Photodecarbonylation of 2(3*H*)-Thiophenones[1]

Heiko Hinrichs and Paul Margaretha*

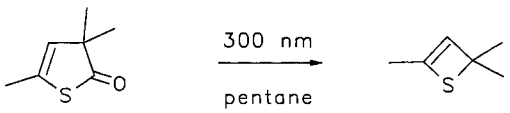
Institut für Organische Chemie der Universität Hamburg,
Martin-Luther-King-Platz 6, W-2000 Hamburg 13, F.R.G.

Received April 8, 1992

Key Words: Photochemistry / Thietes / Thiophenes / Homothiophenes / 2*H*-Thiins

Light-induced (300 nm) loss of CO converts 2(3*H*)-thiophenones to either thietes, thiophenes, homothiophenes, or thiopyrans, the product distribution being strongly influenced by the alkyl substitution pattern on the thiolactone.

We have recently presented preliminary results[2] on the light-induced decarbonylation of 3,3,5-trimethyl-2(3*H*)-thiophenone (**1**) to 2,2,4-trimethyl-2*H*-thiete (**2**). We have now synthesized 3,3-dialkyl-, 3,3,4- and 3,3,5-trialkyl- as well as 3,3,4,5-tetraalkyl-2(3*H*)-thiophenones and report here that both the substituents and the substitution pattern exert a pronounced effect on the product distribution on irradiation (300 nm) of these unsaturated thiolactones in pentane. Interestingly, this further investigation has revealed that the reactions of these compounds are mechanistically more complex than originally thought.



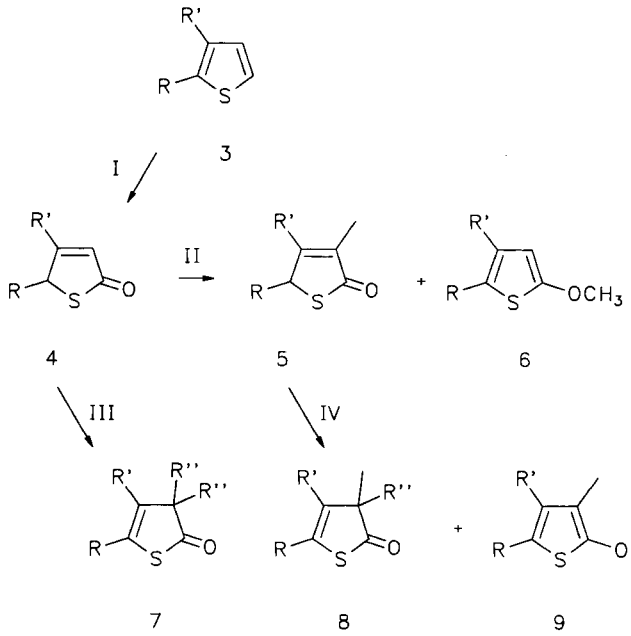
1 2

Results

The synthetic paths to the 2(3*H*)-thiophenones are summarized in Scheme 1. Thus thiophenes **3** are converted to 2(5*H*)-thiophenones **4** according to ref.[3]. Methylation of **4** according to refs.[4 or 5] affords mixtures of thiophenones **5** and methoxythiophenes **6** which are easily separated by chromatography on SiO_2. *Bis*-alkylation of **4** according to refs.[4 or 5] affords the 2(3*H*)-thiophenones **7** selectively, while alkylation of **5** under these conditions affords mixtures of 2(3*H*)-thiophenones **8** and alkoxythiophenes **9**, which are again easily separated by chromatography. Differentiation between 2(5*H*)-thiophenones (**4** and **5**) and 2(3*H*)-thiophenones (**7** and **8**) by spectroscopic means is easy both by ^{13}C-NMR ($\delta_{C=O}$ = 199–201 vs. 210–212) and by IR ($\nu_{C=O}$ = 1680 vs. 1710 cm^{-1}).

Irradiation (λ = 300 nm) of 10^{-1} M pentane solutions of thiophenones **7** and **8** affords different decarbonylated S heterocycles depending on the substitution pattern and on the alkyl groups themselves. Thus 5-*tert*-butylthiophenones **7d**, **8d**, and **8i** are converted to thietes **10**–**12** in 31–47% isolated yield (Scheme 2). Spiro compound **7c** gives a 2:1 mixture of thiete **13** and cyclopenta[*b*]thiophene **14**. In contrast, 4-*tert*-butylthiophenone **8j** is converted selectively to thiophene **15**, isolated in 45% yield. Different types of products are formed from 3-(2-propenyl)- and 3-(2-methyl-2-propenyl)-thiophenones **8h**, **7e** and **8e**, allyl compound **8h** affording

Scheme 1



3-6	R	R'
a	H	H
b	tBu	H
c	H	tBu
d	CH_3	CH_3

I: BuLi, $B(OR)_3$, H_2O_2
II: CH_3I
III: R''X, two equiv.
IV: R''X, one equiv.

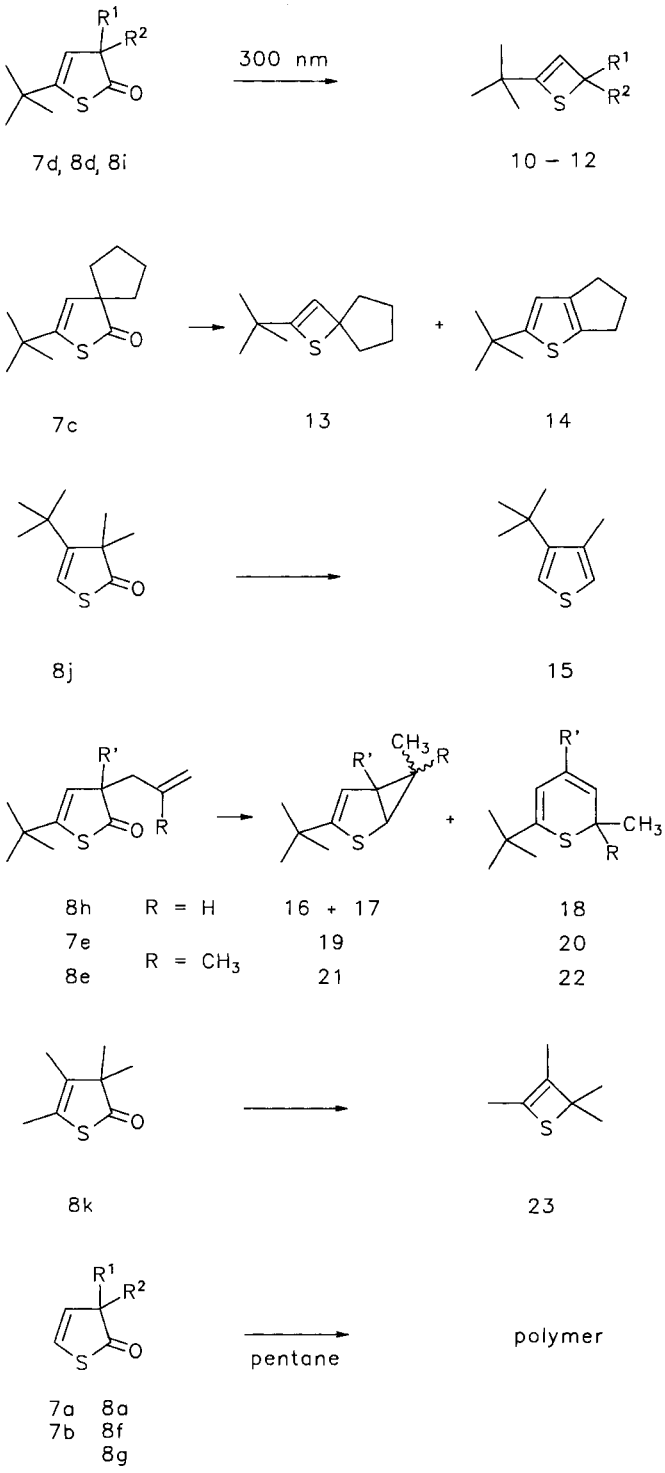
7-9	R	R'	R''
a	H	H	$CH_2C_6H_5$
b	H	H	$CH_2C(CH_3)=CH_2$
c	tBu	H	$(CH_2)_4$
d	tBu	H	$CH_2C_6H_5$
e	tBu	H	$CH_2C(CH_3)=CH_2$
f	H	H	$CH_2CH=CH_2$
g	H	H	CH_3
h	tBu	H	$CH_2CH=CH_2$
i	tBu	H	CH_3
j	H	tBu	CH_3
k	CH_3	CH_3	CH_3

  0009–2940/92/1010–2311 $ 3.50+.25/0

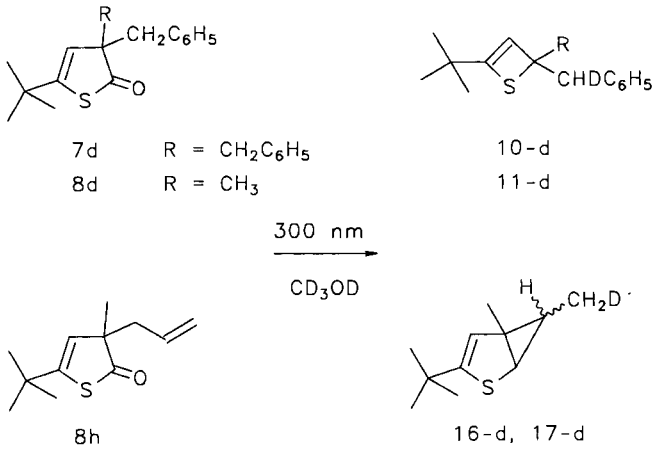
the diastereoisomeric homothiophenes **16** and **17** as major products, while methallyl derivatives **7e** and **8e** preferentially rearrange to 2*H*-thiopyrans **20** and **22**, respectively. Tetramethylthiophenone **8k** is again selectively transformed into tetramethylthiete **23** but this compound decomposes on attempted purification and/or isolation. Finally, thiophenones **7a**, **7b**, **8a**, **8f** and **8g**, unsubstituted on C-4 *and* C-5, polymerize on irradiation in pentane, no monomeric products being detected from these thiolactones either on irradiations in the presence of 2-methylpropene or in 2-propanol as solvent.

In order to obtain additional mechanistic insight, some of the 2(3*H*)-thiophenones were irradiated in CD_3OD. In these experiments 5-*tert*-butylthiophenones **7d** and **8d** afford thietes **10**–**d** and **11**–**d**, respectively, both compounds having deuterium incorporated on the exocyclic benzylic carbon atom (Scheme 3). Similarly, irradiation of **8h** affords a mixture of diastereoisomeric homothiophenes **16**–**d** and **17**–**d**, both compounds carrying the deuterium label on the newly formed methyl group.

Scheme 2



Scheme 3



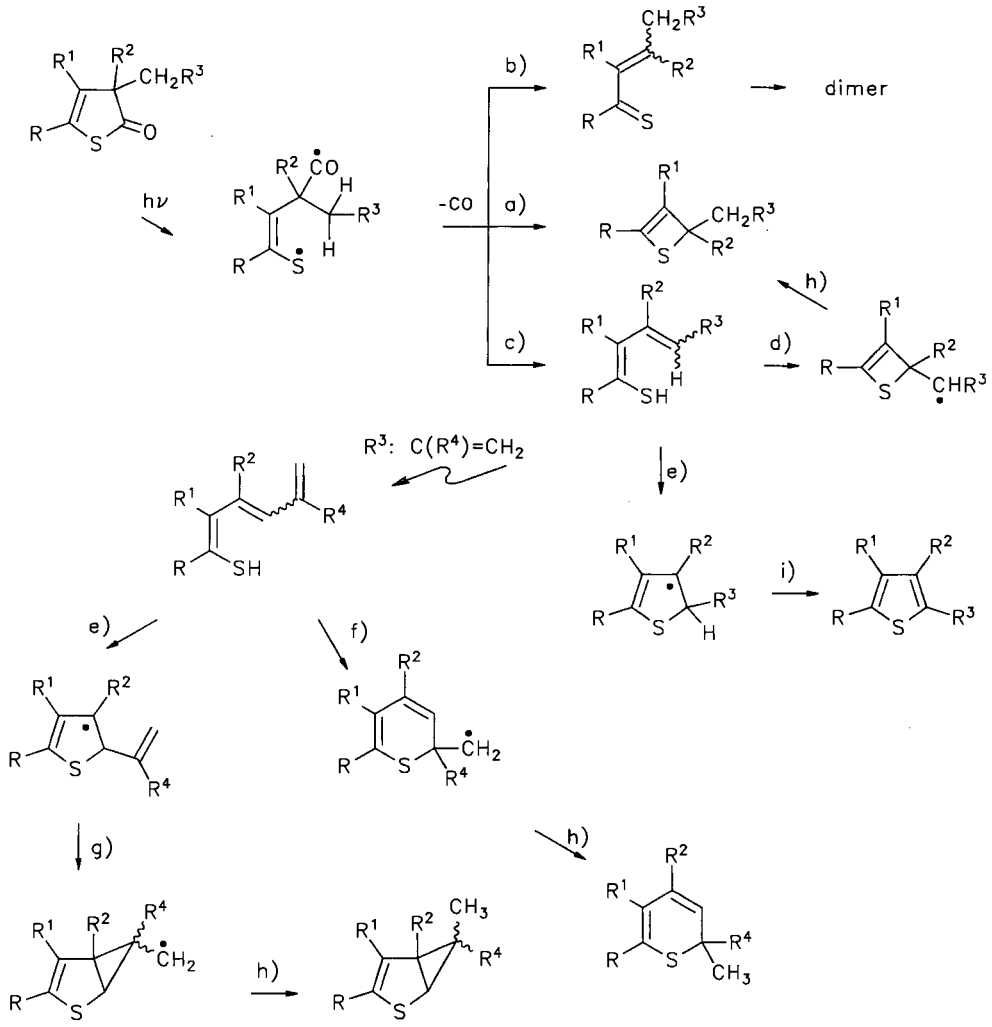
Discussion

The outcome of the photochemical reactions of 2(3*H*)-thiophenones presented in Schemes 2 and 3 suggests a more complex mechanistic behaviour than originally[2] assumed, since not only thietes, but also thiophenes, homothiophenes and 2*H*-thiopyrans are formed as products (Scheme 4). In our preliminary report we had proposed that thiophenone **1** undergoes cleavage of the S–C(O) bond in the excited state, a process followed by cyclization of the thiyl-acyl 1,5-diradical to thiete **2** with loss of carbon monoxide [path a)]. We noted that an intramolecular radical displacement reaction seemed more likely than decarbonylation *prior* to cyclization, as no formation of an α,β-unsaturated thione or its [4 + 2] dimer [path b)] had been observed. Most obviously we had neglected a third reaction [path c)], i.e. intramolecular H atom abstraction by the thiyl radical moiety with concommitant CO elimination. The thus formed dienethiol probably represents the key intermediate on the way to the final products.

Although to our knowledge no such 1-mercapto-1,3-dienes have been reported, it can be safely assumed that they will easily undergo light-induced S–H bond homolysis followed by cyclization of the thiyl radical, as it is known for 5-mercapto-1-butenes[6] or 5-mercapto-1-pentyne[7].

For thiophenes with R = *t*Bu and $R^3 \neq H$ step c) seems to predominate, since all final products stem from the dienethiol intermediate. For $R^3 = C_6H_5$ 1,4-cyclization [step d)]

Scheme 4



affords a benzylic radical, whose intermediacy is also strongly supported by the formation of **10**–**d** and **11**–**d** in CD_3OD as solvent. Thus step d) and subsequent H atom recombination [step h)] respresent an thiete-forming path alternative to direct cyclization of the thiyl-acyl 1,5-diradical [step a)]. No deuterium incorporation is observed in the conversions **1** → **2**, **8i** → **12**, or **8k** → **23** in CD_3OD suggesting that this latter reaction [step a)] is predominant for thiete formation from thiophenones with R = alkyl and R^3 = H.

A bulky group R^1, e.g. R^1 = *t*Bu in **8j**, seems to prevent both direct or stepwise 1,4-cyclization – possibly for steric reasons – as product **15**, resulting from 1,5-cyclization [step e)] and subsequent aromatization by loss of an H atom [step i)], is formed selectively. The dienethiol derived from spirothiophenone **7c** seems to undergo competitive 1,4- vs. 1,5-cyclization with formation of **13** and **14**, respectively.

Allylic hydrogen abstraction occurs selectively for all 3-allyl- and 3-methallyl-substituted 2(3*H*)-thiophenones with formation of 1-mercapto-1,3,5-trienes, which then undergo competitive 1,5- vs. 1,6-cyclization [steps e) and f)]. The result that methallyl derivatives (R^4 = CH_3) afford 2*H*-thiopyrans as main products might be due to a specific configuration of the trienes. The cyclization of a sulfur-substituted 3-buten-1-yl radical to a cyclopropylcarbinyl radical [step g)] has precedents[8].

Finally, it is interesting to note that polymerization is efficient for all thiophenones with R = R^1 = H as the intermediate thiyl radicals could not be trapped by either isobutene or 2-propanol. A speculative interpretation for this observation would be that both R and R^1 have a pronounced effect on charge delocalization (C=C–S$^\bullet$ vs. $^\bullet$C–C=S) in the primarily formed enethiyl radical moiety.

We are grateful to the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* for financial support of this work, and to Mlle *B. Martin*, Université de Rennes, for the preparation of thiophenone **8j**.

Experimental

Qual. GC: 30-m SE 30 capillary column, Fractovap 2150 (Carlo Erba). – UV (cyclohexane): PE 200 (Perkin Elmer/Hitachi). – IR (CCl_4): PE 399 (Perkin Elmer). – ^1H and ^{13}C NMR ($CDCl_3$): 400 and 100.63 MHz, resp., WM 400 (Bruker). – MS: 70 eV, 311 A (Varian Mat). – Photolyses: Rayonet RPR 100 photoreactor equipped with 300-nm lamps.

Preparation of Compounds **4**

2(5H)-Thiophenone (**4a**) was prepared from thiophene (**3a**) according to ref.[3]

5-tert-Butyl- and 4-tert-butyl-2(5H)-thiophenone (**4b** and **4c**): To 70 g (0.5 mol) of a 3:1 mixture of 2-*tert*-butyl- and 3-*tert*-butylthiophene[9] in 400 ml of THF is added dropwise during 30 min 325 ml (0.52 mol) of a 1.6 M butyllithium solution in hexane according to ref.[3]. After refluxing for 30 min the solution is cooled to 40°C, 37.8 ml (0.34 mol) of trimethyl borate is added and the solution refluxed for 90 min. The mixture is then cooled to 0°C and partially neutralized with 95 ml of HCl (1:1); after dropwise addition of 120 ml of H_2O_2 (30%) stirring is continued overnight at room temp. The acidified solution is then poured into Et_2O/H_2O, the organic layer separated and the aqueous phase further extracted with Et_2O. The combined organic layers are washed with aq. $FeSO_4$, then with water and dried with $MgSO_4$. Evaporation of the solvent and distillation at 15 Torr gives 45 g of a 3:1 mixture of **4b** and **4c** (b.p. 119°C). Chromatography (SiO_2/CH_2Cl_2) affords first **4b**: 26.3 g (45%), m.p. 32°C. – IR (CCl_4): $\tilde{\nu}$ = 1688 cm^{-1} (C=O). – ^1H NMR ($CDCl_3$): δ = 7.47 (dd, *J* = 6.4/2.4 Hz), 6.32 (dd, *J* = 6.4/2.4 Hz), 4.35 (t, *J* = 2.4 Hz), 1.08 (s, 9H). – ^{13}C NMR ($CDCl_3$): δ = 200.3 (s), 156.5 (d), 133.5 (d), 66.4 (d), 35.3 (s), 27.6 (q). – MS (70 eV): *m/z* (%) = 156 (3) [M^+], 57 (100).

$C_8H_{12}OS$ (156.2) Calcd. C 61.50 H 7.74
Found C 61.41 H 7.82

The second fraction consists of **4c**: 8.1 g (41%), colourless oil. – IR (CCl_4): $\tilde{\nu}$ = 1685 cm^{-1} (C=O). – ^1H NMR ($CDCl_3$): δ = 6.13 (t, *J* = 1.6 Hz), 4.05 (d, *J* = 1.6 Hz, 2H), 1.25 (s, 9H). – ^{13}C NMR ($CDCl_3$): δ = 198.4 (s), 179.3 (s), 126.7 (d), 36.3 (t), 35.3 (s), 28.9 (q). – MS (70 eV): *m/z* (%) = 156 (74) [M^+], 57 (100).

$C_8H_{12}OS$ (156.2) Calcd. C 61.50 H 7.74
Found C 61.55 H 7.71

4,5-Dimethyl-2(5H)-thiophenone (**4d**): As above from 56 g (0.5 mol) of 2,3-dimethylthiophene[10] are obtained 31 g (48%) of **4d**, b.p. 107°C/15 Torr. – IR (CCl_4): $\tilde{\nu}$ = 1684 cm^{-1} (C=O). – ^1H NMR ($CDCl_3$): δ = 5.99 (q, *J* = 1.0 Hz), 4.29 (q, *J* = 7.2 Hz), 2.15 (d, *J* = 1.0 Hz, 3H), 1.58 (d, *J* = 7.2 Hz, 3H). – ^{13}C NMR ($CDCl_3$): δ = 198.4 (s), 172.0 (s), 128.8 (d), 50.4 (d), 19.2 (q), 16.8 (q). – MS (70 eV): *m/z* (%) = 128 (100) [M^+].

C_6H_8OS (128.2) Calcd. C 56.22 H 6.29
Found C 56.31 H 6.24

Preparation of Compounds **5** *and* **6**

3-Methyl-2(5*H*)-thiophenone (**5a**) and 2-methoxythiophene (**6a**) were synthesized according to ref.[5]

Methylation of (**4b**): According to ref.[4], a solution of 15.6 g (0.1 mol) of **4b** in 50 ml of DMSO is added dropwise to a suspension of 3.0 g (0.1 mol) of 80% NaH in 150 ml DMSO, stirring is continued at room temp. for 1 h, then 6.2 ml (0.1 mol) of CH_3I in 20 ml of DMSO is added and the solution heated to 80°C for 1 h. After cooling the mixture is poured onto Et_2O/H_2O, the organic layer separated and the aqueous phase further extracted with Et_2O. The combined ethereal layers are washed with water and dried with $MgSO_4$. After evaporation of the solvent the residue is treated with 20 ml of pentane and left overnight at –10°C. Thiophenone **5b** is filtered off and crystallized from pentane affording 12.6 g (74%), m.p. 86°C. – IR(CCl_4): $\tilde{\nu}$ = 1687 cm^{-1} (C=O). – ^1H NMR ($CDCl_3$): δ = 7.17 (dq, *J* = 2.2/1.6 Hz), 4.20 (dq, *J* = 2.2/2.0 Hz), 1.92 (dd, *J* = 2.0/1.6 Hz, 3H), 1.05 (s, 9H). – ^{13}C NMR ($CDCl_3$): δ = 200.5 (s), 150.0 (d), 141.6 (s), 62.6 (d), 35.1 (s), 27.5 (q), 11.7 (q). – MS (70 eV): *m/z* (%) = 170 (1) [M^+], 114 (100).

$C_9H_{14}OS$ (170.3) Calcd. C 63.48 H 8.29
Found C 63.52 H 8.22

The filtrate is evaporated and then chromatographed (SiO_2, CH_2Cl_2) to afford 0.92 g (5%) of *5-tert-butyl-2-methoxythiophene* (**6b**) as colourless oil. – ^1H NMR ($CDCl_3$): δ = 6.38 (d, *J* = 4.2 Hz), 5.97 (d, *J* = 4.2 Hz), 3.84 (s, 3H), 1.31 (s, 9H). – ^{13}C NMR ($CDCl_3$): δ = 163.7 (s), 143.5 (s), 121.5 (d), 102.6 (d), 60.1 (q), 34.2 (s), 32.2 (q). – MS (70 eV): *m/z* (%) = 170 (38) [M^+], 155 (100).

$C_9H_{14}OS$ (170.3) Calcd. C 63.48 H 8.29
Found C 63.39 H 8.32

Methylation of **4c**: As above, from 15.6 g (0.1 mol) of **4c**. Subsequent chromatography (SiO_2/CH_2Cl_2) affords first 1.2 g (7%) of *4-tert-butyl-2-methoxythiophene* (**6c**), colourless liquid. – ^1H NMR ($CDCl_3$): δ = 6.19 (d, *J* = 1.8 Hz), 6.15 (d, *J* = 1.8 Hz), 3.85 (s, 3H), 1.24 (s, 9H). – MS (70 eV): *m/z* (%) = 170 (19) [M^+], 75 (100).

$C_9H_{14}OS$ (170.3) Calcd. C 63.48 H 8.29
Found C 63.52 H 8.22

The next fraction consisted of 2.8 g (16%) of *4-tert-butyl-3-methyl-2(5H)-thiophenone* (**5c**), colourless oil. – IR (CCl_4): $\tilde{\nu}$ = 1684 cm^{-1} (C=O). – ^1H NMR ($CDCl_3$): δ = 3.91 (q, *J* = 1.8 Hz, 2H), 2.01 (t, *J* = 1.8 Hz, 3H), 1.30 (s, 9H). – ^{13}C NMR ($CDCl_3$): δ = 201.4 (s), 169.2 (s), 134.8 (s), 36.1 (s), 35.7 (t), 28.9 (q), 12.3 (q). – MS (70 eV): *m/z* (%) = 170 (13) [M^+], 57 (100).

$C_9H_{14}OS$ (170.3) Calcd. C 63.48 H 8.29
Found C 63.55 H 8.19

Methylation of **4d**: As above, from 12.8 g (0.1 mol) of **4d**. Subsequent chromatography (SiO_2/CH_2Cl_2) affords first 0.72 g (5%) of *5-methoxy-2,3-dimethyl-thiophene* (**6d**), colourless liquid. – ^1H NMR ($CDCl_3$): δ = 5.87 (s, 1H), 3.79 (s, 3H), 2.20 (s, 3H), 2.02 (s, 3H). – ^{13}C NMR ($CDCl_3$): δ = 161.8 (s), 129.8 (s), 118.5 (s), 106.6 (d), 60.0 (q), 13.9 (q), 12.5 (q). – MS (70 eV): *m/z* (%) = 142 (100) [M^+].

$C_7H_{10}OS$ (142.2) Calcd. C 59.12 H 7.09
Found C 59.20 H 7.11

The second fraction contained 5.5 g (38%) of *3,4,5-trimethyl-2(5H)-thiophenone* (**5d**), colourless oil. – IR (CCl_4): $\tilde{\nu}$ = 1680 cm^{-1} (C=O). – ^1H NMR ($CDCl_3$): δ = 4.14 (q, *J* = 7.2 Hz), 2.07 (s, 3H), 1.81 (s, 3H), 1.54 (d, *J* = 7.2 Hz, 3H). – ^{13}C NMR ($CDCl_3$): δ = 199.4 (s), 163.2 (s), 134.5 (s), 48.2 (d), 19.4 (q), 15.3 (q), 10.2 (q). – MS (70 eV): *m/z* (%) = 142 (100) [M^+].

$C_7H_{10}OS$ (142.2) Calcd. C 59.12 H 7.09
Found C 59.18 H 7.12

Preparation of Thiophenones **7**

From **4a**: According to ref.[5], to a solution of 10 (0.1 mol) of **4a** and 0.2 mol of R″X in 250 ml of $CHCl_3$ is added dropwise a solution of 8 g (0.2 mol) of NaOH and 10 g of $Bu_4N^+HSO_4^-$ in 250 ml of H_2O. The mixture is then stirred for 14 h. After separation of the two layers the aq. phase is extracted twice with $CHCl_3$, the combined phases are evaporated, and the residue is dissolved in Et_2O. After filtration of the insoluble material the ethereal solution is washed with H_2O, dried with $MgSO_4$, and evaporated. Chromatography (SiO_2) affords thiophenones **7a** and **7b**.

3,3-Dibenzyl-2(3H)-thiophenone (**7a**): From 25.2 g of benzyl chloride as above with toluene as eluent 6.5 g (23%) of **7a** is obtained, m.p. 108°C. – UV (C_6H_{12}): λ_{max} (lgε) = 274 nm (3.202). – ^1H NMR ($CDCl_3$): δ = 7.25–7.06 (m, 10 H), 6.30 (d, *J* = 7.6 Hz), 5.86 (d, *J* = 7.6 Hz), 3.14 and 2.90 (AB, *J* = 13.2 Hz, 4H). – ^{13}C NMR

($CDCl_3$): δ = 211.3 (s), 135.7 (s), 130.2 (d), 128.4 (d), 128.0 (d), 126.9 (d), 122.4 (d), 65.4 (s), 43.6 (t).

$C_{18}H_{16}OS$ (280.4) Calcd. C 77.11 H 5.75
Found C 77.04 H 5.70

3,3-Bis(2-methyl-2-propenyl)-2(3H)-thiophenone (**7b**): From 18 g (0.2 mol) of 3-chloro-2-methyl-1-propene by using CH_2Cl_2 as eluent 1.5 g (7%) of **7b** is obtained as colourless oil. – ^{1}H NMR ($CDCl_3$): δ = 6.59 (d, *J* = 7.6 Hz), 5.91 (d, *J* = 7.6 Hz), 4.82 (m, 2H), 4.71 (m, 2H), 2.49 and 2.36 (AB, *J* = 13.4 Hz, 4H), 1.71 (s, 6H). – ^{13}C NMR ($CDCl_3$): δ = 211.2 (s), 140.7 (s), 130.6 (d), 121.4 (d), 115.4 (t), 63.4 (s), 46.2 (t), 24.2 (q).

$C_{12}H_{16}OS$ (208.3) Calcd. C 69.19 H 7.74
Found C 69.14 H 7.83

From **4b**: To a suspension of 6.5 g (0.21 mol) of 80% NaH in 250 ml of DMSO is added 15.6 g (0.1 mol) of **4b** in 50 ml of DMSO according to ref.[4]. Stirring is continued for 1 h, followed by the addition of 0.2 mol of R″X (or 0.1 mol of $X-[CH_2]_n-X$) in 50 ml of DMSO and stirring overnight. The mixture is then poured onto Et_2O/H_2O, the ethereal phase separated and the aq. phase further extracted with Et_2O. The combined ethereal layers are washed with H_2O and dried with $MgSO_4$. After evaporation of the solvent the residue is treated with pentane and left at –10°C for several hours. The crystals of **7c–e** are then filtered off and recrystallized from pentane.

3-tert-Butyl-2-thiaspiro[4.4]non-3-en-1-one (**7c**): From 30.8 g (0.1 mol) of 1,4-diiodobutane; yield 2.7 g (13%) of **7c**, m.p. 54°C. – IR (CCl_4): $\tilde{\nu}$ = 1714 cm^{-1} (C=O). – ^{1}H NMR ($CDCl_3$): δ = 5.48 (s, 1H), 2.10–1.64 (m, 8H), 1.20 (s, 9H). – ^{13}C NMR ($CDCl_3$): δ = 210.9 (s), 147.3 (s), 122.3 (d), 67.8 (s), 37.6 (t), 34.8 (s), 29.4 (q), 26.3 (t). – MS (70 eV): *m/z* (%) = 210 (24) [M^+], 95 (100).

$C_{12}H_{18}OS$ (210.3) Calcd. C 68.52 H 8.63
Found C 68.43 H 8.59

3,3-Dibenzyl-5-tert-butyl-2(3H)-thiophenone (**7d**): From 25.2 g (0.2 mol) of benzly chloride; yield 13.1 g (39%) of **7d**, m.p. 135°C. – UV (C_6H_{12}): λ_{max}(lgε) = 265 nm (3.023). – ^{1}H NMR ($CDCl_3$): δ = 7.24–7.05 (m, 10H), 5.40 (s, 1H), 3.13 and 2.86 (AB, *J* = 13.2 Hz, 4H), 0.89 (s, 9H). – ^{13}C NMR ($CDCl_3$): δ = 211.8 (s), 149.6 (s), 136.0 (s), 130.1 (d), 127.8 (d), 126.6 (d), 119.2 (d), 67.7 (s), 43.9 (t), 34.7 (s), 29.0 (q). – MS (70 eV): *m/z* (%) = 336 (18) [M^+], 91 (100).

$C_{22}H_{24}OS$ (336.5) Calcd. C 78.53 H 7.19
Found C 78.61 H 7.15

5-tert-Butyl-3,3-bis(2-methyl-2-propenyl)-2(3H)-thiophenone (**7e**): From 18 g (0.2 mol) of 3-chloro-2-methyl-1-propene; yield 3.1 g (11%) of **7e**, m.p. 48°C. – UV (C_6H_{12}): λ_{max}(lgε) = 267 nm (3.094). – IR (CCl_4): $\tilde{\nu}$ = 1709 cm^{-1} (C=O). – ^{1}H NMR ($CDCl_3$): δ = 5.43 (s, 1H), 4.81 (m, 2H), 4.65 (m, 2H), 2.47 & 2.30 (AB, *J* = 13.0 Hz, 4H), 1.70 (s, 6H), 1.19 (s, 9H). – ^{13}C NMR ($CDCl_3$): δ = 211.4 (s), 148.5 (s), 140.8 (s), 121.2 (d), 115.0 (t), 65.6 (s), 46.4 (t), 35.0 (s), 29.3 (q), 24.2 (q). – MS (70 eV): *m/z* (%) = 264 (2) [M^+], 181 (100).

$C_{16}H_{24}OS$ (264.4) Calcd. C 72.68 H 9.15
Found C 72.72 H 9.22

Preparation of Compounds **8** *and* **9**

From **5a**: According to ref.[5] From 5.7 g (0.05 mol) of **5a** and 0.05 mol of R″X, and subsequent purification.

Benzylation of **5a**: With 6.3 g of benzyl chloride. – Chromatography with toluene as eluent yields first 0.73 g (7%) of *2-(benzyloxy)-3-methylthiophene* (**9a**), colourless oil. – ^{1}H NMR ($CDCl_3$): δ = 7.45–7.30 (m, 5H), 6.61 (d, *J* = 5.6 Hz), 6.56 (d, *J* = 5.6 Hz), 5.04 (s, 2H), 2.05 (s, 3H). – ^{13}C NMR ($CDCl_3$): δ = 157.8 (s), 136.5 (s), 136.2 (s), 130.1 (d), 128.5 (d), 128.1 (d), 127.8 (d), 122.2 (d), 77.3 (t), 11.5 (q).

$C_{12}H_{12}OS$ (204.3) Calcd. C 70.55 H 5.92
Found C 70.54 H 5.95

The second fraction contained 1.65 g (15%) of *3-benzyl-3-methyl-2(3H)-thiophenone* (**8a**), m.p. 46°C. – UV (C_6H_{12}): λ_{max}(lgε) = 270 nm (3.214). – IR (CCl_4): $\tilde{\nu}$ = 1723 cm^{-1} (C=O). – ^{1}H NMR ($CDCl_3$): δ = 7.27–7.06 (m, 5H), 6.43 (d, *J* = 7.6 Hz), 5.83 (d, *J* = 7.6 Hz), 3.02 and 2.81 (AB, *J* = 13.2 Hz), 1.27 (s, 3H). – ^{13}C NMR ($CDCl_3$): δ = 211.8 (s), 136.2 (s), 130.8 (d), 130.0 (d), 128.0 (d), 126.8 (d), 120.7 (d), 60.2 (s), 44.0 (t), 22.5 (q). – MS (70 eV): *m/z* (%) = 204 (13) [M^+], 91 (100).

$C_{12}H_{12}OS$ (204.3) Calcd. C 70.55 H 5.92
Found C 70.62 H 5.88

Preparation of 3-Methyl-3-(2-propenyl)-2(3H)-thiophenone (**8f**): From 6 g of 3-bromopropene as above; subsequent distillation (69°C/2 Torr) affords 0.99 g (13%) of **8f** as colourless liquid. – UV (C_6H_{12}): λ_{max}(lgε) = 267 nm (3.195). – IR (CCl_4): $\tilde{\nu}$ = 1712 cm^{-1} (C=O). – ^{1}H NMR ($CDCl_3$): δ = 6.56 (d, *J* = 7.6 Hz), 5.85 (d, *J* = 7.6 Hz), 5.67 (m, 1H), 5.14–5.07 (m, 2H), 2.42 and 2.32 (AB, *J* = 13.6 Hz), 1.24 (s, 3H). – ^{13}C NMR ($CDCl_3$): δ = 211.3 (s), 132.2 (d), 130.9 (d), 120.7 (d), 118.9 (t), 59.0 (s), 42.2 (t), 22.2 (q).

$C_8H_{10}OS$ (154.2) Calcd. C 62.30 H 6.54
Found C 62.24 H 6.50

Methylation of **5a**: The preparation of 2-methoxy-3-methylthiophene (**9g**) and of 3,3-dimethyl-2(*H*)-thiophenone (**8g**) has been reported in ref.[5]

From **5b**. From 8.5 g (0.05 mol) **5b** and 0.05 mol of R″X according to ref.[4] and subsequent purification.

3-Benzyl-5-tert-butyl-3-methyl-2(3H)-thiophenone (**8d**): From 6.33 g of benzyl chloride as above and chromatography with toluene as eluent 3.1 g (24%) of **8d** is obtained, m.p. 54°C. – UV (C_6H_{12}): λ_{max}(lgε) = 265 nm (3.091). – IR (CCl_4): $\tilde{\nu}$ = 1705 cm^{-1} (C=O). – ^{1}H NMR ($CDCl_3$): δ = 7.25–7.07 (m, 5H), 5.38 (s), 3.01 and 2.76 (AB, *J* = 13.1 Hz), 1.28 (s, 3H), 1.06 (s, 9H). – ^{13}C NMR ($CDCl_3$): δ = 212.0 (s), 148.1 (s), 136.4 (s), 130.0 (d), 127.8 (d), 126.6 (d), 121.2 (d), 62.5 (s), 44.8 (t), 34.8 (s), 29.2 (q), 22.8 (q). – MS (70 eV): *m/z* (%) = 260 (11) [M^+], 141 (100).

$C_{16}H_{20}OS$ (260.4) Calcd. C 73.80 H 7.74
Found C 73.74 H 7.81

5-tert-Butyl-3-methyl-3-(2-propenyl)-2(3H)-thiophenone (**8h**): From 6.0 g of 3-bromo-1-propene as above and subsequent distillation (135°C/15 Torr). Yield 7.4 g (70%) of **8h** as colourless liquid. – UV (C_6H_{12}): λ_{max}(lgε) = 266 nm (3.033). – IR (CCl_4): $\tilde{\nu}$ = 1708 cm^{-1} (C=O). – ^{1}H NMR ($CDCl_3$): δ = 5.67 (m, 1H), 5.41 (s), 5.11–5.01 (m, 2H), 2.39 & 2.27 (AB, *J* = 13.4 Hz), 1.21 (s, 3H), 1.20 (s, 9H). – ^{13}C NMR ($CDCl_3$): δ = 211.3 (s), 148.1 (s), 132.4 (d), 121.2 (d), 118.5 (t), 61.3 (s), 42.6 (t), 34.9 (s), 29.5 (q), 22.5 (q). – MS (70 eV): *m/z* (%) = 210 (5) [M^+], 141 (100).

$C_{12}H_{18}OS$ (210.3) Calcd. C 68.52 H 8.63
Found C 68.57 H 8.57

5-tert-Butyl-3-methyl-3-(2-methyl-2-propenyl)-2(3H)-thiophenone (**8e**): From 4.55 g of 3-chloro-2-methyl-1-propene as above. After chromatography with CH_2Cl_2 as eluent yield 8.5 g (76%) of **8e**, colourless oil. – UV (C_6H_{12}): λ_{max}(lgε) = 268 nm (2.979). – IR (CCl_4): $\tilde{\nu}$ = 1708 cm^{-1} (C=O). – ^{1}H NMR ($CDCl_3$): δ = 5.43 (s), 4.78 (m, 1H), 4.67 (m, 1H), 2.51 and 2.26 (AB, *J* = 13.6 Hz), 1.63 (s, 3H), 1.23 (s, 3H), 1.20 (s, 9H). – ^{13}C NMR ($CDCl_3$): δ = 211.8 (s), 147.5 (s), 141.3 (s), 122.3 (d), 114.4 (t), 61.5 (s), 46.1 (t), 34.9 (s),

29.4 (q), 24.4 (q), 23.9 (q). – MS (70 eV): *m/z* (%) = 224 (11) [M^+], 141 (100).

$C_{13}H_{20}OS$ (224.4) Calcd. C 69.59 H 8.98
Found C 69.66 H 9.06

Methylation of **5b**: From 7.05 g of CH_3I as above. Chromatography with CH_2Cl_2 as eluent first leads to 0.31 g (3%) of *5-tert-butyl-2-methoxy-3-methylthiophene* (**9i**) as colourless liquid. – ^1H NMR ($CDCl_3$): δ = 6.31 (s), 3.83 (s, 3H), 2.01 (s, 3H), 1.33 (s, 9H). – MS (70 eV): *m/z* (%) = 184 (21) [M^+], 16 (100).

$C_{10}H_{16}OS$ (184.3) Calcd. C 65.17 H 8.75
Found C 65.10 H 8.80

The second fraction consisted of 4.1 g (45%) of *5-tert-butyl-3,3-dimethyl-2(3H)-thiophenone* (**8i**), m.p. 46°C. – UV (C_6H_{12}): λ_{max}(lgε) = 266 nm (3.002). – IR (CCl_4): $\tilde{\nu}$ = 1718 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 5.42 (s), 1.22 (s, 6H), 1.20 (s, 9H). – ^{13}C NMR ($CDCl_3$): δ = 212.2 (s), 146.8 (s), 123.6 (d), 57.8 (s), 34.9 (s), 29.9 (q), 24.2 (q). – MS (70 eV): *m/z* (%) = 184 (19) [M^+], 99 (100).

$C_{10}H_{16}OS$ (184.3) Calcd. C 65.17 H 8.75
Found C 65.12 H 8.77

From **5c**: These compounds are prepared from 8.5 g (0.05 mol) of **5c** and 0.05 mol of R″X, according to ref.[3] with subsequent chromatography (SiO_2/C_6H_6).

Methylation of **5c**: From 7.05 g of CH_3I as above first 1.43 g (16%) of *4-tert-butyl-2-methoxy-3-methylthiophene* (**9j**) is obtained as colourless liquid. – ^1H NMR ($CDCl_3$): δ = 6.27 (s), 3.86 (s, 3H), 2.17 (s, 3H), 1.29 (s, 9H). – ^{13}C NMR ($CDCl_3$): δ = 160.2 (s), 148.8 (s), 117.0 (s), 103.9 (d), 61.4 (q), 34.6 (s), 29.9 (q), 12.3 (q). – MS (70 eV): *m/z* (%) = 184 (94) [M^+], 169 (100).

$C_{10}H_{16}OS$ (184.3) Calcd. C 65.17 H 8.75
Found C 65.24 H 8.71

The second fraction contained 1.85 g (20%) of *4-tert-butyl-3,3-dimethyl-2(3H)-thiophenone* (**8j**), colourless liquid. – UV (C_6H_{12}): λ_{max}(lgε) = 275 nm (3.334). – IR (CCl_4): $\tilde{\nu}$ = 1716 cm^{-1} (C=O). – ^1H NMR ($CDCl_3$): δ = 6.29 (s), 1.38 (s, 6H), 1.24 (s, 9H). – ^{13}C NMR ($CDCl_3$): δ = 213.3 (s), 151.1 (s), 112.5 (d), 58.7 (s), 36.3 (s), 31.0 (q), 25.3 (q). – MS (70 eV): *m/z* (%) = 184 (58) [M^+], 169 (100).

$C_{10}H_{16}OS$ (184.3) Calcd. C 65.17 H 8.75
Found C 65.11 H 8.68

From **5d**: These compounds were prepared from 7.1 g (0.05 mol) of **5d** and 0.05 mol of R″X according to ref.[4] with subsequent chromatography (SiO_2/CH_2Cl_2).

Methylation of **5d**: From 7.05 g of CH_3I as above first 0.66 g (8%) of *2-methoxy-3,4,5-trimethylthiophene* (**9k**) is obtained; colourless liquid. – ^1H NMR ($CDCl_3$): δ = 3.80 (s, 3H), 2.24 (s, 3H), 1.95 (s, 3H), 1.93 (s, 3H). – MS (70 eV): *m/z* (%) = 156 (95) [M^+], 141 (100).

$C_8H_{12}OS$ (156.3) Calcd. C 61.50 H 7.74
Found C 61.59 H 7.81

Then 2.82 g (36%) of *3,3,4,5-tetramethyl-2(3H)-thiophenone* (**8k**) is eluted; colourless oil. – ^1H NMR ($CDCl_3$): δ = 2.02 (s, 3H), 1.74 (s, 3H), 1.19 (s, 6H). – ^{13}C NMR ($CDCl_3$): δ = 212.8 (s), 131.8 (s), 121.4 (s), 59.5 (s), 23.1 (q), 14.1 (q), 10.8 (q). – MS (70 eV): *m/z* (%) = 156 (100) [M^+].

$C_8H_{12}OS$ (156.3) Calcd. C 61.50 H 7.74
Found C 61.57 H 7.69

Photochemical Experiments

Preparative Photolyses: 0.1 M solutions of **7** or **8** in pentane, degassed by flushing with Argon, were irradiated at 300 nm followed by evaporation of the solvent and workup.

Preparation of Thietes **10**–**12**

2,2-Dibenzyl-4-tert-butyl-2H-thiete (**10**): From 336 mg (10^{-3} mol) of **7d** after irridation for 70 h and chromatography (SiO_2/C_6H_6); yield 144 mg (47%) of **10**, colourless liquid. – ^1H NMR ($CDCl_3$): δ = 7.26 (s, 10 H), 5.51 (s), 3.06 (s, 4H), 0.87 (s, 9H). – ^{13}C NMR ($CDCl_3$): δ = 155.8 (s), 137.3 (s), 129.6 (d), 125.7 (d), 119.5 (d), 57.9 (s), 43.8 (t), 33.2 (s), 27.3 (q). – MS (70 eV): *m/z* (%) = 308 (3) [M^+], 291 (100).

$C_{21}H_{24}S$ (308.5) Calcd. C 81.76 H 7.84
Found C 81.81 H 7.81

2-Benzyl-4-tert-butyl-2-methyl-2H-thiete (**11**): From 260 mg (10^{-3} mol) of **8d** after irradiation for 65 h and chromatography (SiO_2/C_6H_6); yield 72 mg (31%) of **11**, colourless liquid. – ^1H NMR ($CDCl_3$): δ = 7.27 (s, 5H), 5.52 (s), 3.11 (s, 2H), 1.53 (s, 3H), 1.10 (s, 9H). – ^{13}C NMR ($CDCl_3$): δ = 156.1 (s), 137.9 (s), 129.3 (d), 127.2 (d), 125.8 (d), 122.1 (d), 54.9 (s), 46.9 (t), 33.4 (s), 27.6 (q), 24.7 (q). – MS (70 eV): *m/z* (%) = 232 (28) [M^+], 57 (100).

$C_{15}H_{20}S$ (232.4) Calcd. C 77.53 H 8.67
Found C 77.62 H 8.66

4-tert-Butyl-2,2-dimethyl-2H-thiete (**12**): From 184 mg (10^{-3} mol) of **8i** after irradiation for 60 h and chromatography (SiO_2/C_6H_6); yield 53 mg (34%) of **12**, colourless liquid. – ^1H NMR ($CDCl_3$): δ = 5.41 (s), 1.65 (s, 6H), 1.12 (s, 9H). – ^{13}C NMR ($CDCl_3$): δ = 156.3 (s), 124.5 (d), 52.6 (s), 34.1 (s), 28.6 (q), 28.2 (q). – MS (70 eV): *m/z* (%) = 156 (28) [M^+], 99 (100).

$C_9H_{16}S$ (156.3) Calcd. C 69.17 H 10.32
Found C 69.09 H 10.21

Irradiation of **7c** (*Formation of* **13** *and* **14**): From 210 mg (10^{-3} mol) of **7c** after irradiation for 40 h and chromatography (SiO_2/pentane). First 20 mg (11%) of *2-tert-butyl-5,6-dihydro-4H-cyclopenta[b]thiophene* (**14**) is obtained, colourless liquid. – ^1H NMR ($CDCl_3$): δ = 7.43 (tt, *J* = 2.2/2.0 Hz), 2.74–2.41 (m, 6H), 1.29 (s, 9H). – MS (70 eV): *m/z* (%) = 180 (14) [M^+], 165 (100).

$C_{11}H_{16}S$ (180.3) Calcd. C 73.27 H 8.94
Found C 73.19 H 9.00

The second fraction contained 48 mg (26%) of *2-tert-butyl-1-thiaspiro[3,4]oct-2-ene* (**13**), colourless liquid. – ^1H NMR ($CDCl_3$): δ = 5.46 (s), 1.99–1.72 (m, 8H), 1.12 (s, 9H).

$C_{11}H_{18}S$ (182.3) Calcd. C 72.46 H 9.55 Found C 72.58 H 9.45

3-tert-Butyl-4-methylthiophene (**15**): From 184 mg (10^{-3} mol) of **8j** after irradiation for 45 h and chromatography (SiO_2/C_6H_6); yield 70 mg (45%) of **15**, colourless liquid. – UV (C_6H_{12}): λ_{max}(lgε) = 236 nm (3.276). – ^1H NMR ($CDCl_3$): δ = 6.95 (d, *J* = 3.6 Hz), 6.89 (dq, *J* = 3.6/0.8 Hz), 2.39 (d, *J* = 0.8 Hz, 3H), 1.36 (s, 9H). – ^{13}C NMR ($CDCl_3$): δ = 153.3 (s), 140.0 (s), 126.4 (d), 122.5 (d), 37.4 (s), 33.5 (q), 20.8 (q). – MS (70 eV): *m/z* (%) = 154 (24) [M^+], 139 (100).

$C_9H_{14}S$ (154.3) Calcd. C 70.07 H 9.15 Found C 70.00 H 9.05

Preparation of Homothiophenes and 2H-Thiopyrans

From 5-tert-Butyl-3-methyl-3-(2-propenyl)-2(3H)-thiophenone (**8h**): Irradiation of 210 mg (10^{-3} mol) of **8h** for 55 h and subsequent chromatography with pentane as eluent affords 123 mg (67%) of a 3:1 mixture of *endo- and exo-3-tert-butyl-5,6-dimethyl-2-thiabicyclo[3.1.0]hex-3-ene* (**16**/**17**), b.p. 90°C/15 Torr. – *endo* compound: ^1H NMR ($CDCl_3$): δ = 5.15 (s), 2.56 (d, *J* = 7.6 Hz), 1.34 (s, 3H), 1.16 (s, 9H), 0.84 (d, *J* = 8.4 Hz, 3H), 0.77 (dq, *J* = 7.6/8.4 Hz). – ^{13}C NMR ($CDCl_3$): δ = 155.3 (s), 116.8 (d), 40.4 (s), 34.9 (d), 34.4 (s), 30.6 (q), 21.9 (q), 14.7 (d), 7.2 (q). – MS (70 eV): *m/z* (%) = 182 (19) [M^+], 167 (100). – *exo* Derivative: ^1H NMR ($CDCl_3$): δ =

5.29 (s), 2.04 (d, J = 3.8 Hz), 1.29 (s, 3H), 1.12 (s, 9H), 1.10 (d, J = 6.4 Hz, 3H), 0.55 (dq, J = 3.8/6.4 Hz). – ^{13}C NMR ($CDCl_3$): δ = 153.3 (s), 122.5 (d), 39.5 (s), 34.3 (d), 33.9 (s), 30.6 (q), 29.5 (q), 23.2 (d), 12.9 (q). – MS (70 eV): m/z (%) = 182 (19) [M^+], 167 (100).

Analysis of the crude photolysate by GC/^{1}H NMR indicates the presence of 1–2% of *6-tert-butyl-2,4-dimethyl-2H-thiopyran* (**18**). ^{1}H NMR ($CDCl_3$): δ = 5.96 (s), 5.25 (m, 1H), 3.38 (m, 1H), 1.77 (t, J = 1.2 Hz, 3H), 1.22 (d, J = 7.2 Hz, 3H), 1.18 (s, 9H). – MS (70 eV): m/z (%) = 182 (21) [M^+], 167 (100).

From 5-tert-Butyl-3,3-bis(2-methyl-2-propenyl)-2(3H)-thiophene (**7e**): Irradiation of 264 mg (10^{-3} mol) of **7e** for 50 h and subsequent chromatography with pentane as eluent affords first 23 mg (10%) *3-tert-butyl-6,6-dimethyl-5-(2-methyl-2-propenyl)-2-thiabicyclo[3.1.0]hex-3-ene* (**19**), colourless liquid. – ^{1}H NMR ($CDCl_3$): δ = 5.16 (s), 4.79 (m, 1H), 4.66 (m, 1H), 2.68 (s), 2.43 and 2.35 (AB, J = 13.5 Hz), 1.77 (s, 3H), 1.27 (s, 3H), 1.18 (s, 9H), 1.11 (s, 3H).

$C_{15}H_{24}S$ (236.4) Calcd. C 76.21 H 10.23
Found C 76.30 H 10.11

The second fraction consisted of 93 mg (40%) of *6-tert-butyl-2,2-dimethyl-4-(2-methyl-2-propenyl)-2H-thiopyran* (**20**), colourless liquid. – ^{1}H NMR ($CDCl_3$): δ = 5.96 (s), 5.11 (s), 4.76 (m, 1H), 4.72 (m, 1H), 2.77 (s, 2H), 1.65 (s, 3H), 1.30 (s, 6H), 1.15 (s, 9H).

$C_{15}H_{24}S$ (236.4) Calcd. C 76.21 H 10.23
Found C 76.12 H 10.29

From 5-tert-Butyl-3-methyl-3-(2-methyl-2-propenyl)-2(3H)-thiophenone (**8e**): Irradiation of 224 mg (10^{-3} mol) of **8e** for 63 h and subsequent chromatography with pentane as eluent affords first 26 mg (13%) of *3-tert-butyl-5,6,6-trimethyl-2-thiabicyclo[3.1.0]hex-3-ene* (**21**) as colourless liquid. – ^{1}H NMR ($CDCl_3$): δ = 5.07 (s), 2.22 (s), 1.32 (s, 3H), 1.16 (s, 3H), 1.14 (s, 9H), 0.88 (s, 3H). – ^{13}C NMR($CDCl_3$): δ = 154.9 (s), 119.5 (d), 44.7 (s), 40.9 (d), 34.3 (s), 30.5 (q), 22.1 (q), 16.6 (q), 15.6 (s), 15.5 (q). – MS (70 eV): m/z (%) = 196 (16) [M^+], 181 (100).

$C_{12}H_{20}S$ (196.4) Calcd. C 73.40 H 10.27
Found C 73.48 H 10.20

The second fraction consisted of 39 mg (20%) of *6-tert-butyl-2,2,4-trimethyl-2H-thiopyran* (**22**), b.p. 70°C/15 Torr. – ^{1}H NMR ($CDCl_3$): δ = 5.92 (s), 5.04 (m, 1H), 1.81 (d, J = 1.6 Hz, 3H), 1.30 (s, 6H), 1.19 (s, 9H). – ^{13}C NMR ($CDCl_3$): δ = 146.6 (s), 131.8 (s), 123.6 (d), 116.9 (d), 41.1 (s), 36.6 (s), 29.2 (q), 28.7 (q), 22.0 (q). – MS (70 eV): $m7z$ (%) = 196 (30) [M^+], 181 (100).

$C_{12}H_{20}S$ (196.4) Calcd. C 73.40 H 10.27
Found C 73.33 H 10.30

Irradiation of Thiophenones **7a**, **7b**, **8a**, **8f** *and* **8g**: On irradiation of solutions containing 10^{-3} mol of one of these thiophenones a white precipitate is formed. After total converson of starting material the precipitate is filtered off and washed with pentane. The ^{1}H-NMR spectrum shows only broad undefined signals. Elemental analysis suggests loss of CO from the starting material, as C + H + S = 100%.

Labelling Experiments

Irradiation of 3,3,4,5-Tetramethyl-2(3H)-thiophenone (**8k**): A solution of 10 mg (0.08 mmol) of **8k** in 0.8 ml of CD_3OD is irradiated in a quartz NMR tube for 4 h. GC analysis indicates formation of 75% of *2,2,3,4-tetramethyl-2H-thiete* (**23**). ^{1}H-NMR- and MS analysis indicate no incorporation of deuterium into the photoproduct. – ^{1}H NMR (CD_3OD): δ = 1.90 (q, J = 1.2 Hz, 3H), 1.54 (s, 6H), 1.51 (q, J = 1.2 Hz, 3H). – MS (70 eV): m/z (%) = 128 (52) [M^+], 127 (100).

Irradiation of 3,3-Dibenzyl-5-tert-butyl-2(3H)-thiophenone (**7d**) *in CD_3OD*: A solution of 27 mg (0.08 mmol) of **7d** in 0.8 ml of CD_3OD is irradiated in a quartz NMR tube for 5 h. One deuterium atom is incorporated to about 80% at one benzylic methylene group of thiete **10–d**. – ^{1}H NMR (CD_3OD): δ = 7.28–7.05 (m, 10 H), 5.55 (s), 3.02 (s, 3.2H), 0.82 (s, 9H). – MS (70 eV): m/z (%) = 309 (7%) [M^+], 292 (100).

Irradiation of 3-Benzyl-5-tert-butyl-3-methyl-2(3H)-thiophenone (**8d**) *in CD_3OD*: A solution of 21 mg (0.08 mmol) of **8d** in 0.8 ml of CD_3OD is irradiated in a quartz NMR tube for 6 h. One deuterium atom is incorporated to about 80% at the benzylic methylene group of thiete **11–d**. – ^{1}H NMR (CD_3OD): δ = 7.26 (s, 5H), 5.56 (s), 3.10 (s, 1.2H), 1.49 (s, 3H), 1.07 (s, 9H). – MS (70 eV): m/z (%) = 233 (15) [M^+], 57 (100).

Irradiation of 5-tert-Butyl-3-methyl-3-(2-propenyl)-2(3H)-thiophenone (**8h**) *in CD_3OD*: A solution of 18 mg (0.08 mmol) of **8h** in 0.8 ml of CD_3OD is irradiated in a quartz NMR tube for 7 h. One deuterium atom is incorporated to about 90% at the C-methyl group of homothiophenes **16–d** and **17–d** according to ^{1}H NMR. – MS (70 eV): m/z (%) = 183 (12) [M^+], 168 (100).

[1] Dedicated to Prof. Dr. *Hans Paulsen* on the occasion of his 70th birthday.
[2] H. Hinrichs, P. Margaretha, *Angew. Chem.* **1989**, *101*, 1546; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1499.
[3] R. T. Hawkins, *J. Heterocl. Chem.* **1974**, *11*, 291–294.
[4] J. Brunet, D. Paquer, P. Rioult, *Phosphorus Sulfur* **1977**, *3*, 377–379.
[5] B. Cederlund, A. B. Hörnfeldt, *Chem. Scr.* **1975**, *8*, 140–144.
[6] R. Kiesewetter, P. Margaretha, *Helv. Chim. Acta* **1989**, *72*, 83–92.
[7] C. Dupuy, M. P. Crozet, J. M. Surzur, *Bull. Soc. Chim. Fr.* **1980**, 361–373.
[8] R. Kiesewetter, P. Margaretha, *Helv. Chim. Acta* **1987**, *70*, 125–128.
[9] M. Sy, N. P. Buu-Hoi, N. D. Xuong, *J. Chem. Soc.* **1954**, 1975–1978.
[10] S. Gronowitz, P. Moses, A. B. Hörnfeldt, R. Hakanson, *Ark. Kemi* **1961**, *17*, 165–177.

[163/92]

CAS Registry Numbers

4a: 3354-32-3 / **4b**: 17171-84-5 / **4c**: 142396-67-6 / **4d**: 35983-76-7 / **5a**: 33687-85-3 / **5b**: 142396-71-2 / **5c**: 142396-70-1 / **5d**: 142396-73-4 / **6a**: 16839-97-7 / **6b**: 142396-68-7 / **6c**: 142396-69-8 / **6d**: 142396-72-3 / **7a**: 37723-53-8 / **7b**: 142396-74-5 / **7c**: 142396-75-6 / **7d**: 142396-76-7 / **7e**: 142396-77-8 / **8a**: 142396-79-0 / **8d**: 142396-81-4 / **8e**: 142396-83-6 / **8f**: 142396-80-3 / **8g**: 33687-82-0 / **8h**: 142396-82-5 / **8i**: 142396-85-8 / **8j**: 142396-87-0 / **8k**: 142396-89-2 / **9a**: 142396-78-9 / **9g**: 33687-87-5 / **9i**: 142396-84-7 / **9j**: 142396-86-9 / **9k**: 142396-88-1 / **10**: 142396-90-5 / **10d**: 142397-03-3 / **11**: 142396-91-6 / **12**: 142396-92-7 / **13**: 142396-93-8 / **14**: 142396-94-9 / **15**: 142396-95-0 / *endo*-**16**: 142396-96-1 / *endo*-**16d**: 142397-04-4 / *exo*-**16**: 142436-33-7 / **17d**: 142436-34-8 / **18**: 142396-97-2 / **19**: 142396-98-3 / **20**: 142396-99-4 / **21**: 142397-00-0 / **22**: 142397-01-1 / **23**: 142396-02-2