255. Light-Induced Synthesis of Thiolanes and 2,3-Dihydrothiophenes by Addition of (*E*)-4-Mercapto-2-butenoates to Alkenes or Alkynes

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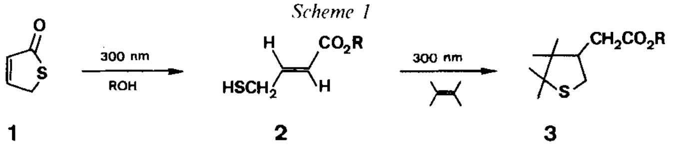
Summary

Irradiation (λ = 300 nm) of methyl 4-mercaptocrotonate (**2a**) in the presence of alkenes or alkynes affords methyl 3-thiolaneacetates **7** and methyl 2,3-dihydro-3-thiopheneacetates **13**. The unsaturated heterocycles **13** undergo further light-induced isomerization to methyl 2,3-dihydro-2-thiopheneacetates **15**. Both **13** and **15** are readily dehydrogenated to thiophenes **17** and **18**, respectively.

We have recently [1] reported on the photochemical formation of 4-mercaptocrotonates **2** from 2(5*H*)-thiophenone (**1**) in alcohols, and on their further photochemical conversion to thiolanes **3** when the experiments were run in the presence of 2,3-dimethyl-2-butene *(Scheme 1)*. We now present additional evidence on the assignment of the reactive excited state of **1**, give an account of the scope of the photochemical addition of **2** to alkenes, and finally discuss the formation of 2,3-dihydrothiophenes from **2** and alkynes as well as some of the subsequent thermal and photochemical reactions of these unsaturated heterocycles.

Scheme 1



Regarding the photosolvolysis **1**→**2**, we had found that the reaction was not slowed down when adding up to tenfold molar 2,5-dimethyl-2,4-hexadiene as triplet quencher [1] and, therefore, we had suggested that **2** was formed from the excited singlet state of **1**. This interpretation is corroborated by the results of xanthone-sensitized reactions of **1** in alcohols or cyclohexane as solvent. Indeed, no esters **2** are formed in alcohols, but only the *RH*-reduction products **4** and the solvent adducts **5**, the relative amount of **4** and **5** depending on the ease of oxidation of the alcohol ($E_{p/2}$: i-PrOH < EtOH < MeOH [2]). In cyclohexane, the *RH*-reduction product **6** is formed selectively *(Scheme 2)*. The spectroscopic data of compounds **4**–**6** are summarized in *Table 1*.

As for the formation of **3** in the irradiation of **1** in alcohols in the presence of 2,3-dimethyl-2-butene, we had shown [1] that **3** was formed by a consecutive light-in-

Table 1. *Spectroscopic Data of* **2a**, **4**, **5** *and* **6**

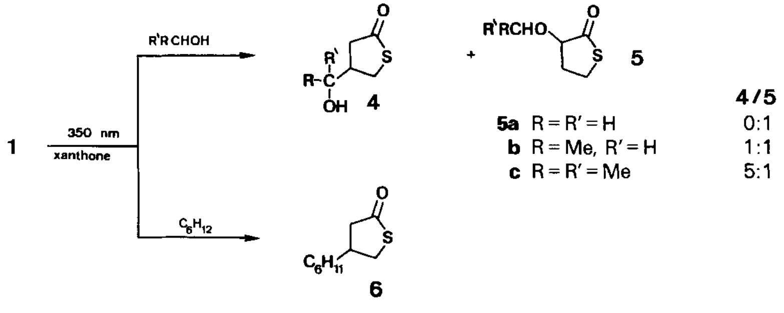
Compound[a])	IR (CCl_4)	^1H-NMR ($CDCl_3$)	^{13}C-NMR ($CDCl_3$)	MS
2a	1730	6.92 (*dt*, J = 15.2, 7.2); 5.94 (*dt*, J = 15.2, 1.5); 3.72 (*s*, 3H); 3.28 (*m*, 2H); 1.54 (*t*, J = 8.2, SH)	166.4 (*s*); 146.1 (*d*); 121.6 (*d*); 51.6 (*q*); 25.6 (*t*)	132 (M^+) 100
4b[b])	1695	2.93 (*quint.*, J = 6.2); 2.80 (*dd*, J = 10.8, 6.2)[c]); 2.40 (*dd*, J = 10.8, 6.2); 2.21 (*dd*, J = 16.8, 7.4); 2.12 (*dd*, J = 16.8, 11.8); 1.71 (*m*); 0.52 (*d*, J = 6.3, CH_3)	207.0 (*s*); 70.1 (*s*); 50.2 (*d*); 43.1 (*t*); 34.6 (*t*); 22.3 (*q*)	146 (M^+) *41*
4c	1697	3.13 (*dd*, J = 10.4, 6.4); 3.02 (*dd*, J = 10.4, 1.4); 2.32 (*dd*, J = 16.2, 9.4); 2.28 (*dd*, J = 16.2, 11.8); 2.22 (*dddd*, J = 11.8, 9.4, 6.4, 1.4); 0.98 and 0.95 (*s*, CH_3)	207.2 (*s*); 70.1 (*s*); 50.2 (*d*); 43.3 (*t*); 33.1 (*t*); 29.5 (*q*); 28.6 (*q*)	160 (M^+) *59*
5a	1695	3.82 (*dd*, J = 7.3, 5.6); 3.53 (*s*, 3H); 3.36 (*ddd*, J = 11.2, 6.0, 5.6); 3.23 (*ddd*, J = 11.2, 7.3, 6.4); 2.41 (*dt*, J = 13.2, 5.6); 2.16 (*ddt*, J = 13.2, 6.0, 7.3)		132 (M^+) *58*
5b	1695	3.92 (*dd*, J = 7.6, 5.8); 3.86 (*q*, 2H); 3.36 (*m*); 3.21 (*m*); 2.38 (*m*); 2.18 (*m*); 1.15 (*t*, 3H)		146 (M^+) *102*
5c	–	4.03 (*dd*, J = 7.6, 5.8); 4.02 (*sept.*, J = 6.2); 3.36 (*m*); 3.22 (*m*); 2.36 (*m*); 2.11 (*m*); 1.12 (*d*, J = 6.2, 2 CH_3)		160 (M^+) *43*
6[b])	1695	2.60 (*dd*, J = 10.8, 6.0); 2.35 (*t*, J = 10.8)[c]); 2.15 (*dd*, J = 15.8, 6.0); 1.65 (*dd*, J = 15.8, 12.4); 1.62 (*m*); 1.60–0.50 (*m*, 11H)		184 (M^+) *108*

[a]) All new compounds gave satisfactory elemental anylses.

[b]) Mixture of diastereomers; NMR data for major isomer.

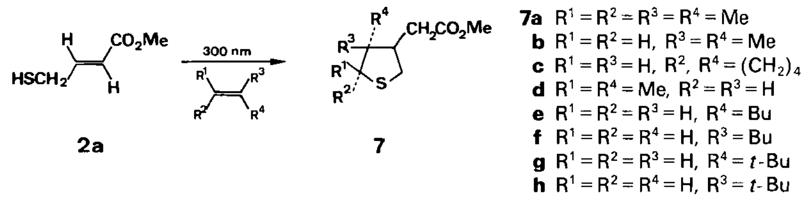
[c]) In (D_6)benzene.

Scheme 2



duced reaction (most probably homolytic cleavage of the S–H bond[1]) of **2** with the olefin. We have now irradiated **1** (resp. **2a**) in MeOH in the presence of several alkenes. The reaction is regiospecific for terminal alkenes (formation of **7b** from 2-methylpropene, **7e** and **7f** from 1-hexene and **7g** and **7h** from 3,3-dimethyl-1-butene). From both (*Z*)- or (*E*)-2-butene the *all-trans*-isomer **7d** is the main product. Addition to cyclohexene gives the *cis*-fused (J(H,H) = 4.2 Hz) perhydrobenzothiophene **7c** as major product *(Scheme 3)*. The spectroscopic data of thiolanes **7** is summarized in *Table 2*.

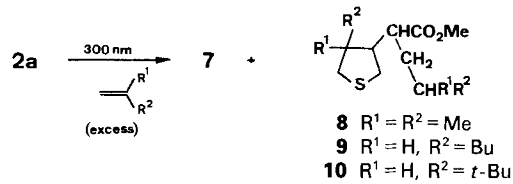
Scheme 3



Irradiation of **2a** in the presence of a large excess of 2-methylpropene afforded the (1 + 2) adduct **8** as main product [1]. With increasing chain length and bulkiness of the terminal alkene the ratio of (1 + 2) to (1 + 1) adducts decreases sharply, *e.g.* only 10% **9** are formed when using 1-hexene in excess and almost no product **10** is formed from **2a** and 3,3-dimethyl-1-butene, as estimated from GC/MS analysis *(Scheme 4)*.

The photochemical reactions of **2a** with alkynes take a similar course as those with alkenes discussed before. Addition to terminal acetylenes as 1-hexyne and 3,3-di-

Scheme 4



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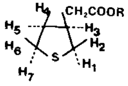
[1] For examples of intramolecular additions of alkylthio radicals to C–C double or triple bonds *cf.* [3] and [4].

Table 2. *Spectroscopic Data of Compounds* **7**, **8** *and* **9**

Compound[a]	IR (CCl_4)	^{1}H-NMR[b] ($CDCl_3$)								^{13}C-NMR ($CDCl_3$)	MS
		H–C(1)	H–C(2)	H–C(3)	H–C(4)	H–C(5)	H–C(6)	H–C(7)	C*H*$_2$COOR		
7a	1735	3.03	2.53	2.60	–	–	–	–	2.48 2.24	173.2 (*s*); 57.8 (*s*); 51.6 (*q*); 47.2 (*s*); 46.6 (*d*); 35.3 (*t*); 33.4 (*t*); 30.4, 24.7, 20.8 and 18.0 (*q*)	216 (M^+) *88*
7b	1732	3.09	2.54	2.15	–	–	2.57	2.75	2.46 2.15	–	188 (M^+) *114*
7c	1735	2.86	2.45	2.39	1.76	–	3.70	–	2.40 2.25	172.6 (*s*); 51.4 (*q*); 44.3 (*d*); 44.2 (*d*); 34.5, 34.0, 27.2, 24.6, 20.6 and 19.7 (*t*)	214 (M^+) *140*
7d	1734	2.95	2.50	2.67	1.85	–	–	2.90	2.30 2.29		188 (M^+) *114*
7e	1734	2.82	2.51	2.14	1.86	–	2.40	2.87	2.52[c] 2.36[c]		216 (M^+) *142*
7f	1734	2.91	2.61	2.14	–	1.75	2.64	2.98	2.48[c] 2.36[c]		216 (M^+) *142*
7g	–	*	*	*	1.90	–	*	*	*[c]		216 (M^+) *85*
7h	–	*	*	*	–	1.73	*	*	*[c]		216 (M^+) *85*
8	1734	3.03	2.54	2.03	–	–	2.58	2.80	2.42		244 (M^+) *87*
9	1735	2.90	2.57	2.27	2.08	–	2.57	2.90	2.40		300 (M^+) *158*

[a] All new compounds gave satisfactory elemental analyses.

[b]

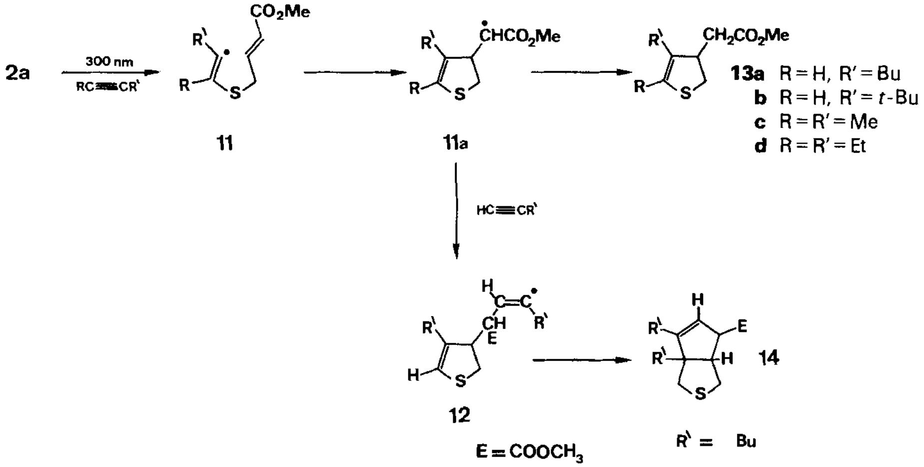


$J(H_1,H_2) = J(H_6,H_7) = 8.6–11.5$
$J(H_1,H_3) = J(H_4,H_6) = J(H_5H_7) = 4.2–6.8$
$J(H_2,H_3) = J(H_4,H_7) = J(H_5,H_6) = 6.0–10.8$
$J(CH_2COOR) = 15–16$

[c] NMR data from product mixture, compounds not isolated (* means exact assignment not possible).

methyl-1-butyne is again regiospecific, the alkylthio radical adding to the unsubstituted carbon atom of the C≡C bond. With a large excess of 1-hexyne the thiabicyclo[3.3.0]octene **14** – formed from **2a** and 2 molecules of the alkyne – becomes the major product. No such reaction is observed for 3,3-dimethyl-1-butyne. Disubstitued alkynes (2-butyne, 3-hexyne) afford the expected 4,5-dialkyl-2,3-dihydrothiophene-3-acetates **13c** and **13d** *(Scheme 5)*.

Scheme 5



All these reactions are somehow complicated by a further light-induced isomerization of **13** to 2,3-dihydrothiophene-2-acetates **15**. This rearrangement probably occurs *via* the cyclopropyl thione **16** [5]. Moreover both **13** and **15** are easily dehydrogenated to thiophenes **17** and **18**, respectively, only the *tert*-butyl compounds **13b** and **15b** being stable for longer periods *(Scheme 6)*. For preparative purposes compounds

Scheme 6

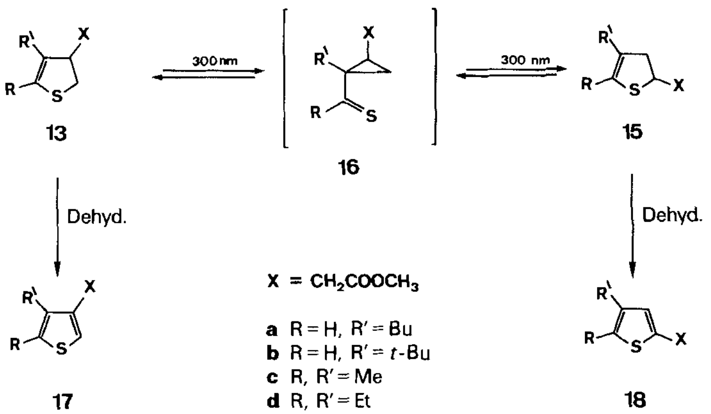


Table 3. *Spectroscopic Data of* **13, 14, 15, 17** *and* **18**

Compound[a])	IR (CCl_4)	^1H-NMR ($CDCl_3$)	^{13}C-NMR ($CDCl_3$)	MS
13a	1735	5.71 (*s*); 3.72 (*s*, 3H); 3.42 (*dd*, *J* = 11.4, 8.4); 3.21 (*m*); 2.94 (*m*); 2.94 (*m*); 2.43 (*m*, 2H); 2.05–0.84 (*m*, 9H)		214 (M^+) *141*
13b	1735	5.82 (*s*); 3.72 (*s*, 3H); 3.39 (*ddd*, *J* = 11.0, 7.0, 2.0); 3.28 (*ddd*, *J* = 10.5, 7.0, 2.0); 2.98 (*d*, *J* = 11.0); 2.81 (*dd*, *J* = 16.8, 10.8); 2.30 (*ddd*, *J* = 16.0, 2.0, 2.0); 1.12 (*s*, 9H)	173.0 (*s*); 149.0 (*s*); 118.6 (*d*); 51.4 (*q*); 43.4 (*d*); 40.3 (*t*); 34.4 (*t*); 33.8 (*s*); 30.4 (*q*)	214 (M^+) *57*
13c[b])		3.65 (*s*, 3H); 3.33 (*dd*, *J* = 11.2, 8.4); 3.27 (*ddt*, *J* = 8.4, 4.4, 7.4); 2.84 (*dd*, *J* = 11.2, 4.4); 2.42 (*d*, *J* = 7.4, 2H); 1.78 and 1.60 (*s*, CH_3)		186 (M^+) *113*
14	1732	5.33 (*dt*, *J* = 1.4, 1.7); 3.70 (*s*, 3H); 3.60 (*ddt*, *J* = 7.9, 1.4, 3.0); 2.96–2.85 (*m*, 2H); 2.83 (*d*, *J* = 11.6); 2.60 (*d*, *J* = 11.6); 2.55 (*dd*, *J* = 10.5, 8.0); 1.90 (*m*, 2H); 1.70–0.85 (*m*, 16H)	173.3 (*s*); 150.1 (*s*); 119.9 (*d*); 67.0 (*s*); 53.5 (*q*); 51.5 and 51.0 (*d*); 42.3, 37.7, 36.4, 29.9, 27.0, 26.9, 23.3, and 22.8 (*t*); 9.3 and 7.9 (*q*)	296 (M^+) *91*
15b	1732	5.68 (*d*, *J* = 2.2); 3.98 (*dq*, *J* = 3 × 8.0, 4.0); 3.72 (*s*, 3H); 2.92 (*ddd*, *J* = 16.0, 8.0, 2.0); 2.70 (*dd*, *J* = 16.0, 8.0); 2.62 (*dd*, *J* = 16.0, 8.0); 2.50 (*dd*, *J* = 16.0, 4.0); 1.02 (*s*, 9H)	172.0 (*s*); 144.7 (*s*); 114.3 (*d*); 51.6 (*q*); 44.5 (*d*); 40.9 (*t*); 40.8 (*t*); 34.0 (*s*); 29.2 (*q*)	214 (M^+) *57*
17a[b])		7.10 (*d*, *J* = 3.0); 6.89 (*d*, *J* = 3.0); 3.70 (*s*, 3H); 3.57 (*s*, 2H); 2.05–0.84 (*m*, 9H)		212 (M^+) *111*
17c	1730	6.88 (*s*); 3.72 (*s*, 3H); 3.56 (*s*, 2H); 2.38 (*s*, 3H); 2.08 (*s*, 3H)		184 (M^+) *125*
17d	1730	6.90 (*s*); 3.62 (*s*, 3H); 3.53 (*s*, 2H); 2.73 and 2.48 (*q*, CH_2); 1.25 and 1.04 (*t*, CH_3)	171.6 (*s*); 141.4 (*s*); 137.6 (*s*); 133.0 (*s*); 119.5 (*d*); 51.7 (*q*); 34.8, 21.6 and 19.8 (*t*); 16.0 and 14.6 (*q*)	212 (M^+) *197*
18c	1730	6.57 (*s*); 3.72 (*s*, 3H); 3.47 (*s*, 2H); 2.28 and 2.06 (*s*, CH_3)		184 (M^+) *125*

[a]) All new compounds gave satisfactory elemental analyses.

[b]) Not isolated; NMR data from spectrum of product mixture; MS data from GC/MC analysis.

13 are best obtained at low degree of conversion of **1**, resp. **2a** and compounds **15** after prolonged irradiation. Isolation of the 4,5-dialkyl-2,3-dihydrothiophenes **13c** and **13d** is cumbersome, as dehydrogenation to **17** and **18** already occurs partially during workup. On the other hand, these thiophenes can be obtained in good yiels by bubbling air through the reaction mixture after irradiation or by treating it with an ethanolic H_2O_2 solution. The spectroscopic data of these products are summarized in *Table 3*.

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Experimental Part

General. Absorptions in the IR spectra are given in cm^{-1}. Chemical shifts in the 400-MHz ^1H- and 100.63-MHz ^{13}C-NMR spectra are given in ppm relative to TMS ($\delta = 0$ ppm) as internal standard. The mass spectra were measured at 70 eV, GC was performed on a *SE 30* capillary column, TLC and prep. chromatography were carried out on SiO_2.

Starting Materials. 2(5*H*)-Thiophenone (**1**) was synthesized according to [6]. Alkenes and alkynes were purchased from *Fluka AG*. Xanthone was recrystallized from EtOH.

Photolyses. These were run in a *Rayonet RPR-100* photoreactor on N_2-degassed solutions using lamps of $\lambda = 300$ nm for direct and $\lambda = 350$ nm for sensitized irradiations.

Sensitized Irradiation of **1** *in Alcohols.* Solutions of 400 mg ($4 \cdot 10^{-3}$ mol) **1** and 90 mg xanthone in 40 ml ROH (R = CH_3, C_2H_5, $(CH_3)_2CH$) were irradiated for 60 h to a conversion of 40–50% of starting material. Evaporation of the solvent and chromatography afforded: a) 80 mg (15%) **5a**, eluent Et_2O/pentane 2:1; b) 48 mg (8%) **5b** and 195 mg (32%) **4b**, the latter as a 5:4 mixture of diastereomers, eluent Et_2O; c) 20 mg (4%) **5c** and 160 mg (25%) **4c**, eluent Et_2O. All these saturated thiolactones are colourless oils.

Sensitized Irradiation of **1** *in Cyclohexane.* Irradiation and workup as above (chromatography: eluent pentane/Et_2O 2:1) afforded 285 mg (38%) **6** as a colourless oil.

Methyl 3-Thiolaneacetates **7**. A soln. of 400 mg ($4 \cdot 10^{-3}$ mol) **1** and 1.10^{-2} mol alkene in 40 ml MeOH was irradiated for 60 h up to total conversion of starting material. Evaporation of the solvent and workup as described below afforded: *a*) bulb-to-bulb distillation (150°/0.02 Torr), 750 mg (85%) *methyl 4,4,5,5-tetramethyl-3-thiolaneacetate* (**7a**), m.p. 33–35°; *b*) chrom. (CH_2Cl_2), 260 mg (35%) *methyl 4,5-dimethyl-3-thiolaneacetate* (**7b**); *c*) chrom. (pentane/Et_2O 9:1), 270 mg (32%) *methyl 7-thiabicyclo[4.3.0]nonane-9-acetate* (**7c**) of 85% purity, contaminated with one unidentified isomer; *d*) chrom. (CH_2Cl_2), 250 mg (32%) **7d** of 65% purity, contaminated with at least four other minor isomers (GC); *e,f*) chrom. (pentane/Et_2O 2:1), 345 mg (40%) of a 2:1 mixture of *methyl 4-butyl-3-thiolaneacetate* (**7e** and **7f**); *g,h*) chrom. (CH_2Cl_2), 385 mg (45%) of a 1:1 mixture of *methyl 4-(*tert*-butyl)-3-thiolaneacetate* (**7g** and **7h**). All compounds except **7a** are colourless oils.

Methyl 2-(4,4-Dimethyltetrahydrothien-3-yl)-4-methylpentanoate (**8**). A soln. of 400 mg **1** in 40 ml MeOH was saturated with 2-methylpropene and irradiated for 60 h. Evaporation of the solvent and chrom. (CH_2Cl_2) afforded 250 mg (26%) **8** as a colourless oil.

Methyl 2-(4-Butyltetrahydrothien-3-yl)octanoate (**9**). A soln. of 400 mg **1** and 4 g 1-hexene in 40 ml MeOH was irradiated for 60 h. Chromatography (pentane/Et_2O 2:1) afforded 50 mg (4%) **9** as a colourless oil.

Methyl 4-Butyl-2,3-dihydro-3-thiopheneacetate (**13a**). A soln. of 400 mg **1** and 365 mg ($4.4 \cdot 10^{-3}$ mol) 1-hexyne in 40 ml MeOH was irradiated for 30 h. Evaporation of the solvent and chrom. (CH_2Cl_2) afforded 515 mg (60%) **13a** of 75% purity, contaminated with 6% *methyl 4-butyl-2,3-dihydro-2-thiopheneacetate* (**15a**) and 19% *methyl 4-butyl-3-thiopheneacetate* (**17a**), as a colourless oil.

*Methyl 4-(*tert*-Butyl)-2,3-dihydro-3-thiopheneacetate* (**13b**). A soln. of 400 mg **1** and 800 mg 3,3-dimethyl-1-butyne in 40 ml MeOH was irradiated for 5 h (50% conversion). Evaporation of the solvent and chrom. (pentane/Et_2O 9:1) afforded 130 mg (15%) **13b** as a colourless oil.

*Methyl 4-(*tert*-Butyl)-2,3-dihydro-2-thiopheneacetate* (**15b**). The same soln. as above was irradiated for 30 h. Chromatography (CH_2Cl_2) afforded 220 mg (26%) **15b** as colourless oil.

Methyl 1,2-Dibutyl-7-thiabicyclo[3.3.0]oct-2-ene-4-carboxylate (**14**). A soln. of 400 mg **1** and 10 ml 1-hexyne in 30 ml MeOH was irradiated for 60 h. Evaporation of the solvent, bulb-to-bulb distillation (250°/0.1 Torr) and chrom. (CH_2Cl_2) afforded 360 mg (30%) **14** as colourless oil.

Methyl 4,5-Dimethyl-3-thiopheneacetate (**17c**). A soln. of 400 mg **1** and 1 ml 2-butyne in 40 ml MeOH was irradiated for 8 h (50% conversion). Evaporation of the solvent, treatment of the residue with a 1% ethanolic H_2O_2 solution, addition of H_2O and Et_2O, separation of the org. layer, further extraction with Et_2O, drying (Na_2SO_4), evaporation of the solvent and chrom. (CH_2Cl_2) afforded 290 mg (40%) **17c** as colourless oil.

Methyl 4,5-Dimethyl-2-thiopheneacetate (**18c**). The same soln. as above was irradiated for 120 h. Similar workup afforded 480 mg (65%) **18c** as colourless oil.

Methyl 4,5-Diethyl-3-thiopheneacetate (**17d**). A soln. of 400 mg **1** and 500 mg 3-hexyne in 40 ml MeOH was irradiated for 40 h. Workup as for **17c** and chromatography (pentane/Et_2O 2:1) afforded 520 mg (61%) **17d** as a colourless oil.

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