

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

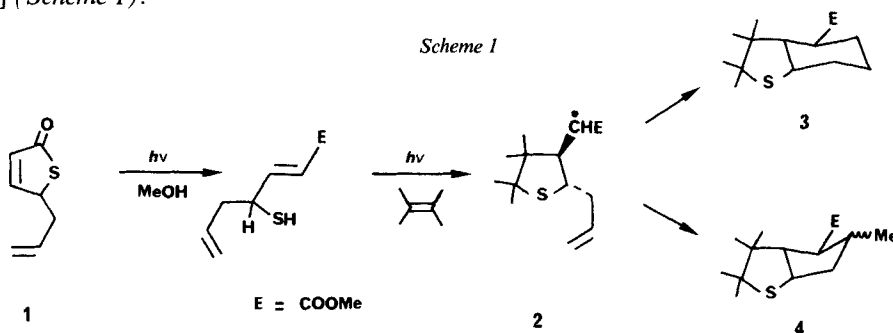
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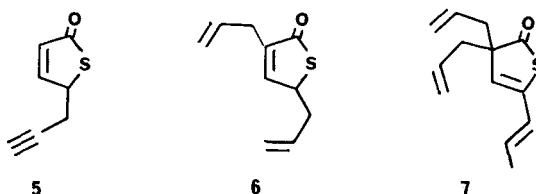
Two α,β -unsaturated thiolactones, 5-(2-propynyl)-2(5*H*)-thiophenone (**5**) and 3,5-di(2-propenyl)-2(5*H*)-thiophenone (**6**), were newly synthesized. Irradiation ($\lambda = 300$ nm) of **5** in MeOH containing cyclopentene afforded a 3:1 mixture of diastereoisomeric methyl 7-thiatricyclo[6.4.0.0^{2,6}]dodec-10-ene-12-carboxylates (**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 reagents¹⁾ 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).



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

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

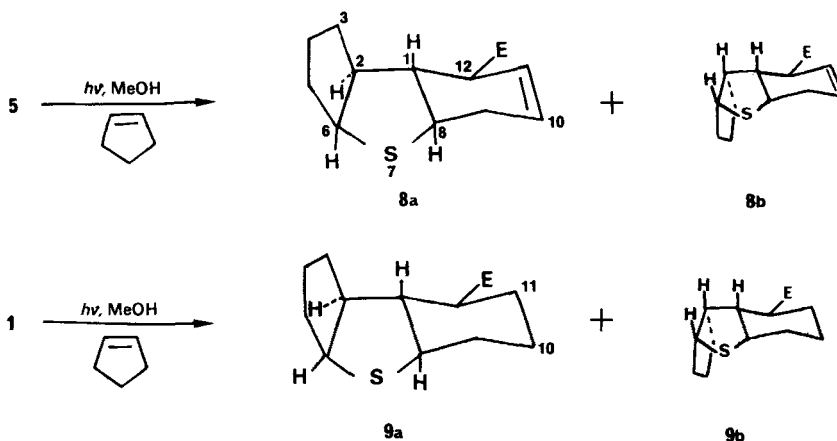


considered: irradiating **5** (or **1**) in alcohol in the presence of a cyclic alkene, and b) irradiating **6** in alcohol containing an acyclic olefin. The preparation of 5-(2-propynyl)-2(5*H*)-thiophenone (**5**) was accomplished in analogy to that of **1** *via* metallation and alkylation of 2-(*tert*-butoxy)thiophene [7] [8]. Diallylthiophene **6** was prepared from **1** by treatment with Na and 3-bromopropene in EtOH/Et₂O 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*).

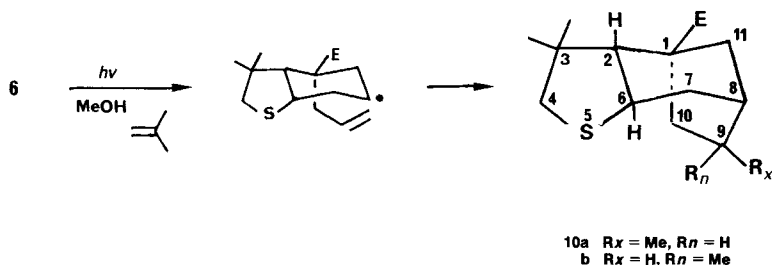
Irradiation ($\lambda = 300$ nm) of **5** in MeOH containing cyclopentene affords a 3:1 mixture (yield by GC 80%) of **8a** and **8b**, whose identical MS with M^+ at m/z 238 indicate that they are diastereoisomers, formed from one molecule of **5**, MeOH and cyclopentene, respectively. The thiatriacyclododecene structure of **8**, foreseen from predicted guidelines for ring closure of substituted hexenyl radicals [10–12], results from the ¹H-NMR spectrum of the main product **8a** indicating a *trans*-fusion between the thiolane and the cyclohexene rings ($J(\text{H}-\text{C}(1), \text{H}-\text{C}(8)) = 12$ 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 ¹H-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**. ¹H-NMR analysis indicates that both compounds **10** possess the expected thiatriacyclo-

Scheme 2



Scheme 3



undecane skeleton, the thiolane ring being *trans*-fused to the bicyclo[3.2.1]octane moiety ($J(\text{H}-\text{C}(2), \text{H}-\text{C}(6)) = 12 \text{ Hz}$), 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 ($J(\text{H}, \text{H}) = 11\text{--}12 \text{ vs. } 7\text{--}9 \text{ Hz}$), 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 ^1H -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. $130^\circ/15 \text{ Torr}$. ^1H -NMR (CDCl_3): 6.57, 6.16 ($\text{CH}=\text{}$); 3.60 (CH_2); 2.15 ($\text{CH}\equiv$); 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 ($90\text{--}100^\circ/0.1 \text{ Torr}$) 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 ($200^\circ/0.1 \text{ Torr}$) 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 ₆ H ₁₂)	MS	¹ H-NMR (CDCl ₃)	¹³ C-NMR (CDCl ₃)
5	264 (3.35)	138 (20, M ⁺), 110	7.57 (<i>dd</i> , <i>J</i> = 6.0, 2.6); 6.37 (<i>dd</i> , <i>J</i> = 6.0, 2.0); 4.61 (<i>dddd</i> , <i>J</i> = 8.0, 6.6, 2.6, 2.0); 2.80 (<i>ddd</i> , <i>J</i> = 16.6, 6.6, 2.5); 2.70 (<i>ddd</i> , <i>J</i> = 16.6, 8.0, 2.5); 2.14 (<i>t</i> , <i>J</i> = 2.5)	198, 156 (<i>d</i>), 133 (<i>d</i>), 79 (<i>d</i>), 71, 52 (<i>d</i>), 24 (<i>t</i>)
	263 (3.51)	180 (4, M ⁺), 111	7.10 (<i>dt</i> , <i>J</i> = 3.0, 1.4); 5.86 (<i>m</i> , 2 H); 5.17 (<i>dq</i> , <i>J</i> = 17.2, 1.4); 5.15 (<i>dq</i> , <i>J</i> = 9.6, 1.4); 5.08 (<i>dq</i> , <i>J</i> = 9.6, 1.4); 5.07 (<i>dq</i> , <i>J</i> = 17.2, 1.4); 4.34 (<i>dddt</i> , <i>J</i> = 8.0, 6.2, 3.0, 1.4); 3.02 (<i>m</i> , 2 H); 2.66 (<i>dddt</i> , <i>J</i> = 14.2, 8.0, 6.8, 1.0); 2.50 (<i>dddt</i> , <i>J</i> = 14.2, 6.8, 6.2, 1.0)	198, 151 (<i>d</i>), 143, 134 (<i>d</i>), 133 (<i>d</i>), 118 (<i>t</i>), 117 (<i>t</i>), 50 (<i>d</i>), 38 (<i>t</i>), 30 (<i>t</i>)
7	226 (4.17)	220 (7, M ⁺), 179	6.27 (<i>m</i> , 1 H); 5.72–5.58 (<i>m</i> , 4 H); 5.08–5.02 (<i>m</i> , 4 H); 2.43–2.39 (<i>m</i> , 4 H); 1.84 (<i>dd</i> , <i>J</i> = 6.6, 1.4, CH ₃)	209, 136, 132 (3 <i>d</i>), 126 (2 <i>d</i>), 119 (2 <i>t</i>), 65, 42 (3 <i>t</i>), 18 (<i>q</i>)
8a		238 (80, M ⁺), 145 ^a)	5.83 (<i>ddt</i> , <i>J</i> = 9.8, 5.2, 2.4, H–C(5)); 5.73 (<i>ddt</i> , <i>J</i> = 9.8, 3.0, 1.4, H–C(4)); 3.86 (<i>dt</i> , <i>J</i> = 3.4, 7.0, H–C(9)); 3.73 (<i>s</i> , 3 H); 3.17 (<i>dt</i> , <i>J</i> = 5.2, 11.2, H–C(7)); 3.15 (<i>m</i> , H–C(3)); 2.92 (<i>dddd</i> , <i>J</i> = 9.5, 8.1, 7.0, 6.2, H–C(1)); 2.50 (<i>ddt</i> , <i>J</i> = 17.0, 1.4, 5.2, H _a –C(6)); 2.23 (<i>dt</i> , <i>J</i> = 6.2, 11.2, H–C(2)); 2.15– 1.45 (<i>m</i> , 7 H)	
9a		240 (60, M ⁺), 146 ^a) ^b)	3.59 (<i>dt</i> , <i>J</i> = 3.4, 7.0, H–C(9)); 3.36 (<i>s</i> , 3H); 2.68 (<i>dq</i> , <i>J</i> = 6.2, 8.0, H–C(1)); 2.62 (<i>dt</i> , <i>J</i> = 3.9, 11.2, H–C(7)); 2.16 (<i>dt</i> , <i>J</i> = 3.6, 11.2, H–C(3)); 1.93 (<i>dt</i> , <i>J</i> = 6.2, 11.2, H–C(2)); 1.91–0.81 (<i>m</i> , 12 H)	
10a		268 (100, M ⁺), 221, (98 ^a) ^c)	3.64 (<i>s</i> , 3 H); 3.46 (<i>dt</i> , <i>J</i> = 4.8, 11.6, H–C(6)); 2.74, 2.50 (<i>AB</i> , <i>J</i> = 10.4, H–C(4)); 2.22 (<i>ddd</i> , <i>J</i> = 14.0, 8.2, 2.2, H _{endo} –C(10)); 1.94 (<i>m</i> , H _a –C(7)); 1.93–1.75 (<i>m</i> , 3 H); 1.74 (<i>d</i> , <i>J</i> = 11.6, H–C(2)); 1.73–1.52 (<i>m</i> , 3 H); 1.07, 0.98 (2 <i>s</i> , CH ₃); 0.85 (<i>d</i> , <i>J</i> = 6.8, CH ₃)	
10b		268 (93, M ⁺), 221 ^a) ^c)	3.64 (<i>s</i> , 3 H); 3.54 (<i>dt</i> , <i>J</i> = 5.2, 11.6, H–C(6)); 2.76, 2.53 (<i>AB</i> , <i>J</i> = 10.4, H–C(4)); 2.40 (<i>dd</i> , <i>J</i> = 14.0, 11.8, H _{exo} –C(10)); 2.08 (<i>m</i> , H _{exo} –C(9), H _a –C(7)); 1.93–1.82 (<i>m</i> , 2 H); 1.81 (<i>d</i> , <i>J</i> = 11.6, H–C(2)); 1.80–1.52 (<i>m</i> , 2 H); 1.47 (<i>ddd</i> , <i>J</i> = 14.0, 6.8, 2.0, H _{endo} –C(10)); 1.03, 0.98 (<i>s</i> , CH ₃); 0.90 (<i>d</i> , <i>J</i> = 6.9, CH ₃)	

a) 2D Spectrum. b) In C₆D₆. c) In C₅D₅N.

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 containing **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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