Strain-Assisted α-Cleavage Reactions of Thioketones: Cyclobutanethiones

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Photochemical α-cleavage from the lowest triplet state ($n\pi^*$, T_1), resulting in the generation of a diradical intermediate, appears to be general for cyclobutanethiones. The diradical intermediate derived from 1,3-dithione is observed to undergo ring expansion to carbene or close to either dithione or dithiolactone. The photochemical behavior reported here for cyclobutanethiones is different from that of the corresponding cyclobutanones. α-Cleavage processes in the case of cyclobutanethiones are not efficient and are often accompanied by side reactions.

Ketone photochemistry has received considerable mechanistic attention and some synthetic application.[1] In contrast, the photochemical behavior of thiocarbonyl compounds has been explored less than that of the analogous carbonyl compounds.[2] Further, thiocarbonyls are rarely reported to undergo one of the primary photoreactions of ketones, namely, the Norrish type I-α-cleavage process. Perhaps because of the rarity of its occurrence the photochemical α-cleavage process is one of the least studied excited-state transformations of thioketones. However, the possibility of such a process in thiocarbonyl systems is suggested by scattered reports. For example, trithiocarbonates are reported to undergo elimination of carbon disulfide[3] and carbon monosulfide[4] through an α-cleavage process. Photo-Fries rearrangement involving α-cleavage is known with thiocarboxylic *O*-esters.[5] Photochemical decomposition of *O*-ethyl *S*-benzyl xanthate, which involves homolytic scission of the S—(C=S) bond, has been used as an efficient initiating process for polymerization.[6] Possible involvement of α-cleavage in thioketones is reported on two strained systems.[7] On the other hand, cyclic and acyclic thioketones, which on analogy to ketones are expected to undergo α-cleavage, have resisted such a process.[8] Therefore, no general picture has emerged regarding the Norrish type I process in thioketones. The rarity of α-cleavage in thioketones could be due to either thermodynamic or electronic factors. It was anticipated that release of ring strain would have a pronounced effect upon the reactivity of molecules in an electronically excited state and might favor the α-cleavage process in thioketones. In the hope of removing thermodynamic impediment for α-cleavage, cyclobutanethiones 1–4 were chosen for photochemical investigation. The results presented herein illustrate that our expectation has been realized and that thioketones do undergo α-cleavage, although inefficiently, once sufficient energy is provided.[9]

Results

Since di-*tert*-butyl thioketone upon excitation to S_1 and S_2 failed to produce products resulting from α-cleavage,[10] it was suspected that internal strain might be one of the factors favoring occurrence of α-cleavage. With this in view, excitation of 2,2,4,4-tetramethylcyclobutanethione (1) was conducted. Irradiation of 1 (450-W medium-pressure mercury lamp) in cyclohexane and methanol gave two products–disulfide **6** and sulfur-incorporating product **5** as shown in Scheme I. One of the products, on the basis of carbonyl photochemistry,[1] namely, the one formed by trapping of the intermediate thiacarbene with methanol solvent, was not isolated. Although the formation of **5**, which has incorporated sulfur, suggested the occurrence of α-cleavage, the absence of a methanol adduct was interpreted to mean that the diradical intermediate had failed to rearrange to thiacarbene. It is in this connection that 2,2,4,4-tetramethyl-1,3-cyclobutanedithione (**2**), dispiro[5.1.5.1]tetradecane-7,14-dithione (**3**), and dispiro-[4.1.4.1]dodecane-6,12-dithione (**4**)[11] were studied. Spectral properties of **1–4** are shown in Table I. Excitation of **2–4** either to the S_1 or S_2 level resulted in the same set of products (Schemes I and II). Irradiation of **2** in cyclohexane gave sulfur-incorporating product **7** and disulfide **8**, whereas excitation in methanol resulted in the formation of cyclic thioacetals **10** and **11** in addition to **7** and **8**. Similarly, excitation of **3** and **4** resulted in the formation of sulfur-incorporating products and cyclic thioacetals. Along with these, dithiolactones **13** and **17** were also formed both in benzene and methanol (Scheme II). Formation of all these products was shown to be light induced as **2–4** were stable in the dark indefinitely, both in benzene and methanol. In the case of **2**, no corresponding dithiolactone was formed. Spectral properties of all products are tabulated in Tables II–IV.

Triplet energies of **1–4** were estimated to be in the range of 48–50 kcal/mol from their phosphorescence spectra. Triplet sensitizers, such as biacetyl, 2-acetylnaphthalene, fluorenone, and benzil, having energies above 50 kcal/mol were found to sensitize the formation of products shown in Scheme I, in the case of **1** and **2**. Consistent with this observation, the triplet quenchers alloocimene and cyclooctatetraene quenched the formation of products upon direct excitation of **1** and **2**. No quantitative studies were conducted in any of these cases due to experimental difficulties. Excitation of **1–4** under comparable conditions revealed that of these four **4** reacted more readily than the rest.

Discussion

The slow nature of reactions of **1–4** (~25% conversion in 2–3 days) and in some cases the accompanying side reactions (mostly polymerization) prevented quantitative investigation of the α-cleavage. Therefore, we have limited

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Scheme I. Photolysis of 2,2,4,4-Tetramethylcyclobutanethione and 2,2,4,4-Tetramethyl-1,3-cyclobutanedithione

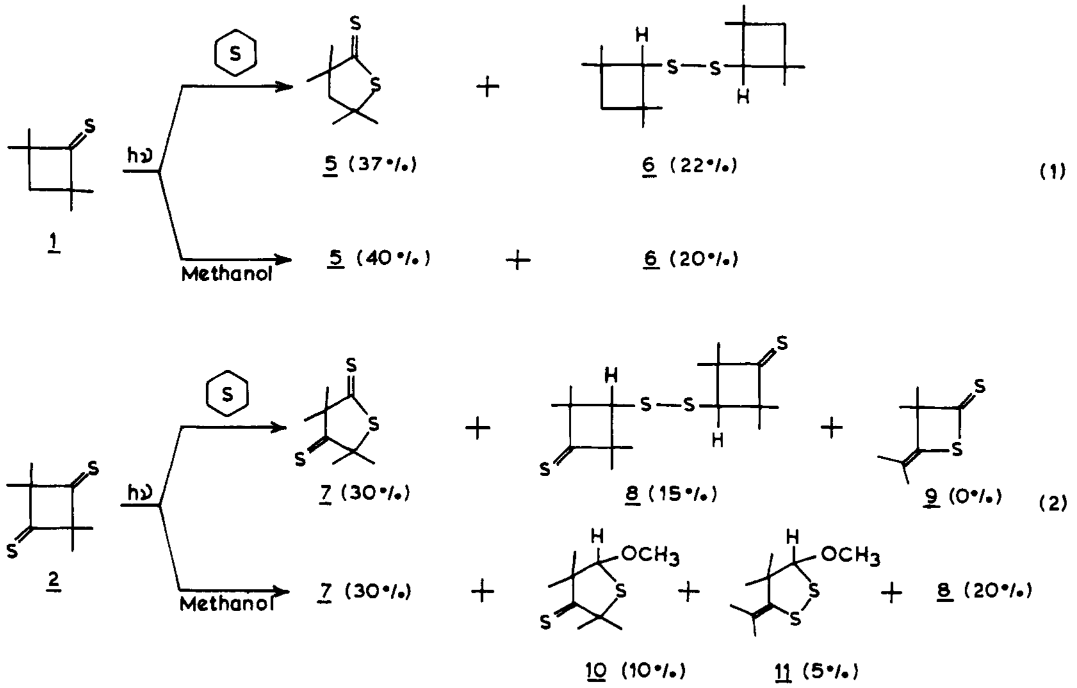


Table I. Spectral Data of Thioketones Investigated

thioketone	UV-vis λ_{max}, nm (ϵ, M^{-1} cm^{-1})	infrared spectrum ν, cm^{-1} (C=S)	^1H NMR,[g] δ (Me_4Si)	^{13}C NMR,[f,g] δ (Me_4Si)
1	215 (5000), 230 (7000), 500 (12)[a]	1140[c]	1.27 (s, 12 H), 2.23 (s, 2 H)[e]	27.95 (q), 47.04 (t), 56.48 (s), 289.12 (s)
2	227 (21600), 298 (410), 500 (22.4)[a]	1080[d]	1.40 (s)[e]	25.81 (q), 80.51 (s), 276.06 (s)
3	244 (15900), 310 (1100), 504 (37)[b]	1130[d]	1.45-1.58 (broad peak, 4 H), 1.70-1.86 (broad peak 16 H)[f]	21.79 (t), 25.23 (t), 35.50 (t), 83.52 (s), 275.38 (s)
4	263 (2240), 298 (420), 492 (12)[b]	1120[d]	1.84-1.92 (m, 8 H),[f] 2.03-2.12 (m, 8 H)	26.93 (t), 37.12 (t), 87.01 (s) 275.43 (s)

[a] In hexane. [b] In chloroform. [c] Neat. [d] In Nujol. [e] In CCl_4. [f] In $CDCl_3$. [g] s = singlet; t = triplet; q = quartet; m = multiplet.

Table II. Spectral Data of Photoproducts: Sulfur-Incorporated Products

compd	UV-vis λ_{max}, nm (ϵ, M^{-1} cm^{-1})	IR (neat) ν, cm^{-1} (C=S)	^1H NMR,[e] δ (Me_4Si)	^{13}C NMR,[e] δ ($CDCl_3$, Me_4Si)	mass spectra (70 eV) and elemental analysis
5	312 (16 000), 470 (22)[a]	1120	1.35 (s, 6 H), 1.63 (s, 6 H), 2.35 (s, 2 H)[c]	31.55 (q), 31.92 (q), 55.29 (s), 58.44 (t), 62.53 (s), 254.02 (s)	*m/e* at 174 (M^+ ion)
7	268 (16 300), 310 (17 200), 480 (40)[a]	1070	1.58 (s, 6 H), 1.80 (s, 6 H)[c]	33.56 (q), 33.72 (q), 70.96 (s), 77.89 (s), 245.17 (s), 267.67 (s)	*m/e* at 204 (M^+ ion) CI (CH_4), *m/e* at 205, $[M + 1]^+$ ion calcd for $C_8H_{12}S_3$: C, 47.06; H, 5.92 found: C, 46.71; H, 6.40
12	260 (13 100), 310 (14 000), 497 (25)[b]	1110	1.40-1.95 (broad multiplet)[d]	20.62 (t), 22.69 (t), 23.90 (t), 25.42 (t), 40.18 (t), 42.60 (t), 66.50 (s), 77.84 (s), 246.52 (s), 266.64 (s)	*m/e* at 284 (M^+ ion), 252, 176, 126
16	260 (13 800), 311 (15 500), 480 (32)[b]	1110	1.70-2.45 (broad multiplet)[d]	25.65 (t), 27.61 (t), 46.59 (t), 47.03 (t), 69.65 (s), 77.40 (s), 245.68 (s), 265.50 (s)	*m/e* at 256 (M^+ ion), 224, 148, 112

[a] In cyclohexane. [b] In chloroform. [c] In CCl_4. [d] In $CDCl_3$. [e] s = singlet, t = triplet, q = quartet.

ourselves to a qualitative study.

(a) Products. Excitation of **1**–**4** resulted in the formation of sulfur-incorporating products (**5**, **7**, **12**, and **16**), dithiolactones (**13** and **17**), solvent adducts (**10**, **11**, **14**, and **18**), and disulfides (**6** and **8**) as shown in Schemes I and II. Structures of these products were deduced from their UV, IR, ^1H NMR, ^{13}C NMR, and mass spectra. We discuss below the spectral features of products derived from **2** as a typical example; products from **1**, **3**, and **4** possess closely similar spectra (Tables II–IV).

Scheme II. Photolysis of Dispiro[5.1.5.1]tetradecane-7,14-dithione and Dispiro[4.1.4.1]dodecane-6,12-dithione

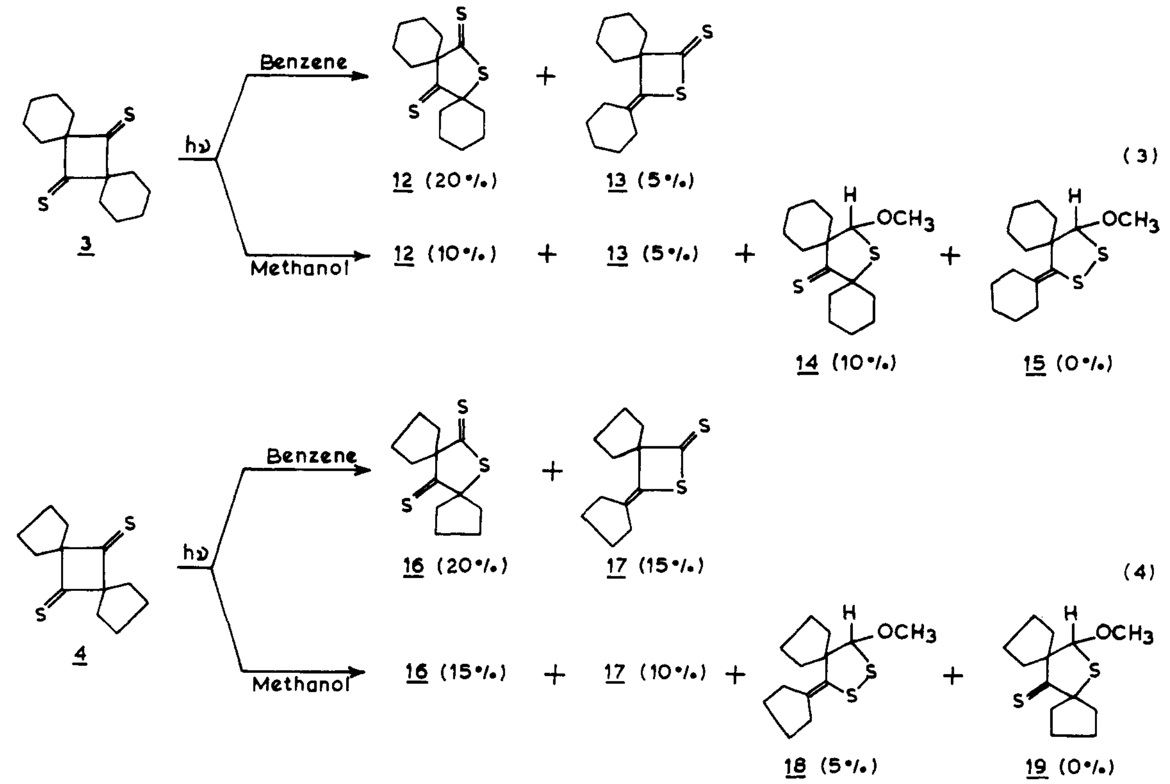


Table III. Spectral Data of Photoproducts: β-Dithiolactones

compd	UV–vis λ_{max}, nm (ϵ, $M^{-1}\,cm^{-1}$)	IR spectrum ν, cm^{-1}	^{1}H NMR,^{g} δ (Me_4Si)	^{13}C NMR,^{g} δ ($CDCl_3$, Me_4Si)
9	244 (3800), 340 (4500), 460 (12)^a	1235, 1160, 1070, 865, 825^d	1.41 (s, 6 H), 1.70 (s, 3 H), 1.86 (s, 3 H)^e	19.98 (q), 21.82 (q), 25.25 (q), 74.16 (s), 122.27 (s), 131.18 (s), 242.90 (s)
13	246 (4800), 353 (7000), 463 (42)^b	1180, 1120, 930, 835^b	1.57-2.02 (bm, 18 H), 2.18-2.27 (bm, 2 H)^f	21.10 (t), 25.37 (t), 26.25 (t), 27.41 (t), 27.49 (t), 30.77 (t), 33.24 (t), 34.04 (t), 76.64 (s), 126.30 (s), 129.98 (s), 242.66 (s)
17	270 (12 750), 350 (9450), 410 (shoulder)^c	1250, 1175, 1150, 980, 855^d	1.68-1.97 (bm, 8 H), 2.05-2.39 (bm, 8 H)^f	25.99 (t), 26.87 (t), 27.79 (t), 30.46 (t), 32.57 (t), 38.27 (t), 84.61 (s), 126.22 (s), 131.77 (s), 245.72 (s)

[a] In cyclohexane. [b] In chloroform. [c] In benzene. [d] Neat. [e] In CCl_4. [f] In $CDCl_3$. [g] s = singlet, t = triplet, q = quartet, bm = broad multiplet.

Table IV. Spectral Data of Photoproducts: Methanol Adducts

compd	UV–vis λ_{max}, nm (ϵ, $M^{-1}\,cm^{-1}$)	IR (neat) ν, cm^{-1}	^{1}H NMR,^{c} δ ($CDCl_3$, Me_4Si)	^{13}C NMR,^{c} δ ($CDCl_3$, Me_4Si)	mass spectra (70 eV) and elemental analysis
10			1.35 (s, 3 H), 1.39 (s, 3 H), 1.59 (s, 6 H), 3.35 (s, 3 H), 4.81 (s, 1 H)		
11	250 (4300), 345 (300)^a	1450, 1360, 1190, 1090, 730	1.34 (s, 3 H), 1.43 (s, 3 H), 1.85 (s, 3 H), 1.89 (s, 3 H), 3.49 (s, 3 H), 4.61 (s, 1 H)	21.55 (q), 23.13 (q), 26.48 (q), 26.83 (q), 51.49 (s), 58.29 (q), 105.79 (d), 123.53 (s), 137.09 (s)	*m/e* at 204 (m^+ ion), 172, 141, 139, 128, 108, 96, 86, 81, 71, 59 calcd for $C_9H_{16}OS_2$: C, 52.45; H, 7.84 found: C, 52.77; H, 7.70
14	264 (11000), 510 (295)^b	1450, 1210 1100	1.45-2.35 (bm, 20 H), 3.46 (s, 3 H), 5.02 (s, 1 H)		
18	263 (5000), 320 (250)^b	1440, 1110	1.54-1.92 (bm, 10 H), 2.17-2.24 (m, 2 H), 2.30 (t, 2 H), 2.42 (t, 2 H), 3.47 (s, 3 H), 4.60 (s, 1 H)	25.85 (t), 26.41 (t), 28.13 (t), 30.93 (t), 31.49 (t), 36.40 (t), 40.00 (t), 57.62 (q), 64.65 (s), 103.37 (d), 132.78 (s), 135.33 (s)	

[a] In cyclohexane. [b] In carbon tetrachloride. [c] s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, bm = broad multiplet.

Sulfur-incorporating product **7** has mass spectra (chemical ionization and electron impact) and an elemental analysis corresponding to molecular formula $C_8H_{12}S_3$, indicating that a sulfur atom has been added to the parent compound **2**. The presence of a thiocarbonyl chromophore is deduced from its visible (480 nm) absorption and IR spectra (1070 cm^{-1}). The presence of two such chromophores is supported by the ^{13}C NMR spectrum, which contains signals at δ 245.17 and 267.67. Absence of olefinic carbon signals in ^{13}C NMR spectra suggested a cyclic structure **7** (Scheme I). ^1H NMR and ^{13}C NMR spectral data are consistent with the proposed structure. As would be expected, a dithioester carbon (δ 245.17) absorbs at a field higher than a thioketone carbon (δ 267.67).

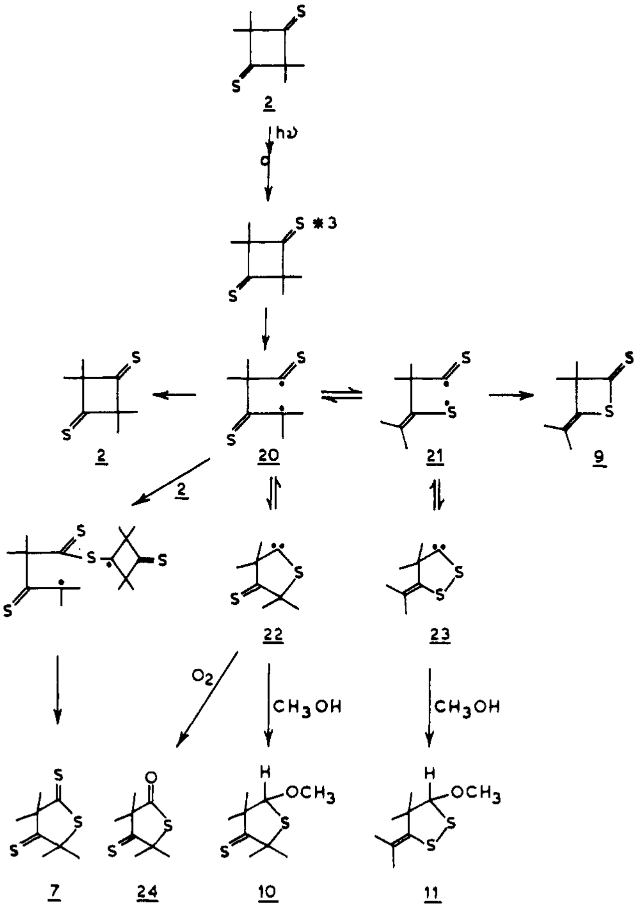
Excitation of **2–4** in methanol gave also solvent adduct(s). The presence of two such 1:1 solvent adducts in the case of **2** became evident from the ^1H NMR spectra of the crude irradiation mixture. Adduct **10** obtained in the case of **2** could not be completely separated from the sulfur-incorporating product **7**. Hence, full spectral data for this adduct could not be obtained and only ^1H NMR data are given in Table IV.

The molecular ion and the elemental analysis for the second adduct (**11**) from **2** correspond to the molecular formula $C_9H_{16}S_2O$. This suggests that a molecule of solvent methanol has added to parent compound **2**. Consistent with this, signals corresponding to OCH_3 and $CHOCH_3$ were seen at δ 3.49 and 4.61 in the ^1H NMR spectrum and at δ 58.29 (q) and 105.79 (d) in ^{13}C NMR spectrum, respectively. Absence of the thiocarbonyl chromophore is inferred from the lack of color and from the absence of a thiocarbonyl carbon signal in the ^{13}C NMR spectrum. On the other hand, the presence of a fully substituted double bond is evident [δ 137.09 (s), 123.53 (s)]. These spectral features can be accommodated by structure **11**. Although the presence of a disulfide linkage could not be confirmed in the infrared spectra, the expected weak $n\sigma^*$ absorption is observed at λ_{max} 345 nm. Adducts from **3** and **4** exhibited similar spectral features. On the basis of ^1H NMR spectra, structure **10** has been assigned to the first adduct. As would be expected, adduct **14**, which is similar to **10**, showed an absorption in the visible region (λ_{max} 510 nm) corresponding to the thiocarbonyl chromophore.

Another product obtained upon excitation of **3** and **4** is the corresponding dithiolactone. This was confirmed by comparing the spectral data (Table III) with authentic samples.[12]

(b) Reactive State. The formation of products shown in Schemes I and II was independent of the excitation band (S_2 and S_1) as was the relative efficiency of the formation of these products. Therefore, involvement of higher excited states was ruled out. Quenching and sensitization studies were conducted with **1** and **2**. Triplet sensitizers such as fluorenone, 2-acetylnaphthalene, benzil, and biacetyl were found to sensitize the formation of products shown in Scheme I. Further, triplet quenchers alloocimene (E_T < 47 kcal/mol) and cyclooctatetraene (E_T < 40 kcal/mol) quenched the formation of these products upon direct excitation. Owing to the difficulty in following the appearance of products, the disappearance of **1** and **2** was followed by their UV–vis absorption in the presence of added quencher. A linear Stern–Volmer plot was obtained, indicating the involvement of the triplet state in these reactions. In cyclobutanones, S_1 is generally the precursor of the ring-expanded oxacarbene and other photoproducts.[13] The triplet state has been found not to produce α-cleavage in cyclobutanones. On the other hand, cyclobutanethiones cleave via the lowest triplet state.

Scheme III. Schematic Representation of the α-Cleavage Process of Cyclobutanethiones



(c) Mechanism. As discussed above, direct and sensitized excitation of **1–4** results in the formation of four types of products–dithiolactones, sulfur-incorporating products, solvent adducts, and disulfides. The formation of disulfides has been reported earlier in other systems, and its origin and mechanism are fairly well understood.[2] Therefore, our mechanistic discussion can be limited to the other three products. Possible mechanistic pathways involving α-cleavage as the primary process are outlined in Scheme III.

That thiacarbene is an intermediate in these photoreactions is suggested by the formation of thioacetals when irradiation of **1–4** was conducted in methanol. Additional evidence foavoring the existence of a carbene intermediate was provided as follows. Irradiation of **2** in cyclohexane, under aerated conditions, gave in addition to **7** and **8** a product **24** incorporating oxygen. Trapping of carbenes from cyclobutanones and related systems is known.[14] Analogous oxacarbene formation during photochemical formation of ring-expanded acetals from ketones in alcoholic solvents was originally suggested by Yates and Kilmurry.[15] The formation of two types of thioacetals from **2–4** clearly calls for the involvement of two thiacarbenes **22** and **23** (Scheme III). Although one could imagine a totally concerted pathway for the formation of thiacarbene **22** from excited cyclobutanethiones, involvement of a di-

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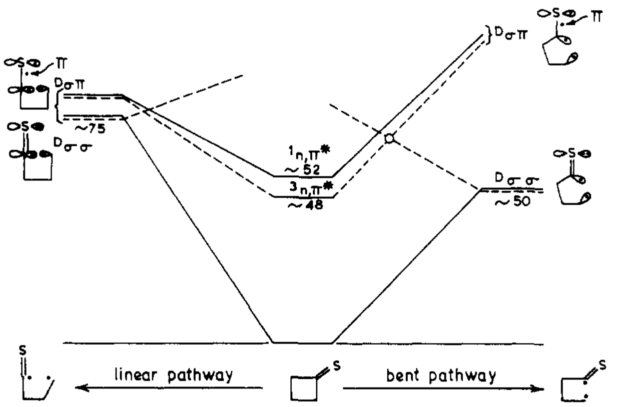

Figure 1. Approximate Salem correlation diagram for the α-cleavage of cyclobutanethiones.

radical as an intermediate in this rearrangement is suggested by the formation of an adduct corresponding to a rearranged thiacarbene **23** and by the isolation of a dithiolactone in the case of **3** and **4**. Formation of two such thioacetals indicates that the initially formed diradical exists also in the other tautomeric form, **21**. Absence of lactones and the other cyclic acetals corresponding to the rearranged oxacarbene **23** (where S=O) in the case of 1,3-cyclobutanediones is understandable[16] because the diradical derived from 1,3-cyclobutanediones would not prefer to exist in the tautomeric form corresponding to **21** (S=O)–carbon-centered radical would be more stable than that centered on oxygen.

Thus, in analogy to carbonyls, migration of the γ-carbon atom to the electron-deficient thiyl radical would afford the thiacarbene, precursor of the cyclic thioacetals. Alternatively, these radicals could decompose to thioketenes through β-cleavage and/or undergo dethiocarbonylation. In **1**–**4** only the former process occurs. The large size of the sulfur 3p orbital and the resonance stabilization of thiacarbenes by adjacent sulfur can be expected to favor ring expansion. The absence of ring expansion in cyclobutane-1,3-diones can be attributed to the reduction in the nucleophilicity of the attacking carbon radical by an adjacent electron-withdrawing carbonyl function[16] whereas such reduction is not expected in the case of thiocarbonyl functionality.

Interestingly, 2,2,4,4-tetramethylcyclobutanethione (**1**) failed to undergo ring expansion to thiacarbene. This is important because the major photochemical behavior of 2,2,4,4-tetramethylcyclobutanone is the ring expansion to oxacarbene (~70% in methanol[14]). Further, irradiation of **1** in an aerated atmosphere did not produce any products analogous to **24**–an oxygen-trapped carbene adduct. This difference in behavior can be rationalized in terms of Salem diagrams (Figure 1).[17] On the basis of this model, formation of a linear $D_{\sigma\pi}$ diradical is expected for 2,2,4,4-tetramethylcyclobutanone, and this diradical would rearrange to an oxacarbene. On the other hand, owing to the lower S_1 and T_1 energies of 2,2,4,4-tetramethylcyclobutanethione, formation of both $D_{\sigma\pi}$ linear and $D_{\sigma\sigma}$ bent diradicals would be activated in the reactive nπ* triplet state. However, cleavage to $D_{\sigma\sigma}$ bent diradical vs. a $D_{\sigma\pi}$ linear diradical would be favored by the presence of a surface crossing. This behavior is reminiscent of that of cyclohexanones. Therefore, we suggest that **1** undergoes α-cleavage in the nπ* triplet state to produce a $D_{\sigma\sigma}$ bent diradical, and owing to its geometry it would require activation energy to rearrange to a thiacarbene, and this it may fail to acquire. On the other hand, 2,2,4,4-tetramethylcyclobutanone, which generates a $D_{\sigma\pi}$ diradical, is suitably disposed for rearrangement, and oxacarbene formation is observed. This accounts for the interesting difference in behavior between carbonyl and thiocarbonyl compounds. Hence, $D_{\sigma\sigma}$ bent diradicals capable of acquiring activation energy would undergo ring expansion. We believe that this may be the case with **2**–**4**.

Sulfur-incorporating products **5**, **7**, **12**, and **16** are formed upon excitation of **1**–**4**, respectively, either in cyclohexane/benzene or in methanol. These can arise through trapping of the intermediate diradical or carbene. Formation of sulfur-incorporating product is accompanied by cyclic thioacetals in all cases except **1**. Since sulfur-incorporating product **5** is produced even in **1**, where thiacarbene is not formed, we are of the view that these products (**5**, **7**, **12**, and **16**) derive from the trapping of a intermediate diradical of the type **20** by a ground-state thione. Such sulfur incorporations in other systems have been reported.[18] However, we do not understand the fate of the sulfur-transferring ground-state thione.

Conclusions. We have established the occurrence of a Norrish type I α-cleavage process in thiocarbonyl systems. Photochemical α-cleavage from the lowest triplet state (nπ*, T_1) resulting in the generation of a diradical intermediate, appears to be general for cyclobutanethiones. It is suggested that the diradical intermediate derived from a 1,3-dithione can undergo ring expansion or close to either a dithiolactone or starting the dithione. Although both ketones and thiones undergo α-cleavage, the behavior of the resulting diradicals is different. The α-cleavage reported here for cyclobutanethiones is not efficient and is often accompanied by side reactions. Further, α-cleavage is restricted to systems having internal strain. The generality of this process with related strained systems and the feasibility of α-cleavage in unstrained systems at higher temperature is yet to be established.

Experimental Section

2,2,4,4-Tetramethylcyclobutanone, 2,2,4,4-tetramethyl-1,3-cyclobutanedione, dispiro[5.1.5.1]tetradecane-7,14-dione, and dispiro[4.1.4.1]dodecane-6,12-dione were prepared by reported procedures.[19]

Synthesis of 1 and 2. Through 10 g of 2,2,4,4-tetramethylcyclobutanone in 125 mL of ethanol were passed dry H_2S and HCl gases for 7 h, and then H_2S alone for another 10 h. During the bubbling of H_2S gas, the temperature was maintained below −5 °C. The red solution obtained at the end of the reaction was poured slowly into crushed ice and extracted with ether. The red viscous solution obtained upon evaporation of the solvent was purified by being passed through a silica gel column (yield 60%).

2,2,4,4-Tetramethyl-1,3-cyclobutanedithione was prepared by following the reported procedure[12] and was purified by column chromatography (silica gel, hexane).

Synthesis of Dispiro[5.1.5.1]tetradecane-7,14-dithione (3).[11] A pyridine solution (30 mL) of the diketone (5 g) and P_2S_5 (10 g) was refluxed for 2 h, at the end of which the reaction mixture was poured into water and extracted with ether. Evaporation of ether gave a monothione (14-oxodispiro[5.1.5.1]tetradecane-7-thione) in 70% yield. A pyridine solution (25 mL) of the monothione (4 g) and P_2S_5 (4 g) was refluxed again with vigorous

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stirring for 2 h. The cooled reaction mixture was poured into water and extracted with ether. Evaporation of ether followed by chromatographic (silica gel, hexane) separation gave **3** in 45% yield. However, continuous refluxing of the diketone with P_2S_5 for 4 h did not yield **3**.

Synthesis of Dispiro[4.1.4.1]dodecane-6,12-dithione (4).[11] HCl gas was bubbled through a methanolic solution (50 mL) of the diketone (5 g) and zinc chloride (freshly fused, 10 g) at -5 °C for 1 h. H_2S gas was then passed through the solution for 10 h during which the solution turned red. The red solution was poured into water and extracted with ether, the ether was evaporated off, and the resultant dithione was purified by column chromatography (silica gel, hexane); yield 70%.

Interestingly, refluxing the diketone in pyridine with P_2S_5 gave β-dithiolactone **17**.

General Photolysis Procedure. All irradiations were conducted either in methanol or benzene under an N_2 atmosphere at room temperature with 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. Concentration of dithiones varied between 0.008 and 0.05 M. Progress of the reaction was followed by TLC (silica gel, hexane/benzene), and, after about 30-40% completion of the reaction, solvent was evaporated off and the products were characterized by their spectral properties. All irradiations were repeated at least three times, and the required duration of irradiation for 30-40% conversion varied with the thioketones.

Photolysis of 2 in Aerated Solvent. A cyclohexane solution of dithione **2** (0.275 g, 80 mL) was irradiated in a Pyrex vessel for 72 h under aerated conditions. At the end of the irradiation, solvent was distilled off under reduced pressure and the residue that remained was chromatographed (silica gel, hexane) to give the sulfur-incorporation product **7**, disulfide **8**, 2,2,4,4-tetramethyl-3-oxo-1-cyclobutanethione, and the oxygen-trapped product **24** (yield ~10%). **24** had the following spectral properties: IR (CCl_4) 1690 (C=O stretching), 1095 cm^{-1} (C=S stretching); ^1H NMR (CCl_4) δ 1.41 (s, 6 H), 1.84 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 29.61 (q), 34.80 (q), 67.57 (s), 68.21 (s), 206.60 (s), 266.43 (s); mass spectrum (70 eV); M^+ ion at *m/e* 188.

Quenching and Sensitization Studies. Quenching and sensitization studies were carried out only for 2,2,4,4-tetramethylcyclobutanethione (**1**) and 2,2,4,4-tetramethyl-1,3-cyclobutanedithione (**2**).

Biacetyl ($E_T \sim 55$ kcal/mol), 2-acetonaphthone ($E_T \sim 59.4$), benzil ($E_T \sim 53.4$), and fluorenone ($E_T \sim 53$) were used as sensitizers. In a typical experiment, a solution of **1** or **2** (100 mg) and sensitizer (50 mg) in cyclohexane or methanol (25 mL) was irradiated with a 450-W medium-pressure mercury lamp. Selective excitation of the sensitizer was achieved with Corning glass filter CS 7.60. Products were isolated and identified as described earlier for direct excitation.

Quenching studies were carried out with alloocimene ($E_T \sim 47$ kcal/mol) and cyclooctatetraene ($E_T \sim 40$ kcal/mol) as quenchers. This was conducted in a merry-go-round apparatus with solutions varying in quencher concentration (0-0.03 M) and fixed thione concentration (0.05 M). The progress of the reaction was followed by UV-vis absorption spectroscopy (disappearance of thione). In both cases linear Stern-Volmer plots were obtained, indicating the involvement of triplet state in the reaction.

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Asymmetric Induction in the Intramolecular 1,3-Diyl Trapping Reaction through the Use of Menthyl and 8-Phenylmenthyl Esters. An Unexpected Result

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Diazenes **4a** and **4b** bearing (-)-menthyl and (-)-8-phenylmenthyl ester units as chiral auxiliaries were prepared and converted into the linearly fused tricyclopentanoid ring system through utilization of the intramolecular 1,3-diyl trapping reaction. The idealized transition state representations **4a**‡ and **4b**‡ were shown to be inadequate, for while they were useful in predicting the observed decrease in the cis,anti to cis,syn ring-fusion product ratio as the size of the ester unit increased, they provided an overly simplified view of the expectations associated with asymmetric induction. In no instance was a synthetically useful *de* value obtained. A brief mechanistic rationale which focuses upon the presumed stepwise nature of the trapping reaction is presented.

The achievement of asymmetric induction in the synthesis of complex natural products constitutes a noteworthy challenge and objective. During the past decade, considerable progress in this area of research has been recorded.[1] However, with the exception of a few reports,[2] comparatively little progress has been made with respect to the enantioselective construction of the linearly fused tricyclopentanoid ring system. In this paper we describe our efforts to achieve this objective through utilization of the intramolecular 1,3-diyl trapping reaction. As it has thus far been applied, this reaction can be described as one which involves an intramolecular cycloaddition reaction between a cyclopentane-1,3-diyl related to trimethylenemethane and a diylophile which is linked to the five-membered ring by a three-carbon tether. In this way, two

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* Alfred P. Sloan Foundation Fellow, 1980-1984.

(1) For example, see: (a) "Asymmetric Reactions and Processes in Chemistry"; Eliel, E. L., Otsuka, S., Ed.; American Chemical Society: Washington, DC, 1982; *ACS Symp. Ser.* 1982, No. 185. (b) "Modern Synthetic Methods, 1980"; Scheffold, R., Ed.; Verlag Chemie: Frankfurt, 1980.

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