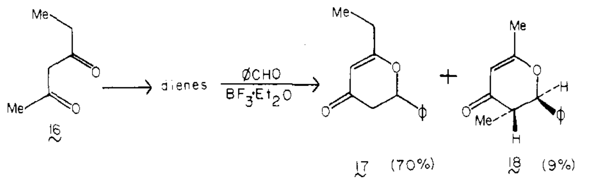
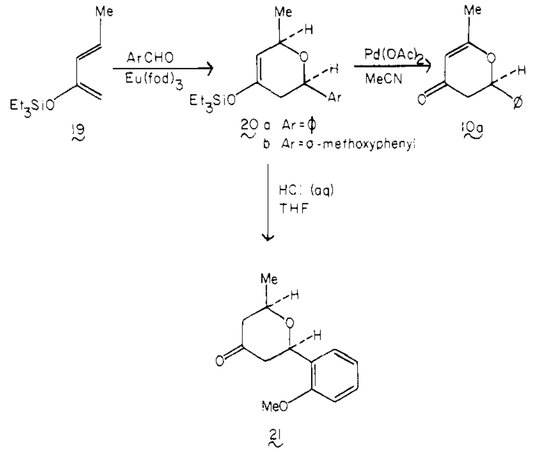


usual conditions (vide supra),[7] a mixture of dienes was produced.[11] Reaction of this mixture with benzaldehyde in the presence of $BF_3{\cdot}Et_2O$ provided a 70% yield of **17**.[6] The trans-trisubstituted isomer **18**[6] was also obtained in 9% yield. While we have no data on the efficacy of the participation of the individual dienes in the process, the product distribution suggests that the major product of bissilylation is the 1-ethyl-1,3-bis(silyloxy) system.[10] While the extendability of this preferential silylation to other systems remains to be determined, the ability to use nonsymmetrical β-diketones in an effective way is encouraging for future possibilities.

Finally, we record the feasibility of using 1-alkyl-3-oxygenated dienes in the cyclocondensation reaction.



Through the use of Eu(fod)$_3$ catalysis,[5] the silyloxy diene **19**[12] reacts with the appropriate aromatic aldehyde to give enol ethers **20a**[6] and **20b**[6] in nearly quantitative yield. Compound **20b** was hydrolyzed to the 2,6-disubstituted tetrahydropyrone **21**[6] with aqueous HCl–THF. Thus, the endo selectivity of the europium-induced pericyclic reaction[5] provides a stereospecific entry to cis-2,6-disubstituted tetrahydropyrones.

Alternative possibilities for taking advantage of the intermediate silyl enol ether functionality have been realized. For instance, transformation of **20a** → **10a**[13] (previously obtained from **8**) suggests some of the potentialities in this direction. Applications of these findings to the synthesis of aryl glycosides and other natural products are being examined in our laboratory.

These significant expansions in the scope of the cyclocondensation reaction are being applied to a variety of total synthesis undertakings. The results will be described in due course.

Acknowledgment. This research was supported by PHS Grant HL49784. A Kent Fellowship to D. F. H. is gratefully acknowledged. NMR spectra were obtained through the auspices of the Northeast Regional NSF/NMR Facility at Yale University, which was supported by NSF Chemistry Division Grant CHE 7916210.

Registry No. **5**, 61539-61-5; **6a**, 88083-77-6; **6b**, 88083-78-7; **7a**, 123-54-6; **7b**, 815-57-6; (*E*)-**8**, 63446-76-4; (*Z*)-**8**, 63446-77-5; (*E*)-**9**, 81942-45-2; (*Z*)-**9**, 81942-37-2; **10a**, 88083-79-8; **10b**, 88083-80-1; **11a**, 88083-81-2; **11b**, 88083-82-3; **12**, 7424-54-6; **13**, 88083-83-4; **14a**, 88083-84-5; **14b**, 88083-85-6; **15a**, 88083-86-7; **15b**, 88083-87-8; **17**, 88083-88-9; **18**, 88083-89-0; **16**, 3002-24-2; **19**, 88083-96-9; **20a**, 88083-97-0; **20b**, 88083-98-1; **21**, 88083-99-2; (*E*)-i, 88083-90-3; (*Z*)-i, 88083-91-4; (*Z,Z*)-ii, 88083-92-5; (*Z,E*)-ii, 88083-93-6; (*E,E*)-ii, 88083-94-7; (*E,Z*)-ii, 88083-95-8; Me_3SiOTf, 27607-77-8; Et_3SiCl, 994-30-9; benzaldehyde, 100-52-7; *n*-heptanal, 111-71-7; pent-3-en-2-one, 625-33-2.

Supplementary Material Available: Representative experimental procedures and spectral data for all compounds (6 pages). Ordering information is given on any current masthead page.

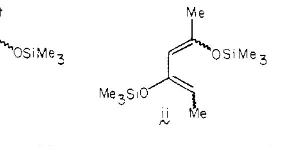
Samuel Danishefsky,* Daniel F. Harvey
George Quallich, Biing Jiun Uang
Department of Chemistry, Yale University
New Haven, Connecticut 06511

Received September 24, 1983

---

[10] 2,4-Hexanedione was purchased from Pfaltz and Bauer, Inc.

[11] Analysis of the 270-MHz ^{1}H NMR spectrum suggests this mixture to be composed of approximately 85% of a 1:1 mixture of dienes i and 15% of one of the isomeric dienes ii. The NMR portion of the spectrum attributable to i is very similar to that of isomers **8** while that portion assignable to ii is very similar to the spectrum previously seen for compounds **13**.



[12] This diene was prepared by silylation (LDA/TESCl) of a mixture of 3-penten-2-one and 4-methyl-3-penten-2-one (from Aldrich) followed by distillation (87–93 °C (10 mmHg)).

[13] Ito, Y.; Hirao, T.; Saegusa, T. *J. Org. Chem.* **1978**, *43*, 1011.

Upper Excited State Reactions of Thioketenes: Di-*tert*-butylthioketene

Summary: Di-*tert*-butylthioketene, while unreactive upon excitation to S_1, produces thiirenylidene carbene and zwitterionic intermediates upon excitation to S_2.

Sir: Photochemistry of ketenes, allenes, and related cumulenes is of contemporary interest.[1] Though the photobehavior of parent thioketene in an argon and nitrogen matrix at low temperatures ($\sim$8 K)[2] has received a great deal of attention, largely due to their involvement in the matrix isolation of thiirenes, no report has appeared on the photochemistry of thioketenes in solution. Photolysis (λ 215–260 nm) of parent thioketene in the above matrix results in photodecomposition and conversion to ethynyl mercaptan.[2] Interestingly, it is stable to light of wavelength above 280 nm. It has been suggested that the interconversion of thioketene to ethynethiol takes place via thiirenyledene carbene and thiirene.[3] We describe the first account of the photochemical behavior of a stable thioketene—di-*tert*-butylthioketene (**1**)—in solution. Results presented in this report support some of the earlier sug-

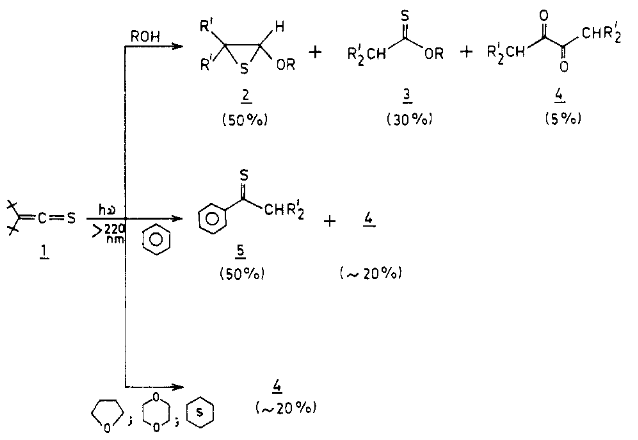
---

[1] (a) Russel, R.; Rowland, F. S. *J. Am. Chem. Soc.* **1970**, *92*, 7508. (b) Kirmse, W.; Spaleck, W. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 776. (c) Klett, M. W.; Johnson, R. P. *Tetrahedron Lett.* **1983**, *24*, 1107. (d) Klett, M. W.; Johnson, R. P. *Ibid.* **1983**, *24*, 2523. (e) Stierman, T. J.; Johnson, R. P. *J. Am. Chem. Soc.* **1983**, *105*, 2492. (f) Steinmetz, M. G.; Mayers, R. T.; Yang, J. C. *Ibid.* **1982**, *104*, 3518. (b) Fujita, K.; Matsni, K.; Shono, T. *Ibid.* **1975**, *97*, 6256. (h) Carlsen, L.; Schaumann, E. *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 2624. (i) Zwanenburg, B. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 1.

[2] Kranz, A.; Laureni, J. *J. Am. Chem. Soc.* **1981**, *103*, 486.

[3] Trorres, M.; Loron, E. M.; Gunning, H. E.; Stransz, O. P. *Pure Appl. Chem.* **1980**, *52*, 1263.

Scheme I[a]



[a] R' = $(CH_3)_3C$; R = CH_3, CH_3CH_2, $(CH_3)_2CH$.

gestions and observations made with the parent system in matrix. Importantly, 1 shows wavelength-dependent behavior. Products isolated upon S_2 irradiation suggest zwitterions and thiirenylidene carbene as intermediates in the photoreactions.

Photolysis of di-*tert*-butylthioketene (**1**)[4] in various solvents (benzene, cyclohexane, dioxane, tetrahydrofuran, methanol, ethanol, and 2-propanol) using a low-pressure mercury arc lamp (>220 nm) resulted in rapid loss of thioketene color (6 h). Evaporation of the solvent and separation of products by preparative TLC gave the products shown in Scheme I. Photolysis of **1** in dioxane, tetrahydrofuran, and cyclohexane gave a complex mixture of products from which 2,2,7,7-tetramethyl-3,6-di-*tert*-butyl-4,5-octanedione (**4**) could be isolated in 20% yield. Irradiations in alcoholic solvents were clean and gave 2-alkoxy-3,3-di-*tert*-butylthiirane (**2**) as the major product (~50%) along with thiopivalic acid ester **3** and diketone **4**. Irradiation in benzene where most of the light was absorbed by **1** gave 2,2-di-*tert*-butylthioacetophenone (**5**) and **4**. All products were characterized by their spectral properties (UV, IR, ^1H and ^{13}C NMR, and mass spectra).[5] Consistent with the proposed structure, Raney nickel desulfurization of **2** gave 2,2-di-*tert*-butylethanol.

The electronic absorption spectra of di-*tert*-butylthioketene show three bands due to the thiocarbonyl group around 211 ($n\sigma^*$, ϵ 32 300); 239 ($\pi\pi^*$, 4200), and 570 nm ($n\pi^*$, 8). 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. The triplet energy (T_1) based on the emission from a glassy matrix at 77 K is near 43 kcal/mol.

The photochemical process resulting in the products shown in Scheme I is believed to originate from an upper excited state, based on selective excitation and sensitization studies. Selective excitation of **1** to $n\pi^*$ singlet state using 500-W tungsten lamps or 450-W medium-pressure mercury lamps with Corning glass filter CS-3.70 (>480 nm) in all the above solvents for over a month did not result in any reaction. This establishes that the lowest excited singlet S_1 is not the reactive species. Triplet sensitization in ethanol and benzene was conducted with benzil (53 kcal/mol), Michler's ketone (62 kcal/mol), and benzophenone (69 kcal/mol). These have triplet energies higher than T_1 of **1** and have high intersystem-crossing efficiencies. It would be expected, thus, that energy transfer should be efficient and near diffusion controlled. However, none of the above sensitizers brought forth any change over **1**, 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 ca. 105 kcal/mol and that of S_1 is ca. 46 kcal/mol, the energy of any chemically active higher triplet must be between these limits. Because of absorption and other difficulties, an unambiguous triplet quencher for this range was unavailable. Due to absorption problems only two triplet sensitizers, xanthone (74 kcal/mol) and acetone (79 kcal/mol) could be used. Xanthone and acetone effected some change after 30 h of irradiation. Irradiation of these sensitizers in presence of **1** in ethanol gave **4** and **2** in extremely low yields, and, importantly, **3** was not among the products. Similarly, in benzene **5** and **4** were formed but in very low yields. Since these sensitizations did not result in the same product distribution as upon direct excitation (>220 nm) we believe that these may not truly be a triplet process. Therefore, we tentatively regard the higher excited singlet (S_2) as the reactive state upon direct excitation. Upper excited state reactions in thiocarbonyl systems have been reported earlier.[6]

For a complete description of the photochemistry of thioketenes, it is necessary to have information on the nature of the potential surfaces for the ground and excited states as a function of geometrical parameters. However, such information is not available. On the other hand, quantum mechanical calculations on the ground and excited states of related systems such as allenes and ketenes have been reported,[7,8] and these are useful in drawing some conclusions regarding the photobehavior of thioketenes. Proposed mechanistic schemes for the formation of **2**–**5** are shown in Scheme II, and this involves zwitterions **6** and **7** and thiirenylidene carbene **10** as intermediates. Addition of alcohols to thioketene **1** is undoubtedly an excited-state process as no addition occurs at room temperature even in presence of acids (in dark) after 3 days.[4] We suggest that there is an increase in positive charge at the thiocarbonyl carbon and a corresponding negative charge at the terminal atoms of thioketene in the excited state. We believe that thiopivalic acid esters **3** result from protonation of the zwitterion **6** having the above features. On the basis of ab intio MCSCF calculations, it has been concluded that two energetically proximate suddenly polarized zwitterions corresponding to **6** and **7** (where S = CH_2) are

---

(4) Elam, E. U.; Rash, F. H.; Dougherty, J. T.; Goodlett, V. W.; Brannock, K. C. *J. Org. Chem.* **1968**, *33*, 2738.

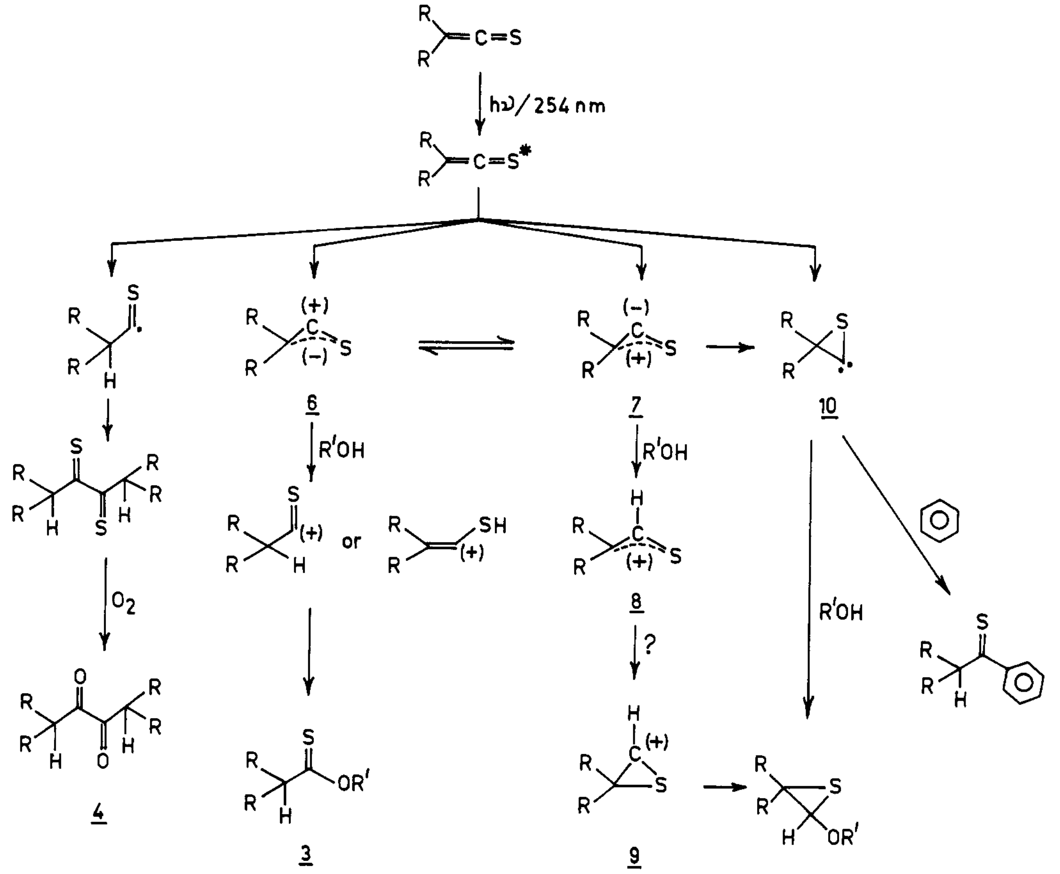
(5) Spectral properties of **2–6** are provided below; all compounds gave satisfactory elemental analyses. **2** (R = CH_3): IR (neat) 2900, 1440, 1380 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0 (9 H, s), 1.05 (9 H, s), 3.3 (3 H, s), 5.0 (1 H, s); ^{13}C NMR ($CDCl_3$) δ 31.24 (q), 31.3 (q), 38.63 (s), 39.92 (s), 58.4 (s), 85.15 (d); mass spectra (70 eV), *m/z* 202, 187, 170. **3** (R = CH_3): IR (neat) 2950, 1395, 1366, 1242, 1185, 1121 cm^{-1}, ^1H NMR ($CDCl_3$) δ 1.0 (18 H, s) 2.5, 3.0 (1 H, s), 3.9, 4.0 (3 H, s); mass spectra (70 eV), *m/z* 202, 146, 137, 57. **4** (mp 61 °C): IR ($CHCl_3$) 2930, 1710, 1490, 1380, 1340 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.1 (18 H, s), 2.2 (1 H, s); ^{13}C NMR ($CDCl_3$) δ 30.8 (q), 39.6 (s), 64.8 (d), 181.2 (s); mass spectra (70 eV), *m/z* 310, 254, 155. **5**: UV (cyclohexane) λ_{max} nm (ϵ) 595 (54), 315 (7080), 250 (3300), 227 (6000), 205 (6660); IR (neat) 3050, 2950, 1600, 1440, 1420, 1380, 1210, 1190 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0 (18 H, s), 4.3 (1 H, s), 7.0–8.0 (5 H, m); ^{13}C NMR ($CDCl_3$) δ 31.2 (q), 31.3 (q), 71.9 (d), 126.9 (d), 128.1 (d), 131.2 (d), 158.8 (s), 252.6 (s); mass spectra (70 eV), *m/z* 248, 204, 202, 192, 127, 121. **6** (R = Me): IR (neat) 2930, 1380, 1260 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0 (18 H, s), 2.2 (1 H, t), 3.2 (3 H, s), 3.45 (2 H, d); mass spectra (70 eV), *m/z* 172, 116, 101.

(6) de Mayo, P. *Acc. Chem. Res.* **1976**, *9*, 52. Turro, N. J.; Ramamurthy, V.; Cherry, W.; Farneth, W. *Chem. Rev.* **1978**, *78*, 125.

(7) Harding, L. B.; Goddard, W. A.; III. *J. Am. Chem. Soc.* **1976**, *98*, 6093. Del Bene, J. E. *Ibid.* **1972**, *94*, 3713.

(8) Seeger, R.; Krishnan, R.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1977**, *99*, 7103. Johnson, R. P.; Lam, B. "Abstract of Papers", 17th Midwest Regional Meeting of the American Chemical Society, Columbus, OH, Nov 5–6, 1981.

Scheme II[a]



[a] R = $(CH_3)_3C$; R' = CH_3, CH_2CH_3, $CH(CH_3)_2$.

present on the excited-state surface of allenes.[8] Similar calculations suggest a partial negative change on the carbonyl carbon of ketenes in the excited state.[7] Based on the above features of ketenes and allenes, we speculate that there might be another zwitterion (7) being oppositely polarized to that of 6. But, products corresponding to the protonation of the central carbon in 7 have not been isolated by us. Protonation of 7 would lead to a stable allyl cation 8, and this would be trapped to give thioaldehyde, a fairly unstable compound.[9] 8, present in the ground-state surface, might cyclize to 9, and this may be lead to thiirane 2. On energy grounds this mechanism seems unlikely for the formation of 2. One of the likely pathways for the decay of 7 is electrocyclization to thiirenylidene carbene 10. An alternate mechanism, a direct cyclization of the excited state of 1 is also conceivable for the formation of 10. If the bent geometry is favored for the excited state of thioketene, as is often suggested in the case of ketenes and allenes,[7,8] such an intramolecular rearrangement to 10 should indeed be favored in the upper excited state. The thiirane 2 and thione 6[10] are the products resulting from trapping of this novel intermediate. α-Diketone 4 probably results from photoreduction and ground-state oxidation.[11]

The photobehavior of thioketenes, established in solution for the first time, differs significantly from that of ketenes. Generally, solution-phase photolysis of ketenes results in the loss of carbon monoxide, but such behavior has not been observed for thioketenes. Quite recently, sterically hindered ketenes were found to undergo novel photoreactions indicating "umpolung" of the excited state.[1b] However, no evidence for oxirenylidene carbene was reported. The behavior of thioketenes to undergo rearrangement to thiirenylidene carbene is reminescent of the excited-state behavior of cyclobutanethiones and cyclopropenethiones.[12] A detailed understanding of the photobehavior of thioketenes awaits our further investigation with related thioketenes.

Acknowledgment. Department of Science and Technology, Government of India, is thanked for financial support. Initial experimental assistance by Mr. V. Jayathirtha Rao is gratefully acknowledged. Spectral help by Mr. N. Omkaran is greatly appreciated.

Registry No. 1, 16797-75-4; 2 (R = Me), 88181-00-4; 3 (R = Me), 16797-77-6; 4, 29679-00-3; 5, 88181-01-5; 6 (R = Me), 44158-23-8.

Sharat Singh, V. Ramamurthy*
Department of Organic Chemistry
Indian Institute of Science
Bangalore 560 012, India

Received July 8, 1983

---

[9] Vedejs, E.; Perry, D. A. *J. Am. Chem. Soc.* **1983**, *105*, 1683. Vedejs, E.; Eberlein, T. H.; Varie, D. L. *Ibid.* **1982**, *104*, 1445. Okazaki, R.; Ishii, A.; Fukuda, N.; Oyama, H.; Inamoto, N. *J. Chem. Soc., Chem. Commun.* **1982**, 1187.

[10] Experiments are underway to explore to generality of addition of thioketenes to aromatics and to understand the mechanism of this addition.

[11] Jayathirtha Rao, V.; Muthuramu, K.; Ramamurthy, V. *J. Org. Chem.* **1982**, *47*, 127. Ramnath, N.; Ramesh, V.; Ramamurthy, V. *Ibid.* **1983**, *48*, 214.

[12] Muthuramu, K.; Sundari, B. S.; Ramamurthy, V. *J. Org. Chem.*, in press. Sharat, S.; Bhadbhade, M. M.; Venkatesan, K.; Ramamurthy, V. *Ibid.* **1982**, *47*, 3550. Muthuramu, K.; Sundari, B. S.; Ramamurthy, V. *Tetrahedron* **1983**, *39*, 2719.