13. Photochemical Synthesis of Octahydro- and 3a,4,5,6,7,7a-Hexahydrobenzo[*b*]thiophenes from Methyl (*E*)-4-Mercapto-2,6-heptadienoate and Alkenes or Alkynes *via* Consecutive Radical Ring Closure

Preliminary Communication

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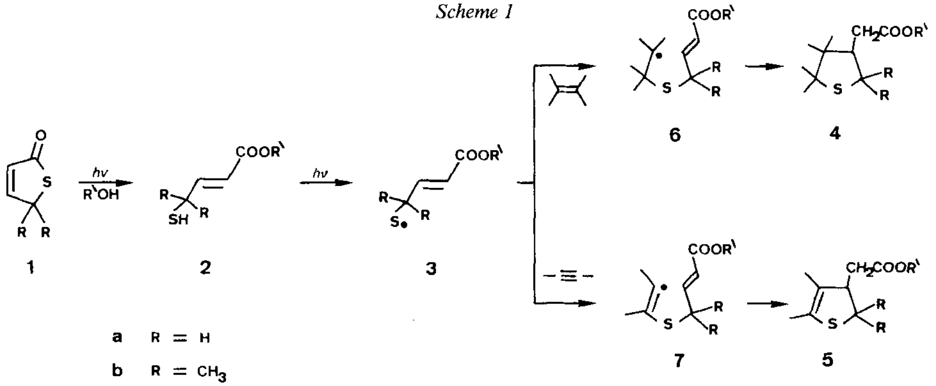
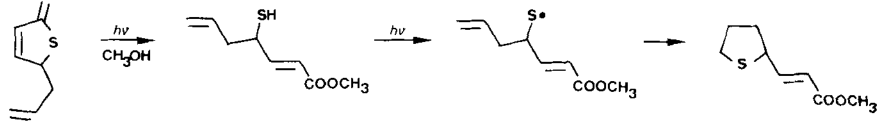
On irradiation (λ = 300 nm) in MeOH 5-(2-propenyl)-2(5*H*)-thiophenone (**1c**) affords methyl (*E*)-4-mercapto-2,6-heptadienoate (**2c**) which undergoes light-induced homolysis of the S–H bond to give the alkylthio radical **3c**. This species can be trapped by 2,3-dimethyl-2-butene or 2-butyne to afford octahydrobenzo-[*b*]thiophene **9** or 3a,4,5,6,7,7a-hexahydrobenzo[*b*]thiophene **13**, respectively, as main products *via* consecutive radical ring closure. In the absence of unsaturated hydrocarbons, **3c** cyclizes to give methyl (*E*)-3(thiolan-2-yl)-2-propenoate (**8**).

We have recently presented results on the photochemical behaviour of the 2(5*H*)-thiophenones **1a** [1] and **1b** [2] which react with alcohols to give 4-mercaptocrotonates **2a** and (*E*)-4-methyl-2-pentenoates **2b** (*Scheme 1*). These esters undergo a subsequent light-induced homolysis of the S–H bond giving alkylthio radicals **3** which add to alkenes or alkynes to afford thiolanes **4** or 2,3-dihydrothiophenes **5** *via* radical ring closure of **6** or **7**, respectively.

Scheme 1



We have now synthesized 5-(2-propenyl)-2(5*H*)-thiophenone (**1c**) in order to investigate the effect of the additional C=C bond on the photochemistry of unsaturated thiolactones **1** and on the reactivity of radicals **3**, **6**, and **7**. Compound **1c** has, up to now, only been observed by ^{1}H-NMR in a product mixture [3]. In contrast to the corresponding furan derivative [4], **1c** does not undergo intramolecular [2 + 2] photocycloaddition, *Scheme 2*

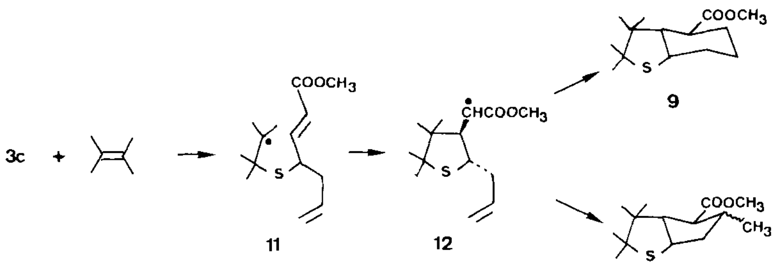


1c **2c** **3c** **8**

but in analogy to **1a** and **1b** affords methyl (*E*)-4-mercapto-2,6-heptadienoate (**2c**) on irradiation (λ = 300 nm) in MeOH (*Scheme 2*). Prolonged irradiation affords methyl (*E*)-3-(thiolan-2-yl)-2-propenoate (**8**) *via* radical ring closure of the alkylthio radical **3c**. Examples of such intramolecular additions of thioradicals to C=C bonds have been reported [5].

Thiolane **8** is not formed when the irradiation of **1c** in MeOH is run in the presence of alkenes or alkynes. With 2,3-dimethyl-2-butene, both *trans*-fused octahydrobenzo[*b*]thiophene **9** (70%) and hexahydro-2*H*-cyclopenta[*b*]thiophene **10** (25%)[1]) are formed (*Scheme 3*). These products arise *via* trapping of the alkylthio radical **3c** by the alkene

Scheme 3



11 **12** **9** **10**

(→**11**). The 3-thiahex-5-enyl radical **11** undergoes regio- and stereospecific ring closure to **12**, itself a hex-5-enyl radical. *trans*-Radical **12** now undergoes preferential 1,6-ring closure (→**9**), the usually favoured 1,5-ring closure (→**10**) being slowed down because of the strain energy of the thiabicyclo[3.3.0]octane system which, nevertheless, is expected to be less strained than the corresponding hydrocarbon system according to molecular-mechanic calculations [6]. All these steps occur in very good agreement with the predicted guidelines for ring closure of substituted hexenyl radicals [7–9].

Similarly, with 2-butyne, the *trans*-fused 3a,4,5,6,7,7a-hexahydrobenzo[*b*]thiophene **13** (45%) and the thiatricyclononane **14** (15%) are formed *via* vinyl radical **15** which undergoes ring closure to **16** and **17** (*Scheme 4*). *trans*-Radical **16** undergoes only 1,6-ring closure to **13**, while *cis*-radical **17** gives 1,5-ring closure to **18** exclusively. Radical **18**, again a hex-5-enyl radical, then gives **14** *via* selective '*exo*'-ring closure [10]. The spectroscopic data of the new compounds is summarized in the *Table*.

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[1]) The yields indicated were determined by GC analysis and, therefore, reflect ratios of products only.

Scheme 4

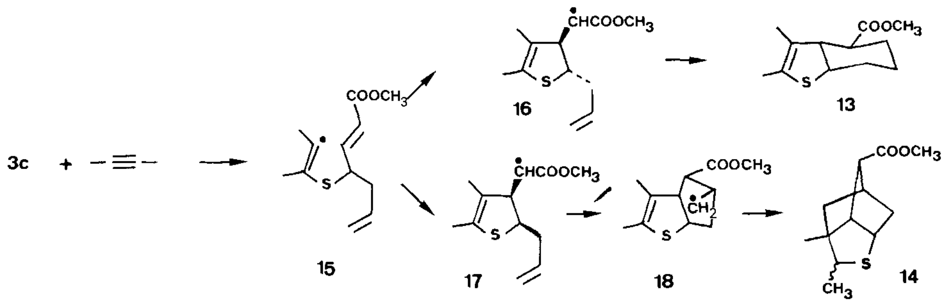

Table. *Spectroscopic Data of Compounds* **1c**, **2c**, **8**, **9**, **10**, **13**, *and* **14**

Compound	^{1}H-NMR ($CDCl_3$)	^{13}C-NMR ($CDCl_3$)	MS
1c	a) 6.83 (*dd*, *J* = 6.0, 2.6); 5.97 (*dd*, *J* = 6.0, 1.8); 5.54 (*dddd*, *J* = 17.0, 10.4, 7.0, 6.8); 4.96 (*ddd*, *J* = 10.4, 3.0, 1.0); 4.95 (*ddd*, *J* = 17.0, 3.0, 1.4); 4.01 (*dddd*, *J* = 8.2, 6.0, 2.6, 1.8); 2.21 (*dddd*, *J* = 14.2, 6.8, 6.0, 1.4); 2.09 (*dddd*, *J* = 14.2, 8.2, 7.0, 1.0)	199 (*s*); 158 (*d*); 133 (*d*); 132 (*d*); 119 (*t*); 54 (*d*); 38 (*t*)	140 ($M^{+\cdot}$) *99*
2c	a) 6.90 (*dd*, *J* = 15.6, 8.4); 5.75 (*dd*, *J* = 15.6, 1.0); 5.45 (*dddd*, *J* = 17.0, 10.2, 7.4, 6.8); 4.89 (*ddd*, *J* = 10.2, 3.4, 1.0); 4.85 (*ddd*, *J* = 17.0, 3.4, 1.4); 3.74 (*s*, 3H); 3.04 (*ddddd*, *J* = 8.4, 7.4, 7.2, 6.2, 1.0); 2.02 (*dddd*, *J* = 14.4, 7.7, 6.8, 1.4); 2.00 (*dddd*, *J* = 14.4, 7.4, 7.2, 1.4); 1.31 (*d*, SH)	166 (*s*); 148 (*d*); 134 (*d*); 122 (*t*); 118 (*d*); 51 (*q*); 42 (*t*); 40 (*d*)	172 ($M^{+\cdot}$) *79*
8	6.75 (*dd*, *J* = 15.4, 9.0); 5.76 (*dd*, *J* = 15.4, 0.6); 4.00 (*dddd*, *J* = 9.0, 7.0, 6.0, 0.6); 3.74 (*s*, 3H); 3.00 (*ddd*, *J* = 10.2, 7.8, 6.2); 2.90 (*ddd*, *J* = 10.2, 6.4, 5.6); 2.25–1.72 (*m*, 4H)	166 (*s*); 148 (*d*); 122 (*d*); 51 (*q*); 49 (*d*); 37 (*t*); 34 (*t*); 33 (*t*)	172 ($M^{+\cdot}$) *140*
9	3.68 (*s*, 3H); 2.93 (*dt*, *J* = 3.4, 11.2); 2.43 (*dt*, *J* = 3.6, 11.2); 2.04 (*ddddd*, *J* = 13.2, 4.0, 3.6, 3.0, 2.6); 2.02 (*t*, *J* = 11.2); 1.92 (*ddddd*, *J* = 13.2, 4.4, 3.6, 2.6, 1.4); 1.85 (*ddddd*, *J* = 13.2, 3.6, 3.4, 3.3, 1.4); 1.58 (*dddd*, *J* = 13.2, 13.0, 11.2, 4.0); 1.39 (*dddd*, *J* = 13.2, 13.0, 11.2, 3.0); 1.33 (*ddq*, *J* = 4.4, 3.4, 13.1); 1.30 (*s*, 3H); 1.22 (*s*, 3H); 0.95 (*s*, 3H); 0.75 (*s*, 3H)	175 (*s*); 57 (*s*); 56 (*q*); 51 (*d*); 48 (*d*); 47 (*s*); 45 (*d*); 33 (*t*); 32 (*q*); 31 (*t*); 25 (*t*); 24 (*q*); 21 (*q*); 19 (*q*)	256 ($M^{+\cdot}$) *122*
10b)	3.69 (*s*, 3H); 3.20 (*dt*, *J* = 5.8, 11.4); 2.81 (*t*, *J* = 11.4); 2.67 (*m*, 1H); 2.15 (*m*, 1H); 1.43 (*s*, 3H); 1.30–1.20 (*m*, 2H); 1.30 (*s*, 3H); 0.99 (*d*, *J* = 6.9, 3H); 0.88 (*s*, 3H); 0.82 (*s*, 3H)	–	256 ($M^{+\cdot}$) *123*
13	3.71 (*s*, 3H); 3.17 (*ddd*, *J* = 13.6, 12.2, 3.2); 2.71 (*ddq*, *J* = 13.6, 11.2, 1.3); 2.37 (*dt*, *J* = 3.4, 11.2); 2.07–1.35 (*m*, 6H); 1.84 (*d*, *J* = 1.3, 3H); 1.55 (*s*, 3H)	176 (*s*); 129 (*s*); 128 (*s*); 58 (*q*); 55 (*d*); 52 (*d*); 47 (*d*); 31 (*t*); 29 (*t*); 25 (*t*); 15 (*q*); 13 (*q*)	226 ($M^{+\cdot}$) *125*
14c)	3.67 (*s*, 3H); 3.50 (*ddd*, *J* = 9.3, 4.8, 1.6); 3.34 (*dq*, *J* = 1.6, 6.7); 2.90 (*dd*, *J* = 3.0, 1.6); 2.50 (*dt*, *J* = 4.8, 1.0); 2.46 (*ddt*, *J* = 2.0, 1.0, 3.2); 2.09 (*ddt*, *J* = 12.6, 9.3, 3.1); 1.66–1.54 (*m*, 2H); 1.40 (*ddd*, *J* = 12.6, 2.0, 1.0); 1.20 (*d*, *J* = 6.7, 3H); 1.09 (*s*, 3H)	–	*226* ($M^{+\cdot}$)

a) In C_6D_6.

b) ^{1}H-NMR from 1:1 mixture of **10** and **9**. Configuration at C(5) unknown.

c) ^{1}H-NMR from 3:1 mixture of **14** and **13**. Configuration at C(2) unknown.

To our knowledge, ring systems like **10** or **13** have not yet been reported in the literature. The reaction of easily accessible alkylthio radicals containing an additional C=C bond like **3c** with alkenes or alkynes, therefore, seems to represent an excellent method for the synthesis of cycloalkane-annellated thiolanes and dihydrothiophenes. We are now investigating the scope of this reaction.

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Experimental Part

General. See [1]. Irradiations were performed in a *Rayonet-RPR-100* photoreactor on N_2-degassed solns. using 300-nm lamps.

*5-(2-Propenyl)-2(5*H*)-thiophenone* (**1c**). The mixture of thiolactone **1c** and the corresponding β,γ-unsat. thiolactone is prepared from 2-(*tert*-butoxy)-5-(2-propenyl)thiophene according to [3]. Stirring of this mixture with Et_3N in Et_2O at 5° for 15 h and subsequent workup according to [11] affords 64% of **1c**, b.p. 41–42°/0.01 Torr.

Photolysis of **1c** *in MeOH.* A N_2-degassed soln. of 420 mg ($3 \cdot 10^{-3}$ mol) of **1c** in 15 ml of MeOH is irradiated for 90 h. Evaporation and chromatography (SiO_2, CH_2Cl_2) afford *methyl (*E*)-4-mercapto-2,6-heptadienoate* (**2c**) in 12% yield and *methyl (*E*)-3-(thiolan-2-yl)-2-propenoate* (**8**) in 15% yield. Both products were further purified by bulb-to-bulb distillation (120°/0.1 Torr) and are colourless oils.

Photolysis of **1c** *in MeOH Containing 2,3-Dimethyl-2-butene.* A N_2-degassed soln. of 420 mg of **1c** and 4.20 g ($5 \cdot 10^{-2}$ mol) of 2,3-dimethyl-2-butene in 15 ml of MeOH is irradiated for 30 h. After evaporation and bulb-to-bulb distillation (130°/0.2 Torr), chromatography (SiO_2, C_6H_6) affords *methyl octahydro-2,2,3,3-tetramethyl-*trans*-benzo[*b*]thiophene-4-carboxylate* (**9**) in 15% yield and a 1:1 mixture of **9** and *methyl hexahydro-2,2,3,3,5-pentamethyl-2*H*-*trans*-cyclopenta[*b*]thiophene-4-carboxylate* (**10**) in 6% yield, all colourless oils.

Photolysis of **1c** *in MeOH Containing 2-Butyne.* A soln. of 420 mg **1c** in 15 ml of MeOH is saturated with 2-butyne and irradiated for 53 h. After evaporation of the solvent and bulb-to-bulb distillation (140°/0.2 Torr), chromatography (SiO_2, CH_2Cl_2) affords *methyl 3a,4,5,6,7,7a-hexahydro-2,3-dimethyl-*trans*-benzo[*b*]thiophene-4-carboxylate* (**13**) in 39% and a 3:1 mixture of *methyl 5,6-dimethyl-4-thiatricyclo[4.2.1.0^{3,7}]nonane-8-carboxylate* (**14**) and **13** in 15% yield. Both compounds are colourless oils.

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