39. Photochemistry of Tetraalkyl-2*H*-thietes

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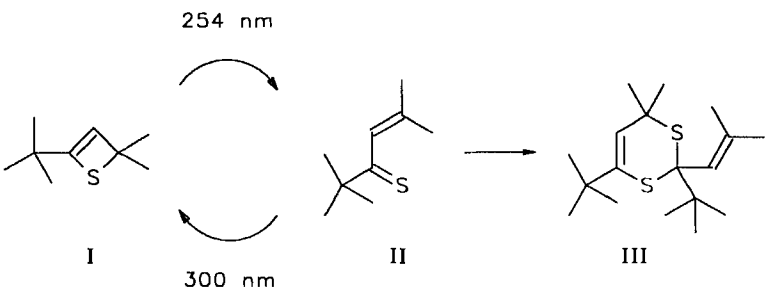
The 3-alkyl-2,2-dimethyl-4-(*tert*-butyl)-2*H*-thietes **9a–c** were obtained in several steps from the corresponding, newly synthesized, 3-alkyl-2-(*tert*-butyl)thiophenes **5a–c**. Irradiation (254 nm) of these tetraalkylated four-membered S-heterocycles leads to a photostationary equilibrium with enethiones **10a–c** (thiete/enethione 3:1)

Introduction. – We have recently presented preliminary results [1] on the first example of a light-induced interconversion of a 2,2,4-trialkyl-2*H*-thiete and its valence isomer, an acyclic α,β-unsaturated thione. Irradiation (254 nm) of 4-(*tert*-butyl)-2,2-dimethyl-2*H*-thiete (**I**) afforded 2,2,5-trimethylhex-4-ene-3-thione (**II**), which reclosed to **I** on irradiation with light of 300 nm or greater than 450 nm. In contrast to cyclic α,β-unsaturated thiones with fixed s-*trans*-conformation, *e.g.*, 3-methylcyclopent-2-ene-1-thione [2], acyclic enethiones as **II** readily undergo [4 + 2] dimerization (at 25°: $\tau_{II} = 18$ h) to a 2*H*,4*H*-1,3-dithiin **III** (*Scheme 1*).

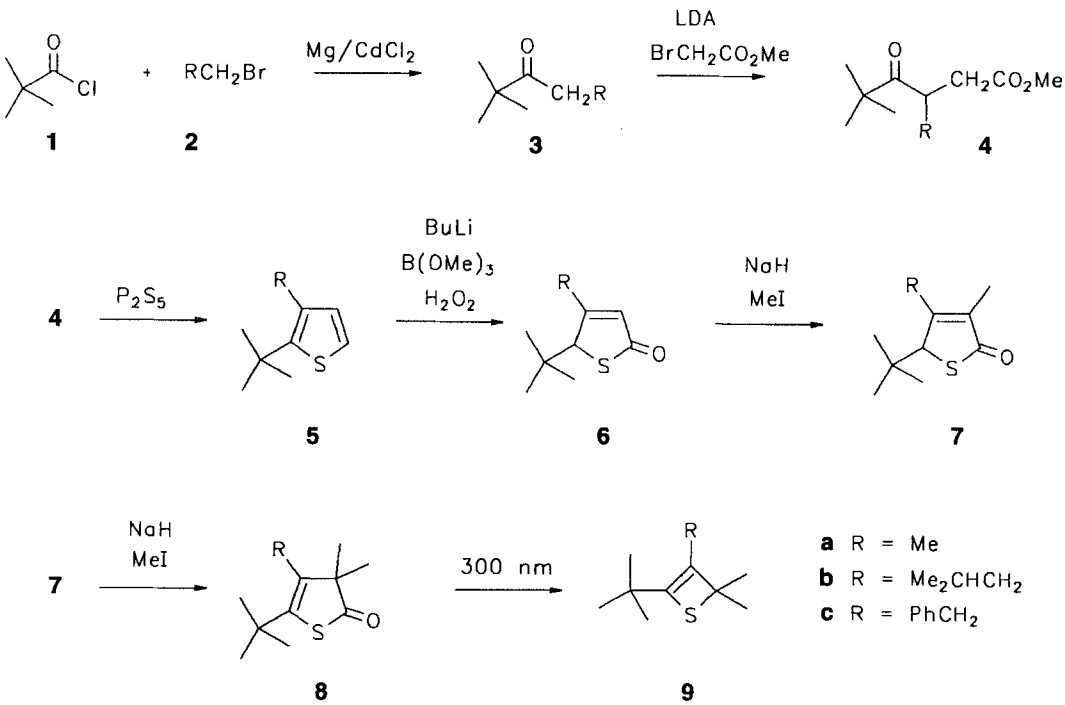
Scheme 1



We expected that the replacement of the vinyl H-atom in **II** by a (bulkier) alkyl group would stabilize the s-*trans*- relative to the s-*cis*-conformation of the acyclic enethione, and thus *a*) decelerate its thermal dimerization, and *b*) allow the number of cycles for the photochromic system 2*H*-thiete/enethione to increase. Here, we report on the synthesis of tetraalkyl-2*H*-thietes and on their photochemistry.

Results. – The synthetic route to the target 2*H*-thietes is summarized in *Scheme 2*. Pivaloyl chloride (**1**) reacted with the organocadmium [3] derivatives of bromoalkanes **2** to alkyl *tert*-butyl ketones **3**. *C*-Alkylation of the enolates of **3** with methyl bromoacetate afforded keto esters **4** which cyclized to 3-alkyl-2-(*tert*-butyl)thiophenes **5** on treatment

Scheme 2

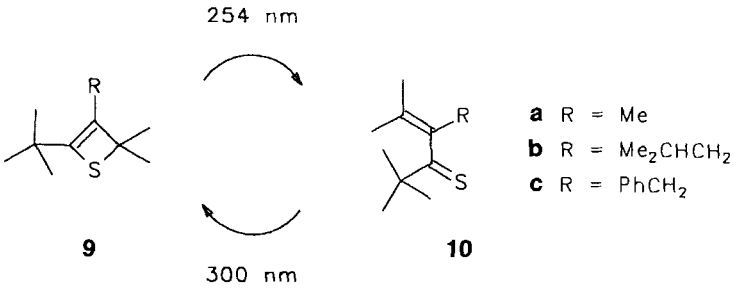


with P_2S_5 at 160° in tetralin [4]. The oxidation/alkylation sequence **5** → **6** → **7** → **8** as well as the photodecarbonylation of 2(3*H*)-thiophenones **8** to 2*H*-thietes **9** had already been used [5] [6] for the synthesis of 2,2,4-trialkyl-2*H*-thietes. Overall yields of isolated tetraalkyl-2*H*-thietes from 2,3-dialkylthiophenes **5a–c** are 10% for **9a** and **9b**, and 2% for **9c**.

On irradiation (254 nm) of **9** ($3 \cdot 10^{-1}$M in CD_3CN) the solution turns purple. Monitoring the reaction by ^{1}H-NMR indicates no further change after 25% conversion of starting material to a new product, identified as enethione **10** on the basis of the spectral data (*cf. Exper. Part*). Solutions containing **10** can be stored unchanged for weeks at −10°. Irradiation of these 3:1 mixtures of **9** and **10** at 300 nm leads to almost quantitative (> 95% as determined by ^{1}H-NMR or UV) back-formation of **9**. The interconversion **9a** ⇌ **10a** can also be monitored by GC, whereas enethiones **10b** and **10c** decompose thermally (as does **II**) (*Scheme 3*).

Discussion. – Except for 2,3-di(*tert*-butyl)thiophene, which has been obtained in very low yield in a multistep synthesis starting from 3,4-di(*tert*-butyl)-1,2-dithiete [7], 2,3-dialkylthiophenes with *t*-Bu group at C(2) have not been reported [8]. Whereas treating 3-methyl-4-oxopentanoic acid with P_2S_5 at 130° gave 2,3-dimethylthiophene in only 3% isolated yield [9], similar treatment of esters **4** in tetralin at 160° affords thiophenes **5** in reasonable yield (36–53%). Regarding the photochemical ring opening of the 2*H*-thiete to the unsaturated thione, the introduction of a fourth alkyl group turns out to be a

Scheme 3



double-edged sword, as, on the one side, enethiones **10** are indeed thermally more stable than **II**, but, on the other side, their absorption spectra now substantially overlap with those of the thiete precursors.

In contrast to enethione **II**, compounds **10a–c** do not undergo (thermal) dimerization at room temperature and can, therefore, be stored in solution for long periods. 2,2,4,5-Tetramethylhex-4-ene-3-thione (**10a**) is even stable under analytical GC conditions thus allowing to record its mass spectrum.

It is known [10] for acyclic α,β-unsaturated ketones that the interaction of an alkyl group at C(α) with that on the carbonyl C-atom leads to twisting around the C(O)–C(α) bond inducing significant deviations from a planar conformation. In the case of the corresponding enethiones **10**, this twisting around the C(S)–C(α) bond apparently reduces the intensity [11] of the π-π^* absorption band ($\lambda_{max} \approx 320$ nm) and induces a more than tenfold increase of the extinction coefficient for the n-σ^* absorption band ($\lambda_{max} \approx 225$ nm, $\log \varepsilon \approx 4.3$). Unfortunately, this latter band overlaps with the 2*H*-thiete absorption ($\lambda_{max} \approx 240$ nm, $\log \varepsilon \approx 3.7$), and, therefore, irradiation with light of 254 nm now leads to a photostationary equilibrium thiete/enethione 3:1, thus preventing a higher degree of conversion **9** → **10**.

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Experimental Part

General. Photolyses: *Rayonet RPR-100* photoreactor equipped with either 254-nm or 300-nm lamps. GC: 30-m *SE 30* capillary column. UV Spectra: in nm (log ε). ^{1}H- and ^{13}C-NMR Spectra: at 400 and 100.63 MHz, resp.; chemical shifts in ppm rel. to TMS (= 0 ppm), coupling constants *J* in Hz. MS: at 70 eV; in *m/z* (rel. intensity in %).

Ketones **3**. To 24.3 g (1.0 mol) of Mg turnings in 100 ml of Et_2O are added dropwise 1.0 mol of **2** (**a**: 109 g of bromoethane, **b**: 151 g of 1-bromo-3-methylbutane, **c**: 185 g of 1-bromo-2-phenylethane) in 300 ml of Et_2O. The mixture is refluxed for 1 h. After cooling, 95.6 g (0.54 mol) of $CdCl_2$ are added at r.t., and the mixture is stirred for 1 h. Under reflux, 108 g (0.9 mol) of *pivaloyl chloride* (**1**) in 200 ml of Et_2O are added, and the mixture is refluxed for 6 h. After cooling to 0°, 400 ml of 10% HCl are added dropwise, the org. phase is separated, washed with sat. aq. $NaHCO_3$ and NaCl solns., and dried ($MgSO_4$). After evaporation of the solvent the ketone **3** is obtained by distillation.

2,2-Dimethylpentan-3-one (**3a**): 36.5 g (32%). B.p. 125°/1013 hPa [12]. *2,2,6-Trimethylheptan-3-one* (**3b**): 80.1 g (51%). B.p. 55°/15 hPa [12]. *4,4-Dimethyl-1-phenylpentan-3-one* (**3c**): 59.1 g (31%). B.p. 114°/15 hPa [13].

Keto Esters **4**. To 44 g (0.44 mol) of $(i\text{-}Pr)_2NH$ in 200 ml of THF are added dropwise 275 ml of BuLi (1.6M in hexane, 0.44 mol). After stirring for 30 min and cooling to −78°, a soln. of 0.44 mol of ketone **3** (**3a**: 48 g, **3b**: 66 g, **3c**: 81.46 g) in 300 ml of THF is added dropwise, the mixture then being stirred for 30 min at −78° and for

1 h at r.t. After cooling to −78°, a soln. of 138 g (0.9 mol) of $BrCH_2COOMe$ in 100 ml of THF is added dropwise and the mixture stirred for 1 h at −78° and then for 12 h at r.t. After addition of Et_2O (300 ml) and H_2O (500 ml), the org. phase is separated, washed with sat. aq. $NaHCO_3$ and NaCl solns., and dried ($MgSO_4$). After evaporation of the solvent keto esters **4** are obtained by distillation.

Methyl 3,5,5-Trimethyl-4-oxohexanoate (**4a**): 49.9 g (61%). B.p. 125°/15 hPa [14].

Methyl 5,5-Dimethyl-3-(2-methylpropyl)-4-oxohexanoate (**4b**): 90.2 g (90%). B.p. 98°/1.33 hPa. ^{1}H-NMR ($CDCl_3$): 3.63 (*s*, 3H); 3.47 (*m*, 1H); 2.68 (*dd*, *J* = 8.6, 16.3); 2.36 (*dd*, *J* = 5.1, 16.3); 1.56 (*m*, 1H); 1.40 (*m*, 1H); 1.19 (*m*, 1H); 1.20 (*s*, 9H); 0.94 (*d*, *J* = 7.6, 3H); 0.92 (*d*, *J* = 7.5, 3H). ^{13}C-NMR ($CDCl_3$): 217.0 (*s*); 172.1 (*s*); 50.9 (*q*); 43.9 (*s*); 40.8 (*t*); 39.3 (*d*); 35.4 (*t*); 26.4 (*q*); 25.2 (*d*); 22.8 (*q*); 21.2 (*q*). MS: 228 (0.1, M^+), *111*.

Methyl 3-Benzyl-5,5-dimethyl-4-oxohexanoate (**4c**): 66.9 g (58%). B.p. 107°/0.2 hPa. ^{1}H-NMR ($CDCl_3$): 7.25–7.14 (*m*, 5H); 3.68 (*m*, 1H); 3.58 (*s*, 3H); 2.96 (*dd*, *J* = 6.6, 13.5); 2.63 (*dd*, *J* = 7.6, 16.5); 2.51 (*dd*, *J* = 7.6, 13.5); 2.31 (*dd*, *J* = 6.1, 16.5); 1.07 (*s*, 9H). ^{13}C-NMR ($CDCl_3$): 217.0 (*s*); 172.3 (*s*); 138.7 (*s*); 129.2 (*d*); 128.5 (*d*); 126.6 (*d*); 51.6 (*q*); 44.7 (*s*); 43.9 (*d*); 38.5 (*t*); 36.2 (*t*); 26.5 (*q*). MS: 262 (7, M^+), *173*.

Thiophenes **5**. A soln. of 0.31 mol of **4** (**a**: 57.7 g, **b**: 70.7 g, **c**: 81.2 g) in 75 ml of tetralin is added dropwise at 160° to a suspension of 70 g (0.31 mol) of P_2S_5 in 175 ml of tetralin, stirring then being continued for 1 h. After cooling, Et_2O (300 ml) is added, the mixture washed with sat. aq. $NaHCO_3$, NaOCl, and NaCl solns., and dried ($MgSO_4$). After evaporation of the Et_2O, the thiophene is distilled through a spinning band column (for **5a**) or tetralin distilled through a *Vigreux* column (for **5b** and **5c**) at 16 hPa and the residual thiophene then obtained by distillation.

*2-(*tert*-Butyl)-3-methylthiophene* (**5a**): 20.5 g (42%). B.p. 180°/1013 hPa. ^{1}H-NMR ($CDCl_3$): 6.89 (*d*, *J* = 5.1); 6.73 (*d*, *J* = 5.1); 2.31 (*s*, 3H); 1.41 (*s*, 9H). ^{13}C-NMR ($CDCl_3$): 147.8 (*s*); 132.5 (*d*); 131.2 (*s*); 119.1 (*d*); 34.5 (*s*); 31.1 (*q*); 16.1 (*q*). MS: 154 (20, M^+), *139*.

*2-(*tert*-Butyl)-3-(2-methylpropyl)thiophene* (**5b**): 21.9 g (36%). B.p. 65°/0.07 hPa. ^{1}H-NMR ($CDCl_3$): 6.91, 6.81 (*d*, *J* = 5.1, 2H); 2.58 (*d*, *J* = 7.6, 2H); 1.94 (*m*, 1H); 1.42 (*s*, 9H); 0.94 (*d*, *J* = 6.6, 6H). ^{13}C-NMR ($CDCl_3$): 142.8 (*s*); 135.8 (*s*); 130.9 (*d*); 119.2 (*d*); 38.8 (*t*); 36.6 (*s*); 32.0 (*q*); 29.8 (*d*); 22.7 (*q*). MS: 196 (34, M^+), *181*.

*3-Benzyl-2-(*tert*-butyl)thiophene* (**5c**): 37.8 g (53%). Purified by chromatography (SiO_2, hexane). ^{1}H-NMR ($CDCl_3$): 7.25–7.11 (*m*, 5H); 6.92, 6.63 (*d*, *J* = 5.1, 2H); 4.12 (*s*, 2H); 1.44 (*s*, 9H). ^{13}C-NMR ($CDCl_3$): 149.1 (*s*); 141.3 (*s*); 134.2 (*q*); 131.8 (*d*); 128.6 (*d*); 128.3 (*d*); 125.9 (*d*); 119.7 (*d*); 35.5 (*t*); 34.6 (*s*); 31.8 (*q*). MS: 230 (0.2, M^+), *91*.

Thiophen-2(5H)-ones **6**. Prepared from thiophenes **5** (0.22 mol), BuLi, trimethyl borate, and H_2O_2 according to [6] and purified by chromatography on SiO_2.

*5-(*tert*-Butyl)-4-methylthiophen-2(5H)-one* (**6a**): 24 g (64%), (CH_2Cl_2). Oil. ^{1}H-NMR ($CDCl_3$): 6.04 (*s*); 4.23 (*s*); 2.21 (*s*, 3H); 1.13 (*s*, 9H). ^{13}C-NMR ($CDCl_3$): 198.6 (*s*); 169.6 (*s*); 132.4 (*d*); 68.1 (*d*); 35.8 (*s*); 28.5 (*q*); 21.1 (*q*). MS: 170 (0.25, M^+), *114*.

*5-(*tert*-Butyl)-4-(2-methylpropyl)thiophen-2(5H)-one* (**6b**): 30.8 g (66%), (pentane/acetone 19:1). Oil. ^{1}H-NMR ($CDCl_3$): 6.04 (*d*, *J* = 1.0); 4.26 (*d*, *J* = 1.0); 2.39 (*d*, *J* = 7.1, 2H); 1.94 (*m*, 1H); 1.12 (*s*, 9H); 0.97 (*d*, *J* = 6.6, 3H); 0.91 (*d*, *J* = 6.6, 3H). ^{13}C-NMR ($CDCl_3$): 197.9 (*s*); 172.6 (*s*); 131.3 (*d*); 66.1 (*d*); 42.8 (*t*); 35.5 (*s*); 28.2 (*q*); 27.5 (*d*); 22.2 (*q*); 21.6 (*q*). MS: 212 (0.1, M^+), *57*.

*4-Benzyl-5-(*tert*-butyl)thiophen-2(5H)-one* (**6c**): 24.3 g (45%), (CH_2Cl_2). Oil. ^{1}H-NMR ($CDCl_3$): 7.30–7.13 (*m*, 5H); 5.82 (*s*); 4.31 (*s*); 3.89, 3.68 (*AB*, *J* = 16.8, 2H); 1.16 (*s*, 9H). ^{13}C-NMR ($CDCl_3$): 198.1 (*s*); 172.8 (*s*); 133.3 (*d*); 129.0 (*d*); 128.9 (*d*); 127.1 (*d*); 66.8 (*d*); 40.6 (*t*); 36.1 (*s*); 22.8 (*q*). MS: 246 (1, M^+), *190*.

3-Methylthiophen-2(5H)-ones **7**. Prepared from thiophen-2(5*H*)-ones **6** (0.13 mmol), NaH and MeI in DMSO according to [6] and purified by chromatography on SiO_2.

*5-(*tert*-Butyl)-3,4-dimethylthiophen-2(5H)-one* (**7a**): 12.0 g (50%), (CH_2Cl_2). M.p. 57°. ^{1}H-NMR ($CDCl_3$): 4.08 (*s*); 2.12 (*s*, 3H); 1.80 (*s*, 3H); 1.10 (*s*, 9H). ^{13}C-NMR ($CDCl_3$): 199.4 (*s*); 160.9 (*s*); 137.1 (*s*); 66.1 (*d*); 36.0 (*s*); 28.7 (*q*); 19.4 (*q*); 10.3 (*q*). MS: 141 (5, $[M-43]^+$), *128*.

*5-(*tert*-Butyl)-4-methyl-4-(2-methylpropyl)thiophen-2(5H)-one* (**7b**): 14.4 g (46%), (pentane/acetone 19:1). Oil. ^{1}H-NMR ($CDCl_3$): 4.19 (*s*); 2.45 (*d*, *J* = 7.5, 2H); 1.95 (*m*, 1H); 1.82 (*s*, 3H); 1.09 (*s*, 9H); 1.02 (*d*, *J* = 6.5, 3H); 0.80 (*d*, *J* = 6.5, 3H). ^{13}C-NMR ($CDCl_3$): 199.9 (*s*); 164.4 (*s*); 138.0 (*s*); 63.4 (*d*); 40.6 (*t*); 36.1 (*s*); 28.8 (*q*); 28.0 (*d*); 23.3 (*q*); 21.4 (*q*); 10.9 (*q*). MS: 211 (0.1, $[M-15]^+$), *128*.

*4-Benzyl-5-(*tert*-butyl)-3-methylthiophen-2(5H)-one* (**7c**): 18.9 g (56%), (pentane/Et_2O 4:1). Oil. ^{1}H-NMR ($CDCl_3$): 7.30–7.06 (*m*, 5H); 4.10 (*s*, 2H); 3.79 (*s*); 1.89 (*s*, 3H); 1.07 (*s*, 9H). ^{13}C-NMR ($CDCl_3$): 199.6 (*s*); 162.2 (*s*); 139.4 (*s*); 137.0 (*s*); 128.5 (*d*); 127.8 (*d*); 126.3 (*d*); 63.4 (*d*); 37.0 (*t*); 36.0 (*s*); 28.9 (*q*); 10.9 (*q*). MS: *204* ($[M-56]^+$).

3,3-Dimethylthiophen-2(3H)-ones **8**. Prepared from **7** (0.07 mol), NaH, and MeI in DMSO according to [6] and purified by chromatography on SiO_2.

*5-(*tert*-Butyl)-3,3,4-trimethylthiophen-2(3H)-one* (**8a**): 5.8 g (42%), (CH_2Cl_2). M.p. 37°. ^{1}H-NMR (CD_3CN): 1.86 (*s*, 3H); 1.31 (*s*, 9H); 1.13 (*s*, 6H). ^{13}C-NMR ($CDCl_3$): 212.2 (*s*); 136.0 (*s*); 130.5 (*s*); 61.6 (*s*); 35.2 (*s*); 30.8 (*q*); 23.1 (*q*); 13.1 (*q*). MS: 198 (30, M^+), *113*.

*5-(*tert*-Butyl)-3,3-dimethyl-4-(2-methylpropyl)thiophen-2(3H)-one* (**8b**): 10.2 g (61%), (pentane/Et_2O 9:1). Oil. ^{1}H-NMR (CD_3CN): 2.29 (*d*, *J* = 8.1, 2H); 2.05 (*m*, 1H); 1.33 (*s*, 9H); 1.20 (*s*, 6H); 0.95 (*d*, *J* = 6.6, 6H). ^{13}C-NMR ($CDCl_3$): 210.0 (*s*); 136.8 (*s*); 132.6 (*s*); 60.3 (*s*); 34.7 (*t*); 34.0 (*s*); 29.6 (*q*); 25.7 (*d*); 22.6 (*q*); 20.8 (*q*). MS: 240 (17, M^+), *197*.

*4-Benzyl-5-(*tert*-butyl)-3,3-dimethylthiophen-2(3H)-one* (**8c**): 3.3 g (17%), (pentane/Et_2O 19:1). Oil. ^{1}H-NMR (CD_3CN): 7.30–7.21 (*m*, 5H); 3.81 (*s*, 2H); 1.30 (*s*, 9H); 1.04 (*s*, 6H). ^{13}C-NMR ($CDCl_3$): 211.5 (*s*); 140.5 (*s*); 139.6 (*s*); 131.4 (*s*); 128.4 (*d*); 128.2 (*d*); 126.2 (*d*); 62.2 (*s*); 36.4 (*s*); 32.9 (*t*); 31.1 (*q*); 24.3 (*q*). MS: 274 (24, M^+), *259*.

2H-Thietes **9**. Ten glass tubes, each one containing an Ar-degassed soln. of **8** (1 mmol) in pentane (10 ml), are irradiated with light of 300 nm for 70 h. After evaporation of the solvent the residue is purified by chromatography on SiO_2.

*4-(*tert*-Butyl)-2,2,3-trimethyl-2H-thiete* (**9a**): 1.4 g (80%), (pentane). Oil. UV (C_6H_{12}): 237 (3.60). ^{1}H-NMR (CD_3CN): 1.61 (*s*, 3H); 1.49 (*s*, 6H); 1.13 (*s*, 9H). ^{13}C-NMR (CD_3CN): 145.8 (*s*); 132.8 (*s*); 51.5 (*s*); 34.9 (*s*); 29.2 (*q*); 25.9 (*q*); 11.6 (*q*). MS: 170 (12, M^+), *113*.

*4-(*tert*-Butyl)-2,2-dimethyl-3-(2-methylpropyl)-2H-thiete* (**9b**): 1.0 g (44%), (pentane). Oil. UV (C_6H_{12}): 243 (3.68). ^{1}H-NMR (CD_3CN): 1.89 (*d*, *J* = 7.5, 2H); 1.73 (*m*, 1H); 1.46 (*s*, 6H); 1.04 (*s*, 9H); 0.81 (*d*, *J* = 6.6, 6H). ^{13}C-NMR ($CDCl_3$): 147.9 (*s*); 136.4 (*s*); 52.0 (*s*); 38.0 (*t*); 35.0 (*s*), 29.6 (*q*); 27.4 (*d*); 27.0 (*q*); 22.6 (*q*). MS: 212 (34, M^+), *155*.

*3-Benzyl-4-(*tert*-butyl)-2,2-dimethyl-2H-thiete* (**9c**): 0.9 g (35%), (pentane). Oil. UV (C_6H_{12}): 248 (3.80). ^{1}H-NMR (CD_3CN): 7.28 (*m*, 5H); 3.48 (*s*, 2H); 1.35 (*s*, 6H); 1.21 (*s*, 9H). ^{13}C-NMR (CD_3CN): 148.7 (*s*); 140.0 (*s*); 134.5 (*s*); 129.2 (*d*); 128.8 (*d*); 126.5 (*d*); 52.6 (*s*); 35.2 (*s*); 34.2 (*t*); 29.4 (*q*); 27.1 (*q*). MS: 246 (23, M^+), *189*.

Enethiones **10**. Ar-Degassed solns. of **9** (0.3 mmol) in CD_3CN (1 ml) in a quarz NMR tube were irradiated with light of 254 nm for 2 h. The reaction can be monitored by GC, UV, and ^{1}H-NMR (for **9a** → **10a**, 26% conversion), and by UV and ^{1}H-NMR only (for **9** → **10b**, 22%, and **9c** → **10c**, 20%, resp.). Irradiation of these solns. with light of 300 nm leads to almost quantitative (> 95%) back-formation of **9**. Attempted separation and isolation of **10** by chromatography on both SiO_2 and Al_2O_3 failed due to decomposition. Spectroscopic data for **10** were thus obtained directly from irradiated solns. of **9**.

2,2,4,5-Tetramethylhex-4-ene-3-thione (**10a**): UV (C_5H_{12}): 554 (1.45), 315 (3.38), 224 (> 4.3). ^{1}H-NMR (CD_3CN): 1.81 (*s*, 3H); 1.68 (*s*, 3H); 1.52 (*s*, 3H); 1.35 (*s*, 9H). ^{13}C-NMR (CD_3CN): 278.4 (*s*); 141.4 (*s*); 122.9 (*s*); 52.7 (*s*); 31.3 (*q*); 22.2 (*q*); 19.7 (*q*); 19.2 (*q*). MS: 170 (20, M^+), *113*.

2,2,5-Trimethyl-4-(2-methylpropyl)hex-4-ene-3-thione (**10b**): UV (C_5H_{12}): 551 (1.72), 315 (3.06), 227 (> 4.2). ^{1}H-NMR (CD_3CN): 2.31 (*dd*, *J* = 10.0, 14.0); 2.21 (*dd*, *J* = 6.0, 14.0); 1.84 (*m*, 1H); 1.71 (*s*, 3H); 1.55 (*s*, 3H); 1.35 (*s*, 9H); 0.89 (*d*, *J* = 7.0, 3H); 0.84 (*d*, *J* = 7.0, 3H). ^{13}C-NMR (CD_3CN): 277.7 (*s*); 146.7 (*s*); 124.9 (*s*); 52.9 (*s*); 41.0 (*t*); 32.2 (*q*); 27.8 (*d*); 23.6 (*q*); 23.0 (*q*); 21.6 (*q*); 20.2 (*q*).

4-Benzyl-2,2,5-trimethylhex-4-ene-3-thione (**10c**): UV (C_5H_{12}): 548 (2.06), 315 (3.46), 220 (> 4.4). ^{1}H-NMR (CD_3CN): 7.20 (*m*, 5H); 3.72 (*s*, 2H); 1.77 (*s*, 3H); 1.61 (*s*, 3H); 1.35 (*s*, 9H). ^{13}C-NMR (CD_3CN): 276.2 (*s*); 144.6 (*s*); 139.6 (*s*); 129.4 (*d*); 128.4 (*d*); 126.4 (*d*); 126.0 (*s*); 53.1 (*s*); 38.9 (*t*); 32.1 (*q*); 23.0 (*q*); 20.6 (*q*).

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