

42. Photochemical Reactions

149th Communication¹⁾

Photochemistry of 7,8-Dihydro-4-hydroxy- β -Ionone and Derivatives

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The photolysis of 7,8-dihydro-4-hydroxy- β -ionone (**6**) was investigated together with its acetate and isopropyl ether **7** and **8**, respectively. Irradiation ($\lambda > 245$ nm) of **6** in MeCN or i-PrOH at temperatures between 25° and –65° leads to the tricyclic ethers **9**, **10**, and **13A + B**, and to the spirocyclic ethers **11** and **12**, which are all known types of photoproducts, previously obtained on photolysis of 7,8-dihydro- β -ionone (**1**). The same types of products are obtained on irradiation of the acetate **7** and the isopropyl ether **8**. On the other hand, irradiation of the hydroxy compound **6** in MeCN or i-PrOH at temperatures between –35° and –65° leads to the new tricyclic tertiary alcohols **14** and **15** as the major products. Their formation involves an intramolecular trapping of a carbocation by the neighbouring OH group, thus, supporting the previously proposed mechanism of the transformation **1**→**5**. For structure proof, the tricyclic alcohol **14** and the phenyl carbamate **42**, derived from **9**, were subjected to X-ray analysis.

1. Introduction. – In [2] [3], we have shown that the photochemistry of 7,8-dihydro- β -ionone⁴⁾ (**1**) depends on temperature, polarity and viscosity of the solvent. Thus, irradiation ($\lambda \geq 245$ nm) at 25° in pentane converts **1** to the isomeric cyclic ethers **2** and **3**. On photolysis of **1** in protic solvents such as EtOH or i-PrOH between 0° and –65°, in addition to the transformation **1**→**2 + 3**, the alternative [2 + 2] photocycloaddition leading to **4** and transformation to the novel spirocyclic ketone **5** takes place (*Scheme 1*).

Continuing our studies of the photochemistry of γ,δ -unsaturated ketones, we describe in this paper the photolyses of compounds **6–8** incorporating in ε -position an OH, an AcO, and an i-PrO group, respectively. The photochemical behaviour of **6** with an allylic alcohol moiety seemed to be of particular interest, since it was reported previously [5] that aliphatic γ,δ -unsaturated ε -hydroxy ketones exclusively undergo [2 + 2] photocycloaddition leading to products of type **4**. The alternative cyclization products of type **2** were, however, not detected [5]. Hence, the photolyses of **6–8** were expected to give further information of the influence of various ε -substituents on the formation of products of type **2** and **4**. Furthermore, the OH group of **6** was thought to be in a strategic position for an intramolecular trapping of the intermediate cation proposed previously in the mechanism of the formation of **5** [3].

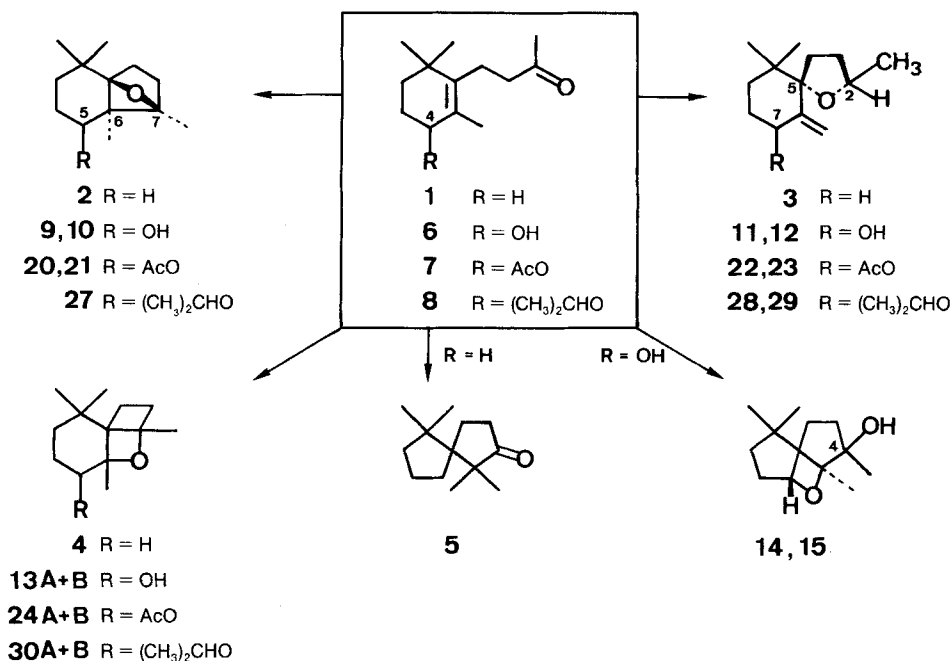
¹⁾ 148th Communication: see [1].

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⁴⁾ Numbering according to the carotenoid nomenclature [4].

Scheme 1



2. Preparation of 6–8. – Compound **6** was obtained by reduction of 4-hydroxy- β -ionone [**6**] with Ph₃SnH [**7**] (80%). Acetylation (Ac₂O/pyridine) of **6** afforded **7** (92%), and the reaction of **6** with *i*-PrOH and TsOH gave **8** (87%).

3. Photolyses of 6–8. – The results are given in *Tables 1–3*, and the products are shown in *Schemes 1* and *2*.

Scheme 2

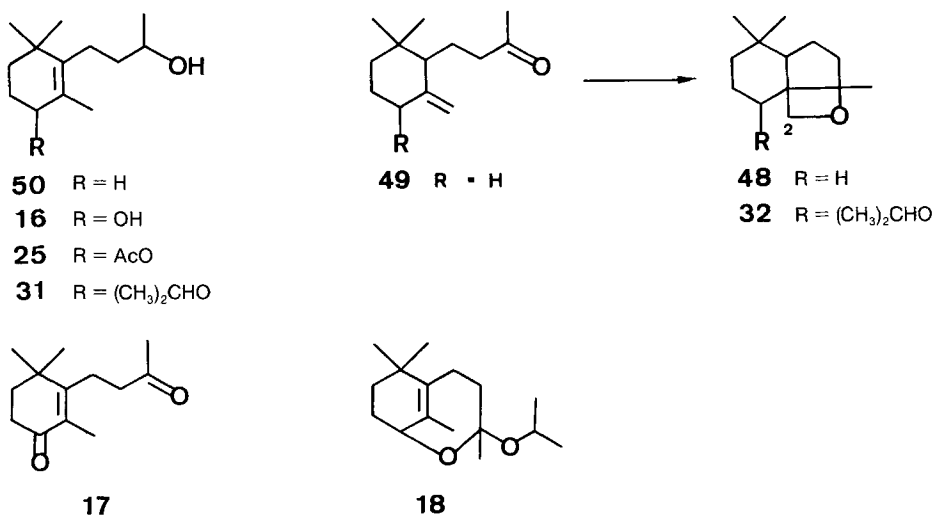


Table 1. Results of the Photolyses of **6** ($\lambda > 245$ nm)

Solvent	Temp. [°C]	Conversion [%]	Product distribution [%] ^{a)}										
			9	10	11 + 12 ^{b)}	13A ^{c)}	13B ^{c)}	14	15	16	17	18	19
MeCN	25	85	5	5	6	19	13	5	5	–	12	–	–
MeCN	–35	85	–	–	–	–	–	15	9	–	4	–	2
i-PrOH	25	90	1	1	9	18	12	–	–	3	–	27	7
i-PrOH ^{d)}	25	95	7	5	5	16	10	5	6	–	–	–	–
i-PrOH ^{d)}	–45	90	–	–	1	–	–	26	11	–	–	–	–
i-PrOH ^{d)}	–65	75	–	–	1	–	–	20	8	–	–	–	–

^{a)} Yields were determined, after CC on SiO₂, by ¹H-NMR and GC of the fractions and are based on converted starting material.

^{b)} Ca. 3:2 mixture.

^{c)} The terms **A** and **B** indicate diastereoisomers whose configurations were not assigned conclusively.

^{d)} In the presence of Na₂CO₃.

Table 2. Results of the Photolyses of **7** ($\lambda > 245$ nm, i-PrOH^{a)})

Temp. [°C]	Conversion [%]	Product distribution [%] ^{b)}						
		20	21	22 + 23 ^{c)}	24A ^{d)}	24B ^{d)}	25	26
25	95	7	5	3	18	5	4	–
–65	83	4	8	2	3	–	5	7

^{a)} In the presence of Na₂CO₃.

^{b)} Yields were determined, after CC on SiO₂, by ¹H-NMR and GC of the fractions and are based on converted starting material.

^{c)} Ca. 3:2 mixture.

^{d)} The terms **A** and **B** indicate diastereoisomers whose configurations were not assigned conclusively.

Table 3. Results of the Photolyses of **8** ($\lambda > 245$ nm, i-PrOH^{a)})

Temp. [°C]	Conversion [%]	Product distribution [%] ^{b)}						
		27	28	29	30A ^{c)}	30B ^{c)}	31	32
25	83	12	5	4	32	7	10	–
–65	85	13	6	1	5	1	9	1

^{a)} In the presence of Na₂CO₃.

^{b)} Yields were determined, after CC on SiO₂, by ¹H-NMR and GC of the fractions and are based on converted starting material.

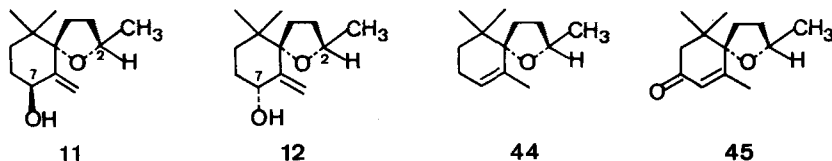
^{c)} The terms **A** and **B** indicate diastereoisomers whose configurations were not assigned conclusively.

4. Structure of the Products. – The structures of all new photoproducts were deduced from their spectral data. Since most of the products obtained are analogs of known compounds formed on photolysis of **1** [2] [3], only the most relevant spectral data are discussed below, together with decisive chemical transformations which confirmed the assigned structures. For full spectral data and the NMR assignments, see *Exper. Part*.

10-Oxatricyclo[5.2.1.0^{1,6}]decanes **9**, **10**, **20**, **21**, and **27** (cf. Scheme 1). These compounds show ¹H- and ¹³C-NMR signals similar to **2**. Oxidation of the alcohols **9** and **10** to the ketone **33** (Scheme 3) proves that **9** and **10** are epimers at C(5). Analogous to **2**, the tricyclic ethers **9**, **10**, **20**, **21**, and **27** are acid-sensitive. Thus, on treatment

of **10**, **20**, **21**, and **27** with HCl in CCl_4 , the bicyclic alcohols **19**, **26**, **34**, and **35**, corresponding to **36** [2], were obtained. Surprisingly, however, treatment of **9**, a diastereoisomer of **10**, under the same conditions gave – via elimination of H_2O – the bicyclic diene alcohol **37** (cf. Scheme 3; UV: $\lambda = 262 \text{ nm}$, $\epsilon = 2360$). It is noteworthy that **2** undergoes acid-catalyzed rearrangement involving 1,2-migration of a geminal Me group leading to the tricyclic ether **38** [3] (cf. Scheme 3), whereas on treatment of **9**, **10**, **20**, **21**, and **27** with acid, the corresponding isomers of structure **39–41** were not detected. To confirm the assigned structure and, in particular, to determine the relative configuration, **9** was transformed to the carbamate **42** which was subjected to X-ray analysis (see below).

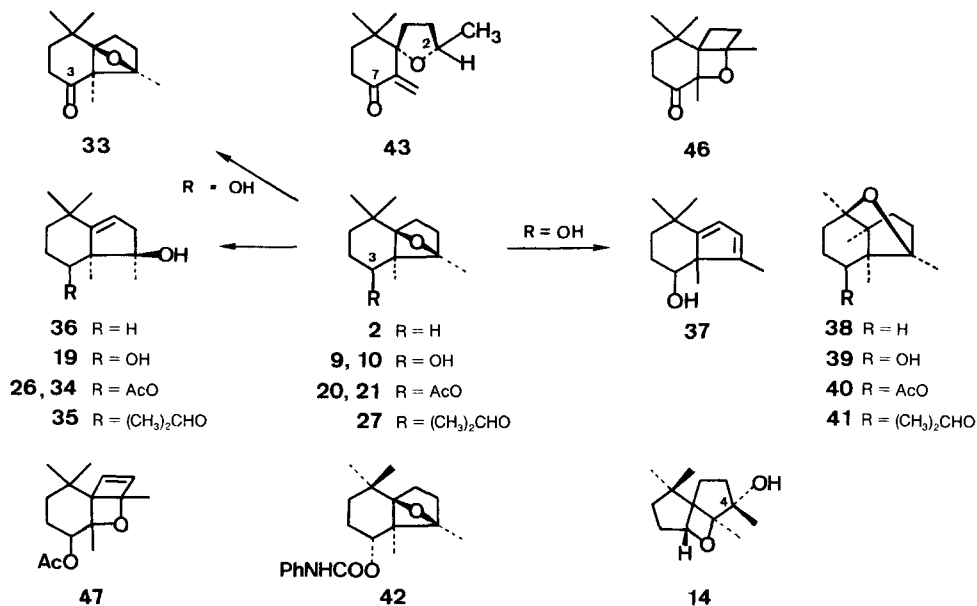
1-Oxaspiro[4.5]decanes 11, 12, 22, 23, 28, and 29 (Scheme 1). The structures were derived by comparison of the spectra with those of **3** [8]. As shown by oxidation of **11** and **12** to the enone **43** (Scheme 3), **11** and **12** and – due to the similarity of their spectra – also **22** and **23** as well as **28** and **29** are pairs of epimers at C(7) with the same relative configuration at C(2). The relative configuration at C(2) could finally be assigned by comparison of the $^1\text{H-NMR}$ spectra of the alcohols **11** and **12** with published data for **11** [9], which had been previously correlated with the natural products theaspirane A (**44**) and theaspirone A (**45**), respectively, of known configuration [9].



2-Oxatricyclo[4.4.0.0^{3,6}]decanes 13A + B, 24A + B, and 30A + B (Scheme 1). The structures were assigned by comparison of their spectra with those of **4**. The epimers **13A** and **13B** were oxidized to the ketone **46** as well as acetylated leading to **24A** and **24B**, respectively. Furthermore, the acetate **24A** was obtained by catalytic hydrogenation of **47** (Scheme 3), the acetate of a photocyclization product of 4-hydroxy- β -ionone [10].

2-Oxatricyclo[5.3.0.0^{3,7}]decanols 14 and 15 (Scheme 1). The finding that compounds **14** and **15** were not oxidized with chromium reagents (PCC [11] and $\text{CrO}_3/\text{pyridine}$ [12]) indicated that they could be tertiary alcohols. On the basis of the spectra, the structures could, however, not be assigned conclusively. Therefore, **14** (Scheme 3) was subjected to X-ray analysis (see below). On the basis of the aforementioned similarity of their properties, it is most likely that **15** is an epimer of **14** at C(4).

Scheme 3



Bicyclic Acetal 18 (Scheme 2). The proposal for this structure is based on the similarity of its NMR spectra with those of the ketones **6** and **8**. The hydrolysis of the acetal **18**→**6** could, however, not be achieved. Even under very mild conditions (oxalic acid/dioxane/H₂O/r.t.) only unspecific decomposition of **18** was observed.

The 3-Oxatricyclo[5.4.0.0^{1,4}]undecane **32** (Scheme 2) yields spectral data similar to that of the analogous compound **48** [2] (a photoproduct of dihydro- γ -ionone (**49**), see Scheme 2) without an i-PrO substituent. Particularly characteristic are in the ¹H-NMR the AB system at 3.95 ppm ($J = 7$ Hz) of 2 H–C(2) and in the MS the loss of CH₂O ($M^+ - 30$).

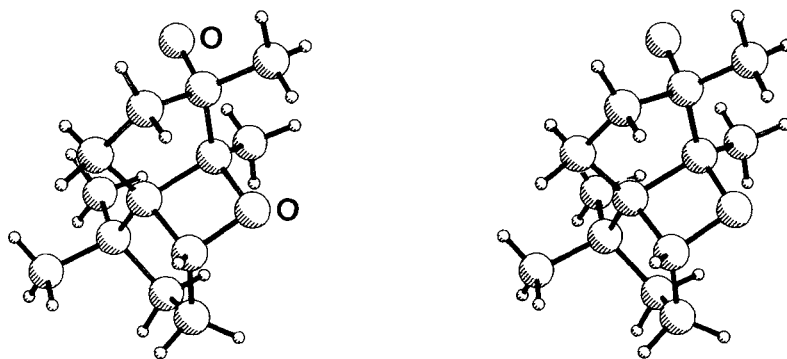


Fig. 1. Stereoview of the molecule **14** drawn by PLUTO 78 [16]

X-Ray Analyses of 14 and 42. – The crystallographic data concerning intensity measurements and the final R values are given in Table 4. Intensity measurements were carried out at room temperature with an *Enraf-Nonius CAD4* diffractometer (graphite monochromator, MoK α radiation $\lambda = 0.7107$ Å). The structures were solved by direct methods with SHELX76 [13] and refined by full-matrix-least-squares⁵⁾ analysis (SHELX [13], XRAY-72 [14]). H-atoms were located at an intermediate stage and included in the refinement with isotropic vibrational parameters (other atoms anisotropic⁶⁾).

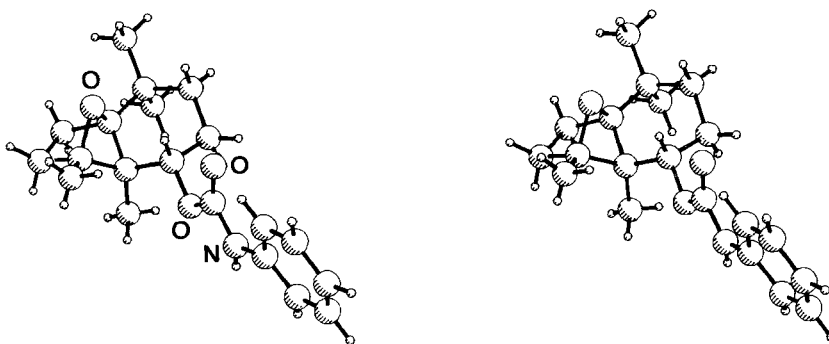


Fig. 2. Stereoview of the molecule **42** drawn by PLUTO 78 [16]

⁵⁾ The weighting schemes $\sigma^{-2}(F)$ and $\sigma^{-1}(F_o) \exp(5 \cdot \sin^2\theta/\lambda^2)$ were used for the refinement [15].

⁶⁾ Atomic parameters have been deposited with the Cambridge Crystallographic Data Centre, Lensfield Road, Cambridge CB2 1EW, England.

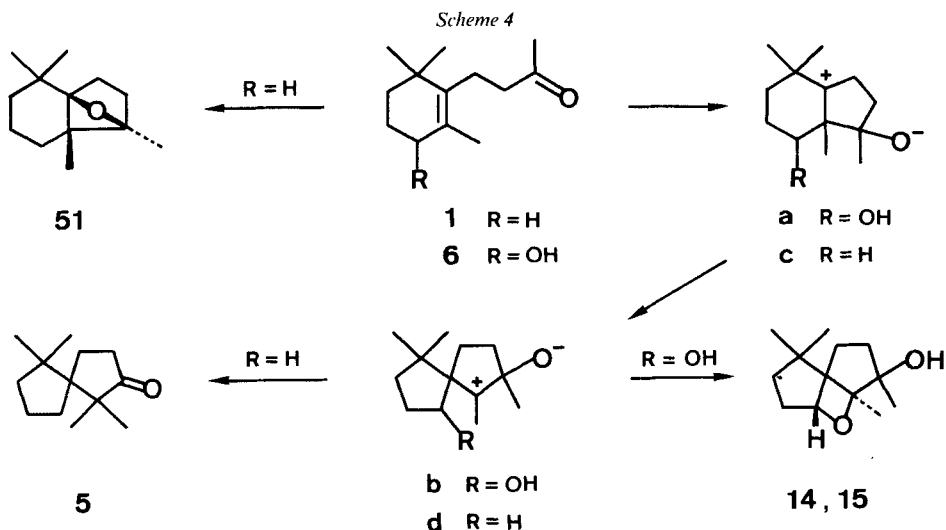
Table 4. Crystallographic and Experimental Data of the X-Ray Analyses of **14** and **42**

Compound	14	42	Compound	14	42
Space group	<i>Pbca</i>	<i>P2₁/n</i>	Reflections measured	2150	3282
<i>a</i> [Å]	11.55	7.54	Reflections of <i>I</i> > 3 σ _{<i>I</i>}	1067	1788
<i>b</i> [Å]	12.84	17.03	<i>R</i>	0.039	0.043
<i>c</i> [Å]	16.48	14.60	<i>R</i> _w	0.040	0.044
α [°]	90	90			
β [°]	90	93.067			
γ [°]	90	90			
<i>Z</i>	8	4			

5. Discussion. – As mentioned in the *Introduction*, the present investigation was undertaken to study the influence of an OH, an AcO, or an *i*-PrO group in ε -position of γ,δ -unsaturated ketones of the ionone series on their photochemical behaviour. Thus, the results of the photolyses of compounds **6–8** (*Scheme 1*) were compared with each other and with those previously reported for **1** [2] [3]. Irradiation ($\lambda > 245$ nm) of the hydroxy ketone **6** in MeCN or *i*-PrOH at temperatures between 25° and –65° leads to the tricyclic ethers **9**, **10**, and **13A + B**, the spirocyclic ethers **11** and **12** (*Scheme 1*), and to the reduction product **16** (*Scheme 2*), which are all known types of products (*cf.* **2**, **3**, and **4**, *Scheme 1*, and **50**, *Scheme 2*), previously obtained on photolysis of 7,8-dihydro- β -ionone (**1**) [2] [3]. The same types of photoprocesses were observed on irradiation of the acetate **7** ($\rightarrow$ **20–25**) and the isopropyl ether **8** ($\rightarrow$ **27–31**). The ε -substituents, however, had an interesting temperature effect on the regioselectivity of the *Paterno-Büchi* reaction. Thus, as for acyclic ε -hydroxy- γ,δ -unsaturated ketones [5], the tricyclic ethers **13A + B**, **24A + B**, and **30A + B** are formed on photolysis of **6**, **7**, and **8**, respectively, in MeCN or *i*-PrOH at room temperature already. On the other hand, the corresponding compound **4** was isolated on photolysis of **1** in *i*-PrOH only between –7° and –65°, and it could not be detected on irradiation of **1** in MeCN.

It is noteworthy that on photolysis of **6**, **7**, and **8** the tricyclic ethers **9** and **10**, **20** and **21**, and **27**, respectively, the products of the alternative *Paterno-Büchi* reaction, are also obtained, whereas according to published reports [5], irradiation of acyclic ε -hydroxy- γ,δ -unsaturated ketones did not give rise to the formation of such type of compounds. The aforementioned tricyclic ethers correspond to compound **2** (*Scheme 1*) and have the same relative configuration at C(6) and C(7). The tricyclic ether **2** was the minor and less stable diastereoisomer, obtained on photolysis of **1**, together with **51** (*Scheme 4*). On photolysis of the ε -O-substituted ketones **6**, **7**, and **8**, however, diastereoisomeric tricyclic ethers corresponding to **51** were not detected, which may be interpreted as due to steric effects of the ε -substituents.

The new tricyclic tertiary alcohols **14** and **15** are formed as the major products on irradiation of the hydroxy compound **6** in MeCN or *i*-PrOH between –35° and –65° (see *Table 1*). Their formation may be indeed explained by an intramolecular trapping of a carbocation by the ε -OH group. Thus, excitation of **6** may lead to the intermediate **a** (*Scheme 4*) which subsequently undergoes rearrangement to **b**. The latter carbocation may then be trapped by the neighbouring OH group furnishing the diastereoisomers **14** and **15**. The corresponding intermediates **c** and **d** have previously been proposed for the transformation of **1** $\rightarrow$ **5** (*Scheme 4*) [3]. With the isolation of **14** and **15** the suggested mechanism should be substantiated. Thus, in the absence of the OH group, the inter-



mediate **d** undergoes a 1,2 Me shift, a process suppressed in **b** by the rapid intramolecular trapping of the carbocation by the neighbouring OH group.

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Experimental Part

General. See [17], except as noted below. In general, photolyses were carried out using a 125-W Hg medium-pressure lamp behind a quartz cooling finger [17]; for a description of the low-temperature photolysis apparatus, see [3]. Anal. GC was performed using a 25 m $\times$ 0.33 mm UCON HB-5100 glass capillary. Column chromatographies (CC) were carried out on silica gel (SiO₂) 60 Merck, 0.040–0.063 mm, 230–400 mesh ASTM according to [18]. Anal. pure samples were obtained, in general, after repeated CC. All UV spectra were taken in MeCN solns. ¹H-NMR spectra were recorded on a Varian HA-100 instrument (100 MHz) in CCl₄ solns. or, exceptionally (as indicated below), in CDCl₃ solns. and, in some cases, on a Bruker WP-80/CW (80 MHz) instrument in CDCl₃ solns.

1. Preparation of 6–8. – 1.1. 7,8-Dihydro-4-hydroxy- β -ionone (**6**). A soln. of 4-hydroxy- β -ionone [**6**] (1.27 g, 6.11 mmol) and Ph₃SnH [**7**] (6.50 g, 18.5 mmol) in abs. benzene (50 ml) was heated under reflux for 4 d. To the cold soln., MeOH (100 ml) was added, the mixture was stirred at r.t. for 4 h and filtered through Celite. CC (600 g SiO₂, hexane/Et₂O 1:4) afforded **6** (1.02 g, 80%).

4-(3'-Hydroxy-2',6',6'-trimethyl-1'-cyclohexen-1'-yl)-2-butanone (**6**). B.p. 120°/0.06 Torr. UV (1.895 mg in 2 ml): 282 (30). IR: 3610w, 3480w (br.), 2960s, 2940s, 2910m (sh), 2860m, 1718s, 1470m, 1450w, 1435w, 1410w, 1380w (sh), 1370m (sh), 1360m, 1305w, 1275w (br.), 1225w (br.), 1200w, 1160m, 1065w (br.), 1035m, 1010m, 995m, 960w, 925w (br.), 900w, 870w. ¹H-NMR: 0.94, 1.00 (2s, 2 CH₃-C(6')); 1.64 (s, CH₃-C(2')); 2.03 (s, 3 H-C(1)); 1.10–1.90 (m, OH, 2 H-C(4'), 2 H-C(5')); 2.05–2.60 (m, 2 H-C(3), 2 H-C(4)); 3.62–3.85 (m, H-C(3')). ¹³C-NMR: 16.7, 27.0, 28.3, 29.7 (4q, C(1), CH₃-C(2'), 2 CH₃-C(6')); 22.3, 28.6, 34.6, 43.8 (4t, C(3), C(4), C(4'), C(5')); 69.7 (d, C(3')); 35.4 (s, C(6')); 129.8, 140.4 (2s, C(1'), C(2')); 208.7 (s, C(2)). MS: 210 (0.5, M⁺, C₁₃H₂₂O₂), 192 (38), 177

(12), 152 (48), 139 (15), 137 (10), 136 (32), 135 (11), 134 (17), 122 (18), 121 (59), 120 (14), 119 (100), 111 (33), 109 (12), 107 (38), 105 (18), 95 (16), 93 (32), 91 (25), 79 (16), 77 (16), 69 (12), 67 (10), 55 (15), 53 (11), 43 (69), 41 (24). Anal. calc. for $C_{13}H_{22}O_2$ (210.32): C 74.24, H 10.54; found: C 74.25, H 10.64.

1.2. Transformation of **6** to **7**. A mixture of **6** (7.69 g, 36.6 mmol), pyridine (40 ml), Ac_2O (20 ml), and 4-(dimethylamino)pyridine was stirred at r.t. for 2 h. Workup in Et_2O by washing with aq. $CuSO_4$ soln. and CC (600 g SiO_2 , hexane/ Et_2O 1:3) gave **7** (8.50 g, 92%).

2,4,4-Trimethyl-3-(3'-oxo-1'-butyl)-2-cyclohexen-1-yl Acetate (**7**). B.p. $90^\circ/0.01$ Torr. M.p. $52-53^\circ$. UV (1.947 mg in 10 ml): 279 (130). IR: 2960m, 2940m, 2865w, 1735s, 1720s, 1470w, 1450w, 1430w, 1410w, 1370m, 1240s, 1230s (sh), 1160m, 1150w, 1010m, 990w (sh), 960m, 930w, 870w. 1H -NMR: 0.96, 1.02 (2s, 2 $CH_3-C(4)$); 1.52 (s, $CH_3-C(2)$); 1.94 (s, CH_3-COO); 2.03 (3 H-C(4')); 1.20–2.60 (m, 2 H-C(5), 2 H-C(6), 2 H-C(1'), 2 H-C(2')); 5.00 (m, with t character, $J = 4$, H-C(1)). ^{13}C -NMR: 16.4, 21.3, 26.8, 28.2, 29.7 (5q, $CH_3-C(2)$, 2 $CH_3-C(4)$, C(4'), CH_3-COO); 22.3, 25.4, 34.8, 43.6 (4t, C(5), C(6), C(1'), C(2')); 72.4 (d, C(1)); 35.4 (s, C(4)); 125.9, 143.4 (2s, C(2), C(3)); 170.8 (s, COO); 207.7 (s, C(3')). MS: 192 (39, $M^+ - AcOH$), 177 (16), 149 (11), 136 (52), 134 (15), 122 (29), 121 (76), 119 (84), 107 (72), 105 (24), 95 (18), 93 (48), 91 (38), 79 (25), 77 (22), 60 (26), 55 (16), 53 (13), 45 (35), 43 (100), 41 (30). Anal. calc. for $C_{15}H_{24}O_3$ (252.35): C 71.39, H 9.59; found: C 71.21, H 9.72.

1.3. Transformation of **6** to **8**. A soln. of **6** (2.67 g, 12.6 mmol) and $TsOH \cdot H_2O$ (2.4 g, 12.6 mmol) in *i*-PrOH (150 ml) was stirred at r.t. for 3 h. Workup of the mixture in Et_2O by washing with aq. $NaHCO_3$ soln. and CC (270 g SiO_2 , hexane/ Et_2O 4:1) yielded **8** (2.76 g, 87%).

4-(3'-Isopropoxy-2',6',6'-trimethyl-1'-cyclohexen-1'-yl)-2-butanone (**8**). B.p. $90^\circ/0.01$ Torr. UV (5.312 mg in 10 ml): 284 (35). IR: 2960s, 2930s, 2860s, 1715s, 1465m, 1450m, 1435m (sh), 1410m, 1380m, 1360s, 1345m, 1315m, 1270w (br.), 1230w, 1200w, 1175m, 1155s, 1140s, 1120s, 1065m, 1040s, 1020s, 1000m, 980m, 940w, 915w, 895w, 880w. 1H -NMR: 0.92, 0.99 (2s, 2 $CH_3-C(6')$); 1.09 (d, $J = 6$, $(CH_3)_2CH$); 1.57 (s, $CH_3-C(2')$); 2.02 (s, 3 H-C(1)); 0.8–2.6 (m, 2 H-C(3), 2 H-C(4), 2 H-C(4'), 2 H-C(5')); 3.30–3.46 (m, H-C(3')); 3.54 (sept., $J = 6$, $(CH_3)_2CH$). ^{13}C -NMR: 16.7, 22.1, 23.9, 26.9, 28.3, 29.6 (6q, C(1), $CH_3-C(2')$, 2 $CH_3-C(6')$, $(CH_3)_2CH$); 22.3, 25.2, 34.8, 43.8 (4t, C(3), C(4), C(4'), C(5')); 69.8 (d, C(3')); 75.2 (d, $(CH_3)_2CH$); 35.4 (s, C(6')); 128.6, 140.8 (2s, C(1'), C(2')); 207.6 (s, C(2)). MS: 252 (1, M^+ , $C_{16}H_{28}O_2$), 194 (27), 192 (28), 177 (14), 154 (11), 152 (33), 149 (13), 138 (31), 136 (32), 135 (16), 134 (13), 133 (11), 122 (11), 121 (60), 119 (82), 111 (32), 109 (12), 107 (51), 105 (24), 95 (20), 93 (39), 91 (35), 81 (12), 79 (25), 77 (22), 69 (15), 67 (12), 55 (20), 53 (14), 46 (61), 43 (100), 41 (41). Anal. calc. for $C_{16}H_{28}O_2$ (252.40): C 76.14, H 11.18; found: C 76.00, H 11.02.

2. Photolyses. – 2.1. Photolysis of **6**. 2.1.1. In *MeCN* at 25° . A soln. of **6** (3.0 g, 14.3 mmol) in *MeCN* (300 ml) was irradiated (85% conversion). CC (500 g SiO_2 , hexane/ Et_2O 1:3) followed by CC of the fractions (pentane/DME 15:1 and $AcOEt/CH_2Cl_2$ /pentane 1:1:1) yielded the following compounds⁷: **9** (5%), **10** (5%), **11** + **12** (6%), **13A** (19%), **13B** (13%), **14** (5%), **15** (5%), **17** (12%), and intractable material.

2.1.2. In *MeCN* at -35° . A soln. of **6** (2.86 g, 13.6 mmol) in *MeCN* (300 ml) was irradiated (85% conversion). CC (340 g SiO_2 , hexane/ Et_2O 1:3) followed by CC of the fractions (pentane/DME 15:1, hexane/ Et_2O 1:1, and hexane/ Et_2O 2:1) gave the following compounds: **14** (15%), **15** (9%), **17** (4%), **19** (2%) and intractable material.

2.1.3. In *i*-PrOH at 25° . A soln. of **6** (3.30 g, 15.7 mmol) in *i*-PrOH (350 ml) was irradiated (90% conversion). The mixture was separated by CC as described in Sect. 2.1.1 giving the following products⁷: **9** (1%), **10** (1%), **11** + **12** (9%), **13A** (18%), **13B** (12%), **16** (3%)⁸, **18** (27%), **19** (7%), and intractable material.

2.1.4. In *i*-PrOH at 25° in the Presence of Na_2CO_3 . A soln. of **6** (1.09 g, 5.19 mmol) in *i*-PrOH (120 ml) was irradiated (95% conversion) in the presence of solid Na_2CO_3 (100 mg). Separation of the mixture by CC as described in Sect. 2.1.1 gave the following product distribution⁷: **9** (7%), **10** (5%), **11** + **12** (5%), **13A** (16%), **13B** (10%), **14** (5%), **15** (6%), and intractable material.

2.1.5. In *i*-PrOH at -45° in the Presence of Na_2CO_3 . A soln. of **6** (3.03 g, 14.5 mmol) in *i*-PrOH (350 ml) was irradiated (90% conversion) in the presence of solid Na_2CO_3 (1 g). Separation of the mixture by CC as described in Sect. 2.1.1 gave the following product distribution⁷: **11** + **12** (1%), **14** (26%), **15** (11%), an alcohol of unknown structure (8%), and intractable material.

2.1.6. In *i*-PrOH at -65° in the Presence of Na_2CO_3 . A soln. of **6** (3.34 g, 15.85 mmol) in *i*-PrOH (350 ml) was irradiated (75% conversion) in the presence of solid Na_2CO_3 (1.10 g). Separation of the mixture by CC as described in Sect. 2.1.1 gave the following product distribution⁷: **11** + **12** (1%), **14** (20%), **15** (8%), an alcohol of unknown structure (7%), and intractable material (mainly polymers).

⁷) Yields were determined, after CC on SiO_2 , by 1H -NMR and GC of the fractions and are based on converted starting material.

⁸) The diol **16** was obtained as a ca. 1:1 mixture with **19**, which could not be separated. After Collins oxidation of this mixture, the diketone **17** could be separated from the ketone corresponding to **19**.

(1RS,5RS,6RS,7RS)-2,2,6,7-Tetramethyl-10-oxatricyclo[5.2.1.0^{1,6}]decan-5-ol (9). M.p. 83–85° (hexane). IR: 3620w, 3460w (br.), 2960s, 2940s, 2920s (sh), 2860m, 1465m (sh), 1450m, 1435w (sh), 1380s, 1360m, 1300w, 1275w, 1225w, 1190w, 1160w, 1150w, 1130w, 1100w, 1085m, 1070m, 1045m, 1000m, 990m, 920w, 900w, 880m. ¹H-NMR (CDCl₃): 0.77, 0.80, 0.84, 1.30 (4s, 4 CH₃); 1.20–1.90 (m, 4 CH₂, OH); 4.36–4.62 (m, H–C(5)). ¹³C-NMR: 10.6, 15.4, 23.0, 23.3 (4q, 4 CH₃); 27.3, 27.9, 32.6, 37.0 (4t, C(3), C(4), C(8), C(9)); 69.4 (d, C(5)); 32.2 (s, C(2)); 53.2 (s, C(6)); 90.2, 97.6 (2s, C(1), C(7)). MS: 210 (1, M⁺, C₁₃H₂₂O₂), 192 (10), 182 (28), 154 (13), 153 (13), 152 (55), 149 (12), 139 (32), 137 (17), 136 (17), 135 (16), 125 (11), 124 (17), 123 (15), 121 (26), 119 (17), 111 (75), 110 (14), 109 (26), 108 (12), 107 (20), 105 (10), 98 (17), 97 (19), 96 (23), 95 (36), 94 (34), 93 (31), 91 (16), 83 (11), 81 (18), 79 (18), 77 (15), 71 (17), 69 (20), 67 (25), 55 (34), 53 (17), 43 (100), 41 (51). Anal. calc. for C₁₃H₂₂O₂ (210.32): C 74.24, H 10.54; found: C 74.07, H 10.63.

(1RS,5SR,6RS,7RS)-2,2,6,7-Tetramethyl-10-oxatricyclo[5.2.1.0^{1,6}]decan-5-ol (10). B.p. 50°/0.04 Torr. IR: 3490m (br.), 2960s, 2940s, 2930s, 2860m, 1465m (sh), 1460m (br.), 1435m, 1410m, 1380m, 1360m, 1300m, 1290m, 1250w, 1200w, 1170w, 1145w, 1130w (sh), 1110w, 1085m, 1050m, 1030m, 1010m, 965w, 950w, 900w, 870w, 855w. ¹H-NMR: 0.69, 0.82, 0.88, 1.50 (4s, 4 CH₃); 1.0–2.0 (m, 4 CH₂); 3.76 (br. AB system, J = 11, δ_A = 3.69, H–C(5), δ_B = 3.83, OH). ¹³C-NMR: (ca. 90% pure): 16.4, 17.1, 23.7, 23.9 (4q, 4 CH₃); 26.4, 26.5, 30.4, 34.3 (4t, C(3), C(4), C(8), C(9)); 72.2 (d, C(5)); 32.3 (s, C(2)); 51.5 (s, C(6)); 92.6, 99.5 (2s, C(1), C(7)). MS: 210 (2, M⁺, C₁₃H₂₂O₂), 192 (58), 177 (21), 159 (31), 149 (52), 139 (23), 137 (24), 136 (41), 135 (46), 123 (45), 121 (57), 119 (29), 111 (43), 110 (27), 109 (42), 108 (23), 107 (50), 95 (37), 94 (25), 93 (61), 91 (26), 88 (23), 81 (28), 79 (28), 77 (18), 69 (28), 67 (27), 55 (33), 43 (100), 41 (40). Anal. calc. for C₁₃H₂₂O₂ (210.32): C 74.24, H 10.54; found: C 74.16, H 10.72.

(2RS,7RS)-2,10,10-Trimethyl-6-methylidene-1-oxaspiro[4.5]decan-7-ol (11). B.p. 70°/0.005 Torr. IR: 3620m, 3470w (br.), 3100w, 2970s, 2940s, 2930s (sh), 2890m, 2870s, 1640w, 1470m, 1455m, 1445m (sh), 1380m, 1360m, 1285w (br.), 1225w (br.), 1195w, 1170w, 1150w, 1120m, 1085s, 1055m, 1035m (sh), 1025m, 990m (sh), 980m, 960w, 935w, 920m, 910m, 870w. ¹H-NMR: 0.78, 0.87 (2s, 2 CH₃–C(10)); 1.10–2.20 (m, 4 CH₂); 1.14 (d, J = 6, CH₃–C(2)); 1.39 (m, w_{1/2} = 5, OH); 3.83 (ddd, J = 6, H–C(2)); 4.24–4.48 (m, H–C(7)); 4.83, 5.09 (2m, w_{1/2} = 3, CH₂=C(6)). ¹³C-NMR: 21.1, 23.6 (3q, 2q overlapping at 23.6, 3 CH₃); 28.3, 32.2, 33.2, 34.7 (4t, C(3), C(4), C(8), C(9)); 106.6 (t, CH₂=C(6)); 70.7, 73.3 (2d, C(2), C(7)); 37.7 (s, C(10)); 90.1 (s, C(5)); 152.1 (s, C(6)). MS: 210 (15, M⁺, C₁₃H₂₂O₂), 195 (11), 193 (30), 181 (19), 177 (18), 168 (24), 165 (31), 163 (22), 154 (22), 153 (88), 150 (20), 141 (77), 140 (26), 139 (29), 137 (33), 126 (30), 125 (44), 121 (23), 112 (18), 111 (36), 110 (19), 109 (28), 107 (23), 101 (31), 98 (22), 97 (31), 95 (42), 93 (32), 91 (26), 85 (100), 83 (31), 81 (31), 79 (27), 77 (24), 70 (34), 69 (35), 67 (31), 56 (31), 55 (77), 53 (32), 43 (66), 41 (78). Anal. calc. for C₁₃H₂₂O₂ (210.32): C 74.24, H 10.54; found: C 74.29, H 10.65.

(2RS,7SR)-2,10,10-Trimethyl-6-methylidene-1-oxaspiro[4.5]decan-7-ol (12). B.p. 70°/0.01 Torr. IR: 3620w, 3600w (sh), 3470m (br.), 3080w, 2970s, 2940s (sh), 2930s, 2870s, 1645w, 1470m, 1455m, 1440m, 1385s, 1360m, 1330w, 1305w, 1285w (br.), 1240w, 1190w, 1155m, 1120m, 1095m, 1075s, 1040s, 1015s, 990m, 960w, 910w, 890w, 870w. ¹H-NMR: 0.80, 0.84 (2s, 2 CH₃–C(10)); 0.90–2.20 (m, 4 CH₂); 1.19 (d, J = 6, CH₃–C(2)); 2.00–2.50 (m, OH); 3.78–4.10 (m, H–C(2), H–C(7)); 4.93 (m, w_{1/2} = 5, CH₂=C(6)). ¹³C-NMR (ca. 90% pure): 20.7, 23.0, 23.6 (3q, 3 CH₃); 30.3, 31.7, 33.5, 33.8 (4t, C(3), C(4), C(8), C(9)); 106.4 (t, CH₂=C(6)); 72.9, 74.1 (2d, C(2), C(7)); 37.8 (s, C(10)); 90.6 (s, C(5)); 151.1 (s, C(6)). MS: 210 (13, M⁺, C₁₃H₂₂O₂), 193 (22), 181 (14), 177 (15), 168 (18), 165 (21), 163 (18), 154 (16), 153 (71), 150 (15), 141 (67), 140 (22), 139 (23), 137 (28), 126 (24), 125 (37), 121 (18), 112 (15), 111 (32), 110 (15), 109 (24), 107 (19), 101 (31), 98 (17), 97 (26), 95 (37), 93 (28), 91 (22), 85 (100), 83 (25), 81 (25), 79 (23), 77 (20), 70 (31), 69 (28), 67 (30), 56 (24), 55 (66), 53 (29), 43 (65), 41 (77).

1,3,7,7-Tetramethyl-2-oxatricyclo[4.4.0.0^{3,6}]decan-10-ol. Isomer A (13A). M.p. 169–171° (hexane). IR: 3610w, 3510s (br.), 2970s, 2940s, 2930s, 2870m, 1460m, 1440m, 1420w, 1385m, 1375s, 1365m, 1350w, 1330w, 1290m, 1230w (br.), 1155m, 1135m, 1100m, 1060m, 1030m, 975w, 910m, 875m, 860m, 840w. ¹H-NMR: 0.61, 0.96, 1.24, 1.40 (4s, 4 CH₃); 1.10–2.70 (m, 4 CH₂); 3.78 (d, J = 3, OH); 3.90–4.18 (m, H–C(10)). ¹³C-NMR: 15.2, 22.8, 23.7, 25.5 (4q, 4 CH₃); 21.6, 26.2, 34.0, 37.7 (4t, C(4), C(5), C(8), C(9)); 79.0 (d, C(10)); 33.0 (s, C(7)); 58.4 (s, C(6)); 90.5 (2s, overlapping, C(1), C(3)). MS: 210 (0.2, M⁺, C₁₃H₂₂O₂), 153 (16), 152 (69), 139 (44), 137 (17), 124 (19), 121 (20), 119 (16), 111 (66), 109 (26), 107 (14), 97 (13), 96 (11), 95 (20), 93 (22), 91 (11), 79 (13), 77 (11), 69 (13), 67 (17), 55 (21), 53 (12), 43 (100), 41 (31). Anal. calc. for C₁₃H₂₂O₂ (210.32): C 74.24, H 10.54; found: C 74.07, H 10.55.

Isomer B (13B). M.p. 57–60° (hexane). IR: 3500m (br.), 2960s, 2930s, 2870m, 1460m, 1450m, 1435m (sh), 1420s, 1390m, 1385m, 1370s, 1290m, 1240w, 1210w, 1160m, 1150m, 1100m, 1080m, 1065s, 1025m, 1000w, 970m (sh), 965m, 950w (sh), 910m, 870m, 845w. ¹H-NMR: 0.60, 0.94, 1.33, 1.38 (4s, 4 CH₃); 0.95–2.40 (m, 4 CH₂); 2.90 (m, w_{1/2} = 5, OH); 3.38–3.54 (m, H–C(10)). ¹³C-NMR: 22.1, 22.7, 23.9, 26.1 (4q, 4 CH₃); 19.8, 25.1, 32.0, 33.9 (4t, C(4), C(5), C(8), C(9)); 71.5 (d, C(10)); 31.6 (s, C(7)); 55.7 (s, C(6)); 84.7, 90.5 (2s, C(1), C(3)). MS: 210 (1, M⁺, C₁₃H₂₂O₂), 154 (10), 153 (17), 152 (63), 139 (45), 137 (16), 124 (20), 121 (22), 111 (70), 109 (24), 107 (17), 97 (14), 96 (10), 95 (21), 93 (24), 91 (12), 81 (14), 79 (12), 69 (14), 67 (16), 55 (19), 44 (11), 43 (100), 41 (25). Anal. calc. for C₁₃H₂₂O₂ (210.32): C 74.24, H 10.54; found: C 74.10, H 10.61.

(1RS,3SR,4SR,7SR)-3,4,8,8-Tetramethyl-2-oxatricyclo[5.3.0.0^{3,7}]decan-4-ol (**14**). M.p. 81–83° (hexane). IR: 3620m, 3450w (br.), 2960s, 2930s (sh), 2910s (sh), 2870m, 1470m, 1455m, 1440m (sh), 1430m (sh), 1385w, 1370m, 1335w, 1300w, 1210w, 1175m, 1155w, 1120w, 1090m, 1060m, 1045m, 1035m, 1020m (sh), 1010m, 960m, 940w, 925m, 915m, 895w, 870m. ¹H-NMR: 0.72, 1.03, 1.10, 1.30 (4s, 4 CH₃); 0.80–2.40 (m, 4 CH₂, OH); 4.26–4.38 (m, H–C(1)). ¹³C-NMR: 17.4, 20.0, 21.0, 27.4 (4q, 4 CH₃); 26.2, 31.6, 37.7, 40.4 (4t, C(5), C(6), C(9), C(10)); 87.1 (d, C(1)); 41.9 (s, C(8)); 63.9 (s, C(7)); 81.5, 94.3 (2s, C(3), C(4)). MS: 210 (1, M⁺, C₁₃H₂₂O₂), 167 (10), 149 (69), 139 (10), 123 (17), 121 (18), 109 (52), 107 (27), 97 (11), 95 (11), 93 (27), 91 (11), 88 (68), 81 (15), 79 (13), 77 (12), 71 (20), 69 (15), 67 (18), 55 (19), 53 (11), 43 (100), 41 (26). Anal. calc. for C₁₃H₂₂O₂ (210.32): C 74.24, H 10.54; found: C 74.07, H 10.46.

(1RS,3SR,4RS,7SR)-3,4,8,8-Tetramethyl-2-oxatricyclo[5.3.0.0^{3,7}]decan-4-ol (**15**). B.p. 60°/0.005 Torr. IR: 3540m, 3440w (br.), 2990s (sh), 2960s, 2935s (sh), 2870s, 1465m, 1450m, 1440m, 1430w, 1385s, 1375m, 1365m, 1355m, 1335m, 1310w, 1300w, 1270w (br.), 1225m, 1210m (sh), 1195s, 1175m, 1160m, 1145m (br.), 1120m, 1105w, 1085w, 1065m, 1035s, 1025m, 1000m, 980w, 960s, 940m, 925w, 910w, 900w, 855m, 840w. ¹H-NMR: 0.70, 0.92, 1.01, 1.16 (4s, 4 CH₃); 1.08–2.50 (m, 4 CH₂); 2.11 (m, w_{1/2} = 4, OH); 4.36–4.48 (m, H–C(1)). ¹³C-NMR: 18.0, 20.9, 22.1, 26.6 (4q, 4 CH₃); 25.3, 31.6, 38.6, 40.5 (4t, C(5), C(6), C(9), C(10)); 87.6 (d, C(1)); 41.8 (s, C(8)); 61.7 (s, C(7)); 79.0, 92.3 (4s, C(3), C(4)). MS: 210 (1, M⁺, C₁₃H₂₂O₂), 167 (10), 159 (25), 150 (10), 149 (81), 139 (10), 137 (10), 135 (14), 123 (18), 121 (18), 109 (54), 107 (29), 97 (12), 95 (20), 93 (28), 91 (10), 88 (77), 81 (16), 79 (11), 71 (21), 69 (14), 67 (18), 55 (14), 43 (100), 41 (16).

2,4,4-Trimethyl-3-(3'-oxobutyl)-2-cyclohexen-1-one (**17**). B.p. 90°/0.005 Torr. UV (0.167 mg in 10 ml): 245 (15800); (3.762 mg in 10 ml): 332 (20) (sh), end absorption to 380. IR: 2960m, 2920m, 2860w, 1720s, 1670s, 1610m, 1470w, 1440w (br.), 1420w, 1410w (sh), 1375w, 1360m (sh), 1350m, 1330m, 1310m, 1270w (br.), 1225w (br.), 1195w, 1160m, 1085w (br.), 1070w (br.), 1025w (br.), 995w. ¹H-NMR: 1.12 (2s, 2 CH₃–C(4)); 1.64 (s, CH₃–C(2)); 1.66–1.88 (m, 2 H–C(5)); 2.08 (s, 3 H–C(4')); 2.24–2.60 (m, 2 H–C(6), 2 H–C(1'), 2 H–C(2')). ¹³C-NMR (75 MHz): 11.4, 29.7 (2q, CH₃–C(2), C(4')); 26.7 (2q, 2 CH₃–C(4)); 24.0, 34.1, 37.3, 42.1 (4t, C(5), C(6), C(1'), C(2')); 36.4 (s, C(4)); 131.0 (s, C(2)); 163.3 (s, C(3)); 198.2 (s, C(1)); 206.7 (s, C(3')). MS: 208 (42, M⁺, C₁₃H₂₀O₂), 166 (13), 165 (100), 151 (18), 138 (16), 137 (59), 135 (38), 134 (15), 123 (38), 122 (10), 109 (50), 107 (37), 95 (17), 93 (21), 91 (23), 81 (21), 79 (25), 77 (19), 67 (23), 65 (11), 55 (23), 53 (19), 43 (86), 41 (36). Anal. calc. for C₁₃H₂₀O₂ (208.32): C 74.96, H 9.68; found: C 74.83, H 9.73.

3-Isopropoxy-3,7,7,10-tetramethyl-2-oxabicyclo[4.3.1]dec-6(10)-ene (**18**). B.p. 80°/0.01 Torr. IR: 2980s, 2930s (sh), 2910s, 2850s, 1480w (sh), 1460m, 1450m, 1435m (sh), 1400w, 1380s, 1360m, 1335w, 1325w, 1285w, 1270w, 1235w, 1190w, 1165m, 1140s, 1120s (sh), 1070s, 1055s, 1040s, 1010s, 990m, 955w, 935w, 910m, 890w, 860w. ¹H-NMR: 0.69, 1.00 (2s, 2 CH₃–C(7)); 1.05, 1.12 (2d, J = 6.5, (CH₃)₂CH); 1.62 (br. s, CH₃–C(10), CH₃–C(3)); 0.6–2.4 (m, 4 CH₂); 3.80 (sept., J = 6.5, (CH₃)₂CH); 4.40–4.60 (m, H–C(1)). ¹³C-NMR (ca. 90% pure): 12.4, 14.4, 22.2, 23.9, 24.5, 25.1 (6q, 6 CH₃); 28.8, 34.0, 36.1 (4t, 2t at 36.1, C(4), C(5), C(8), C(9)); 69.3 (d, (CH₃)₂CH); 96.5 (d, C(1)); 36.9 (s, C(7)); 93.6 (s, C(3)); 133.8, 135.1 (2s, C(6), C(10)). MS: 252 (0.1, M⁺, C₁₆H₂₈O₂), 192 (4), 174 (37), 160 (21), 159 (94), 144 (32), 143 (12), 136 (29), 135 (17), 131 (19), 129 (26), 128 (25), 121 (22), 119 (14), 117 (14), 115 (20), 111 (26), 105 (24), 91 (26), 86 (30), 79 (14), 77 (20), 67 (12), 65 (11), 58 (18), 55 (14), 53 (13), 51 (11), 45 (100), 43 (29), 41 (42). Anal. calc. for C₁₆H₂₈O₂ (252.40): C 76.14, H 11.18; found: C 76.26, H 10.98.

(5RS,6SR,7SR)-2,2,6,7-Tetramethylbicyclo[4.3.0]non-9-ene-5,7-diol (**19**). M.p. 109–111° (hexane). IR: 3610w, 3560w, 3300m (br.), 3050w, 2960s, 2925s, 2860s, 1460m (sh), 1450m, 1380m, 1360m, 1340m, 1290w (br.), 1260w, 1230w, 1200m, 1175m, 1155m, 1090m, 1070m, 1050m, 1020m, 1000m, 965m, 945w, 920w, 900m, 870w, 850m, 675m. ¹H-NMR: 0.92, 1.05, 1.14, 1.28 (4s, 4 CH₃); 1.35–1.95 (m, 2 H–C(3), 2 H–C(4)); 2.07 (dd, J = 16, 3, H–C(8)); 2.37 (dd, J = 16, 2, H–C(8)); 3.80–3.95 (m, H–C(5)); 3.6–5.2 (br. m, 2 OH); 5.36–5.44 (m, H–C(9)). ¹³C-NMR: 22.8, 30.7, 31.1 (4q, 2q at 22.8, 4 CH₃); 27.2, 32.8, 46.1 (3t, C(3), C(4), C(8)); 73.5 (d, C(5)); 119.4 (d, C(9)); 33.3 (s, C(2)); 53.0 (s, C(6)); 86.3 (s, C(7)); 154.6 (s, C(1)). MS: 193 (15), 192 (93, M⁺ – H₂O), 177 (18), 159 (30), 150 (12), 149 (87), 137 (34), 136 (83), 135 (87), 133 (16), 122 (24), 121 (100), 119 (40), 111 (10), 109 (14), 108 (22), 107 (72), 105 (27), 95 (27), 94 (16), 93 (59), 91 (36), 81 (26), 79 (27), 77 (24), 69 (36), 67 (16), 65 (12), 57 (12), 55 (31), 53 (16), 43 (95), 41 (47). Anal. calc. for C₁₃H₂₂O₂ (210.32): C 74.24, H 10.54; found: C 74.43, H 10.39.

2.2. Photolysis of **7**. 2.2.1. In *i*-PrOH at 25° in the Presence of Na₂CO₃. A soln. of **7** (2.25 g, 8.93 mmol) in *i*-PrOH (300 ml) was irradiated (95% conversion) in the presence of solid Na₂CO₃ (100 mg). Separation of the mixture by CC (320 g SiO₂, hexane/Et₂O 4:1) followed by further CC of the fractions (hexane/Et₂O 10:1, 4:1, and 1:1) yielded the following compounds⁹: **20** (7%), **21**⁹ (5%), **22** + **23** (3%), **24A** (18%), **24B** (5%), **25** (4%), and intractable material.

⁹ Compound **21** could only be obtained in ca. 60% purity; this mixture was treated with acid furnishing **34** (see Sect. 3.2.1.2).

2.2.2. In *i*-PrOH at -65° in the Presence of Na_2CO_3 . A soln. of **7** (1.42 g, 5.63 mmol) in *i*-PrOH (300 ml) was irradiated (83% conversion) in the presence of solid Na_2CO_3 (150 mg). Separation of the mixture by CC as described in Section 2.2.1 gave the following product distribution⁷: **20** (4%), **21**⁹ (8%), **22** + **23** (2%), **24A** (3%), **25** (5%), **26** (7%), and intractable material.

(1RS,2RS,3RS)-1,2,6,6-Tetramethyl-10-oxatricyclo[5.2.1.0^{2,7}]dec-3-yl Acetate (**20**). B.p. $50^\circ/0.01$ Torr. 2970s, 2950s, 2930m (sh), 2870m, 1740s, 1465m, 1455m (br.), 1440w, 1435w (sh), 1395w, 1380s, 1375m (sh), 1355m, 1305w, 1240s, 1225m (sh), 1190w, 1165m, 1155m, 1140w, 1100w (sh), 1090m, 1060m, 1040m, 1020m, 995m, 970m, 910w (br.), 885m. ¹H-NMR: 0.84, 0.90, 0.92, 1.13 (4s, 4 CH₃); 1.91 (s, CH₃COO); 0.90–2.10 (m, 4 CH₂); 5.40–5.62 (m, H–C(3)). ¹³C-NMR: 11.4, 14.7, 21.1, 22.9, 23.0 (5q, 5 CH₃); 24.1, 27.1, 32.4, 36.6 (4t, C(4), C(5), C(8), C(9)); 73.1 (d, C(3)); 32.1 (s, C(6)); 52.3 (s, C(2)); 89.6, 97.0 (2s, C(1), C(7)); 170.0 (s, COO). MS: 192 (16, $M^+ - \text{AcOH}$), 177 (13), 159 (11), 152 (57), 149 (32), 136 (19), 135 (14), 123 (13), 122 (10), 121 (42), 119 (28), 111 (15), 109 (13), 108 (14), 107 (28), 105 (12), 95 (18), 94 (14), 93 (33), 91 (15), 81 (12), 79 (14), 77 (10), 69 (17), 67 (14), 55 (19), 43 (100), 41 (28). Anal. calc. for C₁₅H₂₄O₃ (252.35): C 71.39, H 9.59; found: C 71.35, H 9.64.

2,10,10-Trimethyl-6-methylidene-1-oxaspiro[4.5]decan-7-yl Acetate (**22** + **23**; ca. 1:1 mixture). IR: 2970s, 2930s, 2870m, 1740s, 1720m, 1645w, 1460m (br.), 1385m, 1370m, 1360m, 1240s, 1160m, 1090m, 1030m, 910m. ¹H-NMR: 0.88 (d, $J = 7$, CH₃–C(2)); 0.90 (s, CH₃–C(10)); 0.96 (s, CH₃–C(10)); 2.07 (s, CH₃COO); 2.12 (s, CH₃COO); 0.75–2.75 (m, 16 H); 3.80–4.25 (m, H–C(2)); 4.82 (1 H), 5.02 (1 H), 5.07 (2 H) (3m, $w_{1/2} = 5$, CH₂=C(6)); 5.12–5.28, 5.43–5.72 (2m, H–C(7)).

1,3,7,7-Tetramethyl-2-oxatricyclo[4.4.0.0^{3,6}]dec-10-yl Acetate. Isomer A (**24A**). B.p. $70^\circ/0.01$ Torr. IR: 2960s, 2920s, 2860m, 1730s, 1455m, 1440m, 1420w, 1380m (sh), 1370s, 1360s, 1335w, 1320w, 1285m, 1240s, 1190m, 1155m, 1145m, 1115w, 1075m, 1055m, 1040m, 1020s, 1000m, 970m, 915m, 880m, 865w, 845w, 670w. ¹H-NMR: 0.63, 0.98, 1.26, 1.42 (4s, 4 CH₃); 1.98 (s, CH₃COO); 1.10–2.65 (m, 4 CH₂); 5.13 (dd, $J = 12, 4$, H–C(10)). ¹³C-NMR: 15.8, 21.2, 22.9, 23.6, 25.5 (5q, 5 CH₃); 21.4, 23.8, 34.0, 37.1 (4t, C(4), C(5), C(8), C(9)); 81.7 (d, C(10)); 32.8 (s, C(7)); 58.7 (s, C(6)); 86.6, 90.2 (2s, C(1), C(3)); 170.3 (s, CH₃–COO). MS: 192 (5, $M^+ - \text{AcOH}$), 153 (10), 152 (67), 149 (13), 139 (12), 121 (24), 119 (33), 111 (11), 109 (10), 107 (16), 93 (17), 91 (11), 79 (10), 55 (11), 43 (100), 41 (18). Anal. calc. for C₁₅H₂₄O₃ (252.35): C 71.39, H 9.59; found: C 71.30, H 9.44.

Isomer B (**24B**). B.p. $55^\circ/0.005$ Torr. IR: 2960s, 2930m, 2870w, 1740s, 1465w, 1455w (sh), 1450w, 1440w, 1420w, 1385m (sh), 1370s, 1365m (sh), 1290w, 1240s, 1195w, 1170w, 1160m, 1145m, 1110m, 1085m, 1045m, 1025m, 990w, 980w, 970w, 950w, 915m, 880w, 860w. ¹H-NMR: 0.65, 0.96, 1.34, 1.36 (4s, 4 CH₃); 1.98 (s, CH₃COO); 1.20–2.40 (m, 4 CH₂); 4.68–4.84 (m, H–C(10)). ¹³C-NMR: 21.3, 22.2, 25.2, 26.7 (5q, 2q at 22.2, 5 CH₃); 19.3, 23.1, 33.1, 33.9 (4t, C(4), C(5), C(8), C(9)); 74.1 (d, C(10)); 31.6 (s, C(7)); 56.3 (s, C(6)); 83.3, 89.0 (2s, C(1), C(3)); 170.7 (s, COO). MS: 192 (3, $M^+ - \text{AcOH}$), 152 (65), 149 (15), 139 (15), 121 (25), 119 (32), 111 (11), 109 (11), 107 (15), 93 (17), 91 (10), 79 (10), 67 (10), 55 (12), 43 (100), 41 (17). Anal. calc. for C₁₅H₂₄O₃ (252.35): C 71.39, H 9.59; found: C 71.22, H 9.60.

3-(3'-Hydroxy-1'-butyl)-2,4,4-trimethyl-2-cyclohexen-1-yl Acetate (**25**). B.p. $90^\circ/0.01$ Torr. IR: 3620w, 3450w (br.), 2960s, 2940s (sh), 2870m, 1730s, 1470w (sh), 1450w, 1370m, 1240s, 1230s (sh), 1170w (br.), 1140w (br.), 1110w (br.), 1015m, 995w (sh), 960m, 930w, 870w. ¹H-NMR: 0.97, 1.06 (2s, 2 CH₃–C(4)); 1.15 (d, $J = 6, 3$ H–C(4')); 1.56 (s, CH₃–C(2)); 1.96 (s, CH₃COO); 0.70–2.40 (m, 4 CH₂, OH); 3.69 (sext., $J = 6$, H–C(3')); 5.02 (m with t character, $J = 3$, H–C(1)). ¹³C-NMR: 16.6, 21.4, 23.4, 27.0, 28.5 (5q, 5 CH₃); 25.1, 25.4, 34.9, 39.1 (4t, C(5), C(6), C(1'), C(2')); 68.4, 72.9 (2d, C(1), C(3')); 35.3 (s, C(4)); 125.0, 144.5 (2s, C(2), C(3)); 171.3 (s, COO). MS: 194 (6, $M^+ - \text{AcOH}$); 149 (14), 139 (14), 138 (100), 135 (15), 123 (17), 121 (37), 120 (10), 119 (50), 109 (24), 107 (19), 105 (17), 96 (32), 95 (20), 93 (18), 91 (18), 83 (19), 82 (30), 81 (13), 79 (16), 77 (13), 69 (16), 67 (14), 60 (14), 59 (18), 57 (12), 55 (26), 45 (18), 43 (70), 41 (32). Anal. calc. for C₁₅H₂₆O₃ (254.37): C 70.83, H 10.30; found: C 70.91, H 10.28.

(1RS,2SR,9RS)-9-Hydroxy-1,5,5,9-tetramethylbicyclo[4.3.0]non-6-en-2-yl Acetate (**26**). B.p. $60^\circ/0.01$ Torr. IR: 3590m, 3470w (br.), 3050w, 2960s, 2940m, 2900m (sh), 2860m, 2840w, 1740s, 1455w (br.), 1385m, 1370m, 1360m (sh), 1345w, 1320w, 1255m (sh), 1240s (sh), 1230s, 1210m, 1175w, 1140w, 1095w, 1070w, 1040m, 1020m, 990w, 975w, 950w, 925w, 915w, 890w, 860w, 675w. ¹H-NMR: 1.02, 1.11, 1.16, 1.19 (4s, 4 CH₃); 1.92 (s, CH₃COO); 1.00–2.00 (m, 2 H–C(3), 2 H–C(4)); 2.18 (AB system, $J = 16$, $\delta_A = 2.08$, split into d , $J = 3$, $\delta_B = 2.19$, split into d , $J = 2$, 2 H–C(8)); 2.28–2.44 (m, OH); 5.03 (dd, $J = 6, 3$, H–C(2)); 5.45 (dd, $J = 3, 2$, H–C(7)). MS: 234 (10, $M^+ - \text{H}_2\text{O}$), 174 (23), 160 (14), 159 (100), 119 (17), 118 (17), 105 (10), 91 (14), 43 (38), 41 (10).

2.3. Photolysis of **8**. 2.3.1. In *i*-PrOH at 25° in the Presence of Na_2CO_3 . A soln. of **8** (2.52 g, 10.0 mmol) in *i*-PrOH (250 ml) was irradiated (83% conversion) in the presence of solid Na_2CO_3 (250 mg). CC of the mixture (340 g SiO₂, hexane/Et₂O 4:1) followed by CC of the fractions (hexane/Et₂O 20:1 to 1:1) yielded the following compounds⁷: **27** (12%), **28** (5%), **29** (4%), **30A** (32%), **30B** (7%), **31** (10%), and intractable material (mainly polymers).

2.3.2. *In i-PrOH at -65° in the Presence of Na₂CO₃*. A soln. of **8** (2.05 g, 8.13 mmol) in i-PrOH (250 ml) was irradiated (85% conversion) in the presence of solid Na₂CO₃ (250 mg). Separation of the mixture by CC as described in Section 2.3.1 gave the following product distribution: **27** (13%), **28** (6%), **29** (1%), **30A** (5%), **30B** (1%), **31** (9%), **32** (1%), and intractable material (mainly polymers).

(1RS,2RS,3RS,7RS)-1,2,6,6-Tetramethyl-10-oxatricyclo[5.2.1.0^{2,7}]dec-3-yl Isopropyl Ether (**27**). B.p. 80°/0.01 Torr. IR: 2970s, 2930s, 2870m, 1465m (sh), 1460m, 1455m, 1445m (sh), 1380s, 1360m, 1345w, 1330m, 1310w, 1305w (sh), 1270w, 1195w, 1175m (sh), 1160m, 1155m, 1120s, 1100m, 1090m, 1075s, 1060m (br.), 1035m, 1020s, 1005m, 990m, 925w (br.), 880m. ¹H-NMR: 0.68, 0.78, 1.21 (4s, 2s at 0.78, 4 CH₃); 1.09 (d, J = 6, (CH₃)₂CH); 0.80–1.90 (m, 4 CH₂); 3.68 (sept., J = 6, (CH₃)₂CH); 3.96–4.16 (m, H–C(3)). ¹³C-NMR (75 MHz, ca. 90% pure): 11.4, 15.8, 22.8, 23.1, 23.3, 23.8 (6q, 6 CH₃); 24.6, 27.3, 33.0, 37.0 (4t, C(4), C(5), C(8), C(9)); 68.7, 75.0 (2d, C(3), (CH₃)₂CH); 32.4 (s, C(6)); 53.8 (s, C(2)); 90.0, 97.4 (2s, C(1), C(7)). MS: 252 (3, M⁺, C₁₆H₂₈O₂), 192 (11), 191 (16), 177 (17), 176 (40), 162 (14), 161 (100), 159 (32), 147 (12), 139 (11), 136 (17), 135 (53), 133 (23), 123 (14), 121 (29), 120 (71), 119 (43), 117 (11), 107 (20), 105 (26), 93 (14), 91 (32), 81 (10), 79 (13), 77 (16), 69 (11), 57 (15), 55 (14), 45 (11), 43 (51), 41 (39). Anal. calc. for C₁₆H₂₈O₂ (252.40): C 76.14, H 11.18; found: C 76.02, H 11.08.

(2RS,7RS)-2,10,10-Trimethyl-6-methylidene-1-oxaspiro[4.5]dec-7-yl Isopropyl Ether (**28**). B.p. 60°/0.008 Torr. IR: 3090w, 2970s, 2930s, 2870m, 1640w, 1465m, 1450m, 1380m, 1365m, 1360m (sh), 1330w, 1320w, 1280w, 1230w (br.), 1200w, 1180w (sh), 1150m, 1120s, 1105m, 1090s, 1075m, 1065m, 1050s, 1035m, 1005m, 980m, 970w, 935w, 915m, 890w, 870w. ¹H-NMR: 0.79, 0.84 (2s, 2 CH₃C(10)); 1.07 (d, J = 6, (CH₃)₂CH); 1.14 (d, J = 6, CH₃–C(2)); 0.80–2.05 (m, 4 CH₂); 3.50 (sept., J = 6, H–C(2)); 3.74–4.08 (m, H–C(7), (CH₃)₂CH); 4.88, 5.01 (2m, w_{1/2} = 4, CH₂=C(6)). ¹³C-NMR (75 MHz): 21.3, 22.0, 22.9, 23.8 (5q, 5 CH₃); 28.8, 30.5, 33.2, 35.0 (4t, C(3), C(4), C(8), C(9)); 108.3 (t, CH₂=C(1)); 68.9, 73.4, 75.7 (3d, C(2), C(7), (CH₃)₂CH); 37.8 (s, C(10)); 90.8 (s, C(5)); 149.8 (s, C(6)). MS: 252 (3, M⁺, C₁₆H₂₈O₂), 209 (30), 194 (39), 193 (100), 192 (13), 177 (13), 153 (19), 141 (36), 139 (22), 138 (12), 137 (49), 125 (19), 121 (20), 111 (12), 109 (25), 107 (18), 105 (11), 97 (13), 95 (21), 93 (22), 91 (19), 85 (26), 83 (38), 81 (23), 79 (18), 77 (15), 69 (18), 67 (21), 56 (12), 55 (59), 53 (29), 43 (53), 41 (60). Anal. calc. for C₁₆H₂₈O₂ (252.40): C 76.14, H 11.18; found: C 76.29, H 10.99.

(2RS,7RS)-2,10,10-Trimethyl-6-methylidene-1-oxaspiro[4.5]dec-7-yl Isopropyl Ether (**29**). B.p. 65°/0.006 Torr. IR: 3100w (br.), 3040w (sh), 2970s, 2930s, 2870s, 1645w, 1475w, 1460w (sh), 1455m (sh), 1450m, 1380s, 1365m, 1330m, 1305w, 1285w, 1250w (br.), 1195w, 1160s, 1120m, 1105s, 1080s, 1050m, 1035s, 1020m, 995m, 935w, 910s, 890w, 870w. ¹H-NMR: 0.79, 0.82 (2s, 2 CH₃–C(10)); 1.10, 1.11 (2d, J = 6, (CH₃)₂CH); 1.21 (d, J = 6, CH₃–C(2)); 1.0–2.2 (m, 4 CH₂); 3.54 (sept., J = 6, (CH₃)₂CH, overlapping with m); 3.35–3.65, 3.75–4.15 (2m, H–C(2), H–C(7)); 4.93 (m, w_{1/2} = 3, CH₂=C(6)). ¹³C-NMR: 20.5, 21.9, 22.5, 22.9, 24.0 (5q, 5 CH₃); 30.6, 33.4, 34.4, 35.5 (4t, C(3), C(4), C(8), C(9)); 102.5 (t, CH₂=C(6)); 70.4, 74.1, 76.1 (3d, C(2), C(7), (CH₃)₂CH); 38.0 (s, C(10)); 89.7 (s, C(5)); 152.1 (s, C(6)). MS: 252 (2, M⁺, C₁₆H₂₈O₂), 209 (28), 194 (38), 193 (100), 183 (12), 177 (12), 153 (17), 141 (34), 139 (17), 137 (18), 125 (14), 109 (16), 95 (12), 85 (18), 83 (22), 81 (12), 67 (12), 55 (37), 53 (18), 43 (37), 41 (44). Anal. calc. for C₁₆H₂₈O₂ (252.40): C 76.14, H 11.18; found: C 76.32, H 10.89.

1,3,7,7-Tetramethyl-2-oxatricyclo[4.4.0.0^{3,6}]dec-10-yl Isopropyl Ether. Isomer A (**30A**). B.p. 90°/0.005 Torr. IR: 2970s, 2930s, 2870m, 1465m, 1455m, 1440m, 1420w, 1375s (sh), 1370s, 1340m, 1335m, 1285m, 1230w, 1225w (sh), 1195w, 1165m, 1150s, 1135m, 1120s, 1095s, 1070m, 1060s, 1045m, 1020s, 1000m, 975w, 955w, 910m, 880m, 865m, 845w. ¹H-NMR: 0.60, 0.95, 1.21, 1.36 (4s, 4 CH₃); 1.09 (d, J = 6, (CH₃)₂CH); 0.7–2.6 (m, 4 CH₂); 3.60–3.90 (m, H–C(10), (CH₃)₂CH). ¹³C-NMR (75 MHz): 15.8, 21.7, 22.8, 23.0, 23.9, 25.6 (6q, 6 CH₃); 21.6, 25.6, 34.0, 37.9 (4t, C(4), C(5), C(8), C(9)); 70.1, 83.7 (2d, C(10), CH(CH₃)₂); 32.8 (s, C(7)); 58.7 (s, C(6)); 89.4 (2s overlapping, C(1), C(3)). MS: 252 (1, M⁺, C₁₆H₂₈O₂), 194 (13), 192 (31), 177 (14), 152 (20), 149 (15), 139 (21), 136 (33), 135 (15), 134 (15), 122 (22), 121 (69), 120 (16), 119 (100), 111 (21), 109 (12), 107 (61), 105 (27), 95 (18), 93 (44), 91 (45), 81 (13), 79 (26), 77 (27), 69 (15), 67 (12), 65 (13), 55 (19), 53 (16), 45 (66), 43 (87), 41 (42). Anal. calc. for C₁₆H₂₈O₂ (252.40): C 76.14, H 11.18; found: C 76.02, H 11.01.

Isomer B (**30B**). B.p. 85°/0.003 Torr. IR: 2970s, 2930s, 2870m, 1465m, 1450m, 1435m (sh), 1420w, 1395w, 1385m (sh), 1380s, 1370s, 1345w (br.), 1325w (br.), 1290m, 1245w, 1210w, 1180m, 1165m, 1150m, 1130s, 1120s, 1110m, 1080s, 1070s (sh), 1030m, 1005w, 980w, 965m, 950w, 940w, 915m, 885w, 855w. ¹H-NMR: 0.60, 0.93, 1.32, 1.38 (4s, 4 CH₃); 1.08, 1.12 (2d, J = 6, (CH₃)₂CH); 1.0–2.4 (m, 4 CH₂); 3.24 (dd, J = 6.5, 4, H–C(10)); 3.66 (sept., J = 6, (CH₃)₂CH). ¹³C-NMR: 22.0, 22.5, 22.9, 26.7, 27.3 (6q, 2q at 22.5, 6 CH₃); 18.8, 24.4, 33.9, (4t, 2t at 33.9, C(4), C(5), C(5), C(8), C(9)); 71.1, 77.5 (2d, C(10), (CH₃)₂CH); 31.4 (s, C(7)); 56.5 (s, C(6)); 84.6, 88.4 (2s, C(1), C(8)). MS: 252 (ca. 1, M⁺, C₁₆H₂₈O₂), 194 (15), 154 (12), 152 (31), 139 (44), 135 (10), 121 (15), 111 (35), 109 (14), 107 (15), 95 (14), 93 (15), 91 (11), 81 (12), 79 (12), 69 (11), 67 (12), 57 (11), 55 (17), 43 (100), 41 (32). Anal. calc. for C₁₆H₂₈O₂ (252.40): C 76.14, H 11.18; found: C 76.02, H 11.05.

4-(3'-Isopropoxy-2',6',6'-trimethyl-1'-cyclohexen-1'-yl)-2-butanol (**31**). B.p. 100°/0.001 Torr. IR: 3620w, 3480w (br.), 2970s, 2930s, 2870s, 1465m (sh), 1450m, 1380m (sh), 1370m, 1360m (sh), 1375m, 1320m, 1240w (br.),

1200w, 1175m, 1140m, 1120s, 1070m, 1040s, 1020m, 1000m, 980w, 950w, 930w. ¹H-NMR: 0.94, 1.02 (2s, 2 CH₃–C(6'')); 1.10 (d, *J* = 6, (CH₃)₂CH); 1.14 (d, *J* = 7, 3 H–C(1)); 1.61 (m, *w*_{1/2} = 3, CH₃–C(2'')); 1.0–2.4 (m, 4 CH₂, OH); 3.30–3.80 (m, H–C(2), H–C(3'), (CH₃)₂CH). ¹³C-NMR: 16.8, 22.1, 23.3, 23.9, 27.2, 28.5 (6q, 6 CH₃); 25.1, 25.4, 35.0, 39.3 (4t, C(3), C(4), C(4'), C(5'')); 68.5, 70.0, 75.6 (3d, C(2), C(3'), (CH₃)₂CH); 35.4 (s, C(6'')); 127.8, 142.0 (2s, C(1'), C(2'')). MS: 254 (ca. 1, *M*⁺, C₁₆H₃₀O₂), 194 (6), 139 (36), 138 (100), 123 (13), 121 (19), 119 (27), 109 (19), 107 (12), 105 (10), 96 (14), 95 (13), 93 (10), 91 (13), 82 (15), 79 (11), 55 (17), 45 (34), 43 (28), 41 (25). Anal. calc. for C₁₆H₃₀O₂ (254.42): C 75.54, H 11.89; found: C 75.42, H 11.80.

4,8,8-Trimethyl-3-oxatricyclo[5.4.0.0^{1,4}]undec-11-yl Isopropyl Ether (32). B.p. 65°/0.01 Torr. IR: 2965s, 2930s, 2880s, 1465m, 1450m, 1440w, 1370m, 1365m (sh), 1340w, 1330w, 1180m, 1170m, 1135m (sh), 1120s, 1090w, 1060m, 1055m, 1030m, 1000m, 980m, 970m, 930w, 895w, 880w. ¹H-NMR: 0.68, 0.89, 1.24 (3s, CH₃–C(4), 2 CH₃–C(8)); 1.10, 1.13 (2d, *J* = 6, (CH₃)₂CH); 0.80–2.50 (m, 4 CH₂, H–C(7)); 3.58 (sept., *J* = 6, (CH₃)₂CH); 3.68–3.92 (m, H–C(11)); 3.95 (AB system, *J* = 7, *δ*_A = 3.80, *δ*_B = 4.10, H–C(2)). MS: 252 (1, *M*⁺, C₁₆H₂₈O₂), 222 (27), 180 (20), 166 (30), 163 (23), 162 (30), 161 (18), 151 (17), 147 (35), 135 (20), 133 (17), 125 (18), 124 (100), 123 (25), 121 (28), 119 (32), 111 (73), 109 (60), 107 (47), 106 (45), 105 (41), 99 (21), 95 (41), 93 (48), 91 (57), 81 (75), 79 (47), 77 (30), 69 (34), 67 (27), 65 (12), 57 (30), 55 (48), 53 (21), 45 (19), 43 (67), 41 (82).

3. Additional Experiments. – 3.1. *With 6 and its Photoproducts.* 3.1.1. *Oxidation of 6 with MnO₂.* A slurry of **6** (125 mg, 0.595 mmol) and MnO₂ (800 mg) in CH₂Cl₂ (35 ml) was stirred at r.t. for 20 h and filtered through *Celite*. CC (8 g SiO₂, hexane/Et₂O 1:1) afforded **17** (110 mg, 89%).

3.1.2. *Oxidations with PCC [11].* 3.1.2.1. *Oxidation of 11 + 12.* A mixture of PCC (140 mg, 0.650 mmol), NaOAc (8.9 mg, 0.110 mmol), and **11** + **12** (103 mg, 0.480 mmol) in CH₂Cl₂ (7 ml) was stirred at r.t. for 4 h. CC (20 g SiO₂, hexane/Et₂O 1:1) gave **43** (48 mg, 47%).

2,10,10-Trimethyl-6-methylidene-1-oxaspiro[4.5]decan-7-one (43). B.p. 50°/0.005 Torr. UV (0.208 mg in 10 ml): 222 (3850). UV (2.00 mg in 10 ml): end absorption to 400. IR: 3020w (sh), 2960s, 2920s, 2900m (sh), 2860m, 1690s, 1620m, 1465m, 1450m, 1442m (sh), 1410m, 1380s, 1375m (sh), 1360m, 1320w, 1305w, 1270m, 1215w, 1200m, 1170w, 1155w, 1135m (sh), 1125m (br.), 1080s, 1060m, 1015m, 940m, 910w, 890w, 870w. ¹H-NMR: 0.97 (2s overlapping, 2 CH₃–C(10)); 1.17 (d, *J* = 6, CH₃–C(2)); 1.0–2.4 (m, 4 CH₂); 4.09 (ddq, *J* = 6, H–C(2)); 5.14, 5.55 (2d, *J* = 2.5, CH₂=C(6)). ¹³C-NMR (75 MHz): 21.5, 22.5, 23.6 (3q, 3 CH₃); 30.5, 32.5, 33.7, 36.8 (4t, C(3), C(4), C(8), C(9)); 116.8 (t, CH₂=C(6)); 75.2 (d, C(2)); 36.7 (s, C(10)); 90.3 (s, C(5)); 152.2 (s, C(6)); 203.2 (s, C(7)). MS: 208 (78, *M*⁺, C₁₃H₂₀O₂), 193 (36), 179 (14), 166 (18), 165 (40), 153 (23), 152 (20), 151 (20), 139 (100), 137 (25), 125 (10), 124 (26), 123 (16), 111 (31), 110 (26), 109 (42), 107 (11), 105 (12), 97 (18), 96 (12), 95 (18), 93 (13), 91 (14), 83 (32), 81 (16), 79 (14), 77 (12), 70 (12), 60 (22), 67 (17), 57 (13), 56 (12), 55 (36), 53 (13), 43 (38), 41 (46).

3.1.2.2. *Oxidation of 13A.* A mixture of PCC (148 mg, 0.756 mmol), NaOAc (9.4 mg, 0.154 mmol), and **13A** (100 mg, 0.476 mmol) in CH₂Cl₂ (7 ml) was stirred at r.t. for 4 h. The crude product was recrystallized from hexane, yielding **46** (88 mg, 89%).

1,3,7,7-Tetramethyl-2-oxatricyclo[4.4.0.0^{3,6}]decan-10-one (46). M.p. 51–53° (hexane). UV (11.230 mg in 10 ml): 304 (30). IR: 2960s, 2920s, 2860m, 2820w, 1720s, 1465m (sh), 1450m, 1440m, 1420m, 1385w, 1375m, 1365m, 1320w, 1290m, 1260w, 1195w, 1165w (sh), 1155m, 1135w, 1110m, 1095w, 1065m, 1020w (sh), 1000w, 970w, 950w, 915m, 895w, 865m, 855w. ¹H-NMR: 0.79, 1.03, 1.26, 1.29 (4s, 4 CH₃); 1.50–2.60 (m, 4 CH₂). ¹³C-NMR: 18.7, 22.1, 24.9 (4q, 2q at 22.1, 4 CH₃); 20.3, 33.7, 35.1, 36.9 (4t, C(4), C(5), C(8), C(9)); 32.6 (s, C(7)); 60.2 (s, C(6)); 86.0, 90.6 (2s, C(1), C(3)); 214.6 (s, C(10)). MS: 208 (8, *M*⁺, C₁₃H₂₀O₂), 166 (13), 165 (100), 151 (17), 138 (19), 137 (60), 135 (36), 134 (14), 123 (41), 109 (50), 107 (46), 95 (20), 93 (18), 91 (15), 81 (26), 79 (19), 77 (11), 67 (26), 55 (21), 53 (12), 43 (86), 41 (30). Anal. calc. for C₁₃H₂₀O₂ (208.30): C 74.96, H 9.68; found: C 74.84, H 9.68.

3.1.2.3. *Oxidation of 13B.* A mixture of PCC (24.7 mg, 0.126 mmol), NaOAc (1.5 mg, 0.025 mmol), and **13B** (16.2 mg, 0.077 mmol) in CH₂Cl₂ (5 ml) was stirred for 29 h. The crude product consisted of **46** (11 mg, 65%) contaminated with ca. 5% of **13B**.

3.1.2.4. *Oxidation of 14.* After analogous treatment of **14** (16.1 mg, 0.077 mmol) for 50 h, only starting material was recovered.

3.1.2.5. *Oxidation of 15.* After analogous treatment of **15** (41.0 mg, 0.196 mmol) for 21 h, the starting material was not converted.

3.1.3. *Oxidations with Collins' Reagent [12].* 3.1.3.1. *Oxidation of 9.* A slurry of CrO₃ (43 mg, 0.428 mmol) and pyridine (68 mg, 0.857 mmol) in CH₂Cl₂ (1.5 ml) was stirred vigorously for 30 min; afterwards a soln. of **9** (15 mg, 0.072 mmol) in CH₂Cl₂ (1.5 ml) was added, and the mixture was allowed to react for 30 min. Filtration through *Celite* yielded **33** (9 mg, 60%).

(1RS,2RS,7RS)-1,2,6,6-Tetramethyl-10-oxatricyclo[5.2.1.0^{2,7}]decan-3-one (33). B.p. 45°/0.001 Torr. IR: 2960s, 2950s (sh), 2920m, 2870m, 1710s, 1470w, 1465m, 1455w, 1445w, 1435w, 1415w, 1385m, 1370m, 1365w, 1340w, 1325w, 1305w, 1280m, 1220w, 1210w, 1195w, 1165w, 1150w, 1115w, 1090m, 1060m, 1035w, 1020m, 1010w,

905w, 885w. ¹H-NMR: 0.80, 0.94, 0.98, 1.29 (4s, 4 CH₃); 1.10–2.40 (m, 4 CH₂). ¹³C-NMR: 15.5, 16.5, 21.8, 23.2 (4q, 4 CH₃); 25.7, 33.5, 35.8, 36.5 (4t, C(4), C(5), C(8), C(9)); 32.3 (s, C(6)); 59.8 (s, C(2)); 91.3, 98.5 (2s, C(1), C(7)); 214.9 (s, C(3)). MS: 208 (18, M⁺, C₁₃H₂₀O₂), 193 (36), 166 (16), 165 (100), 152 (29), 151 (19), 147 (16), 138 (20), 137 (75), 136 (10), 135 (37), 134 (13), 124 (54), 123 (50), 122 (22), 121 (13), 111 (34), 110 (56), 109 (87), 107 (36), 96 (11), 95 (27), 93 (21), 91 (18), 82 (13), 81 (28), 79 (22), 77 (16), 71 (13), 70 (15), 69 (19), 67 (35), 65 (10), 55 (36), 53 (23), 43 (97), 41 (60). Anal. calc. for C₁₃H₂₀O₂ (208.32): C 74.96, H 9.68; found: C 74.92, H 9.79.

3.1.3.2. *Oxidation of 10*. Similarly, **10** (102 mg, 0.486 mmol) was oxidized with CrO₃ (295 mg, 2.92 mmol) and pyridine (461 mg, 5.83 mmol) in CH₂Cl₂ (7 ml) to yield **33** (81 mg, 80%).

3.1.3.3. *Oxidation of 11 + 12*. According to 3.1.3.1, **11 + 12** (37 mg, 0.176 mmol) was oxidized with CrO₃ (107 mg, 1.07 mmol) and pyridine (170 mg, 2.14 mmol) in CH₂Cl₂ (3 ml). CC of the crude mixture (15 g SiO₂, hexane/Et₂O 2:1) yielded **43** (15 mg, 41%).

3.1.3.4. *Oxidation of 15*. Analogously, **15** (13.7 mg, 0.065 mmol) was treated with CrO₃ (51 mg, 0.51 mmol) and pyridine (80 mg, 1.02 mmol) in CH₂Cl₂ (1.5 ml). After 6 h, no reaction of **15** was observed.

3.1.4. *Treatment with HCl in CCl₄* [3]. 3.1.4.1. *Treatment of 9*. A soln. of **9** (98 mg, 0.429 mmol) in CCl₄ (15 ml) was stirred vigorously in the presence of a few drops of conc. HCl for 30 min. After adding an excess of NaHCO₃ and MgSO₄, CC (9 g SiO₂, hexane/Et₂O 2:1) yielded **37** (65 mg, 73%).

(1RS,2RS)-1,5,5,9-Tetramethylbicyclo[4.3.0]nona-6,8-dien-2-ol (**37**). B.p. 50°/0.01 Torr. UV (0.440 mg in 10 ml): 262 (2360). IR: 3620m, 3500w (br.), 3065w, 3045w, 2960s, 2940s, 2910s, 2865s, 2850m, 1615w, 1560w (br.), 1470m, 1455m, 1445m, 1380m, 1360m, 1270w (br.), 1245w (br.), 1190w (br.), 1075w (sh), 1055m, 1050m (sh), 1035s, 1005m, 965w, 940w, 930w, 905w, 860w, 650w. ¹H-NMR (CDCl₃): 1.09, 1.13, 1.16 (3s, CH₃-C(1), 2 CH₃-C(5)); 0.8–2.0 (m, 2 CH₂, OH); 1.97 (d, J = 1, CH₃-C(9)); 3.00 (dd, J = 11, 5, H-C(2)); 5.87 (m, w_{1/2} = 2, H-C(7), H-C(8)). ¹³C-NMR: 14.3, 14.9, 25.5, 30.4 (4q, 4 CH₃); 29.5, 39.8 (2t, C(3), C(4)); 77.3 (d, C(2)); 122.1, 124.1 (2d, C(7), C(8)); 34.4 (s, C(5)); 58.3 (s, C(1)); 154.0, 159.0 (2s, C(6), C(9)). MS: 192 (52, M⁺, C₁₃H₂₀O), 177 (39), 159 (42), 137 (12), 136 (100), 135 (56), 134 (18), 133 (32), 131 (10), 123 (15), 121 (26), 119 (30), 118 (10), 117 (12), 107 (14), 105 (18), 95 (18), 94 (22), 93 (15), 91 (30), 81 (12), 79 (17), 77 (16), 55 (11), 43 (18), 41 (21).

3.1.4.2. *Treatment of 10*. Similarly, **10** (98 mg, 0.420 mmol) was treated (25 min). CC (10 g SiO₂, hexane/Et₂O 2:1) afforded **19** (44 mg, 50%).

3.1.5. *Reaction of 13A with TsOH in i-PrOH*. A soln. of **13A** (33.3 mg, 0.157 mmol) and TsOH (27.5 mg, 0.157 mmol) in i-PrOH (10 ml) was stirred at r.t. for 2 h. TLC (hexane/Et₂O 1:3) and GC indicated a quantitative conversion to **8**.

3.1.6. *Phenylurethane of 9*. A soln. of **9** (25 mg, 0.119 mmol) in phenylisocyanate (3 ml) was kept at r.t. for 5 min, hexane (10 ml) was added and the new soln. heated up to 80° for 2 h. After cooling, the mixture was poured onto ice-water and worked up as usual. Repeated CC (10 g SiO₂, hexane/Et₂O 1:1) and recrystallization from hexane yielded **42** (17 mg, 42%).

(1RS,2RS,3RS,7RS)-1,2,6,6-Tetramethyl-10-oxatricyclo[5.2.1.0^{2,7}]dec-3-yl N-Phenylcarbamate (**42**). M.p. 124–125° (hexane). IR: 3440m, 3060w, 3030w, 2960m, 2950m, 2920m, 2890w (sh), 2870w, 1740s, 1600m, 1590m, 1515s, 1465w, 1460w, 1450w, 1435s, 1395w (sh), 1385m, 1380m (sh), 1360w, 1320m, 1310m, 1270w, 1245w, 1205s, 1185m, 1180m, 1165w, 1155m, 1140w (sh), 1090w, 1080m, 1060m, 1050m, 1025m, 1005w, 995w, 970w, 925w, 910w, 895w, 885w, 690m. ¹H-NMR (80 MHz, CDCl₃): 0.87 (6 H); 0.90 (3 H); 1.31 (3 H); (3s, 2 CH₃-C(6), CH₃-C(1), CH₃-C(2)); 1.25–2.00 (m, 4 CH₂); 5.60–5.85 (m, H-C(3)); 6.40–6.70 (m, NH); 6.90–7.60 (m, Ph). ¹³C-NMR: 11.7, 15.1, 23.0, 23.2 (4q, 4 CH₃); 24.7, 27.3, 32.5, 36.7 (4t, C(4), C(5), C(8), C(9)); 74.8 (d, C(3)); 118.7, 123.4, 129.0 (3d, 5 arom. C); 32.3 (s, C(6)); 52.6 (s, C(2)); 89.9, 97.3 (2s, C(1), C(7)); 138.1 (s, arom. C-N); 153.0 (s, NH-COO). MS: 329 (2, M⁺, C₂₀H₂₇NO₃), 194 (11), 193 (78), 192 (28), 176 (14), 175 (95), 152 (23), 149 (31), 137 (15), 136 (15), 135 (74), 134 (13), 133 (76), 123 (30), 121 (37), 120 (14), 119 (73), 113 (11), 111 (14), 109 (58), 108 (10), 107 (39), 105 (18), 95 (55), 94 (16), 93 (85), 92 (13), 91 (26), 81 (26), 79 (22), 77 (29), 71 (18), 69 (32), 67 (27), 65 (16), 57 (12), 55 (32), 53 (10), 43 (100), 41 (36).

3.2. *With 7, 8 and their Photoproducts*. 3.2.1. *Treatment with HCl in CCl₄*. 3.2.1.1. *Treatment of 20*. A soln. of **20** (44 mg, 0.175 mmol) in CCl₄ (8 ml) was treated as described in Section 3.1.4.1. CC (5 g SiO₂, hexane/Et₂O 2:1) gave **26** (30 mg, 68%).

3.2.1.2. *Treatment of 21*. A soln. of **21** (150 mg, ca. 60% purity, ca. 0.36 mmol) in CCl₄ (30 ml) was treated as described in Sect. 3.1.4.1. CC of the crude product (10 g SiO₂, hexane/Et₂O 1:1) yielded **34** (36 mg, ca. 40%).

(1RS,2RS,9RS)-9-Hydroxy-1,5,5,9-tetramethylbicyclo[4.3.0]non-6-en-2-yl Acetate (**34**). M.p. 111–113° (hexane). IR: 3580w, 3490w (br.), 3060w, 2980m, 2960m, 2940m, 2890m (sh), 2870w, 2850w, 1740m, 1715s, 1460w, 1445w, 1435w, 1380m, 1375m, 1365m, 1360m, 1340w, 1320w, 1300w, 1255s, 1245s (sh), 1185w, 1160w (br.), 1135w, 1090w, 1085w, 1065w (br.), 1030m, 1020m, 1000w, 980m, 970w, 950w, 925w, 905w, 860w. ¹H-NMR: 1.01, 1.08, 1.09, 1.10 (4s, 4 CH₃); 1.98 (s, CH₃COO); 1.00–2.00 (m, 2 H-C(3), 2 H-C(4)); 2.0–2.4 (m, 2 H-C(8)); 2.4–2.6 (m, OH);

5.12 (*dd*, $J_1 = 11$, 6, H–C(2)); 5.34 (*m* with *t* character, $J = 2$, H–C(7)). Irradiation at 5.34 changed *m* at 2.0–2.4 to *AB* system at 2.18 ($J = 16$, $\delta_A = 2.08$, $\delta_B = 2.28$). ^{13}C -NMR: 16.8, 21.4, 23.3, 29.2, 30.6 (5*q*, 5 CH_3); 24.8, 37.9, 45.0 (3*t*, C(3), C(4), C(8)); 74.0 (*d*, C(2)); 120.0 (*d*, C(7)); 33.3 (*s*, C(5)); 55.5 (*s*, C(1)); 81.7 (*s*, C(9)); 154.8 (*s*, C(6)); 171.5 (*s*, CH_3COO). MS: 192 (21, $M^+ - \text{AcOH}$), 177 (13), 159 (13), 152 (39), 149 (58), 135 (13), 121 (44), 119 (23), 107 (31), 105 (11), 93 (32), 91 (16), 79 (12), 77 (11), 69 (10), 55 (16), 43 (100), 41 (22). Anal. calc. for $\text{C}_{15}\text{H}_{24}\text{O}_3$ (252.35): C 71.39, H 9.59; found: C 71.19, H 9.69.

3.2.1.3. *Treatment of 27*. A soln. of **27** (77 mg, 0.305 mmol) in CCl_4 (15 ml) was treated as described in Sect. 3.1.4.1. CC (6 g SiO_2 , hexane/ Et_2O 10:1) afforded **35** (54 mg, 70%).

(5*RS*,6*RS*,7*RS*)-5-Isopropoxy-2,2,6,7-tetramethylbicyclo[4.3.0]non-9-en-7-ol (**35**). B.p. $70^\circ/0.01$ Torr. IR: 3620*w* (br.), 3580*w*, 3050*w*, 2960*s*, 2930*s*, 2900*s* (sh), 2870*m*, 2840*m*, 1460*m*, 1450*m*, 1440*w*, 1380*s*, 1365*s*, 1345*s*, 1340*m* (sh), 1260*w*, 1220*m*, 1205*w*, 1190*w*, 1170*m*, 1120*s*, 1080*s*, 1070*s*, 1060*s* (sh), 1040*m*, 1020*w*, 1000*w*, 990*w*, 970*w*, 960*w*, 930*m*, 920*m*, 870*w*, 855*m*, 695*w*, 640*w*. ^1H -NMR: 0.96, 1.04, 1.26 (4*s*, 2*s* at 1.04, 4 CH_3); 1.09 (*d*, $J = 6$, $(\text{CH}_3)_2\text{CH}$); 1.00–1.80 (*m*, 2 H–C(3), 2 H–C(4), OH); 2.02 (*dd*, $J = 16$, 3, H_A –C(8)); 2.36 (*dd*, $J = 16$, 2, H_B –C(8)); 3.50–3.84 (*m*, H–C(5), $(\text{CH}_3)_2\text{CH}$); 5.27 (*dd*, $J = 3$, 2, H–C(9)). ^{13}C -NMR: 16.4, 22.6, 23.7, 29.3, 30.8 (6*q*, 2*q* at 22.6, 6 CH_3); 25.1, 38.6, 45.6 (3*t*, C(3), C(4), C(8)); 69.1, 75.8 (2*d*, C(5), $(\text{CH}_3)_2\text{CH}$); 118.6 (*d*, C(9)); 33.5 (*s*, C(2)); 56.2 (*s*, C(6)); 82.8 (*s*, C(7)); 157.2 (*s*, C(1)). MS: 252 (*ca.* 1, M^+ , $\text{C}_{16}\text{H}_{28}\text{O}_2$), 237 (39), 192 (9), 177 (38), 176 (17), 154 (14), 153 (88), 152 (14), 149 (24), 139 (14), 137 (15), 136 (53), 135 (34), 133 (13), 121 (35), 119 (20), 111 (17), 109 (14), 107 (26), 105 (13), 99 (69), 95 (21), 93 (23), 91 (18), 81 (16), 79 (15), 69 (24), 57 (95), 55 (22), 43 (100), 41 (37). Anal. calc. for $\text{C}_{16}\text{H}_{28}\text{O}_2$ (252.40): C 76.14, H 11.18; found: C 76.23, H 11.15.

3.2.2. Collins' Oxidation of **31**. Compound **31** (57 mg, 0.225 mmol) was oxidized with CrO_3 (135 mg, 1.35 mmol) and pyridine (214 mg, 270 mmol) in CH_2Cl_2 (5 ml) according to Sect. 3.1.3.1 producing **8** (48 mg, 85%).

3.2.3. Preparation of **24A**. A soln. of **13A** (127 mg, 0.605 mmol), pyridine (2 ml), and Ac_2O (1 ml) was stirred at r.t. for 18 h and worked up furnishing **24A** (126 mg, 83%).

3.2.4. Preparation of **24B**. A soln. of **13B** (124 mg, 0.590 mmol), Ac_2O (1 ml), pyridine (4 ml), and traces of 4-(*N,N*-dimethylamino)pyridine was stirred at r.t. for 1 h giving **24B** (121 mg, 82%).

3.2.5. Preparation of **20**. Similarly to Sect. 3.2.4, **9** (15 mg, 0.071 mmol) was treated during 150 min. After workup, only impure **20** was obtained.

3.2.6. Reduction of **24B** and **21** with LiAlH_4 . A soln. of **24B** and **21** (3:2, 191 mg, 0.756 mmol) in Et_2O (20 ml) was reduced with LiAlH_4 (30 mg) at r.t. with stirring for 30 min. After workup, a crude mixture **13B/10** (3:2) was obtained in quant. yield.

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