

(2%) of an additional phenol (*M*, 136) were detected but could not be isolated in a pure form.

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## Regioselectivity in $\alpha$ -Cleavage Reactions: Arylalkylcyclopropenethiones

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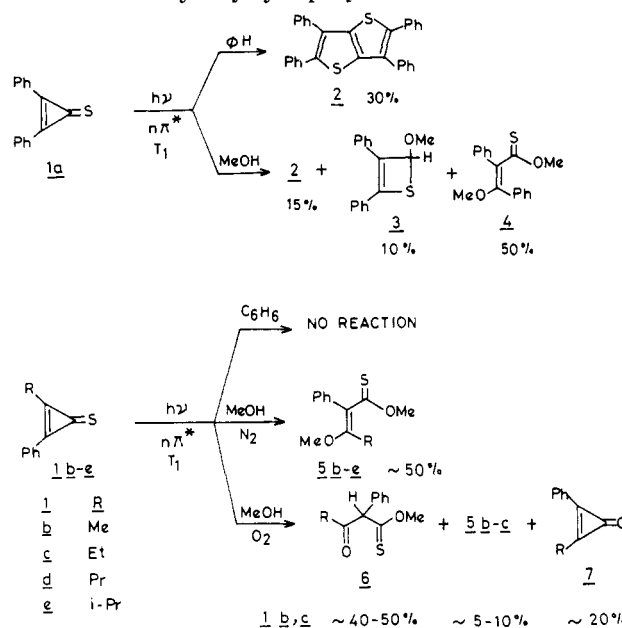
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Photoreactions of several arylalkylcyclopropenethiones (**1b-e**) have been investigated. The products formed have been rationalized on the basis of  $\alpha$ -cleavage as the primary photoprocess. The photochemical  $\alpha$ -cleavage is presumed to originate from the lowest excited  $n\pi^*$  triplet state. A regioselective  $\alpha$ -cleavage reaction has been observed and this unusual regioselectivity is explained on the basis of close approach of the ground-state energy surface of the diradical/carbene, the primary intermediates, to the excited triplet-state surface of cyclopropenethiones. Reactions originating from both triplet and singlet thioketene carbene have been observed upon photolysis of arylalkylcyclopropenethiones.

The Norrish type I  $\alpha$ -cleavage reaction has recently been established as one of the primary photoreactions of strained thiocarbonyls.<sup>1</sup> Cyclobutanethiones<sup>2</sup> and diphenylcyclopropenethiones<sup>3</sup> have been shown to undergo  $\alpha$ -cleavage from the lowest triplet state. A natural extension of the above investigation is the study of selectivity in the  $\alpha$ -cleavage processes. Selectivity in  $\alpha$ -cleavage reactions of ketones has been extensively investigated.<sup>4</sup> Introduction of different substituents on the  $\alpha$  and  $\alpha'$  carbons of ketones results in a preferential  $\alpha$ -cleavage that gives the more stable of the two diradicals. In this context thiones with different  $\alpha, \alpha'$  substituents were chosen for investigation and alkyl- and phenyl-substituted cyclopropenethiones **1** appeared to be suitable substrates. Earlier we had shown<sup>3</sup> that diphenylcyclopropenethione in benzene affords 2,3,5,6-tetraphenylthieno[3,2-*b*]thiophene upon excitation (Scheme I, of top). However, in methanol two additional products namely 2-methoxy-3,4-diphenylthiethene (10%) and methyl 3-methoxy 2-phenylthiocinnamate (50%) were isolated. These products have been rationalized on the basis of the Norrish type I  $\alpha$ -cleavage process, and 1,3-diradical and thioketene carbene have been postulated to be the primary intermediates. Results on the photobehavior of methyl-, ethyl-, propyl-, and isopropylphenylcyclopropenethiones **1b-e** presented below show some similarity with those of diphenylcyclopropenethione. The most interesting aspect of the present study is related to the observed unusual

Scheme I. Photoproducts upon Irradiation of Diphenylcyclopropenethione and Arylalkylcyclopropenethiones



selectivity in the  $\alpha$ -cleavage.

### Results

Cyclopropenethiones **1a-e** chosen for investigation were prepared by standard procedures<sup>5</sup> and were characterized by their spectral properties. The data summarized in Table I are consistent with the literature reports. Of these, electronic absorption spectra are relevant to understanding their excited behavior. The electronic absorption spectrum

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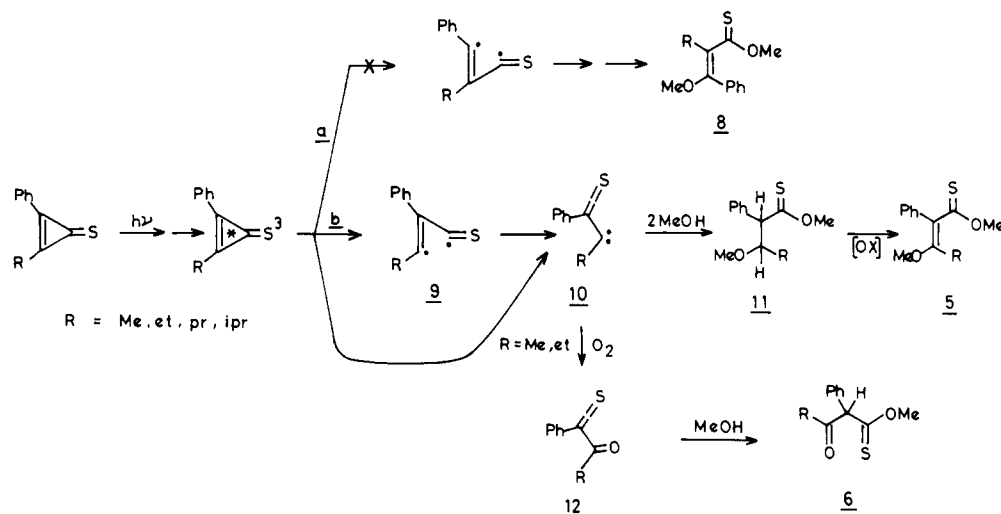
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Scheme II. Mechanism of Product Formation upon Photolysis of Arylalkylcyclopropenethiones



of diphenylcyclopropenethione in cyclohexane shows a band at 360 nm and a number of bands in the region 290–230 nm (Table I). Alkylphenylcyclopropenethiones **1b–e** exhibit bands at 320, 292, and 251 nm. The absorptions of **1b–e** have a tail up to 400 nm. While diphenylcyclopropenethione was slightly yellow in color, arylalkylcyclopropenethiones were either colorless or light yellow. Generally, thiones are bright colored (red, blue, and green) with large separation between  $n\pi^*$  ( $S_1$ ) and  $\pi\pi^*$  ( $S_2$ ) absorptions. However, thio esters, thioamides, and related thione derivatives are known to possess only mild yellow color. Therefore, we believe that the  $n\pi^*$  transition of cyclopropenethiones **1a–e** is buried underneath the intense  $\pi\pi^*$  transition. No emission was seen from **1** at room temperature in cyclohexane or 3-methylpentane. However, a weak emission was detected from **1b–e** in a glassy matrix (3-methylpentane) at 77 K. The excitation spectra corresponded to their absorption spectra, thus confirming the origin of emission to be from **1b–e**. This emission is believed to be phosphorescence. Although several thiones have been reported<sup>6</sup> to show emission from  $S_2$ , the absence of  $S_2$  emission in **1b–e** is not surprising. The energy gap between  $S_2$  and  $S_1$  is expected to be small as there is a good overlap between  $S_1$  ( $n\pi^*$ ) and  $S_2$  ( $\pi\pi^*$ ) transitions. A small energy gap would facilitate internal conversion from  $S_2$  to  $S_1$ , and, therefore, absence of emission from  $S_2$  is expected. Absence of fluorescence from  $S_1$  is consistent with the general behavior of thiones.<sup>1</sup> Thiones in general are established to possess unit intersystem crossing efficiency from  $S_1$  to  $T_1$ . Consequently, thus far no emission is seen from  $S_1$ . Further investigation is required to identify the origin of the various bands in the absorption spectra of **1**. For our purposes based on analogy with other thiones, we have assumed that the lowest excited singlet ( $S_1$ ) and triplet ( $T_1$ ) have  $n\pi^*$  character. At this stage we are not able to provide further support for such an assignment.

Excitation of methylphenylcyclopropenethione (**1b**) into its  $n\pi^*$  excited  $S_1$  state (500-W tungsten lamp) in nitrogen-purged methanol afforded a reddish orange liquid identified to be methyl 1-methoxy-2-phenyl-2-butenethioate (**5b**, 50%) along with a nonidentifiable red polymeric liquid (Scheme I, bottom). Excitation of **1b** (0.005 to 0.05 M) with either a 500-W tungsten lamp or a 450-W

medium pressure mercury lamp in deaerated benzene for 7 days gave only polymer (~30%) along with unreacted **1b**. Under similar conditions of irradiation ethylphenylcyclopropenethione (**1c**), propylphenylcyclopropenethione (**1d**), and isopropylphenylcyclopropenethione (**1e**) behaved in an analogous manner both in benzene and in methanol. However, when excitation of **1b** was conducted in oxygen-purged methanol, the expected oxidation product,<sup>7</sup> methylphenylcyclopropenone (**7**) was obtained only in small amounts (~20%) along with **5b** (~10%). However, an unexpected product, namely, 1:1 methanol adduct identified to be 2-phenyl-3-oxabutenethioate (**6b**) was obtained as the major product (~50%) (Scheme I, bottom). Under identical conditions **1c** gave **6c** (~40%). Although **1b–e** were not readily oxidized upon self-sensitization, dye-sensitized (rose bengal and methylene blue) oxidation of **1b–e** in chloroform and methanol gave the corresponding cyclopropenethiones in moderate yields (60–70%). Singlet oxygen generated from an alternative source, triphenyl phosphite ozonide, also oxidized **1b–e** to the corresponding cyclopropenones.

**1b** was selected for sensitization and quenching studies. Triplet sensitizer Michler's ketone (~62 kcal/mol) was found to sensitize the formation of **5b**. Consistent with this observation, triplet quenchers phenanthrene, naphthalene, and acenaphthene quenched the formation of **5b** on excitation of **1b**. No quantitative studies were conducted in any of these cases due to experimental difficulties.

## Discussion

The structural characterization, the mechanism of product formation, and the reactive state involved in these reactions are presented in this section. The slow nature of the reaction (~50% conversion in ~36 h of irradiation) and the accompanying side reaction (polymerization) prevented quantitative investigation.

**Products.** Structures of products **5b–e** and **6b,c** were established on the basis of their spectral properties (UV, IR, <sup>1</sup>H NMR, and mass spectra) and chemical reactions. The spectral data are presented in Table II. The names of **5b–e** are as follows: methyl 3-methoxy-2-phenyl-2-butenethioate (**5b**), methyl 3-methoxy-2-phenyl-2-pentene-

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Table I. Spectral Data of Cyclopropenethiones

compd	IR spectrum (cm <sup>-1</sup> )	UV (nm) (cyclohexane)	<sup>1</sup> H NMR (δ, CDCl <sub>3</sub> )	<sup>13</sup> C NMR (δ, CDCl <sub>3</sub> )	mass spectrum (mu)
1a	1800, 1600, 1340	360 (6400), 264 (12400), 234 (11000), 227 (12000)	7.4-8.4 (m)	178.2 (s), 153.8 (s), 133.8 (d), 132.1 (d), 129.6 (d), 122.9 (s)	222, 178, 77
1b	1800, 1600, 1340	320 (3000), 251 (7000), 226 (6000)	2.7 (3 H, s), 7.8-8.2 (5 H, m)	114 (q), 122.5 (s), 129.5 (d), 131.7 (d), 133.8 (d), 129.2 (s)	160, 145, 116, 115
1c	1800, 1600, 1360	320 (2500), 252 (6000), 228 (5500)	1.4 (t), 3.0 (2 H, q), 7.4-8.4 (5 H, m)	10.5 (q), 20.0 (t), 118.0 (s), 125.0 (d), 128.0 (d), 130 (d), 154 (s), 158 (s), 175 (s)	
1d	1800, 1600, 1360	319 (3500), 251 (8500), 228 (8000)	1.1 (3 H, t), 1.9 (2 H, m), 3.0 (2 H, t), 7.4-8.2 (5 H, m)		
1e	1800, 1600, 1380, 1360	320 (1000), 250 (3000), 224 (3000)	1.5 (6 H, d), 3.3 (1 H, m), 7.5-8.2 (5 H, m)		

Table II. Spectral Properties of Photoproducts

compd	mass spectrum (mu) (electron ionization 40 eV or 70 eV)	IR spectrum (cm <sup>-1</sup> ) (neat or chloroform solution)	UV (nm) (cyclohexane)	<sup>1</sup> H NMR (δ, CCl <sub>4</sub> /Me <sub>2</sub> Si)	<sup>13</sup> C NMR (δ, CDCl <sub>3</sub> /Me <sub>2</sub> Si)
5b	222, 207, 171, 127	1600, 1440, 1200, 1140, 1080	409 (600), 310 (15000)	1.8 (s), 2.2 (s) (3 H), 3.4 (s), 3.6 (s) (3 H), 4.0 (3 H, s), 7.0-7.6 (5 H, m)	
5c	236, 234, 211, 205	1600, 1440, 1200, 1140, 1080	409 (500), 307 (15000)	1.2 (3 H, t, t), 2.6 (2 H, m), 3.4 (s), 3.6 (s) (3 H), 4.0 (3 H, s), 7.0-7.6 (5 H, m)	
5d	250, 248, 235, 221	1600, 1430, 1200, 1140, 1080	407 (600), 307 (14000)	0.9 (3 H, m), 1.4 (2 H, m), 2.6 (2 H, m), 3.4 (s), 3.6 (s) (3 H), 4.0 (3 H, s), 7.0-7.6 (5 H, m)	
5e	250, 235, 217, 202	1600, 1440, 1380, 1200, 1140, 1090	409 (600), 307 (15000)	0.9 (d), 1.2 (d) (6 H), 3.0 (1 H, m), 3.4 (s), 3.8 (s) (3 H), 4.0 (s), 4.05 (s) (3 H), 7.0-7.6 (5 H, m)	
4	284, 151, 105, 77	1600, 1460, 1320, 1220, 1100	418 (600), 314 (8300), 233 (14000)	3.2 (s), 3.3 (s) (3 H), 3.6 (s), 4.0 (s) (3 H), 7.0-7.4 (5 H, m)	216.37 (s), 216.05 (s), 159.55 (s), 156.43 (s), 138.17 (s), 137.25 (s), 135.07 (s), 133.29 (s), 130.3-126.9 (eight peaks), 58.62 (q), 58.38 (q), 58.18 (q), 58.06 (q)
6b	208, 193, 166, 134	1720, 1560, 1440, 1200, 1180	336 (150), 207 (10000)	keto form: 2.2 (s), 4.0 (s), 5.2 (s) chloroform: 1.8 (s), 3.8 (s) common signals: 7.0-7.8 (m)	29.1 (q), 59.6 (q), 75.5 (d), 201.1 (s), 207.6 (s), 22.0 (q), 58.4 (q), 117.7 (s), 176.9 (s), 207.6 (s), 127.1 (d), 128.3 (d), 128.7 (d), 129.5 (d), 130.9 (s), 137.2 (s)
6c	222, 221, 207, 166	1720, 1560, 1440, 1200, 1080	336 (170), 207 (9500)	1.2 (3 H, t, t), 3.0 (2 H, m), 3.8 (s), 4.0 (s) (3 H), 5.3 (s), 7.0-8.0 (5 H, m)	11.0 (q), 18.4 (q), 28.2 (t), 35.5 (t), 56.7 (q), 58.3 (q), 74.5 (d), 116.3 (s), 127.1 (d), 128.1 (d), 128.3 (d), 128.7 (d), 129.5 (d), 130.1 (d), 130.6 (d), 130.8 (s), 134.4 (s), 136.9 (s), 180.8 (s), 204 (s), 207 (s), 216.5 (s)

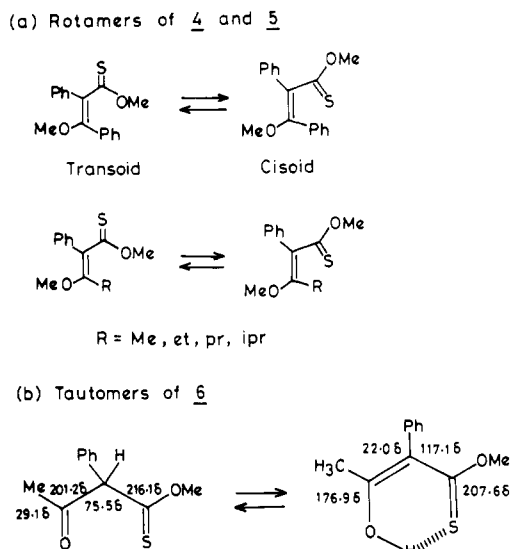


Figure 1. Rotamers of **5** and tautomers of **6**.

thioate (**5c**), methyl 3-methoxy-2-phenyl-2-hexenethioate (**5d**), and methyl 4-methyl-3-methoxy-2-phenyl-2-pentenethioate (**5e**). For the sake of brevity only the spectral features of **5b** are highlighted and appropriate comparisons are made wherever necessary. **5b** has a molecular ion peak at  $m/e$  222 in the mass spectrum (electron ionization 70 eV) corresponding to the molecular formula  $C_{12}H_{14}SO_2$ , indicating the addition of two methoxy groups to **1b**. Since the IR and electronic absorption spectra of **5b** are similar to those of methyl 3-methoxy-2-phenylthiocinnamate<sup>3</sup> (**4**) (Table II) it was presumed that **5b** has an analogous structure. This conclusion is also supported by the molecular ion peak (222) in the mass spectrum. Thus **5b** has a double bond substituted with methoxy, thioacetate, methyl and phenyl groups. Since we already know from **4** that thioacetate and methoxy are trans 1,2-disposed, the other two groups, namely, methyl and phenyl, can be arranged in either of two ways (**5** or **8**; Scheme II). These result from cleavages of different  $\alpha$ -bonds. <sup>1</sup>H NMR is helpful in identifying the relative disposition of alkyl and thio ester moieties in **5b–e**. Although total integration of the peaks in the <sup>1</sup>H NMR spectrum of **5b** corresponds to the compound having methyl, thioacetate, methoxy, and phenyl groups, methyl and methoxy were found to appear as two individual sets of doublets (four peaks) of unequal height. Vinylic methyl appeared at  $\delta$  1.8 and 2.2 and vinylic methoxy at  $\delta$  3.4 and 3.6. Only the total integration of these peaks corresponded to 3 H each. This suggested the presence of an equilibrium of two conformational/rotational isomers. It has been documented earlier<sup>3</sup> that s-transoid and s-cisoid rotamers arising due to the restricted rotation of the thio ester moiety substituted on the double bond (Figure 1) are responsible for the observed two sets of methoxy signals in methyl 3-methoxy-2-phenylthiocinnamate (**4**) whose structure has been confirmed by X-ray crystallographic studies. It is important to note that the thioacetate of **4** gives two <sup>1</sup>H NMR signals and the chemical shift difference between them is substantial ( $\delta$  4.0 and 3.3). It was argued that in the s-cisoid arrangement the phenyl group at the position-1 is tilted with respect to the double bond in a way so as to shield the thioacetate group (Figure 1). Under conditions wherein the phenyl group is replaced by a smaller alkyl group, the anisotropic effect on the thioacetate group should be small. This is indeed what seems to happen in **5b–e**. Molecular models further favor this argument. The thioacetate group is hardly affected by its rotation in **5b–d**

whereas in **5e** the thio ester group itself is slightly out of plane due to the interaction with the bulky isopropyl group. This may be responsible for the slight difference in the chemical shift for the two rotamers in **5e** ( $\delta$  4.0 and 4.05). On the basis of arguments, the alkyl group is assigned to be at position-1, i.e., the alkyl and the thio ester moiety are cis 1,2-disposed on the tetrasubstituted double bond. Had the structure been **8** (Scheme II) instead of **5** as proposed above, one would have expected a large difference in chemical shift for the thioacetate group in the two rotamers. Further support for the proposed structure comes from the acid hydrolysis of **5b** which gave the corresponding methyl 2-phenyl-3-oxobutanethioate (**6b**) whose structure has been established by spectral data as described below.

Spectral features of **6b** and **6c** are identical. For the sake of brevity only the structure of methyl 2-phenyl-3-oxobutanethioate (**6b**) is discussed below. Photolysis of **1b** in oxygen-purged methanol gave **6b** as a yellowish orange liquid. It has the molecular ion peak at  $m/e$  208 in the mass spectrum (electron ionization 70 eV) corresponding to a molecular formula  $C_{11}H_{12}SO_2$ , indicating the addition of a molecule of methanol and an oxygen atom to the parent compound. The presence of the ketone moiety is discernible from the IR spectrum ( $1720\text{ cm}^{-1}$ ). The electronic absorption spectrum suggested the presence of a thio ester functionality (336 nm,  $\epsilon$  150). Further, the <sup>13</sup>C NMR data substantiated the presence of these chromophores,  $\delta$  216.1 (s) and 201.2 (s). The presence of acetyl and methoxy groups became evident from the <sup>1</sup>H and <sup>13</sup>C NMR spectra: <sup>1</sup>H,  $\delta$  2.2 and 4.0; <sup>13</sup>C,  $\delta$  29.1 (q), 201.2 (s), and 59.6 (q). In the <sup>1</sup>H NMR spectrum, a singlet at  $\delta$  5.2 having one-third the intensity of these methoxy and acetyl signals is present, suggesting that this set of signals (i.e.,  $\delta$  2.2, 4.0, and 5.2) belongs to one compound. The carbon bearing the proton having a signal at  $\delta$  5.2 appears as a doublet in the <sup>13</sup>C NMR spectrum at  $\delta$  75.5. This suggested that the carbon is  $\alpha$  to phenyl, ketone, and thio ester groups. This set of signals along with the phenyl group is consistent with the structure-methyl 2-phenyl-3-oxobutanethioate (**6b**). Perusal of the literature<sup>8</sup> reveals that this type of compounds exists in equilibrium with its tautomer enol (Figure 1). Indeed, in addition to the signals discussed above, another set of signals of approximately 30% of the parent compound's intensity is observed. These are attributed to the enol form (Figure 1). The signals at  $\delta$  1.8 in <sup>1</sup>H NMR and at  $\delta$  22.0 (q) in <sup>13</sup>C NMR are attributed to the methyl that is adjacent to a double bond. In 1,3-diones it has been established<sup>9</sup> that the hydroxy-substituted olefinic carbon of the enol form appears very much downfield in the <sup>13</sup>C NMR spectrum. Indeed it is found to be so in our case also ( $\delta$  176.9 (s)). It is also reported<sup>8</sup> that intramolecular hydrogen-bonded enol does not show up in the IR spectrum, because of extreme broadening. This is also consistent with our observation of the absence of a hydroxyl peak in the IR spectrum. On the basis of distinctive spectral features, the structure is assigned to be methyl 2-phenyl-3-oxobutanethioate (**6b**) and is believed to exist in equilibrium with the enol tautomer.

**Reactive State.** In order to characterize the excited state involved in the  $\alpha$ -cleavage process, selective excitation, triplet sensitization, and quenching studies were conducted with **1b**. Thiocarbonyls in general have been established<sup>10</sup> to undergo reactions from both lower and

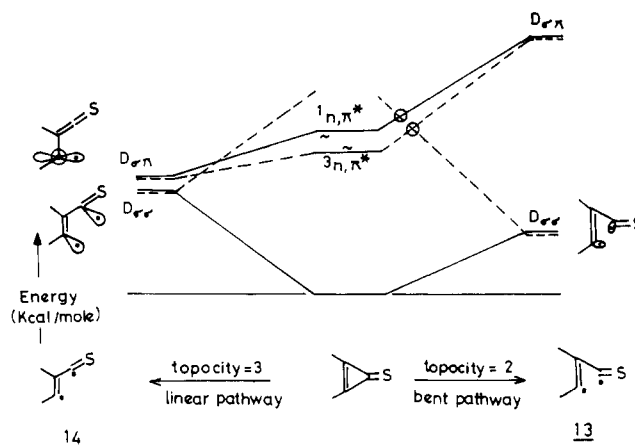
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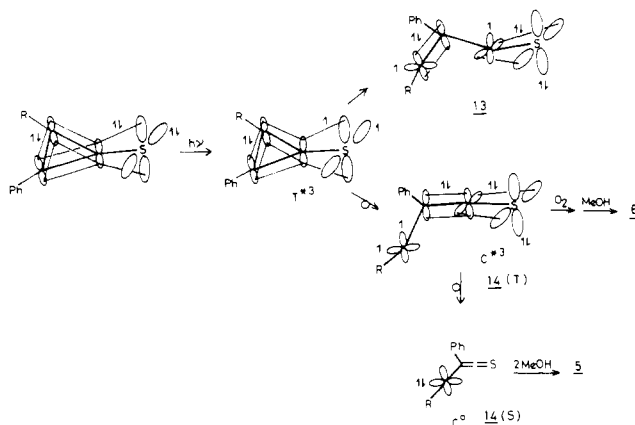
higher excited states. Therefore, the possibility of a reaction occurring from higher  $S_2$  and lower  $S_1$  and  $T_1$  excited states was considered. From the absorption spectrum of **1b** it is clear that the difference in energies between  $S_1$  and  $S_2$  is small (23 kcal/mol) on comparison to other thiones. The triplet energy ( $T_1$ ) based on the emission from a glassy matrix at 77 K is near 62 kcal/mol. Formation of the products shown in Scheme I, bottom, was independent of the excitation band ( $S_1$  or  $S_2$ ). Further, no new products were formed upon irradiation of **1b** to the higher energy band. Therefore the participation of a higher excited state was excluded. Selective excitation into the  $S_1$  level (500-W tungsten lamp) resulted in the formation of the products **5b** and **6b**. Thus, the reactive state is narrowed down to  $S_1$  and  $T_1$ . Triplet sensitizer Michler's ketone sensitized the formation of **5b**. Under the conditions of irradiation (450-W medium pressure mercury lamp with Corning glass 0.52 filter; transmission above 350 nm), more than 90% of the incident light was absorbed by the sensitizer. Consistent with the above sensitization studies, the triplet quenchers phenanthrene, naphthalene, and acenaphthene quenched the formation of photoproducts (**5b** and **6b**) upon excitation of **1b** into the  $S_1$  band ( $> 350$  nm). On the basis of these results, the reactive state is suggested to be the lowest excited triplet state. However, the characteristics of the state ( $n\pi^*$  or  $\pi\pi^*$ ) being quenched could not be inferred.

**Mechanism.** Direct or triplet-sensitized excitation of diphenylcyclopropenethione resulted in the formation of three products, namely, dimer and 1:1 and 1:2 methanol adducts, as illustrated in Scheme I, top.<sup>3</sup> These products have been rationalized on the basis of  $\alpha$ -cleavage and as involving diradicals and carbenes as reactive intermediates. To explore the possibility of observing regioselective  $\alpha$ -cleavage, the excited-state behavior of arylalkylcyclopropenethiones **1b-e** was investigated. Two different modes of  $\alpha$ -cleavage can be visualized, one to give a stable phenyl-substituted diradical/carbene and another to form a less stable alkyl-substituted diradical/carbene. According to the mechanism involving diradical/carbene, preferential formation of a more stable diradical/carbene might be expected, but the excited-state behavior of these systems is substantially different from what one would generally expect.

Irradiation of **1b-e** in deaerated methanol gave 3-methoxy-2-phenyl-2-butenethioate and related products as shown in Scheme I, bottom. Close following of the reaction by GC with respect to time did not reveal any new products. At all stages of irradiation **5**, **6**, and **7** were identified as the only products. This suggested that **5**, **6**, and **7** are primary photoproducts and are not the result of secondary photoprocesses. Thus, the products obtained are derived from preferential cleavage of the cyclopropenethione single bond which is alkyl rather than phenyl substituted. Possible mechanistic paths are indicated in Scheme II. On the basis of a Salem correlation diagram, assuming that the reaction originates from  $n\pi^*$  triplet state,  $\alpha$ -cleavage of cyclopropenethiones can result either in a  $D_{\sigma\sigma}$  bent diradical or a  $D_{\sigma\pi}$  linear diradical/carbene. The correlation diagrams for these two pathways are illustrated in Figure 2. Energies of these  $D_{\sigma\sigma}$  and  $D_{\sigma\pi}$  states are unknown. One can conclude from these qualitative diagrams that cleavage from the triplet state of cyclopropenethione is electronically allowed to the  $D_{\sigma\pi}$  diradical/carbene but not to the  $D_{\sigma\sigma}$  bent diradical. Electronic structures of these two intermediates are dip-



**Figure 2.** Approximate Salem correlation diagram for the  $\alpha$ -cleavage of cyclopropenethiones.



**Figure 3.** Electronic orbital picture for the  $\alpha$ -cleavage of arylalkylcyclopropenethiones.

icted in Figure 3. It appears from the correlation diagram and Figure 3 that smooth conversion of the triplet state of cyclopropenethione to the triplet thioketene carbene **14(T)** can occur. We believe that it is this intermediate which plays an important role in the formation of products **5** and **6**.

The mechanistic rationale for the formation of methyl 2-phenyl-3-oxo-4-alkylbutanethioates **6b** and **6c** is given in Scheme II. An electronic orbital picture of the rearrangement is illustrated in Figure 3. Thioketene carbene **10** (Scheme II) is identical with the one shown as **14** in Figure 3. Thioketene carbene which can exist in singlet and triplet electronic configurations are labeled as **14(S)** and **14(T)**, respectively. We propose that the triplet excited thione rearranges directly to triplet thioketene carbene **10** (**14(T)**) and this is trapped by oxygen to yield the intermediate **12**. Trapping of triplet carbenes with oxygen is a well-known phenomenon.<sup>11</sup> The intermediate **12** reacts with a molecule of methanol to form **6b** and **6c**. In the absence of oxygen, the triplet thioketene carbene undergoes intersystem crossing to the singlet state. We believe that this reactive intermediate **14(S)** is trapped by two molecules of methanol to form **11** which undergoes facile oxidation to **5**. Attempts to seek evidence for **11** were not successful; however, this appears to be the most reasonable pathway for the formation of **5**.

A reasonable explanation can be offered to account for the formation of products derived from the less stable

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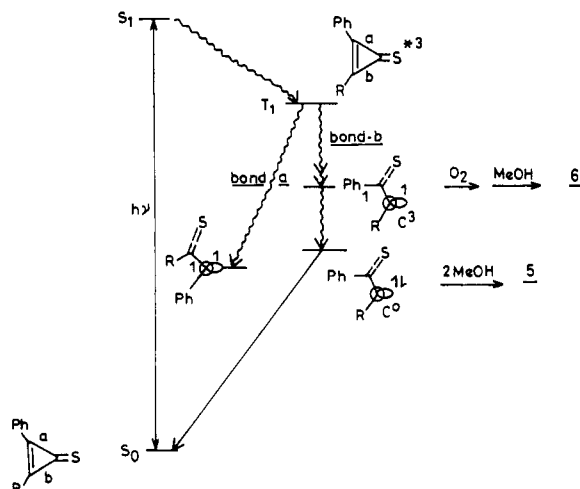


Figure 4. Pathways for the decay of the excited triplet of arylalkylcyclopropanethiones.

diradical/carbene. If it is assumed that the excited-state triplet surface of cyclopropanethione approaches more closely the ground-state of diradicals/carbenes, that is alkyl substituted rather than phenyl substituted (Figure 4), then preferential cleavage of the cyclopropanethione bond attached to alkyl group agrees well with the funnel theory of excited-state to ground-state conversion.<sup>12</sup> Close approach of the two surfaces greatly enhances internal conversion and since the alkyl-substituted biradical/carbene is higher lying than phenyl substituted, it could be easily funnelled into from the triplet excited surface of **1b-e**. A similar explanation has been forwarded to rationalize the unusual photochemistry of arylalkylcyclopropenes by Padwa and co-workers.<sup>13</sup> These upon excitation to  $S_1$ , undergo bond cleavage to predominately form the less stable alkyl-substituted biradical or carbene. Recently, Steinmetz and co-workers<sup>14</sup> have invoked an analogous hypothesis to explain the difference in the photochemical and thermal reactions of spiro[2.4]hept-1-ene. Perusal of the literature reveals that this anomalous behavior is unique for cyclopropane derivatives.

### Conclusions

We have demonstrated the occurrence of regioselective  $\alpha$ -cleavage reactions in arylalkylcyclopropanethiones. The unexpected regioselectivity is explained on the basis of close approach of the ground-state energy surface of the biradical/carbene to the excited triplet surface of cyclopropanethione followed by funneling. Products derived from both triplet and singlet thioketene carbene have been observed. Though the regioselectivity observed is identical with that already reported<sup>13,14</sup> in substituted cyclopropenes, the reactive states are different. Cyclopropanethiones undergo cleavage from the excited triplet state while cyclopropenes do not undergo cleavage from the triplet state but do so from excited singlet state. The light-induced reactions of cyclopropanethiones are totally different from those of the corresponding cyclopropenes,<sup>15</sup> which un-

dergo photoextrusion of carbon monoxide. Thus the photoreactivity of substituted cyclopropanethiones is unique and cannot be extrapolated from that of cyclopropenes and the corresponding carbonyls.

### Experimental Section

UV-vis absorption spectra were recorded on a Shimadzu UV-180 double beam spectrophotometer. IR data were obtained on a Perkin-Elmer Model 730 infrared spectrophotometer. Varian T-60 and Bruker HW-270 FT NMR spectrometers were used for recording  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. Emission spectra were recorded on either a Shimadzu Model RF-540 spectrofluorimeter or a Perkin-Elmer Model MPF-44 spectrofluorimeter. Phosphorescence spectra were recorded at 77 K in 3-methylpentane, using the accessory provided with MPF-44.

Arylalkylcyclopropanethiones **1b-e** were prepared from the corresponding arylalkylcyclopropenes by reported procedure.<sup>5</sup> Spectral data for **1** are provided in Table I. These were purified by column chromatography (silica gel/hexane). Solvents for irradiation were distilled once prior to use. A 450-W Hanovia medium pressure mercury lamp was used as the source of UV radiation and was contained in a water-cooled Pyrex immersion well. The 450-mL irradiation vessel had a provision for gas inlet. Irradiations were conducted while oxygen-free nitrogen (passed through alkaline pyrogallol solution followed by concentrated sulfuric acid and potassium hydroxide pellet traps) was bubbled through. Irradiation in the visible region was conducted with 500-W tungsten lamps as external sources. The sample to be irradiated was contained in a water-cooled irradiation vessel containing a gas inlet. All irradiations were monitored by TLC and were run until essential disappearance of the starting material.

**1. Irradiation of Arylalkylcyclopropanethiones **1b-e** in Methanol.** Arylalkylcyclopropanethiones **1b-e** (0.02 M, 1.5 g in 400 mL of methanol) were irradiated (450 W medium pressure mercury lamp or 500-W tungsten lamp) for 24 h while nitrogen was continuously bubbled through. After complete conversion of the starting material as monitored by tlc, solvent was evaporated, and the products were separated by repetitive column and preparative TLC (silica gel/hexane) and identified by their spectral properties. In all cases only **5b-e** were obtained, in 50% yield. Their spectral data are provided in Table II.

**Irradiations of **1b,c**** were also carried out in methanol with continuous bubbling of oxygen under analogous conditions. Column chromatography (silica gel/hexane-chloroform) of the product mixture gave **6b** (50%), **5b** (5%), and the corresponding cyclopropanone **7** (20%) in the case of **1b** and **6c** (40%), **5c** (10%), and cyclopropanone (20%) in the case of **1c**. Spectral data of **6b** and **6c** are provided in Table II.

**2. Irradiation of Arylalkylcyclopropanethiones in Benzene.** Irradiation of **1b-c** in benzene at different concentrations (0.005 to 0.05 M) in nitrogen atmosphere was conducted as above. However, evaporation of the solvent after complete disappearance of the starting material gave only polymeric material.

**3. Control Experiments.** (a) A solution of **1b-e** in benzene or methanol (0.02 M) was kept in dark for a week. No reaction was detected. (b) Refluxing of **1b** in both methanol and benzene for 24 h did not result in any observable reaction; **1b** was recovered quantitatively.

**4. Sensitization and Quenching Studies.** Sensitization and quenching studies were carried out for **1b** alone. Michler's ketone was used as the sensitizer. In a typical experiment, a solution of **1b** (0.04 M) and sensitizer (0.2 M) in 50 mL of methanol was irradiated by using a 450-W medium pressure mercury lamp with a Corning glass filter 0.52 (transmission above 350 nm) as the external source. As selective excitation of the sensitizer could not be achieved, high concentration of the sensitizer was used so that >90% of the incident light is absorbed by the sensitizer. A blank solution without the sensitizer was irradiated simultaneously, and the extent of conversions were compared in the sensitized and unsensitized cases. Sensitization afforded a larger yield of the product **5b** as determined by  $^1\text{H}$  NMR with an internal standard.

Quenching studies were carried out with fluorene ( $E_T \approx 68$  kcal/mol), phenanthrene (62), naphthalene (60), and ace-

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naphthene (59) as quenchers. These were conducted in a merry-go-round apparatus (Corning glass filter 0.52, medium pressure mercury lamp) with a quencher concentration of 0.06 M and a thione concentration of 0.04 M. A control having 0.04 M thione without quencher was also irradiated. After 25 h of irradiation, the solvent was evaporated under reduced pressure and the products were chromatographed. The thioacetoxo signal was monitored with respect to the internal standard. The reaction was quenched by phenanthrene, naphthalene, and acenaphthene, while fluorene was not effective. Therefore the triplet  $T_1$  is concluded to be the reactive state.

**5. Oxidation of Arylalkylcyclopropenethiones.** Dye-sensitized oxidation of **1b-e** was conducted by irradiating aerated solutions of **1b-e** (0.01 M in benzene, chloroform, and acetonitrile) in the presence of appropriate dyes ( $10^{-4}$  M methylene blue or rose bengal). Selective excitation of the dye was achieved by using Corning glass filter CS-2.58 (transmission above 630 nm). Corresponding cyclopropenones **7** were isolated in 60% yield as the only products in all four cases.

Triphenyl phosphite ozonide was prepared at  $-78$  °C in dichloromethane by following the reported procedure.<sup>16</sup> The above solution was warmed to  $-10$  °C at which time oxygen evolution was visible and at this stage **1b-e** were added. After the reaction mixture was kept at room temperature for about an hour, the solvent was evaporated and the products were separated by

column chromatography. Similar to dye-sensitized oxidation, the corresponding cyclopropenones **7** were isolated as the only products.

**6. Miscellaneous Experiments. (a) Photolysis of Arylalkylcyclopropenones.** Irradiation of arylalkylcyclopropenones (corresponding to **1b-e**) in methanol and benzene with a 450-W medium pressure mercury lamp for 20 h resulted in the formation of the corresponding acetylenes. These were identified by their spectral properties and by comparison with authentic samples.

**(b) Acid Hydrolysis of Methyl 3-Methoxy-2-phenylbutenethioate (5b).** To 100 mg of **5b** in 20 mL of methanol was added a drop of dilute hydrochloric acid, and the mixture was stirred at room temperature for 2 h. The reaction mixture was poured into water, extracted with ether, and dried over anhydrous sodium sulfate. Evaporation of the solvent gave **6b** (90%). Spectral data of **6b** are provided in Table II.

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**Registry No.** **1a**, 2570-01-6; **1b**, 56764-07-9; **1c**, 77853-14-6; **1d**, 97703-38-3; **1e**, 97703-39-4; **2**, 35093-32-4; **3**, 82246-85-3; **4**, 97703-40-7; **5b**, 97703-41-8; **5c**, 97703-42-9; **5d**, 97703-43-0; **5e**, 97703-44-1; **6b**, 97703-45-2; **6c**, 97703-46-3; **7a**, 26307-30-2; **7c**, 5909-87-5; **7d**, 97703-47-4; **7e**, 69425-02-1; Michler's ketone, 90-94-8; triphenyl phosphite ozonide, 29833-83-8.

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## Total Synthesis of Halogenated Monoterpene Marine Natural Products via the Diels-Alder Reaction

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This work represents the first de novo synthetic approach to the halogenated, monocyclic monoterpenes isolated from red algae belonging to the genus *Plocamium*. The total syntheses of two natural products, i.e., *epi*-plocamene D (**2**) and the allylic chloride **3**, are presented along with an approach to the synthesis of violacene (**1**). A key step in the construction of the terpenoid skeleton is the Diels-Alder reaction utilizing a  $\beta$ -halogenated dienophile. The stereochemistry, regiochemistry, yields, and rates are compared for Diels-Alder reactions between the  $\beta$ -halogenated dienophiles *cis*- or *trans*-3-chloro-2-methylpropenal (**5** and **6**) and the dienes butadiene, isoprene, or cyclopentadiene. These results are compared with the corresponding Diels-Alder reactions of nonhalogenated dienophiles. All of the known, halogenated monocyclic *Plocamium* monoterpenes are classified according to a Diels-Alder retrosynthetic analysis.

### Introduction

An unusual set of halogenated monoterpenes has been isolated from red algae belonging to the genus, *Plocamium*.<sup>1</sup> Violacene (**1**), isolated by Mynderse and Faulkner in 1974,<sup>2</sup> was the first monocyclic monoterpene in this series to be described. Compound **1** exhibits the most complex pattern of halogenation yet found among the monocyclic *Plocamium* metabolites. The correct structure for **1** was confirmed by X-ray diffraction analysis after some initial confusion about the location of the bromine atom.<sup>3,4</sup> Violacene (**1**) is relatively ubiquitous with respect

to other *Plocamium* metabolites, since it was isolated from several sources in combination with other monoterpenes.<sup>5</sup> Its unique pattern of halogenation poses an unprecedented challenge for the stereo- and regiospecific introduction of halogen into organic molecules. Although a total synthesis

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