# 125. Photochemical Synthesis and Some Reactions of 7-Oxa- and 7-Thiatricyclo[3.2.1.$0^{3,6}$]octan-2-ones

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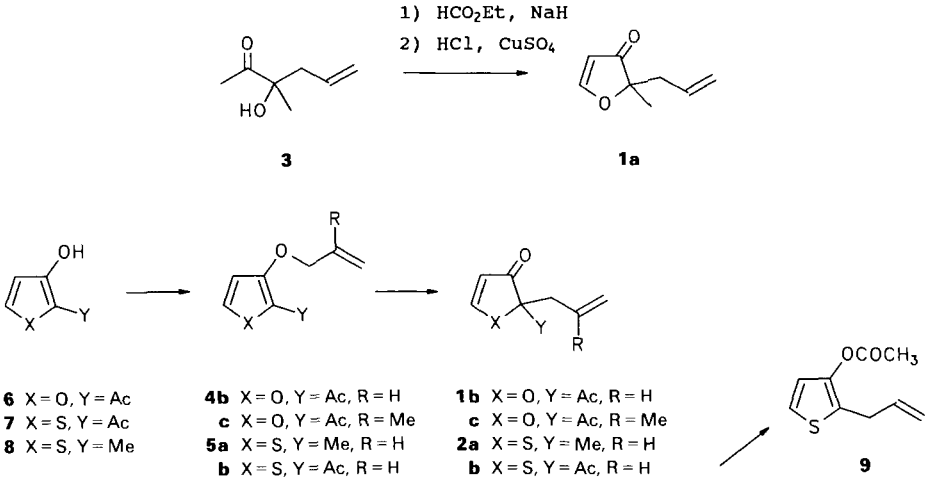
Irradiation ($\lambda$ = 350 nm) of newly synthesized 2-acetyl- *or* 2-methyl-2-(alk-2-enyl)furan-3(2*H*)-ones **1** and 2-acetyl- or 2-methyl-2-(prop-2-enyl)thiophen-3(2*H*)-ones **2** affords the corresponding 1-acetyl- *or* 1-methyl-substituted 7-oxa- and 7-thiatricyclo[3.2.1.$0^{3,6}$]octan-2-ones **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 $\alpha,\beta$-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].

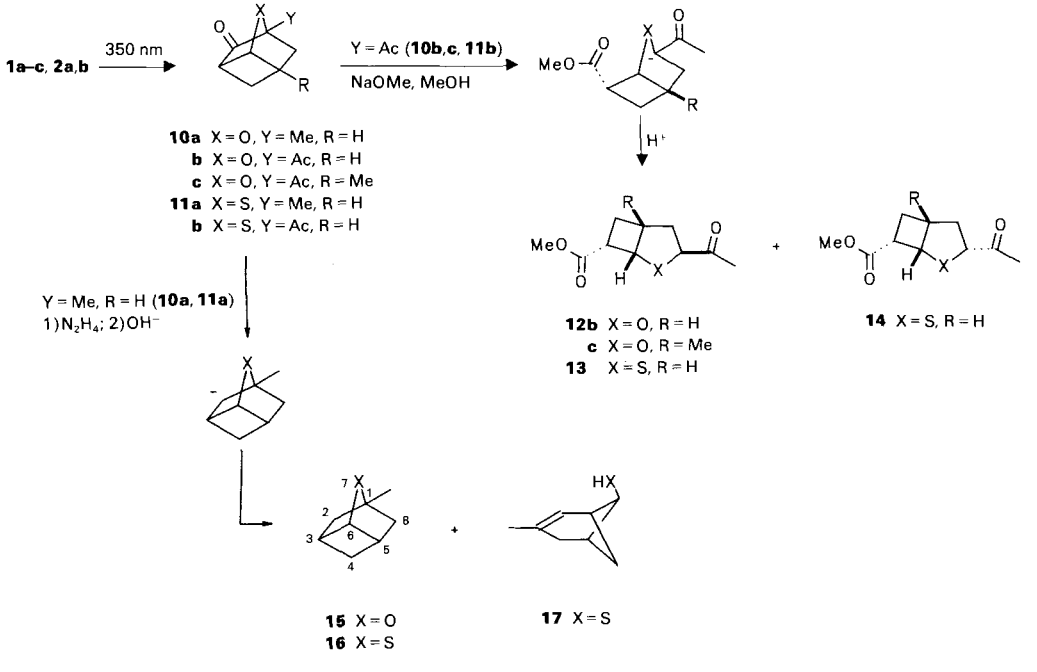
*Scheme 1*




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

Table. *Selected $^1$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 |

$J(3,4_{exo}) = 7$–10, $J(3,5) = 5$–6, $J(3,6) = 4$–5, $J(3,8_{anti}) = 0$–1, $J(4_{exo},4_{endo}) = 9$–11, $J(4_{exo},5) = 6$–6.5, $J(4_{exo},8_{anti}) = 3$–4, $J(5,6) = 4$–5, $J(5,8_{anti}) = 6$–7, $J(8_{anti},8_{syn}) = 12$–13.

| $C_6D_6$ Solution | **12a** | **12b** | **13** | **14** | |
|---|---|---|---|---|---|
| H–C(1) | 4.35 | 3.99 | 3.85 | 3.85 | $J(1,5) = 6$–8, |
| H–C(3) | 4.00 | 4.06 | 4.12 | 3.43 | $J(1,6_{exo}) = 2$–2.5, |
| $H_{exo}$–C(4) | 1.80 | 1.55 | 1.83 | 1.35 | $J(1,7_{exo}) = 6$–8, |
| $H_{endo}$–C(4) | 1.95 | 2.17 | 1.57 | 2.62 | $J(5,6_{exo}) = 7$–8, |
| H–C(5) | 2.20 | – | 2.71 | 2.58 | $J(5,6_{endo}) = 7$–8, |
| $H_{exo}$–C(6) | 1.80 | 1.43 | 1.68 | 1.68 | $J(6_{exo},7_{exo}) = 6$–8, |
| $H_{endo}$–C(6) | 2.05 | 2.21 | 2.00 | 2.28 | $J(6_{endo},7_{exo}) = 6$–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* $\beta$-elimination of an $RS^-$ moiety.

## Experimental Part

*General.* The 3-hydroxy-3-methylhex-5-en-2-one (**3**) was synthesized form 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 $\varepsilon$). IR Spectra: in $cm^{-1}$. $^1H$- and $^{13}C$-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 $Et_2O$ (150 ml) is added a soln. of ethyl formate (22.1 g, 0.29 mol) and **3** (24.8 g, 0.19 mol) in $Et_2O$ (100 ml). After stirring for 5 h at r.t., anh. $CuSO_4$ (30 g) is added and the mixture saturated with HCl gas. After filtration, the soln. is neutralized with aq. $NaHCO_3$ soln. and the $Et_2O$ soln. then dried ($MgSO_4$). Evaporation affords 6.2 g (25%) of **1a**. B.p. 160°/760 Torr. $^1H$-NMR ($CDCl_3$): 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). $^{13}C$-NMR ($CDCl_3$): 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. $K_2CO_3$ (17 g, 0.12 mol) in dry acetone (120 ml) is refluxed for 18 h. After addition of $H_2O$ and $Et_2O$, the org. phase is separated, washed with $NaHCO_3$ and NaCl solns., dried ($MgSO_4$), and evaporated: 6.1 g (52%) of crude **4b**, > 90% pure. $^1H$-NMR ($CDCl_3$): 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 ($CDCl_3$): 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 $H_2$). 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. $NaHCO_3$ soln., $H_2O$, and aq. NaCl soln., dried ($MgSO_4$), 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). $^{13}C$-NMR ($CDCl_3$): 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 ($CDCl_3$): 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(2*H*)-one* (**1b**). From **4b**, 5 h at 195°. Distillation at 170°/0.25 Torr: 76% yield. M.p. 41°. $^1$H-NMR ($CDCl_3$): 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). $^{13}$C-NMR ($CDCl_3$): 198 (*s*); 197 (*s*); 178 (*d*); 129 (*d*); 121 (*t*); 107 (*d*); 97 (*s*); 38 (*t*); 25 (*q*). MS: 124 (100, $M^+$), *95*.

*2-Acetyl-2-(2-methylprop-2-enyl)furan-3(2*H*)-one* (**1c**). From **4c**, 4 h at 160°. Distillation at 175°/0.25 Torr: 77% yield. M.p. 64°. $^1$H-NMR ($CDCl_3$): 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). $^{13}$C-NMR ($CDCl_3$): 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(2*H*)-one* (**2a**). From **5a**, 5 h at 180°. Distillation at 100°/0.25 Torr: 87% yield. Oil. $^1$H-NMR ($CDCl_3$): 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). $^{13}$C-NMR ($CDCl_3$): 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(2*H*)-one* (**2b**). From **5b**, 30 min at 180°. Distillation at 165°/0.25 Torr: 72% yield. Oil. $^1$H-NMR ($CDCl_3$): 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). $^{13}$C-NMR ($CDCl_3$): 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. $^1$H-NMR ($CDCl_3$): 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). $^{13}$C-NMR ($CDCl_3$): 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** ($^1$H-NMR, see *Table*).

*1-Methyl-7-oxatricyclo[3.2.1.0$^{3,6}$]octan-2-one* (**10a**). From **1a**: 62%. Liquid. IR ($CCl_4$): 2981*m*, 1762*s*. $^{13}$C-NMR ($CDCl_3$): 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 ($CCl_4$): 2983*m*, 1733*s*. $^{13}$C-NMR ($CDCl_3$): 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 ($CCl_4$): 2956*m*, 1767*m*, 1718*m*. $^{13}$C-NMR ($CDCl_3$): 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 ($CCl_4$): 2851*m*, 1733*s*. $^{13}$C-NMR ($CDCl_3$): 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 ($CCl_4$): 2978*m*, 1735*m*, 1708*m*. $^{13}$C-NMR ($CDCl_3$): 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 $H_2O$ and $Et_2O$, the org. phase separated, washed with aq. $NH_4Cl$ soln. and then with $H_2O$, dried ($MgSO_4$), and evaporated and the residue bulb-to-bulb distilled at 170°/0.25 Torr: **12**–**14** ($^1$H-NMR, see *Table*).

*Methyl 3-*exo*-Acetyl-2-oxabicyclo[3.2.0]heptane-7-*endo*-carboxylate* (**12b**). From **10b**: 65%. Liquid. $^{13}$C-NMR ($CDCl_3$): 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. $^{13}$C-NMR ($CDCl_3$): 209 (*s*); 172 (*s*); 87 (*d*); 86 (*d*); 52 (*d*); 44 (*s*); 43 (*t*); 37 (*q*); 32 (*t*); 25 (*q*). 23 (*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. $H_2O$ is added to the distillate, the org. phase separated, dried (little $CaCl_2$), 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. $^1$H-NMR: *Table*. $^{13}$C-NMR ($C_6D_6$): 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 ($SiO_2$, pentane) of **16**/**17** (1:2) affords first 29 mg (7%) of **16** and then 63 mg (15%) of **17**.

**16**: Colorless liquid. $^1$H-NMR: *Table*. $^{13}$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. $^1$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). $^{13}$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*.

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