from the homonuclear decoupled ^{1}H NMR spectrum of the cyclopropane region gave somewhat limited information since all four protons are coupled to each other. The irradiation of the ^{1}H δ 0.36 caused a collapse of the ^{1}H δ 0.74 into an apparent six-line multiplet and an irradiation of the ^{1}H signal δ 0.74 caused a collapse of the ^{1}H δ 0.36 into a similar six-line multiplet. One would have expected either a triplet or doublet of doublets from these decoupling experiments. We, however, believe this suggests that the ^{1}H signals at δ 1.4 and 0.89 are due to attachment to the methylene carbon trans to the benzyl ring, and the geminal ^{1}H's δ 0.74 and 0.36 to be attached to the methylene cis to the benzyl ring since similar results were obtained in the homonuclear decoupling experiments at δ 0.74 and δ 0.36. To substantiate that the ^{13}C signal downfield (δ 19.46) is the methylene cis to the benzyl and that the protons which resonate at δ 0.74 and 0.36 are attached to said carbon and that the ^{13}C signal at δ 17.02 is trans to the benzyl group and coupled to the protons at δ 1.4 and 0.89, the selective proton-decoupled ^{13}C spectrum shown in Figure 1 was recorded. Figure 1 shows the ^{13}C spectrum with the ^{1}H at δ 0.36 selectively irradiated at various decoupling powers. The ^{13}C spectra with the ^{1}H at δ 0.74, 0.89, and 1.4, each irradiated at equivalent decoupling powers, gave results comparable to those shown in Figure 1. These selective ^{1}H-decoupled ^{13}C spectra provide further evidence that the ^{1}H's at δ 0.74 and 0.36 are attached to the ^{13}C at δ 19.46 which is the cyclopropane methylene carbon cis to the benzyl group in the diketopiperazine cyclo[ACC-L-Phe]. Recently the group of Hill et al.[17] has synthesized (*R*)- and (*S*)-[2,2-^{2}H$_2$]ACC by two independent routes and incorporated one of the enantiomers into a diketopiperazine with L-(*S*)-phenylalanine. The ^{1}H NMR spectrum of the diketopiperazine cyclo[D-(*R*)-ACC-L-Phe] gave two sharp doublets at δ 0.36 and 0.74 (J = 5.2 Hz). Subramanian et al.[18] have also synthesized (*R*)- and (*S*)-[2,2-^{2}H$_2$]ACC by a third method. The ^{1}H NMR spectra of the diketopiperazines derived from L-(*S*)-phenylalanine and each of their individual enantiomers gave results consistent with the assignments made in this paper and that of Hill.[17]

Conclusion

In order to determine the stereochemical mechanism of the enzyme 1-aminocyclopropane-1-carboxylic acid synthase one will have to analyze the position of the deuterium(s) in ACC obtained from the feeding of regio- or stereospecific deuterated *S*-adenosyl-L-methionine. We have shown in the present study that it is possible to distinquish between the enantiotopic methylene groups of ACC by derivatizing ACC with L-phenylalanine (or D-phenylalanine). The ^{13}C NMR signal of the L-methylene carbon of ACC will be shifted downfield[19,20] and the D-methylene carbon will be shifted upfield. The ^{1}H NMR signal of the hydrogen atoms attached to the L-methylene carbon of ACC will be shifted upfield.

Acknowledgment. This work was supported by U.S. Public Health Service Grant GM30097.

Registry No. c[L-Ala-L-Ala], 5845-61-4; c[L-Ala-L-Phe], 15180-22-0; c[D-Ala-L-Phe], 15136-19-3; c[A^{i}BA-L-Ala], 98735-75-2; c[A^{i}BA-D-Phe], 98735-76-3; c[ACC-D-Phe], 98735-77-4; c(ACC-L-Ala], 98735-78-5; c[ACC-D-Ala], 98735-79-6; c[A^{i}BA-L-Phe], 95235-24-8; c[ACC-L-Phe], 98735-80-9; 1-aminocyclopropane-1-carboxylic acid, 22059-21-8.

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(19) The opposite results would be obtained if one used D-phenylalanine, i.e., the D-methylene carbon of ACC would be shifted downfield, and the L-methylene carbon would be shifted upfield.

(20) Since deuterium has a nuclear spin of one in a proton-decoupled ^{13}C NMR spectrum, a carbon with deuterium attached directly to it would appear as a triplet, whose lines would be of equal intensity. In addition, the signal is usally centered 0.3–0.6-ppm upfield of the normal proton signal and the $J(^{13}\text{C}-^{2}\text{H})$ values are one-sixth those of the equivalent $J(^{13}\text{C}-^{1}\text{H})$.

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Photochemical Behavior of Thioketenes in Solution: Reaction from S$_2$

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The higher excited-state reactions of sterically encumbered thioketenes **1a–d** in solution were investigated. Substituted thiiranes, thio esters, thioacetophenones, and 1,2-diones are formed on photoexcitation of thioketenes in hydroxylic and nonhydroxylic solvents. Thioketenes while unreactive upon excitation to S$_1$ produce thiiranylidene carbene and zwitterionic intermediates upon excitation to S$_2$. The reactive state is identified to be S$_2$ ($\pi\pi^*$). The excited thioketene resists carbon monosulfide elimination but undergoes rearrangement. The photobehavior of thioketenes, established in solution for the first time, differs significantly from that of ketenes, and it cannot be extrapolated from that of structurally analogous ketenes and allenes.

The photochemistry of ketenes is well documented,[1] while that of allenes and cumulenes has been of recent interest.[2] Thioketenes, which are structurally analogous to the above systems, have received only scant attention due to their poor stability. However, in the last decade

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[†] Indian Institute of Science.

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0022-3263/85/1950-4799$01.50/0

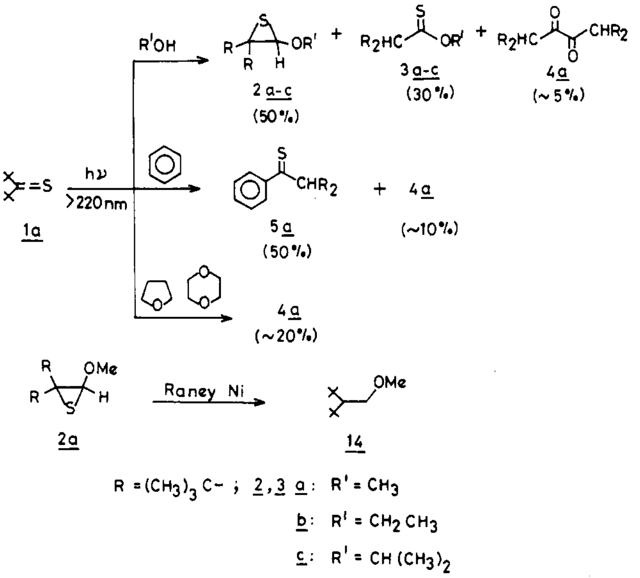
several thioketenes with bulky alkyl substituents have been synthesized and their thermal reactions have been thoroughly explored.[3] Recently singlet oxygen oxidations of a few thioketenes have also been investigated.[4] The excited-state behavior of parent thioketene in argon and nitrogen matrix at low temperatures has received considerable attention.[5] Though systematic investigations could not be carried out under these constraints a few interesting and rather intriguing facets of the excited-state behavior of thioketenes were revealed. This prompted us to undertake a study of the photochemical behavior of a few stable thioketenes in detail. We describe below the first systematic account of the photochemical behavior of a few stable thioketenes (**1a–d**) in solution.

Results

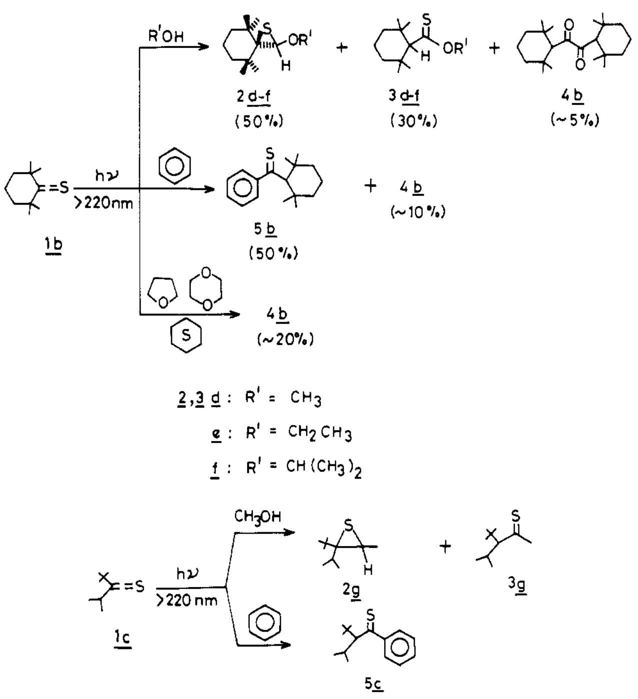
Among the various thioketenes reported in the last decade, di-*tert*-butylthioketene (**1a**) and 2,2,6,6-tetramethylcyclohexylidenemethanethione (**1b**) are reasonably stable and relatively easy to synthesize[3] and were therefore selected for the detailed study of the excited-state behavior. Only preliminary studies could be carried out on *tert*-butylisopropylthioketene (**1c**) and 2,6-di-*tert*-butylcyclohexylidenemethanethione (**1d**).

The electronic absorption spectrum of **1a** in cyclohexane shows three bands with $\lambda_{\max}$ at 570 ($n\pi^*$, ϵ 8), 239 ($\pi\pi^*$, ϵ 4200), and 211 nm ($n\sigma^*$, ϵ 3230). **1b** also exhibits similar bands at 575 ($n\pi^*$, ϵ 4), 239 ($\pi\pi^*$, ϵ 3325), and 219 nm ($n\sigma^*$, ϵ 6000). No fluorescence has been detected, and the S_1 and S_2 energies can only be approximated from the absorption spectrum. Values of near 46 and 105 kcal/mol, respectively, seem probable. Also no phosphorescence was seen from any of these four thioketenes either at room or at low (77 K) temperatures. Therefore the triplets of **1a** and **1b** were probed by laser flash photolysis studies.[6] Laser excitation (532 nm) of thioketenes **1a–c** show transients that can be attributed to their triplets. A weak absorption due to triplet is observed in all three cases in the range 260–500 nm. Triplet energies of **1a** and **1b** were estimated by measuring the rates of quenching of the triplets of a series of organic molecules with varying triplet energies by **1a** and **1b** (Sandros plot). The triplet energy based on these studies is near 43–45 kcal/mol. Some of the interesting features that came to light during this study are that these triplets have a short lifetime (5–20 ns), and the quantum yield of intersystem crossing from S_1 to T_1 is low (~0.1). The self-quenching rate is estimated to be near diffusion. Details of the photophysical studies on thioketenes will be published elsewhere.

Scheme I. Products upon Photolysis of Di-*tert*-butylthioketene



Scheme II. Products upon Excitation of 2,2,6,6-Tetramethylcyclohexylidenemethanethione and *tert*-Butylisopropylthioketene



All photolyses for chemical investigations were carried out under nitrogen atmosphere to approximately 20% conversion, and the products were separated by column or preparative thin-layer chromatography. Photolysis of **1a** (low-pressure mercury arc lamp >220 nm) in nonhydroxylic solvents such as dioxane, tetrahydrofuran, and cyclohexane gave a complex mixture of products from which only 2,2,7,7-tetramethyl-3,6-di-*tert*-butyl-4,5-octanedione (**4a**) was isolated in 20% yield. Irradiations in alcoholic solvents (methanol, ethanol, and isopropyl alcohol) were clean and gave 2-alkoxy-3,3-di-*tert*-butylthiirane (**2a–c**) as the major product (50%) along with thiobutyric acid ester **3a** (30%) and dione **4a** (5%) (Scheme I). Irradiation in benzene where most of the light (>70%) is absorbed by **1a** gave 2,2-di-*tert*-butylthioacetophenone (**5a**) (50%) and dione **4a** (10%). Photolysis of **1b** under similar conditions gave an analogous set of products (Scheme II). The thiirane **2** and thio ester **3** do not clearly separate either on preparative TLC or on column chromatography under various conditions. Therefore, only in the case of di-*tert*-butylthioketene (**1a**) were the thiiranes **2a–c** sep-

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Table I. Spectral Data of Photoproducts 2–5

compd	ms,[a] mu	IR,[b] cm^{-1}	^{1}H NMR,[c] δ	^{13}C NMR,[c] δ
2a	202, 146, 131, 115, 57	2975, 1470, 1380, 1230, 1060	1.05 (9 H, s), 1.1 (9 H, s), 3.4 (3 H, s), 5.0 (1 H, s)	85.15 (d), 67.5 (s), 58.4 (q), 39.0 (s), 38.6 (s), 32.26 (q), 30.26 (q)
2b	216, 172, 160, 156, 101, 99, 57	2975, 1470, 1380, 1230, 1060	1.0 (9 H, s), 1.1 (9 H, s), 1.15 (t, 3 H), 3.6 (q, 2 H), 5.05 (s, 1 H)	83.2 (d), 67.2 (t), 67.0 (s)8, 38.9 (s), 38.4 (s), 32.1 (q), 31.6 (q), 30.2 (q)
2c		1.0 (9 H, s), 1.1 (9 H, s), 1.15 (d, 6 H), 3.8 (m, 1 H), 5.05 (1 H, s)	1.0 (9 H, s), 1.1 (9 H, s), 1.15 (d, 6 H), 3.8 (m, 1 H), 5.05 (1 H, s)	
2d	214, 181, 171, 149, 131, 123, 99	0.65 (s, 3 H), 0.95 (s, 3 H), 1.3 (s, 6 H), 1.5 (m, 6 H), 3.45 (s, 3 H), 5.0 (s, 1 H)	0.65 (s, 3 H), 0.95 (s, 3 H), 1.3 (s, 6 H), 1.5 (m, 6 H), 3.45 (s, 3 H), 5.0 (s, 1 H)	83.2 (d), 65.1 (s), 58.6 (q), 38.5 (s), 36.2 (q), 30.2 (q), 25.3 (t), 23.2 (q), 20.5 (t), 20.1 (t)
2e		2950, 1450, 1380, 1240, 1120, 1050	0.65 (3 H, s), 0.95 (3 H, s), 1.3 (6 H, s), 1.2 (3 H, t), 1.5 (m, 6 H), 3.8 (2 H, q), 5.0 (s, 1 H)	
2f		2950, 1450, 1380, 1360, 1240, 1120, 1050	0.65 (s, 3 H), 0.95 (s, 3 H), 1.3 (s, 6 H), 1.5 (d, 6 H), 1.6 (m, 6 H), 3.7 (m, 1 H), 5.05 (s, 1 H)	
2g			0.95 (s, 9 H), 1.05 (d, 6 H), 2.0 (m, 1 H), 3.35 (s), 3.4 (s, 3 H), 4.9k (s), 5.0 (s 1 H)	
3a		2970, 1490, 1380, 1270, 1150	1.0 (s, 18 H), 2.5 (s), 3.0 (d, 1 H), 4.0 (s, 3 H)	
3b		2970, 1490, 1380, 1270, 1150	1.05 (s, 18 H)8, 1.1 (t, 3 H), 2.5 (s), 3.0 (s, 1 H), 4.5 (q, 2 H)	
3c		2970, 1490, 1380, 1360, 1270, 1150	1.05 (s, 18 H)8 1.15 (d, 6 H), 2.2 (s), 2.5 (s, 1 H), 3.0 (s, 3 H), 5.5 (m, 1 H)	
3d	214, 181, 171, 149, 131, 126, 118, 99	2925, 1460, 1380 1240, 1120	0.95 (s, 6 H), 1.10 (s, 6 H), 1.5 (m, 6 H), 2.9 (s, 1 H), 4.05 (s, 3 H)	225.4 (s), 73.6 (q), 60.2 (d), 42.5 (q), 39.8 (s)8 40.1 (s), 39.6 (q), 34.3 (t), 21.6 (t), 20.6 (t)
3e		2925, 1460, 1380, 1240, 1120	0.95 (s, 6 H), 1.1 (s, 6 H), 1.4 (t, 3 H), 1.5 (m, 6 H), 2.8 (s, 1 H), 4.25 (q, 2 H)	
3f		2920, 1460, 13808 1360, 1240, 1120	0.95 (s, 6 H), 1.10 (s, 6 H), 1.4 (d, 6 H), 1.6 (m, 6 H), 2.8 (s, 1 H),5.8 (m, 1 H)	
3g			0.95 (s, 9 H), 1.05 (d, 6 H), 2.1 (m, 1 H), 2.8 (d, 1 H), 4.0 (s, 3 H)	
4a	310, 155,166, 101	2950, 1720, 1440, 1380	1.1 (s, 18 H), 2.2 (s, 1 H)	181.3 (s), 64.2 (d), 34.7 (s), 30.9 (q)
4b	334, 184, 166, 124	2900, 1720,1380, 1240	1.0 (s, 6 H), 1.2 (s, 6 H), 1.6 (m, 6 H), 2.1 (s, 1 H)	
5a	248, 204, 202, 192, 188, 177, 159, 136, 121	2970, 1600, 1490, 1380, 1250	1.1 (s, 18 H), 4.05 (s, 1 H), 7.2–8.2 (m, 5 H)	252.5 (s), 151.7 (s), 131.3 (d)8 128.2 (d), 126.9 (d), 72 (d), 37.4 (s), 31.7 (q)
5b	260, 182, 167, 99	2950, 2900, 1600, 1440, 1380, 1200	1.1 (s, 12 H), 1.4 (m, 6 H), 4.0 (s, 1 H), 7.5 (m, 5 H)	
5c			1.15 (s, 9 H), 1.3 (d, 6 H), 2.04 (m, 1 H), 4.0 (d, 1 H)	

[a] All mass spectra were recorded with electron ioinization 40 or 70 eV). [b] IR spectra were recorded either neat or in chloroform solution. [c] ^{1}H NMR and ^{13}C NMR in CCl_4 and $CDCl_3$ solutions, respectively, with Me_4Si as internal standard.

arated. **2d** and **3d** could not be separated and the spectra comprised of signals due to both the compounds. All the products were characterized on the basis of their spectral properties (UV, IR, ^{1}H and ^{13}C NMR, and mass spectra).

Raney nickel desulfurization of **2a** gave 2,2-di-*tert*-butylethyl methyl ether as the major product (~50%). The other products could not be identified as they were obtained in small quantities. 2,2-Di-*tert*-butylethyl methyl ether was characterized on the basis of its spectral properties.

The thio ester was characterized by comparison with the authentic compound.[3,7] The formation of thioester is a photochemical process as thioketene does not react with methanol in dark even after a week. Refluxing of thioketene in methanol for 12 h did not afford thio ester, while refluxing in acidic methanol for 2 h gave thioester in quantitative yield.

Test irradiations of **1c** and **1d** were conducted only in methanol and benzene due to paucity of the material. Characteristic signals due to thiirane (**2**), thioester (**3**), and thioacetophenone (**5**) were looked for in the ^{1}H NMR spectrum. All three compounds were formed in low yields in the case of **1c**, whereas these compounds could not be detected by ^{1}H NMR during the photolysis of **1d**.

Discussion

The structural characterization, the reactive state involved in the reaction, and the mechanism of product formation upon excitation of **1a–c** are presented in this section.

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Structural Characterization. Structures of the products were deduced from their spectral properties (UV, IR, ^{1}H and ^{13}C NMR, and mass spectra). Spectral data are summarized in Table I. Products **2a**, **3a**, *4* and *5* gave satisfactory analytical data.

The structure of 2-methoxy-3,3-di-*tert*-butylthiirane (**2a**) alone will be discussed in detail. Other thiiranes possess similar spectral features. Substituted 2-alkoxythiiranes are formed as major products during the photolysis of thioketenes **1a–c** in alcoholic solvents. **2a** has the molecular ion peak at m/e 202 in the mass spectrum (electron ionization, 70 eV) corresponding to the molecular formula $C_{11}H_{22}SO$, indicating the addition of a molecule of methanol to the thioketene **1a**. The absence of unsaturated chromophores like olefins, ketones, and thio esters in the molecule is apparent from the IR and ^{13}C NMR spectra. The presence of a doublet at δ 85.15 in the ^{13}C NMR spectrum indicates that the carbon is secondary and is substituted by heteroatoms. Lack of symmetry in the molecule is discernible by the presence of two signals corresponding to *tert*-butyl groups in the molecule. A signal at δ 67.5 in the ^{13}C NMR spectrum can be attributed to the quaternary carbon substituted by a sulfur and two *tert*-butyl groups. In the absence of unsaturation, the molecular formula can be accommodated only by a cyclic structure. On the basis of the above spectral properties, the structure is assigned to be 2-methoxy-3,3-di-*tert*-butylthiirane (**2a**). Raney nickel desulfurization of **2a** gave 2,2-di-*tert*-butylethyl methyl ether as a major product, which was identified on the basis of its spectral properties. This provided further support to the above structural assignment.

The thio esters formed on photolysis were found to be identical with the authentic compounds prepared by an independent method.[3,7] The structural elucidation of 2,2-di-*tert*-butylthioacetophenone (**5a**) is presented in detail below. Compounds **5b** and **5c** possess analogous spectral properties. 2,2-Di-*tert*-butylthioacetophenone (**5a**) is formed as a major product in the photolysis of di-*tert*-butylthioketene in benzene. **5a** has the molecular ion peak at m/e 248 in the mass spectrum (electron ionization, 70 eV) corresponding to the molecular formula $C_{16}H_{24}S$, indicating the addition of a benzene molecule to thioketene. The presence of a phenyl-substituted thioketone moiety is apparent from the absorption spectrum (cyclohexane; λ_{max} 595 nm) and ^{13}C NMR spectrum (δ 252.5, 151.7), the signal at δ 151.7 corresponding to the thioketone-substituted carbon on benzene. A singlet at δ 4.0 corresponding to one hydrogen in the ^{1}H NMR spectrum indicates that hydrogen could be α to both the thioketone as well as to the two *tert*-butyl groups. ^{13}C NMR data at δ 72.0 (d) favors this assignment. The two *tert*-butyl groups appear as a singlet at δ 1.1 (18 H). On the basis of these spectral features, the structure has been assigned as 2,2-di-*tert*-butylthioacetophenone (**5a**). The presence of a strong characteristic McLafferty fragmentation signal at 192 mass units due to the loss of isobutylene further supports the proposed structure.

The structure of 2,2,7,7-tetramethyl-3,6-di-*tert*-butyl-4,5-octanedione (**4a**) is described below. Product **4b** has an analogous structure. **4a** is formed as a minor product in the photolysis of **1a** in alcoholic solvents and as the only isolable product in nonhydroxylic solvents. **4a** is a white crystalline solid (mp 65 °C) and has the molecular ion peak at m/e 310 in the mass spectrum (electron ionization, 40 eV) corresponding to molecular formula $C_{20}H_{38}O_2$, indicating a dimeric structure of **1a** in which sulfur is replaced by oxygen. The presence of ketone is shown by the IR spectrum (1720 cm^{-1}) and by a quaternary carbon peak at δ 181.3 in the ^{13}C NMR spectrum. ^{1}H NMR exhibits two singlets at δ 1.1 (18 H) and 2.2 (1 H), while ^{13}C NMR displays only four signals indicating a symmetric structure for the product. The presence of a diketone is indicated by the doublet at 1720 cm^{-1} in the IR spectrum, and the symmetric nature of the diketone is apparent by the appearance of a single peak at δ 181.3 in the ^{13}C NMR spectrum. On the basis of these spectral characteristics, the structure has been assigned to be 2,2,7,7-tetramethyl-3,6-di-*tert*-butyl-4,5-octanedione (**4a**). A strong signal at 155 mass units corresponding to half the molecular weight of **4a** in the mass spectrum further supports this structural assignment.

Reactive State. Since it has been well established that thiocarbonyls are capable of reacting from higher and lower excited states,[8] the possibility of reaction occurring from S_2, T_2, S_1, and T_1 excited states were considered. The products shown in Schemes I and II were formed only when thioketenes were excited to the S_2 state (220 nm). Selective excitation of **1a** and **1b** to the $n\pi^*$ singlet state using a 500-W tungsten lamp or a 450-W medium-pressure mercury lamp with Corning glass filter CS-3.70 (>480 nm) in all the above solvents in sealed Pyrex tubes for a period of 1 month did not result in any reaction. This establishes that the lowest singlet state S_1 is not the reactive species. Triplet senesitization in methanol and benzene was conducted with benzil (E_T, 53 kcal/mol), Michler's ketone (E_T, 62 kcal/mol), and benzophenone (E_T, 69 kcal/mol). None of the above sensitizers brought about any change in **1a** and **1b** suggesting that the lowest triplet T_1 is not the reactive state.

The lowest triplet and singlet excluded, S_2 itself or higher states in the triplet manifold must now be considered as the chemically active state. Since the energy of S_2 is ~105 kcal/mol and that of S_1 is ~46 kcal/mol, the energy of any chemically active higher triplet must be between these limits. Due to absorption problems and other difficulties, an unambiguous triplet quencher for this range was not available. Again because of absorption problems only two triplet sensitizers namely xanthone (E_T, 74 kcal/mol) and acetone E_T, 79 kcal/mol) could be used. Xanthone and acetone effected some change only after 24 h of irradiation. Excitation of these sensitizers in the presence of **1a** in methanol gave **2a** and **4a** in extremely low yield (~5%), and importantly **3a** was not among the products. Similarly, in benzene **5a** and **4a** were formed in low yields (~5%). Since these sensitizations did not result in the same product distribution as upon direct irradiation (>220 nm), we believe that the reaction may not truly be a triplet process. Therefore, we tentatively regard the higher excited state S_2 as the reactive state upon direct excitation.

Mechanism. For a complete understanding of the photochemistry of thioketenes, it is necessary to have information on the nature of their potential surfaces for the ground and excited states as a function of geometrical parameters. Although on the basis of theoretical calculations some knowledge on the ground and excited triplet states of thioketene is available,[9] little is known regarding the excited singlet state potential energy surfaces. Since the products in the present study are established to derive

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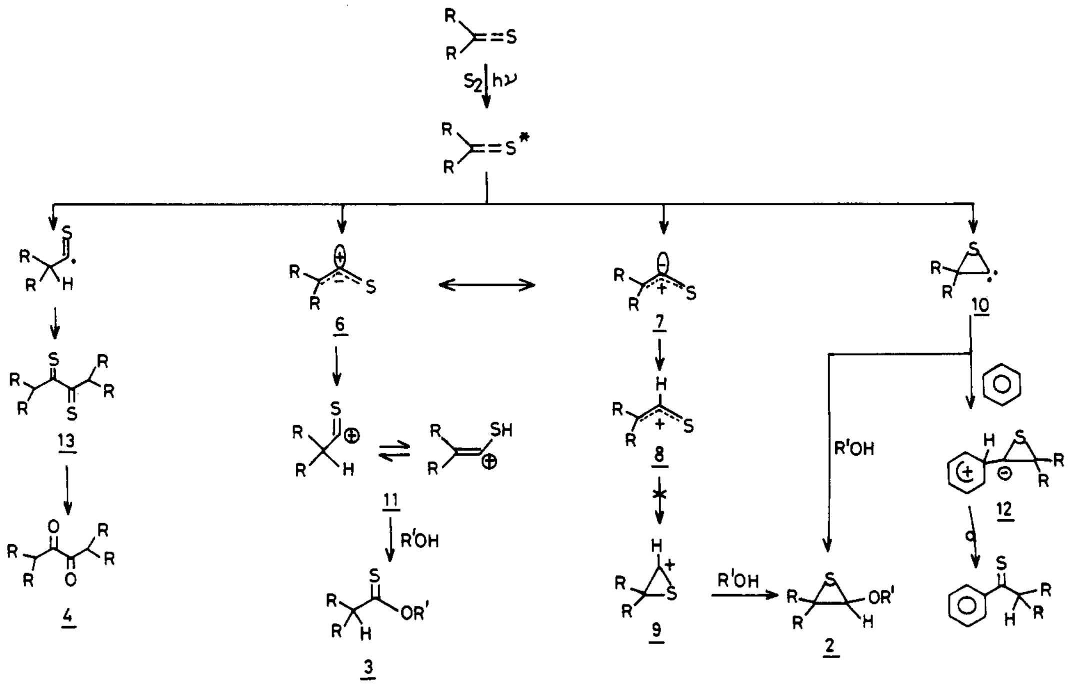
Scheme III. Proposed Mechanism for the Formation of Products from Excited State of Thioketenes



from the second excited singlet state, their mechanistic discussion is limited by the absence of such useful information. Therefore, although it is speculative, one could benefit by extrapolating the theory of ketene and allene, structurally analogous systems, to thioketenes. Detailed ab initio FORS MCSCF and CI calculations have recently been reported[10] for low lying electronic states of allene. Previously in addition to a number of semiempirical calculations,[11] ab initio[12] studies of allene excited states have also been reported. Allenes, like most alkenes, have long been believed to twist to planar geometries in their lowest singlet and triplet excited states. Recent calculations have established that in addition to the planar geometry (with D_{2h} symmetry), another minimum with a bent (C_{2v}) geometry is present in the excited singlet surface. Furthermore, these two nearly isoenergetic minima (D_{2h} and C_{2v}) are strongly polarized but in opposite directions. The lowest singlet and triplet states of ketenes have been predicted on the basis of ab initio SCF and SCF–CI calculations[13] to be planar with C_s symmetry. Furthermore, the molecule is bent (∠C–C–O 130°) in the molecular plane. In the excited state, the negatively charged methylene carbon of the ground state becomes positively charged while the carbonyl carbon positively charged in the ground state becomes negatively charged in the excited state. Interestingly, a bent geometry appears to be preferred in the excited singlet states of both allene and ketene. Recent theoretical study (SCF gradient and CI methods)[9] on thioketene triplet also suggests that the optimized geometry for the lowest triplet state of thioketene corresponds to a bent geometry (∠C–C–S 137.1°). However no information is available regarding the preferred geometry of the excited singlet state, which is the point of interest in this study. On the basis of the information available on the excited-state potential energy surfaces of ketenes and allenes, we have proposed a simple mechanism for the formation of products **2**–**5** from the second excited singlet state of thioketenes (Scheme III). Such a mechanism involves thiiranylidene carbene **10** and zwitterions **6** and **7** as intermediates.

The above discussion, is consistent with the involvement of thiiranylidene carbene **10** as an intermediate in the photoreactions of thioketenes. If the bent geometry is indeed preferred in the excited singlet state of thioketene, as has been suggested in the case of allenes and ketenes, an intramolecular rearrangement of the bent thioketene to thiiranylidene carbene seems likely. On the basis of theoretical calculations energies of singlet and triplet thiiranylidene carbene have been computed.[9] While the energy of the singlet carbene **10** is estimated to be 45.2 kcal/mol with respect to ground state thioketene, that of triplet **10** is 76.6 kcal/mol. These energies are reliable as there is an excellent agreement between the computed (42.6 kcal/mol) and experimental (43–45 kcal/mol) triplet energies of thioketene. The lowest triplet would not be expected to give carbene **10** as it involves an endothermic process. On the basis of the above energy consideration, formation of **10** via a bent geometry of the S_2 thioketene seems probable. Substituted thiiranes and thioacetophenones are products resulting from trapping of this novel intermediate (**10**). Addition of alcohols to thioketenes is undoubtedly an excited state process as no addition occurs at room temperature (in the absence of light) even in the presence of acids. Most probable pathway for the formation of thiobutyric acid ester **3** appears to be via the zwitterionic intermediate **6**. Two zwitterionic intermediates **6** and **7** have been invoked on the basis of the presence of similar polarized intermediates in the singlet excited states of allene. While both zwitterionic forms **6** and **7** may exist in the singlet excited surface of thioketene, the product corresponding to **6** alone has been identified. Products corresponding to protonation of the central carbon in **7** have not been isolated. Protonation of **7** would lead to thioacyl carbenium ion **8**, which on reaction with OR$^-$ could give thioaldehyde. Although thioaldehydes possessing bulky substituents have been reported to be

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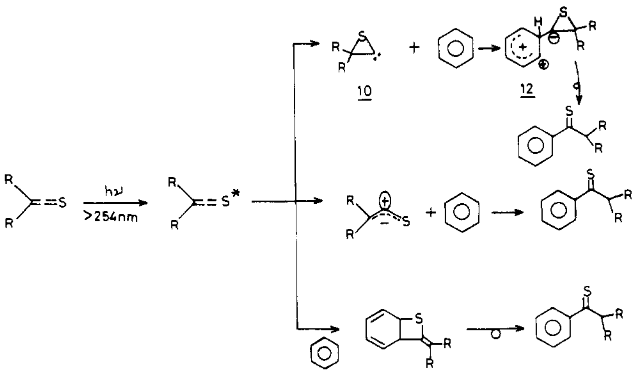
Scheme IV. Mechanism of Addition of Thioketene to Benzene



stable,[14] we did not isolate any such products upon photolysis of thioketene. Another likely pathway for the decay of **7** is electrocyclization to thiiranylidene carbene **10**. However, an alternative pathway, namely, the direct cyclization of the excited thioketene to **10**, seems more probable. Thus on the basis of product studies we speculate that thioketenes in the excited singlet states possess a bent geometry and have a minimum corresponding to a zwitterionic species. Potential involvement of a polarized state corresponding to **7** is not warranted by the products isolated.

For the sake of clarity the mechanisms leading to the formation of each products are briefly summarized below (Schemes III and IV). Substituted 2-alkoxythiiranes are formed by trapping of the thiiranylidene carbene by alcoholic solvents. An alternative pathway involves protonation of zwitterion **7** to form α-thioacyl carbenium ion **8**. Alkoxythiiranes can be formed by the addition of alcohol to α-thia carbenium ion **9**, which in turn is formed by the cyclization of **8**. On energy grounds, this appears to be less likely, since the α-thioacyl carbenium ion (**8**) which is isomorphous to allyl cation is not expected to form a relatively unstable and strained three-membered α-thia carbenium ion **9**. Therefore the pathway involving thiiranylidene carbene **10** appears more probable. Thio esters (**3**) are formed by the capture of the zwitterion (**6**) by alcoholic solvents. The first step involves the protonation of **6** to give thioacyl carbenium ion **11**. Thio esters are formed from **11** through the addition of alcohols. On the other hand, when the irradiation is conducted in benzene thiiranylidene carbene **10** is trapped by benzene to form an intermediate **12**, which rearranges to substituted thioacetophenones. Thioacetophenones can also be formed by the capture of the zwitterion (**6**) by benzene. The addition of carbenes to aromatic systems is known. On the basis of energy grounds the electrophilic substitution of benzene by **10** is more probable than the addition of benzene to zwitterion **6**. An alternative pathway involves the addition of thioketene in a (2 + 2) fashion to benzene to form an adduct (Scheme IV) that can be expected to undergo rearrangement to **5**. Though we cannot rule out this mechanism, it would be appropriate to point out that allenes undergo meta cycloaddition to excited benzene.[15] Photoreduction of thioketene leads to the formation of a thioacyl radical which dimerizes to α-dithiones **13**. However, under our experimental conditions facile oxidation of **13** occurs to yield α-dione **4**. Ground-state oxidation of thiones by oxygen has been documented.[16]

It is appropriate to compare the excited-state behavior of thioketenes, ketenes, allenes, and other heterocumulenes.[2] These cumulated systems have been proposed to have a zwitterionic minima in their excited-state surface. Label scrambling on excitation of ketenes has been rationalized by invoking the intermediacy of oxiranylidene carbene and oxirene. However, these intermediates have neither been trapped nor detected. Cyclic allenes cyclize from their triplet state to form cyclopropylidene carbene, which is trapped intramolecularly. Sulfines also cyclize on excitation to a novel three-membered heterocyclic system.[17] The present results demonstrate that thioketenes also cyclize to thiiranylidene carbene when excited to the S_2 state. In this respect the excited-state behavior of these cumulated systems are similar. However the differences are many. The major pathway of an excited ketene is to extrude carbon monoxide while allenes undergo diverse reactions which include concerted cyclization to cyclopropenes and 1,2-shifts to vinyl carbenes. Thioketenes exhibit a different behavior. They undergo photoreaction from the S_2 state and do not eliminate carbon monosulfide nor undergo concerted cyclization to thiirene or 1,2-shift to thioketone carbene.

Conclusions

The photochemistry of a few thioketenes in solution has been established for the first time. Thioketenes are photoactive only from their higher excited singlet state (S_2). Photorearrangement to thiiranylidene carbene is unique. The formation of thioester is a photochemical process. Structurally interesting products like α-dithione vis-à-vis α-diketone and sterically congested aryl alkyl thioketones are formed from the excited thioketene. The excited thioketene resists carbon monosulfide elimination but undergoes rearrangement. In this respect it resembles the photochemistry of substituted cyclopropenethiones and cyclobutanethiones.[18] Thus the light-induced reactions of thioketene are distinctive and cannot be extrapolated from that of structurally analogous ketenes and allenes.

Experimental Section

General Photolysis Procedure. All the irradiations were carried out at room temperature (~30 °C) in quartz tubes using low-pressure mercury arc lamps (>220 nm) in nitrogen atmosphere. Selective excitation to $n\pi^*$ singlet state was conducted with 500-W tungsten lamps or 450-W medium-pressure mercury arc lamp. Rayonet RPR 3000-Å low-pressure mercury lamps were used in sensitization experiments. A Corning glass filter (CS-3.70) was used to isolate bands above 480 nm from a 450-W medium-pressure mercury lamp for selective excitation. Progress of the reaction was monitored by TLC (silica gel, hexane), and in general after ~20% conversion the reaction was discontinued. The solvent was evaporated, and the products were isolated by repetitive column and thin-layer chromatography (silica gel, hexane) and identified on the basis of their spectral properties or by comparison with authentic samples wherever accessible.

Photolysis of Thioketenes 1a and 1b. A solution of thioketene **1a** or **1b** (0.02 M) in alcoholic solvents (methanol, ethanol,

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and isopropyl alcohol) or in nonhydroxylic solvents (acetonitrile, cyclohexane, dioxane, and tetrahydrofuran) was irradiated (after the solution was thoroughly purged with N_2 for 30 min) in a quartz tube with a low-pressure mercury arc lamp to approximately 20% conversion. After the irradiation, the solvent was distilled off, and the products were separated and purified by preparative TLC (silica gel, hexane). Generally it was not possible to separate thiiranes **2** from thioesters **3**. Only in the case of **1a** could thiirane **2a** and thioester **3a** be separated by repeated column chromatography. In the case of the other thioketenes (**1b** and **1c**) the spectra of the mixture were recorded. Products formed; their yields are shown in Schemes I and II, and the spectral data of the products are provided in Table I. Analytical data for **2–5**, where they could be obtained pure, are provided below.

Anal. Calcd for $C_{11}H_{22}SO$ (**2a**): C, 65.31; H, 10.96. Found: C, 64.98; H, 10.27. Anal. Calcd for $C_{11}H_{22}SO$ (**3a**): C, 65.31; H, 10.96. Found: C, 65.54; H, 11.02. Anal. Calcd for $C_{20}H_{38}O_2$ (**4a**): C, 77.36; H, 12.33. Found: C, 77.78; H, 12.05. Anal. Calcd for $C_{22}H_{38}O_2$ (**4b**): C, 78.99; H, 11.45. Found: C, 78.12; H, 11.61. Anal. Calcd for $C_{16}H_{24}S$ (**5a**): C, 77.38; H, 9.74. Found: C, 77.64; H, 9.64. Anal. Calcd for $C_{17}H_{24}O_2$ (**5b**): C, 78.42; H, 9.29. Found: C, 77.98; H, 9.56. Anal. Calcd for $C_{15}H_{22}O_2$ (**5c**): C, 76.88; H, 9.46. Found: C, 77.02; H, 9.38.

Photolysis of Thioketenes in Benzene. A solution of thioketene **1a** or **1b** (0.1 M) in benzene was irradiated under above conditions to 10% conversion. The workup, separation, and characterization of products were done in an analogous manner. Products and their yields are given in Schemes I and II. Spectral data are provided in Table I.

Control Experiment. Solutions of thioketenes **1a** and **1b** (0.02 M) in methanol, benzene, and acetonitrile were kept in dark at room temperature (30 °C). After 4 days the solutions were checked spectrophotometrically (monitored at 570 nm). Practically no change in the OD was observed, indicating that products **2–5** were derived from light-induced reaction of thioketenes and not by thermal means. Even refluxing in the above solvents for 6 h did not show any change.

Selective Excitation and Sensitization Studies: Selective Excitation to S_1. Solutions of **1a** and **1b** (0.02 M) in solvents (methanol, ethanol, acetonitrile, cyclohexane, dioxane, tetrahydrofuran, and benzene) were degassed and sealed in Pyrex tubes. Irradiation was conducted for about 30 days either with 500-W tungsten lamps or with a 450-W medium-pressure mercury arc lamp with Corning glass filter C.S.-3.70. No reaction could be detected both by UV (OD at 570 nm) and by ^1H NMR. Therefore S_1 is excluded as the reactive state.

Sensitization Studies. Triplet sensitization was carried out only in benzene and methanol. Benzil (53 kcal/mol), Michler's ketone (62 kcal/mol), benzophenone (69 kcal/mol), xanthone (74 kcal/mol), and acetone (79 kcal/mol) were used as sensitizers. In a typical experiment, a solution of thioketene **1a** or **1b** (100 mg, 0.03 M) and sensitizer (0.01 M) in methanol and benzene (40 mL) was irradiated after bubbling with nitrogen for 30 min (Rayonet RPR 3000-Å low-pressure mercury arc lamps). Under analogous conditions 10 mL of acetone and 100 mg of thioketene in 40 mL of methanol and benzene was irradiated. Under these conditions only the sensitizer is excited. A blank solution was also irradiated in an identical manner. After 24 h these solutions were analyzed spectrophotometrically and by ^1H NMR. No reaction could be detected both in the blank solution and in the solution containing the sensitizers benzil, Michler's ketone, and benzophenone. Partial reaction was detected in the case of xanthone and acetone as sensitizers. Under these conditions in methanol only **2** and **4** were formed in low yields (~10%) while **3** was not formed. In benzene **4** and **5** were obtained in low yields (~10%). In brief, acetone- and xanthone-sensitized reactions were very slow, the product yields were low, and moreover, **3** was not formed in methanol. Therefore it was concluded that the reaction is not a triplet process.

Preparation of Thio Esters 3a and 3b.[7] A solution of thioketene **1** (200 mg) in 25 mL of dry methanol containing a drop of sulfuric acid was refluxed for 1 h. The reaction mixture was passed through anhydrous sodium sulfate to remove acid and evaporated. The thio ester thus obtained (yield 90%) was purified on preparative TLC. The spectral data are summarized in Table I.

Raney Nickel Desulfurization of 2a. To a solution of 150 mg of **2a** in 25 mL of petroleum ether (40–60 °C) was added excess of Raney nickel (1 g), and the mixture was refluxed for 12 h. After the reaction, the catalyst was removed by filtering through Whatman No. 1 filter paper and the solvent evaporated. The colorless liquid was purified by TLC (silica gel, hexane) to give 70 mg (yield 50%) of a volatile product identified to be 2,2-di-*tert*-butylethyl methyl ether on the basis of its spectral properties: mass spectrum (70 eV), 172, 116, 101, 57 mass units; ^1H NMR (CCl_4) δ 1.0 (s, 18 H), 2.2 (t, 1 H), 3.2 (s, 3 H), 3.35 (d, 2 H); IR (neat) 2970, 1470, 1380, 1230 cm^{-1}.

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Registry No. **1a**, 16797-75-4; **1b**, 54440-00-5; **1c**, 54439-99-5; **1d**, 57738-75-7; **2a**, 88181-00-4; **2b**, 98687-81-1; **2c**, 98687-82-2; **2d**, 98687-84-4; **2e**, 98687-85-5; **2f**, 98687-86-6; **2g**, 98687-92-4; **3a**, 16797-77-6; **3b**, 16797-70-9; **3c**, 98687-93-5; **3d**, 98687-87-7; **3e**, 98687-88-8; **3f**, 98687-89-9; **3g**, 98687-94-6; **4a**, 29679-00-3; **4b**, 98687-83-3; **5a**, 88181-01-5; **5b**, 98687-90-2; **5c**, 98687-95-7; **14**, 98687-91-3.

6,6-Dimethyl-2,4-diphenylcyclohexadienyl Anion and the Failure of Carbanion Homoaromaticity

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The title carbanion was generated by methyllithium deprotonation of 6,6-dimethyl-2,4-diphenyl-1,4-cyclohexadiene in tetrahydrofuran. Attempted generation of the identical carbanion using potassium (methylsulfinyl)methide in Me_2SO led to cyclopropanation only via isomerization to the 1,3-diene followed by addition/elimination of (methylsulfinyl)methide anion. Except for modest changes in carbon chemical shifts, the title compound exhibits little thermodynamic driving force toward ring closure or homoaromaticity. The NMR spectra at all temperatures were consistent with a planar nonaromatic anion, again failing to establish the existence of homoaromaticity in such carbanions.

Unconventional forms of aromaticity—e.g., spiroaromaticity, Y-aromaticity, homoaromaticity, antiaromaticity—have been significant in testing theoretical concepts against the demands of experiment. Of the