14. Formation of 2,3-Dihydrothiophene-3-carboxylates from 2(5*H*)-Thiophenones *via* Sequential Cyclization and Ring-Opening Reactions of 3-Thiahexa-1,5-dienyl Radicals

Preliminary Communication

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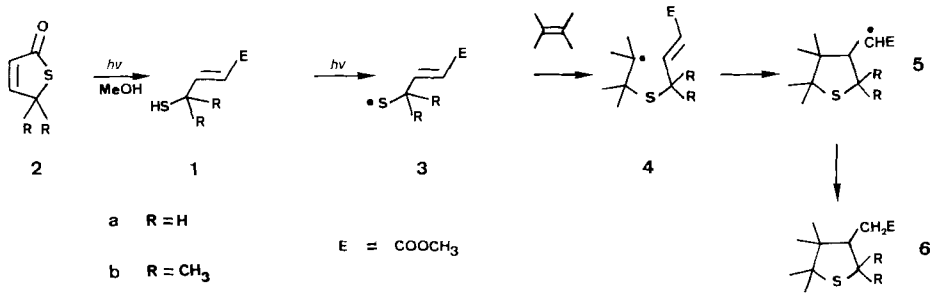
Methyl 4-mercapto-2-alkenoates **1**, obtained by irradiation of 2(5*H*)-thiophenones **2** in MeOH, undergo light-induced S–H bond homolysis to give thio radicals **3** which can be trapped with 2-butyne to afford 3-thiahexa-1,5-dienyl radicals **12**. Intermediates **12** undergo selective 1,5-ring closure to allylcarbinyl radicals **18**, which cyclize to cyclopropylcarbinyl radicals **19**. A novel rearrangement of **19** to **23**, the direct precursors of title compounds **15** and **17**, occurs *via* two additional ring-opening and one 1,5-ring-closure step.

We have recently reported that methyl 4-mercapto-2-alkenoates **1**, obtained by irradiation of 2(5*H*)-thiophenones **2** in MeOH, undergo light-induced S–H bond homolysis to give thio radicals **3** *(Scheme 1)* [1] [2]. Intermediates **3** can be trapped by alkenes to afford 3-thiahex-5-enyl radicals **4**, which cyclize selectively to radicals **5**, precursors of thiolane-3-acetates **6**.

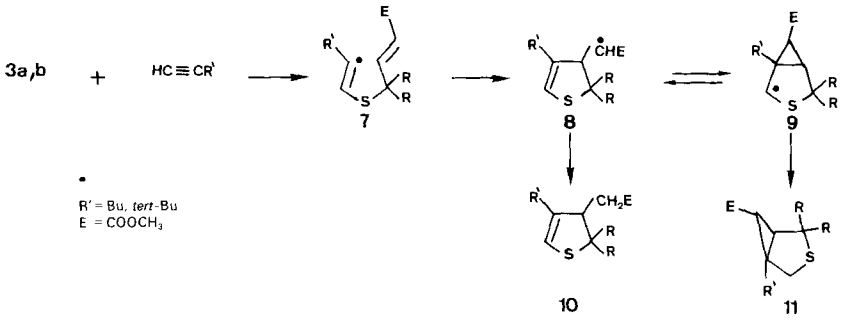
Scheme 1



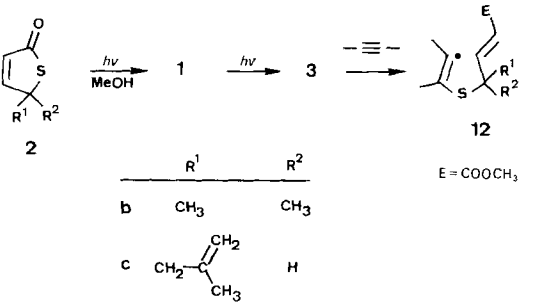
Reaction of **3** with terminal alkynes occurs regioselectively giving 3-thiahexa-1,5-dienyl radicals **7** which also undergo selective 1,5-ring closure to allylcarbinyl radicals **8** *(Scheme 2)*. Depending on the substitution pattern, radicals **8** rearrange to cyclopropylcarbinyl radicals **9**. From **8** and **9**, 2,3-dihydrothiophene-3-acetates **10** and 3-thiabicyclo-[3.1.0]hexane-6-carboxylates **11** are formed, respectively [1] [2].

We now report a novel rearrangement observed with 3-thiahexa-1,5-dienyl radicals **12b** and **12c** formed by addition of 2-butyne to **3b** and **3c**, respectively *(Scheme 3)*. Thio

Scheme 2



Scheme 3

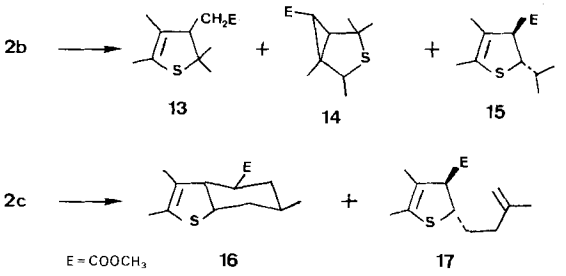


radical **3c** is obtained from newly synthesized 5-(2-methyl-2-propenyl)-2(5*H*)-thiophenone (**2c**).

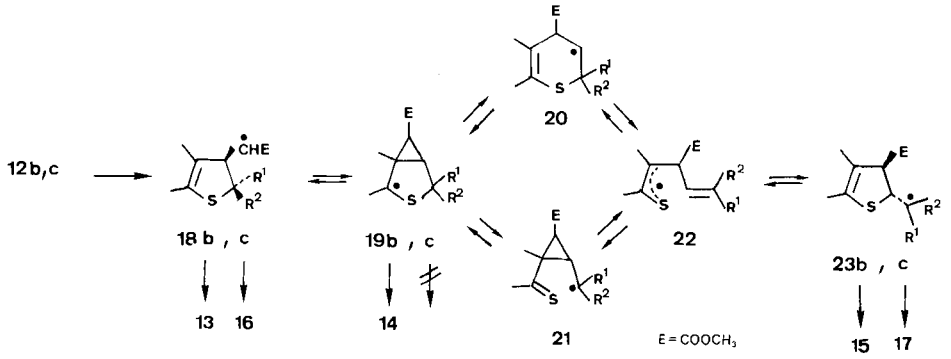
Irradiation of **2b** in MeOH saturated with 2-butyne affords 2,3-dihydrothiophene-3-acetate **13**, 3-thiabicyclo[3.1.0]hexane **14**, and 2,3-dihydrothiophene-3-carboxylate **15** in a 1:1:1 ratio *(Scheme 4)*. From **2c** under similar conditions, a 1:1 mixture of *trans*-fused 3a,4,5,6,7,7a-hexahydrobenzo[*b*]thiophene **16** and of 2,3-dihydrothiophene-3-carboxylate **17** is formed.

The 2-bicyclo[3.1.0]hexyl radicals are known to undergo cyclopropylcarbinyl→allylcarbinyl rearrangement to either (primary) (3-cyclopentenyl)methyl or to (secondary) 3-cyclohexenyl radicals by cleavage of one of the cyclopropane bonds adjacent to the radical center [3] [4]. While the formation of **13** from allylcarbinyl radical **18b**, that of **14**

Scheme 4



Scheme 5



from cyclopropylcarbinyl radical **19b** and that of **16** by selective 1,6-ring closure [5] of *trans*-radical **18c** occur in analogy to previously reported examples, the formation of **15** and **17** represents a novel reaction type *(Scheme 5)*. Either the 3-thiabicyclo[3.1.0]hex-2-yl radical **19** does not rearrange to intermediate **20**, as no dihydrothine derivatives are observed, but instead undergoes S–C-bond cleavage to cyclopropylcarbinyl radical **21** which rearranges to resonance-stabilized radical **22**, or **19** does rearrange to **20** which then undergoes immediate ring opening to **22**. The 1-thiahexa-2,5-dienyl radical **22** then undergoes 1,5-ring closure to radical **23** which leads to **15** and **17**, respectively. The configuration of the alkyl and the ester group in these 2,3-dihydrothiophene-3-carboxylates is most probably *trans* as hex-5-enyl radicals with substituents on C(4) are known to undergo preferential *trans*-1,5-ring closure [6]. Conversion of **20** to **23** corresponds to an (intramolecular) 1,2-thio migration [7]. Interaction of the acyclic C=C bond and the radical center in **18c** or **19c** apparently prevents H-abstraction by these species and, therefore, no dihydrothiophene-3-acetate or 3-thiabicyclo[3.1.0]hexane-6-carboxylate is formed from **2c**. In **16**, the methoxycarbonyl group is equatorial, the position of the CH_3 group on C(6) being unknown. The spectroscopic data of the products is summarized in the *Table*.

Table. *Spectroscopic Data of Compounds* **13–17**

Compound	^{1}H-NMR ($CDCl_3$)	MS
13	3.68 (*s*, 3H); 2.84 (*dd*, *J* = 8.0, 5.6); 2.58 (*dd*, *J* = 16.0, 5.6); 2.30 (*dd*, *J* = 16.0, 5.6); 1.80 (*s*, 3H); 1.63 (*s*, 3H); 1.48 (*s*, 3H); 1.28 (*s*, 3H)	214 ($M^{+\cdot}$) *141*
14	3.69 (*s*, 3H); 3.67 (*q*, *J* = 6.4); 2.24 (*d*, *J* = 4.3); 1.84 (*d*, *J* = 4.3); 1.52 (*s*, 3H); 1.32 (*s*, 3H); 1.30 (*s*, 3H); 1.24 (*d*, *J* = 6.4, 3H)	214 ($M^{+\cdot}$) *127*
15	3.92 (*d*, *J* = 4.6); 3.75 (*s*, 3H); 3.33 (*m*, CHS); 2.10 (*m*, $(CH_3)_2CH$); 1.80 (*s*, 3H); 1.62 (*s*, 3H); 0.92 (*d*, *J* = 7.0, 3H); 0.81 (*d*, *J* = 7.0, 3H)	214 ($M^{+\cdot}$) *171*
16	3.72 (*s*, 3H); 3.21 (*ddd*, *J* = 13.8, 12.0, 3.2); 2.69 (*t*, *J* = 12.0); 2.43 (*dt*, *J* = 3.6, 12.0); 2.07–1.05 (*m*, 5H); 1.85 (*s*, 3H); 1.59 (*s*, 3H); 0.94 (*d*, *J* = 6.4, 3H)	240 ($M^{+\cdot}$) *125*
17	4.79 and 4.68 (*m*, $C=CH_2$); 3.84 (*d*, *J* = 3.4); 3.74 (*s*, 3H); 3.26 (*m*, CHS); 2.04 (*t*, *J* = 7.8, 2H); 1.81 (*s*, 3H); 1.74 (*s*, 3H); 1.70–1.62 (*m*, 2H); 1.66 (*s*, 3H).	240 ($M^{+\cdot}$) *125*

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Experimental Part

General. See [1]. Thiophenone **2b** was synthesized according to [2]. GC was performed on a *SE-30*-capillary column. Irradiation were performed in a *Rayonet-RPR-100* photoreactor using 300-nm lamps.

*5-(2-Methyl-2-propenyl)-2(5*H*)-thiophenone* (**2c**). The procedure is analogous to the one used for the synthesis of 5-(2-propenyl)-2(5*H*)-thiophenone [5] [8] [9]. Metallation and alkylation of 2-(*tert*-butoxy)thiophene affords 2-(*tert*-butoxy)-5-(2-methyl-2-propenyl)thiophene, b.p. 63–65°/0.2 Torr in 70% yield, which is then treated with TsOH at 160°. The mixture of **2c** and the corresponding β,γ-unsat. thiolactone is equilibrated with Et_3N in Et_2O. Distillation affords 60% of **2c**, b.p. 45–46°/0.01 Torr; ^{1}H-NMR ($CDCl_3$): 7.51 (*dd*, 1 H); 6.30 (*dd*, 1 H); 4.95 (*m*, 1 H); 4.86 (*m*, 1 H); 4.67 (*dddd*, 1 H); 2.69 (*dd*, 1 H); 2.45 (*dd*, 1 H); 1.87 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 199.3 (*s*); 158.0 (*d*); 141.5 (*s*); 132.0 (*d*); 113.5 (*t*); 52.4 (*d*); 42.4 (*t*); 22.3 (*q*). MS: 154 ($M^{+\cdot}$), 55.

Irradiations. Solns. of $3 \cdot 10^{-3}$ M **2b** or **2c** in MeOH with a tenfold molar excess of 2-butyne (in all, 15 ml of soln. are irradiated (time given below). After evaporation of the MeOH, the residue is bulb-to-bulb distilled (150°/0.01 Torr). The products are then obtained by chromatography on SiO_2.

From **2b**. Irradiation time, 15 h. Chromatography: with hexane/AcOEt 7:1. Elution order: *methyl 1,2,4,4-tetramethyl-3-thiabicyclo[3.1.0]hexane-6-carboxylate* (**14**, 22%), *methyl 2,3-dihydro-2,2,4,5-tetramethylthiophene-3-acetate* (**13**, 20%), and *methyl 2,3-dihydro-2-isopropyl-4,5-dimethylthiophene-3-carboxylate* (**15**, 28%), all colourless oils.

From **2c**. Irradiation time, 45 h. Chromatography: with benzene. Elution order: *methyl 2,3-dihydro-4,5-dimethyl-2-(3-methyl-3-butenyl)thiophene-3-carboxylate* (**17**, 39%) and *methyl 3a,4,5,6,7,7a-hexahydro-2,3,6-trimethyl-*trans*-benzo[*b*]thiophene-4-carboxylate* (**16**, 51%), both colourless oils.

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