74947-72-1; **6**, 104-46-1; **7a**, 74947-73-2; **7b**, 74947-74-3; **8a**, 74984-76-2; **8b**, 74984-77-3; **9**, 74947-75-4; Al_2O_3, 74947-76-5; **5b**, 1344-28-1.

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Photochemistry of Dimethylthioketene Dimers

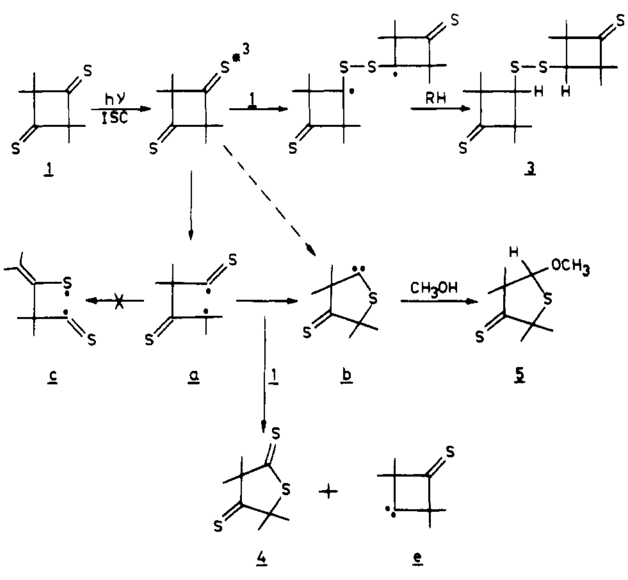
Summary: Thioketones and dithioesters, using 1,3-cyclobutanedithione and 3-mercapto-2,2,4-trimethyldithio-3-pentenoic acid β-thiolactone as models are found to undergo α-cleavage to give the diradical and carbene as reactive intermediates.

Sir: During the past several years, considerable research has been directed toward an understanding of the chemistry of electronically excited thioketones.[1] Analyses of the data from this research have revealed that thioketones are capable of undergoing three general types of reactions from both lower and higher excited states: (a) photoreduction, (b) cycloaddition to multiple bonds, and (c) intramolecular cyclization. These reactions are also primary photoreactions of ketones. But, thioketones have not yet been reported to undergo one of the primary photoreactions of ketones, namely, Norrish type I α-cleavage. In an attempt to explore the possibility of type I reactions in thioketones, we have studied the photochemistry of tetramethyl-1,3-cyclobutanedithione (**1**) and 3-mercapto-2,2,4-trimethyldithio-3-pentenoic acid β-thiolactone (**2**). The preliminary results are presented in this communication.

The electronic absorption spectrum of **1** shows three bands due to the thiocarbonyl group around 500 nm (n,π^*, ϵ 22), 298 (π,π^*, 409), and 227 (n,σ^*, 21600). That of **2** shows three bands around 460 nm (n,π^*, ϵ 12), 344 ($\pi,\pi^*_{C=S}$, 4500), and 244 ($\pi,\pi^*_{C=C}$, 3800).

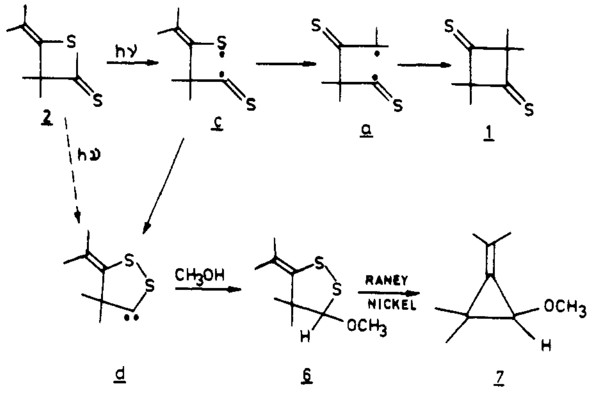
Irradiation of **1** (450-W medium-pressure mercury lamp with Pyrex filter; $\sim 5 \times 10^{-2}$ M) in nonhydroxylic solvents (cyclohexane, benzene, diethyl ether) gives two major products. These were identified as **3** and **4**.[2,3] Irradiation in methanol under similar conditions yields an additional product **5** (a 1:1 adduct) along with **3** and **4**.[3] All of these products are believed to originate from the lowest n,π^* triplet state of **1** since selective excitation of the S_1 band ($\lambda > 450$ nm; isolated by the Corning glass filter CS-3.71) and triplet sensitization (fluorenone, 2-acetylnaphthalene, benzil, and biacetyl) gave all these products. Also, consistent with this, the triplet quenchers alloocimene (47 kcal/mol) and cyclooctatetraene (<40 kcal/mol) quenched the formation of photoproducts **3**–**5** upon direct excitation.

Scheme I



SOLVENT	PRODUCTS
Cyclohexane	3 (15%) ; 4 (45%)
Methanol	3 (20%) ; 4 (30%) ; 5 (< 10%)

Scheme II



SOLVENT	PRODUCT
Cyclohexane	1 (> 60%)
Methanol	6 (80 %)

Irradiation of **2** (450-W medium-pressure mercury lamp with Pyrex filter; $\sim 2 \times 10^{-2}$ M) in nonhydroxylic solvents such as cyclohexane, ether, and benzene gave 1,3-dithione **1** in 60% yield. On the other hand, irradiation of **2** in methanol gave a 1:1 adduct as the major product (80%) identified to be **6**.[4] In accordance with the proposed structure, Raney nickel desulfurization of **6** gave **7**. The appearance of photoproducts **1** and **6** only when the S_1

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(1) de Mayo, P. *Acc. Chem. Res.* 1976, *9*, 52.

(2) In addition to **3** and **4**, we have isolated two products believed to be some type of dimers of the intermediate carbenes **b** and **e**. Characterization of these two products is hampered by the inability to obtain pure samples of these compounds for spectral identification.

(3) All three compounds **3**–**5** gave satisfactory elemental analyses. Their spectral data are shown below. **3**: IR (neat) 2960, 2920, 2860, 1440, 1350, 1290, 1250, 1120, 990, 880 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33 (s, 12 H), 1.382 (s, 12 H), 3.720 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 24.054 (q), 28.569 (q), 63.251 (s), 65.649 (d), 281.536 (s); mass spectrum (70 eV), *m/e* 346 (M^+). Anal. Calcd for $C_{16}H_{26}S_4$: C, 55.48; H, 7.57. Found: C, 56.08; H, 7.87. **4**: IR (neat) 2970, 2920, 2860, 1440, 1360, 1220, 1170, 1060, 960, 900, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.578 (s, 6 H), 1.802 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 33.563 (q), 33.723 (q), 70.963 (s), 77.891 (s), 245.175 (s), 267.671 (s); mass spectrum (70 eV), *m/e* 204 (100%), 172 (17.9), 141 (42.9), 128 (59.5), 113 (40.5), 96 (38.1), 86 (83.3), 85 (48.8), 81 (53.6), 71 (57.1), 59 (33.3), 41 (35.7). Anal. Calcd for $C_8H_{12}S_3$: C, 47.06; H, 5.92. Found: C, 46.71; H, 6.401. **5**: ^1H NMR ($CDCl_3$) δ 1.352 (s, 3 H), 1.393 (s, 3 H), 1.593 (s, 6 H), 3.349 (s, 3 H), 4.809 (s, 1 H). A careful search for **2** during the irradiation of **1** failed to show the presence of any **2**.

(4) Compound **6** gave satisfactory elemental analysis and had the following spectral properties: IR (neat) 2970, 2930, 2860, 1450, 1360, 1190, 1090, 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.341 (s, 3 H), 1.431 (s, 3 H), 1.847 (s, 3 H), 1.891 (s, 3 H), 3.495 (s, 3 H), 4.609 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 21.546 (q), 23.131 (q), 26.478 (q), 26.830 (q), 51.489 (s), 58.299 (q), 105.796 (d), 123.526 (s), 137.087 (s); mass spectrum (70 eV), *m/e* 204 (100%), 172 (47.0), 141 (45.5), 139 (37.9), 128 (36.4), 108 (50.0), 96 (56.1), 86 (51.5), 85 (50.0); 81 (86.4), 71 (39.4), 59 (62.1), 41 (77.3). Anal. Calcd for $C_9H_{16}OS_2$: C, 52.93; H, 7.90. Found: C, 52.77; H, 7.702.

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band of **2** is selectively excited ($\lambda > 420$ nm, isolated by Corning glass filter CS-3.73) and not upon photosensitization (benzophenone, *p,p'*-dibromobiphenyl and fluorenone) demonstrates that these originate from the lowest n,π^* singlet state of **2**. In conformity with this, alloocimine, a triplet quencher, failed to quench the formation of **1** and **6**.

The above results are summarized below: (a) 1,3-Dithione **1** gives **3** and **4** in nonhydroxylic solvents and **3–5** in methanol from the *first excited triplet state*.[5] (b) Dithiolactone **2** gives 1,3-dithione **1** in nonhydroxylic solvents and a 1:1 adduct (**6**) in methanol from the *first excited singlet state*.

The results of our study can be rationalized by the occurrence of an unprecedented (in thiocarbonyls) α-cleavage in **1** and **2** as illustrated in Schemes I and II. The suggested mechanism for these reactions involve diradical and/or carbene intermediates. Photoproduct **3** must arise through sulfur incorporation of the intermediate carbene or diradical (**a** or **b**) by the ground-state thione. Though substantial evidence for this carbene pathway is not provided, such sulfur incorporation in other systems has been reported.[2,6]

Interestingly, the photochemical behavior of **1** and **2** is different from that of the corresponding carbonyl compounds.[7] The diradical derived from analogous oxygenated compounds either eliminates carbon monoxide or cleaves to give dimethylketene, whereas evidence for like products are not to be seen in **1** and **2**. In the case of 1,3-diketone **1** (S = O) and the corresponding β-lactone **2** (S = O), no evidence for the formation of a carbene intermediate is reported.[7]

In summary, we have established the occurrence of Norrish type I α-cleavage in thiocarbonyl compounds.[8,9] A detailed understanding of the mechanism of the above reactions and a study of related thiocarbonyl systems await our further investigation.

Acknowledgment. We are grateful to the Department of Science and Technology, Government of India, for financial support and to Professors R. S. H. Liu and N. J. Turro for mass spectra. K.M. thanks the University Grants Commission, New Delhi, for a Junior Research Fellowship.

Registry No. **1**, 10181-56-3; **2**, 10181-61-0; **3**, 74835-36-2; **4**, 74835-37-3; **5**, 74835-38-4; **6**, 74835-39-5; **7**, 74835-40-8.

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[5] The irradiation of 1 in an oxygen atmosphere was reported earlier to give the corresponding 1,3-diketones (1, S = O) only: Worman, J. J.; Shen, M.; Nichols, P. C. *Can. J. Chem.* **1972**, *50*, 3923.

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[7] Turro, N. J.; Cole, T. *Tetrahedron Lett.* **1969**, 3451.

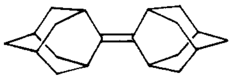
[8] The photochemical cleavage reactions of *S*-aryl and *S*-acyl xanthates, dithio- and trithiocarbonates, and thiocarboxylic *O*-esters have been reported: Barton, D. H. R.; George, M. V.; Tomeda, M. *J. Chem. Soc.* **1962**, 1967; Singh, S. N.; George, M. V. *J. Org. Chem.* **1972**, *37*, 1375; Schonberg, A.; Sodete, U. *Tetrahedron Lett.* **1967**, 4977; Heine, H.; Metzner, W. *Justus Liebigs Ann. Chem.* **1969**, *724*, 223; Lundersdorf, R.; Martens, J.; Pakzad, B.; Praefeke, K. *Ibid.* **1977**, 1992; Rungwerth, D.; Schwetlick, K. *Z. Chem.* **1974**, *14*, 17; Schmidt, V.; Kabitzke, K. H. *Angew. Chem.* **1964**, *76*, 687.

[9] The direct comparison of the behavior of diradical and carbene intermediates (**a–d**) derived from **1** and **2** is not possible due to the different spin states involved in the reaction.

Unusual Reactions of Adamantylideneadamantane with Metal Oxidants. Isolation of Stable Chloronium Salts

Summary: Reaction of adamantylideneadamantane with OsO_4 has provided the first spectroscopic evidence for coordination of an olefin to a d^0 metal species, while its reactions with $SbCl_5$ or $MoOCl_4$ give remarkably stable chloronium salts $[AdAdCl^+][SbCl_6^-]$ and $[AdAdCl^+][Mo_2O_2Cl_7^-]$.

Sir: The initial step in the reaction of olefins with metal oxidants has been proposed[1] to be coordination of the reactants to form a complex. Virtually nothing is known about these key intermediates, possibly because they rapidly collapse to organometallic species[1] and ultimately to products. Because of its unusual structure, adamantylideneadamantane,[2] I, fails to undergo[3] many addition reactions typical of olefins and yet forms complexes with a variety of Lewis acids.[4] Therefore, it was expected that complexes between I and metal oxidants might be directly observable. This expectation was borne out for reactions involving I and OsO_4. However, I readily reacted with metal chloride oxidants such as $MoOCl_4$ in an unexpected way as described below.



I

In general, the rate of reaction of olefins with OsO_4 increases with increasing alkyl substitution of the olefinic double bond along the series mono- < di- < tri- < tetrasubstituted.[5] In contrast, tetrasubstituted I reacted with 0.1 M OsO_4 in hexane 370 times more slowly than even monosubstituted 1-octene.[6,7] A solution containing 0.05 M OsO_4 and 0.05 M I in heptane was pale red-orange in color. The electronic spectrum of such a solution immediately on mixing showed a new absorbance in the visible region not present in solutions containing only OsO_4 or I (see Figure 1). Subtraction of the contribution due to unreacted OsO_4 indicated an absorbance maximum at 415 nm. We assign this absorbance to ligand to metal charge transfer in a weak complex involving OsO_4 and I. Consistent with this assignment, the intensity of this band did not increase with time but gradually diminished as the reactants were consumed.

Antimony pentachloride and molybdenum oxytetrachloride are members[8,9] of a class[10] of oxidants which in-

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[1] Sharpless, K. B.; Teranishi, A. Y.; Backvall, J. E. *J. Am. Chem. Soc.* **1977**, *99*, 3120–3128.

[2] I utilized in this study was prepared by the procedure of McMurry and was additionally purified by chromatography (alumina) and repeated recrystallization from 1:1 $EtOH/CHCl_3$: McMurry, J. E.; Fleming, M. P. *J. Am. Chem. Soc.* **1974**, *96*, 4708–4709.

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[5] Sharpless, K. B.; Williams, D. R. *Tetrahedron Lett.* **1975**, 3045–3046.

[6] Pseudo-first-order rate constants were determined for the reaction of I and of 1-octene with a large excess of 0.1 M OsO_4 in hexane at 22.5 °C. These rates were, respectively, 8.3×10^{-6} and 3.1×10^{-3} s^{-1}. Reactions were followed by monitoring the disappearance of starting olefin.

[7] The product of this interaction is the osmate ester derived from I. This was converted upon reductive workup ($LiAlH_4$) to the corresponding glycol, with properties identical with those produced by reductive coupling of adamantanone: Wynberg, H.; Boelman, E.; Wieringa, J. H.; Strating, J. *Tetrahedron Lett.* **1970**, 3613–3614.

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