23. Photochemical Reactions

141st Communication[1])

Photochemistry of α,β-Unsaturated δ,ε-Epoxyketones of the Ionone Series

by **Peter Mathies**[2])[3]), **Bruno Frei**, and **Oskar Jeger***

Laboratorium für Organische Chemie der Eidgenössischen Technischen Hochschule, Universitätstrasse 16, CH-8092 Zürich

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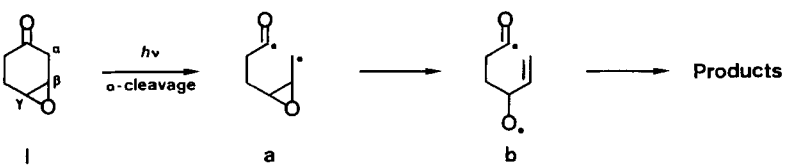
On n,π*- as well as on π,π*-excitation, the 4,5-epoxy-α-ionones (*E*)-**1**, (*E*)-**2**, and (*E*)-**3** undergo (*E*)/(*Z*)-isomerization and subsequent γ-H-abstraction leading to the corresponding 4-hydroxy-β-ionones (*E*/*Z*)-**9**, (*E*/*Z*)-**13**, and (*E*/*Z*)-**17** as primary photoproducts. On photolysis of (*E*)-**3**, as an additional primary photoproduct, the β,γ-unsaturated δ,ε-epoxy ketone **18** was obtained. The other isolated compounds, namely the 2*H*-pyrans **10A** + **B** and **14A** + **B** as well as the *retro*-γ-ionones **11** and **15A** + **B**, represent known types of products, which are derived from the 4-hydroxy-β-ionones (*E*/*Z*)-**9** and (*E*/*Z*)-**13**, respectively.

1. Introduction. – It has been shown previously [2] that irradiation of β,γ-epoxyketones such as **I** *(Scheme 1)* initially causes *Norrish*-type-I bond cleavage leading to a

Scheme 1



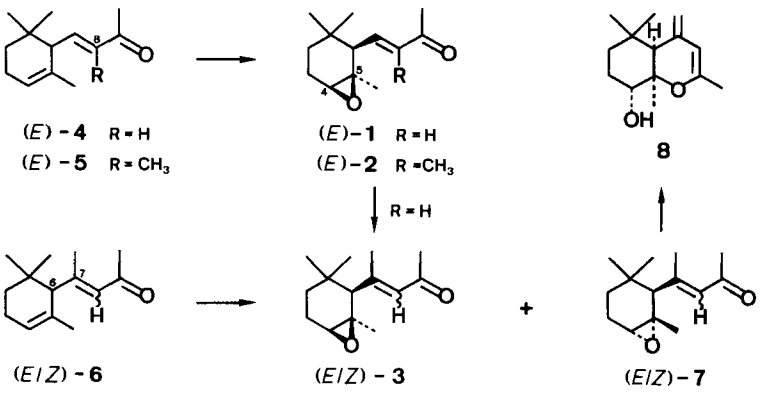
diradical **a** which undergoes subsequent opening of the oxirane ring. The hereby formed acyl alkoxy diradical **b** reacts further to give various types of products. These findings made it of interest to examine, whether an oxirane cleavage could also be induced by initial abstraction of a γ-H-atom in α,β-unsaturated δ,ε-epoxyketones, and what type of products would be formed. We decided to investigate the behavior of the 4,5-epoxy-4,5-dihydro-α-ionones (*E*)-**1**, (*E*)-**2** and (*E*)-**3** *(Scheme 2)*, since α-ionone ((*E*)-**4**) undergoes photoisomerization involving γ-H-abstraction [3]. In addition, comparison of the photochemical behavior of (*E*)-**1** with that of its methyl homologs (*E*)-**2** and (*E*)-**3** was expected to give information about the influence of a CH_3-substituent in α- or β-position of the enone chromophore. This comparison was of particular inter-

[1]) 140th Communication: [1].

[2]) Taken in part from the Ph. D. thesis of *P. M.*, ETHZ No. 7679 (1984).

[3]) Presented in part by *P. M.* at the 'Herbstversammlung der Schweizerischen Chemischen Gesellschaft', October 14, 1983, Bern.

Scheme 2



est, since, in contrast to α-ionone ((*E*)-**4**), 8-methyl-α-ionone ((*E*)-**5**)[4]) did not show photo-isomerization *via* γ-H-abstraction [5]. Furthermore, from NMR measurements at low temperature it was evident that, in contrast to (*E*)-**4** and (*E*)-**5**, in 7-methyl-α-ionone ((*E*)-**6**), the rotation of the side chain around the C(6),C(7)-bond is hindered due to steric interaction of the CH_3-group at C(7) with the geminal CH_3-groups [6].

2. Preparation and Stereochemical Assignment of the Epoxyenones (*E*)-1, (*E*)-2 and (*E*)-3. – Compound (*E*)-**1** was obtained by treatment of (*E*)-**4** with monoperphthalic acid in Et_2O according to *Karrer* and *Stürzinger* [7]. Analogously, the previously unknown epoxyenone (*E*)-**2** was prepared in 82% yield by stereoselective epoxidation of (*E*)-**5**. The reaction of (*E*)-**6** [8] with monoperphthalic acid led to a 1:1 mixture of the diastereomeric epoxyenones (*E*)-**3** (36%) and (*E*)-**7** (36%; see *Scheme 2*). The epoxidation of (*Z*)-**6** was fairly stereoselective, however; thus the epoxides (*Z*)-**3** and (*Z*)-**7** were obtained in 76% and 10% yields, respectively. Treatment of both (*E*)- and (*Z*)-**3** with a *ca.* 0.3M solution of NaOMe in MeOH at reflux temperature led to a 9:2 mixture of (*E*/*Z*)-**3** (*ca.* 88%). On the other hand, analogous treatment of their diastereomers (*E*)- and (*Z*)-**7** afforded in each case the bicyclic enol ether **8** in *ca.* 95% yield. This different behavior of the diastereomeric epoxyenones (*E*/*Z*)-**3** and (*E*/*Z*)-**7** allows their stereochemistry to be assigned. Only (*Z*)-**7** fulfils the stereoelectronic requirements for facile oxirane ring opening, *i.e.*, the *trans*-diaxial arrangement of the two O-atoms involved. Therefore, the epoxide O-atom and the enone side chain must be in *trans*-relation in (*E*/*Z*)-**7**, and in *cis*-relation in (*E*/*Z*)-**3**. Furthermore, the epoxyenones (*E*/*Z*)-**3** were obtained in 23% yield by alkylation of the epoxyenone (*E*)-**1**, furnishing further confirmation of the previously assigned stereochemistry of the latter [7].

3. Photolyses. – Irradiation of *ca.* 0.05M solutions of the epoxyenones (*E*)-**1**, (*E*)-**2**, and (*E*)-**3** in MeCN and $\lambda > 280$ nm (n,π*-excitation) and $\lambda = 254$ nm (π,π*-excitation), respectively, up to *ca.* 90% conversion (details are given in the *Exper. Part*) gave the following product distributions.

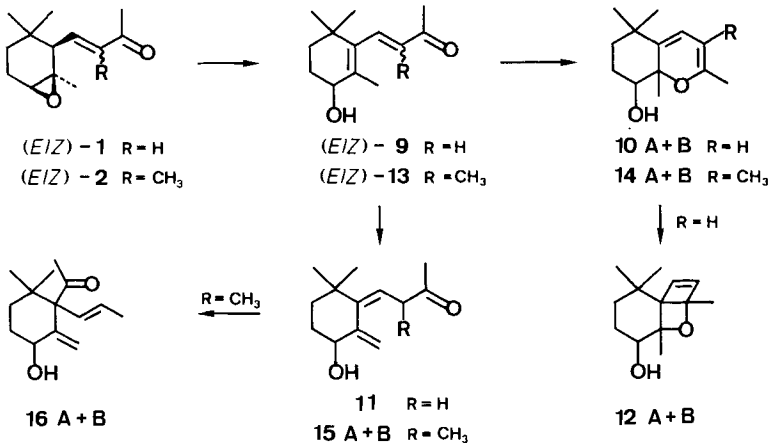
[4]) In ionone derivatives, numbering according to the carotinoid nomenclature is used [4].

3.1. *Photolyses of* (E)-**1** *(Scheme 3).* – 3.1.1. *n,π*-Excitation:* (*Z*)-**1** (1%), (*E*)-**9** (13%), **10A** (33%), **10B** (37%), **11** (3%), **12A** (1%), and **12B** (3%)[5]).

3.1.2. *π,π*-Excitation:* (*Z*)-**1** (6%), (*E*)-**9** (14%), **10A** (4%), **10B** (5%), and **11** (33%)[5]).

3.2. *Photolyses of* (E)-**2** (see *Scheme 3*). 3.2.1. *n,π*-Excitation:* (*Z*)-**2** (2%), (*E*)-**13** (26%), (*Z*)-**13**[6]) (15%), **14A** (9%), **14B** (11%), **15A** (9%), **15B** (9%), **16A** (4%), and **16B** (2%).

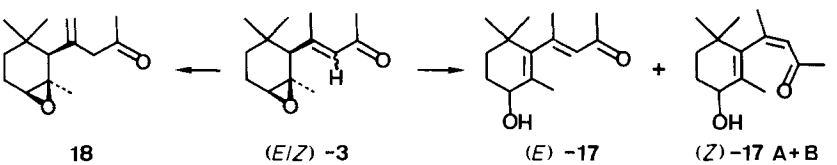
Scheme 3



3.2.2. *π,π*-Excitation:* (*Z*)-**2** (6%), (*E*)-**13** (17%), (*Z*)-**13** (30%)[6]), **14A** (2%), **14B** (2%), **15A** (14%), and **15B** (16%).

3.3. *Photolyses of* (E)-**3** (see *Scheme 4*). – 3.3.1. *n,π*-Excitation:* (*Z*)-**3** (39%), (*E*)-**17** (16%), (*Z*)-**17A** (13%), (*Z*)-**17B** (25%), **18** (1%), and additional photoproducts arising from (*E*/*Z*)-**17** (2%)[7]).

Scheme 4



3.3.2. *π,π*-Excitation:* (*Z*)-**3** (19%), (*E*)-**17** (12%), (*Z*)-**17A** (12%), (*Z*)-**17B** (22%), **18** (8%), and additional photoproducts arising from (*E*/*Z*)-**17** (4%)[7]).

4. Structure of the Products. – The structures of all new compounds were deduced from their spectral data. Since OH-free analogs of most of the products obtained here are known from the photolyses of β-ionone [10], only the most relevant spectral data are discussed herein together with the chemical transformations which confirmed the assigned structures. Full spectral data and the assignment of the NMR data are given in the *Exper. Part.*

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[5]) With the exception of (*Z*)-**1**, the same products were obtained on photolysis of (*E*)-**9** under these conditions (see *Exper. Part*).

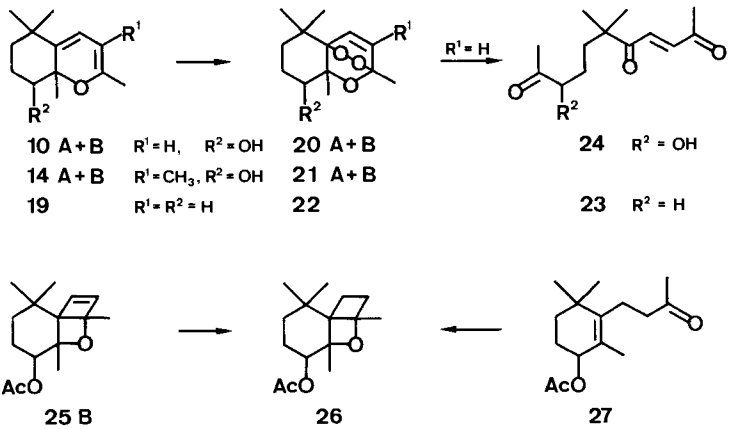
[6]) Chromatography fractions containing (*Z*)-**13** gradually changed to a mixture **14A**/**14B** in a 3:1 equilibrium ratio.

[7]) The results of the photolyses of (*E*/*Z*)-**17** will be reported in a forthcoming paper [9].

Epoxyenones (E/Z)-**1**, (E/Z)-**2**, (E/Z)-**3**, *and* (E/Z)-**7** (*Scheme 2* and *3*). The stereochemical relation of the epoxide moiety and the enone side chain of compounds (*E*/*Z*)-**3** and (*E*/*Z*)-**7** was established by their reactivity upon treatment with base and on the transformation of the epoxyenone (*E*)-**1** of known configuration [7] to (*E*/*Z*)-**3** (see *Sect. 2*). The inspection of models indicated that the epoxidation of (*E*)-**5** occurs from the same side as in (*E*)-**4**, thus leading to the epoxyenone (*E*)-**2** with the same relative configuration as (*E*)-**1**. The configuration of the enone double bond of (*E*)- and (*Z*)-**1** was assigned unequivocally from the ^{1}H-NMR-coupling constants of the olefinic H-atoms ((*E*)-**1**: J = 16 [7b], (*Z*)-**1**: J = 11.5). On the other hand, the configuration of the double bond of (*E*/*Z*)-**2**, (*E*/*Z*)-**3**, and (*E*/*Z*)-**7** was correlated with the chemical shift of the allylic H–C(6)[4]). Due to the anisotropic effect of the carbonyl group, this signal of (*Z*)-**2** is shifted downfield to 2.85 ppm whereas the corresponding signal of (*E*)-**2** appears at 2.47 ppm. This effect is even more profound in the case of (*Z*)-**3** and (*Z*)-**7**, in the spectra of which the signals of H–C(6)[4]) are shifted in both cases to *ca.* 4.2 ppm, whereas the corresponding signals of (*E*)-**3** and (*E*)-**7** appear at 2.15 and 2.35 ppm, respectively.

4-Hydroxy-β-ionones (E)-**17** *and* (Z)-**17A** + **B** (*Scheme 4*) were independently prepared *via* alkylation of (*E*)-**9** [11]. It is noteworthy that two conformers (*Z*)-**17A** and (*Z*)-**17B** arising from hindered rotation around the C(6),C(7)-bond[4]) could be separated by chromatography, however, heating them separately to 80° for 5 h led in both cases to 1:1 mixtures.

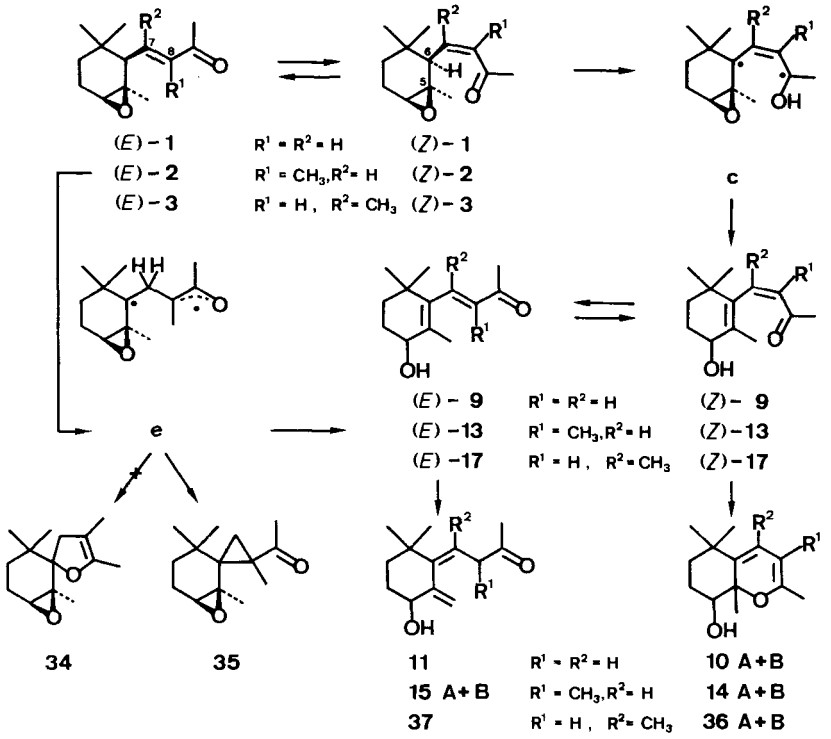
Scheme 5



2H-*Pyrans* **10A** + **B** *and* **14A** + **B** (*Scheme 3*). The structures were deduced from their spectral data and by comparing them with that of **19** (*Scheme 5*), a known product of the photolysis of β-ionone [10]. Reaction of **10A** + **B** and **14A** + **B** with $^1O_2$ gave the endoperoxides **20A** + **B** and **21A** + **B**, respectively. Analogous to the acid-catalyzed transformation of **22**→**23** [12], the endoperoxides **20A** + **B** were converted to the acyclic triketone **24**. Photolysis ($\lambda > 280$ nm) of **10A** and **10B** led to a 1:2 mixture of the tricyclic oxetans **12A** + **B**. The acetate **25B** derived from the alcohol **12B** was hydrogenated to the saturated compound **26**, which was also obtained as a photoproduct of 4-acetoxy-7,8-dihydro-β-ionone (**27**) [13].

5. Discussion. – n,π*- as well as π,π*-excitation of the epoxyenone (*E*)-**1**, (*E*)-**2**, and (*E*)-**3** causes rapid (*E*)/(*Z*)-isomerization and formation of the 4-hydroxy-β-ionones (*E*/*Z*)-**9**, (*E*/*Z*)-**13**, and (*E*/*Z*)-**17** as primary photoproducts. On photolysis of (*E*)-**3**, as an additional primary photoproduct, the β,γ'-unsaturated δ,ε-epoxy ketone **18** (*Scheme 4*) was obtained in low yield. The formation of these compounds can be explained by γ-H-abstraction of the epoxyenones (*Z*)-**1**, (*Z*)-**2**, and (*Z*)-**3** at C(6) leading to the diradical intermediates of type **c**. Analogously to the oxirane cleavage **a**→**b** (*Scheme 1*), the intermediate **c** undergoes scission of the C(5),O-bond of the oxirane, which is followed by H-transfer (*Scheme 6*). Compound **18** (*Scheme 4*) arises by an alternative γ-H-abstraction from CH_3–C(7)-group in (*E*)-**3**.

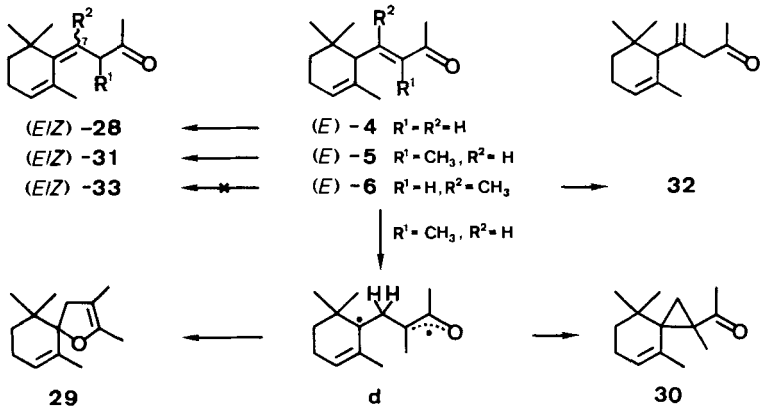
Scheme 6



The other isolated compounds **10A + B, 11, 12A + B, 14A + B, 15A + B,** and **16A + B** are all secondary photoproducts derived from (*E*/*Z*)-**9**, (*E*/*Z*)-**13**, and (*E*/*Z*)-**17**, respectively.

Comparison of the behavior of the epoxyenones (*E*)-**1**, (*E*)-**2**, and (*E*)-**3** with that of the parent α-ionones (*E*)-**4**, (*E*)-**5**, and (*E*)-**6** *(Scheme 7)* is of interest. Thus, it has

Scheme 7



been reported that (*E*)-**4** efficiently undergoes photo-isomerization to the *retro*-α-ionones (*E*/*Z*)-**28** *via* a γ-H-abstraction at C(6) [3]. On the other hand, photolysis of (*E*)-**5** in neutral solvents led to the compounds **29** and **30** involving as first step a 1,2-H-shift ((*E*)-**5**→**d**; see *Scheme 7*)[8]). The *retro*-α-ionones (*E*/*Z*)-**31** were only formed on photolysis of (*E*)-**5** in acidic or basic media. Finally, (*E*)-**6** was shown to be quite unreactive. Besides (*E*)/(*Z*)-isomerization, only the formation of the deconjugated compound **32** *(Scheme 7)* arising from γ-H-abstraction at CH_3–C(7) was observed to a small extent [11]. The lack of formation of the *retro*-α-ionones (*E*/*Z*)-**33** is apparently due to an unfavorable steric interaction between the two substituents at C(7) and the ring CH_3-groups.

On the basis of the differing behavior of (*E*)-**4**, (*E*)-**5**, and (*E*)-**6**, it was surprising that irradiation of the derived epoxyenones (*E*)-**1**, (*E*)-**2**, and (*E*)-**3** should lead to the same types of primary products. However, the formation of (*E*/*Z*)-**9**, (*E*/*Z*)-**13**, and (*E*/*Z*)-**17** may not necessarily imply the same reaction mechanism. In particular, for the transformation of (*E*)-**2**→(*E*/*Z*)-**13** an alternative mechanism could be considered *(Scheme 6)*. Thus, analogous to the transformation of (*E*)-**5**→**d** *(Scheme 7)*, a 1,2-H-shift in (*E*)-**2** could lead to the diradical intermediate **e**. Instead of ring closure analogous to **d**→**29** + **30** *(Scheme 7)* leading to compounds **34** and **35**, the intermediate **e** could undergo rapid cleavage of the C(5),O-bond of the oxirane followed by a 1,5-H-shift furnishing (*E*)- or (*Z*)-**13**[9]).

The 4-hydroxy-β-ionones (*E*/*Z*)-**9**, (*E*/*Z*)-**13** and (*E*/*Z*)-**17** show the same behavior as their analogs without an OH-function in 4-position (*cf.* [5] [9] [10]). Thus, the 2*H*-pyrans **10A** + **B** and **14A** + **B** are formed by thermal or photochemical cyclization of the dienones (*Z*)-**9** and (*Z*)-**13**, respectively. On the other hand, cyclization of the dienones (*Z*)-**17A** + **B** to the 2*H*-pyrans **36A** + **B** does not occur due to an unfavorable steric interaction between the CH_3-group at C(7) and the geminal CH_3-groups. Due to this steric repulsion, the two conformers (*Z*)-**17A** and (*Z*)-**17B** arising from hindered rotation around the C(6),C(7)-bond could be isolated.

Also in analogy to the β-ionone derivatives without an OH-function in 4-position, the hydroxylated compounds (*E*)-**9**, (*E*)-**13**, and (*E*)-**17** undergo a 1,5-sigmatropic H-shift leading to the *retro*-γ-ionones **11**, **15A** + **B**, and **37**[7])[10]).

Furthermore, on n,π*-excitation of the epoxyenones (*E*)-**1** and (*E*)-**2**, the compounds **12A** + **B** and **16A** + **B**, respectively, are formed in low yield *(Scheme 3)*. The tricyclic oxetanes **12A** + **B** are products of an electrocyclic reaction of the 2*H*-pyrans

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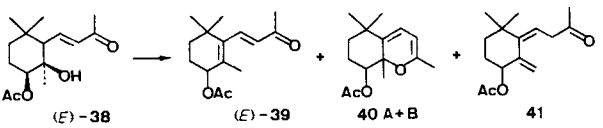
[8]) The labile compound **30** which was previously postulated [5] has been recently isolated by flash chromatography [11].

[9]) This hypothesis may be supported by the detection of traces (*ca.* 2%) of two diastereomeric compounds of structure **35**, they could, however, not be isolated in pure form.

[10]) *Etoh et al.* [14] reported that π,π*-excitation of the hydroxyacetate (*E*)-**38** gave rise to a photochemically induced dehydration *via* a γ-H-abstraction furnishing the compound (*E*)-**39** and its secondary products **40A** + **B** and **41** *(Scheme 8)*.

Scheme 8



10A + B as was demonstrated by photolysis of the latter. The compounds **16A + B** presumably arise from the homoconjugated ketones **15A + B** *via* a 1,3-acyl shift, which was previously reported for retro-α-ionone (*E*/*Z*)-**28** [3].

Conclusion. – The aforementioned results demonstrate that, on n,π*- as well as on π,π*-excitation, the 4,5-epoxy-α-ionones (*E*/*Z*)-**1**, (*E*/*Z*)-**2**, and (*E*/*Z*)-**3** may be converted efficiently to the corresponding 4-hydroxy-β-ionones (*E*/*Z*)-**9**, (*E*/*Z*)-**13**, and (*E*/*Z*)-**14** *via* initial γ-H-abstraction.

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Experimental Part

General. See [15], except as noted below. Analytical gas chromatography was performed using a 25 m × 0.33 mm *Ucon 50 HB 5100* glass capillary. Column chromatography was carried out on silica gel *60 Merck* 0.040–0.063 mm, 230–400 mesh ASTM (SiO_2) according to [16] ('flash chromatography'). Analytically pure samples were obtained, in general, after repeated column chromatography on SiO_2; in some cases further purification was necessary with an HPLC (*Du Pont Instruments*, Model *830*, UV detector), using a 25 cm × 23.6 mm SiO_2 column. In general, ^{1}H-NMR spectra were taken on a *Bruker WP-80 CW* (80 MHz) or *WM 300* (300 MHz) instrument in $CDCl_3$-soln. or, exceptionally (as indicated below), in CCl_4-soln. on a *Varian HA-100* instrument (100 MHz).

Alcohols were acetylated by reaction with 2 equiv. of Ac_2O in *ca.* 0.5M pyridine soln. In some cases a catalytic amount of *N*,*N*-dimethylaminopyridine was added. The mixture was worked up in Et_2O and the org. phase washed with sat. aq. $NaHCO_3$ and sat. aq. $CuSO_4$.

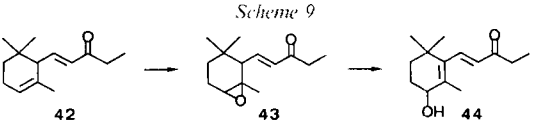
1. Preparations. – 1.1. *Epoxidation of (*E*)-3-Methyl-4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-one (= (*E*)-8-Methyl-α-ionone, (E)-***5***).* To a soln. of (*E*)-**5** (513 mg, 2.49 mmol; containing *ca.* 7% of the isomeric ethyl ketone **42**)[11]) in Et_2O (20 ml) a soln. of monoperphthalic acid in Et_2O [17] (0.50M, 6.00 ml, 3.00 mmol) was added at 0°, the mixture first stirred for 1 h at 0° and then for 12 h at r.t. The org. phase was washed with $Na_2S_2O_3$-soln. (sat. aq.), $NaHCO_3$-soln. (sat.) and worked up. Chromatography (Et_2O/pentane 4:1) afforded a mixture of (*E*)-**2** and **43** (453 mg, 82%).

Treatment of crude (*E*)-**2** (1.26 g, 5.67 mmol) with NaOMe (380 mg, 7.03 mmol) in MeOH (25 ml) at reflux temp. for 24 h afforded after workup and chromatography (SiO_2, Et_2O/pentane 1:1) pure (*E*)-**2** (1.09 g, 87%)[11]).

*(*E,*1′*RS,2′*RS,3′*SR)-4-(2′,3′-Epoxy-2′,6′,6′-trimethylcyclohexyl)-3-methyl-3-buten-2-one* ((*E*)-**2**). B.p. 80°/0.01 Torr. UV (0.249 mg in 25 ml MeCN): 232 (15600). UV (6.010 mg in 10 ml MeCN): 317 (50). IR: 3055*w*, 2960*s*, 2925*m*, 2865*w*, 1670*s*, 1640*w*, 1470*w* (sh), 1460*w* (sh), 1445*m*, 1435*w*, 1420*w* (sh), 1385*w*, 1375*m*, 1365*m*, 1345*w*, 1315*w* (sh), 1305*w* (sh), 1300*w*, 1290*w* (sh), 1260*w* (sh), 1250*m*, 1240*w* (sh), 1205*w*, 1180*w* (sh), 1175*w*,

[11]) Compounds (*E*)-**5** and **42** as well as the epoxides (*E*)-**2** and **43** could not be separated. However, on treatment of (*E*)-**2** and **43** with NaOMe only **43** was transformed into the hydroxydienone **44** as described for the conversion of α-iononepoxide (*E*)-**1** to (**E**)-4-hydroxy-β-ionone (*E*)-**9** [7]. Compound (*E*)-**2** could easily be separated from **44** by chromatography.

Scheme 9



1145*w*, 1090*w*, 1050*w*, 980*w*, 965*w*, 910*m*, 880*w*. ^{1}H-NMR: 0.74, 0.93, 1.21 (3*s*, 2 CH_3–C(6'), CH_3–C(2')); 0.9–1.6 (*m*, 2H–C(5')); 1.82 (*d*, J = 1.5, CH_3–C(3)); 1.8–2.1 (*m*, 2H–C(4')); 2.32 (*s*, 3H–C(1)); 2.47 (*d*, J = 10.0, H–C(1')); 3.06 (*dd*, $J_1 = J_2$ = 2.0, H–C(3')); 6.62 (*dq*, J_1 = 10.0, J_2 = 1.5, H–C(4)). ^{13}C-NMR (20 MHz): 12.0, 24.3, 25.6, 26.6, 28.5 (5*q*, 5 CH_3); 21.9, 29.2 (2*t*, C(4'), C(5')); 32.0 (*s*, C(6')); 47.8 (*d*, C(1')); 59.3 (*s*, C(2')); 59.7 (*d*, C(3')); 139.0 (*s*, C(3)); 141.7 (*d*, C(4)); 199.6 (*s*, C(2)). MS: 222 (2, M^+, $C_{14}H_{22}O_2$), 207 (3), 193 (6), 179 (10), 137 (16), 125 (20), 123 (60), 111 (18), 109 (36), 95 (14), 81 (15), 69 (16), 55 (19), *43* (100), 41 (15). Anal. calc. for $C_{14}H_{22}O_2$ (222.23): C 75.63, H 9.97; found: C 75.94, H 10.01.

1.2. *Epoxidation of (*E*)-4-(2,6,6-Trimethyl-2-cyclohexen-1-yl)-3-penten-2-one (= (*E*)-7-Methyl-α-ionone; (*E*)-***6***).* A soln. of (*E*)-**6** (1.120 g, 5.43 mmol) in Et_2O (50 ml) was treated with a soln. of monoperphthalic acid in Et_2O (0.50M, 13.0 ml, 6.50 mmol) and worked up as described for (*E*)-**5** (see *Sect. 1.1*). Chromatography (Et_2O/pentane 4:1) of the crude product afforded (*E*)-**3** (432 mg, 36%) and (*E*)-**7** (438 mg, 36%).

*(*E*,1'*RS*,2'*RS*,3'*SR*)-4-(2',3'-Epoxy-2',6',6'-trimethylcyclohexyl)-3-penten-2-one* ((*E*)-**3**). B.p. 70°/0.01 Torr. UV (0.339 mg in 25 ml MeCN): 241 (12800). UV (3.644 mg in 2 ml MeCN): 325 (65). IR: 2970*s*, 2950*s* (sh), 2930*s*, 2870*m*, 2850*m* (sh), 1710*w* (sh), 1685*s*, 1605*s*, 1470*w* (sh), 1460*m* (sh), 1450*m*, 1435*m*, 1425*m* (sh), 1385*m*, 1375*m*, 1365*m*, 1350*m*, 1320*w*, 1305*w*, 1290*w*, 1205*s*, 1180*m*, 1165*m*, 1105*w*, 1065*w*, 1015*w*, 1005*w*, 965*m*, 950*w*, 900*w*, 865*w*. ^{1}H-NMR: 0.92 (*s*, 2 CH_3–C(2')); 0.80–1.70 (*m*, 2H–C(5')); 1.80–2.20 (*m*, 2H–C(4')); 2.15 (*s*, H–C(1')); 2.23 (*s*, 3H–C(1)); 2.28 (*d*, J = 1.5, 3H–C(5)); 2.94 (*dd*, $J_1 = J_2$ = 3, H–C(3')); 6.29 (*m*, $w_{1/2}$ = 3, H–C(3)). ^{13}C-NMR (20 MHz): 21.1, 23.5, 24.2, 31.5, 32.1 (5*q*, 5 CH_3); 21.6, 34.2 (2*t*, C(4'), C(5')); 33.0 (*s*, C(6')); 57.9, 58.8 (2*d*, C(1'), C(3')); 59.1 (*s*, C(2')); 128.5 (*d*, C(3)); 157.1 (*s*, C(4)); 198.4 (*s*, C(2)). MS: 222 (2, M^+, $C_{14}H_{22}O_2$), 179 (10), 151 (12), 137 (12), 125 (17), 124 (10), 123 (70), 109 (47), 107 (12), 95 (11), 93 (11), 81 (15), 69 (17), 55 (20), *43* (100), 41 (29). Anal. calc. for $C_{14}H_{22}O_2$ (222.33): C 75.63, H 9.97; found: C 75.61, H 9.89.

*(*E*,1'*RS*,2'*SR*,3'*RS*)-4-(2',3'-Epoxy-2',6',6'-trimethylcyclohexyl)-3-penten-2-one* ((*E*)-**7**). B.p. 70°/0.01 Torr. UV (0.380 mg in 25 ml MeCN): 241 (13400). UV (3.118 mg in 2 ml MeCN): 326 (65). IR: 3000*w* (sh), 2960*s*, 2930*s*, 2870*m*, 1685*s*, 1600*s*, 1475*w*, 1460*m* (sh), 1445*m* (sh), 1435*m*, 1420*m* (sh), 1385*s*, 1380*s*, 1365*m*, 1350*m*, 1310*w*, 1230*w* (sh), 1200*s*, 1170*m*, 1160*m*, 1150*m* (sh), 1070*w*, 1015*w* br., 960*m*, 900*w*, 875*w*, 855*w* (sh), 845*w*. ^{1}H-NMR: 0.82, 1.00 (2*s*, 2 CH_3–C(6')); 1.23 (*s*, CH_3–C(2)); 1.10–1.50 (*m*, 2H–C(5')); 1.90–2.30 (*m*, 2H–C(4')); 2.16 (*m*, $w_{1/2}$ = 6, 3H–C(5)); 2.21 (*s*, 3H–C(1)); 2.35 (*s*, H–C(1')); 3.05 (*dd*, $J_1 = J_2$ = 2.5, H–C(3')); 6.18 (*m*, $w_{1/2}$ = 6, H–C(3)). ^{13}C-NMR (75 MHz, CD_3CN): 20.2, 24.1, 24.1, 29.3, 31.0 (5*q*, 5 CH_3)); 22.3, 32.8 (2*t*, C(4'), C(5')); 32.5 (*s*, C(6')); 59.6 (*s*, C(2')); 59.7, 60.6 (2*d*, C(1'), C(3')); 129.8 (*d*, C(3)); 157.1 (*s*, C(4)); 198.5 (*s*, C(2)). MS: 222 (3, M^+, $C_{14}H_{22}O_2$), 207 (4), 189 (5), 179 (10), 161 (15), 151 (11), 137 (10), 125 (12), 123 (53), 111 (13), 109 (26), 107 (11), 95 (11), 93 (16), 55 (20), *43* (100), 41 (30). Anal. calc. for $C_{14}H_{22}O_2$ (222.33): C 75.63, H 9.97; found: C 75.47, H 9.92.

1.3. *Epoxidation of (*Z*)-***6***.* A soln. of (*Z*)-**6** (1.782 g, 8.64 mmol) in Et_2O (50 ml) was treated with a soln. of monoperphthalic acid in Et_2O (0.50M, 20.7 ml, 10.4 mmol) and worked up as described for (*E*)-**5** (see *Sect. 1.1*). Chromatography (Et_2O/pentane 9:1 to 4:1) of the crude product yielded (*Z*)-**3** (1.466 g, 76%) and (*Z*)-7 (196 mg, 10%).

*(*Z*,1'*RS*,2'*RS*,3'*SR*)-4-(2',3'-Epoxy-2',6',6'-trimethylcyclohexyl)-3-penten-2-one* ((*Z*)-**3**). B.p. 80°/0.01 Torr. UV (0.303 mg in 25 ml MeCN): 244 (10900). UV (5.061 mg in 2 ml MeCN): 327 (55), end absorption to 390. IR: 3000*w* (sh), 2960*s*, 2940*s* (sh), 2920*s*, 2870*m*, 2850*w* (sh), 1680*s*, 1600*s*, 1470*w* (sh), 1460*m* (sh), 1450*m*, 1435*m*, 1420*m*, 1385*m*, 1375*m*, 1360*m*, 1350*m*, 1300*w*, 1230*w*, 1220*w*, 1200*m*, 1190*m*, 1170*s*, 1140*w*, 1095*w*, 1060*m*, 1015*w*, 970*m*, 920*w*, 910*w*, 900*m*, 855*m*. ^{1}H-NMR: 0.83, 0.94 (2*s*, 2 CH_3–C(6')); 1.18 (*s*, CH_3–C(2')); 0.80–1.80 (*m*, 2H–C(5')); 1.80–2.10 (*m*, 2H–C(4')); 2.04 (*d*, J = 1.5, 3H–C(5)); 2.17 (*s*, 3H–C(1)); 2.94 (*dd*, $J_1 = J_2$ = 2.5, H–C(3')); 4.22 (*s*, H–C(1')); 6.32 (*m*, $w_{1/2}$ = 3, H–C(3)). ^{13}C-NMR (20 MHz): 23.7, 24.1, 25.8, 30.2 (5*q*, 2*q* overlapping, 5 CH_3); 22.0, 32.7 (2*t*, C(4'), C(5')); 32.2 (*s*, C(6')); 45.9 (*d*, C(1')); 58.0 (*d*, (C(3')); 58.8 (*s*, C(2')); 128.9 (*d*, C(3)); 158.1 (*s*, C(4)); 198.3 (*s*, C(2)). MS: 222 (12, M^+, $C_{14}H_{22}O_2$), 207 (20), 204 (31), 189 (20), 165 (10), 161 (31), 151 (14), 149 (31), 148 (91), 147 (19), 137 (17), 133 (50), 125 (11), 124 (12), 123 (88), 121 (12), 119 (18), 109 (29), 108 (26), 107 (16), 105 (33), 95 (12), 91 (26), 77 (21), 55 (22), *43* (100), 41 (41). Anal. calc. for $C_{14}H_{22}O_2$ (222.33): C 75.63, H 9.97; found: C 75.65, H 9.87.

*(*Z*,1'*RS*,2'*SR*,3'*RS*)-4-(2',3'-Epoxy-2',6',6'-trimethylcyclohexyl)-3-penten-2-one* ((*Z*)-**7**). UV (0.340 mg in 25 ml MeCN): 243 (9900). UV (4.888 mg in 2 ml MeCN): 327 (50), end absorption to 390. IR: 3000*w*, 2960*s*, 2930*s*, 2910*m* (sh), 2870*m*, 1685*s*, 1605*s*, 1470*w*, 1460*m* (sh), 1450*m*, 1440*m*, 1420*m*, 1385*m*, 1380*m*, 1370*m*, 1360*m*, 1350*m*, 1310*w*, 1240*w*, 1215*w*, 1205*w*, 1180*s*, 1170*s*, 1100*w*, 1070*w*, 965*m*, 870*w*. ^{1}H-NMR: 0.81, 1.13 (2*s*, 2 CH_3–C(6')); 1.19 (*s*, CH_3–C(2')); 0.80–1.80 (*m*, 2H–C(5')); 1.92 (*d*, J = 1.5, 3H–C(5)); 2.21 (*s*, 3H–C(1)); 1.80–2.20 (*m*, 2H–C(4')); 3.01 (*m*, $w_{1/2}$ = 7, H–C(3')); 4.23 (*s*, H–C(1')); 6.23 (*m*, $w_{1/2}$ = 4, H–C(3)). MS: 222

(12, M^+, $C_{14}H_{22}O_2$), 204 (6), 189 (5), 161 (8), 18 (17), 139 (20), 133 (11), 124 (12), *123* (100), 109 (10), 105 (9), 43 (46), 41 (15). Anal. calc. for $C_{14}H_{22}O_2$ (222.33): C 75.63, H 9.97; found: C 75.48, H 9.90.

1.4. *Treatment of (*E*)- and (*Z*)-***3*** with Base. a*) A suspension of (*Z*)-**3** (3.00 g, 13.5 mmol), NaOMe (3.00 g, 55.5 mmol) and MeOH (150 ml) was heated under reflux for 5 h. The mixture was concentrated *in vacuo* and the residue extracted with Et_2O/pentane 1:1. Workup and chromatography (Et_2O/pentane 1:9) afforded (*E*)-**3** (2.17 g, 72%) and (*Z*)-**3** (0.47 g, 16%). *b*) The analogous reaction with (*E*)-**3** (723 mg, 3.25 mmol) lead to a mixture of (*E*)- and (*Z*)-**3** (662 mg, 92%, 9:2).

1.5. *Treatment of (*E*)- and (*Z*)-***7*** with Base. a*) A suspension of (*E*)-**7** (763 mg, 3.43 mmol), NaOMe (770 mg, 14.3 mmol) and MeOH (50 ml) was heated under reflux for 3 h. The mixture was concentrated *in vacuo* and the residue extracted with Et_2O/pentane 1:1. Workup afforded compound **8** (750 mg, 98%). *b*) The reaction of (*Z*)-**7** (220 mg, 0.99 mmol) with NaOMe (212 mg, 3.92 mmol) in MeOH (20 ml) was complete after refluxing for 30 min, affording **8** (206 mg, 94%).

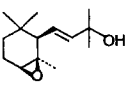
10-Hydroxy-1,3,7,7-tetramethyl-5-methylidene-2-oxabicyclo[4.4.0]dec-3-ene (**8**). B.p. 80°/0.01 Torr. UV (0.514 mg in 25 ml MeCN): 257 (13400). UV (3.630 mg in 2 ml MeCN): end absorption to 300. IR: 3635*m*, 3500*w* (br.), 3080*w*, 3050*w*, 2980*s*, 2970*s*, 2940*s*, 2920*s*, 2870*s*, 1745*w*, 1650*s*, 1605*w*, 1470*w*, 1455*m*, 1450*m*, 1440*m*, 1430*m*, 1415*m*, 1385*s* (sh), 1380*s*, 1370*m*, 1360*m*, 1340*s*, 1290*m*, 1240*w*, 1200*m*, 1170*s*, 1120*s*, 1065*s*, 990*s*, 960*m*, 950*m*, 930*w*, 910*w*, 885*m*, 870*s*, 855*m*. ^{1}H-NMR: 0.80, 0.92 (2*s*, 2 CH_3–C(7)); 1.20 (*s*, CH_3–C(1)); 1.72 (*s*, CH_3–C(3)); 0.80–2.50 (*m*, 2H–C(8), 2H–C(9), OH); 1.95 (*m*, $w_{1/2}$ = 3, H–C(6)); 3.75 (*dd*, $J_1 = J_2 = 2.5$, H–C(10)); 4.46, 4.82 (2*m*, $w_{1/2}$ = 4, 2 CH_2=C(5)); 5.22 (*m*, $w_{1/2}$ = 3, H–C(4)). ^{13}C-NMR (20 MHz): 20.1, 21.8, 22.6 (3*q*, 3 CH_3); 25.3, 33.4 (2*t*, C(8), C(9)); 32.1 (*q*, CH_3–C(3)); 33.1 (*s*, C(7)); 49.3 (*d*, C(6)); 72.3 (*d*, C(10)); 78.5 (*s*, C(1)); 103.3 (*d*, C(4)); 109.1 (*t*, C=C(5)); 138.5 (*s*, C(5)); 150.2 (*s*, C(3)). MS: 222 (12, M^+, $C_{14}H_{22}O_2$), 139 (20), 124 (12), *123* (100), 43 (38). Anal. calc. for $C_{14}H_{22}O_2$ (222.33): C 75.63, H 9.97; found: C 75.34, H 10.04.

1.6. *Preparation of (*E*/*Z*)-***3*** from (*E*)-4-(2,3-Epoxy-2,6,6-trimethylcyclohexyl)-3-buten-2-one (= (*E*)-4,5-Epoxy-α-ionone; (*E*)-***1***).* To a suspension of CuI (5.08 g, 26.7 mmol) in Et_2O (250 ml), a solution of MeLi in Et_2O (1.6M, 32.7 ml, 52.3 mmol) was added at −40° and the mixture was stirred for 20 min. (*E*)-**1** [7] (4.54 g, 21.8 mmol) in Et_2O (30 ml) was then added slowly at −40°, and the mixture was allowed to warm to −10° over 20 min. Again at −40° a soln. of phenylselenyl bromide in THF (45 ml) (prepared by reaction of diphenyl diselenide (8.41 g, 26.9 mmol) and Br_2 (0.95 ml, 18.5 mmol) in THF at 0°) was added rapidly. The cooling bath was removed and the mixture was allowed to warm up to r.t., poured into Et_2O/pentane 1:1 (300 ml) and aq. NH_4Cl (sat., 200 ml) and worked up. The crude product was dissolved in pyridine (6.40 ml) and CH_2Cl_2 (300 ml), and H_2O_2 (15%, 32 ml, 141 mmol) was added dropwise at r.t. (the reaction was highly exothermic). After 1 h at r.t., aq. $NaHCO_3$ (10%, 70 ml) was added, the org. phase washed with 1M aq. HCl and worked up. Column chromatography (acetone/CH_2Cl_2 1:100) yielded the starting material ((*E*)-**1**, 160 mg, 4%), (*E*)-**3** (292 mg, 6%), (*Z*)-**3** (805 mg, 17%), **45**[12]) (1.64 g, 34%), and **46**[12]) (164 mg, 3%).

2. Photolysis Experiments. – 2.1. *Photolyses of (*E*)-***1*** in MeCN.* – 2.1.1. *At λ > 280 nm.* A solution of (*E*)-**1** [7] (5.00 g, 24.0 mmol) in MeCN (600 ml) was irradiated (*Pyrex*, lamp *B*, 97% conversion). Chromatography (Et_2O/pentane 1:1), gave mixed fractions; from their ^{1}H-NMR analysis, the following product distribution was determined: (*Z*)-**1** (1%), **10A** (33%), **10B** (37%), **11** (3%), (*E*)-**9** [18] (13%), **12A** (1%) and **12B** (3%). Compounds **11** and **12B** were purified and isolated as their acetates.

(Z,1′RS,2′RS,3′SR)-4-(2′,3′-Epoxy-2′,6′,6′-trimethylcyclohexyl)-3-buten-2-one ((*Z*)-**1**). B.p. 70°/0.01 Torr. UV (0.254 mg in 25 ml pentane): 231 (9400). UV (5.678 mg in 10 ml pentane): 335 (40). IR: 3020*w*, 2960*s*, 2930*s*, 2870*m*, 2850*m* (sh), 1715*w* (sh), 1690*s*, 1685*m* (sh), 1665*m* 1610*m*, 1460*m* (sh), 1445*m*, 1435*m* (sh), 1410*m*, 1385*w* (sh), 1380*m*, 1365*m*, 1350*m*, 1305*w*, 1245*w*, 1170*s*, 1145*w*, 1095*w*, 965*m*, 895*m*. ^{1}H-NMR (C_6D_6): 0.80, 0.82 (2*s*, 2 CH_3–C(6′)); 1.24 (*s*, CH_3–C(2′)); 1.78 (*s*, 3H–C(1)); 0.75 (*dddd*, J_1 = 13.4, J_2 = 5.7, J_3 = 3.6, J_4 = 1.2, H–C(5′)); 1.37 (*ddd*, J_1 = 13.4, J_2 = 10.8, J_3 = 5.5, H–C(5′)); 1.55 (*dddd*, J_1 = 15.3, J_2 = 10.8, J_3 = 5.7, J_4 = 2.5, H–C(4′)); 1.77 (*dddd*, J_1 = 15.3, J_2 = 5.5, J_3 = 3.6, J_4 = 1.5, H–C(4′)); 2.74 (*m*, $w_{1/2}$ = 5.5, H–C(3′)); 3.90 (*dm*, J = 10.8, $w_{1/2}$ = 2.5, H–C(1′)); 6.01 (*AB*-system, J = 11.5, δ_A = 5.93, H–C(3), δ_B = 6.09, B part split

[12]) The spectral data of these compounds are given in the Ph. D. thesis of *P. M.*



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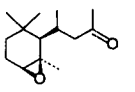

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to *d*, J = 10.8, H–C(4)). ^{13}C-NMR (C_6D_{12}): 24.0, 26.8, 28.1, 31.4 (4*q*, 4 CH_3); 22.6, 29.3 (2*t*, C(4'), C(5')); 31.5 (*s*, C(6')); 44.8 (*d*, C(1')); 58.8 (*s*, C(2')); 59.3 (*d*, C(3')); 128.7 (*d*, C(4)); 145.8 (*d*, C(3)); 196.7 (*s*, C(2)). MS: 208 (19, M^+, $C_{13}H_{20}O_2$), 193 (18), 190 (12), 179 (28), 175 (23), 165 (16), 151 (13), 147 (16), 134 (33), 123 (18), 109 (73), 95 (24), 91 (16), 86 (18), 84 (35), 79 (13), 69 (16), 57 (82), 56 (64), 55 (25), *43* (100), 42 (31), 41 (73). Anal. calc. for $C_{13}H_{20}O_2$ (208.30): C 74.96, H 9.68; found: C 74.79, H 9.73.

10-Hydroxy-1,3,7,7-tetramethyl-2-oxabicyclo[4.4.0]deca-3,5-diene, Isomer A (**10A**). IR: 3680*s*, 3070*w*, 3050*w*, 2960*s*, 2935*s*, 2920*s* (sh), 2870*s*, 1730*w*, 1660*s*, 1650*m* (sh), 1600*m*, 1465*m* (sh), 1460*m* (sh), 1450*s*, 1445*m* (sh), 1430*m*, 1385*s*, 1375*s*, 1360*s*, 1340*m*, 1330*m*, 1315*s*, 1280*m*, 1255*s*, 1235*m*, 1205*s*, 1180*m*, 1155*s*, 1145*m*, 1125*m*, 1075*s*, 1060*s*, 1050*s* (sh), 1030*m*, 1000*m* (sh), 995*m*, 975*m*, 965*s*, 945*m*, 930*w*, 915*m*, 885*w*, 875*w*, 860*w*, 845*m*, 670*m*, 620*w*. ^{1}H-NMR (C_6D_6, 300 MHz): 0.98, 1.12 (2*s*, 2 CH_3–C(7)); 1.22 (*s*, CH_3–C(1)); 1.59 (*m*, $w_{½}$ = 2.5, CH_3–C(3)); 1.01 (*td*, overlapping with *s*, J_1 = 13, J_2 = 7, H–C(8)); 1.58 (*m*, H–C(8)); 1.91 (*dq*, J_1 = 14, J_2 = 4, H–C(9)); 2.17 (*dt*, broadened to *m*, J_1 = 14, J_2 = 4, $w_{½}$ = 3, H–C(9)); 2.90 (*m*, $w_{½}$ = 20, OH); 3.76 (*m*, $w_{½}$ = 8, H–C(10)); 4.93 (*dq*, J_1 = 6.0, J_2 = 1.1, H–C(4)); 5.71 (*dm*, J = 6, $w_{½}$ = 2, H–C(5)). ^{13}C-NMR (C_6D_{12}): 19.8, 22.6, 30.7, 31.6 (4*q*, 4 CH_3); 25.0, 32.8 (2*t*, C(8), C(9)); 34.6 (*s*, C(7)); 72.5 (*d*, C(10)); 81.1 (*s*, C(1)); 99.0, 116.3 (2*d*, C(4), C(5)); 137.9, 148.7 (2*s*, C(3), C(6)).

Isomer B (**10B**). IR: 3610*m*, 3070*w*, 3050*w*, 2980*s* (sh), 2960*s*, 2940*s*, 2920*s* (sh), 2870*m*, 1720*w*, 1660*m*, 1650*m* (sh), 1600*w*, 1460*m*, 1445*m*, 1395*w*, 1380*m*, 1370*m*, 1350*m*, 1320*m*, 1315*m*, 1285*m*, 1260*m*, 1210*w*, 1180*w*, 1150*m* (sh), 1125*s*, 1085*m*, 1060*s*, 1025*m*, 1000*m*, 975*w*, 940*w*, 935*w*, 865*w*. ^{1}H-NMR (C_6D_6, 300 MHz): 0.94, 0.98 (2*s*, 2 CH_3–C(7)); 1.48 (*s*, CH_3–C(1)); 1.68 (*s*, CH_3–C(3)); 1.10–1.32 (*m*, 2H–C(8)); 1.51–1.80 (*m*, overlapping with *s*, 2H–C(9)); 2.05–2.35 (*m*, OH); 3.99 (*dd*, J_1 = 12.0, J_2 = 5.0, H–C(10)); 4.93 (*dq*, J_1 = 6.0, J_2 = 1.1, H–C(4)); 5.60 (*dm*, J = 6.0, $w_{½}$ = 2.0, H–C(5)). ^{13}C-NMR (C_6D_{12}): 17.2, 19.9, 30.7, 31.5 (4*q*, 4 CH_3); 26.9, 38.1 (2*t*, C(8), C(9)); 35.3 (*s*, C(7)); 77.6 (*d*, C(10)); 83.0 (*s*, C(1)); 98.5, 116.3 (2*d*, C(4), C(5)); 138.3, 149.8 (2*s*, C(3), C(6)). MS: 208 (6, M^+, $C_{13}H_{20}O_2$), 193 (7), 190 (13), 175 (8), 165 (3), 151 (5), 147 (6), 135 (13), *134* (100), 133 (11), 119 (7), 106 (19), 91 (24), 57 (13), 43 (17), 41 (16). Anal. calc. for $C_{13}H_{20}O_2$ (208.30): C 74.96, H 9.68; found: C 74.86, H 9.85.

4,4-Dimethyl-2-methylidene-3-(3'-oxobutylidene)cyclohexyl Acetate (Acetate of **11**). B.p. 70°/0.01 Torr. UV (0.290 mg in 25 ml MeCN): 220 (sh, 6000). UV: (2.653 mg in 2 ml MeCN): 284 (290). IR: 3080*w* (sh), 2960*m*, 2945*m*, 2920*m* (sh), 2870*w*, 2850*w*, 1735*s*, 1720*s*, 1635*w*, 1470*w*, 1460*w*, 1405*w*, 1385*w*, 1370*m*, 1360*m*, 1310*w*, 1325*s*, 1160*m*, 1070*w* (sh), 1040*m*, 1030*m*, 1015*m* (sh), 990*w*, 965*w*, 910*w* (br.), 875*w*. ^{1}H-NMR: 1.03 (*s*, 2 CH_3–C(4)); 1.2–2.2 (*m*, 2H–C(5), 2H–C(6)); 2.01, 2.08 (2*s*, 3H–C(4'), CH_3CO_2); 3.20 (*d*, J = 7, 2H–C(2')); 4.72, 5.18 (2*m*, $w_{½}$ = 4, 2H–C=C(2)); 5.03–5.23 (*m*, overlapping with *m* at 5.18, H–C(1)); 5.48 (*t*, J = 7, H–C(1')). ^{13}C-NMR: 21.1, 27.0, 27.0, 29.6 (4*q*, 4 CH_3); 28.5, 37.1, 43.5 (3*t*, C(2'), C(5), C(6)); 37.7 (*s*, C(4)); 75.0 (*d*, C(1)); 112.7 (*t*, *C*=C(2)); 115.0 (*d*, C(1')); 143.2, 149.1 (2*s*, C(2), C(3)); 169.9 (*s*, CH_3CO_2); 206.9 (*s*, C(3')). MS: 250 (2, M^+, $C_{15}H_{22}O_3$), 235 (4), 208 (3), 190 (18), 175 (11), 165 (11), 148 (22), 147 (62), 134 (17), 133 (63), 119 (23), 105 (42), 92 (31), 91 (29), 55 (14), *43* (100), 41 (17). Anal. calc. for $C_{15}H_{22}O_3$ (250.34): C 71.97, H 8.86; found: C 72.09, H 8.88.

7-Hydroxy-4,6,10,10-tetramethyl-5-oxatricyclo[4.4.0.0^{1,4}]dec-2-ene, Isomer A (**12A**). B.p. 90°/0.01 Torr. IR: 3560*w*, 3510*w* (br.), 3120*w*, 3040*w*, 2960*s*, 2940*s*, 2920*s* (sh), 2870*s*, 1460*w* (sh), 1450*m*, 1435*w*, 1390*m*, 1370*s*, 1365*m*, 1315*m*, 1305*w*, 1280*m*, 1240*w*, 1135*w*, 1090*w*, 1065*s*, 1060*s* (sh), 1040*m*, 1000*w*, 970*w*, 960*w*, 900*w*, 885*m*, 870*m*, 840*m*. ^{1}H-NMR: 0.84, 0.89 (2*s*, 2 CH_3–C(1)); 1.18 (*s*, CH_3–C(6)); 1.49 (*s*, CH_3–C(4)); 1.0–2.2 (*m*, 2H–C(8), 2H–C(9)); 3.25 (*m*, $w_{½}$ = 6, OH); 3.64 (*m*, $w_{½}$ = 10 with fine structure, H–C(7)); 6.46 (*AB*, J = 3, δ_A = 6.43, δ_B = 6.49, H–C(2), H–C(3)). ^{13}C-NMR: 17.7, 22.6, 26.7, 26.7 (4*q*, 4 CH_3); 25.1, 31.9 (2*t*, C(8), C(9)); 30.6 (*s*, C(10)); 63.9 (*s*, C(1)); 71.1 (*d*, C(7)); 79.6, 90.6 (2*s*, C(4), C(6)); 140.6, 143.5 (2*d*, C(2), C(3)). MS: 208 (11, M^+, $C_{13}H_{20}O_2$), 193 (46), 151 (23), 147 (14), 139 (17), 137 (17), 135 (22), 134 (18), 133 (13), 123 (21), 121 (24), 119 (22), 109 (57), 107 (22), 105 (23), 95 (18), 93 (19), 91 (33), 81 (16), 79 (20), 77 (19), 55 (19), 53 (14), *43* (100), 41 (32). Anal. calc. for $C_{13}H_{20}O_2$ (208.30): C 74.96, H 9.68; found: C 74.89, H 9.56.

4,6,10,10-Tetramethyl-5-oxatricyclo[4.4.0.0^{1,4}]dec-2-en-7-yl Acetate, Isomer B (**25B**). B.p. 90°/0.01 Torr. IR: 3040*w*, 2960*m*, 2940*m* (sh), 2925*m*, 2870*w*, 2860*w* (sh), 1740*s*, 1455*w*, 1445*w* (sh), 1370*m*, 1365*m* (sh), 1315*w*, 1295*w*, 1240*s*, 1190*w*, 1160*w*, 1135*w*, 1125*w* (sh), 1090*m*, 1065*w*, 1045*s*, 1020*m*, 1000*m*, 990*w* (sh), 975*w*, 915*w*, 890*m*, 870*w*, 840*w*. ^{1}H-NMR (300 MHz): 0.88, 0.98 (2*s*, 2 CH_3–C(10)); 1.22, 1.52 (2*s*, CH_3–C(4), CH_3–C(6)); 1.10–1.85 (*m*, H–C(8), 2 H–C(9)); 1.90–2.04 (*m*, H–C(8)); 2.11 (*s*, CH_3CO_2); 5.05 (*dd*, J_1 = 9.5, J_2 = 4.0, H–C(7)); 6.50 (*AB*, J = 3.0, δ_A = 6.48, δ_B = 6.52, H–C(2), H–C(3)). ^{13}C-NMR: 17.9, 21.3, 21.6, 27.4, 28.4 (5*q*, 5 CH_3); 23.0, 32.9 (2*t*, C(8), C(9)); 30.3 (*s*, C(10)); 64.8 (*s*, C(1)); 74.0 (*d*, C(7)); 78.7, 88.7 (2*s*, C(4), C(6)); 139.7, 143.7 (2*d*, C(2), C(3)); 170.9 (*s*, CH_3CO_2–). MS: 250 (2, M^+, $C_{15}H_{22}O_3$), 235 (21), 207 (13), 190 (47), 175 (40), 151 (11), 147 (23), 135 (25), 134 (47), 109 (26), 105 (17), 91 (30), *43* (100), 41 (21). Anal. calc. for $C_{15}H_{22}O_3$ (250.34): C 71.97, H 8.86; found: C 71.98, H 8.75.

2.1.2. *At λ = 254 nm.* A soln. of (*E*)-**1** (1.00 g, 4.80 mmol) in MeCN (200 ml) was irradiated (quartz, lamp *A*, 91% conversion). Chromatography of the mixture (Et_2O/pentane 1:1) gave mixed fractions from which the following product distribution was determined (^{1}H-NMR): (*Z*)-**1** (6%), **10A** (4%), **10B** (5%), **11** (33%) and (*E*)-**9** [18] (14%).

2.2. *Photolysis of (*E*)-**1** in Acetone at λ > 280 nm.* A soln. of (*E*)-**1** (1.00 g, 4.80 mmol) in acetone (100 ml) was irradiated (*Pyrex*, lamp *B*, 2 h). Chromatography (Et_2O/pentane 1:2) afforded (*E*)-**1** (184 mg, 18%), and (*Z*)-**1** (736 mg, 74%).

2.3. *Photolyses of (*E*)-**9** in MeCN.* – 2.3.1. *At λ > 280 nm.* A soln. of (*E*)-**9** (1.12 g, 5.38 mmol) in MeCN (100 ml) was irradiated (*Pyrex*, lamp *B*, 84% conversion). After chromatography (Et_2O/pentane 1:1 to 3:1), the following product distribution was determined (^{1}H-NMR): **10A** (17%), **10B** (22%), **11** (31%), **12A** (3%), and **12B** (8%).

2.3.2. *At λ = 254 nm.* A soln. of (*E*)-**9** (412 mg, 1.98 mmol) in MeCN (200 ml) was irradiated (quartz, lamp *A*, 88% conversion). Chromatography (Et_2O/pentane 1:1 to 3:1) afforded **10A** (3%), **10B** (3%) and **11** (57%).

2.4. *Photolyses of* **10A** *and* **10B** *in MeCN at λ > 280 nm.* Two separate samples of **10A** and **10B** (50 mg, 0.24 mmol) in MeCN (10 ml) were irradiated (*Pyrex*, lamp *B*, *ca.* 50% conversion, *ca.* 40°). Capillary GC and ^{1}H-NMR analysis showed for both samples the same ratio (1:2) of the oxetanes **12A** and **12B** as well as a ratio (*ca.* 1:1) of the pyrans **10A** and **10B**.

2.5. *Photolyses of (*E*)-**2** in MeCN.* – 2.5.1. *At λ > 280 nm.* A soln. of (*E*)-**2** (5.00 g, 22.5 mmol) in MeCN (720 ml) was irradiated (*Pyrex*, lamp *B*, 99% conversion). After chromatography (Et_2O/pentane 1:1 to 3:1), the following product distribution was determined (^{1}H-NMR): (*Z*)-**2** (2%), **14A** (9%), **14B** (11%), (*E*)-**13** (26%), (*Z*)-**13** (15%), **15A** (9%), **15B** (9%), **16A** (4%), **16B** (2%), and **35** (*ca.* 2%).

(Z,1′RS,2′RS,3′SR)-4-(2′,3′-Epoxy-2′,6′,6′-trimethylcyclohexyl)-3-methyl-3-buten-2-one ((*Z*)-**2**). B.p. 65°/0.01 Torr. UV (0.439 mg in 25 ml MeCN): 237 (5400). UV (4.791 mg in 2 ml MeCN): end absorption to 390. IR: 2960*s*, 2925*s*, 2870*m*, 1690*s*, 1685*s* (sh), 1620*m* (br.), 1460*m*, (sh), 1450*m*, 1435*m* (sh), 1375*m*, 1365*s*, 1350*m*, 1305*w*, 1225*m*, 1200*m*, 1180*m*, 1145*w*, 1125*m*, 1090*w*, 1065*w*, 965*m*, 910*m*, 875*w*. ^{1}H-NMR: 0.73, 0.86 (2*s*, 2 CH_3–C(6′)); 1.20 (*s*, CH_3–C(2′)); 0.7–1.6 (*m*, 2H–C(5′)); 1.8–2.1 (*m*, 2H–C(4′)); 1.99 (*d*, *J* = 1.5, CH_3–C(3)); 1.22 (*s*, 3H–C(1)); 2.85 (*d*, *J* = 11.0, H–C(1′)); 3.01 (*dd*, $J_1 = J_2 = 2$, H–C(3′)); 5.61 (*dq*, $J_1 = 11.0$, $J_2 = 1.5$, H–C(4)). ^{13}C-NMR (20 MHz): 21.2, 24.2, 26.9, 28.0, 29.8 (5*q*, 5 *C*H_3); 22.0, 28.7 (2*t*, C(4′), C(5′)); 31.4 (*s*, C(6′)); 45.7 (*d*, C(1′)); 59.5 (*s*, C(2′)); 59.8 (*d*, C(3′)); 135.1 (*d*, C(4)); 137.6 (*s*, C(3)); 203.0 (*s*, C(2)). MS: 222 (6, M^+, $C_{14}H_{22}O_2$), 207 (18), 153 (11), 137 (26), 125 (14), 123 (85), 111 (14), 109 (35), 107 (13), 95 (14), 69 (15), 55 (23), 53 (12), *43* (100), 41 (33). Anal. calc. for $C_{14}H_{22}O_2$ (222.33): C 75.63, H 9.97; found: C 75.43, H 9.93.

10-Hydroxy-1,3,4,7,7-pentamethyl-2-oxabicyclo[4.4.0]deca-3,5-diene, Isomer A (**14A**). IR: 3575*s*, 3030*w* (sh), 2960*s*, 2935*s*, 2920*s*, 2870*s*, 1670*m*, 1600*w*, 1460*m* (sh), 1450*m*, 1435*m* (sh), 1390*s*, 1385*s* (sh), 1365*m*, 1295*m* (sh), 1280*s*, 1225*s*, 1210*m* (sh), 1190*m*, 1150*s*, 1120*m*, 1080*m* (sh), 1060*s*, 1000*m*, 970*m*, 915*w*, 890*w*, 860*m*. ^{1}H-NMR (80 MHz): 1.11, 1.16, 1.27 (3*s*, CH_3–C(1), 2 CH_3–C(7)); 0.9–2.3 (*m*, 2H–C(8), 2H–C(9)); 1.68, 1.79 (2*m*, $w_{½} = 3$, CH_3–C(3), CH_3–C(4)); 2.95 (*m*, $w_{½} = 3$, OH); 3.75 (*m*, $w_{½} = 7$, H–C(10)); 5.64 (*s*, H–C(5)). ^{13}C-NMR (20 MHz): 15.4, 16.2, 22.6, 30.3, 31.2, (5*q*, 5 CH_3); 24.4, 32.4 (2*t*, C(8), C(9)); 34.1 (*s*, C(7)); 72.3 (*d*, C(10)); 79.3 (*s*, C(1)); 104.6 (*s*, C(4)); 120.5 (*d*, C(5)); 138.5, 142.2 (2*s*, C(3), C(6)). MS: 222 (38, M^+, $C_{14}H_{22}O_2$), 208 (15), 207 (99), 177 (18), 165 (27), 163 (50), 153 (23), 151 (23), 150 (38), 149 (31), 148 (26), 137 (26), 135 (20), 123 (80), 122 (22), 109 (19), 105 (19), 91 (20), 77 (17), 55 (16), *43* (100), 41 (26).

Isomer B (**14B**). IR: 3610*m*, 3040*w* (sh), 2980*s* (sh), 2960*s*, 2940*s*, 2920*s*, 2860*s*, 1740*w*, 1670*m*, 1600*w*, 1460*m*, 1440*m* (sh), 1380*m*, 1365*m*, 1320*w*, 1275*m*, 1255*m*, 1230*m*, 1190*m*, 1150*m*, 1130*s*, 1070*s*, 1060*s*, 1050*s*, 1030*m*, 960*w*, 865*m*. ^{1}H-NMR: 1.06, 1.10 (2*s*, 2 CH_3–C(7)); 1.26 (*s*, CH_3–C(1)); 1.00–2.10 (*m*, 2H–C(8), 2H–C(9)); 1.64, 1.74 (2*m*, $w_{½} = 3$, CH_3–C(3), CH_3–C(4)); 2.87 (*m*, $w_{½} = 9$, OH); 3.78–4.00 (*m*, H–C(10)); 5.52 (*s*, H–C(5)). ^{13}C-NMR (20 MHz): 15.3, 16.3, 17.0, 30.3, 31.2 (5*q*, 5 CH_3); 26.2, 37.4 (2*t*, C(8), C(9)); 34.7 (*s*, C(7)); 77.6 (*d*, C(10)); 81.5 (*s*, C(1)); 104.2 (*s*, C(4)); 120.3 (*d*, C(5)); 139.3, 143.1 (2*s*, C(3), C(6)). MS: 222 (35, M^+, $C_{14}H_{22}O_2$), 208 (16), *207* (100), 189 (9), 177 (13), 165 (28), 163 (24), 153 (23), 151 (22), 149 (30), 148 (26), 137 (27), 123 (80), 109 (18), 105 (19), 91 (19), 77 (16), 55 (15), 43 (90), 41 (27).

(E)-4-(3′-Hydroxy-2′,6′,6′-trimethyl-1′-cyclohexenyl)-3-methyl-3-buten-2-one ((*E*)-**13**). B.p. 100°/0.01 Torr. UV (0.517 mg in 25 ml MeCN): 228 (8400), 266 (3800). UV (2.130 mg in 2 ml MeCN): end absorption to 380. IR: 3610*w*, 3480*w* (br.), 2960*s*, 2930*s*, 2860*m*, 1670*s*, 1620*w*, 1445*m* (sh), 1435*m*, 1380*m*, 1360*s*, 1335*w*, 1285*w*, 1245*s*, 1200*w*, 1170*w*, 1100*m*, 1070*m*, 1030*m*, 1020*m*, 990*m*, 960*m*, 905*w*, 865*w*. ^{1}H-NMR: 0.96, 1.01 (2*s*, 2 CH_3–C(6′)); 1.60, 1.65 (2*m*, $w_{½} = 3$, CH_3–C(3), CH_3–C(2′)); 1.20–2.10 (*m*, 2H–C(4′), 2H–C(5′)); 2.32 (*s*, 3H–C(1)); 2.25–2.45 (*m*, OH); 4.00 (*m*, $w_{½} = 12$, H–C(3′)); 7.04 (*m*, $w_{½} = 6$, H–C(4)). ^{13}C-NMR (contaminated with 30% of **15A**): 12.2, 17.3, 25.0, 26.6, 27.6 (5*q*, 5*C*H_3); 27.9, 33.9 (2*t*, C(4′), C(5′)); 34.6 (*s*, C(6′)); 68.1 (*d*, C(3′)); 130.8, 137.0, 138.9 (3*s*, C(3), C(1′), C(2′)); 139.4 (*d*, C(4)); 199.3 (*s*, C(2)). MS: 222 (5, M^+,

$C_{14}H_{22}O_2$), 207 (9), 204 (8), 189 (25), 161 (14), 137 (18), 123 (41), 105 (13), 91 (15), 77 (13), 55 (12), *43* (100), 41 (24). Anal. calc. for $C_{14}H_{22}O_2$ (222.33): C 75.63, H 9.97; found: C 75.49, H 9.91.

(Z)-4-(3'-Hydroxy-2',6',6'-trimethyl-1'-cyclohexenyl)-3-methyl-3-buten-2-one ((*Z*)-**13**). ^{1}H-NMR (3:2 mixture of (*Z*)- and (*E*)-**13**): 1.03, 1.07 (2*s*, 2 CH_3–C(6')); 1.66 (*m*, *J* = 1.0, CH_3–C(2')); 1.97 (*m*, *J* = 1.5, CH_3–C(3)); 0.8–2.1 (*m*, 2H–C(4'), 2H–C(5'), OH); 2.21 (*s*, 3H–C(1)); 3.8–4.2 (*m*, H–C(3')); 6.32 (*m*, $w_{½}$ = 6, H–C(4)).

(E)-4-(3'-Hydroxy-6',6'-dimethyl-2'-methylidenecyclohexylidene)-3-methyl-2-butanone, Isomer A (**15A**). B.p. 90°/0.01 Torr. UV (0.373 mg in 25 ml MeCN): 215 (sh, 5500). UV (4.450 mg in 10 ml MeCN): 290 (200). IR: 3620*w*, 3490*w* (br.), 3080*w*, 2960*s*, 2930*s*, 2870*m*, 2850*m*, 1710*s*, 1635*w*, 1470*w* (sh), 1455*m*, 1420*m*, 1380*m*, 1365*m*, 1355*s*, 1215*m*, 1170*m*, 1130*w*, 1070*m*, 1060*m*, 1045*m*, 1000*w*, 980*w*, 965*m*, 915*s*, 890*w*, 870*w*. ^{1}H-NMR: 1.02 (*s*, 2 CH_3–C(6')); 1.11 (*d*, *J* = 7, CH_3–C(3)); 1.00–2.10 (*m*, 2H–C(4'), 2H–C(5')); 2.11 (*s*, 3H–C(1)); 3.57 (*qd*, J_1 = 7, J_2 = 10, H–C(3)); 4.12 (*m*, $w_{½}$ = 15, H–C(3')); 4.74 (*m*, $w_{½}$ = 5, H–C=C(2')); 5.21 (*d*, *J* = 10, H–C(4)); 5.26 (*m*, $w_{½}$ = 4, H–C=C(2')). ^{13}C-NMR (*ca.* 80% pure): 17.1, 26.2, 26.5, 27.3 (4*q*, 4 *C*H_3); 31.0, 36.7 (2*t*, C(4'); C(5')); 37.1 (*s*, C(6')); 46.2 (*d*, C(3)); 72.6 (*d*, C(3')); 109.7 (*t*, *C*=C(2')); 120.8 (*d*, C(4)); 147.7, 148.9 (2*s*, C(1'), C(2')); 211.1 (*s*, C(2)). MS: 222 (4, M^+, $C_{14}H_{22}O_2$), 189 (11), 179 (42), 165 (12), 162 (26), 161 (80), 148 (22), 147 (66), 135 (21), 133 (23), 123 (58), 121 (24), 119 (54), 109 (22), 107 (35), *106* (100), 105 (62), 95 (27), 93 (23), 91 (34), 81 (28), 79 (20), 69 (28), 67 (17), 55 (37), 43 (72), 41 (35).

Isomer B (**15B**). B.p. 90°/0.01 Torr. UV (0.471 mg in 25 ml MeCN): 215 (4250). UV (1.311 mg in 2 ml MeCN): 292 (240). IR: 3620*w*, 3470*w* (br.), 3080*w*, 2960*s*, 2930*s*, 2870*m*, 2850*m*, 1710*s*, 1630*w*, 1460*m* (sh), 1450*m*, 1415*w* (sh), 1380*w* (sh), 1370*w* (sh), 1350*m*, 1210*w*, 1180*w* (sh), 1165*m* 1065*m*, 1050*m* (sh), 960*w*, 910*m*, 870*w*. ^{1}H-NMR: 1.00, 1.04 (2*s*, 2 CH_3–C(6')); 1.12 (*d*, *J* = 7.0, CH_3–C(3)); 1.0–2.1 (*m*, 2H–C(4'), 2H–C(5')); 2.04 (*s*, 3H–C(1)); 2.22 (*m*, $w_{½}$ = 10, OH); 3.62 (*qd*, J_1 = 7.0, J_2 = 10.0, H–C(3)); 3.96–4.20 (*m*, H–C(3')); 4.76, 5.31 (2*m* with *t*-character, $w_{½}$ = 5, 2H–C=C(2')); 5.18 (*d*, *J* = 10.0, H–C(4)). ^{13}C-NMR: (*ca.* 90% pure): 17.2, 26.4, 27.5, 28.2 (4*q*, 4 *C*H_3); 31.9, 37.8 (2*t*, overlapping with *s* at 37.8, C(4'), C(5')); 37.8 (*s*, C(6')); 46.9 (*d*, C(3)); 73.2 (*d*, C(3')); 109.3 (*t*, *C*=C(2')); 121.3 (*d*, C(4)); 148.4, 150.0 (2*s*, C(1'), C(2')); 211.0 (*s*, C(2)). MS: 222 (4, M^+, $C_{14}H_{22}O_2$), 207 (4), 204 (5), 189 (10), 179 (30), 161 (67), 148 (18), 147 (19), 133 (20), 123 (49), 119 (43), 107 (26), 106 (38), 105 (50), 95 (25), 93 (20), 91 (31), 81 (28), 79 (22), 77 (24), 69 (28), 55 (41), *43* (100), 41 (54). Anal. calc. for $C_{14}H_{22}O_2$ (222.33): C 75.63, H 9.97; found: C 75.74, H 10.05.

(E)-3-Hydroxy-6,6-dimethyl-2-methylidene-1-(1'-propenyl)cyclohexyl Methyl Ketone, Isomer A (**16A**). IR: 3610*w*, 3450*w* (br.), 3020*w*, 2960*m* (sh), 2950*m*, 2920*s*, 2870*m*, 1705*s*, 1635*w*, 1475*w*, 1450*m*, 1380*m*, 1360*w*, 1350*m*, 1270*w*, 1190*w*, 1170*m*, 1115*s*, 1040*m*, 985*m*, 940*w*, 910*m*, 900*m* (sh), 870*w*. ^{1}H-NMR: 0.73, 1.08 (2*s*, 2 CH_3–C(6)); 1.78 (*dd*, J_1 = 6.0, J_2 = 1.5, 3H–C(3')); 1.95 (*s*, CH_3CO), 0.80–2.40 (*m*, 2H–C(4), 2H–C(5)); 3.14 (*m*, $w_{½}$ = 10, OH); 3.66–3.96 (*m*, H–C(3)); 5.41 (*AB*, *J* = 16.0, δ_A = 5.15, δ_B = 5.73, *A* part split to *q*, J_1 = 6.0, H–C(2'), *B* part split to *q*, J_2 = 1.5, H–C(1')); 5.26, 5.57 (2*m*, $w_{½}$ = 4.0, 2H–C=C(2)). ^{13}C-NMR: 18.6, 25.2, 25.7, 27.9 (4*q*, 4 *C*H_3); 32.4, 34.6 (2*t*, C(4), C(5)); 38.2 (*s*, C(6)); 67.1 (*s*, C(1)); 70.7 (*d*, C(3)); 109.8 (*t*, *C*=C(2)); 128.3, 128.8 (2*d*, C(1'), C(2')); 150.5 (*s*, C(2)); 109.3 (*s*, CH_3–O). MS: 222 (2, M^+, $C_{11}H_{22}O_2$), 189 (11), 179 (19), 161 (22), 148 (11), 136 (26), 123 (19), 119 (29), 105 (22), 91 (18), 84 (24), 69 (17), 55 (24), 45 (28), *43* (100), 41 (37).

Isomer B (**16B**), (*ca.* 75% pure). IR: 3610*w*, 3460*w* (br.), 3080*w*, 3010*w* (sh), 2960*s*, 2925*s*, 2865*s*, 1705*s*, 1630*w*, 1440*w* (br.), 1380*m*, 1360*m*, 1345*m*, 1210*m*, 1170*m*, 1115*m*, 1045*m*, 980*m*, 965*m*, 910*s*. ^{1}H-NMR (80 MHz): 0.80, 1.15 (2*s*, 2 CH_3–C(6)); 1.80 (*dd*, J_1 = 6.0, J_2 = 1.5, 3H–C(3')); 2.06 (*s*, CH_3–CO); 0.70–2.50 (*m*, 2H–C(4), 2H–C(5), OH); 4.27–4.45 (*m*, H–C(3)); 5.46 (*AB*, *J* = 16.0, δ_A = 5.24, δ_B = 5.68, *A* part split to *q*, J_1 = 6.0, H–C(2'), *B* part split to *m*, $w_{½}$ = 3, H–C(1')); 5.20, 5.38 (2*m*, $w_{½}$ = 3, 2H–C=C(2)). ^{13}C-NMR: 18.7, 25.2, 25.5, 28.8 (4*q*, 4 *C*H_3); 30.6, 31.7 (2*t*, C(4), C(5)); 38.0 (*s*, C(6)); 72.9 (*d*, C(3)); 115.7 (*t*, *C*=C(2)); 129.3 (2*d*, C(1'), C(2')); 150.0 (*s*, C(2)); 208.5 (*s*, CH_3–CO). MS: 222 (5, M^+, $C_{14}H_{22}O_2$), 204 (35), 189 (41), 161 (31), 159 (18), 148 (34), 147 (44), 136 (38), 135 (35), 133 (45), 119 (41), 105 (55), 91 (66), 85 (45), 83 (70), 79 (35), 77 (37), 55 (3), 47 (30), *43* (100), 41 (68).

4,5-Epoxy-1,4,8,8-tetramethylspiro[2.5]oct-1-yl Methyl Ketone (**35**). IR: 2960*s*, 2930*s*, 2870*m*, 1705*s*, 1450*m*, 1380*m*, 1355*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.73 (*d*, *J* = 5.5, H–C(2)); 0.87, 0.98 (2*s*, 2 CH_3–C(8)); 1.19 (*s*, CH_3–C(1)); 1.15–1.35 (*m*, H–C(7)); 1.51 (*s*, CH_3–C(4)); 1.55–1.75 (*m*, H–C(7)); 1.91 (*d*, *J* = 5.5, H–C(2)); 1.94–2.04 (*m*, H–C(6)); 2.04–2.16 (*m*, H–C(6)); 2.32 (*s*, CH_3CO); 2.87 (*dm*, *J* = 3.5, $w_{½}$ = 2.5, H–C(5)). ^{13}C-NMR (25 MHz, contains *ca.* 30% of (*E*)-**2**): 17.2 (*dd*, C(2)); 18.9, 24.4, 26.3, 27.1 (4*q*, 4 *C*H_3); 21.8, 31.9 (2*t*, C(7), C(6)); 34.5, 38.2, 42.1 (3*s*, C(1), C(3), C(8)); 59.5 (*s*, C(4)); 60.5 (*d*, C(5)); 207.0 (*s*, C=O).

2.5.2. *At λ = 254 nm.* A soln. of (*E*)-**2** (180 mg, 0.81 mmol) in MeCN (15 ml) was irradiated (quartz, lamp *A*, 91% conversion). After chromatography (Et_2O/pentane 1:1), the following product distribution was determined (^{1}H-NMR) (*Z*)-**2** (6%), **14A** (2%), **14B** (2%), (*E*)-**13** (17%), (*Z*)-**13** (30%), **15A** (14%) and **15B** (16%).

2.6. *Photolyses of (E)-3 in MeCN.* – 2.6.1. *At λ > 280 nm.* A soln. of (*E*)-**3** (510 mg, 2.29 mmol) in MeCN (100 ml) was irradiated (*Pyrex*, lamp *B*, 93% conversion). Chromatography (Et_2O/pentane 1:1) gave mixed fractions from which the following product distribution was determined (^{1}H-NMR): (*Z*)-**3** (39%), **18** (1%), (*E*)-**17** (16%), (*Z*)-**17A** (13%), (*Z*)-**17B** (25%), and additional photoproducts arising from (*E*/*Z*)-**17** (2%)[7]. Compounds (*E*)-**17**, (*Z*)-**17A**, and (*Z*)-**17B** were purified and isolated as their acetates.

(Z)-2,4,4-Trimethyl-3-(4'-oxo-2'-penten-2'-yl)-2-cyclohexenyl Acetate, Conformer A (Acetate of (*Z*)-**17A**). UV (0.601 mg in 25 ml MeCN): 233 (10600). UV (5.942 mg in 2 ml MeCN): 322 (75). IR: 3010*w* (sh), 2960*m*, 2940*m*, 2920*m*, 2870*w*, 2855*w*, 1730*s*, 1695*m*, 1665*m*, 1600*m*, 1470*w*, 1460*w* (sh), 1450*m*, 1435*m*, 1370*s*, 1360*m* (sh), 1240*s*, 1190*m*, 1170*w*, 1160*w*, 1135*w*, 1010*m*, 990*w* (sh), 960*m*, 940*w*, 875*w*. ^{1}H-NMR: 1.00, 1.11 (2*s*, 2 CH_3–C(4)); 1.55 (*s*, CH_3–C(2)); 1.98 (*d*, *J* = 1.5, 3H–C(1)); 2.08, 2.20 (2*s*, 3H–C(5'), CH_3CO_2); 0.80–2.30 (*m*, 2H–C(5), 2H–C(6)); 5.24 (*m*, $w_{½}$ = 10, H–C(1)); 6.13 (*m*, $w_{½}$ = 4, H–C(3')). ^{13}C-NMR: 17.7, 21.2, 26.9, 27.6, 29.4, 29.8 (6*q*, 6 CH_3); 25.5, 35.4 (2*t*, C(5), C(6)); 34.7 (*s*, C(4)); 70.9 (*d*, C(1)); 124.6, 145.2, 151.9 (3*s*, C(2), C(3), C(2')); 129.2 (*d*, C(3')); 170.9 (*s*, CH_3CO_2); 198.2 (*s*, C(4')); MS: 204 (27, $M^+ - CH_3CO_2H$), 189 (22), 161 (36), 149 (32), *148* (100), 147 (25), 133 (74), 119 (24), 108 (31), 105 (50), 91 (29), 79 (17), 77 (21), 45 (29), 43 (87), 41 (28). Anal. calc. for $C_{16}H_{24}O_3$ (264.37): C 72.69, H 9.15; found: C 72.78, H 9.25.

Conformer B (Acetate of (*Z*)-**17B**). UV (0.604 mg in 25 ml MeCN): 233 (9900). UV (6.886 mg in 2 ml MeCN): 326 (70). IR: 3000*w* (sh), 2970*w* (sh), 2960*m*, 2940*m*, 2915*w*, 2860*w*, 1730*s*, 1690*m*, 1665*w*, 1600*m*, 1435*w* br., 1365*m*, 1360*w* (sh), 1350*w*, 1240*s*, 1195*m*, 1160*w*, 1010*m*, 955*w*, 935*w*. ^{1}H-NMR: 0.91, 1.13 (2*s*, 2 CH_3–C(4)); 1.50 (*s*, CH_3–C(2)); 1.98 (*d*, *J* = 1.5, 3H–C(1')); 2.08, 2.13 (2*s*, 3H–C(5'), CH_3CO_2); 0.80–2.30 (*m*, 2H–C(5), 2H–C(6)); 5.18–5.40 (*m*, H–C(1)); 6.16 (*m*, $w_{½}$ = 4, H–C(3')). ^{13}C-NMR: 17.0, 21.3, 26.9, 27.0, 30.2, 30.5 (6*q*, 6 CH_3); 25.5, 36.2 (2*t*, C(5), C(6)); 35.0 (*s*, C(4)); 72.3 (*d*, C(1)); 124.9, 144.4, 152.7 (3*s*, C(2), C(3), C(2')); 127.6 (*d*, C(3')); 170.9 (*s*, CH_3CO_2), 197.4 (*s*, C(4')). MS: 204 (30, $M^+ - CH_3CO_2H$), 189 (22), 161 (34), 149 (31), *148* (100), 147 (22), 133 (68), 119 (21), 108 (27), 105 (45), 91 (30), 84 (22), 77 (23), 45 (30), 43 (87), 41 (33). Anal. calc. for $C_{16}H_{24}O_3$ (264.37): C 72.69, H 9.15; found: C 72.77, H 9.03.

(1'RS,2'SR,3'RS)-4-(2',3'-Epoxy-2',6',6'-trimethylcyclohexyl)-4-penten-2-one (**18**). (Obtained in a mixture containing 57% of (*E*)-**3**.) Signals assigned to **18**: IR: 3080*w*, 1725*m* (sh), 1710*s*, 905*m*. ^{1}H-NMR: 0.86, 0.93 (2*s*, 2 CH_3–C(6')); 1.26 (*s*, CH_3–C(2')); 2.22 (*s*, 3H–C(1)); 0.80–2.30 (*m*, H–C(1'), 2H–C(4'), 2H–C(5')); 2.80–3.02 (*m*, H–C(3')); 3.29 (*AB*, *J* = 15, δ_A = 3.08, δ_B = 3.50, 2H–C(3)); 5.05, 5.22 (2*m*, $w_{½}$ = 3, 2H–C(5)). ^{13}C-NMR (75 MHz): 49.9 (*t*, C(3)); 54.3, 57.5 (2*d*, C(1'), C(3')); 58.3 (*s*, C(2')); 119.2 (*t*, C(5)); 140.7 (*s*, C(4)); 204.5 (*s*, C(2)).

2.6.2. *At λ = 254 nm.* A soln. of (*E*)-**3** (629 mg, 2.83 mmol) in MeCN (150 ml) was irradiated (quartz, lamp *A*, 86% conversion). After chromatography (Et_2O/pentane 1:1 to 3:1), the following product distribution was determined (^{1}H-NMR): (*Z*)-**3** (19%), **18** (8%), (*E*)-**17** (12%), (*Z*)-**17A** (22%), (*Z*)-**17B** (15%), and additional photoproducts arising from (*E*/*Z*)-**17** (4%)[7].

3. Additional Experiments. – 3.1. *Photooxygenation of* **10A** *and* **10B**. *a*) A suspension of **10A** (120 mg, 0.58 mmol), *Sensitox I* (*ca.* 20 mg) in CH_2Cl_2 (15 ml) was irradiated in the presence of O_2 ($K_2Cr_2O_7$-filter, lamp *B*, conversion > 95%). Chromatography (Et_2O/pentane 2:1) yielded **20A** (65 mg, 47%). *b*) Analogously, photooxygenation of **10B** (106 mg, 0.51 mmol) afforded **20B** (70 mg, 57%).

5-Hydroxy-2,2,6,8-tetramethyl-7,9-10-trioxatricyclo[6.2.2.0^{1,6}]dodec-11-ene, Isomer A (**20A**). IR: 3575*m*, 3060*w*, 3010*m* (sh), 2980*m* (sh), 2960*s* (sh), 2940*s*, 2870*m*, 1740*w* (sh), 1720*m* (sh), 1700*m*, 1675*s*, 1655*m* (sh), 1615*w* (br.), 1465*m* (sh), 1445*m*, 1390*m* (sh), 1380*s*, 1375*s* (sh), 1365*m*, 1350*m* (sh), 1330*m*, 1310*w*, 1295*m*, 1245*m*, 1195*m*, 1170*m*, 1160*s*, 1105*s*, 1070*s*, 1030*m*, 1005*m*, 970*s*, 935*m*, 930*m*, 920*w* (sh), 900*w*, 870*m*, 850*m*. ^{1}H-NMR (80 MHz): 1.03, 1.15, 1.15, (3*s*, 2 CH_3–C(2), CH_3–C(6)); 1.58 (*s*, CH_3–C(8)); 1.00–2.40 (*m*, 2H–C(3), 2H–C(4)); 3.45–3.65 (*m*, OH); 3.70–3.90 (*m*, H–C(5)); 6.53 (*AB*, *J* = 8.0, δ_A = 6.45, δ_B = 6.60, H–C(11), H–C(12)). ^{13}C-NMR: 19.6, 20.8, 24.5, 26.1 (4*q*, 4 CH_3); 27.0, 33.7 (2*t*, C(3), C(4)); 35.6 (*s*, C(2)); 73.5 (*d*, C(5)); 81.2, 83.2, 95.0 (3*s*, C(1), C(6), C(8)); 128.7, 133.4 (2*d*, C(11), C(12)).

Isomer B (**20B**). IR: 3610*m*, 3480*w* (br.), 3060*w*, 2990*m*, 2950*s*, 2930*s* (sh), 2870*m*, 1740*s*, 1735*s* (sh), 1725*m* (sh), 1715*m* (sh), 1625*w* (br.), 1475*w* (sh), 1465*m* (sh), 1460*m*, 1445*m*, 1380*s*, 1350*m* (sh), 1325*m*, 1285*w*, 1260*m*, 1240*s*, 1205*m*, 1195*m*, 1170*m*, 1155*m*, 1115*s*, 1100*s*, 1075*s*, 1040*s*, 1015*s*, 980*m*, 965*s*, 940*w*, 925*w*, 905*s*, 875*m*, 855*w*. ^{1}H-NMR (80 MHz): 1.00, 1.08, 1.12 (3*s*, 2 CH_3–C(2), CH_3–C(6)); 1.52 (*s*, CH_3–C(8)); 1.00–2.50 (*m*, 2H–C(3), 2H–C(4), OH); 4.20–4.50 (*m*, H–C(5)); 6.47 (*AB*, *J* = 8.0, δ_A = 6.40, δ_B = 6.54, H–C(11), H–C(12)). ^{13}C-NMR (70% pure): 19.5, 20.7, 24.4, 26.1 (4*q*, 4 CH_3); 27.0, 33.7 (2*t*, C(3), C(4)); 35.5 (*s*, C(2)); 73.4 (*d*, C(5)); 81.0, 83.1, 94.9 (3*s*, C(1), C(6), C(8)); 128.6, 133.4 (2*d*, C(11), C(12)).

3.2. *Acid-Catalyzed Transformation of* **20A** *and* **20B** *to* **24**. A soln. of **20A** (107 mg, 0.45 mmol) in THF (15 ml) and aq. HCl (1M, 1.5 ml) was stirred for 20 h at r.t. Chromatography (AcOEt/CH_2Cl_2/pentane 2:1:1)

yielded **24** (26 mg, 24%). The analogous transformation of **20B** (86 mg, 0.36 mmol) in THF (15 ml) and aq. HCl (1M, 1.5 ml) afforded **24** (19 mg, 22%), which was purified as its acetate.

1-Acetyl-4,4-dimethyl-5,8-dioxo-6-nonenyl Acetate (Acetate of **24**). B.p. 110°/0.01 Torr. UV (0.233 mg in 25 ml MeCN): 233 (12100). UV (2.150 mg in 2 ml MeCN): 342 (80), end absorption to 415. IR: 3010*w* (sh), 2965*m*, 2930*m*, 2870*w*, 1745*s*, 1735*s*, 1705*s* (sh), 1685*s*, 1615*w*, 1470*m*, 1425*m*, 1390*m*, 1370*s*, 1360*s*, 1320*m*, 1285*s*, 1260*m* (sh), 1230*s*, 1190*m*, 1160*m*, 1155*m* (sh), 1085*m* (sh), 1065*m*, 1040*m*, 980*m*. ^{1}H-NMR: 1.16 (*s*, 2 CH_3–C(4)); 1.63 (*m*, $w_{1/2}$ = 6, 2H–C(3), 2H–C(2)); 2.11, 2.11, 2.34 (3*s*, 3H–C(9), CH_3–CO, CH_3CO_2); 4.86–5.00 (*m*, H–C(1)); 7.11 (*AB*, *J* = 15, δ_A = 6.96, δ_B = 7.26, H–C(6), H–C(7)). ^{13}C-NMR: 20.6, 23.7, 23.7, 26.1, 29.3 (5*q*, 5 CH_3); 25.5, 34.1 (2*t*, C(2), C(3)); 46.7 (*s*, C(4)); 78.4 (*d*, C(1)); 132.2, 137.6 (2*d*, C(6), C(7)); 170.5 (*s*, CH_3CO_2); 197.7, 203.5, 204.8 (3*s*, C(5), C(8), CH_3CO). MS: 240 (2, $M^+ - C_2H_2O$), 239 (3), 197 (7), 125 (23), 98 (43), *43* (100). Anal. calc. for $C_{15}H_{22}O_5$ (282.34): C 63.81, H 7.85; found: C 63.67, H 7.97.

3.3. *Catalytic Hydrogenation of* **25B**. A soln. of **25B** (30 mg, 0.11 mmol) in EtOH (1 ml) was added to an activated (H_2-saturated) suspension of Pd/$BaSO_4$ (*ca.* 5 mg) in EtOH (3 ml) and stirred for 2 h at ambient temp. The catalyst was filtered off and the solvent removed *in vacuo* to give a quantitative yield of the pure product **26** [13].

3.4. *Photooxygenation of* **14A** *and* **14B**. Solns. of **14A** (93 mg, 0.42 mmol) and **14B** (75 mg, 0.34 mmol) in CH_2Cl_2 (15 ml) were photooxygenated as described in *Sect. 3.1* affording **21A** (50 mg, 47%), and **21B** (45 mg, 52%), respectively.

5-Hydroxy-2,2,6,8,12-pentamethyl-7,9-10-trioxatricyclo[6.2.2.0^{1,6}]dodec-11-ene, Isomer A (**21A**). IR: 3580*m*, 3050*w*, 3000*m* (sh), 3060*s* (sh), 3045*s*, 3025*s* (sh), 2890*m* (sh), 2870*m*, 1750*m* (br.), 1475*w* (sh), 1465*m* (sh), 1450*s*, 1435*m*, 1395*s*, 1385*s*, 1375*s*, 1335*w*, 1290*w*, 1340*m*, 1215*m*, 1185*m*, 1165*m*, 1125*s*, 1085*s*, 1075*s*, 1025*m*, 970*s*, 930*m*. ^{1}H-NMR: 1.00, 1.08, 1.10 (3*s*, 2 CH_3–C(2), CH_3–C(6)); 1.50 (*s*, CH_3–C(8)); 1.93 (*d*, *J* = 1.5, CH_3–C(12)); 0.90–1.20 (*m*, 2H–C(3), 2H–C(4)); 3.50–3.90 (*m*, H–C(5), OH); 6.20 (*m*, $w_{1/2}$ = 5, H–C(11)). ^{13}C-NMR: 16.8, 18.2, 24.4, 26.3, 26.3 (5*q*, 5 CH_3); 26.0, 29.1 (2*t*, C(3), C(4)); 35.4 (*s*, C(2)); 71.4 (*d*, C(5)); 78.2, 83.7 (2*s*, C(1), C(6)); 97.5 (*s*, C(8)); 123.0 (*d*, C(11)); 141.2 (*s*, C(12)). MS: 254 (6, M^+, $C_{14}H_{22}O_4$), 236 (2), 211 (4), 193 (16), 179 (6), 167 (8), 151 (14), 139 (23), 137 (21), 125 (14), 121 (12), 111 (22), 109 (22), 95 (15), 81 (15), 71 (15), 69 (18), 55 (19), *43* (100), 41 (28).

Isomer B (**21B**). IR: 3610*m*, 3490*w* (br.), 3050*w*, 3000*m*, 2970*s* (sh), 2950*s*, 2930*m*, 2900*m* (sh), 2870*m*, 1655*w*, 1475*w* (sh), 1470*m* (sh), 1460*m* (sh), 1450*m*, 1440*m*, 1395*m*, 1385*s*, 1375*s*, 1325*m*, 1275*w*, 1340*w*, 1220*w*, 1180*w*, 1145*m*, 1120*s*, 1100*s*, 1075*m*, 1045*s*, 1015*m*, 960*s*, 910*s*, 875*m*, 850*w*. ^{1}H-NMR: 0.97, 1.02, 1.04 (3*s*, 2 CH_3–C(2), CH_3–C(6)); 1.43 (*s*, CH_3–C(8)); 1.90 (*d*, *J* = 1.5, CH_3–C(12)); 0.90–2.20 (*m*, 2H–C(3), 2H–C(4), OH); 4.22–4.46 (*m*, H–C(5)); 6.14 (*m*, $w_{1/2}$ = 5, H–C(11)). ^{13}C-NMR: 16.7, 18.3, 19.6, 24.5, 26.1 (5*q*, 5 CH_3); 27.0, 33.7 (2*t*, C(3), C(4)); 35.6 (*s*, C(2)); 73.4 (*d*, C(5)); 80.9, 83.7 (2*s*, C(1), C(6)); 97.3 (*s*, C(8)); 122.6 (*d*, C(11)); 140.8 (*s*, C(12)). MS: 254 (13, M^+, $C_{14}H_{22}O_4$), 193 (13), 167 (8), 151 (16), 139 (31), 137 (22), 125 (10), 123 (13), 121 (16), 111 (27), 109 (27), 95 (18), 84 (28), 69 (20), 55 (20), *43* (100), 41 (28).

3.5. *Equilibration of the Conformers (Z)-***17A** *and (Z)-***17B**. Two samples of (*Z*)-**17A** and (*Z*)-**17B** (50 mg, 0.19 mmol) in CD_3CN (0.5 ml) were heated in an oil bath to 80° and the reaction was followed by ^{1}H-NMR. After 5 h both samples contained a *ca.* 1:1 mixture of (*Z*)-**17A** and (*Z*)-**17B** as the only products.

3.6. *Treatment of* **18** *with Base*. A mixture of (*E*)-**3** and **18** (*ca.* 1:1, 230 mg, 1.03 mmol), NaOMe (230 mg, 4.26 mmol) and MeOH (10 ml) was heated under reflux for 5 h. The mixture was concentrated *in vacuo* and the residue extracted with Et_2O/pentane 1:1. Workup afforded pure (*E*)- and (*Z*)-**3** (82:18, 215 mg, 93%).

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