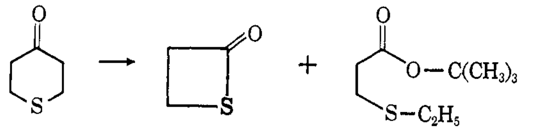
Photolysis of γ-Keto Sulfides

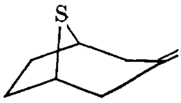
Sir:

The ultraviolet spectra of β-keto sulfides,[1-3] the cyclic γ-keto sulfide thiacyclohexan-4-one[1-3] (**1**), and the cyclic δ-keto sulfide thiacyclooctan-5-one[4,5] show evidence for charge transfer in the excited state as well as perturbation of the n,π^* state of the carbonyl group. We have undertaken a study of the photochemistry of these systems and related systems to investigate possible synthetic applications of these reactions. This communication reports the results of our initial studies with γ-keto sulfides.

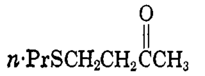
Photolysis[6] of **1**[7,8] as a 0.21% (w/v) solution in *t*-butyl alcohol for 26.4 hr yielded 46.5%[9] β-thiolactone **2**[10,11], 49% ester **3**,[12,13] and 5%[9] unreacted **1**. Photolysis of **1**[6] as a 0.29% solution in Freon-113 for 48.2 hr produced **2** in 51% yield.[9]



1 **2** **3**



4



$n\text{-PrSCH}_2\text{CH}_2\overset{\text{O}}{\overset{\|}{\text{C}}}\text{CH}_3$

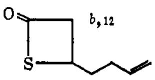
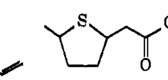
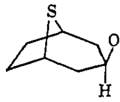
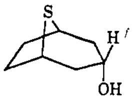
5

Similar studies of the photolysis[6] of 8-thiabicyclo-[3.2.1]octan-3-one[14,15] (**4**) in a variety of solvents yielded the products indicated in Table I.

The ultraviolet spectrum of the acyclic γ-keto sulfide **5** shows no charge-transfer band.[16,17] Photolysis of **5** in Freon-113 with a Pyrex, Corex, or Vycor filter yields only polymeric material; photolysis in *t*-butyl alcohol yields predominately polymeric material plus at least six other products, formed in a total yield of less than 5%.

Since the charge-transfer bands for **1** and **4** extend beyond 280 mμ and overlap with the n,π^* band, our results do not enable us to conclude whether charge transfer or n,π^* excitation is responsible for the observed products.[18]

Table I. Yields of Products from Photolysis of **4**

Solvent	Time, hr	Concn, % (g/ml)	% yield[a]				
			 [b,12]	 [12]	 [f]	 [f]	Unreacted **4**
t-Butyl alcohol	39	0.20	49 (84)	(0)	(6)	(1)	6 (9)
t-Butyl alcohol	95	1.20	43 (67)	0.5 (3)[c]	15	2	36 (33)
Methanol	62.3	0.20	(2)	(4)[d,e]	(42)	(6)	(45)
Cyclohexane	74	0.20	(0)		15	4	70
Freon-113	15.3	0.40	32			0	50

[a] The numbers not in parentheses are isolated yields determined by column chromatography on 80–100 mesh silicic acid followed by distillation or sublimation; the yields in parentheses are determined by gas chromatography as described in ref 9. [b] $\nu_{\text{max}}^{\text{CHCl}_3}$ 1782 (s), 1637 (w), 1000 (m), 910 (m) cm^{-1}; nmr (CCl$_4$): δ 1.7–2.6 (multiplet, 4 H, $-\text{CH}_2\text{CH}_2-$), 3.2–4.4 (multiplet, 3 H, $-\text{CH}-\text{CH}_2-\text{CO}-\text{S}$), 4.8–5.2 (multiplet, 2 H, $=\text{CH}_2$), 5.4–6.3 (multiplet, 1 H, $-\text{CH}=$). [c] R = C(CH$_3$)$_3$. [d] R = CH$_3$. [e] Structure not established; structure based on retention time on gas chromatography. [f] R. E. Ireland and N. H. Smith, *Chem. Ind.* (London), 1252 (1959).

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(1) E. A. Fehnel and M. Carmack, *J. Am. Chem. Soc.*, **71**, 84 (1949).
(2) G. Bergson and A-L. Delin, *Arkiv Kemi*, **18**, 489 (1961).
(3) G. Bergson, G. Claeson, and L. Schotte, *Acta Chem. Scand.*, **16**, 1159 (1962).
(4) N. J. Leonard, T. L. Brown, and T. W. Milligan, *J. Am. Chem. Soc.*, 81, 504 (1959).
(5) N. J. Leonard, T. W. Milligan, and T. L. Brown, *ibid.*, **82**, 4075 (1960).
(6) Hanova Type L 450-w lamp with Pyrex filter.
(7) $\lambda_{\text{max}}^{\text{Freon-113}}$ 230 mμ (ϵ 640), 291 mμ (ϵ 21); $\lambda_{\text{max}}^{(\text{CH}_3)_3\text{COH}}$ 237 mμ (ϵ 435), 287 mμ (ϵ 22).
(8) C. Barkenbuss, V. C. Midkiff, and R. M. Newman, *J. Org. Chem.*, **16**, 232 (1951).
(9) Not isolated yield; the mixture was analyzed by gas chromatography on a 6-ft column of 10% Carbowax on Chromosorb P at 140°. Samples were collected on a 2.5-ft column at 110° for spectra and combustion analysis or comparison with an authentic sample.
(10) British Patent 840,658 (1960); *Chem. Abstr.*, **55**, 1452 (1961).
(11) $\nu_{\text{max}}^{\text{CHCl}_3}$ 1776 cm^{-1}; nmr (CCl$_4$): δ 3.05 and 4.02 ppm, triplets, $J = 6.5$ cps.
(12) Satisfactory analyses have been obtained for all new compounds reported.
(13) The isolated yield of **3** was 36%; isolated by column chromatography on 80–100 mesh silicic acid followed by distillation.
(14) $\lambda_{\text{max}}^{\text{Freon-113}}$ 232 mμ (ϵ 570), 294 mμ (ϵ 20); $\lambda_{\text{max}}^{(\text{CH}_3)_3\text{COH}}$ 238 mμ (ϵ 399), 287 mμ (ϵ 21).
(15) V. Horak, J. Zavada, and A. Pishala, *Acta Chim. Hung.*, 21, 97 (1959).
(16) $\lambda_{\text{max}}^{\text{Freon-113}}$ 283 mμ (ϵ 28); $\lambda_{\text{max}}^{(\text{CH}_3)_3\text{COH}}$ 280 mμ (ϵ 34).
(17) Similar results are reported for other acyclic γ-keto sulfides; see ref 1–3.
(18) This research has been supported by National Science Foundation Grant No. GP-5761.
(19) Alfred P. Sloan Fellow, 1963–1967.

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Received February 27, 1967

Photochemistry of Isothiochroman-4-one

Sir:

We wish to report an interesting photochemical rearrangement of the isothiochroman-4-one system.

Photolysis[1] of **1**[2,3] in cyclohexane (0.20% w/v) for 6–7 hr produced in 20% yield a liquid isomer identified as thiochroman-3-one (**3**) by analysis,[4] spectral data,[5] and the synthesis of an authentic sample by Dieckmann cyclization of **4** followed by acid hydrolysis and decar-

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(1) Hanovia Type L 450-w lamp with Pyrex filter.
(2) C. C. Price, M. Hori, T. Parasaran, and M. Polk, *J. Am. Chem. Soc.*, **85**, 2278 (1963); J. von Braun and K. Weissbach, *Ber.*, **62**, 2416 (1929); P. Cagniant and D. Cagniant, *Bull. Soc. Chim. France*, 2225 (1961).
(3) $\lambda_{\text{max}}^{\text{isooctane}}$ 244.5 mμ (ϵ 10,400), 289 (1540), 348 (149).
(4) Satisfactory analyses have been obtained on all new compounds reported.
(5) $\nu_{\text{max}}^{\text{CCl}_4}$ 1723, 1468, 1443, 1385, 1253, 1236, 951, 500, 440 cm^{-1}; $\lambda_{\text{max}}^{\text{isooctane}}$ 254 mμ (ϵ 6900), 357 (150); nmr: δ 3.15 (2 H, singlet, $-\text{SCH}_2\text{-CO}-$), 3.55 (2 H, singlet, ArCH$_2$CO$-$), 6.9–7.8 (4 H, multiplet, ArH).