42. Photochemical Reactions

149th Communication[1])

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

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(14.I.88)

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-ionone[4]) (**1**) depends on temperature, polarity and viscosity of the solvent. Thus, irradiation ($\lambda \geqslant 245$ 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].

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[1]) 148th Communication: see [1].

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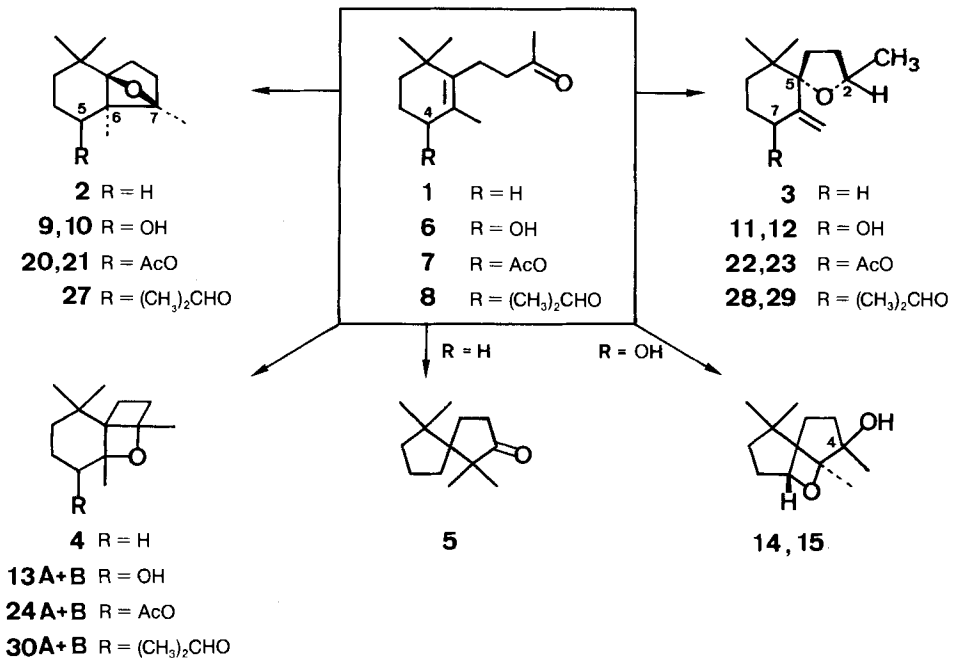
[4]) Numbering according to the carotenoid nomenclature [4].

Scheme 1



2. Preparation of 6–8. – Compound **6** was obtained by reduction of 4-hydroxy-β-ionone [6] with Ph_3SnH [7] (80%). Acetylation (Ac_2O/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

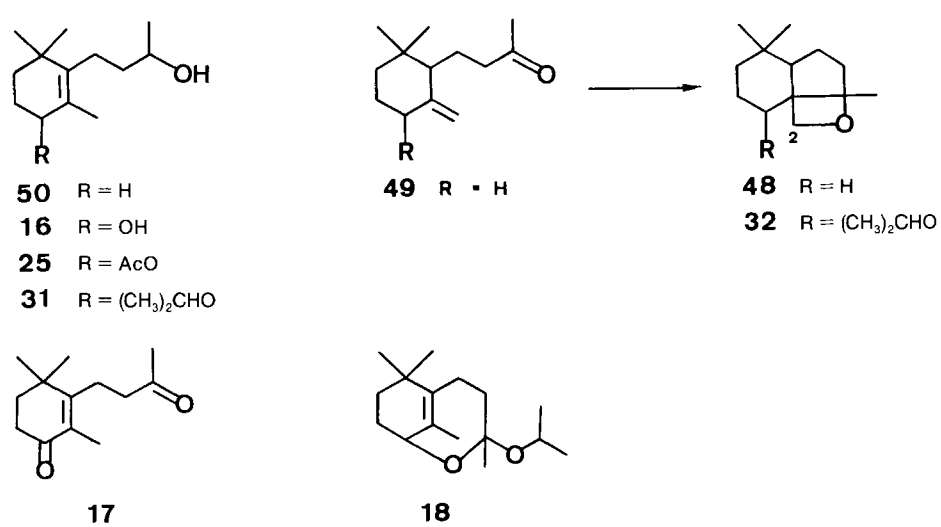


Table 1. *Results of the Photolyses of* **6** ($\lambda > 245$ nm)

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 SiO_2, by ^{1}H-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 Na_2CO_3.

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 Na_2CO_3.
[b]) Yields were determined, after CC on SiO_2, by ^{1}H-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

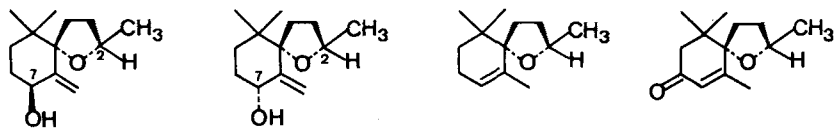
[a]) In the presence of Na_2CO_3.
[b]) Yields were determined, after CC on SiO_2, by ^{1}H-NMR and GC of the fractions and are based on converted starting material.
[c]) The terms **A** and **B** indicate diastereoisomers whose configurations were not assigned conclusively.

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 ^{1}H- and ^{13}C-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 ain 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: λ = 262 nm, ε = 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}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].

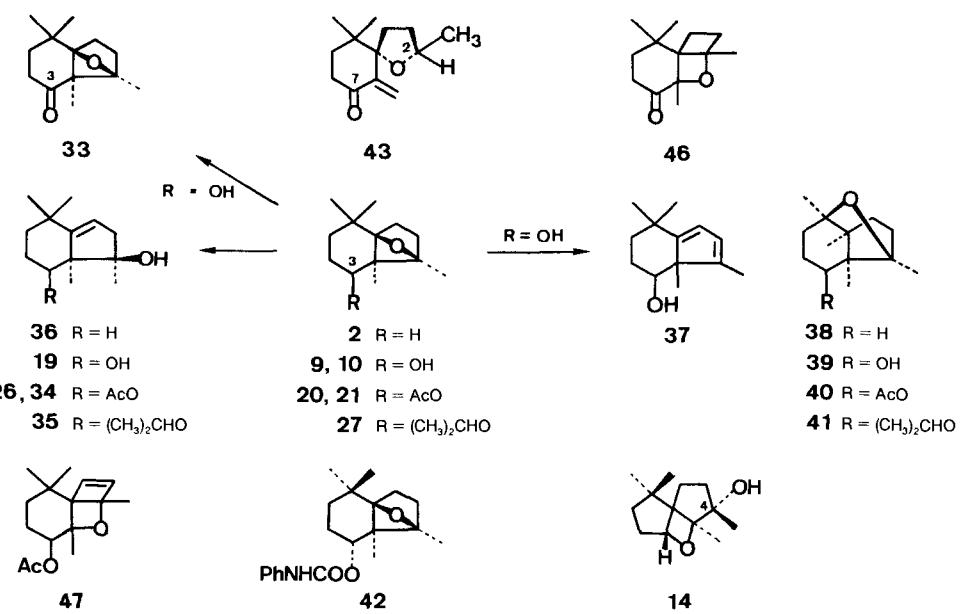


11 **12** **44** **45**

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 CrO_3/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/H_2O/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 ^{1}H-NMR the *AB* system at 3.95 ppm (J = 7 Hz) of 2 H–C(2) and in the MS the loss of CH_2O ($M^{+\cdot} - 30$).

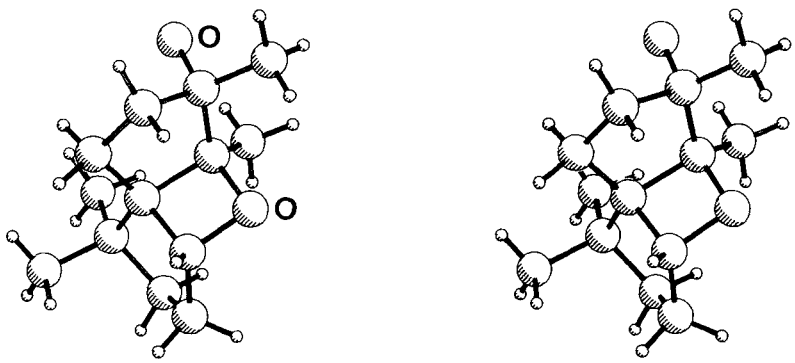


Fig. 1. *Stereoview of the molecule* **14** *drawn by PLUTO 78* [16]

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 λ = 0.7107 Å). The structures were solved by direct methods with SHELX76 [13] and refined by full-matrix-least-squares[5]) 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 anisotropic[6])).

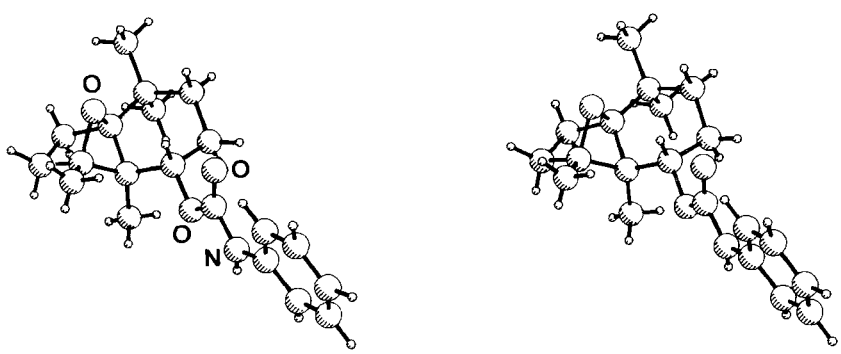


Fig. 2. *Stereoview of the molecule* **42** *drawn by PLUTO 78* [16]

[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**

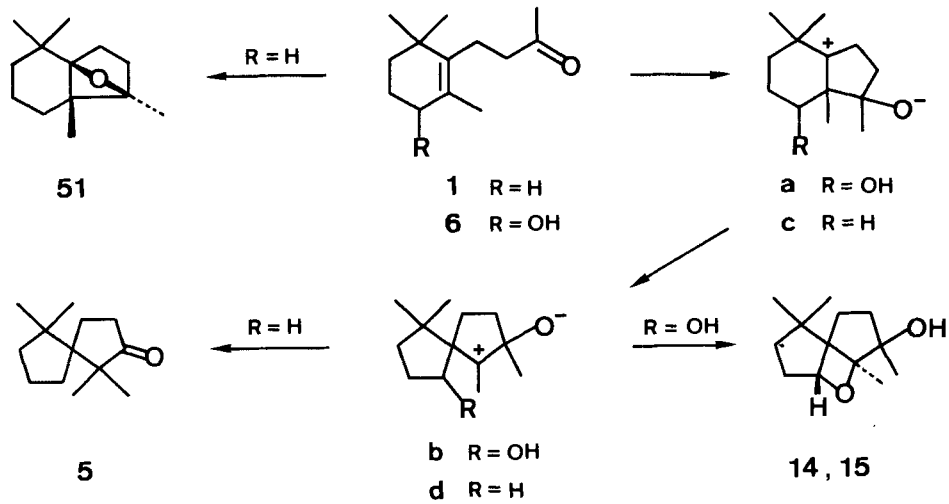
Compound	**14**	**42**	Compound	**14**	**42**
Space group	*Pbca*	$P2_1/n$	Reflections measured	2150	3282
a [Å]	11.55	7.54	Reflections of $I > 3\delta_I$	1067	1788
b [Å]	12.84	17.03	R	0.039	0.043
c [Å]	16.48	14.60	R_w	0.040	0.044
α [°]	90	90			
β [°]	90	93.067			
γ [°]	90	90			
Z	8	4			

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 ($\lambda > 245$ mm) 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** (→**20–25**) and the isopropyl ether **8** (→**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**→**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-

Scheme 4



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.

This work was supported by the *Swiss National Science Foundation* and *Ciba-Geigy Ltd.*, Basel. We are indebted to the following persons for their help: Miss *B. Brandenberg*, Mr. *F.Fehr*, and Mr. *M. Langenauer* (NMR), Mrs. *L. Golgowski* and Prof. *J. Seibl* (MS), and Mr. *D. Manser* (elemental analysis). We are also grateful to Mr. *K. Job* for the preparation of starting materials.

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 × 0.33 mm *UCON HB-5100* glass capillary. Column chromatographies (CC) were carried out on silica gel (SiO_2) *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. ^{1}H-NMR spectra were recorded on a *Varian HA-100* instrument (100 MHz) in CCl_4 solns. or, exceptionally (as indicated below), in $CDCl_3$ solns. and, in some cases, on a *Bruker WP-80/CW* (80 MHz) instrument in $CDCl_3$ 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 Ph_3SnH [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 SiO_2, hexane/Et_2O 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: 3610*w*, 3480*w* (br.), 2960*s*, 2940*s*, 2910*m* (sh), 2860*m*, 1718*s*, 1470*m*, 1450*w*, 1435*w*, 1410*w*, 1380*w* (sh), 1370*m* (sh), 1360*m*, 1305*w*, 1275*w* (br.), 1225*w* (br.), 1200*w*, 1160*m*, 1065*w* (br.), 1035*m*, 1010*m*, 995*m*, 960*w*, 925*w* (br.), 900*w*, 870*w*. ^{1}H-NMR: 0.94, 1.00 (2*s*, 2 CH_3–C(6')); 1,64 (*s*, CH_3–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')). ^{13}C-NMR: 16.7, 27.0, 28.3, 29.7 (4*q*, C(1), CH_3–C(2'), 2 CH_3–C(6')); 22.3, 28.6, 34.6, 43.8 (4*t*, C(3), C(4), C(4'), C(5')); 69.7 (*d*, C(3')); 35.4 (*s*, C(6')); 129.8, 140.4 (2*s*, C(1'), C(2')); 208.7 (*s*, C(2)). MS: 210 (0.5, $M^{+\cdot}$, $C_{13}H_{22}O_2$), 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°/0.01 Torr. M.p. 52–53°. UV (1.947 mg in 10 ml): 279 (130). IR: 2960*m*, 2940*m*, 2865*w*, 1735*s*, 1720*s*, 1470*w*, 1450*w*, 1430*w*, 1410*w*, 1370*m*, 1240*s*, 1230*s* (sh), 1160*m*, 1150*w*, 1010*m*, 990*w* (sh), 960*m*, 930*w*, 870*w*. ^{1}H-NMR: 0.96, 1.02 (2*s*, 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 (5*q*, CH_3–C(2), 2 CH_3–C(4), C(4'), CH_3–COO); 22.3, 25.4, 34.8, 43.6 (4*t*, C(5), C(6), C(1'), C(2')); 72.4 (*d*, C(1)); 35.4 (*s*, C(4)); 125.9, 143.4 (2*s*, C(2), C(3)); 170.8 (*s*, COO); 207.7 (*s*, C(3')). MS: 192 (39, $M^{+\cdot}$ – 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·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'-Isoproxy-2',6',6'-trimethyl-1'-cyclohexen-1'-yl)-2-butanone (**8**). B.p. 90°/0.01 Torr. UV (5.312 mg in 10 ml): 284 (35). IR: 2960*s*, 2930*s*, 2860*s*, 1715*s*, 1465*m*, 1450*m*, 1435*m* (sh), 1410*m*, 1380*m*, 1360*s*, 1345*m*, 1315*m*, 1270*w* (br.), 1230*w*, 1200*w*, 1175*m*, 1155*s*, 1140*s*, 1120*s*, 1065*m*, 1040*s*, 1020*s*, 1000*m*, 980*m*, 940*w*, 915*w*, 895*w*, 880*w*. ^{1}H-NMR: 0.92, 0.99 (2*s*, 2 CH_3–C(6')); 1.09 (*d*, J = 6, $(CH_3)_2$CH); 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 (6*q*, C(1), CH_3–C(2'), 2 CH_3–C(6'), $(CH_3)_2$CH); 22.3, 25.2, 34.8, 43.8 (4*t*, 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 (2*s*, C(1'), C(2')); 207.6 (*s*, C(2)). MS: 252 (1, $M^{+\cdot}$, $C_{16}H_{28}O_2$), 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 compounds[7]: **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 products[7]: **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 distribution[7]: **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 distribution[7]): **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 distribution[7]): **11** + **12** (1%), **14** (20%), **15** (8%), an alcohol of unknown structure (7%), and intractable material (mainly polymers).

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[7]) Yields were determined, after CC on SiO_2, by ^{1}H-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: 3620*w*, 3460*w* (br.), 2960*s*, 2940*s*, 2920*s* (sh), 2860*m*, 1465*m* (sh), 1450*m*, 1435*w* (sh), 1380*s*, 1360*m*, 1300*w*, 1275*w*, 1225*w*, 1190*w*, 1160*w*, 1150*w*, 1130*w*, 1100*w*, 1085*m*, 1070*m*, 1045*m*, 1000*m*, 990*m*, 920*w*, 900*w*, 880*m*. ^{1}H-NMR ($CDCl_3$): 0.77, 0.80, 0.84, 1.30 (4*s*, 4 CH_3); 1.20–1.90 (*m*, 4 CH_2, OH); 4.36–4.62 (*m*, H–C(5)). ^{13}C-NMR: 10.6, 15.4, 23.0, 23.3 (4*q*, 4 CH_3); 27.3, 27.9, 32.6, 37.0 (4*t*, 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 (2*s*, C(1), C(7)). MS: 210 (1, M^+, $C_{13}H_{22}O_2$), 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 $C_{13}H_{22}O_2$ (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: 3490*m* (br.), 2960*s*, 2940*s*, 2930*s*, 2860*m*, 1465*m* (sh), 1460*m* (br.), 1435*m*, 1410*m*, 1380*m*, 1360*m*, 1300*m*, 1290*m*, 1250*w*, 1200*w*, 1170*w*, 1145*w*, 1130*w* (sh), 1110*w*, 1085*m*, 1050*m*, 1030*m*, 1010*m*, 965*w*, 950*w*, 900*w*, 870*w*, 855*w*. ^{1}H-NMR: 0.69, 0.82, 0.88, 1.50 (4*s*, 4 CH_3); 1.0–2.0 (*m*, 4 CH_2); 3.76 (br. *AB* system, J = 11, δ_A = 3.69, H–C(5), δ_B = 3.83, OH). ^{13}C-NMR: (*ca.* 90% pure): 16.4, 17.1, 23.7, 23.9 (4*q*, 4 CH_3); 26.4, 26.5, 30.4, 34.3 (4*t*, 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 (2*s*, C(1), C(7)). MS: 210 (2, M^+, $C_{13}H_{22}O_2$), 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 $C_{13}H_{22}O_2$ (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: 3620*m*, 3470*w* (br.), 3100*w*, 2970*s*, 2940*s*, 2930*s* (sh), 2890*m*, 2870*s*, 1640*w*, 1470*m*, 1455*m*, 1445*m* (sh), 1380*m*, 1360*m*, 1285*w* (br.), 1225*w* (br.), 1195*w*, 1170*w*, 1150*w*, 1120*m*, 1085*s*, 1055*m*, 1035*m* (sh), 1025*m*, 990*m* (sh), 980*m*, 960*w*, 935*w*, 920*m*, 910*m*, 870*w*. ^{1}H-NMR: 0.78, 0.87 (2*s*, 2 CH_3–C(10)); 1.10–2.20 (*m*, 4 CH_2); 1.14 (*d*, J = 6, CH_3–C(2)); 1.39 (*m*, $w_{1/2}$ = 5, OH); 3.83 (*ddq*, J = 6, H–C(2)); 4.24–4.48 (*m*, H–C(7)); 4.83, 5.09 (2*m*, $w_{1/2}$ = 3, CH_2=C(6)). ^{13}C-NMR: 21.1, 23.6 (3*q*, 2*q* overlapping at 23.6, 3 CH_3); 28.3, 32.2, 33.2, 34.7 (4*t*, C(3), C(4), C(8), C(9)); 106.6 (*t*, CH_2=C(6)); 70.7, 73.3 (2*d*, C(2), C(7)); 37.7 (*s*, C(10)); 90.1 (*s*, C(5)); 152.1 (*s*, C(6)). MS: 210 (15, M^+, $C_{13}H_{22}O_2$), 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 $C_{13}H_{22}O_2$ (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: 3620*w*, 3600*w* (sh), 3470*m* (br.), 3080*w*, 2970*s*, 2940*s* (sh), 2930*s*, 2870*s*, 1645*w*, 1470*m*, 1455*m*, 1440*m*, 1385*s*, 1360*m*, 1330*w*, 1305*w*, 1285*w* (br.), 1240*w*, 1190*w*, 1155*m*, 1120*m*, 1095*m*, 1075*s*, 1040*s*, 1015*s*, 990*m*, 960*w*, 910*w*, 890*w*, 870*w*. ^{1}H-NMR: 0.80, 0.84 (2*s*, 2 CH_3–C(10)); 0.90–2.20 (*m*, 4 CH_2); 1.19 (*d*, J = 6, CH_3–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, CH_2=C(6)). ^{13}C-NMR (*ca.* 90% pure): 20.7, 23.0, 23.6 (3*q*, 3 CH_3); 30.3, 31.7, 33.5, 33.8 (4*t*, C(3), C(4), C(8), C(9)); 106.4 (*t*, CH_2=C(6)); 72.9, 74.1 (2*d*, C(2), C(7)); 37.8 (*s*, C(10)); 90.6 (*s*, C(5)); 151.1 (*s*, C(6)). MS: 210 (13, M^+, $C_{13}H_{22}O_2$), 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: 3610*w*, 3510*s* (br.), 2970*s*, 2940*s*, 2930*s*, 2870*m*, 1460*m*, 1440*m*, 1420*w*, 1385*m*, 1375*s*, 1365*m*, 1350*w*, 1330*w*, 1290*m*, 1230*w* (br.), 1155*m*, 1135*m*, 1100*m*, 1060*m*, 1030*m*, 975*w*, 910*m*, 875*m*, 860*m*, 840*w*. ^{1}H-NMR: 0.61, 0.96, 1.24, 1.40 (4*s*, 4 CH_3); 1.10–2.70 (*m*, 4 CH_2); 3.78 (*d*, J = 3, OH); 3.90–4.18 (*m*, H–C(10)). ^{13}C-NMR: 15.2, 22.8, 23.7, 25.5 (4*q*, 4 CH_3); 21.6, 26.2, 34.0, 37.7 (4*t*, 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 (2*s*, overlapping, C(1), C(3)). MS: 210 (0.2, M^+, $C_{13}H_{22}O_2$), 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 $C_{13}H_{22}O_2$ (210.32): C 74.24, H 10.54; found: C 74.07, H 10.55.

Isomer B (**13B**). M.p. 57–60° (hexane). IR: 3500*m* (br.), 2960*s*, 2930*s*, 2870*m*, 1460*m*, 1450*m*, 1435*m* (sh), 1420*s*, 1390*m*, 1385*m*, 1370*s*, 1290*m*, 1240*w*, 1210*w*, 1160*m*, 1150*m*, 1100*m*, 1080*m*, 1065*s*, 1025*m*, 1000*w*, 970*m* (sh), 965*m*, 950*w* (sh), 910*m*, 870*m*, 845*w*. ^{1}H-NMR: 0.60, 0.94, 1.33, 1.38 (4*s*, 4 CH_3); 0.95–2.40 (*m*, 4 CH_2); 2.90 (*m*, $w_{1/2}$ = 5, OH); 3.38–3.54 (*m*, H–C(10)). ^{13}C-NMR: 22.1, 22.7, 23.9, 26.1 (4*q*, 4 CH_3); 19.8, 25.1, 32.0, 33.9 (4*t*, 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 (2*s*, C(1), C(3)). MS: 210 (1, M^+, $C_{13}H_{22}O_2$), 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 $C_{13}H_{22}O_2$ (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: 3620*m*, 3450*w* (br.), 2960*s*, 2930*s* (sh), 2910*s* (sh), 2870*m*, 1470*m*, 1455*m*, 1440*m* (sh), 1430*m* (sh), 1385*w*, 1370*m*, 1335*w*, 1300*w*, 1210*w*, 1175*m*, 1155*w*, 1120*w*, 1090*m*, 1060*m*, 1045*m*, 1035*m*, 1020*m* (sh), 1010*m*, 960*m*, 940*w*, 925*m*, 915*m*, 895*w*, 870*m*. ^{1}H-NMR: 0.72, 1.03, 1.10, 1.30 (4*s*, 4 CH_3); 0.80–2.40 (*m*, 4 CH_2, OH); 4.26–4.38 (*m*, H–C(1)). ^{13}C-NMR: 17.4, 20.0, 21.0, 27.4 (4*q*, 4 CH_3); 26.2, 31.6, 37.7, 40.4 (4*t*, 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 (2*s*, C(3), C(4)). MS: 210 (1, M^+, $C_{13}H_{22}O_2$), 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 $C_{13}H_{22}O_2$ (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: 3540*m*, 3440*w* (br.), 2990*s* (sh), 2960*s*, 2935*s* (sh), 2870*s*, 1465*m*, 1450*m*, 1440*m*, 1430*w*, 1385*s*, 1375*m*, 1365*m*, 1355*m*, 1335*m*, 1310*w*, 1300*w*, 1270*w* (br.), 1225*m*, 1210*m* (sh), 1195*s*, 1175*m*, 1160*m*, 1145*m* (br.), 1120*m*, 1105*w*, 1085*w*, 1065*m*, 1035*s*, 1025*m*, 1000*m*, 980*w*, 960*s*, 940*m*, 925*w*, 910*w*, 900*w*, 855*m*, 840*w*. ^{1}H-NMR: 0.70, 0.92, 1.01, 1.16 (4*s*, 4 CH_3); 1.08–2.50 (*m*, 4 CH_2); 2.11 (*m*, $w_{1/2}$ = 4, OH); 4.36–4.48 (*m*, H–C(1)). ^{13}C-NMR: 18.0, 20.9, 22.1, 26.6 (4*q*, 4 CH_3); 25.3, 31.6, 38.6, 40.5 (4*t*, 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 (4*s*, C(3), C(4)). MS: 210 (1, M^+, $C_{13}H_{22}O_2$), 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: 2960*m*, 2920*m*, 2860*w*, 1720*s*, 1670*s*, 1610*m*, 1470*w*, 1440*w* (br.), 1420*w*, 1410*w* (sh), 1375*w*, 1360*m* (sh), 1350*m*, 1330*m*, 1310*m*, 1270*w* (br.), 1225*w* (br.), 1195*w*, 1160*m*, 1085*w* (br.), 1070*w* (br.), 1025*w* (br.), 995*w*. ^{1}H-NMR: 1.12 (2*s*, 2CH_3–C(4)); 1.64 (*s*, CH_3–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')). ^{13}C-NMR (75 MHz): 11.4, 29.7 (2*q*, CH_3–C(2), C(4')); 26.7 (2*q*, 2 CH_3–C(4)); 24.0, 34.1, 37.3, 42.1 (4*t*, 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^+, $C_{13}H_{20}O_2$), 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 $C_{13}H_{20}O_2$ (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: 2980*s*, 2930*s* (sh), 2910*s*, 2850*s*, 1480*w* (sh), 1460*m*, 1450*m*, 1435*m* (sh), 1400*w*, 1380*s*, 1360*m*, 1335*w*, 1325*w*, 1285*w*, 1270*w*, 1235*w*, 1190*w*, 1165*m*, 1140*s*, 1120*s* (sh), 1070*s*, 1055*s*, 1040*s*, 1010*s*, 990*m*, 955*w*, 935*w*, 910*m*, 890*w*, 860*w*. ^{1}H-NMR: 0.69, 1.00 (2*s*, 2 CH_3–C(7)); 1.05, 1.12 (2*d*, J = 6.5, $(CH_3)_2CH$); 1.62 (br. *s*, CH_3–C(10), CH_3–C(3)); 0.6–2.4 (*m*, 4 CH_2); 3.80 (*sept.*, J = 6,5, $(CH_3)_2CH$); 4.40–4.60 (*m*, H–C(1)). ^{13}C-NMR (*ca.* 90% pure): 12.4, 14.4, 22.2, 23.9, 24.5, 25.1 (6*q*, 6 CH_3); 28.8, 34.0, 36.1 (4*t*, 2*t* at 36.1, C(4), C(5), C(8), C(9)); 69.3 (*d*, $(CH_3)_2CH$); 96.5 (*d*, C(1)); 36.9 (*s*, C(7)); 93.6 (*s*, C(3)); 133.8, 135.1 (2*s*, C(6), C(10)). MS: 252 (0.1, M^+, $C_{16}H_{28}O_2$), 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 $C_{16}H_{28}O_2$ (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: 3610*w*, 3560*w*, 3300*m* (br.), 3050*w*, 2960*s*, 2925*s*, 2860*s*, 1460*m* (sh), 1450*m*, 1380*m*, 1360*m*, 1340*m*, 1290*w* (br.), 1260*w*, 1230*w*, 1200*m*, 1175*m*, 1155*m*, 1090*m*, 1070*m*, 1050*m*, 1020*m*, 1000*m*, 965*m*, 945*w*, 920*w*, 900*m*, 870*w*, 850*m*, 675*m*. ^{1}H-NMR: 0.92, 1.05, 1.14, 1.28 (4*s*, 4 CH_3); 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)). ^{13}C-NMR: 22.8, 30.7, 31.1 (4*q*, 2*q* at 22.8, 4 CH_3); 27.2, 32.8, 46.1 (3*t*, 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, $M^+ - H_2O$), 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 $C_{13}H_{22}O_2$ (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 Na_2CO_3*. A soln. of **7** (2.25 g, 8.93 mmol) in i-PrOH (300 ml) was irradiated (95% conversion) in the presence of solid Na_2CO_3 (100 mg). Separation of the mixture by CC (320 g SiO_2, hexane/Et_2O 4:1) followed by further CC of the fractions (hexane/Et_2O 10:1, 4:1, and 1:1) yielded the following compounds[7]): **20** (7%), **21**[9]) (5%), **22** + **23** (3%), **24A** (18%), **24B** (5%), **25** (4%), and intractable material.

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[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 distribution[7]: **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°/0.01 Torr. 2970*s*, 2950*s*, 2930*m* (sh), 2870*m*, 1740*s*, 1465*m*, 1455*m* (br.), 1440*w*, 1435*w* (sh), 1395*w*, 1380*s*, 1375*m* (sh), 1355*m*, 1305*w*, 1240*s*, 1225*m* (sh), 1190*w*, 1165*m*, 1155*m*, 1140*w*, 1100*w* (sh), 1090*m*, 1060*m*, 1040*m*, 1020*m*, 995*m*, 970*m*, 910*w* (br.), 885*m*. ^{1}H-NMR: 0.84, 0.90, 0.92, 1.13 (4*s*, 4 CH_3); 1.91 (*s*, CH_3COO); 0.90–2.10 (*m*, 4 CH_2); 5.40–5.62 (*m*, H–C(3)). ^{13}C-NMR: 11.4, 14.7, 21.1, 22.9, 23.0 (5*q*, 5 CH_3); 24.1, 27.1, 32.4, 36.6 (4*t*, 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 (2*s*, C(1), C(7)); 170.0 (*s*, COO). MS: 192 (16, M^+ − 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 $C_{15}H_{24}O_3$ (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: 2970*s*, 2930*s*, 2870*m*, 1740*s*, 1720*m*, 1645*w*, 1460*m* (br.), 1385*m*, 1370*m*, 1360*m*, 1240*s*, 1160*m*, 1090*m*, 1030*m*, 910*m*. ^{1}H-NMR: 0.88 (*d*, *J* = 7, CH_3–C(2)); 0.90 (*s*, CH_3–C(10)); 0.96 (*s*, CH_3–C(10)); 2.07 (*s*, CH_3COO); 2.12 (*s*, CH_3COO); 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) (3*m*, $w_{1/2}$ = 5, CH_2=C(6)); 5.12–5.28, 5.43–5.72 (2*m*, 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°/0.01 Torr. IR: 2960*s*, 2920*s*, 2860*m*, 1730*s*, 1455*m*, 1440*m*, 1420*w*, 1380*m* (sh), 1370*s*, 1360*s*, 1335*w*, 1320*w*, 1285*m*, 1240*s*, 1190*m*, 1155*m*, 1145*m*, 1115*w*, 1075*m*, 1055*m*, 1040*m*, 1020*s*, 1000*m*, 970*m*, 915*m*, 880*m*, 865*w*, 845*w*, 670*w*. ^{1}H-NMR: 0.63, 0.98, 1.26, 1.42 (4*s*, 4 CH_3); 1.98 (*s*, CH_3COO); 1.10–2.65 (*m*, 4 CH_2); 5.13 (*dd*, *J* = 12, 4, H–C(10)). ^{13}C-NMR: 15.8, 21.2, 22.9, 23.6, 25.5 (5*q*, 5 CH_3); 21.4, 23.8, 34.0, 37.1 (4*t*, 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 (2*s*, C(1), C(3)); 170.3 (*s*, CH_3–*C*OO). MS: 192 (5, M^+ − 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 $C_{15}H_{24}O_3$ (252.35): C 71.39, H 9.59; found: C 71.30, H 9.44.

Isomer B (**24B**). B.p. 55°/0.005 Torr. IR: 2960*s*, 2930*m*, 2870*w*, 1740*s*, 1465*w*, 1455*w* (sh), 1450*w*, 1440*w*, 1420*w*, 1385*m* (sh), 1370*s*, 1365*m* (sh), 1290*w*, 1240*s*, 1195*w*, 1170*w*, 1160*m*, 1145*m*, 1110*m*, 1085*m*, 1045*m*, 1025*m*, 990*w*, 980*w*, 970*w*, 950*w*, 915*m*, 880*w*, 860*w*. ^{1}H-NMR: 0.65, 0.96, 1.34, 1.36 (4*s*, 4 CH_3); 1.98 (*s*, CH_3COO); 1.20–2.40 (*m*, 4 CH_2); 4.68–4.84 (*m*, H–C(10)). ^{13}C-NMR: 21.3, 22.2, 25.2, 26.7 (5*q*, 2*q* at 22.2, 5 CH_3); 19.3, 23.1, 33.1, 33.9 (4*t*, 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 (2*s*, C(1), C(3)); 170.7 (*s*, COO). MS: 192 (3, M^+ − 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 $C_{15}H_{24}O_3$ (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°/0.01 Torr. IR: 3620*w*, 3450*w* (br.), 2960*s*, 2940*s* (sh), 2870*m*, 1730*s*, 1470*w* (sh), 1450*w*, 1370*m*, 1240*s*, 1230*s* (sh), 1170*w* (br.), 1140*w* (br.), 1110*w* (br.), 1015*m*, 995*w* (sh), 960*m*, 930*w*, 870*w*. ^{1}H-NMR: 0.97, 1.06 (2*s*, 2 CH_3–C(4)); 1.15 (*d*, *J* = 6, 3 H–C(4')); 1.56 (*s*, CH_3–C(2)); 1.96 (*s*, CH_3COO); 0.70–2.40 (*m*, 4 CH_2, OH); 3.69 (*sext.*, *J* = 6, H–C(3')); 5.02 (*m* with *t* character, *J* = 3, H–C(1)). ^{13}C-NMR: 16.6, 21.4, 23.4, 27.0, 28.5 (5*q*, 5 CH_3); 25.1, 25.4, 34.9, 39.1 (4*t*, C(5), C(6), C(1'), C(2')); 68.4, 72.9 (2*d*, C(1), C(3')); 35.3 (*s*, C(4)); 125.0, 144.5 (2*s*, C(2), C(3)); 171.3 (*s*, COO). MS: 194 (6, M^+ − 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 $C_{15}H_{26}O_3$ (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°/0.01 Torr. IR: 3590*m*, 3470*w* (br.), 3050*w*, 2960*s*, 2940*m*, 2900*m* (sh), 2860*m*, 2840*w*, 1740*s*, 1455*w* (br.), 1385*m*, 1370*m*, 1360*m* (sh), 1345*w*, 1320*w*, 1255*m* (sh), 1240*s* (sh), 1230*s*, 1210*m*, 1175*w*, 1140*w*, 1095*w*, 1070*w*, 1040*m*, 1020*m*, 990*w*, 975*w*, 950*w*, 925*w*, 915*w*, 890*w*, 860*w*, 675*w*. ^{1}H-NMR: 1.02, 1.11, 1.16, 1.19 (4*s*, 4 CH_3); 1.92 (*s*, CH_3COO); 1.00–2.00 (*m*, 2 H–C(3), 2 H–C(4)); 2.18 (*AB* system, *J* = 16, δ_A = 2.08, split into *d*, *J* = 3, δ_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^+ − H_2O), 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 SiO_2, hexane/Et_2O 4:1) followed by CC of the fractions (hexane/Et_2O 20:1 to 1:1) yielded the following compounds[7]: **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 Na_2CO_3.* A soln. of **8** (2.05 g, 8.13 mmol) in i-PrOH (250 ml) was irradiated (85% conversion) in the presence of solid Na_2CO_3 (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: 2970*s*, 2930*s*, 2870*m*, 1465*m* (sh), 1460*m*, 1455*m*, 1445*m* (sh), 1380*s*, 1360*m*, 1345*w*, 1330*m*, 1310*w*, 1305*w* (sh), 1270*w*, 1195*w*, 1175*m* (sh), 1160*m*, 1155*m*, 1120*s*, 1100*m*, 1090*m*, 1075*s*, 1060*m* (br.), 1035*m*, 1020*s*, 1005*m*, 990*m*, 925*w* (br.), 880*m*. ^{1}H-NMR: 0.68, 0.78, 1.21 (4*s*, 2*s* at 0.78, 4 CH_3); 1.09 (*d*, *J* = 6, $(CH_3)_2CH$); 0.80–1.90 (*m*, 4 CH_2); 3.68 (*sept.*, *J* = 6, $(CH_3)_2CH$); 3.96–4.16 (*m*, H–C(3)). ^{13}C-NMR (75 MHz, *ca.* 90% pure): 11.4, 15.8, 22.8, 23.1, 23.3, 23.8 (6*q*, 6 CH_3); 24.6, 27.3, 33.0, 37.0 (4*t*, C(4), C(5), C(8), C(9)); 68.7, 75.0 (2*d*, C(3), $(CH_3)_2CH$); 32.4 (*s*, C(6)); 53.8 (*s*, C(2)); 90.0, 97.4 (2*s*, C(1), C(7)). MS: 252 (3, M^+, $C_{16}H_{28}O_2$), 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 $C_{16}H_{28}O_2$ (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: 3090*w*, 2970*s*, 2930*s*, 2870*m*, 1640*w*, 1465*m*, 1450*m*, 1380*m*, 1365*m*, 1360*m* (sh), 1330*w*, 1320*w*, 1280*w*, 1230*w* (br.), 1200*w*, 1180*w* (sh), 1150*m*, 1120*s*, 1105*m*, 1090*s*, 1075*m*, 1065*m*, 1050*s*, 1035*m*, 1005*m*, 980*m*, 970*w*, 935*w*, 915*m*, 890*w*, 870*w*. ^{1}H-NMR: 0.79, 0.84 (2*s*, 2 CH_3C(10)); 1.07 (*d*, *J* = 6, $(CH_3)_2CH$); 1.14 (*d*, *J* = 6, CH_3–C(2)); 0.80–2.05 (*m*, 4 CH_2); 3.50 (*sept.*, *J* = 6, H–C(2)); 3.74–4.08 (*m*, H–C(7), $(CH_3)_2CH$); 4.88, 5.01 (2*m*, $w_{1/2}$ = 4, CH_2=C(6)). ^{13}C-NMR (75 MHz): 21.3, 22.0, 22.9, 23.4, 23.8 (5*q*, 5 CH_3); 28.8, 30.5, 33.2, 35.0 (4*t*, C(3), C(4), C(8), C(9)); 108.3 (*t*, CH_2=C(1)); 68.9, 73.4, 75.7 (3*d*, C(2), C(7), $(CH_3)_2CH$); 37.8 (*s*, C(10)); 90.8 (*s*, C(5)); 149.8 (*s*, C(6)). MS: 252 (3, M^+, $C_{16}H_{28}O_2$), 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 $C_{16}H_{28}O_2$ (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: 3100*w* (br.), 3040*w* (sh), 2970*s*, 2930*s*, 2870*s*, 1645*w*, 1475*w*, 1460*w* (sh), 1455*m* (sh), 1450*m*, 1380*s*, 1365*m*, 1330*m*, 1305*w*, 1285*w*, 1250*w* (br.), 1195*w*, 1160*s*, 1120*m*, 1105*s*, 1080*s*, 1050*m*, 1035*s*, 1020*m*, 995*m*, 935*w*, 910*s*, 890*w*, 870*w*. ^{1}H-NMR: 0.79, 0.82 (2*s*, 2 CH_3–C(10)); 1.10, 1.11 (2*d*, *J* = 6, $(CH_3)_2CH$); 1.21 (*d*, *J* = 6, CH_3–C(2)); 1.0–2.2 (*m*, 4 CH_2); 3.54 (*sept.*, *J* = 6, $(CH_3)_2CH$, overlapping with *m*); 3.35–3.65, 3.75–4.15 (2*m*, H–C(2), H–C(7)); 4.93 (*m*, $w_{1/2}$ = 3, CH_2=C(6)). ^{13}C-NMR: 20.5, 21.9, 22.5, 22.9, 24.0 (5*q*, 5 CH_3); 30.6, 33.4, 34.4, 35.5 (4*t*, C(3), C(4), C(8), C(9)); 102.5 (*t*, CH_2=C(6)); 70.4, 74.1, 76.1 (3*d*, C(2), C(7), $(CH_3)_2CH$); 38.0 (*s*, C(10)); 89.7 (*s*, C(5)); 152.1 (*s*, C(6)). MS: 252 (2, M^+, $C_{16}H_{28}O_2$), 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 $C_{16}H_{28}O_2$ (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: 2970*s*, 2930*s*, 2870*m*, 1465*m*, 1455*m*, 1440*m*, 1420*w*, 1375*s* (sh), 1370*s*, 1340*m*, 1335*m*, 1285*m*, 1230*w*, 1225*w* (sh), 1195*w*, 1165*m*, 1150*s*, 1135*m*, 1120*s*, 1095*s*, 1070*m*, 1060*s*, 1045*m*, 1020*s*, 1000*m*, 975*w*, 955*w*, 910*m*, 880*m*, 865*m*, 845*w*. ^{1}H-NMR: 0.60, 0.95, 1.21, 1.36 (4*s*, 4 CH_3); 1.09 (*d*, *J* = 6, $(CH_3)_2CH$); 0.7–2.6 (*m*, 4 CH_2); 3.60–3.90 (*m*, H–C(10), $(CH_3)_2CH$). ^{13}C-NMR (75 MHz): 15.8, 21.7, 22.8, 23.0, 23.9, 25.6 (6*q*, 6 CH_3); 21.6, 25.6, 34.0, 37.9 (4*t*, C(4), C(5), C(8), C(9)); 70.1, 83.7 (2*d*, C(10), $CH(CH_3)_2$); 32.8 (*s*, C(7)); 58.7 (*s*, C(6)); 89.4 (2*s* overlapping, C(1), C(3)). MS: 252 (1, M^+, $C_{16}H_{28}O_2$), 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 $C_{16}H_{28}O_2$ (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: 2970*s*, 2930*s*, 2870*m*, 1465*m*, 1450*m*, 1435*m* (sh), 1420*w*, 1395*w*, 1385*m* (sh), 1380*s*, 1370*s*, 1345*w* (br.), 1325*w* (br.), 1290*m*, 1245*w*, 1210*w*, 1180*m*, 1165*m*, 1150*m*, 1130*s*, 1120*s*, 1110*m*, 1080*s*, 1070*s* (sh), 1030*m*, 1005*w*, 980*w*, 965*m*, 950*w*, 940*w*, 915*m*, 885*w*, 855*w*. ^{1}H-NMR: 0.60, 0.93, 1.32, 1.38 (4*s*, 4 CH_3); 1.08, 1.12 (2*d*, *J* = 6, $(CH_3)_2CH$); 1.0–2.4 (*m*, 4 CH_2); 3.24 (*dd*, *J* = 6.5, 4, H–C(10)); 3.66 (*sept.*, *J* = 6, $(CH_3)_2CH$). ^{13}C-NMR: 22.0, 22.5, 22.9, 26.7, 27.3 (6*q*, 2*q* at 22.5, 6 CH_3); 18.8, 24.4, 33.9, (4*t*, 2*t* at 33.9, C(4), C(5), C(5), C(8), C(9)); 71.1, 77.5 (2*d*, C(10), $(CH_3)_2CH$); 31.4 (*s*, C(7)); 56.5 (*s*, C(6)); 84.6, 88.4 (2*s*, C(1), C(8)). MS: 252 (*ca.* 1, M^+, $C_{16}H_{28}O_2$), 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 $C_{16}H_{28}O_2$ (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: 3620*w*, 3480*w* (br.), 2970*s*, 2930*s*, 2870*s*, 1465*m* (sh), 1450*m*, 1380*m* (sh), 1370*m*, 1360*m* (sh), 1375*m*, 1320*m*, 1240*w* (br.),

1200*w*, 1175*m*, 1140*m*, 1120*s*, 1070*m*, 1040*s*, 1020*m*, 1000*m*, 980*w*, 950*w*, 930*w*. ^{1}H-NMR: 0.94, 1.02 (2*s*, 2 CH_3–C(6')); 1.10 (*d*, J = 6, $(CH_3)_2CH$); 1.14 (*d*, J = 7, 3 H–C(1)); 1.61 (*m*, $w_{1/2}$ = 3, CH_3–C(2')); 1.0–2.4 (*m*, 4 CH_2, OH); 3.30–3.80 (*m*, H–C(2), H–C(3'), $(CH_3)_2CH$). ^{13}C-NMR: 16.8, 22.1, 23.3, 23.9, 27.2, 28.5 (6*q*, 6 CH_3); 25.1, 25.4, 35.0, 39.3 (4*t*, C(3), C(4), C(4'), C(5')); 68.5, 70.0, 75.6 (3*d*, C(2), C(3'), $(CH_3)_2CH$); 35.4 (*s*, C(6')); 127.8, 142.0 (2*s*, C(1'), C(2')). MS: 254 (*ca.* 1, M^+, $C_{16}H_{30}O_2$), 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 $C_{16}H_{30}O_2$ (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: 2965*s*, 2930*s*, 2880*s*, 1465*m*, 1450*m*, 1440*w*, 1370*m*, 1365*m* (sh), 1340*w*, 1330*w*, 1180*m*, 1170*m*, 1135*m* (sh), 1120*s*, 1090*w*, 1060*m*, 1055*m*, 1030*m*, 1000*m*, 980*m*, 970*m*, 930*w*, 895*w*, 880*w*. ^{1}H-NMR: 0.68, 0.89, 1.24 (3*s*, CH_3–C(4), 2 CH_3–C(8)); 1.10, 1.13 (2*d*, J = 6, $(CH_3)_2CH$); 0.80–2.50 (*m*, 4 CH_2, H–C(7)); 3.58 (*sept.*, J = 6, $(CH_3)_2CH$); 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^+, $C_{16}H_{28}O_2$), 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* MnO_2. A slurry of **6** (125 mg, 0.595 mmol) and MnO_2 (800 mg) in CH_2Cl_2 (35 ml) was stirred at r.t. for 20 h and filtered through *Celite*. CC (8 g SiO_2, hexane/Et_2O 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 CH_2Cl_2 (7 ml) was stirred at r.t. for 4 h. CC (20 g SiO_2, hexane/Et_2O 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: 3020*w* (sh), 2960*s*, 2920*s*, 2900*m* (sh), 2860*m*, 1690*s*, 1620*m*, 1465*m*, 1450*m*, 1442*m* (sh), 1410*m*, 1380*s*, 1375*m* (sh), 1360*m*, 1320*w*, 1305*w*, 1270*m*, 1215*w*, 1200*m*, 1170*w*, 1155*w*, 1135*m* (sh), 1125*m* (br.), 1080*s*, 1060*m*, 1015*m*, 940*m*, 910*w*, 890*w*, 870*w*. ^{1}H-NMR: 0.97 (2*s* overlapping, 2 CH_3–C(10)); 1.17 (*d*, J = 6, CH_3–C(2)); 1.0–2.4 (*m*, 4 CH_2); 4.09 (*ddq*, J = 6, H–C(2)); 5.14, 5.55 (2*d*, J = 2.5, CH_2=C(6)). ^{13}C-NMR (75 MHz): 21.5, 22.5, 23.6 (3*q*, 3 CH_3); 30.5, 32.5, 33.7, 36.8 (4*t*, C(3), C(4), C(8), C(9)); 116.8 (*t*, CH_2=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^+, $C_{13}H_{20}O_2$), 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 CH_2Cl_2 (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: 2960*s*, 2920*s*, 2860*m*, 2820*w*, 1720*s*, 1465*m* (sh), 1450*m*, 1440*m*, 1420*m*, 1385*w*, 1375*m*, 1365*m*, 1320*w*, 1290*m*, 1260*w*, 1195*w*, 1165*w* (sh), 1155*m*, 1135*w*, 1110*m*, 1095*w*, 1065*m*, 1020*w* (sh), 1000*w*, 970*w*, 950*w*, 915*m*, 895*w*, 865*m*, 855*w*. ^{1}H-NMR: 0.79, 1.03, 1.26, 1.29 (4*s*, 4 CH_3); 1.50–2.60 (*m*, 4 CH_2). ^{13}C-NMR: 18.7, 22.1, 24.9 (4*q*, 2*q* at 22.1, 4 CH_3); 20.3, 33.7, 35.1, 36.9 (4*t*, C(4), C(5), C(8), C(9)); 32.6 (*s*, C(7)); 60.2 (*s*, C(6)); 86.0, 90.6 (2*s*, C(1), C(3)); 214.6 (*s*, C(10)). MS: 208 (8, M^+, $C_{13}H_{20}O_2$), 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 $C_{13}H_{20}O_2$ (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 CH_2Cl_2 (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 CrO_3 (43 mg, 0.428 mmol) and pyridine (68 mg, 0.857 mmol) in CH_2Cl_2 (1.5 ml) was stirred vigorously for 30 min; afterwards a soln. of **9** (15 mg, 0.072 mmol) in CH_2Cl_2 (1.5 ml) was added, and the mixture was allowed to react for 30 min. Filtration through *Celite* yielded **33** (9 mg, 60%).

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

905*w*, 885*w*. ^{1}H-NMR: 0.80, 0.94, 0.98, 1.29 (4*s*, 4 CH_3); 1.10–2.40 (*m*, 4 CH_2). ^{13}C-NMR: 15.5, 16.5, 21.8, 23.2 (4*q*, 4 CH_3); 25.7, 33.5, 35.8, 36.5 (4*t*, C(4), C(5), C(8), C(9)); 32.3 (*s*, C(6)); 59.8 (*s*, C(2)); 91.3, 98.5 (2*s*, C(1), C(7)); 214.9 (*s*, C(3)). MS: 208 (18, M^+, $C_{13}H_{20}O_2$), 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 $C_{13}H_{20}O_2$ (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 CrO_3 (295 mg, 2.92 mmol) and pyridine (461 mg, 5.83 mmol) in CH_2Cl_2 (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 CrO_3 (107 mg, 1.07 mmol) and pyridine (170 mg, 2.14 mmol) in CH_2Cl_2 (3 ml). CC of the crude mixture (15 g SiO_2, hexane/Et_2O 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 CrO_3 (51 mg, 0.51 mmol) and pyridine (80 mg, 1.02 mmol) in CH_2Cl_2 (1.5 ml). After 6 h, no reaction of **15** was observed.

3.1.4. *Treatment with HCl in* CCl_4 [3]. 3.1.4.1. *Treatment of* **9**. A soln. of **9** (98 mg, 0.429 mmol) in CCl_4 (15 ml) was stirred vigorously in the presence of a few drops of conc. HCl for 30 min. After adding an excess of $NaHCO_3$ and $MgSO_4$, CC (9 g SiO_2, hexane/Et_2O 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: 3620*m*, 3500*w* (br.), 3065*w*, 3045*w*, 2960*s*, 2940*s*, 2910*s*, 2865*s*, 2850*m*, 1615*w*, 1560*w* (br.), 1470*m*, 1455*m*, 1445*m*, 1380*m*, 1360*m*, 1270*w* (br.), 1245*w* (br.), 1190*w* (br.), 1150*w* (br.), 1075*w* (sh), 1055*m*, 1050*m* (sh), 1035*s*, 1005*m*, 965*w*, 940*w*, 930*w*, 905*w*, 860*w*, 650*w*. ^{1}H-NMR ($CDCl_3$): 1.09, 1.13, 1.16 (3*s*, CH_3–C(1), 2 CH_3–C(5)); 0.8–2.0 (*m*, 2 CH_2, OH); 1.97 (*d*, *J* = 1, CH_3–C(9)); 3.00 (*dd*, *J* = 11, 5, H–C(2)); 5.87 (*m*, $w_{1/2}$ = 2, H–C(7), H–C(8)). ^{13}C-NMR: 14.3, 14.9, 25.5, 30.4 (4*q*, 4 CH_3); 29.5, 39.8 (2*t*, C(3), C(4)); 77.3 (*d*, C(2)); 122.1, 124.1 (2*d*, C(7), C(8)); 34.4 (*s*, C(5)); 58.3 (*s*, C(1)); 154.0, 159.0 (2*s*, C(6), C(9)). MS: 192 (52, M^+, $C_{13}H_{20}O$), 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 SiO_2, hexane/Et_2O 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/Et_2O 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 SiO_2, hexane/Et_2O 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: 3440*m*, 3060*w*, 3030*w*, 2960*m*, 2950*m*, 2920*m*, 2890*w* (sh), 2870*w*, 1740*s*, 1600*m*, 1590*m*, 1515*s*, 1465*w*, 1460*w*, 1450*w*, 1435*s*, 1395*w* (sh), 1385*m*, 1380*m* (sh), 1360*w*, 1320*m*, 1310*m*, 1270*w*, 1245*w*, 1205*s*, 1185*m*, 1180*m*, 1165*w*, 1155*m*, 1140*w* (sh), 1090*w*, 1080*m*, 1060*m*, 1050*m*, 1025*m*, 1005*w*, 995*w*, 970*w*, 925*w*, 910*w*, 895*w*, 885*w*, 690*m*. ^{1}H-NMR (80 MHz, $CDCl_3$): 0.87 (6 H); 0.90 (3 H); 1.31 (3 H); (3*s*, 2 CH_3–C(6), CH_3–C(1), CH_3–C(2)); 1.25–2.00 (*m*, 4 CH_2); 5.60–5.85 (*m*, H–C(3)); 6.40–6.70 (*m*, NH); 6.90–7.60 (*m*, Ph). ^{13}C-NMR: 11.7, 15.1, 23.0, 23.2 (4*q*, 4 CH_3); 24.7, 27.3, 32.5, 36.7 (4*t*, C(4), C(5), C(8), C(9)); 74.8 (*d*, C(3)); 118.7, 123.4, 129.0 (3*d*, 5 arom. C); 32.3 (*s*, C(6)); 52.6 (*s*, C(2)); 89.9, 97.3 (2*s*, C(1), C(7)); 138.1 (*s*, arom. C–N); 153.0 (*s*, NH–COO). MS: 329 (2, M^+, $C_{20}H_{27}NO_3$), 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* CCl_4. 3.2.1.1. *Treatment of* **20**. A soln. of **20** (44 mg, 0.175 mmol) in CCl_4 (8 ml) was treated as described in *Section 3.1.4.1*. CC (5 g SiO_2, hexane/Et_2O 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 CCl_4 (30 ml) was treated as described in *Sect. 3.1.4.1*. CC of the crude product (10 g SiO_2, hexane/Et_2O 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: 3580*w*, 3490*w* (br.), 3060*w*, 2980*m*, 2960*m*, 2940*m*, 2890*m* (sh), 2870*w*, 2850*w*, 1740*m*, 1715*s*, 1460*w*, 1445*w*, 1435*w*, 1380*m*, 1375*m*, 1365*m*, 1360*m*, 1340*w*, 1320*w*, 1300*w*, 1255*s*, 1245*s* (sh), 1185*w*, 1160*w* (br.), 1135*w*, 1090*w*, 1085*w*, 1065*w* (br.), 1030*m*, 1020*m*, 1000*w*, 980*m*, 970*w*, 950*w*, 925*w*, 905*w*, 860*w*. ^{1}H-NMR: 1.01, 1.08, 1.09, 1.10 (4*s*, 4 CH_3); 1.98 (*s*, CH_3COO); 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, δ_A = 2.08, δ_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^{+} – 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 $C_{15}H_{24}O_3$ (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°/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*. ^{1}H-NMR: 0.96, 1.04, 1.26 (4*s*, 2*s* at 1.04, 4 CH_3); 1.09 (*d*, J = 6, $(CH_3)_2CH$); 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), $(CH_3)_2CH$); 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), $(CH_3)_2CH$); 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^{+}, $C_{16}H_{28}O_2$), 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 $C_{16}H_{28}O_2$ (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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