56. Light-Induced Synthesis of Tricyclic Thiolane Derivatives from 2(5*H*)-Thiophenones *via* Consecutive Radical Ring Closure

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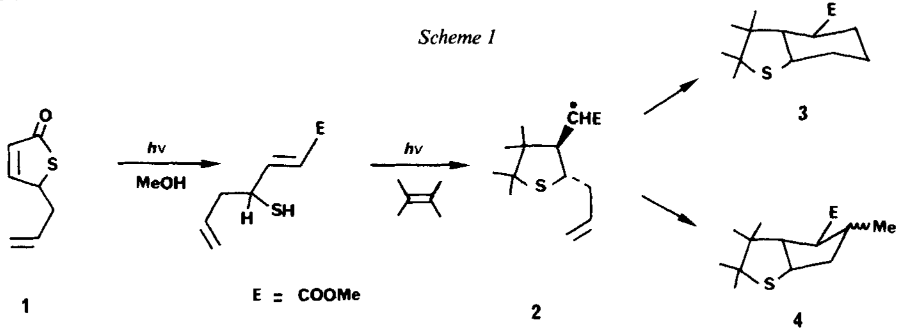
Two α,β-unsaturated thiolactones, 5-(2-propynyl)-2(5*H*)-thiophenone (**5**) and 3,5-di(2-propenyl)-2(5*H*)-thiophenone (**6**), were newly synthesized. Irradiation (λ = 300 nm) of **5** in MeOH containing cyclopentene afforded a 3:1 mixture of diastereoisomeric methyl 7-thiatricyclo[6.4.0.$0^{2,6}$]dodec-10-ene-12-carboxylates (**8a**/**8b**), while irradiation of **6** in MeOH saturated with 2-methylpropene gives a 3:2 mixture of diastereoisomeric methyl 3,3,9-trimethyl-5-thiatricyclo[6.2.1.$0^{2,6}$]undecane-1-carboxylates (**10a**/**10b**).

We have reported on the photochemical conversion of 2(5*H*)-thiophenones to γ-mercapto-α,β-unsaturated esters [1–4] and on the further photochemical transformation of these highly functionalized reagents[1]) to thiolanes and 2,3-dihydrothiophenes. In this context, we have also shown that in the presence of a suitably located C=C bond in the 2(5*H*)-thiophenone, *e.g.* **1**, the thiolane ring closure step afforded again a 5-hexen-1-yl radical (see **2**). Due to the *trans*-configuration of the radical center and the allyl group in **2**, preferential *'endo'* ring closure to **3** and only little *'exo'* ring closure to **4** were observed [7] *(Scheme 1)*.

Scheme 1



We now report on the syntheses of two new 2(*H*)-thiophenones **5** and **6** and on their *one-pot* photochemical conversion to (structurally different) tricyclic thiolane derivatives *via* consecutive radical ring closure. Two strategies for these tandem cyclizations were

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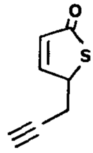
[1]) A (thermal) procedure for the preparation of 4-mercapto-2-butenoates from 2-mercaptoacetaldehyde dimer has been reported recently [5]. Results on *Michael* addition with such compounds had already been reported [6].



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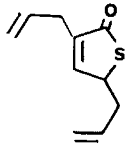

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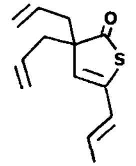

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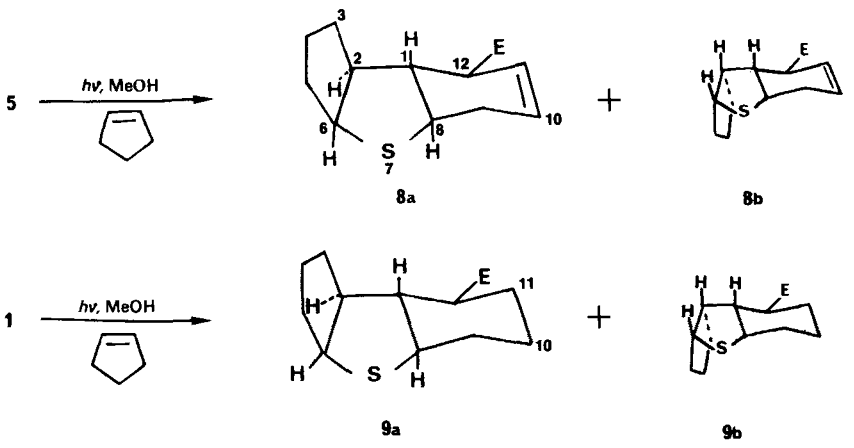
considered: irradiating **5** (or **1**) in alcohol in the presence of a cyclic alkene, and b) irradiating **6** in alcohol containing an acyclic olefin. The preparation of 5-(2-propynyl)-2(5*H*)-thiophenone (**5**) was accomplished in analogy to that of **1** *via* metallation and alkylation of 2-(*tert*-butoxy)thiophene [7] [8]. Diallylthiophene **6** was prepared from **1** by treatment with Na and 3-bromopropene in EtOH/Et$_2$O in analogy to [9]. Minor amounts of the trialkylated β,γ-unsaturated thiolactone **7** were also formed in this reaction. Compound **7** was then independently synthesized by alkylation of **6** with 3-bromopropene (*Scheme 2*).

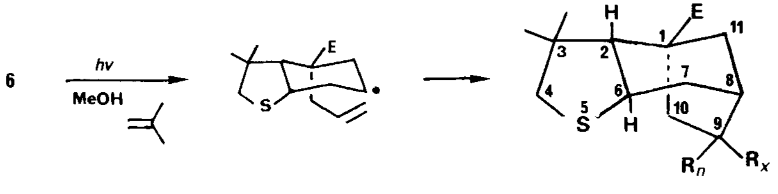
Irradiation (λ = 300 nm) of **5** in MeOH containing cyclopentene affords a 3:1 mixture (yield by GC 80%) of **8a** and **8b**, whose identical MS with M^+ at m/z 238 indicate that they are diastereoisomers, formed from one molecule of **5**, MeOH and cyclopentene, respectively. The thiatricyclododecene structure of **8**, foreseen from predicted guidelines for ring closure of substituted hexenyl radicals [10–12], results from the ^{1}H-NMR spectrum of the main product **8a** indicating a *trans*-fusion between the thiolane and the cyclohexene rings (J(H–C(1), H–C(8)) = 12 Hz). The steric relation to the outer rings most probably are *transoid* in **8a** and *cisoid* in **8b**. Under similar experimental conditions, **1** affords a 6:1 mixture (72% yield by GC) of **9a** and **9b** which again have identical MS (M^+ 240), the ^{1}H-NMR of **9a** suggesting it to have the same configuration as **8a** (*Scheme 2*).

Irradiation of **6** in MeOH saturated with 2-methylpropene gives a 3:2 mixture (yield by GC 91%) of isomers **10a** and **10b** with M^+ 268. Chromatography of **10** affords 2 fractions, the first one containing a 9:1 mixture, the second one a 1:1 mixture **10a**/**10b**. ^{1}H-NMR analysis indicates that both compounds **10** posess the expected thiatricyclo-

Scheme 2



Scheme 3



10a R_x = Me, R_n = H
b R_x = H, R_n = Me

undecane skeleton, the thiolane ring being *trans*-fused to the bicyclo[3.2.1]octane moiety (J(H–C(2), H–C(6)) = 12 Hz), and that they differ by the position of the CH_3 group on C(9). The facts that in norbornanes the vicinal coupling constant of the *exo* protons is bigger than that of the *endo* protons (J(H,H) = 11–12 *vs.* 7–9 Hz), and that *exo* protons are deshielded by *ca.* 0.3 ppm [13] help to assign the CH_3 group in **10a** as being *exo* and the one in **10b** as *endo (Scheme 3)*.

The formation of **8**–**10** from acyclic precursors, *i.e.* the γ-mercapto-α,β-unsaturated esters formed by photosolvolysis of **1**, **5**, and **6**, respectively, thus represent interesting new applications of consecutive radical ring closures, establishing this method as an important and highly versatile one for polycyclic-skeleton construction. The NMR and MS data of the new compounds are summarized in the *Table*.

We are grateful to Dr. *V. Sinnwell* for recording the 2D ^{1}H-NMR spectra and to the *Deutsche Forschungsgemeinschaft* for financial support.

Experimental Part

General. See [2] [3]. Irradiations were performed in a *Rayonet-RPR-100* photoreactor using 300-nm lamps.

5-(2-Propynyl)-2(5H)-thiophenone (**5**). *a) 2-(*tert*-Butoxy)-5-(2-propynyl)thiophene.* From 2-(*tert*-butoxy)thiophene and 3-chloropropyne in analogy to [8] in 84% yield. B.p. 130°/15 Torr. ^{1}H-NMR ($CDCl_3$): 6.57, 6.16 (CH=); 3.60 (CH_2); 2.15 (CH≡); 1.31 (CH_3). MS: 194 (4, M^+), 57.

b) Preparation of **5**. From 2-(*tert*-butoxy)-5-(2-propynyl)thiophene and TsOH at 180° in analogy to [8] in 90% yield, after chromatography (SiO_2, CH_2Cl_2).

3,5-Di(2-propenyl)-2(5H)-thiophenone (**6**). To a soln. of 2.3 g (0.1 mol) of Na in 50 ml of EtOH under N_2 are added 14 g (0.1 mol) of **1** in 50 ml of EtOH and then 25 g (0.2 mol) of 3-bromopropene in 50 ml of Et_2O. The mixture is refluxed for 30 min and, after cooling, poured into a mixture of 100 ml of 6N HCl and 100 ml of Et_2O. The Et_2O phase is separated and the aq. phase extracted with Et_2O. The Et_2O extracts are dried ($MgSO_4$) and evaporated. Distillation (90–100°/0.1 Torr) affords 7.4 g (41%) of a 5:1 mixture **6**/**7**. Compound **6** is then further purified by chromatography (SiO_2, CH_2Cl_2).

5-[(E)-1-Propenyl]-3,3-di(2-propenyl)-2(3H)-thiophenone (**7**). To a soln. of NaOEt prepared from 0.075 g (3 mmol) of Na and 4 ml of EtOH under N_2 are added 0.54 g (3 mmol) of **6** in 5 ml of EtOH and then 1.32 g (11 mmol) of 3-bromopropene in 10 ml of Et_2O. The mixture is refluxed for 1 h. Workup as above for **6** and chromatography (SiO_2, CH_2Cl_2) afford 0.23 g (34%) of **7** as colourless oil.

Photolysis of **5** *in MeOH Containing Cyclopentene.* An Ar-degassed soln. of 90 mg (0.65 mmol) of **5** and 1 g of cyclopentene in 7 ml of MeOH is irradiated for 25 h. Evaporation of the solvent, bulb-to-bulb distillation (200°/0.1 Torr) of the crude mixture containing **8a**/**8b**, chromatography (SiO_2, CH_2Cl_2), and again chromatography (SiO_2, C_6H_6) afford 63 mg (40%) of *methyl 7-thiatricyclo[6.4.0.0^{2,6}]dodec-10-ene-12-carboxylate* (**8a**) as colourless oil.

Table. *Spectroscopic Data of Compounds* **5**–**10**

Compound	UV (C_6H_{12})	MS	^{1}H-NMR ($CDCl_3$)	^{13}C-NMR ($CDCl_3$)
5	264 (3.35)	138 (20, $M^{+\cdot}$), *110*	7.57 (*dd*, J = 6.0, 2.6); 6.37 (*dd*, J = 6.0, 2.0); 4.61 (*dddd*, J = 8.0, 6.6, 2.6, 2.0); 2.80 (*ddd*, J = 16.6, 6.6, 2.5); 2.70 (*ddd*, J = 16.6, 8.0, 2.5); 2.14 (*t*, J = 2.5)	198, 156 (*d*), 133 (*d*), 79 (*d*), 71, 52 (*d*), 24 (*t*)
	263 (3.51)	180 (4, $M^{+\cdot}$), *111*	7.10 (*dt*, J = 3.0, 1.4); 5.86 (*m*, 2 H); 5.17 (*dq*, J = 17.2, 1.4); 5.15 (*dq*, J = 9.6, 1.4); 5.08 (*dq*, J = 9.6, 1.4); 5.07 (*dq*, J = 17.2, 1.4); 4.34 (*dddt*, J = 8.0, 6.2, 3.0, 1.4); 3.02 (*m*, 2 H); 2.66 (*dddt*, J = 14.2, 8.0, 6.8, 1.0); 2.50 (*dddt*, J = 14.2, 6.8, 6.2, 1.0)	198, 151 (*d*), 143, 134 (*d*), 133 (*d*), 118 (*t*), 117 (*t*), 50 (*d*), 38 (*t*), 30 (*t*)
7	226 (4.17)	220 (7, $M^{+\cdot}$), *179*	6.27 (*m*, 1 H); 5.72–5.58 (*m*, 4 H); 5.08–5.02 (*m*, 4 H); 2.43–2.39 (*m*, 4 H); 1.84 (*dd*, J = 6.6, 1.4, CH_3)	209, 136, 132 (3*d*), 126 (2*d*), 119 (2*t*), 65, 42 (3*t*), 18 (*q*)
8a		238 (80, $M^{+\cdot}$), *145*a))	5.83 (*ddt*, J = 9.8, 5.2, 2.4, H–C(5)); 5.73 (*ddt*, J = 9.8, 3.0, 1.4, H–C(4)); 3.86 (*dt*, J = 3.4, 7.0, H–C(9)); 3.73 (*s*, 3 H); 3.17 (*dt*, J = 5.2, 11.2, H–C(7)); 3.15 (*m*, H–C(3)); 2.92 (*dddd*, J = 9.5, 8.1, 7.0, 6.2, H–C(1)); 2.50 (*ddt*, J = 17.0, 1.4, 5.2, H_a–C(6)); 2.23 (*dt*, J = 6.2, 11.2, H–C(2)); 2.15–1.45 (*m*, 7 H)	
9a		240 (60, $M^{+\cdot}$), *146*a))b))	3.59 (*dt*, J = 3.4, 7.0, H–C(9)); 3.36 (*s*, 3H); 2.68 (*dq*, J = 6.2, 8.0, H–C(1)); 2.62 (*dt*, J = 3.9, 11.2, H–C(7)); 2.16 (*dt*, J = 3.6, 11.2, H–C(3)); 1.93 (*dt*, J = 6.2, 11.2, H–C(2)); 1.91–0.81 (*m*, 12 H)	
10a		*268* (100, $M^{+\cdot}$), 221, (98)a))c))	3.64 (*s*, 3 H); 3.46 (*dt*, J = 4.8, 11.6, H–C(6)); 2.74, 2.50 (*AB*, J = 10.4, H–C(4)); 2.22 (*ddd*, J = 14.0, 8.2, 2.2, H_{endo}–C(10)); 1.94 (*m*, H_a–C(7)); 1.93–1.75 (*m*, 3 H); 1.74 (*d*, J = 11.6, H–C(2)); 1.73–1.52 (*m*, 3 H); 1.07, 0.98 (2*s*, CH_3); 0.85 (*d*, J = 6.8, CH_3)	
10b		268 (93, $M^{+\cdot}$), *221*a))c))	3.64 (*s*, 3 H); 3.54 (*dt*, J = 5.2, 11.6, H–C(6)); 2.76, 2.53 (*AB*, J = 10.4, H–C(4)); 2.40 (*dd*, J = 14.0, 11.8, H_{exo}–C(10)); 2.08 (*m*, H_{exo}–C(9), H_a–C(7)); 1.93–1.82 (*m*, 2 H); 1.81 (*d*, J = 11.6, H–C(2)); 1.80–1.52 (*m*, 2 H); 1.47 (*ddd*, J = 14.0, 6.8, 2.0, H_{endo}–C(10)); 1.03, 0.98 (*s*, CH_3); 0.90 (*d*, J = 6.9, CH_3)	

a) 2D Spectrum. b) In C_6D_6. c) In C_5D_5N.

Photolysis of **1** *in MeOH Containing Cyclopentene.* An Ar-degassed soln. of 200 mg (1.43 mmol) of **1** and 3 g of cyclopentene in 15 ml of MeOH is irradiated for 45 h. Workup of the crude mixture certaining **9a/9b** as above affords 189 mg (55%) of *methyl 7-thiatricyclo[6.4.0.0^{2,7}]dodecane-12-carboxylate* (**9a**) as colourless oil.

Photolysis of **6** *in MeOH Saturated with 2-Methylpropene.* A soln. of 1.5 g (8.3 mmol) **6** in 80 ml of MeOH saturated with 2-methylpropene is irradiated for 60 h. Workup as above affords 2 fractions, the first one (800 mg, 36%) consisting of a 9:1 mixture of *methyl 3,3,9-*exo- *and 3,3,9-*endo-*trimethyl-5-thiatricyclo[6.2.1.0^{2,6}]undecane-1-carboxylates* (**10a** and **10b**), resp. the second one (600 mg, 27%) of a 1:1 mixture **10a/10b**, all colourless oils.

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