Photochemical, Photophysical, and Theoretical Studies on Cyclobutanethiones: α-Cleavage Reactions

Bantu Nageshwer Rao, Jayaraman Chandrasekhar,* and Vaidhyanathan Ramamurthy*†

Department of Organic Chemistry, Indian Institute of Science, Bangalore-560 012, India

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Photophysics and photochemistry of cyclobutanethiones 1–5 have been studied with the view to generalize the α-cleavage reactions of cyclobutanethiones. The above cyclobutanethiones possess a unit intersystem crossing efficiency from S_1 to T_1, a high self-quenching rate ($\sim 4 \times 10^9$ M^{-1} s^{-1}), and a short triplet lifetime (<0.50 μs). Photolysis of 1–5 yields in benzene a product resulting from 1,3-transposition and in methanol two cyclic thioacetals. The origin of these products is traced to the triplet excited state. A mechanistic scheme involving α-cleavage as the primary photoprocess and diradicals and thiacarbenes as intermediates has been formulated to rationalize the formation of thioacetals and rearranged products. The proposed mechanistic scheme is supported by UHF MINDO/3 calculations performed on four model systems, cyclobutanethiones and 1,3-cyclobutanedithiones 18–21. These calculations indicate that formation of diradical is favored thermodynamically and kinetically for systems analogous to 19 and 21, while rearrangement to thiacarbene is likely only for those similar to 21.

The Norrish type I α-cleavage process is one of the most commonly observed phototransformations involving carbonyl compounds. However, most cyclic and acyclic thiocarbonyl compounds generally resist undergoing such a reaction.[1] The process has been observed only in a few highly strained ring systems such as cyclobutanethiones[2] and cyclopropenethiones[3]. α-Cleavage reactions of carbonyls have found innumerable application in the synthesis of strained and energy-rich organic molecules and natural products. Thiocarbonyls having absorption in the visible region provide considerable scope to conduct similar syntheses with visible light and in the presence of other chromophores which might absorb only in the UV region. In an attempt to generalize the photofragmentation reactions of cyclobutanethiones, the photophysics and photochemistry of substituted cyclobutanethions 1–5 were investigated and the results are presented here. Flash photolysis studies[4] were conducted to obtain information on the excited state properties of cyclobutanethiones. These were also utilized to search for possible intermediates in the α-cleavage process. Theoretical calculations were performed to obtain some knowledge on the mechanism of α-cleavage. The main goal was to obtain an understanding of the thermodynamic, electronic, and kinetic factors determining the formation of different photoproducts by an examination of selected key regions of the excited hypersurface of cyclobutanethiones and dithiones using the UHF MINDO/3 method.[5] We envision that the present combined experimental and theoretical examination would provide a comprehensive understanding of the excited state behavior of small ring thiocarbonyls.

Results

In continuation of our photochemical investigation on cyclobutanethiones,[2] a study of the photophysical and photochemical behavior of differently 3-substituted tetramethylcyclobutanethione, 14-substituted dispiro-[5.1.5.1]tetradecane-7-thione, and 12-substituted dispiro-[4.1.4.1]dodecane-6-thione was undertaken. Substituents at these positions included dicyanomethylene, cyanocarboethoxymethylene, carbonyl, and phenylimino groups. However, due to difficulties encountered in the stability of some of these thiones and/or products resulting from them, thioketones 1–5 (Schemes I–III) alone could be investigated in detail.

In order to clarify the mechanistic possibilities, UHF MINDO/3 calculations were performed on four model systems, cyclobutanethiones and 1,3-cyclobutanedithiones 18–21. The results for 18 and 20 reflect the intrinsic reactivity preferences of small ring monothiones and 1,3-dithiones. The conclusions derived for 20 are likely to be applicable for the related 3-methylenecyclobutanethione as well. Calculations on the dimethyl derivatives 19 and 21, which most closely resemble the experimentally examined molecules, help to understand the key role of alkyl groups in determining the overall reactivity pattern.

Photophysical Properties. The electronic absorption spectra of 1–4 display three absorption band systems in the 220–600 nm region in cyclohexane and methanol. The absorption spectral data along with other spectral data for these thiones are provided in Table I. For example, 1a possesses three bands with λ_{max} at 503, 301, and 229 nm. Similarly 3 has absorptions at 530, 328, and 228 nm (λ_{max}). On the otherhand, 5 shows only two absorption bands with λ_{max} at 518 and 226 nm. The weak nπ* bands ($\epsilon \sim 10$ M^{-1} cm^{-1}) of all five thioketones are well seperated from the intense ππ* band systems lying at higher energies (220–270 nm). In between these two bands, a band of medium intensity ($\epsilon \sim 100$–300 M^{-1} cm^{-1}) is found for 1–4. In the case of 3 and 4, this band may be attributed to the nπ* transition of the carbonyl chromophore. The transition responsible for this band in the case of 1 and 2 is not obvious.

No emission was seen in 1–5 at room temperature in cyclohexane or 3-methyl pentane. However, a moderate emission (590–700 nm) was detected in all of these cases at 77 K in a glassy matrix (3-methylpentane). The exci-

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<center>Table I. Spectral Data of Cyclobutanethiones 1-5</center>

thione	mp (°C)	UV (MeOH) λ_{max}, nm (ϵ, M^{-1} cm^{-1})	IR (cm^{-1})	^1H NMR (CCl_4)[c] (δ)	^{13}C NMR ($CDCl_3$)[c] (δ)
1a	134–136	503 (11), 301 (376), 229 (3653)	[a]2250, 1640, 1300, 1140	1.58 (s)	268.8 (s), 198.65 (s), 110.0 (s), 82.2 (s), 68.2 (s), 24.03 (q)
1b	83	496 (8), 306 (376), 229 (2339)	[a]2240, 1735, 1645, 1230, 1150	1.43 (t, 3 H), 1.52 (s, 6 H), 1.54 (s, 6 H), 4.32 (q, 2 H)	
2a	86–87	496 (10), 303 (388), 237 (7692)	[a]2250, 1635, 1180, 1130	1.55–2.35 (bm)	270.6 (s), 199.7 (s), 110.3 (s), 79.7 (s), 76.6 (s), 39.5 (t), 27.6 (t)
2b		496 (8), 301 (370), 236 (3043)	[b]2240, 1730, 1640, 1370, 1270, 1100	1.39 (t, 3 H), 1.6–2.5 (bm, 16 H), 4.23 (q, 2 H)	
3		530 (10), 328 (110), 272 (350), 228 (8700)	[b]1810, 1780, 1460, 1300, 1130	1.33 (s)	272.8 (s), 216.1 (s), 76.8 (s), 22.4 (q)
4		528 (9), 330 (115), 275 (340), 226 (8420)	[a]1780, 1240, 1120, 980	1.70 (bm, 20 H)	
5		518 (9), 226 (3340)	[b]1710, 1670, 1220, 1120	1.2 (s, 6 H), 1.5 (s, 6 H), 6.5–7.43 (m, 5 H)	

[a] Nujol. [b] Neat. [c] s = singlet; t = triplet; q = quartet; m = multiplet; bm = broad multiplet.

tation spectra corresponded to their absorption spectra, thus confirming the origin of the emission to be from 1–5. This emission which was independent of the excitation band is believed to be phosphorescence. Importantly, even in the case of 3 no emission corresponding to the carbonyl chromophore was seen. Consistent with this, as to be outlined below, transients corresponding to the triplet of the thiocarbonyl chromophore alone were seen during a flash photolysis investigation of 3. absence of fluorescence from higher excited singlet S_2 and from lower excited singlet S_1 of 1–5 is consistent with the previous reports,[6] suggesting that dialkyl thiones rarely emit from S_2 and S_1. The energies of S_1 and T_1 of 1–5 are estimated to be in the range of 50–55 and 48–52 kcal/mol^{-1} respectively based on absorption and emission spectra.

Thioketones 1a, 1b, 3, and 5 were flash photolyzed[4] by exciting them into the nπ* band by using high intensity laser pulses at 532 nm. A few experiments were also performed by exciting them into the second band (337.1 nm, N_2 laser). Laser flash photolysis (532 nm) of benzene solutions (0.001 M) of the above thioketones resulted in the formation of short-lived transients. The transient absorption spectra were recorded by averaging kinetic traces from 20 to 30 laser shots at each monitoring wavelength. the spectra of all these four thioketones were similar. All four spectra showed similarity both in location and appearance. Intense absorption in the 250–700 nm region was seen with λ_{max} centered around 400–420 nm in all cases. These transients are assigned to be triplets based on efficient self-quenching, quenching by oxygen, and by all-trans-1,6-diphenyl-1,3,5-hexatriene (DPH). No phosphorescence emission was seen from any of these compounds under flash photolytic conditions. Since diradicals and/or carbenes are suspected to be the primary intermediates from α-cleavage of cyclobutanethiones (see below), attempts were made to detect these intermediates upon flash photolysis (532, 337.1, and 266 nm). Under all these excitations, absorptions only due to triplets were observed.

The quantum yield of intersystem crossing from S_1 to T_1 and the rate of self-quenching were estimated indirectly by energy transfer to DPH. The procedure adopted involved monitoring the transient absorbance due to the DPH triplet at 420–430 nm.[7] This was necessary as the signals due to cyclobutanethiones were weak and deteri-

<center>Table II. Kinetic Data Concerning Cyclobutanethione Triplets in Benzene</center>

compd	τ (μs)[a]	$10^9 k_{sq}$ (M^{-1} s^{-1})	$10^9 k_{DPH}$ (M^{-1} s^{-1})	ISC[b] ($S_1 \rightarrow T_1$)
1a	0.20 (0.50)	3.3	5.7	1.2
1b	0.50 (0.30)	4.0	5.8	1.1
3	0.50 (0.30)	3.5	7.7	1.0
5	0.50 (0.80)	2.0	6.5	1.0

[a] Lifetime estimated from the plots of k_{obsd}^T vs [TK] and k_{obsd}^T vs [DPH]. Values in parentheses correspond to the latter; error ±20%. [b] Estimated using p,p'-dimethoxythiobenzophenone as the standard; error ±25%.
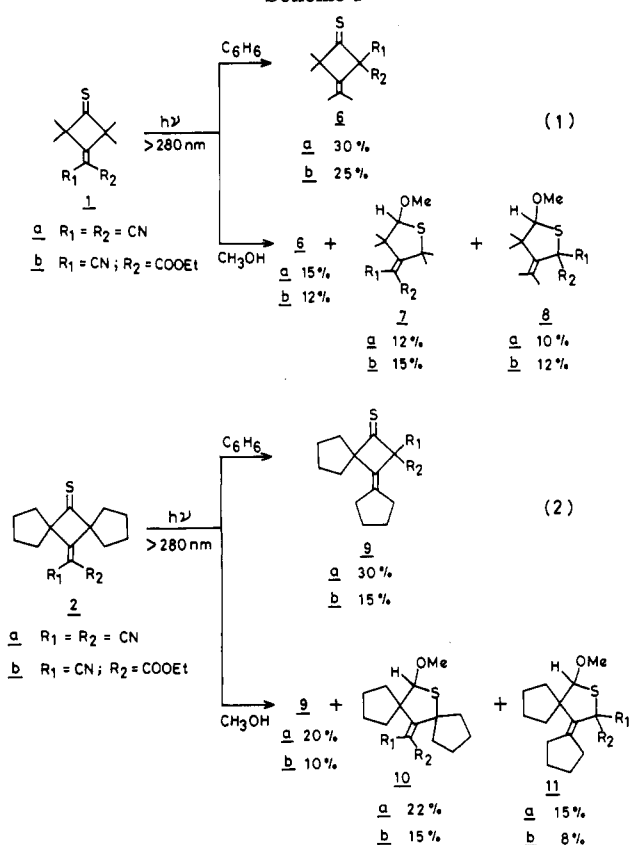
oration of the sample occurred upon large number of pulses. For triplet yields, 4,4'-dimethoxythiobenzophenone in benzene was used as the reference.[8] Using solutions of cyclobutanethiones and 4,4'-dimethoxythiobenzophenone with optical densities matched at 532 nm, the maximum absorbance changes due to the DPH triplet at 420 nm were measured at [DPH] ranging from 0.0025 to 0.02 M. From the linear plots of $1/\Delta OD_{DPH}^T$ vs $1/[DPH]$ the relative intersystem crossing efficiencies were obtained. Knowing the triplet yield of the reference (1.00), those of the others were estimated. Results are given in Table II. The intersystem crossing efficiencies thus estimated were within ±20% of unity. The intrinsic lifetimes of the thioketone triplets were estimated by two independent methods. First with [TK] = 0.001 M, k_{obsd}^T (the pseudo-first-order rate constant) for the growth of DPH triplet absorption as a result of energy transfer from thioketone triplet to DPH were measured for a series of solutions containing variable concentrations of DPH (0.0005–0.004 M). Slopes of plots of k_{obsd}^T vs [DPH] gave the bimolecular energy transfer rate constants from thioketone triplets to DPH and intercepts correspond to the lifetime of the triplets at 0.001 M concentration. Secondly, k_{obsd}^T were obtained for a series of solutions containing variable thioketone concentration (0.0005–0.005 M) and fixed DPH concentration (0.001 M). Slopes of the linear plots of k_{obsd}^T vs [TK] correspond to k_{sq}^T. Data concerning k_{sq}^T and k_{DPH}^T are given in Table II. Intrinsic triplet lifetimes (τ°) were obtained from these two linear plots knowing k_{sq}^T and k_{DPH}^T. The numbers thus estimated are shown in Table II. The disagreement between the two sets of values (Table II) is a reflection of large errors associated with the way they are measured. In spite of the disagreement, both sets suggest submicrosecond intrinsic lifetimes for all four thioketones. Also, the direct monitoring of transient ab-

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Scheme I

Figure 1. Potential energy diagram for the α-cleavage of cyclobutanethiones.

Figure 2. Potential energy diagram for the α-cleavage of α,α'-dimethylcyclobutanethione.

Scheme II

sorption at 0.001 M of thioketone using 532-nm laser excitation gave lifetimes (τ) in reasonable agreement with those measured from DPH quenching.

Photochemical Behavior. Molecules 1a, 1b and 2a, 2b exhibit similar photochemical behavior and, therefore, their results are presented together (Scheme I). Irradiation of 1 and 2 (450-W medium pressure mercury lamp; 280 nm) in benzene resulted in a clean rearrangement to yield products 6 and 9, respectively, via 1,3-migration. Structures of products were deduced from their spectral properties (Table III). Similar irradiation in methanol resulted in the formation of two cyclic thioacetals in easch case (7, 8 and 10, 11, respectively) in addition to 1,3-migration products (Scheme I). Irradiation of the corresponding carbonyl compounds are reported[9] to yield products from the trimethylenemethane intermediate. However, no such products were obtained from 1 and 2. Selective excitation into the S_1 band (Corning filter CS-3.70) and triplet sensitization of 1a (biacetyl, 2-acetylnaphthalene, fluorenone, or benzil as sensitizers; Corning filter CS-7.60) yielded the same set of products as shown in Scheme I. Furthermore, product formation from 1a both in benzene and methanol was quenched by triplet quenchers cyclooctatetraene and alloocimene. Therefore, it was concluded that the reaction originates from T_1. We assume that this conclusion can be extended to 1b, 2a, and 2b.

Behavior of 3 and 4 was similar upon photolysis (Schemes II and III). For example, irradiation of 3 in the nπ* band of the thiocarbonyl group (<460 nm, Corning filter CS-3.70; 450-W medium pressure mercury lamp) in benzene gave a sulfur incorporating product 12 and β-thionolactone 13 (Scheme II). Similar irradiation in
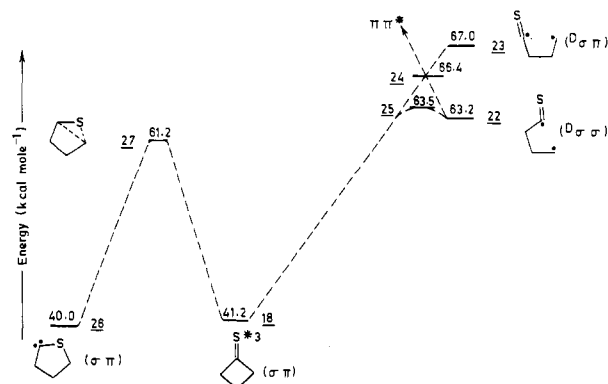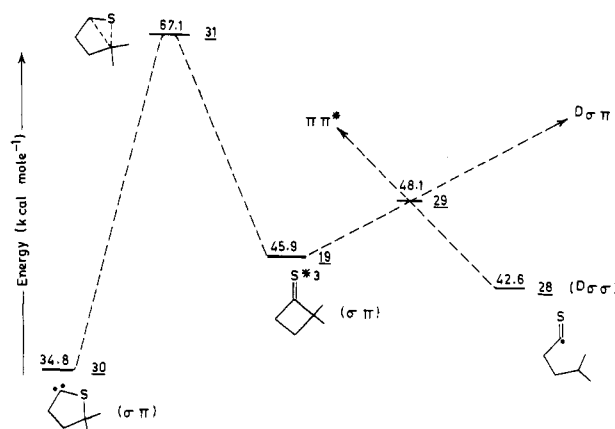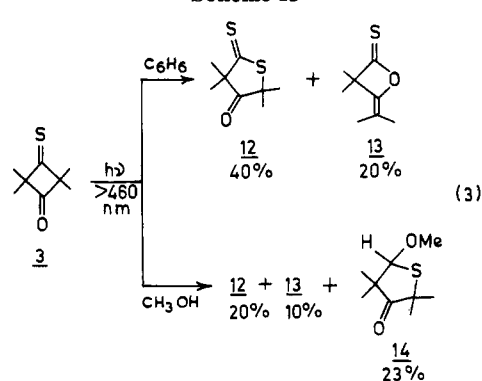
methanol gave a 1:1 adduct of thioacetal 14 along with 12 and 13. No evidence for the formation of dimethylketene and dimethylthioketene was obtained. Products were identified by their spectral properties (Table III). Similar product distribution was obtained in the case of 4 (Scheme III) upon excitation in the long wavelength band. Quenching experiments (λ >480 nm) with alloocimene and cyclooctatetraene as triplet quenchers demonstrated that the products 12, 13, and 14 were formed from the lowest excited triplet state of 3.

Photolysis of 5 in benzene gave the 1,3-migration product, thiolactam 17. Because of poor stability of 5 in methanol, its photolysis in methanol could not be conducted. The spectral data of the 1,3-migration products and the solvent adducts from 1 to 5 are summarized in Table III.
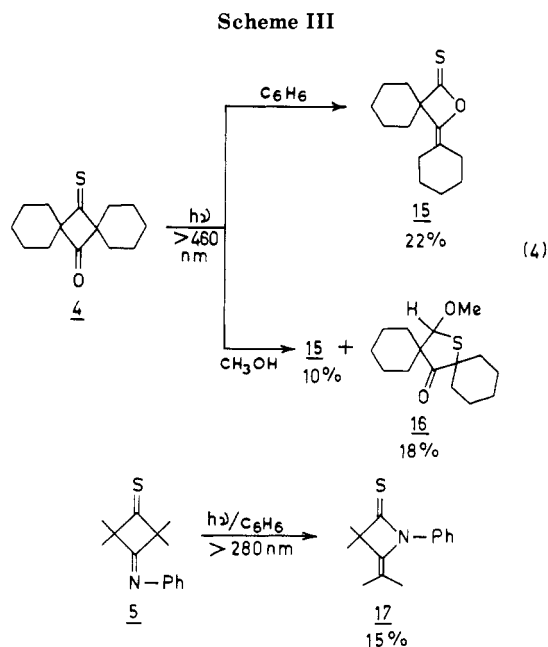
Theoretical Calculations. UHF MINDO/3 calculations[5] were performed on several points of interest on the

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Table III. Spectral Data of Photoproducts

product	IR (neat), cm⁻¹	¹H NMR (CCl₄),[c] δ	mass spectrum (70 eV), m/e
6a[a]	2240, 1640, 1160, 1050	1.54 (s, 6 H), 1.70 (s, 3 H), 2.06 (s, 3 H)	204 (M⁺), 160
6b	2240, 1735, 1645, 1275, 1230, 1150	1.33 (t, 3 H), 1.43 (s, 3 H), 1.52 (s, 3 H), 1.64 (s, 3 H), 1.70 (s, 3 H), 4.32 (m, 2 H)	
7a	2240, 1640, 1190, 1130	1.63 (s, 6 H), 1.66 (s, 6 H), 3.26 (s, 3 H), 3.76 (s, 1 H)	236 (M⁺)
7b	2240, 1760, 1600, 1240, 1100	1.27 (t, 3 H), 1.36 (s, 3 H), 1.45 (s, 3 H), 1.50 (s, 3 H), 1.63 (s, 3 H), 3.30 (s, 3 H), 4.30 (q, 2 H), 4.47 (s, 1 H)	
8a	2240, 1635, 1180, 1130	1.50 (s, 3 H), 1.57 (s, 3 H), 1.86 (s, 3 H), 2.0 (s, 3 H), 3.23 (s, 3 H), 3.80 (s, 1 H)	236 (M⁺)
8b	2230, 1760, 1630, 1240, 1100	1.39 (t, 3 H), 1.45 (s, 3 H), 1.51 (s, 3 H), 1.61 (s, 3 H), 1.79 (s, 3 H), 3.63 (s, 3 H), 4.2 (m, 2 H), 4.37 (s, 1 H)	
9a[b]	2240, 1635, 1250	1.4–2.8 (bm, 16 H)	
9b	2240, 1740, 1640, 1450, 1270, 1240	1.34 (t, 3 H), 1.5–2.53 (bm, 16 H), 4.32 (m, 2 H)	
10a	2250, 1635, 1445, 1180	1.4–2.8 (bm, 16 H), 4.2 (s, 3 H), 4.86 (s, 3 H)	
10b	2220, 1750, 1600, 1240, 1100	1.3 (t, 3 H), 1.1–2.8 (bm, 16 H), 3.64 (s, 3 H), 4.24 (q, 2 H), 4.61 (s, 1 H)	
11a	2240, 1640, 1440, 1175	1.5–2.8 (bm, 16 H), 3.1 (s, 3 H), 4.1 (s, 1 H)	
11b	2240, 1740, 1630, 1230, 1100	1.36 (m, 3 H), 1.4–2.8 (bm, 16 H), 3.36 (s, 3 H), 4.25 (m, 2 H), 4.45 (s, 1 H)	
12	1745, 1115	1.41 (s, 6 H), 1.67 (s, 6 H)	188 (M⁺)
13	1260, 1230, 1100, 1020	1.46 (s, 6 H), 1.64 (s, 3 H), 1.67 (s, 3 H)	156 (M⁺), 124
14	1740, 1370, 1240, 1020	1.18 (s, 3 H), 1.27 (s, 3 H), 1.42 (s, 6 H), 3.32 (s, 3 H), 4.50 (s, 1 H)	188 (M⁺)
15	2920, 2850, 1680, 1300, 1180, 1160	1–2.6 (bm, 20 H)	236 (M⁺)
16	2950, 2870, 740, 1250, 1170	0.8–2.6 (bm, 20 H), 3.65 (s, 3 H), 4.6 (s, 1 H)	268 (M⁺), 236, 224, 208
17	1600, 1150	1.34 (s, 3 H), 1.59 (s, 3 H), 1.62 (s, 3 H), 1.8 (s, 3 H), 6.82–7.4 (m, 5 H)	

[a] ¹³C NMR spectral data of **6a** (CDCl₃): δ 20.5 (q), 25.4 (q), 31.2 (q), 55.8 (s), 66.8 (s), 109.9 (s), 111.18 (s), 194.0 (s), 266.4 (s). [b] ¹³C NMR spectral data of **9a** (CDCl₃): δ 26.3 (t), 27.58 (t), 31.99 (t), 35.9 (t), 39.9 (t), 46.6 (t), 76.1 (s), 110.3 (s), 138.43 (s), 195.3 (s), 264.2 (s). [c] s = singlet; t = triplet; q = quartet; m = multiplet; bm = broad multiplet.
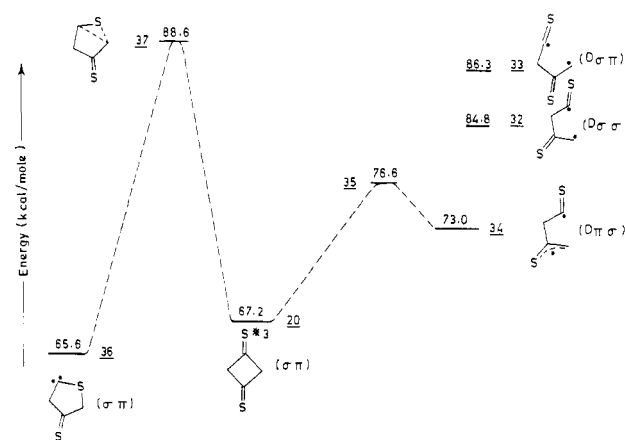
Scheme III

Figure 3. Potential energy diagram for the α-cleavage of cyclobutane-1,3-dithione.
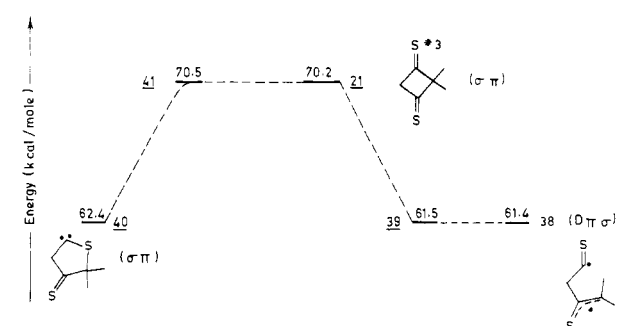
Figure 4. Potential energy diagram for the α-cleavage of α,α'-dimethylcyclobutane-1,3-dithione.

triplet excited surface of the parent and 2,2'-dimethyl-substituted cyclobutanethione and 1,3-cyclobutanedithione **18–21**. The composite potential energy diagrams on the basis of the computed heats of formation are summarized in Figures 1–4. Important geometric parameters of the various stationary points considered in this study are included as supplementary material.

The minima of interest on the excited hypersurface are the nπ* triplet state and the two primary intermediates, viz. 1,4-diradical and ring-expanded thiacarbene. For the diradical derived via α-cleavage from cyclobutanethione, two conformations were considered. In addition to the $D_{\sigma\sigma}$ diradical **22**, another structure ($\Delta_{\sigma\pi}$, **23**) with a linear C—C=S unit was also considered. The latter is of interest because only this form electronically correlates with the nπ* excited state.[10] Similarly, for the diradical derived

from the dithione, the $D_{\sigma\sigma}$ **32** and $D_{\sigma\pi}$ **33** conformers were examined. In this case an additional structure, designated

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as $D_{\pi\sigma}$ 34, with a delocalized thiaallyl radical center was also considered.

A few minimum energy reaction pathways (MERP) were examined to determine the barriers separating the minima. For the reaction profile connecting triplet cyclobutanethione and the corresponding $D_{\sigma\sigma}$ diradical, a surface crossing occurs near structure 24 if a C_s symmetry constraint is imposed. Complete geometry optimization of 24 leads to 25, which represents a good approximation to the true transition state (Figure 1). For the MERP separating triplet cyclobutanedithione and the ring-opened $D_{\pi\sigma}$ diradical computed without any geometry constraints, 35 is found to be the transition structure (Figure 3). Similarly, 27 and 37 correspond to the transition structures for thiacarbene rearrangements of triplet cyclobutanethione and dithione, 18 → 26 and 20 → 36 respectively. The effect of *gem*-dimethyl groups was considered only for the minima, transition states, and surface crossing points. The structures were assumed to be unaffected by the substituents and only the geometric parameters involving the methyl groups were optimized. The resultant energy profiles are shown in Figures 2 and 4.
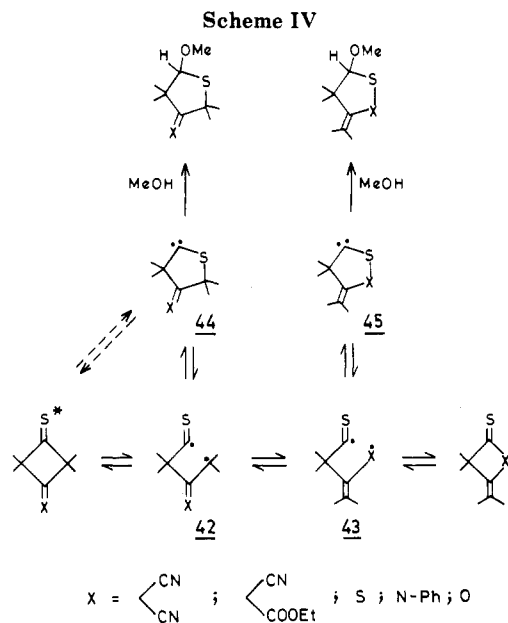
Attempts to obtain the transition state connecting the 1,4-diradicals and thiacarbenes did not lead to unambiguous results. It was difficult to distinguish between the high energy points on such pathways and the transition-state structures obtained above for the rearrangement of the nπ* triplets to thiacarbenes.

Discussion

Photolysis of 1–5 resulted in the formation of 1,3-migration products and cyclic thioacetals as illustrated in Schemes I–III. Structures of these products were deduced from their UV, IR, and ¹H NMR and mass spectral data. Spectral data of all the photoproducts are summarized in Table III. Since the spectral properties of products 1 to 5 are similar to those of analogous products from 2,2′,4,4′-tetramethyl-1,3-cyclobutanedithione and related systems,[2] these are discussed only briefly below.

The presence of two cyclic thioacetals in 1 and 2 became evident from the ¹H NMR spectra of the crude photolysis mixture. Pure samples of these were obtained through preparative TLC. The mass spectral data and the elemental analysis revealed the addition of methanol to the starting thiones 1 and 2. Consistent with this, signals corresponding to OCH₃ were seen in ¹H NMR. The two cyclic thioacetals were distinguished on the basis of ¹H NMR wherein distinct signals due to allylic and vinylic methyls (or methylenes) were seen. Although two geometric isomers are possible in the case of 7b and 8b, only one was seen in each case by ¹H NMR. Formation of rearranged thiones 6 and 9 was evident from UV, IR, and ¹H and ¹³C NMR spectral data. This was further confirmed by mass spectral data and elemental analysis. Formation of thionolactone 13 and 15 was revealed by IR and UV spectra. ¹³C NMR data corresponding to the thionolactone carbon (δ 192.13) was confirmatory. Structures of solvent adducts 14 and 16 were deduced from their spectral data. The presence of carbonyl and absence of thiocarbonyl chromophores were evident from UV and IR spectral data. Elemental analysis data and ¹H NMR spectra provided confirmatory evidences toward the addition of methanol to the starting thiones 3 and 4.

The formation of products shown in Schemes I–III was independent of the excitation band (S_2 or S_1) as was the relative efficiency of the formation of these products. Therefore, involvement of higher excited states was ruled out. Triplet quenching and triplet sensitization studies carried out in the case of 1a suggest that the lowest triplet

Scheme IV

$$X = \begin{array}{c} CN \\ CN \end{array} \quad ; \quad \begin{array}{c} CN \\ COOEt \end{array} \quad ; \; S \; ; \; N\text{-}Ph \; ; \; O$$

state is the immediate precursor for the product formation. This conclusion is further strengthened by the flash photolysis studies.[4] The intersystem crossing efficiency from S_1 to T_1 has been measured to be near unity for all the above cyclobutanethiones (Table II). The absence of detectable emission from S_1 or T_1, triplet sensitization of products from 1a and 3, and triplet quenching of photoproducts suggest that the lowest triplet is the reactive species. Consistent with this conclusion, the efficiency of products formation was inversely proportional to the concentration of thioketone due to the triplet self-quenching process, a process that occurs at a diffusion-controlled limit. It should be noted that cyclobutanones generally undergo α-cleavage from the lowest excited singlet state (S_1).[11]

A plausible mechanism for the formation of photoproducts 1–5 is illustrated in Scheme IV. The formation of 1,3-migration products can be rationalized on the basis of involvement of the diradical 43. The sequence of formation of 43 from cyclobutanethiones can be visualized to involve an α-cleavage process in the excited triplet to yield the diradical 42 followed by a rotation about a single bond. Both diradicals contain a delocalized thiaallyl fragment. Among the many possible pathways for the decay of the diradical one would involve the attack of the thioacetyl carbon one of the two termini of the substituted allyl fragment. While one of these couplings would result in the starting thione, the other combination would yield the 1,3-migration product. The extent of participation of these two processes in the decay of the 1,4-diradical would be expected to depend on the electron densities at the two termini in the highest singly occupied MO. The SOMO coefficients of the allylic and heteroallylic radicals as calculated by the MINDO/3 method are summarized in Scheme V. The coefficients at both termini are sizeable in all the allyl systems, readily accounting for the formation of 1,3-migration products.

Several cyclobutanones, analogous to the systems investigated here, have already been studied.[9,12] In these

(11) (a) Morton, D. R.; Turro, N. J. *Adv. Photochem.* **1974**, *9*, 197. (b) Stohrer, W. D.; Jacobs, P.; Kaiser, K. H.; Wiech, G.; Quinckert, G. *Top. Curr. Chem.* **1974**, *46*, 181.

(12) (a) Turro, N. J.; Leermakers, P. A.; Wilson, H. R.; Neckers, D. C.; Byers, G. W.; Vesley, G. F. *J. Am. Chem. Soc.* **1965**, *87*, 2617. (b) Kimura, K.; Takamura, M.; Kunai, A.; Odaisa, Y. *J. Chem. Soc., Chem. Commun.* **1974**, 685. (c) Turro, N. J.; Cole, T. *Tetrahedron Lett.* **1969**, 3451.

Scheme V

SOMO coefficients of allylic and heteroallylic radicals.
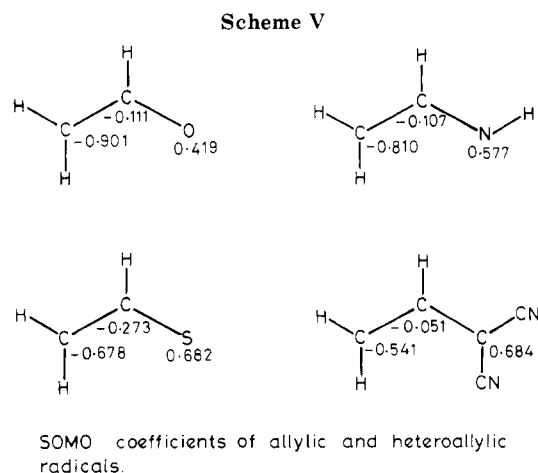
systems, the occurrence of 1,3-migration to give the rearranged product is a rarity. The oxygen analogues of **1a** and **1b** favor the formation of the decarbonylated product along with a cyclic acetal corresponding to the oxacarbene, but the 1,3-migration product was not observed. Differences in the exothermicity for the elimination of carbon monoxide and carbon monosulfide may contribute to the difference in the photobehavior between the corresponding carbonyl and the thiocarbonyl compounds.

The formation of cyclic thioacetals upon excitation of 1–4 in methanol calls for the involvement of thiacarbenes **44** and **45** as reactive intermediates. That both thiacarbenes are intermediates in these phototransformations is suggested by the formation of two different thioacetals. Involvement of a diradical as an intermediate in this process is suggested by the formation of an adduct corresponding to a rearranged thiacarbene **45**. As discussed earlier, such diradical intermediates were also supported by the isolation of 1,3-migration products. Analogous oxacarbene involvement during photochemical formation of ring-expanded acetals from alicyclic ketones in alcoholic solvents is known.[13] In these examples, oxacarbene formation has been proposed to derive directly from the excited ketone.[14] Diradical has not been invoked in this rearrangement.

Two pathways are conceivable for the formation of thiacarbene **44**: (a) via a diradical intermediate and (b) via a concerted rearrangement from the triplet thioketone to triplet thiacarbene. No direct spectroscopic evidence could be obtained for the presence of either diradical or carbene as intermediates during the laser photolysis of cyclobutanethiones. Therefore, attempts to follow these intermediates in the reaction sequence were not successful. Consequently, a plausible mechanistic scheme was sought with the aid of semiquantitative theoretical calculations.

On thermodynamic grounds, α-cleavage is not a favorable process for unsubstituted cyclobutanethiones. Even allowing for the underestimation of ring strain by the MINDO/3 method,[5b] the preferred conformer of the 1,4-diradical, **22**, is much above the nπ* triplet **18**. However, the energy gap between the triplet and the ring-opened diradical is substantially reduced by *gem*-dimethyl sub-
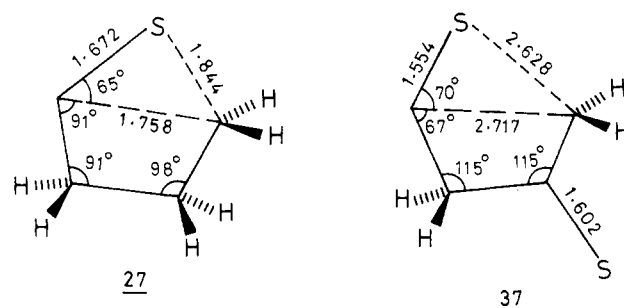

Figure 5. Calculated geometries of transition states **27** and **37** (bond lengths in Å).

stitution as well as by the presence of a second thione group. The alkyl groups tend to destabilize the four-membered ring, while the dithione diradical benefits from allylic conjugation. Due to the combined effect of alkyl and thiaallyl stabiliztaion, α-cleavage from triplet **21** to diradical **38** is clearly a downhill process.

A symmetry imposed barrier[15] may be expected for the α-cleavage of cyclobutanethione since the nπ* triplet correlates with the $D_{\sigma\pi}$ diradical **23** rather than with the more stable $D_{\sigma\sigma}$ diradical **22** (correspondingly, **22** correlates with a high lying $\pi\pi$* excited state).[16] A surface crossing at **24** is indeed calculated when a C_s symmetry constraint is maintained during geometry optimizations. However, the transition state for the reaction is nonplanar **25** in which σ–π mixing occurs. The resultant barrier is not significantly greater than the endothermicity of the process. Even for the dimethyl derivative, a barrier less than 2 kcal/mol is indicated.

Interestingly, α-cleavage from the dithione nπ* triplet **20** is electronically allowed. This is because the product is the $D_{\pi\sigma}$ diradical, and not a $D_{\sigma\sigma}$ diradical as in the monothione case. A natural correlation diagram approach[17] does indicate a barrier even for the formation of **34**, as **20** correlates more directly with the $D_{\sigma\pi}$ diradical containing a linear C—C=S unit. The initial geometric changes in the reaction profile **20** → **34** reflect these orbital effects. However, the onset of thiaallylic conjugation by rotation of a CH$_2$ group[18] obliterates the distinction between σ and π orbitals. Therefore, a smooth reaction profile is obtained (Figure 3). The calculated activation energy (9 kcal/mol) is only slightly larger than the reaction energy. For the corresponding reaction involving the dimethyl derivative, **21** → **38**, no barrier is found at all.

In summary, the α-cleavage process to give a diradical is kinetically feasible in small-ring thiones only when stabilizing alkyl or conjugating groups are present. For exothermic ring opening, little or no kinetic barrier exists. Experimentally, parent cyclobutanethione and -dithione have not been investigated. However, the observed products for all systems related to the models **19** and **21** support the formation of a 1,4-diradical intermediate via α-cleavage.[2b,c]

(13) (a) Kilmurry, L.; Yates, P. *J. Am. Chem. Soc.* **1966**, *98*, 1563. (b) Yates, P.; Loutfy, R. O. *Acc. Chem. Res.* **1975**, *8*, 209.

(14) (a) Quinckert, G.; Jacobs, P.; Stohrer, W. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 197. (b) Quinckert, G.; Kaiser, K. H.; Stohrer, W. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 198. (c) Stohrer, W.; Wiech, G.; Quinckert, G. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 199 and 200. (d) Altmann, J. A.; Csizmadia, I. G.; Robb, M. A.; Yates, K.; Yates, P. *J. Am. Chem. Soc.* **1978**, *100*, 1653.

(15) (a) Michl, J. *Top. Curr. Chem.* **1974**, *46*, 1. (b) Michl, J. *Mol. Photochem.* **1972**, *4*, 243, 257 and 287.

(16) The $D_{\sigma\sigma}$ diradical correlates with a very high energy σ–σ* excited state of cyclobutanethione on the basis of a natural correlation analysis.[17] However, the latter state can mix with the lower lying π–π* excited state, leading to the correlation stated in the text. See ref 10d.

(17) (a) Bigot, B.; Devaquet, A.; Turro, N. J. *J. Am. Chem. Soc.* **1981**, *103*, 6. (b) Devaquet, A.; Sevin, A.; Bigot, B. *J. Am. Chem. Soc.* **1978**, *100*, 2009. (c) Bigot, B.; Sevin, A.; Devaquet, A. *J. Am. Chem. Soc.* **1979**, *101*, 1095.

(18) In general σ bonds can be broken either by a stretching motion or by a twisting process. The one considered here is equivalent to a twisting process.

The alternate reaction pathway of $n\pi^*$ triplet thiones to yield ring-expanded thiacarbene is calculated to be exothermic for all the four systems considered. The relief of ring strain and formation of an additional σ band provide the driving force, especially in the dimethyl derivatives. The concerted ring expansion is also an electronically allowed process, since $\sigma\pi$ triplets are involved in both the reactant and the product. However, due to the extent of bond reorganization involved, sizeable barriers are obtained for the rearrangement of triplet cyclobutanethione and dithione (Figures 1 and 3). Interestingly, the structure of the transition state computed for $18 \rightarrow 26$ is qualitatively different from that for $20 \rightarrow 36$. In the monothione case, a tight structure, 27, is obtained, with relatively short contacts between the migrating carbon and the thione unit. The presence of a second thione group introduces considerable strain is such a structure. The corresponding transition structure 37 is much more open (Figure 5). The migrating carbon interacts weakly with the thione fragment. As a result, the unpaired electron density is large at the migrating carbon, especially compared to that in 27.

The differences in the molecular and electronic structures of 27 and 37 have important consequences with respect to substiuent effects. Additional methyl groups at the migrating carbon atom only serve to increase the steric repulsion in the tight structure of the monothione transition state. Therefore, the relative energies of 19 and 31 change little compared to their unsubstituted counterparts. On the other hand, for the dithione, *gem*-dimethyl groups dramatically stabilize the transition state 41 relative to 21 due to the radicaloid nature of the migrating carbon. Thus, alkyl-substituted dithione 21 is the only system, of the four models considered here which is predicted to give products derived from thiacarbene intermediates. This conclusion is also in accord with experimental observations: there is no evidence for thiacarbene intermediacy in the photochemical reactions of cyclobutanethione, while systems analogous to 21 with additional double bonds and alkyl substituents lead to ring-enlarged thiacarbenes.

In conclusion, we have demonstrated the generality of the α-cleavage process in cyclobutanethione systems. The cleavage occurs from the triplet (T_1) state which is reached with unit efficiency upon excitation of the above molecules to the lowest excited singlet state. The α-cleavage results in 1,4-diradical and thiacarbene intermediates which undergo further reactions to yield stable products. MINDO/3 calculations suggest that direct conversion from the triplet state to the diradical and thiacarbene is feasible for cyclobutane 1,3-dithiones possessing an α-alkyl substitution. However, cyclobutanethiones possessing an α-alkyl substitution are predicted to cleave only to 1,4-diradical. These predictions are in accord with experimental observations.

Experimental Section

Preparations of Cyclobutanethiones. Cyclobutanethiones 1–5 were prepared from the corresponding ketones[19] by using the phosphorus pentasulfide method[2]. A typical procedure consisted of the following: A dry pyridine solution (30 mL) of the corresponding ketone (6 g) and phosphorus pentasulfide (10 g) was refluxed with constant stirring for 2 h. The reaction mixture was cooled, poured into ice water and extracted with ether. Evaporation of the solvent left behind a red viscous liquid. Chromatography of the liquid using a silica gel column (hexane/chloroform 4:1 mixture) gave analytically pure thione. Spectral data are summarized in Table I. All the thiones gave satisfactory elemental analysis data.

General Photolysis Procedure. All irradiations were conducted in methanol or in benzene under a nitrogen atmosphere by using a 450-W medium pressure mercury lamp. Small-scale irradiations (up to 100 mL) were conducted in Pyrex tubes with an external source of irradiation. Large-scale irradiations (250 mL) were conducted in Pyrex immersion wells. The initial concentrations of thiones used for irradiation generally varied between 10^{-2} and 10^{-3} M. For irradiations in the visible region, a Corning glass filter (CS-3.70; transmission >480 nm) was used. The progress of the reaction was monitored by TLC (silica gel hexane/benzene). After about 50% completion of the reaction, the solvent was evaporated and the products were separated by column and preparative thin layer chromatography. They were characterized by their spectral properties (Table III). Satisfactory elemental analysis data were obtained for most of the photoproducts. For a few analytically pure material could not be obtained. Analytical data for 6ab, 7ab, 8ab, 9ab, 10ab, 11ab, 12, and 14 are recorded in the supplementary material.

Quenching and Sensitization Studies. Quenching and sensitization studies were carried out only for 1a and 3. Biacetyl, 2-acetylnaphthalene, benzil, and fluorenone were used as sensitizers. In a typical experiment, a solution of 1a or 3 (100 mg) and sensitizer (100 mg) in cyclohexane or methanol (25 mL) was irradiated with a 450-W medium pressure mercury lamp fitted with a Corning glass filter CS-7.60 (transmission between 320 and 400 nm) for about 24 h. Products of the photolysis were isolated as above and were identified to be the same ones as obtained on direct excitation.

Quenching studies were carried out with alloocimene and cyclooctatetraene as quenchers. This experiment was conducted in a merry-go-round apparatus with solutions varying in quencher concentration (0–0.05 M) and fixed thione concentration (0.02 M). Progress of the reaction was monitored by UV–vis absorption spectroscopy (following the disappearance of thione). In both cases (1a and 3), linear Stern–Volmer plots were obtained, indicating the involvement of the triplet state in the reaction.

Flash Photolysis Studies. Details of the procedure adopted have already been presented.[4,20] For most of the laser flash photolysis experiments, laser pulses at 337.1 nm (3 mJ, 8 ns, Molectron UV-400) or 532 nm (10–100 mJ, 6 ns, Quanta Ray Nd-YAG 2nd harmonic) were used for excitation at both right angle and front face geometries. Rectangular quartz cells of 2 and 3 mm path lengths were used for photolysis in a front face configuration. For measurement of T–T spectra a flow cell was used. Appropriate interference filters (ORIEL) were placed in the paths of the monitoring light, in front of the analyzing monochromator to minimize interference from the scattered light, and before the photolysis cell to minimize photochemical deterioration of the solution.

Supplementary Material Available: Important geometric parameters of the various stationary points as calculated by the MINDO/3 method and analytical data for 6ab, 7ab, 8ab, 9ab, 10ab, 11ab, 12, and 14 (5 pages). Ordering information is given on any current masthead page.

(19) (a) Lalancette, E. A.; Benson, R. E. *J. Am. Chem. Soc.* 1961, *83*, 4867. (b) Hasek, R. H.; Elam, E. V.; Martin, J. C. *J. Org. Chem.* 1961, *26*, 4340.

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