

125. Photochemical Synthesis and Some Reactions of 7-Oxa- and 7-Thiatricyclo[3.2.1.0^{3,6}]octan-2-ones

by Rolf-Christoph Gebel and Paul Margaretha*

Institut für Organische Chemie, Universität, D-2000 Hamburg 13

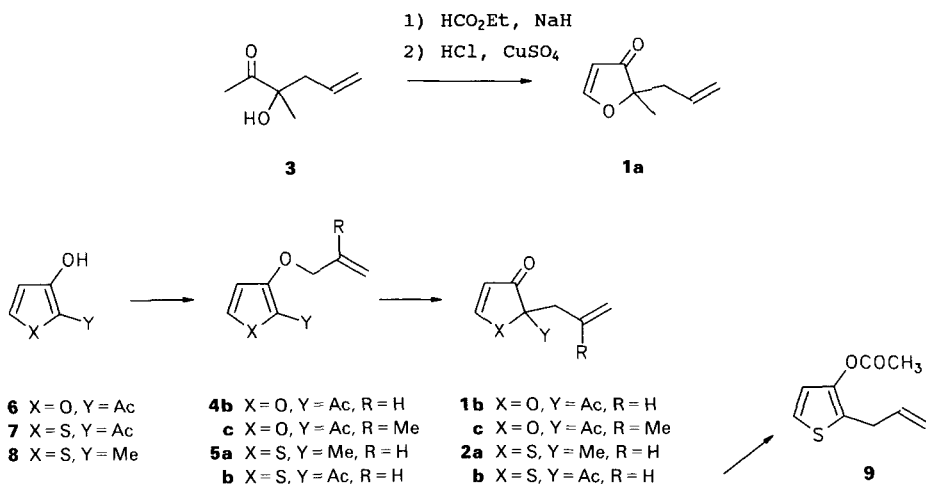
(15.VI.92)

Irradiation ($\lambda = 350$ nm) of newly synthesized 2-acetyl- or 2-methyl-2-(alk-2-enyl)furan-3(2*H*)-ones **1** and 2-acetyl- or 2-methyl-2-(prop-2-enyl)thiophen-3(2*H*)-ones **2** affords the corresponding 1-acetyl- or 1-methyl-substituted 7-oxa- and 7-thiatricyclo[3.2.1.0^{3,6}]octan-2-ones **10** and **11**, respectively, *via* regioselective intramolecular [2 + 2] photocycloaddition in 65–95% yield (*Scheme 2*). The 1-acetyl-substituted O-derivatives **10b** and **10c** undergo ring opening on treatment with MeONa in MeOH at -78° to afford stereoselectively methyl 3-*exo*-acetyl-2-oxabicyclo[3.2.0]heptane-7-*endo*-carboxylates **12b** and **12c**, respectively, while a 2:1 diastereoisomeric mixture of methyl 3-acetyl-2-thiabicyclo[3.2.0]heptane-7-*endo*-carboxylates **13** and **14** is obtained from the corresponding S-derivative **11b**. The outcome of the Huang-Minlon reduction of the 1-methyl-substituted ketones **10a** and **11a** is again influenced by the heteroatom in the tricycle. While 1-methyl-7-oxatricyclo[3.2.1.0^{3,6}]octane (**15**) is the only product from the corresponding oxatricyclooctanone **10a**, a 1:2 mixture of 1-methyl-7-thiatricyclo[3.2.1.0^{3,6}]octane (**16**) and 3-methylbicyclo[3.1.1]hept-2-ene-6-*endo*-thiol (**17**) is obtained from the analogous S-compound **11a**, both products stemming from a common carbanion precursor.

Introduction. – Intramolecular enone/olefin photocycloadditions have gained increasing importance in organic syntheses [1–3]. In the course of our studies on the photochemistry of cyclic α,β -unsaturated carbonyl compounds, we contributed to this topic with results on regiochemical trends in such reactions for 5-(prop-2-enyl)cyclopent-2-enones [4]. We also emphasized on the synthesis of several corresponding heteropentacyclic enones having a heteroatom instead of C(4), *e.g.* O, S, or N, and C(5) substituted with two Me groups to prevent tautomerization to a 3-hydroxy-substituted heterocycle. We observed that such compounds exhibit photochemistry typical for cyclopent-2-enone itself [5–8]. In this paper, we report on the synthesis of 2-acetyl- or 2-methyl-2-(alk-2-enyl)furan-3(2*H*)-ones **1** and 2-acetyl- or 2-methyl-2-(prop-2-enyl)thiophen-3(2*H*)-ones **2**, their regioselective light-induced conversion to 7-oxa- or 7-thiatricyclo[3.2.1.0^{3,6}]octan-2-ones, and further (thermal) transformations of these photoproducts to novel heterocyclic systems.

Results. – Two different synthetic routes were used for preparing (alk-2-enyl)furanones **1** and (prop-2-enyl)thiophenones **2**. Thus, 2-methyl-2-(prop-2-enyl)furan-3(2*H*)-one (**1a**) was obtained from 3-hydroxy-3-methylhex-5-en-2-one (**3**; *Scheme 1*) by a formylation/aldol cyclization sequence, as already used for the synthesis of 2,2-dimethylfuran-3(2*H*)-one [9]. The 2-acetylfuranones **1b** and **1c**, the 2-acetylthiophenone **2b** and the 2-methylthiophenone **2a** were obtained from the corresponding propenyloxy precursors **4** and **5** – obtained in turn from isomaltol (**6**), thioisomaltol (**7**), and 3-hydroxy-2-methylthiophene (**8**), respectively, *via* a Claisen rearrangement, as already used for the synthesis of methyl 2,3-dihydro-3-oxo-2-(prop-2-enyl)thiophene-2-carboxylate [10] [11].

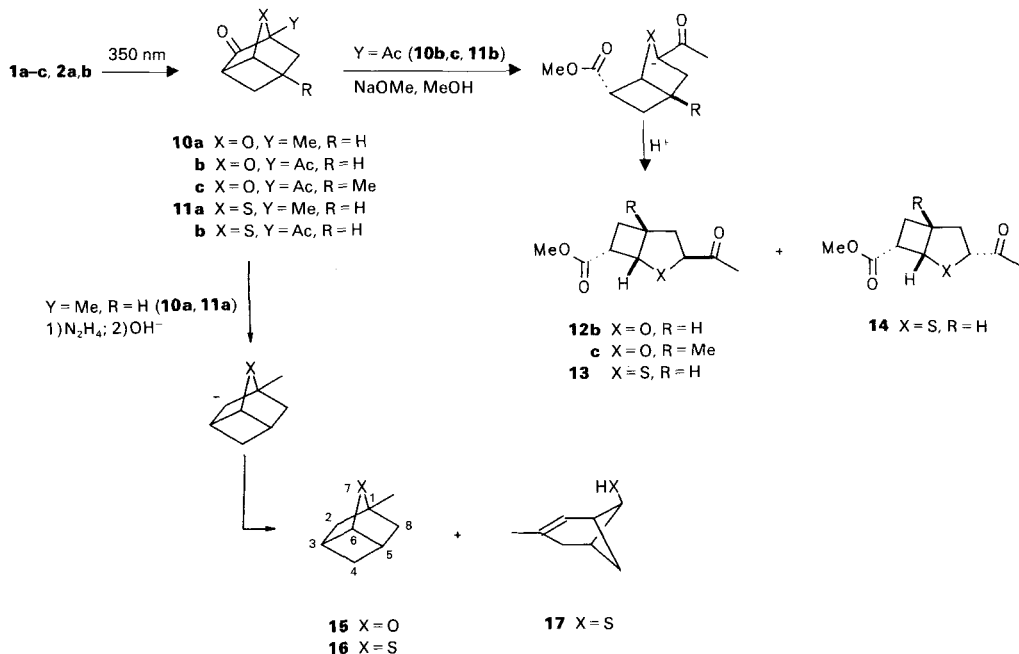
Scheme 1



Prolonged heating in the conversion of **5b** to **2b** has to be avoided, as **2b** rearranged further to 2-(prop-2-enyl)thien-3-yl acetate (**9**).

Irradiation ($\lambda > 340$ nm) of enones **1** and **2** in benzene led in a regioselective and quantitative conversion (Scheme 2) to tricyclooctanones **10** and **11**, respectively. Treat-

Scheme 2



ment of oxatricyclooctanones **10b** and **10c** with NaOMe in MeOH at -78° afforded stereoselectively the methyl 3-*exo*-acetyl-2-oxabicyclo[3.2.0]heptane-7-*endo*-carboxylates **12**. Under the same conditions, thiatricyclooctanone **11b** afforded a 1:2 diastereoisomer mixture of the methyl 3-*exo*- and 3-*endo*-acetyl-2-thiabicyclo[3.2.0]heptane-7-*endo*-carboxylates (**13** and **14**, resp.; *Scheme 2*). Reaction of oxatricyclooctanone **10a** with hydrazine and NaOH in ethylene glycol (*Huang-Minlon* reaction) led to the selective formation of 1-methyl-7-oxatricyclo[3.2.1.0^{3,6}]octane (**15**). Again, under the same conditions, thiatricyclooctanone **11a** gave a 1:2 mixture of 1-methyl-7-thiatricyclo[3.2.1.0^{3,6}]octane (**16**) and 3-methylbicyclo[3.1.1]hept-2-ene-6-*endo*-thiol (**17**) (*Scheme 2*).

Selected $^1\text{H-NMR}$ spectroscopical data of compounds **10–16** is summarized in the *Table*.

Table. Selected $^1\text{H-NMR}$ Data of Compounds **10–16**

CDCl_3 Solution	10a	10b	10c	11a	11b	15	16
H–C(3)	2.80	2.95	2.88	2.76	2.87	2.58	2.65
H _{exo} –C(4)	2.25	2.34	2.11	2.40	2.45	1.88	2.11
H _{endo} –C(4)	1.44	1.59	1.79	1.51	1.62	1.10	1.24
H–C(5)	2.95	3.02	–	3.03	3.09	2.58	2.65
H–C(6)	5.03	5.19	4.78	4.23	4.37	4.78	4.16
H _{anti} –C(8)	1.84	2.03	1.77	2.23	2.33	1.56	1.95
H _{syn} –C(8)	1.74	2.17	2.23	2.06	2.53	1.62	1.79
$J(3,4_{\text{exo}}) = 7\text{--}10$, $J(3,5) = 5\text{--}6$, $J(3,6) = 4\text{--}5$, $J(3,8_{\text{anti}}) = 0\text{--}1$, $J(4_{\text{exo}},4_{\text{endo}}) = 9\text{--}11$, $J(4_{\text{exo}},5) = 6\text{--}6.5$, $J(4_{\text{exo}},8_{\text{anti}}) = 3\text{--}4$, $J(5,6) = 4\text{--}5$, $J(5,8_{\text{anti}}) = 6\text{--}7$, $J(8_{\text{anti}},8_{\text{syn}}) = 12\text{--}13$.							
C_6D_6 Solution	12a	12b	13	14			
H–C(1)	4.35	3.99	3.85	3.85	$J(1,5) = 6\text{--}8$,		
H–C(3)	4.00	4.06	4.12	3.43	$J(1,6_{\text{exo}}) = 2\text{--}2.5$,		
H _{exo} –C(4)	1.80	1.55	1.83	1.35	$J(1,7_{\text{exo}}) = 6\text{--}8$,		
H _{endo} –C(4)	1.95	2.17	1.57	2.62	$J(5,6_{\text{exo}}) = 7\text{--}8$,		
H–C(5)	2.20	–	2.71	2.58	$J(5,6_{\text{endo}}) = 7\text{--}8$,		
H _{exo} –C(6)	1.80	1.43	1.68	1.68	$J(6_{\text{exo}},7_{\text{exo}}) = 6\text{--}8$,		
H _{endo} –C(6)	2.05	2.21	2.00	2.28	$J(6_{\text{endo}},7_{\text{exo}}) = 6\text{--}8$,		
H _{exo} –C(7)	2.75	2.77	3.01	2.89	$J(4,4) = 13$, $J(6,6) = 12$		

Discussion. – The synthetic access to the novel furanones **1** and thiophenones **2** is straightforward, except the conversion of ether **5b** to enone **2b** which has to be monitored by GC to avoid the easily occurring further rearrangement of 2-acetyl-2-(prop-2-enyl)-thiophenone **2b** to thien-3-yl acetate **9**.

The (formal) replacement of C(4) of cyclopent-2-enone by either an O- or an S-atom leads to heteropentacyclic enones (oxa- or thiaenones) which undergo light-induced [2 + 2] cycloadditions to terminal alkenes with a much higher degree of regioselectivity than cyclopent-2-enone itself [5] [7]. This is reflected in the behavior of compounds **1** and **2** in intramolecular photocycloadditions, where always only one orientation of addition of the exocyclic double bond to the enone C=C bond (formation of **10** and **11**) was observed. In the irradiation of 5-(prop-2-enyl)- or 5-(2-methylprop-2-enyl)cyclopent-2-enones, both isomeric tricyclo[3.2.1.0^{3,6}]octan-2-ones and -7-ones were commonly formed [4] [12], the former usually being the major reaction product.

Whereas the reduction of tricyclooctan-2-ones to the parent hydrocarbons was already reported [12], the base-induced ring opening of 1-acetyl-7-heterotricyclo[3.2.1.0^{3,6}]octan-2-ones **10** and **11** (Y = Ac) to 3-acetyl-2-heterobicyclo[3.2.0]heptanes **12–14** represents a novel and useful approach to these cyclobuta[*b*]furanes and -thiophenes. Under kinetic control (–78°), protonation of the carbanionic center C(3) of the intermediate 2-oxabicyclo[3.2.0]heptanes in the O-series occurs selectively from the *endo*-side, the ester group on C(7) possibly assisting *via* intramolecular H-transfer, with exclusive formation of the 3-*exo*-acetyl derivatives ($J(3,4) = 7.0$ and 8.0 Hz). Protonation of the corresponding – thermodynamically more stable – carbanion in the S-series seems to occur slower, and, therefore, the 3-*endo*-acetyl derivative is formed preferentially (Ac group in equatorial position, $J(3,4) = 5.5$ and 10.0 Hz).

Finally, the greater stability of a carbanion center next to an S-atom (as compared to an O-atom) – and the fact that RS is a better anionic leaving group than RO – is reflected in the outcome of the basic decomposition of the hydrazones of **10a** and **11a**. While **10a** was converted selectively to **15** under these conditions, the corresponding S-compound **11a** afforded bicyclic thiol **17** as the major product *via* β -elimination of an RS[–] moiety.

Experimental Part

General. The 3-hydroxy-3-methylhex-5-en-2-one (**3**) was synthesized from diacetyl according to [13], and 1-(3-hydroxyfuran-2-yl)ethanone (= isomaltol; **6**), 1-(3-hydroxythien-2-yl)ethanone (= thioisomaltol; **7**), and 2-methylthiophen-3-ol (**8**) were obtained according to [14–16]. Photolyses: *Rayonet-RPR-100* photoreactor equipped with 350-nm lamps and using a liquid filter with cut-off at 340 nm. Qual. GC: 30-m *SE 30* capillary column. UV Spectra: in nm (log ϵ). IR Spectra: in cm^{–1}. ¹H- and ¹³C-NMR Spectra: at 400 and 100.63 MHz, resp.; chemical shifts in ppm rel. to TMS (= 0 ppm), coupling constants in Hz. MS: at 70 eV.

2-Methyl-2-(prop-2-enyl)furan-3(2H)-one (1a). To a suspension of 80% NaH (16.75 g, 0.58 mol) in Et₂O (150 ml) is added a soln. of ethyl formate (22.1 g, 0.29 mol) and **3** (24.8 g, 0.19 mol) in Et₂O (100 ml). After stirring for 5 h at r.t., anh. CuSO₄ (30 g) is added and the mixture saturated with HCl gas. After filtration, the soln. is neutralized with aq. NaHCO₃ soln. and the Et₂O soln. then dried (MgSO₄). Evaporation affords 6.2 g (25%) of **1a**. B.p. 160°/760 Torr. ¹H-NMR (CDCl₃): 8.20, 5.63 (2d, $J = 2.4$, 2 H); 5.66 (m, 1 H); 5.16–5.09 (m, 2 H); 2.45 (d, $J = 7.4$, 2 H); 1.40 (s, 3 H). ¹³C-NMR (CDCl₃): 207 (s); 176 (d); 130 (d); 120 (t); 106 (d); 89 (s); 41 (t); 21 (q). MS: 138 (30, M⁺), 43.

1-[3-(Prop-2-enyloxy)furan-2-yl]ethanone (4b). A soln. of **6** (8.17 g, 0.072 mol), 3-bromopropene (14.3 g, 0.11 mol), and anh. K₂CO₃ (17 g, 0.12 mol) in dry acetone (120 ml) is refluxed for 18 h. After addition of H₂O and Et₂O, the org. phase is separated, washed with NaHCO₃ and NaCl solns., dried (MgSO₄), and evaporated: 6.1 g (52%) of crude **4b**, > 90% pure. ¹H-NMR (CDCl₃): 7.42, 6.36 (2d, $J = 2.0$, 2 H); 6.02 (m, 1 H); 5.40 (m, 2 H); 4.65 (m, 2 H); 2.47 (s, 3 H).

1-[3-(Prop-2-enyloxy)thien-2-yl]ethanone (5b). As described above, from **7** and 3-bromopropene (2 h reflux): **5b** in 78% yield. ¹H-NMR (CDCl₃): 7.50, 6.84 (2d, $J = 5.5$, 2 H); 6.04 (m, 1 H); 5.40 (m, 2 H); 4.70 (m, 2 H); 2.57 (s, 3 H).

1-[3-(2-Methylprop-2-enyloxy)furan-2-yl]ethanone (4c). To a soln. of 80% NaH (0.68 g, 22 mmol) in DMSO (20 ml) is added a soln. of **6** (2.4 g, 22 mmol) in DMSO (20 ml). Stirring is continued for 1 h (evolution of H₂). Then 3-chloro-2-methylpropene (1.99 g, 22 mmol) is added and the mixture warmed to 40° and stirred for 6 h. After addition of pentane and dil. aq. HCl soln., the org. phase is separated, washed with aq. NaHCO₃ soln., H₂O, and aq. NaCl soln., dried (MgSO₄), and evaporated: 1.61 g (42%) of crude **4c**. ¹H-NMR: 7.43, 6.37 (2d, $J = 2.1$, 2 H); 5.10 (s, 1 H); 5.04 (s, 1 H); 4.55 (s, 2 H); 2.46 (s, 3 H); 1.84 (s, 3 H). ¹³C-NMR (CDCl₃): 185 (s); 154 (s); 146 (d); 140 (s); 138 (s); 114 (t); 103 (d); 75 (t); 27 (q); 19 (q).

2-Methyl-3-(prop-2-enyloxy)thiophene (5a). As described above, from **8** and 3-bromopropene in DMSO at 40°. Stirring for 1 h affords crude **5a** in 47% yield. ¹H-NMR (CDCl₃): 6.76, 6.56 (2d, $J = 5.4$, 2 H); 6.02 (m, 1 H); 5.70 (m, 2 H); 5.30 (m, 2 H); 2.60 (s, 3 H).

Thermolyses of Propenyl Ethers 4 and 5 to Enones 1 and 2, Respectively. The neat propenyl ether (0.01 mol) is heated under Ar at the temp. and for the time given. The enone is then purified by bulb-to-bulb distillation.

2-Acetyl-2-(prop-2-enyl)furan-3(2H)-one (1b). From **4b**, 5 h at 195°. Distillation at 170°/0.25 Torr: 76% yield. M.p. 41°. ¹H-NMR (CDCl₃): 8.45, 5.72 (2d, *J* = 2.4, 2 H); 5.62 (*m*, 1 H); 5.19 (*m*, 2 H); 2.90, 2.75 (*dd*, *J* = 7.4, 14.6, 2 H); 2.22 (*s*, 3 H). ¹³C-NMR (CDCl₃): 198 (*s*); 197 (*s*); 178 (*d*); 129 (*d*); 121 (*t*); 107 (*d*); 97 (*s*); 38 (*r*); 25 (*q*). MS: 124 (100, *M*⁺), 95.

2-Acetyl-2-(2-methylprop-2-enyl)furan-3(2H)-one (1c). From **4c**, 4 h at 160°. Distillation at 175°/0.25 Torr: 77% yield. M.p. 64°. ¹H-NMR (CDCl₃): 8.43, 5.72 (2d, *J* = 2.4, 2 H); 4.90 (*s*); 4.84 (*s*); 2.97, 2.64 (*d*, *J* = 15.0); 2.22 (*s*, 3 H); 1.84 (*s*, 3 H). ¹³C-NMR (CDCl₃): 198 (*s*); 197 (*s*); 178 (*d*); 138 (*s*); 116 (*t*); 106 (*d*); 97 (*s*); 42 (*t*); 25 (*q*); 24 (*q*). MS: 180 (3, *M*⁺), 42.

2-Methyl-2-(prop-2-enyl)thiophen-3(2H)-one (2a). From **5a**, 5 h at 180°. Distillation at 100°/0.25 Torr: 87% yield. Oil. ¹H-NMR (CDCl₃): 8.41, 6.13 (2d, *J* = 5.8, 2 H); 5.66 (*m*, 1 H); 5.16 (*m*, 2 H); 2.44 (*d*, *J* = 7.2, 2 H); 1.40 (*s*, 3 H). ¹³C-NMR (CDCl₃): 207 (*s*); 162 (*d*); 132 (*d*); 121 (*d*); 119 (*t*); 61 (*s*); 43 (*t*); 24 (*q*). MS: 154 (10, *M*⁺), 113.

2-Acetyl-2-(prop-2-enyl)thiophen-3(2H)-one (2b). From **5b**, 30 min at 180°. Distillation at 165°/0.25 Torr: 72% yield. Oil. ¹H-NMR (CDCl₃): 8.47, 6.26 (2d, *J* = 5.8, 2 H); 5.63 (*m*, 1 H); 5.15 (*m*, 2 H); 2.94, 2.79 (*dd*, *J* = 7.0, 14.3, 2 H); 2.14 (*s*, 3 H). ¹³C-NMR (CDCl₃): 202 (*s*); 197 (*s*); 164 (*d*); 131 (*d*); 123 (*d*); 120 (*t*); 72 (*s*); 37 (*t*); 25 (*q*). MS: 182 (0.9, *M*⁺), 85.

2-(Prop-2-enyl)thien-3-yl Acetate (9). From **5b** or from **2b**, 5 h at 180°. Distillation at 165°/0.25 Torr: 76% yield. Oil. ¹H-NMR (CDCl₃): 7.08, 6.82 (2d, *J* = 5.5, 2 H); 5.90 (*m*, 1 H); 5.11 (*m*, 2 H); 3.40 (*m*, 2 H); 2.26 (*s*, 3 H). ¹³C-NMR (CDCl₃): 169 (*s*); 143 (*d*); 135 (*s*); 127 (*s*); 122 (*d*); 121 (*d*); 116 (*t*); 30 (*t*); 21 (*q*). MS: 182 (1, *M*⁺), 140.

Photolyses. Ar-degassed solns. of **1** or **2** (5 mmol) in benzene (5 ml) are irradiated for 15–30 h (GC monitoring up to total conversion). Evaporation of the solvent and bulb-to-bulb distillation (170°/0.25 Torr) give pure **10** or **11** (¹H-NMR, see Table).

1-Methyl-7-oxatricyclo[3.2.1.0^{3,6}]octan-2-one (10a). From **1a**: 62%. Liquid. IR (CCl₄): 2981*m*, 1762*s*. ¹³C-NMR (CDCl₃): 212 (*s*); 85 (*s*); 77 (*d*); 41 (*t*); 39 (*d*); 34 (*t*); 13 (*s*). MS: 138 (3, *M*⁺), 43.

1-Acetyl-7-oxatricyclo[3.2.1.0^{3,6}]octan-2-one (10b). From **1b**: 77%. M.p. 45°. IR (CCl₄): 2983*m*, 1733*s*. ¹³C-NMR (CDCl₃): 206 (*s*); 201 (*s*); 92 (*s*); 78 (*d*); 47 (*d*); 39 (*d*); 38 (*t*); 29 (*t*); 28 (*q*). MS: 166 (1, *M*⁺), 43.

1-Acetyl-5-methyl-7-oxatricyclo[3.2.1.0^{3,6}]octan-2-one (10c). From **1c**: 80%. Oil. IR (CCl₄): 2956*m*, 1767*m*, 1718*m*. ¹³C-NMR (CDCl₃): 200 (*s*); 195 (*s*); 92 (*s*); 81 (*d*); 47 (*s*); 43 (*t*); 43 (*d*); 34 (*t*); 27 (*q*); 21 (*q*). MS: 180 (4, *M*⁺), 42.

1-Methyl-7-thiatricyclo[3.2.1.0^{3,6}]octan-2-one (11a). From **2a**: 70%. Oil. IR (CCl₄): 2851*m*, 1733*s*. ¹³C-NMR (CDCl₃): 208 (*s*); 63 (*s*); 48 (*d*); 47 (*d*); 46 (*t*); 41 (*d*); 33 (*t*); 13 (*q*). MS: 154 (38, *M*⁺), 99.

1-Acetyl-7-thiatricyclo[3.2.1.0^{3,6}]octan-2-one (11b). From **2b**: 80%. Oil. IR (CCl₄): 2978*m*, 1735*m*, 1708*m*. ¹³C-NMR (CDCl₃): 204 (*s*); 202 (*s*); 76 (*s*); 48 (*d*); 47 (*d*); 41 (*d*); 40 (*t*); 34 (*t*); 29 (*q*). MS: 182 (7, *M*⁺), 42.

Cleavage of β-Diketones 10b,c and 11b with Base. To a soln. of NaOMe (60 mg, 1.1 mmol) in MeOH (5 ml) cooled down to –78° is added a soln. of **10b**, **10c**, or **11b** (1 mmol) in MeOH (2 ml). After 1 min, the reaction is quenched by addition of H₂O and Et₂O, the org. phase separated, washed with aq. NH₄Cl soln. and then with H₂O, dried (MgSO₄), and evaporated and the residue bulb-to-bulb distilled at 170°/0.25 Torr: **12–14** (¹H-NMR, see Table).

Methyl 3-exo-Acetyl-2-oxabicyclo[3.2.0]heptane-7-endo-carboxylate (12b). From **10b**: 65%. Liquid. ¹³C-NMR (CDCl₃): 211 (*s*); 175 (*s*); 87 (*d*); 81 (*d*); 50 (*d*); 38 (*d*); 35 (*q*); 34 (*t*); 25 (*t*); 24 (*q*). MS: 167 (2, [*M* – 31]⁺), 69.

Methyl 3-exo-Acetyl-5-methyl-2-oxabicyclo[3.2.0]heptane-7-endo-carboxylate (12c). From **10c**: 55%. Liquid. ¹³C-NMR (CDCl₃): 209 (*s*); 172 (*s*); 87 (*d*); 86 (*d*); 52 (*d*); 44 (*s*); 43 (*t*); 37 (*q*); 32 (*t*); 25 (*q*). MS: 181 (2, [*M* – 31]⁺), 55.

Methyl 3-Acetyl-2-thiabicyclo[3.2.0]heptane-7-endo-carboxylates (13/14). From **11b**: 89% of a 1:2 mixture (GC) of **13** (3-*exo*) and **14** (3-*endo*). MS: 214 (0.6, *M*⁺), 85.

Huang-Minlon Reduction of Ketones 10a and 11a. A soln. of the ketone (1 mmol) and hydrazine (0.16 g, 5 mmol) in ethylene glycol (5 ml) is stirred for 30 min at 110°. After addition of NaOH (0.12 g, 3 mmol), the mixture is heated to 195° and distilled. H₂O is added to the distillate, the org. phase separated, dried (little CaCl₂), and then further processed.

1-Methyl-7-oxatricyclo[3.2.0.1^{3,6}]octane (15). Distillation at 120°/760 Torr affords 119 mg (32%) of **15**. Colorless liquid. ¹H-NMR: Table. ¹³C-NMR (C₆D₆): 83.9 (*s*); 79.1 (*d*); 44.1 (*t*); 40.0 (*d*); 29.0 (*t*); 20.3 (*q*). MS: 124 (13, *M*⁺), 95.

1-Methyl-7-thiatricyclo[3.2.1.0^{3,6}]octane (16) and 3-Methylbicyclo[3.1.1]hept-2-ene-6-endo-thiol (17). Chromatography (SiO₂, pentane) of **16/17** (1:2) affords first 29 mg (7%) of **16** and then 63 mg (15%) of **17**.

16: Colorless liquid. $^1\text{H-NMR}$: *Table*. $^{13}\text{C-NMR}$ (CDCl_3): 54.9 (*d*); 49.6 (*t*); 41.3 (*d*); 34.1 (*t*); 20.0 (*q*). MS: 140 (51, M^+), 99.

17: Colorless liquid. $^1\text{H-NMR}$ (CDCl_3): 5.70 (*d*, $J = 6.0$); 3.75 (*dt*, $J = 5.2, 10.4$); 2.65 (*q*, $J = 5.6$); 2.55 (*tq*, $J = 2.8, 5.6$); 2.33 (*d*, $J = 2.8$); 2.22 (*d*, $J = 2.8$); 1.55 (*dt*, $J = 5.6, 8.1$); 1.73 (*d*, $J = 10.5$), 1.73 (*s*); 1.50 (*d*, $J = 8.4$). $^{13}\text{C-NMR}$ (CDCl_3): 133.3 (*s*); 126.6 (*d*); 39.9 (*d*); 39.6 (*d*); 38.8 (*d*); 34.3 (*t*); 32.2 (*t*); 20.9 (*t*). MS: 140 (50, M^+), 107.

REFERENCES

- [1] M. T. Crimmins, *Chem. Rev.* **1988**, 88, 1453.
- [2] J. Cossy, P. A. Carrupt, P. Vogel, in 'The Chemistry of Double-Bonded Functional Groups', Ed. S. Patai, J. Wiley, New York, 1989, p. 1368.
- [3] D. Becker, N. Haddad, in 'Organic Photochemistry', Ed. A. Padwa, M. Dekker, New York, 1989, Vol. 10, p. 1.
- [4] G. Cruciani, P. Margaretha, *Helv. Chim. Acta* **1990**, 73, 288.
- [5] P. Margaretha, *Chimia* **1975**, 29, 203.
- [6] R. C. Gebel, P. Margaretha, *Chem. Ber.* **1990**, 123, 855.
- [7] E. Anklam, R. Ghaffari-Tabrizi, H. Hombrecher, S. Lau, P. Margaretha, *Helv. Chim. Acta* **1984**, 67, 1402.
- [8] J. Patjens, P. Margaretha, *Helv. Chim. Acta* **1989**, 72, 1817.
- [9] P. Margaretha, *Tetrahedron Lett.* **1971**, 4891.
- [10] M. R. Banks, J. M. Barker, P. R. Huddelston, *J. Chem. Res. (S)* **1984**, 27.
- [11] E. Anklam, S. Lau, P. Margaretha, *Helv. Chim. Acta* **1985**, 68, 1129.
- [12] T. Y. Luh, K. L. Lei, *J. Org. Chem.* **1981**, 46, 5328.
- [13] A. Tougani, R. Couffignal, H. Normant, *C. R. Acad. Sci., Ser. 2* **1985**, 15, 1127.
- [14] J. E. Hodge, E. C. Nelson, *Cereal Chem.* **1961**, 38, 216.
- [15] H. J. Jakobsen, S. O. Lawesson, *Tetrahedron* **1965**, 21, 3331.
- [16] A. B. Hörnfeldt, *Acta Chem. Scand.* **1965**, 19, 1250.