which had been observed in the nmr spectrum. This difference Fourier revealed a channel of electron density almost parallel to the *a* axis and indicated that the ether was not highly ordered in the crystal. Since the main interest of the analysis was the structure of **33** and not the structure of disordered ether molecules, no significant attempt was made to fit approximate ether coordinates. Because the disordered ether molecules occupied positions almost parallel to the *a* axis, the intensities most affected by these ether molecules are contained in the 0*kl* set. Therefore, these intensities were removed from the data and refinement was continued. The hydrogen positions were located by difference Fourier techniques and were added to the structure-factor calculation. Refinement with anisotropic temperature factors reduced the *R* index to 16.1%. A final difference Fourier at this point revealed no missing or misplaced atoms, thus indicating that the model was indeed correct.

Results of X-Ray Analyses.—The three structures obtained in the analyses were stereographically plotted (Figure 1) using the ORTEP computer program of Johnson.[23] An estimate of errors in positional parameters, bond lengths, and bond angles are summarized in Table III. Owing to limitations in space, other pertinent crystallographic data and parameters cannot be listed here. *F* tables, atomic coordinates, anisotropic temperature factors, and bond angles and distances have been filed with NAPS.[24]

(23) C. K. Johnson, ORTEP, ORNL-3794, Oak Ridge National Laboratories, Oak Ridge, Tenn.

Registry No.—**6**, 22932-90-7; **6** methyl ether, 22932-91-8; **10**, 16957-32-7; **10** semicarbazone, 16957-33-8; **12**, 16957-34-9; **12** semicarbazone, 16957-35-0; **14**, 22932-96-3; **15**, 22932-97-4; **18**, 22932-98-5; **19**, 22932-99-6; **20**, 22933-00-2; **21**, 16957-31-6; **22**, 22933-02-4; **22** semicarbazone, 22933-03-5; **24**, 22933-04-6; **24** semicarbazone, 22979-21-1; **30**, 22933-05-7; **31**, 22933-06-8; **32**, 22979-22-2; **33**, 22933-07-9; **34**, 22933-08-0; **35**, 22933-09-1; **36**, 22933-10-4; **37**, 22933-11-5; **38**, 22933-12-6; 4β,7aβ-dimethyl-1-acetoxy-4α-phenyl-*cis*-hexahydro-2-indanone, 22933-13-7; 2α-acetyl-2β,6β-dimethyl-6α-phenylcyclohexanone, 22933-14-8; 4β,7aβ-dimethyl-4α-phenyl-4,5,6,7-tetrahydroindan-1,2-dione, 22933-15-9; *syn*-9-(1,5-dimethyl-2,3-benzobicyclo[3.3.1]nonanyl)-2-ethyl alcohol, 22933-16-0; *syn*-9-(1,5-dimethyl-2,3-benzobicyclo[3.3.1]nonanyl)-acetaldehyde, 22933-17-1.

(24) Material supplementary to this article has been deposited as Document No. NAPS 00647 with the ASIS National Auxiliary Publication Service, % CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and by remitting $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to ASIS-NAPS.

Photochemical Reactions of γ-Keto Sulfides[1,2]

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Irradiation of thiacyclohexan-4-one (**1**) in *t*-butyl alcohol gave thiacyclobutan-2-one (27%) and *t*-butyl 4-thiahexanoate (18%). The photochemical reactions of cyclic γ-keto sulfides **2**–**8** and cyclic δ-keto sulfide **9** in *t*-butyl alcohol were investigated. The irradiation of **1** and **5** was studied under a variety of conditions. Irradiation of 5-thiaoctan-2-one and thiachroman-4-one in *t*-butyl alcohol did not give appreciable quantities of monomeric products.

Photochemical studies of β-keto sulfides[4] have received attention in recent years because of the nature of the excited-state interaction of the two chromophores[5] and the possibility that they might undergo unusual photochemical reaction as a result of this interaction. Acyclic γ-keto sulfides show no evidence of charge-transfer interaction, but cyclic γ-keto sulfides[5] and some cyclic δ-keto sulfides[6] show an excited-state interaction which is probably similar to that observed in β-keto sulfides. The photochemical reactions of a number of γ-keto sulfides and a δ-keto sulfide have been investigated in order to determine the nature of the products under the conditions studied.

The ultraviolet spectra of the cyclic keto sulfides (**1**–**9**) irradiated are listed in Table I with the products formed on irradiation in *t*-butyl alcohol. (See Experimental Section for reaction conditions.) Irradiation of thiacyclohexan-4-one (**1**) in *t*-butyl alcohol until disappearance of 93% of the starting material gave 27% thiacyclobutan-2-one (**10**) and 18% *t*-butyl 4-thiahexanoate (**11**). In order to check the wavelength dependence of this reaction and because the intensity of the charge-transfer band is the same order of magnitude as the n $\rightarrow$ π^* band (shoulder) in the 280–290-nm region, **1** was irradiated with a Vycor filter to effect more excitation *via* the charge-transfer band. Irradiation under these conditions gave 22% **11**, 4% unreacted **1**, and no **10**, although the concentration of **10** was observed to build up to as high as several per cent in the first few hours. Thus irradiation with the Vycor filter appears to effect the same reaction and secondary photochemical polymerization of the thiolactone. Cyclic thiolactones were shown to form polymer upon irradiation at 254 nm. Irradiation of **1** in Freon-113 (1,1,2-trichlorotrifluoroethane) with a Pyrex filter resulted in 74% reaction of **1** after 48 hr and formation of **10** (23%) and some polymeric material. Formation of **11** was observed if *t*-butyl alcohol was added to the photolysis mixture after irradiation of **1** in Freon-113 for a short period of time. This suggests the ketene intermediate, $C_2H_5SCH_2C{=}C{=}O$, in the formation of **11**.

(1) Part of this work was previously reported in communication form: P. Y. Johnson and G. A. Berchtold, *J. Amer. Chem. Soc.*, **89**, 2761 (1967).

(2) This research has been supported by National Science Foundation Grant GP-7831 and by National Institutes of Health Grant AI-09300.

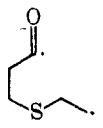
(3) National Institutes of Health Predoctoral Fellow, 1966–1968.

(4) W. C. Lumma and G. A. Berchtold, *J. Org. Chem.*, **34**, 1566 (1969); *J. Amer. Chem. Soc.*, **89**, 2761 (1967); K. K. Maheshwari and G. A. Berchtold, *Chem. Commun.*, 13 (1969); C. Ganter and J.-F. Moser, *Helv. Chim. Acta*, **51**, 300 (1968); J. R. Collier and J. Hill, *Chem. Commun.*, 702 (1968); 700 (1969); A. Schonberg, A. K. Fateen, and S. M. Omran, *J. Amer. Chem. Soc.*, **78**, 1224 (1956); H. Hogeveen and P. J. Smit, *Rec. Trav. Chim. Pays-Bas*, **85**, 489 (1966); R. B. La Count and C. E. Griffin, *Tetrahedron Lett.*, 1549 (1964).

(5) E. A. Fehnel and M. Carmack, *J. Amer. Chem. Soc.*, **71**, 84 (1949); G. Bergson and A.-L. Delin, *Ark. Kemi*, **18**, 489 (1961); G. Bergson, G. Claeson, and L. Schotte, *Acta Chem. Scand.*, **16**, 1159 (1962).

(6) N. J. Leonard, T. L. Brown, and T. W. Milligan, *J. Amer. Chem. Soc.*, **81**, 504 (1959); N. J. Leonard, T. W. Milligan, and T. L. Brown, *ibid.*, **82**, 4075 (1960).

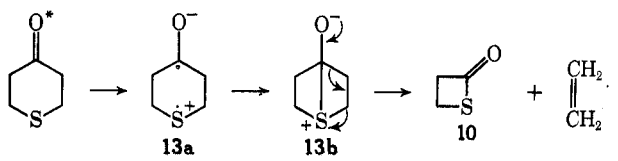
Formation of diradical intermediate **12** prior to formation of the ketene (which reacts with solvent) is a common pathway in the photochemical reactions of cyclic ketones.[7] Elimination of ethylene from a sulfur-



12

stabilized form of diradical **12** to give **10** would appear to be a reasonable process. Cohen[8] has observed that aliphatic sulfides act as physical quenchers for excited benzophenone. The suggested mechanism for ketone quenching by sulfides is similar to that proposed for ketone quenching by amines.[9] In view of Cohen's observations with sulfides, an alternative explanation for the formation of **10** would involve intramolecular electron transfer from sulfur to the excited carbonyl of **1** to generate **13** and fragmentation of dipolar **13** to give **10** and ethylene (Scheme I).

SCHEME I



13a **13b** **10**

Irradiation of **1** in a 2:1 mixture of benzene–*t*-butyl alcohol[10] with a 2537-Å source formed **10** and **11** with no rate enhancement. No phosphorescence spectrum[11] was observed for **1**. The suggestion of intramolecular quenching of excited **1** is supported by these observations. The experiments show no evidence for the triplet state, but they do not discount the likely possibility that the triplet state is involved in the formation of some of the products in the reaction.

It is interesting to note that the major fragmentation of the parent ion of **1** on electron impact also involves loss of the elements of ethylene to give $C_3H_4OS^+$ (**10**?), at *m/e* 88. That the peak at *m/e* 88 was not due to loss of CO from the parent ion was established from the mass spectrum of **1**-d_4 prepared by equilibration of **1** in methanol-O-*d*. The parent ion of **1**-d_4 showed loss of 30 mass units ($C_2H_2D_2$).

Irradiation of 3,3-dimethylthiacyclohexan-4-one (**2**) in *t*-butyl alcohol gave **10** and **14** (see Table I). These products arise from cleavage of the C_3–C_4 bond in **2**; no products were observed from cleavage of the C_4–C_5 bond. Cleavage at the more highly substituted position to a diradical intermediate analogous to **12** is typical in the irradiation of α-alkyl-substituted cyclic ketones.[12] If a dipolar intermediate analogous with **13** is involved in β-thiolactone formation, substitution α to the carbonyl group results in fragmentation of the more highly substituted olefin.

Irradiation of 2,2-dimethylthiacyclohexan-4-one (**3**) in *t*-butyl alcohol gave **10** and **15–18** (see Table I). Since **10** and **16** are formed, substitution β to the carbonyl group shows no effect on the direction of cleavage in thiolactone formation. Alkyl substitution at C_2 may promote Norrish type II cleavage at C_2–C_3. Any acyclic γ-keto sulfide formed as a result of type II cleavage would probably polymerize under the reaction conditions (see below). Whether **18** arises from a secondary reaction of **17** has not been established.

Irradiation of **4** in *t*-butyl alcohol gave **16**, **18**, and large amounts of insoluble polymer possibly resulting from type II cleavage and photopolymerization of the acyclic product formed.

Irradiation of **5** in *t*-butyl alcohol gave predominantly the thiolactone **19** (see Table I). Irradiation of **5** in Freon-113 produced only **19** in good yield. Irradiation in cyclohexane for 78 hr gave the epimeric alcohols **21** and **22** in yields of 15 and 4%, respectively, in addition to bicyclohexane and small amounts of two materials which appeared to be tertiary alcohols resulting from bimolecular photoreduction. Irradiation of **5** in methanol again resulted in photoreduction as the principle course of reaction. (See Experimental Section.)

Isolation of **19** as the major product from irradiation of **5** in *t*-butyl alcohol or Freon-113 verifies olefin formation in the photochemical conversion of thiacyclohexan-4-ones into β-thiolactones. Irradiation of **19** in *t*-butyl alcohol with a 2537-Å source gave only insoluble polymer; no **5** could be detected.

Thiacycloheptan-4-one (**6**) undergoes photochemical reaction in *t*-butyl alcohol to produce γ-thiolactone **23** along with typical products (**24–27**) expected from irradiation of cyclic ketones.[12] β-Thiolactone **10** could not be observed as a product in this reaction. Similar results were obtained from the irradiation of thiacyclooctan-4-one (**7**). Products other than those listed in Table I are present in only trace quantities in the photomixtures. Some of these may have been formed in larger quantity but polymerized under the reaction conditions. Aldehyde **25**, for example, was shown to polymerize under the reaction conditions.

Keto sulfide **8** is particularly interesting in that the uv spectrum indicates charge-transfer interaction and perturbation of the π^*,n state of the carbonyl group, even though the two chromophores are not in the same ring. Dreiding models indicate that the sulfur–carbonyl distance in the chair or twist-boat conformation of **8**, in which the methylthio group is axial, is essentially the same distance as that in the boat conformation of **1**. Irradiation of **8** in *t*-butyl alcohol gave at least 50 products; the monomeric products present in yields of 2% or greater are listed in Table I. Products **36–39** are not unexpected in the reaction. The unsaturated *t*-butyl ester **35** arises at least in part and probably completely from **34**, since **34** was converted into **35** to the extent of 10% on irradiation in *t*-butyl alcohol for 18 hr. Formation of **34** as the major product of this reaction would seem to require interaction of the two chromophores, either through quenching of the excited carbonyl, *i.e.*, **40**, or stabilization of diradical **41**, type I cleavage, by sulfur. It appears

(7) See, *e.g.*, R. O. Kan, "Organic Photochemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, Chapter 3.

(8) J. Guttenplan and S. G. Cohen, *Chem. Commun.*, 247 (1969).

(9) S. G. Cohen and J. B. Guttenplan, *Tetrahedron Lett.*, 5353 (1968); S. G. Cohen and H. M. Chao, *J. Amer. Chem. Soc.*, **90**, 165 (1968); A. Padwa, *et al.*, *ibid.*, **91**, 1857 (1969), and references cited therein.

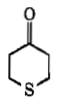
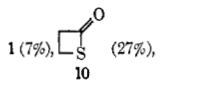
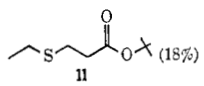
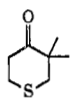
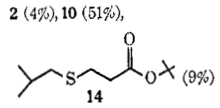
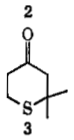
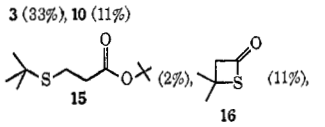
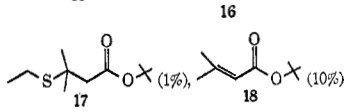
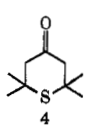
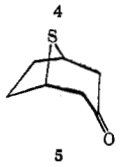
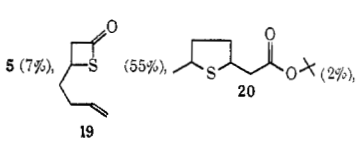
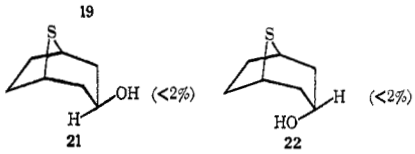
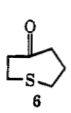
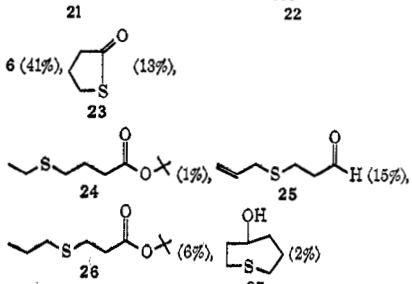
(10) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *ibid.*, **86**, 4537 (1964).

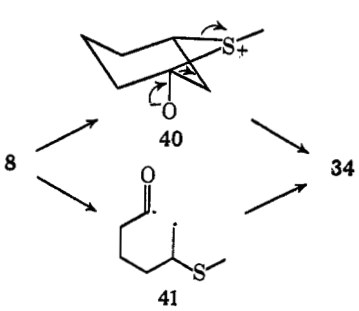
(11) We wish to thank Professor D. Hercules of this department for these measurements.

(12) See, *e.g.*, J. G. Clavert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966, pp 389–427.

TABLE I

ULTRAVIOLET SPECTRA AND PRODUCTS FROM IRRADIATION OF KETO SULFIDES IN *t*-BUTYL ALCOHOL

Keto sulfide	Solvent	λ_{max}, nm (ϵ)	Components of product mixture (% yield)
 1	$(CH_3)_3COH$	237 (435) 287 (22)	 1 (7%), 10 (27%),  11 (18%)
	C_2H_5OH	236 (285) 298 (33)	
	Freon-113 (see ref 5)	230 (650) 291 (21)	
 2	C_2H_5OH	236 (274) 282 (32)	2 (4%), 10 (51%),  14 (9%)
 3	C_2H_5OH	236 (435) 288 (18)	3 (33%), 10 (11%),  15 (2%), 16 (11%),  17 (1%), 18 (10%)
 4	C_2H_5OH	238 (450) 285 (35)	4 (26%), 16 (11%), 18 (3%)
 5	$(CH_3)_3COH$	238 (399) 287 (21)	 5 (7%), 19 (55%), 20 (2%)
	C_2H_5OH	239 (390) 290 (26)	 21 (<2%), 22 (<2%)
	Freon-113	232 (570) 294 (20)	
 6	C_2H_5OH	224 (192) 285 (25)	 6 (41%), 23 (13%), 24 (1%), 25 (15%), 26 (6%), 27 (2%)



unlikely that unstabilized type I diradical intermediate **41** would be converted into **34** in preference to other products.

Irradiation of δ-keto sulfide **9** in *t*-butyl alcohol leads to products from type II cleavage (**42**), type I cleavage (**43**), and photoreduction (**44**).

The uv spectrum of the acyclic δ-keto sulfide, 5-thiaoctan-2-one (**45**), shows no indication of charge transfer in the excited state [$\lambda_{max}^{C_2H_5OH}$ 281 nm (ϵ 35), $\lambda_{max}^{Freon-113}$ 283 nm (ϵ 28)]. Irradiation of this keto sulfide in *t*-butyl alcohol or Freon-113 gave no monomeric products in yields of 2% or greater. Attempts to isolate monomeric products from irradiation of thiachroman-4-one (**46**) were also unsuccessful.

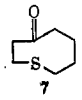
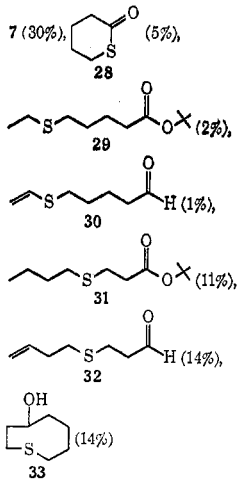
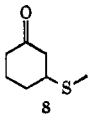
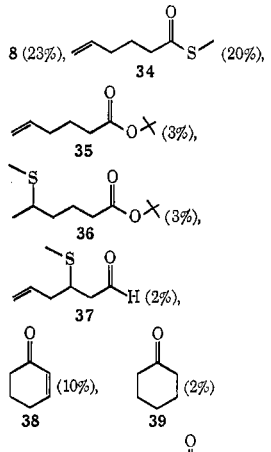
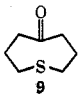
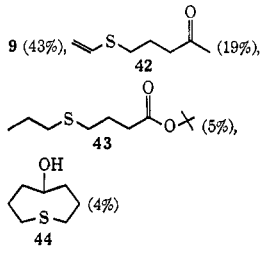
It appears that carbonyl–sulfur interactions in the π^*,n excited state and sulfur stabilization of ground-state radical intermediates may play an important role in the photochemistry of cyclic γ-keto sulfides.

Experimental Section[13]

Photochemical Studies.—All photochemical results are listed in Table II. The ultraviolet sources were as follows: (1) Hanovia 450-W, Type L, medium-pressure, mercury-arc lamp

(13) Infrared spectra were taken on a Perkin-Elmer 237 spectrophotometer. Ultraviolet spectra were taken on a Cary 14 recording spectrophotometer. The nmr spectra were taken on a Varian A-60 spectrometer and are reported in parts per million downfield from tetramethylsilane at 0.00. Mass spectra were run on a Perkin-Elmer Hitachi RMU-6D spectrometer. Melting points were taken on a Thomas–Hoover UniMelt and are corrected. Mallinckrodt 100-mesh silicic acid was used for all column chromatography. All solutions were dried with $MgSO_4$. Microanalyses were determined by the Scandinavian Microanalytical Laboratory, Herlev, Denmark, by Galbraith Laboratories, Knoxville, Tenn., and by Mr. S. Nagy at this institute.

TABLE I
(Continued)

Keto sulfide	Solvent	λ_{max}, nm (ε)	Components of product mixture (% yield)
 7	C_2H_5OH	223 (112) 283 (23)	 7 (30%), 28 (5%), 29 (2%), 30 (1%), 31 (11%), 32 (14%), 33 (14%)
 8	C_2H_5OH	233 (410) 288 (35)	 8 (23%), 34 (20%), 35 (3%), 36 (3%), 37 (2%), 38 (10%), 39 (2%)
 9	C_2H_5OH (see ref 6)	237 (2620) 290 (45)	 9 (43%), 42 (19%), 43 (5%), 44 (4%)

in a water-cooled quartz immersion well with filters of (a) Pyrex, (b) Corex, (c) Vycor; (2) Rayonet Photochemical Reactor, Model RPR 100 (Southern New England Ultraviolet Co., Middletown, Conn.), reactor barrel, 10 (diam) × 15 in. (depth), wavelengths available (16 in circular bank) of (a) 2537, (b) 3000, or (c) 3600 Å.

Photolysis solvents were purified by the following procedures. Cyclohexane (Baker reagent) was passed through Woelm neutral alumina and distilled under N_2 through a 2-ft Vigreux column. Freon-113 (Allied Chemical Co.) was distilled under N_2 from NaH through a 2-ft Vigreux column. *t*-Butyl alcohol (Eastman Chemical Co.) was distilled under N_2 from Na through a 2-ft Vigreux column. Methanol was refluxed for 3 hr over Mg turnings and distilled under N_2 through a 2-ft Vigreux column.

All solutions were degassed for 1–2 hr using oxygen-free N_2 and were irradiated under a blanket of N_2 with stirring. Aliquots were taken through a side arm (capped with a no-air stopper) at time intervals and the reactions were followed by ir or glpc. An F & M Model 810 gas chromatograph equipped with a thermal conductivity detector and a 6-ft 10% Carbowax on Chromosorb P (80–100 mesh) column as well as a 6-ft 15% SE-30 on Chromosorb P (60-80 mesh) column was used for analytical and preparative glpc. Products were collected from glpc and identified by comparison with authentic samples or by spectral characteristics described below. Glpc yields are based on pentadecane as the internal standard unless otherwise indicated. Similar product mixtures were obtained in all cases where uv sources 1a and 2b were compared; consequently, the results are listed in Table II with only one of the two sources.

Thiacyclohexan-4-one (1).—Ketone 1 was prepared in yields of 5–40% by the known procedure.[14] The following procedure was found to be more practical for preparing large quantities of 1.

To a stirred solution of 113 g (1.0 mol) of N-methylpiperidone in 500 ml of ether was added dropwise 150 g (1.06 mol) of methyl iodide in 300 ml of ether. The exothermic reaction was controlled by the rate of addition of methyl iodide and the mixture was stirred for 1 hr after addition was completed. The white solid was filtered off by suction and dried in an oven to yield 245 g (97%) of the amine salt.

To a 5-l., three-necked flask fitted with a stirrer, two addition funnels, N_2 inlet, and two condensers was added 500 ml of H_2O and 1000 ml of ether. The flask was heated on a steam bath while 240 g (1.0 mol) of sodium sulfide in 500 ml of H_2O and 245 g, (0.97 mol) of the amine salt as a saturated solution in water were added simultaneously over 5 hr. Ether was continuously added to make up for that which escaped through the condensers. The reaction was refluxed an additional 2 hr, the ether layer was separated, and the aqueous layer was extracted twice with ether. The combined ether extracts were washed

(14) C. Barkenbuss, V. C. Midkiff, and R. M. Newman, *J. Org. Chem.*, **16**, 232 (1951).

TABLE II
PHOTOCHEMICAL EXPERIMENTS

Keto sulfide (g)	Uv source	Solvent (ml)	Time, hr	Components of product mixture (% yield)
1 (0.6301)	2b	$(CH_3)_3COH$ (250)	11	**1** (7%), **10** (27%), **11** (18%)
1 (1.7434)	1c	$(CH_3)_3COH$ (500)	24	**1** (4%), **11** (22%)[a]
1 (1.4500)	1a	Freon-113 (500)	48	**1** (26%), **10** (23%)[a]
1 (1.2000)	1b	2:1 C_6H_6–$(CH_3)_3COH$ (500)	12	**1** (43%), **10** (13%), **11** (25%)[a]
2 (0.2708)	2b	$(CH_3)_3COH$ (250)	19	**2** (4%), **10** (51%), **14** (9%)
3 (0.4060)	2b	$(CH_3)_3COH$ (250)	12	**3** (33%), **10** (11%), **15** (2%), **16** (11%), **17** (1%), **18** (10%)
4 (0.4718)	2b	$(CH_3)_3COH$ (250)	20	**4** (26%), **16** (11%), **18** (3%)
5 (0.7529)	2b	$(CH_3)_3COH$ (250)	34	**5** (7%), **19** (55%), **20** (2%), **21** (<2%), **22** (<2%)
5 (6.002)	1a	$(CH_3)_3COH$ (500)	95	**5** (36%), **19** (43%), **20** (0.5%), **21** (16%), **22** (3%)[b]
5 (2.2780)	1a	Freon-113 (500)	54	**5** (49%), **19** (41%)[c]
5 (1.0005)	1a	C_6H_{12} (500)	74	**5** (60%), **21** (15%), **22** (4%)[b,d]
5 (1.0030)	1a	CH_3OH (500)	62	**5** (45%), **19** (2%), **21** (42%), **22** (6%)[a]
6 (0.6240)	2b	$(CH_3)_3COH$ (250)	27	**6** (41%), **23** (13%), **24** (1%), **25** (15%), **26** (6%), **27** (2%)
7 (0.085)	2b	$(CH_3)_3COH$ (20)	42	**7** (30%), **28** (5%), **29** (2%), **30** (1%), **31** (11%), **32** (14%), **33** (14%)
8 (2.2080)	2b	$(CH_3)_3COH$ (500)	30	**8** (23%), **34** (20%), **35** (3%), **36** (3%), **37** (2%), **38** (10%), **39** (2%)
9 (1.3378)	2b	$(CH_3)_3COH$ (500)	76	**9** (43%), **42** (19%), **43** (5%), **44** (4%)[e]
34 (0.020)	2b	$(CH_3)_3COH$ (10)	18	**35** (10%)
45 (2.7720)	1a	Freon-113 (500)	44	**45** (66%), no products
45 (2.0045)	1a	$(CH_3)_3COH$ (500)	57	**45** (69%), more than five products (<5%)
46 (0.4554)	2c	$(CH_3)_3COH$ (250)	46	**46** (68%), no products[f]

[a] Area ratios based on injection of constant sample sizes. [b] Yields reported are isolated yields from column chromatography of the photolysis residue (elution with hexane, hexane–ether) and distillation or sublimation. [c] Isolation by column chromatography and sublimation (for **5**) or distillation (for **19**) gave 46% **5** and 32% **19**. [d] Bicyclohexyl (40 mg) was also isolated. [e] Isolation by column chromatography gave **42** in 16% yield. [f] Similar results were obtained with uv sources 2a and 2b.

twice with dilute HCl and H_2O, dried, and evaporated to yield a yellow solid. Sublimation at 40° (1 mm) gave 55 g (48%) of **1**: mp 65–67° (lit.[14] mp 65–66°); ir (CCl_4) 1715 cm^{-1} (C=O); mass spectrum (70 eV) *m/e* (rel intensity) 116 (100, M^+), 88 (40), 60 (35), and 46 (25).

Thiacyclohexan-4-one-3,3,5,5-d_4 was prepared by equilibration of a 2-g sample of **1** with $NaOCH_3$ in CH_3OD prepared by dissolving 0.2 g of Na in 50 ml of CH_3OD. The solution was stirred for 24 hr at 25°. Deuterium oxide was added and the mixture was extracted with ether. The ether extracts were washed with H_2O, dried, and evaporated to give a yellow solid. This procedure was repeated a second time and the deuterated **1** was purified by sublimation: yield 1.6 g (80%); nmr (CCl_4) δ 2.92 (br s); mass spectrum (70 eV) *m/e* (rel intensity) 120 (100), 119 (65), 118 (30), 117 (20), 116 (5), 92 (7), 91 (8), 90 (75), 89 (35), and 88 (10).

3,3-Dimethylthiacyclohexan-4-one (**2**).—Diethyl 2,2-dimethyl-4-thia-1,7-heptandioate was prepared by addition of 11 g (0.195 mol) of KOH to 25 g (0.184 mol, Aldrich) of β-chloropivalic acid in 150 ml of cold H_2O. The solution was added to a solution of 20 g (0.186 mol) of 3-mercaptopropionic acid and 22 g (0.390 mol) of KOH in 150 ml of cold H_2O and stirred at 25° for 8 hr, extracted with ether (discarded), acidified at 0° with concentrated HCl, and extracted with ether. The ether extracts were washed with H_2O, dried, and evaporated. The crude residue was Fisher esterified and distilled: bp 114–116° (0.1 mm); yield 24 g (50%); ir (neat) 2985, 1740, 1360, 1315, 1245, 1180, and 1030 cm^{-1}; nmr (neat) δ 1.18 (t, 6 H), 1.22 (s, 6 H), 2.70 (m, 6 H), and 4.10 (q, 4 H).

Anal. Calcd for $C_{12}H_{22}O_4S$: C, 54.93; H, 8.45; S, 12.22. Found: C, 55.00; H, 8.42; S, 12.43.

The diester (21.5 g, 0.082 mol) in 50 ml of toluene was added dropwise to a mixture of $NaOCH_3$ in toluene (prepared by adding 3.8 g of Na to 50 ml of CH_3OH under N_2, distilling off the excess CH_3OH, and adding 150 ml of toluene). The mixture was refluxed for 8 hr under N_2, cooled to 0°, and acidified with dilute HCl. The organic layer was separated and washed with H_2O, and the toluene was removed at 25° (0.1 mm). To the residue was added 100 ml of concentrated HCl and 1 ml of HOAc. The mixture was heated under reflux for 6 hr, cooled, and extracted with ether. The ether extracts were washed with dilute $NaHCO_3$ and with water, dried, and evaporated to give 2 g of crude **2**. Short-path distillation gave 1.2 g (10%) of pure **2**: ir (neat) 2970, 1711, 1470, 1385, 1320, and 1080 cm^{-1}; nmr (neat) δ

1.22 (s, 6 H) and 2.80 (m, 6 H); mass spectrum (70 eV) *m/e* (rel intensity) 144 (90, M^+), 89 (35), 88 (30), 60 (20), 56 (100), 55 (30), and 41 (25).

Anal. Calcd for $C_7H_{12}OS$: C, 58.29; H, 8.39; S, 22.23. Found: C, 58.22; H, 8.39; S, 21.80.

2,2-Dimethylthiacyclohexan-4-one (3).—Into a Pyrex tube sealed at one end were placed 55 g (0.5 mol) of diethylamine hydrochloride, 42 g (35%, 0.5 mol) of formaldehyde, 58 g (0.5 mol) of diacetone alcohol,[15] 2 ml of concentrated HCl, and 1 g of hydroquinone. The tube was sealed, heated at 100° for 2 hr, cooled, and opened, and the mixture was concentrated under high vacuum at 25°. 5-Methyl-1,4-hexadien-3-one was collected at 150–200° (10–20 mm) and redistilled: yield 19 g (35%); bp 55° (15 mm) [lit.[16] bp 60–61° (22 mm)]; ir (neat) 3100, 3020, 2980, 2920, 1675, 1630, 1610, 1450, 1400, 1240, 1120, 980, 960, 890, and 855 cm^{-1}; nmr (neat) δ 1.95 (s, 3 H), 2.20 (s, 3 H), and 5.30–6.60 (m, 4 H).

Hydrogen sulfide was bubbled into a solution of 10 g of NaOAc in 200 ml of acetone for 0.4 hr, and 35 g (0.32 mol) of the hexadienone was then added over a 1-hr period. The mixture was refluxed for 15 hr and the acetone was evaporated under high vacuum. The residue was extracted with ether, washed with H_2O, dried, and concentrated. The product was distilled at 80–95° (10–15 mm) to give 11 g, which was recrystallized from pentane to give 9.5 g (20%) of keto sulfide **3**: mp 28–29° [lit.[17] bp 85° (11 mm)]; ir (neat) 2960, 1718, 1370, 1318, 1305, 1286, 1220, 1170, and 975 cm^{-1}; nmr (CCl_4) δ 1.25 (s, 6 H), 2.36 (m, 4 H), and 2.80 (m, 2 H); mass spectrum (70 eV) *m/e* (rel intensity) 144 (70, M^+), 129 (30), 89 (20), 88 (20), 87 (20), 74 (25), 61 (20), 60 (30), 59 (35), 56 (100), 55 (30), 45 (20), and 41 (40).

2,2,6,6-Tetramethylthiacyclohexan-4-one (4).—Ketone **4** was prepared in 80% yield as previously described:[18] bp 96° (8 mm) [lit.[18] bp 92–93° (13 mm)]; ir (neat) 2955, 1710, 1448, 1370, 1295, and 1209 cm^{-1}; nmr (CCl_4) δ 1.45 (s, 12 H) and 2.45 (s, 4 H); mass spectrum (70 eV) *m/e* (rel intensity) 172 (70, M^+), 157 (30), 117 (25), 105 (30), 91 (25), 87 (85), 75 (35), 74 (60), 59 (65), 57 (25), 56 (100), 55 (55), 43 (40), and 41 (65).

8-Thiabicyclo[3.2.1]octane-3-one (5).—Ketone **5** was prepared in 68% yield from N-methyl tropinone methiodide as previously described:[19] mp 155–157° (lit. mp 156–157°); mass spectrum (70 eV) *m/e* (rel intensity) 142 (100 M^+), 114 (50), 99 (20), 85 (65), 81 (20), 80 (25), 67 (50), 58 (25), 45 (25), and 41 (35).

Thiacycloheptan-4-one (6), Thiacyclooctan-4-one (7), and Thiacyclooctan-5-one (9).—To a dry flask under N_2 were added 15.0 g (0.13 mol) of **1**, 200 ml of dry ether, and 20.0 g (0.14 mol) of freshly distilled boron trifluoride etherate. Diazomethane (0.156 mol) prepared from 70 g of DFX-101[20] in ether was dried for 6 hr over KOH and poured slowly into the flask containing **1**. The mixture was stirred for 10 min and H_2O was added. The ether layer was separated, washed with dilute $NaHCO_3$, dilute $NaHSO_4$, and water, dried, and concentrated. The mixture was distilled and then chromatographed on a 3-ft silicic acid column (elution with hexane, hexane–ether) to give the following products (**6**, **7**, and **9**) after combination of like fractions and purification by distillation (**6** and **7**) or sublimation (**9**).

Data for **6** follow: yield 4.72 g (29%); bp 70° (1.0 mm) [lit.[21] bp 72–75° (1.5 mm)]; mass spectrum (70 eV) *m/e* (rel intensity) 130 (65, M^+), 102 (80), 60 (25), 55 (65), 46 (25), and 42 (100).

Data for **7** follow: yield 0.45 g (2.5%); bp 75° (1.0 mm); ir (neat) 2925, 2850, 1700, 1450, 1425, 1275, and 815 cm^{-1}; nmr (CCl_4) δ 1.40–2.60 (m, 8 H) and 2.72 (s, 4 H); mass spectrum (70 eV) *m/e* (rel intensity) 144 (100, M^+), 116 (20), 88 (95), 87 (60), 61 (25), 60 (80), 55 (40), 47 (20), 46 (30), 45 (25), and 41 (25).

Anal. Calcd for $C_7H_{12}OS$: C, 58.29; H, 8.38; S, 22.23. Found: C, 58.27; H, 8.33; S, 21.97.

Data for **9** follow: yield 0.75 g (4%); mp 53–54° (lit.[6] mp 53.2–54.2°).

3-Methylthiocyclohexanone (8).—Ketone **8** was prepared in 73% yield and has been described previously:[22] bp 72° (0.6 mm) [lit.[22] bp 55° (0.1 mm)]; mass spectrum (70 eV) *m/e* (rel intensity) 144 (45, M^+), 97 (35), 96 (35), 75 (5), 69 (50), 68 (60), 55 (40), 45 (30), and 41 (100).

Thiacyclobutan-2-one (10).—The authentic sample of **10** was prepared as previously described[23] and was purified by glpc: ir ($CHCl_3$) 1776 cm^{-1}; nmr (CCl_4) 3.05 and 4.02 (t, J = 6.5 Hz); mass spectrum (70 eV) *m/e* (rel intensity) 88 (100, M^+), 60 (20), 59 (20), 46 (35), and 45 (40).

***t*-Butyl 4-Thiahexanoate (11).**—4-Thiahexanoic acid[24] (10 g, 0.075 mol), H_2SO_4 (1 ml), and methylene chloride (100 ml) were placed in a dry 500-ml pressure bottle. The mixture was cooled in Dry Ice–acetone, and isobutylene (100 ml) was condensed into the reaction mixture. The mixture was stoppered, shaken at 25° for 48 hr, vented, diluted with H_2O, and extracted with ether. The ether extracts were washed with dilute $NaHCO_3$ and water, dried, and concentrated. The residue was distilled to give **11**: 9.35 g (66%); bp 56° (0.65 mm); ir ($CHCl_3$) 2975, 2940, 1735, 1370, 1250, and 1150 cm^{-1}; nmr (CCl_4) δ 1.20 (t, 3 H), 1.37 (s, 9 H), and 2.5 (m, 6 H); mass spectrum (70 eV) *m/e* (rel intensity) 190 (30, M^+), 134 (60), 117 (40), 89 (45), 75 (50), 61 (50), 60 (45), 57 (100), and 41 (40).

Anal. Calcd for $C_9H_8O_2S$: C, 56.80; H, 9.53; S, 16.84. Found: C, 56.88; H, 9.58; S, 16.80.

***t*-Butyl 6-Methyl-4-thiaheptanoate (14).**—To 20 g (0.17 mol, Aldrich) of 3-mercaptopropionic acid in 200 ml of a 1:1 H_2O–ethanol mixture was added 15 g (0.39 mol) of KOH. 1-Bromo-2-methylpropane (30 g, 0.22 mol) was added and the mixture was stirred for 24 hr at 25°. The basic layer was washed with ether (discarded), acidified at 0° with concentrated HCl, and extracted with ether. The ether extracts were washed with H_2O, dried, and concentrated. Distillation gave 27.2 g (84%) of 6-methyl-4 thiaheptanoic acid: bp 109° (2 mm); nmr (CCl_4) δ 0.89 (d, 6 H), 1.65 (septet, 1 H), and 2.50 (m, 6 H).

The *t*-butyl ester **14** was prepared in 60% yield as described for **11** from 10 g (0.062 mol) of the above acid: bp 71° (1.0 mm); ir (neat) 2960, 1730, 1460, 1385, 1362, 1248, 1145, and 844 cm^{-1}; nmr (CCl_4) δ 1.00 (d, 6 H), 1.25 (s, 9 H), 1.78 (septet, 1 H), and 2.50 (m, 6 H); mass spectrum (70 eV) *m/e* (rel intensity) 218 (15, M^+), 190 (15), 162 (40), 145 (25), 119 (25), 106 (35), 103 (30), 89 (60), 88 (25), 59 (35), 57 (100), 56 (50), 55 (30), and 41 (65).

Anal. Calcd for $C_{11}H_{22}O_2S$: C, 60.50; H, 10.16; S, 14.69. Found: C, 60.38; H, 10.21; S, 14.42.

***t*-Butyl 5,5-Dimethyl-4-thiahexanoate (15).**—Ester **15** was prepared in 75% yield from 10 g (0.062 mol) of 5,5-dimethyl-4-thiahexanoic acid[25] by the procedure described for **11**: bp 69° (0.9 mm); ir (neat) 2988, 1739, 1460, 1382, 1370, 1250, 1151, and 847 cm^{-1}; nmr (CCl_4) δ 1.25 (s, 9 H), 1.45 (s, 9 H), and 2.50 (m, 4 H); mass spectrum (70 eV) *m/e* (rel intensity) 218 (15, M^+) 162 (35), 145 (15), 107 (20), 106 (55), 89 (25), 57 (100), 56 (45), 55 (20), and 41 (75).

Anal. Calcd for $C_{11}H_{22}O_2S$: C, 60.50; H, 10.16; S, 14.69. Found: C, 60.67; H, 10.24; S, 14.52.

4,4-Dimethylthiacyclobutan-2-one (16).—Thiolactone **16**[26] was identified from its spectral properties after purification from the photoreaction by glpc: ir (CCl_4) 2970, 2930, 2870, 1772, 1410, 1392, 1379, 1254, 1140, and 1021 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 116 (20, M^+), 83 (10), 74 (40), 59 (65), 57 15), 56 ((100), 55 (20), 45 (10), and 41 (60).

***t*-Butyl 3,3-Dimethyl-4-thiahexanoate (17).**—A solution of 20 g (0.145 mol) of ethyl 3,3-dimethylacrylate and 25 g (0.40 mol) of ethyl mercaptan in 100 ml of ethanol was stirred at 25° for 12 hr. Water (100 ml) and KOH (20 g, 0.36 mol) were added and the mixture was heated under reflux for 3 hr, cooled, washed with ether (discarded), acidified at 0° with concentrated HCl, and

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extracted with ether. The ether extracts were washed with H_2O, dried, and concentrated. Distillation gave 18.1 g (77%) of 3,3-dimethyl-4-hexanoic acid: bp 108° (1.5 mm); nmr (CCl_4) δ 1.30 (t, 3 H), 1.42 (s, 6 H), 2.52 (q, 2 H), and 2.58 (s, 2 H).

t-Butyl ester **17** was prepared in 67% yield from 10 g (0.062 mol) of the above acid by the procedure described for **11**: bp 74° (1.3 mm); ir (neat) 2987, 1730, 1460, 1370, 1224, 1170, 1110, 880, and 852 cm^{-1}; nmr (CCl_4) δ 1.15 (t, 3 H), 1.30 (s, 6 H), 1.35 (s, 9 H), 2.35 (s, 2 H), and 2.45 (q, 2 H); mass spectrum (70 eV) *m/e* (rel intensity) 218 (15, M^+), 162 (25), 145 (15), 103 (40), 101 (50), 89 (15), 60 (20), 59 (45), 57 (100), 55 (20), 43 (25), and 41 (25).

Anal. Calcd for $C_{11}H_{22}O_2S$: C, 60.50; H, 10.16; S, 14.69. Found: C, 60.70; H, 10.25; S, 14.72.

t-Butyl 3,3-Dimethylacrylate (18).—Ester **18** was prepared in 78% yield from 10 g (0.10 mol) of 3,3-dimethylacrylic acid (Aldrich) by the procedure described for **11**: bp 30° (0.1 mm); ir (neat) 3050, 2984, 1721, 1660, 1450, 1370, 1243, 1148, 1080, and 858 cm^{-1}; nmr (neat) δ 1.45 (s, 9 H), 1.80 (d, 3 H, J = 1 Hz), 2.12 (d, 3 H, J = 1 Hz), 5.60 (septet, 1 H, J = 1 Hz); mass spectrum (70 eV) *m/e* (rel intensity) 101 (45), 100 (80), 83 (100), 57 (80), 56 (30), 55 (20), and 41 (20).

Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.33. Found: C, 69.05; H, 10.20.

4-(3-Butenyl)thiacyclobutan-2-one (19).—Thiolactone **19** was identified from the following data: bp 66° (0.75 mm); ir ($CHCl_3$) 3060, 1772, 1637, 1000, and 910 cm^{-1}; uv max (ethanol) 233 nm (ε 1730); nmr (CCl_4) δ 1.7–2.6 (m, 4 H, CH_2CH_2), 3.2–4.4 [m, 3 H, $CHCH_2(C{=}O)S$], 4.8–5.2 (m, 2 H, $=CH_2$), and 5.4–6.3 (m, 1 H, CH=); mass spectrum (70 eV) *m/e* (rel intensity) 116 (5), 115 (6), 114 (100), 101 (3), 100 (2), 99 (20), 87 (3), 86 (4), 85 (35), 81 (20), 80 (20), 79 (10), 73 (15), 68 (10), 67 (90), 66 (10), 65 (10), 60 (10), 59 (15), 58 (15), 55 (10), 54 (30), 53 (10), 45 (25), and 41 (80).

Anal. Calcd for $C_7H_{10}OS$: C, 59.12; H, 7.09; S, 22.55. Found: C, 59.11; H, 7.13; S, 22.73.

t-Butyl 2-(3-Methyl-2-thiacyclopentyl)acetate (20).—Ester **20** was identified from the following data: ir (neat) 2980, 2940, 2860, 1730, 1450, 1390, 1360, 1295, 1255, and 1150 cm^{-1}; nmr (CCl_4) δ 1.35 (d, 3 H, CH_3), 1.52 [s, 9 H, $(CH_3)_3C$], 1.50–2.40 (m, 4 H, CH_2CH_2), 2.54 (d, 2 H, $COCH_2$), and 3.40–3.80 (m, 2 H, CHSCH); mass spectrum (70 eV) *m/e* (rel intensity) 216 (25, M^+), 160 (45), 159 (65), 143 (25), 141 (10), 118 (15), 115 (10), 114 (15), 113 (45), 101 (100), 100 (20), 99 (15), 85 (15), 81 (10), 74 (30), 67 (10), 59 (20), 57 (70), 55 (20), and 41 (60).

Anal. Calcd for $C_{11}H_{20}O_2S$: C, 61.01; H, 9.32; S, 14.82. Found: C, 61.11; H, 9.12; S, 14.95.

***exo*- and *endo*-8-Thiabicyclo[3.2.1]octan-3-ol (21 and 22).**—Alcohols **21** and **22** were prepared by reduction of 570 mg of **5** with $NaBH_4$[27] and were purified by chromatography on a 2-ft silicic acid column (elution with hexane, hexane–ether). The *endo* alcohol **22** was eluted first, yield 114 mg (20%) mp 239–240° (lit.[27] mp 238–239°). The *exo* alcohol was eluted second, yield 445 mg (78%), mp 145–148° (lit.[27] mp 150°).

Thiacyclopentan-2-one (23).—Thiolactone **23** (Aldrich) was purified by distillation, bp 115° (70 mm) [lit.[28] bp 77° (13 mm)].

t-Butyl 5-Thiaheptanoate (24).—5-Thiaheptanoic acid,[29] prepared from 4-bromobutyric acid (Aldrich) and ethanethiol by the procedure used to prepare **15**, was converted into the *t*-butyl ester in 53% yield by the procedure described for **11**: bp 75° (1.0 mm); ir (neat) 2960, 1730, 1330, and 1260 cm^{-1}; nmr (neat) δ 1.10 (t, 3 H), 1.35 (s, 9 H), 1.68 (m, 2 H), and 3.30 (m, 6 H); mass spectrum (70 eV) *m/e* (rel intensity) 204 (40, M^+), 148 (85), 131 (100), 103 (35), 101 (80), 94 (40), 89 (30), 88 (50), 87 (35), 85 (30), 75 (35), 61 (20), 60 (30), and 41 (85).

Anal. Calcd for $C_{10}H_{20}O_2S$: C, 58.77; H, 9.87; S, 15.09. Found: C, 58.74; H, 9.85; S, 15.39.

4-Thiahept-6-enal (25).—Sodium (0.1 g) was dissolved in 25 g of allyl mercaptan under N_2, and 5 g (0.089 mol) of acrolein was added dropwise so as to keep the temperature near 30°. The mixture was stirred for 15 min, diluted with H_2O, and extracted with ether. The ether extracts were washed with dilute HCl and water, dried, and concentrated to give 7.9 g (68%) of crude **25**. Distillation gave 4.2 g (36%) of pure **25**: bp 76° (25 mm); ir (neat) 3070, 2905, 2810, 2710, 1725, 1630, 990, and 920 cm^{-1}; nmr (neat) δ 2.70 (s, 4 H), 3.12 (d, 2 H), 4.90–6.00 (m, 3 H), and 9.9 (s, 1 H); mass spectrum (70 eV) *m/e* (rel intensity) 130 (10, M^+), 74 (80), 45 (30), and 41 (100).

Anal. Calcd for $C_6H_{10}OS$: C, 55.34; H, 7.74; S, 24.63. Found: C, 55.60; H, 8.11; S, 24.46.

t-Butyl 4-Thiaheptanoate (26).—4-Thiaheptanoic acid,[30] prepared from 3-bromopropionic acid and 1-propanethiol by the procedure used to prepare **15**, was converted into *t*-butyl ester **26** in 59% yield by the procedure described for **11**: bp 69° (0.1 mm); ir (neat) 2960, 1730, 1340, 1250, and 1145 cm^{-1}; nmr (neat) δ 0.99 (t, 3 H), 1.35 (s, 9 H), 1.48 (m, 2 H), and 2.50 (m, 6 H); mass spectrum (70 eV) *m/e* (rel intensity) 204 (40, M^+), 148 (100), 147 (25), 131 (45), 119 (20), 106 (40), 103 (35), 89 (70), 88 (25), 87 (20), 75 (75), 74 (55), 61 (30), 57 (80), 56 (20), 55 (20), 43 (45), and 41 (90).

Anal. Calcd for $C_{10}H_{20}O_2S$: C, 58.77; H, 9.87; S, 15.09. Found: C, 58.49; H, 10.19; S, 15.19.

Thiacycloheptan-4-ol (27).—Alcohol **27**[21] was prepared by reduction of **6** with $LiAlH_4$: ir (CCl_4) 3625, 3450, 2925, 1445, 1420, and 1027 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 132 (25, M^+), 114 (25), 99 (25), 87 (25), 86 (100), 72 (20), 61 (20), 60 (45), 59 (25), 57 (55), 55 (20), 47 (35), 40 (25), 45 (35), 43 (35), and 41 (45).

Thiacyclohexan-2-one (28).—Thiolactone **28** was prepared as previously described[31] in 36% yield, bp 118° (50 mm) [lit.[31] bp 70–72° (0.8 mm)].

t-Butyl 6-Thiacctanoate (29).—6-Thiaoctanoic acid was prepared by the method described in the preparation of **15** from 5-chloropentanoic acid and ethanethiol in 61% yield, bp 110° (0.55 mm), and was converted into the *t*-butyl ester in 79% yield by the method described for **11**: bp 75° (0.2 mm); ir (neat) 1735, 1368, 1265, and 1160 cm^{-1}; nmr (neat) δ 1.19 (t, 3 H), 1.38 (s, 9 H), 1.55 (m, 4 H), and 2.40 (m, 6 H); mass spectrum (70 eV) *m/e* (rel intensity) 218 (20, M^+), 162 (55), 145 (55), 143 (20), 115 (25), 101 (100), 99 (25), 98 (20), 74 (65), 61 (25), 60 (20), 57 (80), 56 (30), 55 (50), 47 (25), 43 (20), and 41 (80).

Anal. Calcd for $C_{11}H_{22}O_2S$: C, 60.50; H, 10.16; S, 14.69. Found: C, 60.47; H, 10.14; S, 14.78.

6-Thiaoct-7-enal (30).—The structure of **30** is based only on its glpc retention time and its mass spectrum (70 eV): *m/e* (rel intensity) 144 (100, M^+), 126 (60), 119 (40), 116 (80), 91 (65), 88 (60), 87 (50), 84 (35), 83 (75), 73 (30), 61 (20), 60 (50), 57 (30), 56 (30), 55 (95), 54 (20), 53 (20), 45 (50), 44 (30), 43 (50), 42 (30), and 41 (70).

t-Butyl 4-Thiaoctanoate (31).—4-Thiaoctanoic acid was prepared by the method described in the preparation of **15** from 3-chloropropionic acid and 1-butanethiol in 63% yield, bp 114° (0.15 mm) [lit.[32] bp 115–157° (12 mm)]. The above acid was converted into its *t*-butyl ester in 71% yield as previously described for **11**: bp 69° (0.1 mm); ir (neat) 1730, 1360, 1250, and 1150 cm^{-1}; nmr (neat) δ 0.92 (t, 3 H), 1.43 (s, 9 H), 1.50 (m, 4 H), and 2.50 (m, 6 H); mass spectrum (70 eV) *m/e* (rel intensity) 218 (30, M^+), 162 (20), 145 (35), 119 (25), 105 (40), 103 (25), 89 (100), 88 (55), 61 (40), 57 (100), 56 (55), 55 (45), and 41 (70).

Anal. Calcd for $C_{11}H_{22}O_2S$: C, 60.50; H, 10.16; S, 14.69. Found: C, 60 54; H, 10.12; S, 14.72.

4-Thiaoct-7-enal (32).—3-Butenethiol was prepared according to the procedure of Birch and McAllan.[33] The reaction gave, in our hands, at best 70% the desired isomer,[34] ir 920 and 995 cm^{-1}, bp 100° (760 mm) [lit.[33] bp 100–104° (760 mm)], and 30% *trans*-2-butenethiol, ir 965 cm^{-1}.

Acrolein (2 g) was added dropwise over several minutes to 5 g of the mixture of butenethiols. The mixture was stirred for 1 hr and the excess butenethiol was removed under vacuum. Distillation of 1 g of the residue (4.5 g) gave 0.75 g (75%) of a mixture which contained, by glpc and ir, about 60% the desired isomer and 40% 4-thiaoct-6-enal. After several days, the third isomer, 4-thiaoct-5-enal, also appeared. The desired isomer, **32**, was collected by glpc: bp 72° (0.5 mm); ir (neat) 3080, 2925, 2810, 2715, 1727, 1650, 994, and 920 cm^{-1}; mass

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spectrum (70 eV) *m/e* (rel intensity) 144 (25, M^+), 126 (5), 88, (90), 75 (15), 61 (55), 60 (20), 55 (100), 54 (40), 47 (30), and 45 (25).

Anal. Calcd for $C_7H_{12}OS$: C, 58.28; H, 8.39. Found: C, 58.20; H, 8.47.

Thiacyclooctan-4-ol (33).—Alcohol **33** was prepared in the same manner as alcohol **27**: ir (CCl_4) 3630, 3470, 2930, 1440, and 1025 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 146 (95, M^+), 128 (15), 116 (15), 100 (25), 99 (25), 95 (25), 94 (25), 89 (20), 88 (20), 87 (100), 86 (55), 85 (45), 83 (25), 79 (20), 67 (30), 61 (60), 57 (80), 56 (40), 55 (50), 47 (40), 46 (20), 45 (30), 43 (40), and 41 (55).

Methyl 5-Hexenethiolate (34).—5-Hexenoic acid was prepared in 25% yield by the $FeSO_4$–$CuSO_4$ oxidation[35] of the cyclohexanone–hydrogen peroxide adduct,[36] bp 102° (12 mm) [lit.[37] bp 87° (6 mm)].

The above acid (1.08 g, 0.009 mol) in 10 ml of hexane was added to 0.60 g (0.005 mol) of oxaloyl chloride in 20 ml of hexane at 0° under N_2. The solution was refluxed for 4 hr and cooled, and 2 ml of methanethiol was added. After 20 min the solution was extracted with ether. The extract was washed twice with saturated Na_2CO_3 and water, dried, and concentrated. Distillation gave 1.1 g (83%) of **34**: bp 50° (4 mm); ir (CCl_4) 3080, 2928, 1696, 1643, 990, and 918 cm^{-1}; nmr (CCl_4) δ 2.00 (m, 4 H), 2.20 (s, 3 H), 2.45 (t, 2 H), 4.80 (m, 1 H), 5.10 (m, 1 H), and 5.65 (m, 1 H); mass spectrum (70 eV) *m/e* (rel intensity) 97 (85), 96 (15), 75 (10), 69 (60), 55 (40), and 41 (100).

Anal. Calcd for $C_7H_{12}OS$: C, 58.29; H, 8.39; S, 22.23. Found: C, 58.21; H, 8.48; S, 22.37.

***t*-Butyl 5-Hexanoate (35).**—Ester **35** was prepared in 74% yield from 5-hexenoic acid (described in the preparation of **34**) by the procedure for **11**: bp 30°(0.1 mm); ir (neat) 3085, 2985, 2940, 1740, 1645, 1370, 1255, 1160, 990, and 915 cm^{-1}; nmr (neat) δ 1.2–2.3 (m, 6 H), 1.39 (s, 9 H), 4.8 (m, 1 H), 5.05 (m, 1 H), and 5.60 (m, 1 H); mass spectrum (70 eV) *m/e* (rel intensity) 114 (35), 97 (40), 69 (30), 57 (100), and 41 (35).

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.35; H, 10.67. Found: C, 70.11; H, 10.70.

***t*-Butyl 5-Methyl-6-thiaheptanoate (36).**—Solid $NaBH_4$ (1 g, 0.068 mol active H) was added to 10 g (0.069 mol) of methyl 4-acetylbutyrate[38] in 200 ml of methanol at −70° over several minutes. After the reaction mixture had been warmed to room temperature during a 3-hr period with stirring, dilute HCl was added to pH 1 and the mixture was extracted with ether, washed with H_2O, dried, and concentrated under high vacuum at 25°. To 8 g of crude methyl 5-hydroxyhexanoate was added 1 ml of pyridine followed by 20 ml of $SOCl_2$ which was added dropwise over 20 min. The mixture was stirred for 6 hr at 25° and methanol was added to destroy the excess $SOCl_2$. Water was added and the mixture was extracted with ether. The extract was washed with dilute Na_2CO_3 and water, dried, and concentrated. Distillation of the residue gave 4.8 g of methyl 5-chlorohexanoate, bp 55–56° (0.2 mm) [lit.[39] bp 72–77° (5 mm)].

To 4 g (0.041 mol) of this chloro ester in 100 ml of methanol at 0° was added 25 g of cold methanethiol and 4 g of KOH in 50 ml of H_2O. The flask was stoppered, stirred for 20 hr at 25°, and vented, and 5 g of KOH in 50 ml of H_2O was added. The mixture was heated under reflux for 1 hr, washed with ether (discarded), acidified with concentrated HCl, and extracted with ether. The extract was washed with H_2O, dried, and concentrated. Distillation gave 2.3 g (63%) of 5-methyl-6-thiaheptanoic acid, bp 102–106° (0.25 mm) [lit.[40] bp 100–105° (0.8 mm)].

The *t*-butyl ester of the above acid was prepared in 64% yield from 2 g of acid by the same procedure used to prepare **11**: bp 66–68° (0.05 mm); ir ($CHCl_3$) 2960, 2920, 2860, 1727, 1365, and 1152 cm^{-1}; nmr (neat) δ 1.12 (d, 3 H), 1.40 (s, 9 H), 1.70 (m, 4 H), 1.97 (s, 3 H), and 2.20 (m, 3 H); mass spectrum (70 eV) *m/e* (rel intensity) 218 (40, M^+), 162 (40), 161 (55), 145 (80), 143 (25), 115 (45), 114 (20), 113 (30), 101 (50), 97 (30), 75 (65), 69 (30), 57 (100), 55 (25), and 41 (45).

Anal. Calcd for $C_{11}H_{22}O_2S$: C, 60.50; H, 10.16; S, 14.69. Found: C, 60.44; H, 10.07; S, 14.87.

3-Methylthiohex-5-enal (37).—Aldehyde **37** was collected by glpc from the mixture obtained on photolysis of **8** and was identified from the following data: ir (CCl_4) 3075, 2975, 2820, 2805, 2710, 1726, 1640, 1440, 985, and 920 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 144 (10, M^+), 142 (5), 127 (5), 116 (5), 103 (15), 96 (10), 95 (10), 94 (15), 85 (5), 81 (20), 79 (10), 75 (60), 68 (55), 67 (60), 65 (15), 61 (30), 55 (15), 53 (30), 49 (20), 48 (25), 47 (45), 46 (20), 45 (45), and 41 (100).

3-Thiaoct-1-en-7-one (42).—A solution of 25 g (0.45 mol) of KOH and 32 g (0.40 mol) of 2-mercaptoethanol in 100 ml of H_2O was added to 30 g (0.25 mol) of 5-chloro-2-pentanone[41] in 150 ml of ethanol. The mixture was stirred at 25° for 4 hr and extracted with ether. The extract was washed with H_2O, dried, and concentrated. Distillation gave 56 g (88%) of 3-thia-7-oxo-1-octanol: bp 104–106° (0.01 mm); ir (neat) 3440, 2940, 1710, 1420, 1370, and 1050 cm^{-1}; nmr (neat) δ 1.85 (m, 2 H), 2.19 (s, 3 H), 2.65 (m, 6 H), 3.70 (t, 2 H), and 4.35 (s, 1 H). The above alcohol was converted into its acetate in 93% yield with acetic anhydride: bp 138° (1 mm); ir (neat) 2940, 1740, 1710, 1385, 1365, 1260, and 1030 cm^{-1}; nmr (neat) δ 1.85 (m, 2 H), 2.02 (s, 3 H), 2.65 (m, 6 H), and 4.15 (t, 2 H); mass spectrum (70 eV) *m/e* (rel intensity) 204 (5, M^+), 144 (25), 86 (55), 85 (45), and 43 (100).

Anal. Calcd for $C_9H_{16}O_3S$: C, 52.91; H, 7.89; S, 15.69. Found: C, 53.18; H, 7.94; S, 15.45.

The above keto acetate (5 g, 0.024 mol) in 60 ml of solvent (40 ml of hexane, 20 ml of ether) was pyrolyzed under a stream of N_2 at 565° by passing it for 1 hr through a 20-cm-long Pyrex tube that was packed with glass helices. The column was washed with hexane and the organic fractions were combined, washed with dilute Na_2CO_3 and H_2O, dried, and concentrated. Column chromatography of the residue (elution with hexane, hexane–ether) gave, after combination of like fractions and distillation, 0.6 g (19%) of **42**: bp 102–105° (20 mm); ir (neat) 3090, 2960, 2930, 1715, 1585, 1340, 965, and 870 cm^{-1}; nmr (neat) δ 1.85 (m, 2 H), 2.09 (s, 3 H), 2.70 (m, 4 H), 5.02 (d, 1 H), 5.25 (s, 1 H), and 6.30 (m, 1 H); mass spectrum (70 eV) *m/e* (rel intensity) 144 (30, M^+), 86 (50), 85 (40), and 43 (100).

Anal. Calcd for $C_7H_{12}OS$: C, 58.29; H, 8.39; S, 22.23. Found: C, 58.48; H, 8.42; S, 22.33.

***t*-Butyl 5-Thiaoctanoate (43).**—5-Thiaoctanoic acid was prepared in 67% yield from 1-propanethiol and ethyl 4-bromobutyrate by the same procedure used to prepare **15**, bp 111° (1.0 mm) [lit.[42] bp 168–170° (23 mm)]. The *t*-butyl ester was prepared from the above acid in 52% yield by the same procedure used to prepare **11**: bp 74° (0.6 mm); ir (neat) 2970, 2945, 1730, 1330, 1220, 1150, and 845 cm^{-1}; nmr (CCl_4) δ 0.95 (t, 3 H), 1.35 (s, 9 H), 1.68 (m, 4 H), and 2.4 (m, 6 H); mass spectrum (70 eV) *m/e* (rel intensity) 218 (40, M^+), 162 (100), 145 (70), 115 (65), 103 (90), 102 (65), 101 (20), 87 (45), 85 (30), 75 (25), 74 (30), 60 (25), 57 (100), 47 (20), 43 (50), and 41 (95).

Anal. Calcd for $C_{11}H_{22}O_2S$: C, 60.50; H, 10.16; S, 14.69. Found: C, 60.48; H, 10.12; S, 14.71.

Thiacyclooctan-5-ol (44).—Alcohol **44** was prepared from **9** as described previously,[43] mp 25–26°.

5-Thiaoctan-2-one (45).—The preparation of ketone **46** has been described previously,[44] bp 62° (0.6 mm) [lit.[44] bp 91° (16 mm)].

Thiachroman-4-one (46).—Ketone **46** (Aldrich) was purified by distillation: bp 96° (0.075 mm); uv (C_2H_5OH) 242 nm (ε 23,600), 263 (6800), and 348 (2680).

Registry No.—**1**, 1072-72-6; **2**, 22842-38-2; **3**, 2323-13-9; **4**, 22842-41-7; **5**, 16892-50-5; **6**, 22072-22-6; **7**, 22842-44-0; **8**, 22842-45-1; **9**, 20701-80-8; **10**, 2935-95-7; **11**, 16892-49-2; **14**, 22842-49-5; **15**, 22842-50-8; **16**, 22842-51-9; **17**, 22842-52-0; **18**, 22842-54-2; **19**, 22842-56-4; **20**, 22842-57-5; **24**, 22842-58-6; **25**, 22842-59-7; **26**, 22842-60-0; **27**, 18643-31-7; **29**, 22842-62-2; **30**, 22842-63-3; **31**, 22842-64-4; **32**, 22842-65-5; **33**, 22842-66-6; **34**,

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22842-67-7; **35**, 22842-68-8; **36**, 22842-69-9; **37**, 22842-70-2; **42**, 22842-71-3; **43**, 22842-74-6; **45**, 22842-75-7; **46**, 3528-17-4; thiacyclohexan-4-one-3,3,5,5-d_4, 22842-37-1; 5-methyl-1,4-hexadien-3-one, 13058-38-3; 3,3-dimethyl-4-thiahexanoic acid, 22842-53-1; 3,3-dimethylacrylic acid, 541-47-9; 3-thia-7-oxo-1-octanol, 22842-72-4; 3-thia-7-oxo-1-octanol acetate, 22842-73-5.

Rearrangement Reactions of Hexose 4-*O*-Sulfonates in the Presence of Azide and Phthalimide Nucleophiles[1]

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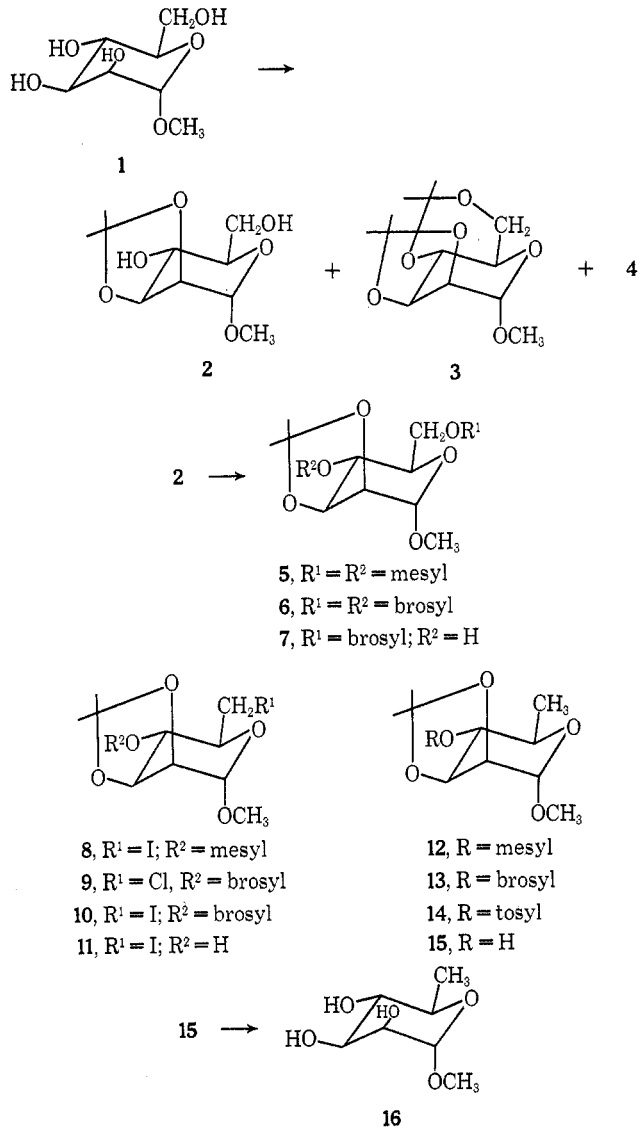
The reaction of various 4-*O*-sulfonates of methyl 6-deoxy-2,3-*O*-isopropylidene-α-D-mannopyranoside (**15**) in the presence of azide and phthalimide nucleophiles was investigated. The expected displacement product, having the α-D-talo configuration, was not detected. Instead, drastic skeletal rearrangement occurred to yield C-5-substituted derivatives of α-D-talofuranoside. The development of two high-yield routes to 4-*O*-sulfonates of compound **15** is discussed. Also, methyl 6-deoxy-α-D-mannopyranoside (**16**) was synthesized by a new route and obtained in crystalline form for the first time.

Since the appearance of our first publication[1] concerning the novel rearrangement reaction of various 4-*O*-sulfonates of methyl 6-deoxy-2,3-*O*-isopropylidene-α-D-mannopyranoside (**15**) with azide (later confirmed by others[2,3]), acetate, and phthalimide anions under conditions[4] expected to yield normal SN2 products, it was found that the tosyl ester of **15** also undergoes rearrangement in the presence of thiobenzoate ion[5] to give crystalline methyl 6-deoxy-2,3-*O*-isopropylidene-5-thiolbenzoyl-α-D-talofuranoside in 10% yield. An earlier erroneous report[6] had assigned the SN2 displacement product structure, methyl 6-deoxy-2,3-*O*-isopropylidene-4-thiobenzoyl-α-L-talopyranoside, to the enantiomer of this crystalline material. These and recent related publications,[7] which describe solvolysis reactions and anhydride formation from various sugar sulfonates by neighboring-group participation, prompt the authors to report in more detail results of the ring-contraction–rearrangement reaction in the presence of nitrogen-containing nucleophiles. The synthetic sequences used to prepare the various 4-*O*-sulfonates of methyl 6-deoxy-2,3-*O*-isopropylidene-α-D-mannopyranoside (**15**) as well as the proof of structure of these compounds will be outlined.

Two routes to compounds **12**, **13**, and **14** were developed. The first sequence was similar to that employed in earlier syntheses.[4] Thus methyl α-D-mannopyranoside (**1**) was heated in acetone under reflux in the presence of zinc chloride to afford a mixture of isopropylidene compounds, **2**, **3**, and **4**, which were separated by a combination of extraction techniques, fractional crystallization, and column chromatography.

SCHEME I



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