10. Photochemistry of Thiophen-2(5*H*)-ones

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Dedicated to Prof. Dr. *O. E. Polansky* on the occasion of his 70th birthday

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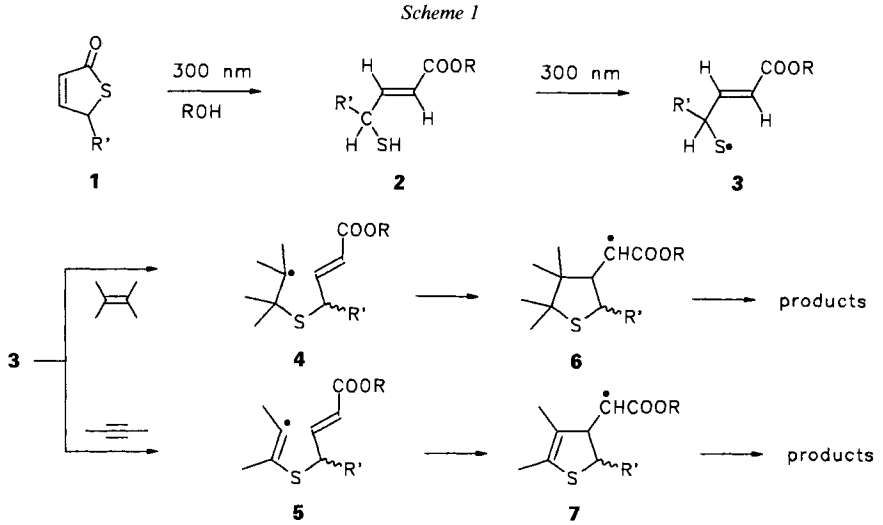
Mechanistic evidence for the light-induced ring opening of thiophen-2(5*H*)-ones **1** in alcohols affording α,β-unsaturated mercapto esters **2** is presented. Regio- and stereochemical aspects of the ring closure of alkenylthio (type **3**) radicals **15** and **17** to S-heterocycles **16** and **18**, of 3-thiahex-5-enyl radicals **4** to (tetrahydrothien-3-yl)methyl radicals **6** and of (2,3-dihydrothien-3-yl)methyl radicals **30** (type **7**, but-3-enyl radicals) to cyclopropanemethyl radicals **29** are discussed. Irradiation (λ 350 nm) of **1** in cyclohexane in the presence of 2,3-dimethylbut-2-ene affords [2 + 2] cycloadducts **14** albeit in very low yields.

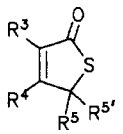
We have recently reported [1–7] that on irradiation thiophen-2(5*H*)-ones **1** behave different from the corresponding O-heterocycles. While furan-2(5*H*)-ones exhibit a typical enone-like behaviour yielding cyclodimers, [2 + 2] cycloadducts with alkenes or photoreduction products in alcohols from their triplet state [8] [9], the unsaturated thiolactones **1** undergo ring opening in alcohols to give α,β-unsaturated mercapto esters **2** from the excited singlet state. Mercapto esters **2** undergo consecutive light-induced S-H homolysis to afford alkenylthio radicals **3** which in reacting with alkenes or alkynes proved to be useful synthetic intermediates for *one-pot* syntheses of thiolanes, 2,3-dihydrothiophenes as well as bi- and tricyclic thiolane derivatives *via* intermediates **4**–**7** *(Scheme 1)*. Such

Scheme 1



polycyclic S-heterocycles [10] have served as starting materials for the synthesis of polyfunctional biologically active compounds [11] and as models in the study of hetero-aromatic compounds in petroleum [12].

In this paper, we present the mechanistic evidence for the ring opening **1**→**2**, showing in this context that **1** also undergoes [2 + 2] photocycloaddition with 2,3-dimethylbut-2-ene in cyclohexane. In addition, we have investigated new reactions of **3** in the absence of alkenes, stereochemical aspects of the cyclization of 3-thiahex-5-enyl radicals **4** to **6** as well as the equilibration of 4-(alkylthio)but-3-enyl radicals **7** to cyclopropanemethyl radicals. Furthermore, we discuss the *non*-photochemical conversion **2**→**3**, and finally, we present results on the formation of cyclohexanols from radical **6** (R′ = CH_2CH_2CHO) *via* intramolecular addition of the radical center to a C=O bond. The following thiophen-2(5*H*)-ones **1** were investigated.

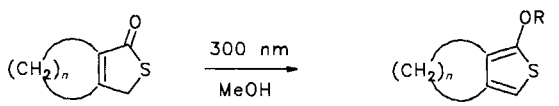


1

	a	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**	**j**	**k**	**l**	**m**
R^3	H	H	H	H	H	H	H	CH_2=$CHCH_2$	CH_2=$CHCH_2$	H	Me	$(CH_2)_4$	$(CH_2)_3$
R^4	H	H	H	H	H	H	H	H	H	Me	Me	$(CH_2)_4$	$(CH_2)_3$
R^5	H	Me	H	H	H	H	H	H	H	H	H	H	H
R^5	H	Me	Me	CH_2=$CHCH_2$	CH≡CCH_2	CH_2=$C(CH_3)CH_2$	$OHCCH_2CH_2$	Me	CH_2=$CHCH_2$	H	H	H	H

Ring-Opening Reaction 1→2. – In comparing the relative rate of conversion of **1** (0.1M) on irradiation (λ 300 nm) in MeOH, it becomes evident that substituents on C(4), *i.e.* $R^4 \neq H$, inhibit the conversion **1**→**2**. While **1a–i** react with similar rates, **1j–m** disappear *ca.* 10 times slower, and no formation of mercapto esters is observed. In MeOH, the bicyclic thiophenones **1l** and **1m** afford the 3,4-annellated 2-methoxythiophenes **8** in low yields [13] *(Scheme 2)*. From **1a–f**, (*E*)-configurated esters **2** are obtained selectively. The substituted thiolactones **1h** and **1i** also afford only one diastereoisomeric mercapto ester, whose configuration has not been assigned, but is again expected to be (*E*).

Scheme 2

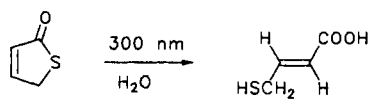


1l $n = 4$
m $n = 3$

8 R = CH_3, $n = 4$ or 3
13 R = H, $n = 4$ or 3

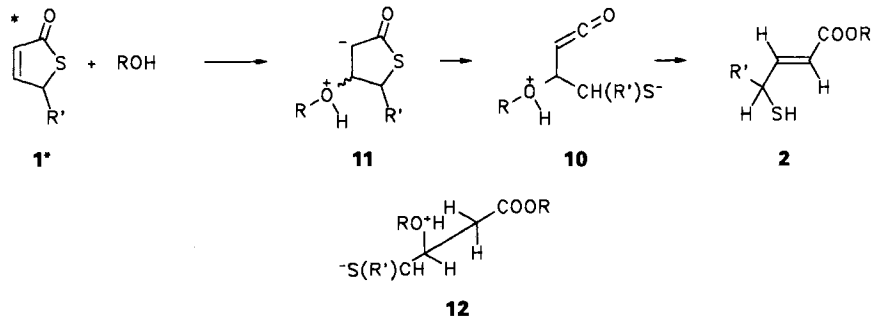
Concerning the solvent, **1a** or **1c** react *ca.* 10 times faster in EtOH than in 2,2,2-trifluoroethanol indicating a preference of excited **1** for the more nucleophilic alcohol. In H_2O, **1a** reacts as fast as in MeOH affording 4-mercaptocrotonic acid (**9**) in 26% isolated yield *(Scheme 3)*; a compound exhibiting similar spectroscopic data as (*E*)-4-mercaptopent-2-enoic acid [14]. All these reactions are *not* quenched by 2,5-dimethylhexa-2,4-diene or naphthalene suggesting a reactive excited singlet state.

Scheme 3



1a **9**

Scheme 4



1* **11** **10** **2**

12

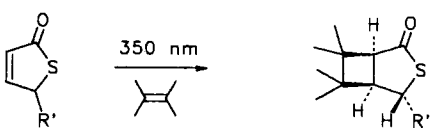
Combination of all these results makes the following mechanism for the conversion **1**→**2** plausible: addition of alcohol on C(4) of excited **1** affords ketene derivative **10** *via* adduct **11**, the formation of **2** then occurring by elimination of alcohol from **12** in the conformation shown *(Scheme 4)*.

The conversion of **1l** or **1m** to **8** is more difficult to explain. It seems to represent an alternative reaction path due to the hindered approach of MeOH to C(4) of **1***, possibly proceeding *via* MeOH addition to photochemically generated 2-hydroxythiophene **13** and subsequent loss of H_2O.

Formation of 3-Thiabicyclo[3.2.0]heptan-2-ones 14. – Under the usual experimental conditions (λ 300 nm, alcohol as solvent), no [2 + 2] photocycloadducts of **1** with alkenes have been observed. On irradiation at 350 nm in cylcohexane or MeCN in the presence of a 20-fold molar excess of 2,3-dimethylbut-2-ene, thiophenones **1a** and **1c–e** do indeed afford cyclobutanes **14a** and **14c–e**, respectively, albeit in low yields (10–12%) together with polymeric material *(Scheme 5)*. The reaction is not quenched by naphthalene up to 2M quencher concentration, again suggesting a reactive excited singlet state of **1**. No such reactions are observed with 2-methylpropene as alkene indicating that excited **1** preferentially interacts with electron-rich alkenes in analogy to the preference of **1*** for better nucleophiles. The rate of conversion **1**→**14** in either C_6H_{12} or MeCN at 350 nm is *ca.* three times slower than the conversion **1**→**2** in MeOH at the same wavelength. At 300 nm, saturated thiolactones **14** undergo slow photodecomposition.

From the magnitude of the $^1H,^1H$ coupling constants, it results that for compounds **14** the ring fusion is *cis* (J(H–C(1), H–C(5)) = 8.5 Hz); and that in **14c–e** the alkyl group on

Scheme 5



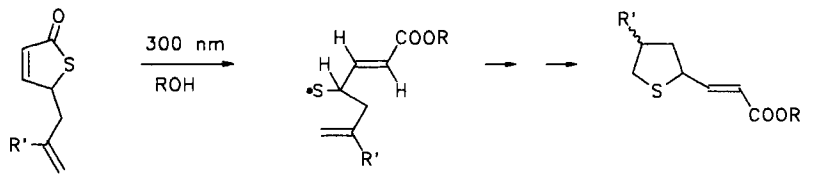
1a R′ = H
c R′ = Me
d R′ = CH_2=$CHCH_2$
e R′ = CH≡CCH_2

14a R′ = H
c R′ = Me
d R′ = CH_2=$CHCH_2$
e R′ = CH≡CCH_2

C(4) is *trans* to the four-membered ring (J(H–C(4), H–C(5)) = 2 Hz) *(Scheme 5)*. The spectroscopic data of compounds **14** are summarized in *Table 1*.

Cyclization of 1-Thiapent-4-enyl Radicals 15 to Thiolanes 16. – Although ring closure of the pent-4-enyl to the cyclopentyl radical – being inconsistent with the rules for ring closure [15] – has not been observed, 1,5-ring closure of substituted pent-4-enyl radicals have been reported [16]. We had already observed [4] that on prolonged irradiation of **1d** in MeOH, thiolane **16a** was formed in low yield (15%). Similar low yields of compounds **16** were now obtained on irradiating **1d** in *t*-BuOH or **1f** in MeOH. Thus, *endo-trig* cyclization of 1-thiapent-4-enyl radicals **15** seems to be less unfavourable than that of the all-C species *(Scheme 6)*.

Scheme 6



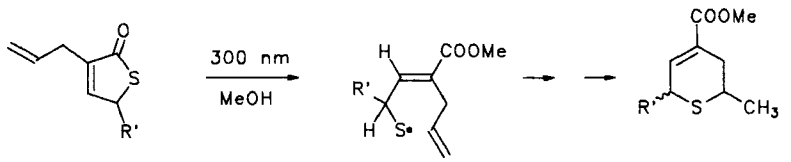
1d R' = H
f R' = CH_3

15

16a R' = H, R = CH_3
b R' = H, R = $(CH_3)_3C$
c R' = CH_3, R = CH_3

Cyclization of 1-Thiahepta-3,6-dienyl Radicals 17 to Dihydro-2*H*-thiins 18. – Stereoelectronic constraints on the regioselectivity of ring closure is less severe for alkenyl radicals with longer chains. Although 1,6-ring closure to hept-6-enyl radicals is relatively slow, some examples for such cyclizations have been reported [17]. Irradiation of thiophenones **1h** and **1i** in MeOH affords diastereoisomeric mixtures of 5,6-dihydro-2*H*-thiine-4-carboxylates **18** *via exo-trig* cyclization of 1-thiahepta-3,6-dienyl radicals **17** in 15% isolated yield *(Scheme 7)*. In this context, it is interesting to note that acetylenic thiols, *e.g.* hex-5-yne-1-thiol, undergo preferential *endo-dig* cyclization to tetrahydrothiepine derivatives [18]. The spectroscopic data of S-heterocycles **16** and **18** are summarized in *Table 2*.

Scheme 7



1h R' = CH_3
i R' = CH_2=$CHCH_2$

17

18a R' = CH_3
b R' = CH_2=$CHCH_2$

Cyclization of 3-Thiahex-5-enyl Radicals 4 to (Tetrahydrothien-3-yl)methyl Radicals 6: Stereochemistry of Ring Closure in the Formation of Thiolanes 19. – In agreement with the stereochemical rules concerning the ring closure of substituted hexenyl radicals [19], 3-thiahex-5-enyl radicals **4** bearing a substituent R' on C(4) (originally on C(5) of the

Table 1. *Spectroscopic Data of Compounds* **14**[a])

Compound	**14a**	**14c**	**14d**	**14e**
UV (C_6H_{12})			235 (3.47)	234 (3.25)
IR (CCl_4)	1700	1690	1690	1690
^{1}H-NMR ($CDCl_3$)	3.52 (*dd*, J = 11.9, 8.8);	3.88 (*dq*, J = 2.0, 7.0);	5.77 (*ddt*, J = 17.2, 9.8, 7.0);	3.86 (*ddd*, J = 7.2, 5.6, 1.6);
	3.34 (*dd*, J = 11.9, 2.1);	2.93 (*d*, J = 8.4);	5.17 (*dq*, J = 10.2, 1.4);	2.94 (*d*, J = 8.2);
	2.83 (*dt*, J = 2.1, 8.8);	2.43 (*dd*, J = 8.4, 2.0);	5.11 (*dq*, J = 17.2, 1.4);	2.70 (*dd*, J = 8.2, 1.6);
	2.80 (*d*, J = 8.8);	1.46 (*d*, J = 7.0, 3 H);	3.82 (*dt*, J = 2.0, 7.0);	2.63 (*ddd*, J = 16.6, 5.6, 2.6);
	1.19, 1.18, 1.07,	1.19, 1.18, 1.09,	2.90 (*d*, J = 8.4);	2.51 (*ddd*, J = 16.6, 7.2, 2.6);
	1.04 (4*s*, CH_3)	1.04 (4*s*, CH_3)	2.55 (*dd*, J = 8.4, 2.0); 2.40 (*m*, 2 H);	2.04 (*t*, J = 2.6); 1.19, 1.18, 1.04,
			1.20, 1.17, 1.07, 1.05 (*s*, CH_3)	1.03 (4*s*, CH_3)
MS	184 (M^+), 83 (100)	198 (M^+), 83 (100)	224 (M^+), 83 (100)	222 (M^+), 83 (100)

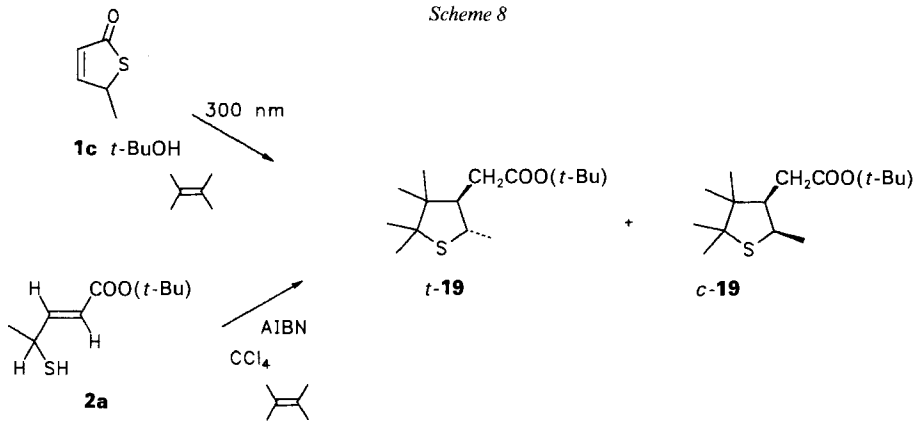
[a]) UV: λ_{max} (log ε) in nm. IR: in cm^{-1}. ^{1}H-NMR: chemical shifts in δ [ppm] rel. to TMS (= 0 ppm), J in Hz. MS: m/z (% rel. int.).

Table 2. *Spectroscopic Data of Compounds* **16** *and* **18**[a])

Compound	**16a**	**16c**	**18a**	**18b**[b])
UV (C_6H_{12})	256 (3.15)		213 (3.58)	217 (3.68)
IR (CCl_4)	1705	1710	1710	1705
^{1}H-NMR ($CDCl_3$)[b])	6.75 (*dd*, J = 15.4, 9.0);	6.86 (*dd*, J = 15.4, 9.0);	7.11 (*ddd*, J = 4.8, 2.2, 1.6);	7.00 (*ddd*, J = 4.6, 2.2, 1.4);
	5.76 (*d*, J = 15.4);	5.86 (*d*, J = 15.4);	3.82 (*s*, 3 H);	5.73 (*ddt*, J = 17.4, 9.8, 7.0);
	4.00 (*ddd*, J = 9.0, 7.0, 6.0);	4.06 (*ddd*, J = 9.0, 7.0, 6.0);	3.61 (*dddq*, J = 4.8, 2.2, 1.6, 7.2);	4.99 (*dq*, J = 17.4, 2.0);
	3.01 (*ddd*, J = 10.2, 7.8, 6.2);	3.72 (*s*, 3 H);	3.04 (*ddq*, J = 9.4, 3.8, 6.8);	4.97 (*dq*, J = 9.8, 2.0);
	2.90 (*ddd*, J = 10.2, 6.4, 5.6);	2.95 (*dd*, J = 10.2, 7.0);	2.80 (*ddt*, J = 17.6, 3.8, 1.6);	3.46 (*m*); 3.30 (*s*, 3 H);
	2.25–1.72 (*m*, 4 H);	2.63 (*t*, J = 10.2);	2.27 (*ddt*, J = 17.6, 9.4, 2.2);	2.67 (*ddt*, J = 16.2, 3.8, 1.4);
	1.50 (*s*, 9 H)	2.59–1.77 (*m*, 3 H);	1.51 (*d*, J = 7.2, 3 H);	2.61 (*m*); 2.20 (*tt*, J = 7.0, 2.0);
			1.39 (*d*, J = 6.8, 3 H)	2.07 (*ddt*, J = 16.2, 8.6, 2.2);
				1.07 (*d*, J = 6.8, 3 H)
MS	no M^+, 140 (100)	186 (M^+), 154 (100)	186 (M^+), 127 (100)	212 (M^+), 171 (100)

[a]) See *Footnote a* in *Table 1*. [b]) ^{1}H-NMR of **18b** in C_6D_6.

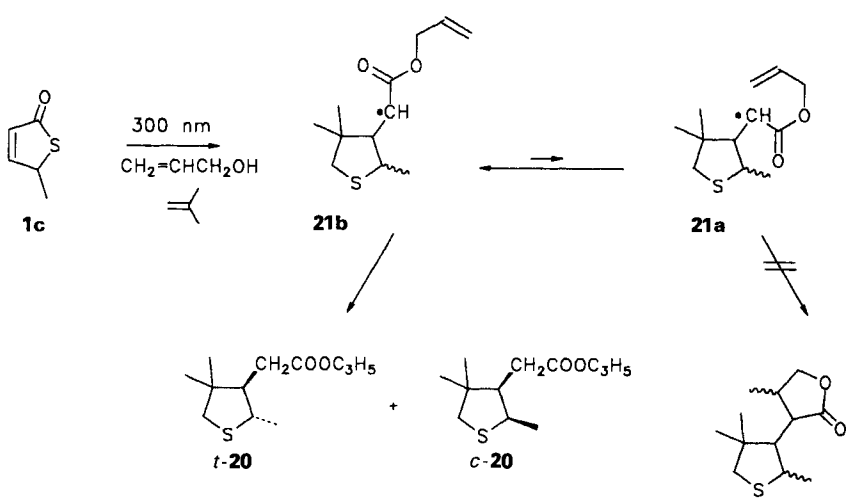
Scheme 8



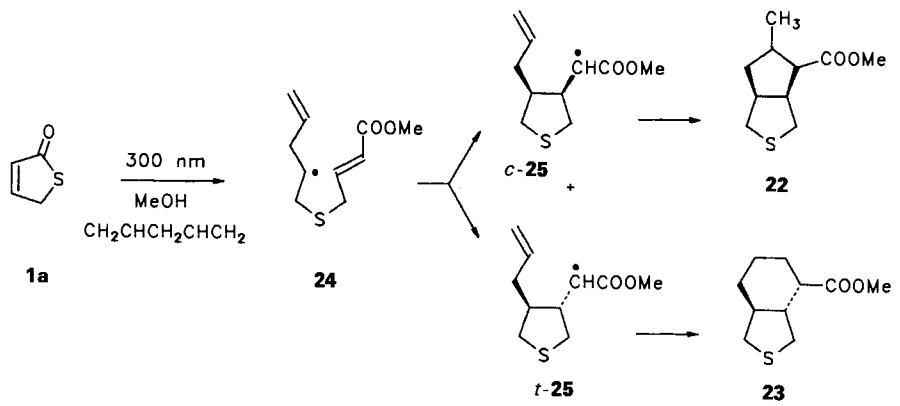
thiophen-2(5*H*)-one **1**) undergo stereoselective ring closure to 2,3-*trans*-disubstituted thiolanes. As an illustrative example, irradiation of **1c** in *t*-BuOH in the presence of 2,3-dimethylbut-2-ene affords a 91:9 mixture (GC) of thiolanes *t*-**19** and *c*-**19**. Similarly, heating the corresponding mercapto ester **2a** with traces of 2,2′-azobis(isobutyronitrile) (AIBN) in CCl_4 containing the same alkene affords a 95:5 mixture of the same compounds *(Scheme 8)*.

A similar *trans*/*cis* (85:15) product ratio for *t*-**20**/*c*-**20** is obtained in the irradiation of **1c** in allyl alcohol containing an excess of 2-methylpropene. In this context, it is interesting to note that the 2-oxo-3-oxahex-5-enyl radical **21** does *not* undergo cyclization to an O-heterocycle, but only H-abstraction to **20**. A similar observation in the irradiation of allyl bromoacetates had been explained [20] by the low relative stability of the *'anti'*-conformer (corresponding to **21a**) and the barrier for its formation from the preferred *'syn'*-conformer corresponding to **21b** *(Scheme 9)*.

Scheme 9



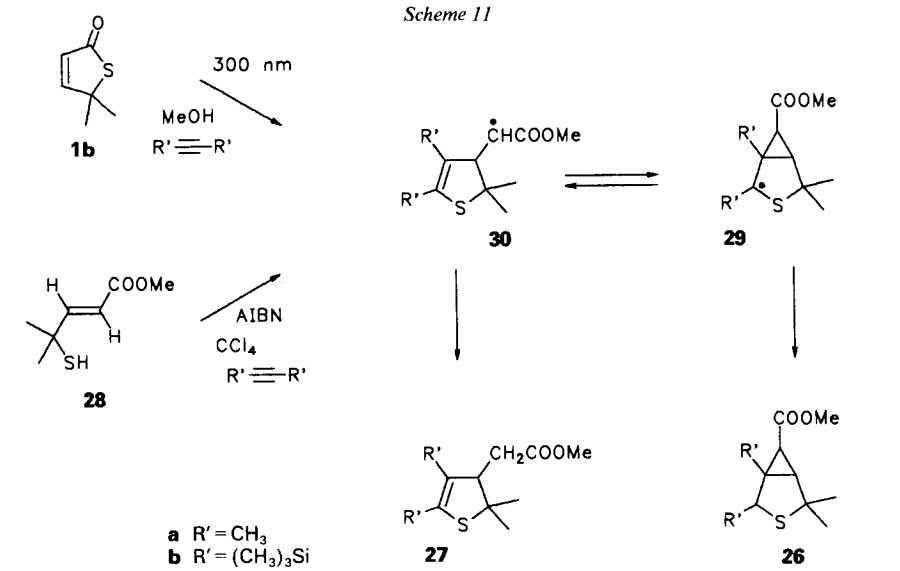
Scheme 10



Again in agreement with [19], radicals **4** bearing a substituent on C(1) (originally on the alkene) undergo stereoselective ring closure to 3,4-*cis*-disubstituted thiolanes. As already reported [7], irradiation of **1a** in MeOH containing penta-1,4-diene affords a 6:1 mixture of **22**/**23** *via* intermediates **24** and **25** *(Scheme 10)*.

Ring Closure of But-3-enyl Radicals 7 to Cyclopropanemethyl Radicals. – With the exception of some norbornenyl systems, the equilibrium between but-3-enyl radicals and cyclopropanemethyl radicals lies strongly in favour of the open-chain species. Already on irradiation of **1b** in MeOH containing but-2-yne, we had observed that 3-thiabicyclo-[3.1.0]hexane **26a** was formed in higher (3:2) amounts than dihydrothiophene **27a** [5]. In using bis(trimethylsilyl)acetylene as alkyne, the ratio for **26b**/**27b** becomes 4:1, and **26b** is formed selectively on treatment of mercapto ester **28** with traces of AIBN in CCl_4 containing the same alkyne *(Scheme 11)*. It, thus, becomes obvious that the S-atom

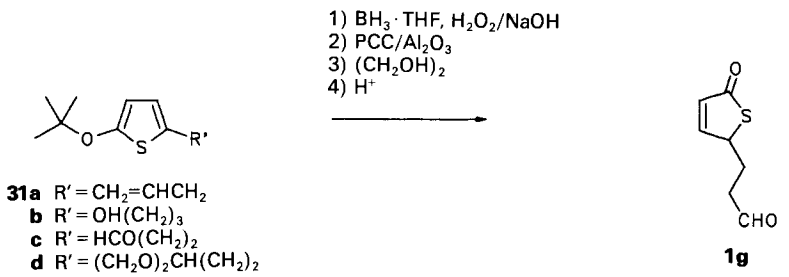
Scheme 11



vicinal to the radical center, as compared to the C-atom, stabilizes the cyclopropane-methyl form, *i.e.* **29**, *vs.* the but-3-enyl form, *i.e.* **30**. A further stabilizing effect comes from the replacement of the C-atom by an Si-atom in R′ as seen in the selective formation of **26b** from **28** and bis(trimethylsilyl)acetylene.

Intramolecular Addition of Radicals to Aldehydes with Formation of Cyclohexanols. – In recent publications [21] [22], it has been shown that radical cyclization on a C=O bond is frequently a highly efficient reaction. To probe such a reaction for the synthesis of bicyclic thiolane derivatives, we have prepared thiophenone **1g** *(Scheme 12)* starting from thiophene ether **31a** [23] *via* alcohol **31b**, aldehyde **31c**, and acetal **31d**. Direct conversion of **31c** to **1g** failed, as only polymeric material was formed.

Scheme 12

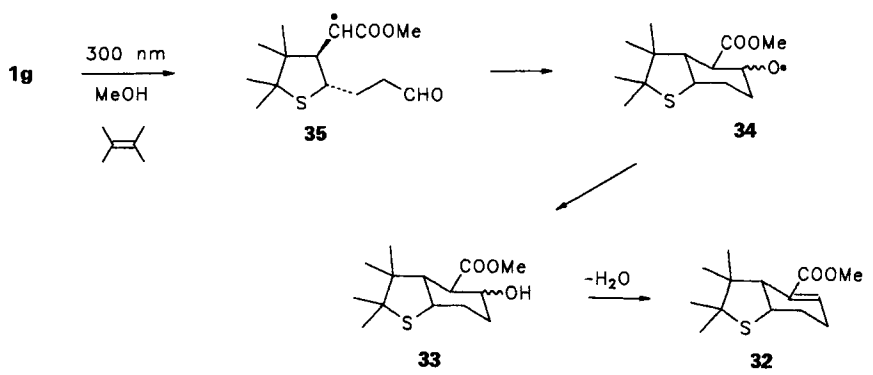


31a R′ = CH_2=$CHCH_2$
b R′ = $OH(CH_2)_3$
c R′ = $HCO(CH_2)_2$
d R′ = $(CH_2O)_2CH(CH_2)_2$

1g

Irradiation of **1g** in MeOH containing 2,3-dimethylbut-2-ene affords only very little (10%) material after distillation consisting of a 3:1 (GC) mixture of **32** (M^+ 244) and **33** (M^+ 262). Chromatography on both SiO_2 and Al_2O_3 led to decomposition of both products. It can be assumed that **33** is indeed the expected bicyclic cyclohexanol – formed *via* radical intermediates **34** and **35** – which then loses H_2O to afford the α,β-unsaturated ester **32** *(Scheme 13)*. Due to the low yield and the difficulty in isolating the products, such cyclizations on C=O bonds were not further investigated.

Scheme 13



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Experimental Part

1. *General.* Photolyses were run in a *Rayonet RPR-100* photoreactor on N_2-degassed solns. using lamps of either 300 (*A*) or 350 nm (*B*). TLC and prep. chromatography: on SiO_2. GC: *SE 30* capillary column. UV Spectra: λ_{max} (log ε) in nm. IR Spectra: in cm^{-1}. ^1H- and ^{13}C-NMR spectra (400 and 100.63 MHz, resp.): chemical shifts in ppm rel. to TMS (= 0 ppm) as internal standard, *J* in Hz. MS (70 eV): *m/z* (rel. intensity in %).

2. *Starting Materials.* Thiophen-2(5*H*)-ones **1a** [24], **1b**, **1j** and **1k** [3], **1c** [23], **1d** [4], **1e** [6], **1f** [5], **1h** and **1i** [25], and **1l** and **1m** [13] were synthesized according to the ref. indicated.

*5-(3'-Oxopropyl)thiophen-2(5*H*)-one* (**1g**). Treatment of 17.8 g (90.8 mmol) of *2-(*tert*-butoxy)-5-(prop-2-enyl)thiophene* (**31a**) [23] with $BH_3 \cdot THF$ at −15° and then with $NaOH/H_2O_2$ afforded 14.4 g (74%) of *5-(*tert*-butoxy)thiophene-2-propanol* (**31b**), b.p. 120–130°/0.02 Torr, which was oxidized with pyridinium chlorochromate (PCC) on Al_2O_3 in hexane to afford 10.8 g (76%) of *5-(*tert*-butoxy)thiophene-2-propanal* (**31c**), b.p. 115–120°/0.02 Torr. Aldehyde **31** was converted to acetal **31d** on treatment with ethylene glycol and TsOH in benzene (yield 85%; b.p. 125–135°/0.02 Torr) which was then heated with traces of TsOH at 180° for 5 min (elimination of 2-methylpropene) and refluxed in 0.5M HCl for 1 h to give 5.2 g (77%) of **1g**. B.p. 130°/0.2 Torr. UV (C_6H_{12}): 264 (3.27). IR (CCl_4): 1730, 1700. ^1H-NMR ($CDCl_3$): 9.80 (*t*, CHO); 7.42 (*dd*, *J* = 6.0, 2.6); 6.32 (*dd*, *J* = 6.0, 2.0); 4.62 (*dddd*, *J* = 7.7, 4.8, 2.6, 2.0); 2.70–2.08 (*m*, 4 H). MS: 156 ($M^{+\cdot}$), 113 (100).

3. *Relative Rates of Conversion of* **1a–m** *in MeOH, and of* **1a** *and* **1c** *in Either EtOH or 2,2,2-Trifluoroethanol.* Irradiation (*A*) of 0.1M solns. were performed in a 'merry-go-round' setup and monitored by GC using tetradecane as standard.

4. *Irradiation of* **1l** *and* **1m**. MeOH solns. of **1l** or **1m** (10^{-3} mol) were irradiated (*A*) for 100 h. Evaporation of the solvent and bulb-to-bulb distillation afforded **8l** (23%; 76% purity) and **8m** (19%; 70% purity), resp.

*4,5,6,7-Tetrahydro-2-methoxybenzo[*c*]thiophene* (**8l**): ^1H-NMR (C_6D_6): 6.02 (*s*); 3.45 (*s*, 3 H); 3.25 (*m*, 2 H); 2.40 (*m*, 2 H); 1.08 (*m*, 4 H).

*5,6-Dihydro-2-methoxycyclopenta[*c*]thiophene* (**8m**): MS: 154 (M^+), 139 (100).

5. *Irradiation of* **1a** *in* H_2O. A soln. of **1a** (500 mg, $5 \cdot 10^{-3}$ mol) in H_2O (50 ml) was irradiated (*A*) for 20 h up to 60% conversion (GC). Extraction with Et_2O, drying of the org. phase, evaporation of the solvent, and bulb-to-bulb distillation afforded 150 mg (26%) of *(*E*)-4-mercaptobut-2-enoic acid* (**9**). B.p. 160°/15 Torr. IR (CCl_4): 1690. ^1H-NMR ($CDCl_3$): 8.50 (*s*, COOH); 7.12 (*ddt*, *J* = 15.4, 0.8, 7.0); 5.97 (*dt*, *J* = 15.4, 1.2); 3.32 (*ddt*, *J* = 8.2, 7.0, 1.2, 2 H); 1.54 (*dt*, SH). MS: no $M^{+\cdot}$, 44 (100).

6. *Irradiation of* **1a** *and* **1c–e** *with 2,3-Dimethylbut-2-ene in* C_6H_{12}. A soln. of **1** (10^{-3} mol) and alkene (1.68 g) in cyclohexane (10 ml) was irradiated (*B*) for 20–25 h. Distillative workup as described above and chromatography (C_6H_6) afforded 20 mg (11%) of *6,6,7,7-tetramethyl-*, 22 mg (11%) of *4,6,6,7,7-pentamethyl-*, 25 mg (12%) of *4-(prop-2-enyl)-6,6,7,7-tetramethyl-*, and 22 mg (10%) of *4-(prop-2-ynyl)-6,6,7,7-tetramethyl-3-thiabicyclo[3.2.0]heptan-2-one* (**14a**, **14c**, **14d**, and **14e**, resp.), all colourless oils. Spectral data: *cf. Table 1.*

7. *Irradiation of* **1d** *in* t-*BuOH*. A soln. of **1d** (200 mg, 1.43 mmol) was irradiated (*A*) in 7 ml of *t*-BuOH for 45 h. Distillative workup as described above and chromatography (CH_2Cl_2) afforded 45 mg (15%) of tert-*butyl (*E*)-3-(thiolan-2-yl)prop-2-enoate* (**16b**) as colourless oil. Spectral data for **16b** and **16c**: *Table 2.*

8. *Irradiation of* **1h** *and* **1i** *in MeOH.* A soln. of **1h** or **1i** (10^{-3} mol) in MeOH (10 ml) was irradiated for 25 h. Distillative workup and chromatography (C_6H_6) afforded 22 mg (13%) of *methyl 2,6-dimethyl-* and 24 mg (11%) of *methyl 3,6-dihydro-2-methyl-6-(prop-2-enyl)-2*H*-thiine-4-carboxylates* (**18a** and **18b**, resp.), resp., as colourless oils. Spectral data: *cf. Table 2.*

9. tert-*Butyl* trans-*2,4,4,5,5-Pentamethylthiolane-3-acetate* (**19t**). 9.1. *Photochemical Conversion.* A soln. of **1c** (228 mg, $2 \cdot 10^{-3}$ mol) and 2,3-dimethylbut-2-ene (2 g) in *t*-BuOH (10 ml) was irradiated (*A*) for 10 h. Distillative workup and chromatography (CH_2Cl_2) afforded 325 mg (60%) of **19t** as colourless oil. IR (CCl_4): 1730. ^1H-NMR ($CDCl_3$): [26]. MS: 272 ($M^{+\cdot}$), 41 (100).

9.2. *Thermal Conversion.* A soln. of tert-*butyl (*E*)-4-mercaptopent-2-enoate* (**2a**; 200 mg, 10^{-3} mol), 1.2 g 2,3-dimethylbut-2-ene (1,2 g) and 2,2'-azobis(isobutyronitrile) (AIBN; 10 mg) in CCl_4 (10 ml) was refluxed under Ar for 3 h. Workup as described above afforded **19t** (contaminated with 5% **19c**) in 82% yield.

10. *Irradiation of* **1c** *and 2-Methylpropene in Allyl Alcohol.* A soln. of **1c** (228 mg, $2 \cdot 10^{-3}$ mol) in prop-2-en-1-ol (20 ml) saturated with 2-methylpropene was irradiated (*A*) for 8 h. Distillative workup as described above and chromatography (C_6H_6) afforded 140 mg (32%) of *prop-2-enyl* trans-*2,4,4-trimethylthiolane-3-acetate* (**20t**) as colourless oil. IR (CCl_4): ^1H-NMR ($CDCl_3$): [26]. 1725. MS: 228 ($M^{+\cdot}$), 128 (100).

11. *Methyl 1,2-Bis(trimethylsilyl)-4,4-dimethyl-3-thiabicyclo[3.1.0]hexane-6-carboxylate* (**26b**). 11.1. *Photochemical Conversion.* A soln. of **1b** (256 mg, $2 \cdot 10^{-3}$ mol) and bis(trimethylsilyl)acetylene (5.5 g) in MeOH (10 ml) was irradiated (*A*) for 20 h. Distillative workup as described above and chromatography (C_6H_6) afforded 220 mg (33%) of **26b**. M.p. 58°. IR (CCl_4): 1730. ^{1}H-NMR ($CDCl_3$): 3.68 (*s*, 3 H); 3.06 (*s*); 2.27, 1.90 (*AB*, $J = 4.4$); 1.43 (*s*, 6 H); 0.17 (*s*, 9 H); 0.13 (*s*, 9 H). ^{13}C-NMR ($CDCl_3$): 23.7, 49.0 (2*d*, each $J = 165$, (2 CH of cyclopropane). MS: 330 ($M^{+\cdot}$), 73 (100).

11.2. *Thermal Conversion.* A soln. of *methyl (*E*)-4-mercapto-4-methylpent-2-enoate* (**29**; 150 mg, 10^{-3} mol), bis(trimethylsilyl)acetylene (3 g) and AIBN (10 mg) in CCl_4 (20 ml) was refluxed for 2 h. Workup as described above afford 165 mg (50%) of **26b**.

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