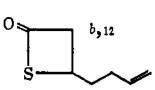
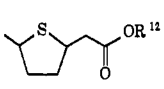
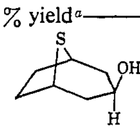
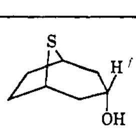
Photolysis of γ-Keto Sulfides

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.

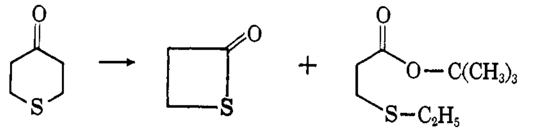
Table I. Yields of Products from Photolysis of **4**

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

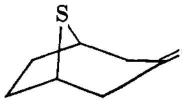
[a] The numbers not in parentheses are isolated yields determined by column chromatography on 80–100 mesh silicic acid followed by distillation or sublimation; the yields in parentheses are determined by gas chromatography as described in ref 9. [b] $\nu_{max}^{CHCl_3}$ 1782 (s), 1637 (w), 1000 (m), 910 (m) cm^{-1}; nmr (CCl$_4$): δ 1.7–2.6 (multiplet, 4 H, $-CH_2CH_2-$), 3.2–4.4 (multiplet, 3 H, $\overline{-CH-CH_2-CO-S}$), 4.8–5.2 (multiplet, 2 H, $=CH_2$), 5.4–6.3 (multiplet, 1 H, $-CH=$). [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).

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.

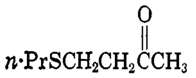
Photolysis[6] of **1**[7,8] as a 0.21% (w/v) solution in *t*-butyl alcohol for 26.4 hr yielded 46.5%[9] β-thiolactone **2**[10,11], 49% ester **3**,[12,13] and 5%[9] unreacted **1**. Photolysis of **1**[6] as a 0.29% solution in Freon-113 for 48.2 hr produced **2** in 51% yield.[9]



1 **2** **3**



4



$$n\text{-}PrSCH_2CH_2\overset{O}{\overset{\|}{C}}CH_3$$

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]

(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) $\lambda_{max}^{Freon\text{-}113}$ 230 mμ (ε 640), 291 mμ (ε 21); $\lambda_{max}^{(CH_3)_3COH}$ 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) $\nu_{max}^{CHCl_3}$ 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) $\lambda_{max}^{Freon\text{-}113}$ 232 mμ (ε 570), 294 mμ (ε 20); $\lambda_{max}^{(CH_3)_3COH}$ 238 mμ (ε 399), 287 mμ (ε 21).

(15) V. Horak, J. Zavada, and A. Pishala, *Acta Chim. Hung.*, **21**, 97 (1959).

(16) $\lambda_{max}^{Freon\text{-}113}$ 283 mμ (ε 28); $\lambda_{max}^{(CH_3)_3COH}$ 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.

Peter Y. Johnson, Glenn A. Berchtold[19]
Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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-

(1) Hanovia Type L 450-w lamp with Pyrex filter.

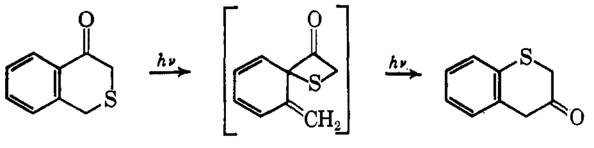
(2) C. C. Price, M. Hori, T. Parasaran, and M. Polk, *J. Am. Chem. Soc.*, **85**, 2278 (1963); J. von Braun and K. Weissbach, *Ber.*, **62**, 2416 (1929); P. Cagniant and D. Cagniant, *Bull. Soc. Chim. France*, 2225 (1961).

(3) $\lambda_{max}^{isooctane}$ 244.5 mμ (ε 10,400), 289 (1540), 348 (149).

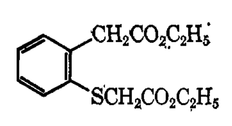
(4) Satisfactory analyses have been obtained on all new compounds reported.

(5) $\nu_{max}^{CCl_4}$ 1723, 1468, 1443, 1385, 1253, 1236, 951, 500, 440 cm^{-1}; $\lambda_{max}^{isooctane}$ 254 mμ (ε 6900), 357 (150); nmr: δ 3.15 (2 H, singlet, $-SCH_2-CO-$), 3.55 (2 H, singlet, $ArCH_2CO-$), 6.9–7.8 (4 H, multiplet, ArH).

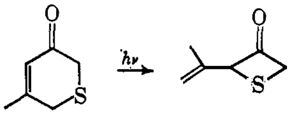
boxylation. Photolysis of **1** under similar conditions in a Rayonet reactor, 3500-A source,[6] resulted in very slow decomposition to polymeric material, indicating excitation of only the long-wavelength band is not sufficient for the reaction.



1 **2** **3**



4



5 **6**

We believe that the initial photoproduct is the triene **2** which undergoes a further photochemically induced rearrangement to **3**. In an effort to obtain evidence for the intermediacy of **2** in the reaction, **5**[4,7] was irradiated under similar conditions in the hope of isolating **6**, which should not undergo further photochemical rearrangement if excitation of the triene system is responsible for further photochemical rearrangement of **2**. Photolysis[1] of **5** in cyclohexane produced **6**[8] in 30% yield. This observation and the appearance of an absorption band at 1770 cm^{-1} in the infrared spectrum of a solution of **1** in cyclohexane which had been photolyzed for a short period of time suggest that **2** is a reasonable intermediate in the formation of **3**.

8-Methyl-, 7-methoxy-, 3-methyl-, and 3,3-dimethylisothiochroman-4-one also undergo this photochemical rearrangement in yields varying from 20 to 40%.[9]

(6) The Southern New England Ultraviolet Co., Middletown, Conn.

(7) $\lambda_{max}^{isooctane}$ 231.5 mμ (ϵ 9340), 270 (302), 347 (97.8).

(8) $\nu_{max}^{CCl_4}$ 1780, 1641, 1448, 1397, 1374, 1168, 1127, 910 cm^{-1}; $\lambda_{max}^{C_2H_5OH}$ 245 mμ (ϵ 912), 330 (166); nmr: δ 4.1 (2 H, broad singlet, $-SCH_2C(=)-$), 1.85 (3 H, broad singlet, CH_3-), 5.0, 5.1, 5.25 (3 H, broad singlets, $CH_2{=}C<$ and $\geqslant CCH(S-)CO-$).

(9) This research has been supported by National Science Foundation Grant No. GP-5761.

(10) Alfred P. Sloan Fellow, 1963–1967.

William C. Lumma, Jr., Glenn A. Berchtold[10]
Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

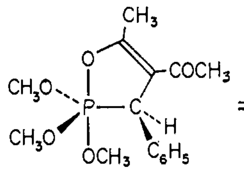
Received February 27, 1967

Inhibited Pseudo-Rotation in a Cyclic Monoalkylphosphorane[1]

Sir:

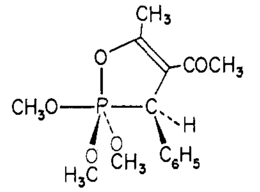
Methyl ethylene phosphate undergoes hydrolysis, both to open the ring and to lose the methoxyl group, at a rate about a million times as great as that for trimethyl phosphate.[2] The driving force for the rapid reactions is presumably ring strain.[3] However, to explain the unexpected rapid hydrolysis of the ester group *external* to the ring in methyl ethylene phosphate and various other cyclic compounds[2,4–6] we recently postulated[7] that the hydrolysis of phosphate esters may, and in some cases must, proceed with pseudo-rotation[8,9] of trigonal-bipyramidal intermediates. In contrast to methyl ethylene phosphate, the methyl ester of the five-membered cyclic phosphinic acid hydrolyzes at a rate comparable to that of the ester of diethylphosphinic acid.[6,10] This fact can be explained by postulating that, in analogy with the known chemistry of the alkylfluorophosphoranes,[11] oxygen atoms preferentially occupy the apical, and alkyl groups the equatorial positions in the trigonal-bipyramidal intermediates formed during hydrolysis. Under these assumptions, the hydrolysis of the ester of the cyclic phosphinic acid is slow, despite the presumed strain in the ring, because, in order to form a trigonal-bipyramidal intermediate, an alkyl group must be forced into an unfavorable axial position, or else the ring angle must be expanded to 120°. Both kinetic[4,7] and X-ray crystallographic[12] evidence as well as theory[3] argue against this latter choice. The chemistry of phostonates[7] can also be rationalized on the assumption of preferential placement of alkyl groups in equatorial positions in trigonal-bipyramidal intermediates in hydrolysis. Ramirez and his co-workers[13] have prepared many cyclic phosphoranes, including[14] I, where an alkyl group is part of a five-membered ring system. According to our postulates,[7] this compound should exist preferentially in a structure where the alkyl group is equatorial, and where therefore the methoxyl groups occupy different positions. However, the nmr spectrum of I, determined at room temperature,[14] shows only one kind of methoxyl group.

We now report that, at low temperatures, the nmr spectrum of I corresponds to that expected for the structure as shown. At room temperature, the three

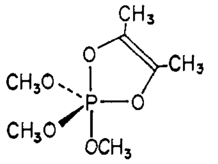


$\rightleftharpoons$

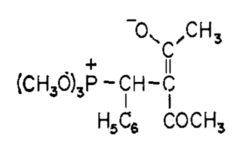
I



II



III



$(CH_3O)_3\overset{+}{P}-\underset{H_5C_6}{CH}-\underset{COCH_3}{C}{=}C(O^-)CH_3$

IV

---

(1) This research was supported by the National Science Foundation under Grant GP-2098.

(2) F. Covitz and F. H. Westheimer, *J. Am. Chem. Soc.*, **85**, 1773 (1963).

(3) E. T. Kaiser, M. Panar, and F. H. Westheimer, *ibid.*, **85**, 602 (1963); D. A. Usher, E. A. Dennis, and F. H. Westheimer, *ibid.*, **87**, 2320 (1965).

(4) P. C. Haake and F. H. Westheimer, *ibid.*, **83**, 1102 (1961).

(5) M. G. Newton, J. R. Cox, Jr., and J. A. Bertrand, *ibid.*, **88**, 1503 (1966).

(6) E. A. Dennis and F. H. Westheimer, *ibid.*, **88**, 3431 (1966).

(7) E. A. Dennis and F. H. Westheimer, *ibid.*, **88**, 3432 (1966).

(8) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

(9) D. Hellwinkel, *Ber.*, **99**, 3628, 3660 (1966), has demonstrated similar pseudo-rotations for pentaarylphosphoranes by stereochemical studies.

(10) G. Aksnes and K. Bergesen, *Acta Chim. Scand.*, **20**, 2508 (1966).

(11) E. Muetterties and R. A. Schonm, *Quart. Rev.* (London), **20**, 245 (1966); R. Schmutzler, *Angew. Chem. Intern. Ed. Engl.*, **4**, 496 (1965).

(12) W. C. Hamilton, S. J. LaPlaca, and F. Ramirez, *J. Am. Chem. Soc.*, **87**, 127 (1965).

(13) F. Ramirez, *Pure Appl. Chem.*, **9**, 337 (1964).

(14) F. Ramirez, O. P. Madan, and S. R. Heller, *J. Am. Chem. Soc.*, **87**, 731 (1965).