16. Photochemical Reactions

134th Communication[1])

Photochemistry of 5,6-Epoxy-5,6-dihydro-3,4-methano-β-ionone: Influence of a Cyclopropane Ring on the Reactivity of an Ylide Intermediate

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Dedicated to Dr. *Arnold Brossi* on the occasion of his 60th birthday

(23.XI.83)

Summary

On ^{1}n,π*-excitation (λ > 347 nm), the diastereomeric methanoepoxyenones (*E*)-**5** and (*E*)-**6** undergo isomerization *via* C,O-cleavage of the oxirane leading to diastereomeric photoproducts ((*E*)-**5**→(*E/Z*)-**13** and **14**; (*E*)-**6**→(*E/Z*)-**16** and **17**). On ^{1}π,π*-excitation (λ = 254 nm) of either (*E*)-**5** or (*E*)-**6** the photoproducts **9**, **10** and **11** are formed. By laser flash photolysis (λ = 265 nm) the ylide intermediate **e** was detected, with a lifetime of 10 μs in MeCN at ambient temperature. *Stern-Volmer* analysis of the ylide quenching by MeOH disclosed that compounds **9** and **10**, but not **11**, arise from the ylide intermediate **e**.

1. Introduction. – Previous works in this series [2] [3] have disclosed that ^{1}π,π*-excitation (λ = 254 nm) of the epoxyenones (*E*)-**1** and (*E*)-**2** induces, as a main process, the cleavage of the C(5),C(6)-bond[3]) leading to the ylide intermediates **a** and **b**, respectively. The ylide **a** undergoes an electrocyclic reaction producing the dihydrofurans (*E/Z*)-**3** [2] whereas a 1,4-O-migration in **b** gives the acetal **4** [3].

In the present investigation, the photolysis of the methano-epoxyenones (*E*)-**5** and (*E*)-**6** was studied to obtain information about the influence of the cyclopropane ring on the formation and reactivity of ylide intermediates.

Compound (*E*)-**5** was obtained in only 14% yield by cyclopropanation of (*E*)-**1** according to the method of *Kawabata et al.* [5][4]). On the other hand, epoxidation of **8** [7] gave (*E*)-**5** in 20% and (*E*)-**6** in 38% yield.

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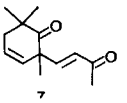
[1]) 133rd Communication see [1].

[2]) Taken in part from the Ph. D. thesis of *N.B.*

[3]) In ionone derivatives numbering of the carotinoid nomenclature [4] is used.

[4]) The low yield of (*E*)-**5** may be due to the lability of (*E*)-**1**; in addition, compound **7** (4%) was obtained presumably by a pinacol rearrangement. For an analogous acid-catalyzed transformation, see [6].



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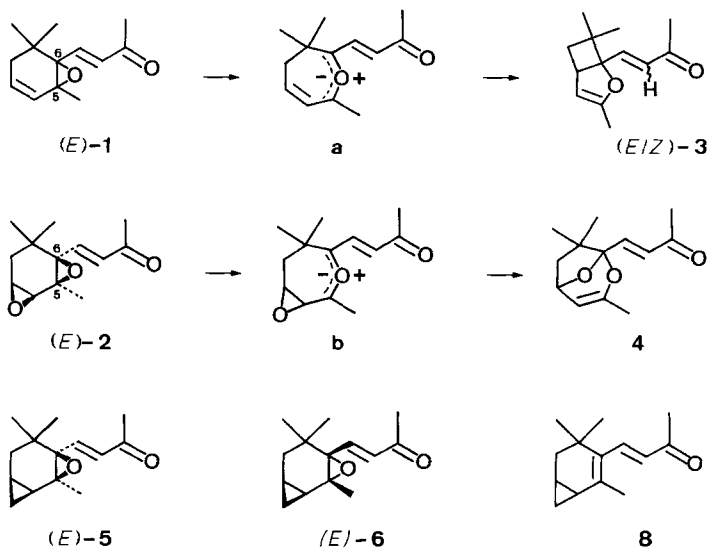
Scheme 1



2. Photolyses. – 2.1. *$^1\pi,\pi^*$-Excitation of (*E*)-5 and (*E*)-6 (λ = 254 nm).* The results are given in *Table 1* and the products are depicted in *Scheme 2*.

Table 1. *Results of the Photolysis (λ = 254 nm) of (*E*)-5 and (*E*)-6*

Substrate	Solvent	Conversion	Product distribution [%][a]					
		[%]	(*Z*)-5[b]	(*Z*)-6[b]	9	10	11	12
(*E*)-5	THF	96[c]	–	–	15	5	23	12
(*E*)-5	THF	72[d]	11	–	11	1	20	–
(*E*)-5	Hexane	81[d]	13	–	9	1	9	–
(*E*)-5	MeCN	98[c]	–	–	16	12	3	10
(*E*)-5	MeCN	70[d]	10	–	18	3	3	–
(*E*)-6	THF	87[c]	–	–	10	2	15	19
(*E*)-6	THF	61[d]	–	10	8	1	11	–
(*E*)-6	Hexane	62[d]	–	11	5	0.5	7	–
(*E*)-6	MeCN	68[d]	–	12	13	1	2	–

[a] Yields are based on converted starting material.

[b] Compounds (*Z*)-5 and (*Z*)-6 were only detected in the photolysis mixture (^{1}H-NMR and GC); on separation (SiO_2) they rearranged to the furan **12.**

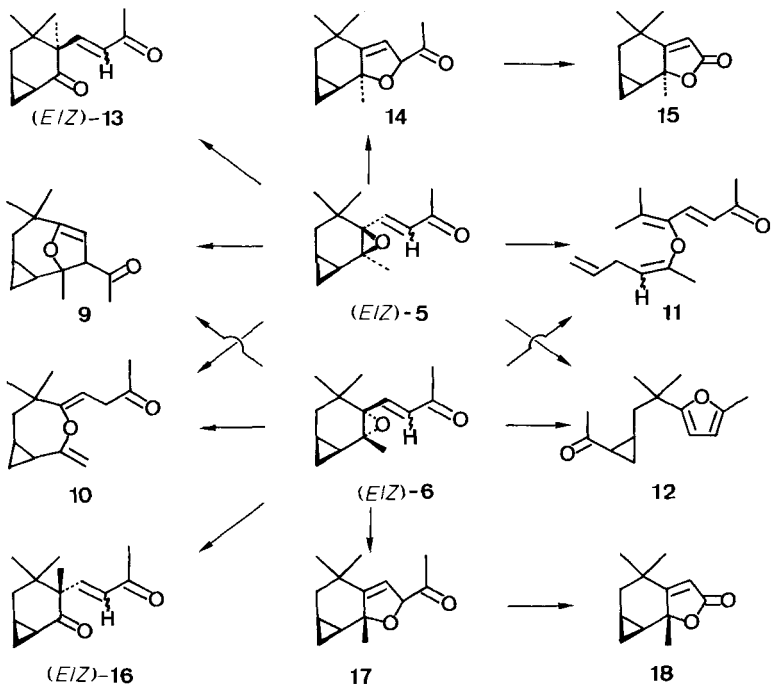
[c] Preparative scale, yields were determined after chromatography on SiO_2 by ^{1}H-NMR- and GC-analysis of the fractions.

[d] Analytical scale, yields were determined by GC-analysis using hexadecane as an internal standard.

2.2. *$^1n,\pi^*$-Excitation of (*E*)-5.* Photolysis of a *ca.* 0.02M solution of (*E*)-**5** in MeCN (λ > 347 nm, 82% conversion) gave the following products[5]): (*E*)-**13** (8%), (*Z*)-**13** (8%), **14** (18%) and **15** (8%) (see *Scheme 2*).

[5]) Yields are based on converted starting material.

Scheme 2

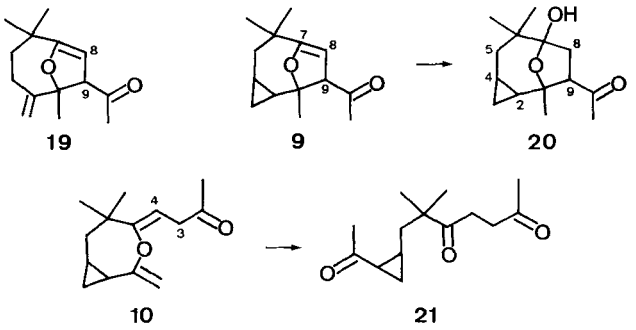


2.3. *$^1n,\pi^*$-Excitation of* (E)-**6**. Photolysis of a *ca.* 0.045M solution of (*E*)-**6** in MeCN ($\lambda > 347$ nm, 94% conversion) gave the following products[5]): **12** (2%) (*E*)-**16** (14%), (*Z*)-**16** (20%), **17** (14%) and **18** (9%) (see *Scheme 2*).

3. Structures of the Compounds. – *Methano-epoxyenones* (E)-**5** *and* (E)-**6**. The structures of the two diastereomers follow from the method of preparation and the spectral data. The enone moiety is evidenced by IR bands at 1695, 1678 cm^{-1} and 1695, 1675 cm^{-1} as well as the UV maxima at 242 nm ($\varepsilon = 11500$) and 231 nm ($\varepsilon = 8900$) for (*E*)-**5** and (*E*)-**6**, respectively. The ^{13}C-NMR spectra show characteristic signals for the oxirane C-atoms at 64.4 and 70.2 ppm for (*E*)-**5** and at 68.2 and 70.1 ppm for (*E*)-**6**. The cyclopropane moiety is evidenced by signals at 5.2 (*d*), 10.1 (*t*) and 12.7 ppm (*d*) in the case of (*E*)-**5**; the corresponding signals in the ^{13}C-NMR spectrum of (*E*)-**6** appear at 9.6 (*t*), 11.3 (*d*) and 15.0 ppm (*d*). The assignment of the relative configuration of (*E*)-**5** and (*E*)-**6** can be discussed on the basis of the method of their preparation. Thus, (*E*)-**5** is obtained as the only diastereomer by cyclopropanation of (*E*)-**1** according to the procedure in [5], which was found to give stereospecifically the product with the methano bridge in *cis*-position to the methyl-ether function in the reaction of 3-methoxycyclohexene.

Dihydrofuran **9**. The structure was derived by comparison of the ^{1}H-NMR spectrum of **9** with that of **19** [8] (see *Scheme 3*). In particular, the *d* at 5.24 and 3.99 ppm ($J = 0.5$ Hz) are characteristic for H–C(8) and H–C(9), respectively. Presumably due to the strained enol-ether moiety, **9** was easily transformed into the hemiacetal **20** by reaction with aq. oxalic acid. The structure of **20** is evidenced by the spectral data. Characteristic signals in the 300-MHz ^{1}H-NMR spectrum are 3 *dd* of 2 H–C(8) and H–C(9) at 1.88, 2.92 and 3.34 ppm (for coupling constants, see *Exper. Part*), an *AB*-system of 2 H–C(5) at 1.93 ppm, which is further split into *d* by coupling with H–C(4), and a *ddd* (0.39 ppm) and 2 *m* (0.54–0.67 and 0.85–0.91 ppm) of the 4 H-atoms of the cyclopropane component. In the ^{13}C-NMR spectrum of **20** the signals of the cyclopropane moiety appear at 3.5(*t*), 15.8(*d*) and 21.5 ppm (*d*), and the 2*s* of the bridgehead C-atoms are at 82.9 and 108.6 ppm. Furthermore the methyl-ketone group is evidenced by an IR band at 1713 cm^{-1} and a *s* at 2.26 ppm in the ^{1}H-NMR-spectrum.

Scheme 3



Bicyclic Divinyl Ether **10.** The structure of **10,** which was also obtained on thermolysis of (*E*)-**5** and (*E*)-(*E*)-**6** at 520° [9], was primarily derived from the spectral data. The ^{1}H-NMR spectrum shows 2*d* at 4.15 and 4.52 ppm with a coupling constant of 2 Hz of the H-atoms of the methylidene group, a *d* (*J* = 7 Hz) at 3.35 ppm of 2 H–C(3), and a *t* (*J* = 7 Hz) at 5.21 ppm of the enol-ether H–C(4). The methyl-ketone moiety is evidenced by the IR band at 1720 cm^{-1} and the *s* at 2.18 ppm in the ^{1}H-NMR spectrum.

Hydrolysis (aq. oxalic acid) of **10** gave the triketone **21** (for the spectral data, see *Exper. Part*).

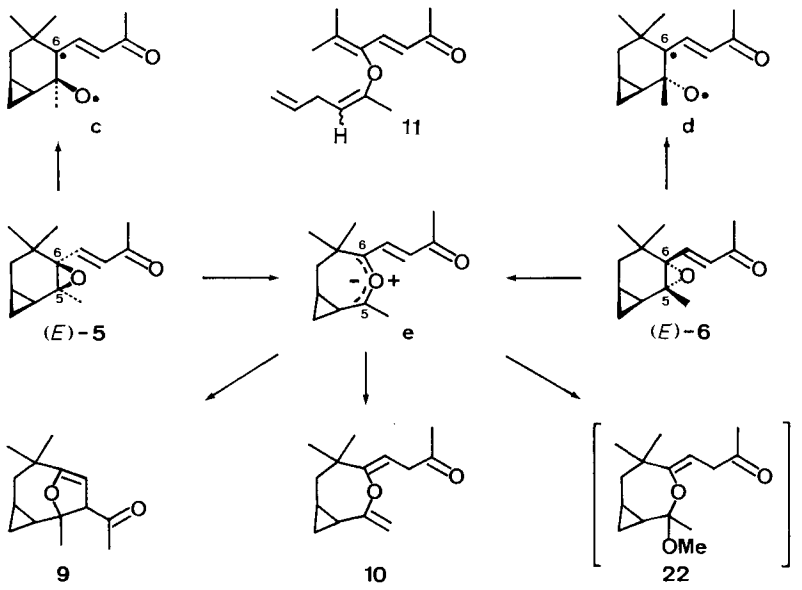
Aliphatic Divinyl Ether **11.** The dienone chromophore is evidenced by the UV maximum at 288 nm (ε = 17000), and the IR spectrum exhibits strong bands of the dienone and enol-ether moieties at 1690, 1668, 1635, 1621 and 1590 cm^{-1}. Most of the structural evidence, however, stems from the ^{1}H- and ^{13}C-NMR spectra; in particular, in the 300-MHz ^{1}H-NMR spectrum every individual H-atom was assigned conclusively and the couplings are in agreement with the proposed structure (see *Exper. Part*).

Compounds **12,** *(*E/Z*)*-**13, 14, 15,** *(*E/Z*)*-**16, 17** *and* **18.** The NMR spectra indicate that the cyclopropane moiety is intact in all these compounds and has spectral characteristics similar to those described for the aforementioned cyclopropyl compounds. The structures became evident after comparison of the spectral data with those of the corresponding compounds obtained on photolysis of (*E*)-**2** [3]; full data are given in the *Exper. Part*. The assignment of the stereochemistry is based on the fact that (*E*)-**5** and (*E*)-**6** stereospecifically produce two sets of diastereomeric compounds: (*E*)-**5**→(*E/Z*)-**13** and **14**; (*E*)-**6**→(*E/Z*)-**16** and **17.** Furthermore the lactones **15** and **18** were obtained by oxidation of **14** and **17,** respectively.

4. Discussion. – As expected, the photolyses of (*E*)-**5** and (*E*)-**6** show a strong dependence of the product formation upon the mode of excitation. On ^{1}n,π*-excitation isomerization *via* C(6),O-bond cleavage of the oxirane occurs ((*E*)-**5**→**c,** (*E*)-**6**→**d,** see *Scheme 4)* leading to the same types of photoproducts as obtained on ^{1}n,π*-excitation of (*E*)-**2** [3] (**c**→(*E/Z*)-**13** and **14; d**→(*E/Z*)-**16** and **17,** see *Scheme 2)*. While on ^{1}n,π*-excitation the diastereomeric epoxyenones (*E*)-**5** and (*E*)-**6** produce the expected two sets of diastereomeric photoproducts, in contrast, ^{1}π,π*-excitation of either (*E*)-**5** or (*E*)-**6** gives rise to the identical photoproducts **9, 10** and **11.** This finding indicates that ^{1}π,π*-excitation of (*E*)-**5** and (*E*)-**6** leads to a common intermediate such as the ylide **e,** which would arise from cleavage of the C(5),C(6)-bond. In fact, by laser flash photolysis (λ = 265 nm, MeCN) of (*E*)-**5** and (*E*)-**6** at ambient temperature, a carbonyl ylide with a lifetime of 10 ± 1 μs and a broad absorption maximum in the visible region was detected. The same species was formed as a persistent blue photoproduct by the 254-nm irradiation of compounds (*E*)-**5** and (*E*)-**6** dissolved in an EPA glass at 77 K *(Fig. 1)* [10].

To determine which of the photoproducts **9–11** are formed *via* the ylide intermediate **e,** a *Stern-Volmer* analysis [11] was carried out. First the lifetimes τ of the ylide

Scheme 4



e in MeCN in the presence of various MeOH-concentrations were measured. The plot of τ^{-1} *vs.* the MeOH-concentration gave a straight line *(Fig. 2)* and, from the *Stern-Volmer* equation $\tau^{-1} = \tau_0^{-1} + k_q[\text{MeOH}]$, a bimolecular quenching constant $k_q = 1.4 \pm 0.2 \cdot 10^5 \text{s}^{-1}\text{M}^{-1}$ was determined.

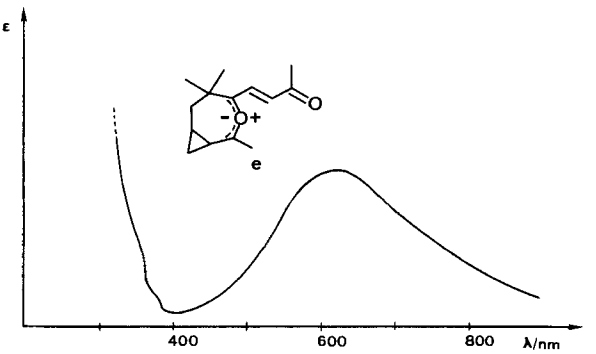


Fig. 1. *Absorbance of the carbonyl ylide* **e** *derived form (*E*)-***5***.* Recorded after 254 nm irradiation of the epoxy precursor in an EPA glass at 77 K (arbitrary ordinate scale).

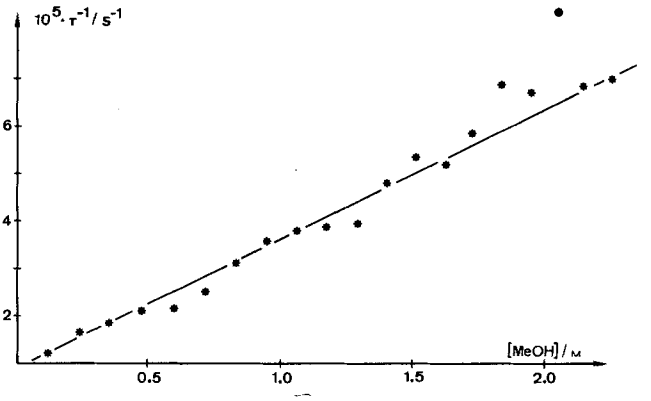


Fig. 2. *Plot of* τ^{-1} *of the ylide* **e** *derived from* (E)-**5** *as a function of the MeOH-concentration*

In a second experiment, the relative quantum yields Φ of the photoproducts **9** and **11** as a function of the MeOH-concentration were determined[6]). The plot of Φ_0/Φ[7]) *vs.* the MeOH-concentration gave straight lines *(Fig. 3)*. From the slopes values for $\tau_0 \cdot k_q$ were determined to be $1.2 \pm 0.1 M^{-1}$ for **9** and $17 \pm 2 M^{-1}$ for **11.** In the case of **9,** the values for $\tau_0 \cdot k_q$ obtained from laser flash experiments ($1.4 \pm 0.2 M^{-1}$) and preparative quenching experiments ($1.2 \pm 0.1 M^{-1}$) are the same within the limits of error. This proves conclusively that **9** is formed *via* the ylide intermediate **e**[8]).

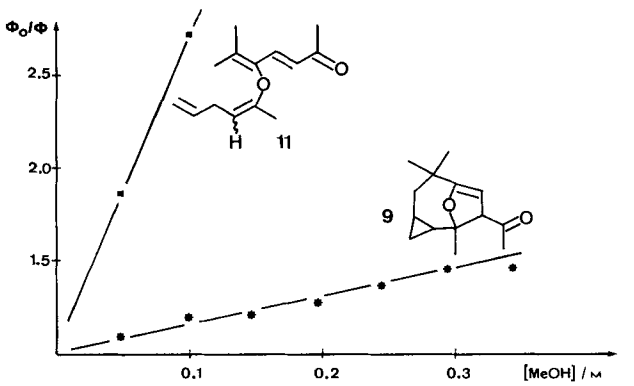


Fig. 3. *Plot of* Φ_0/Φ *of* **9** *and* **11** *as function of the MeOH-concentration*

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[6]) The dependence of the formation of **10** on the MeOH-concentration could not be determined due to the low yield of **10.** Since compound **10** could not be detected on preparative photolysis of (*E*)-**6** in MeOH, it may be assumed that its formation is also quenched by this solvent.

[7]) Φ_0 = Relative quantum yield of the products at [MeOH] = 0.

[8]) The formation of dihydrofurans analogous to **9** *via* carbonyl ylides is a well-known process (see *e.g.* (*E*)-**1**→**a**→(*E/Z*)-**3**); for additional examples see [8] [12]. However, the proof for the intermediacy of a carbonyl ylide by direct kinetic measurements was not given so far.

Thus the main reaction of the $^1\pi,\pi^*$-excited epoxyenones (*E*)-**5** and (*E*)-**6** is cleavage of the C(5),C(6)-bond leading to the ylide intermediate **e.** In the absence of a trapping agent such as MeOH, **e** undergoes an electrocyclic reaction with the neighbouring C,C-double bond (**e**→**9**) or a 1,6-H-shift (**e**→**10**[9])). In the presence of MeOH, however, the ylide is rapidly quenched. As shown on preparative photolysis of (*E*)-**6** in MeOH, apart from the furan **12** (see *Scheme 2*), as main product the triketone **21** (see *Scheme 3*) was formed presumably by hydrolysis of **22,** the primary product of the ylide-trapping (see *Scheme 4*), which could not be detected.

The mechanism for the formation of **11** remains open. From *Fig. 3* it is evident that the intermediate leading to **11** is quenched more rapidly by MeOH ($\tau_0 \cdot k_q = 17 \pm 2 M^{-1}$) than the ylide intermediate **e** ($\tau_0 \cdot k_q = 1.4 \pm 0.2 M^{-1}$). However, on preparative photolysis of (*E*)-**6** in MeOH, apart from **21,** other trapping products or their secondary products could not be detected. Furthermore, the yield of **11** markedly depends on the solvent (see *Table 1*). This solvent effect and the finding that the formation of **11** is quenched by MeOH indicate that a concerted mechanism is not involved, however, the nature of the intermediate still remains open[10])[11]).

Conclusion. – On $^1n,\pi^*$-excitation, of the methano-epoxyenones (*E*)-**5** and (*E*)-**6,** the same types of photoproducts are formed as on $^1n,\pi^*$-excitation of the bis-epoxyenone (*E*)-**2** [3], involving (*E*/*Z*)-isomerization of the enone side chain and/or cleavage of the C(6),O-bond. Both systems show the typical behavior of $^1n,\pi^*$-excited epoxyenones [15], with no participation of the additional three-membered ring.

On $^1\pi,\pi^*$-excitation of (*E*)-**5** and (*E*)-**6,** the main reaction is cleavage of the C(5), C(6)-bond leading to the carbonyl ylide intermediate **e.** Whereas the corresponding ylide intermediates **a** and **b,** derived from (*E*)-**1** and (*E*)-**2,** respectively, react rapidly with participation of the neighbouring C(3),C(4)-double bond (**a**→(*E*/*Z*)-**3**) or the neighbouring oxirane moiety (**b**→**4,** see *Scheme 1*), **e** is transformed to compounds **9** and **10** without cleavage of the cyclopropane ring. This difference in reactivity is also evidenced by the lifetimes of the ylide intermediates **a, b** and **e.** Thus, in contrast to the short lifetimes of **a** (185 ns in Et_2O) and **b** (33 ns in Et_2O), that of **e** is much longer (2700 ns in Et_2O) [10]. Finally it is noteworthy that in contrast to ylides formed from related epoxyenones of the ionone series [10] [16], the ylide **e** does not undergo ring closure to the epoxides (*E*)-**5** and (*E*)-**6.**

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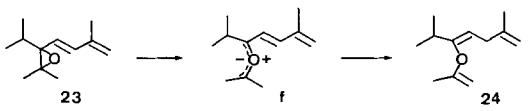
[9]) An analogous transformation was observed on $^1\pi,\pi^*$-excitation of **23**→**f**→**24** [13].

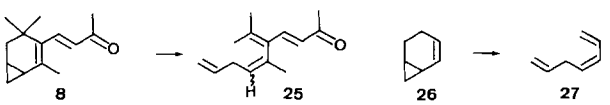
Scheme 5



[10]) An analogous isomerization (**8**→**25**) was found earlier [7].

[11]) For a discussion of a concerted *vs.* a stepwise mechanism of the transformation of **26**→**27** see [14].

Scheme 6



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Experimental Part

General. See [17] except as noted below. Analytical GC was performed using a 25 m × 0.33 mm *Ucon 50 HB 5100* glass capillary. Column chromatographies were carried out on silica gel (SiO_2 *60 Merck*, 0.040–0.063 mm, 230–400 mesh ASTM. Analytically pure samples were obtained, in general, after repeated column chromatography on SiO_2. ^{1}H-NMR spectra were taken in $CDCl_3$-solutions on a *Brucker-WP-80/CW* instrument (80 MHz) exceptions are noted below. *Laser flash photolysis experiments* were carried out as described in [10].

1. Preparation of (*E*)-5 and (*E*)-6. – 1.1. *By Cyclopropanation of* (E)-**4**-*(1',2'-Epoxy-2',6',6'-Trimethyl-3-cyclohexenyl)-3-buten-2-one* ((E)-**1**). According to the procedure described in [5], a solution of (*E*)-**1** [18] (15.6 g, 75.7 mmol) in benzene (60 ml) and CH_2I_2 (25 ml, 310 mmol) and Cu-powder (40 g, 630 mmol) was refluxed for 4 days. After filtration over *Celite* and chromatography of the mixture (SiO_2; Et_2O/hexane 1:2), two fractions were obtained, the first (3.02 g) contained 80% of (*E*)-**5** (14%) and the second (1.58 g) contained 40% of **7** (4%). Pure (*E*)-**5** was obtained by repeated chromatography on SiO_2.

(E,1'R,2'R*,4'S*,7'S*)-4-(2',5',5'-Trimethyl-3'-oxatricyclo[5.1.0.0^{2,4}]oct-4'-yl)-3-buten-2-one* ((*E*)-**5**). B.p. 80°/0.03 Torr. UV (0.204 mg in 10 ml): 242 (115000). UV (2.5 mg in 2 ml): end absorption to 400. IR: 3082*w*, 3010*m*, 2965*s*, 2930*m*, 2900*m* sh, 2875*m*, 2860*w*, 1695*s*, 1678*s*, 1625*s*, 1468*m*, 1461*m*, 1450*m*, 1435*m*, 1425*m*, 1390*m*, 1378*m*, 1365*m*, 1360*s*, 1320*w*, 1301*m*, 1275*s*, 1255*m*, 1250*m* sh, 1202*w*, 1181*m*, 1167*m*, 1135*w*, 1108*w*, 1085*m*, 1049*m*, 1035*m*, 1020*m*, 982*m*, 955*w*, 945*m*, 908*m*, 882*m*, 861*m*, 840*w*. ^{1}H-NMR (100 MHz, CCl_4): 0.28–1.58 (*m*, H–C(1'), H–C(7'), 2 H–C(8'), 2 H–C(6')); 0.81, 1.19, 1.28 (3*s*, CH_3–C(2'), 2 CH_3–C(5')); 2.15 (*s*, 3 H–C(1)); 6.49 (*AB*-system, J = 15, δ_A = 6.12, δ_B = 6.85, H–C(3), H–C(4)). ^{13}C-NMR: 19.7, 23.3, 26.8, 28.1 (4*q*, 4 *C*H_3); 10.1 (*t*, C(8')); 35.3 (*t*, C(6')); 5.2, 12.7 (2*d*, C(1'), C(7')); 132.1, 141.9 (2*d*, C(3), C(4)); 35.3 (*s*, C(5')); 64.4, 70.2 (2*s*, C(2'), C(4')); 196.9 (*s*, C(2)). MS: 220 (2, M^+, $C_{14}H_{20}O_2$), 177 (14), 125 (11), 124 (11), *123* (100), 121 (20), 109 (10), 43 (43), 39 (12). Anal. calc. for $C_{14}H_{20}O_2$ (220.30): C 76.33, H 9.15; found: C 75.94, H 9.20.

(E)-2,6,6-Trimethyl-2-(3'-oxo-1'-butenyl)-3-cyclohexen-1-one (**7**). B.p. 100°/0.02 Torr. IR: 3030*m*, 2970*s*, 2930*m*, 2900*m*, 2870*m*, 2840*w*, 1736*m*, 1709*s*, 1678*s*, 1615*s*, 1469*m*, 1450*m*, 1435*w*, 1382*m*, 1360*s*, 1335*w*, 1302*w*, 1288*w*, 1269*m*, 1250*s*, 1232*m*, 1212*w*, 1173*w*, 1132*w*, 1124*w*, 1089*w*, 1075*w*, 1030*m*, 995*m*, 989*m*, 945*w*, 938*w*. ^{1}H-NMR (100 MHz, CCl_4): 1.06, 1.10, 1.26 (3*s*, CH_3–C(2), 2 CH_3–C(6)); 2.12 (*s*, 3 H–C(4')); 2.23 (*dd*, J_1 = 4, J_2 = 1.5, 2 H–C(5)); 5.78 (*AB*-system, J = 10, δ_A = 5.67, broadened, H–C(3), δ_B = 5.90, split into *t*, J = 4, H–C(4)); 6.22 (*AB*-system, J = 16, δ_A = 5.88, δ_B = 6.56, H–C(1'), H–C(2')). ^{13}C–NMR: 25.4, 26.8 (4*q*, 3 at 25.4, 4 *C*H_3); 38.2 (*t*, C(5)); 129.0, 130.9, 136.1, 149.2 (4*d*, C(3), C(4), C(1'); C(2')); 43.7 (*s*, C(6)); 50.2 (*s*, C(2)); 197.4 (*s*, C(3')); 213.9 (*s*, C(1)). MS: 206 (4, M^+, $C_{13}H_{18}O_2$), 178 (18), 163 (37), 145 (11), 136 (14), 135 (38), 123 (12), 122 (14), 121 (44), 120 (14), 119 (18), 109 (35), 108 (36), 107 (24), 105 (19), 96 (18), 94 (11), 93 (88), 92 (13), 91 (37), 79 (19), 77 (28), 70 (35), 55 (12), 53 (11), *43* (100), 42 (12), 41 (27), 39 (16).

1.2. *By Epoxidation of* **8**. To a solution of **8** [7] (21.31 g, 104 mmol) in CH_2Cl_2 (150 ml) and $NaHCO_3$ (11.5 g, 13.4 mmol) in H_2O (200 ml) was slowly added a solution of *m*-chloroperbenzoic acid (22.7 g, 118 mmol) in CH_2Cl_2 (150 ml) at 0°. The mixture was allowed to warm up to ambient temp. and was stirred for 1 h. Chromatography (SiO_2, hexane/CH_2Cl_2/AcOEt 10:1:1) gave three fractions, the first (3.35 g) contained pure (*E*)-**5**, the second (5.64 g) consisted of (*E*)-**5** (20%) and (*E*)-**6** (65%) and the third (5.12 g) was pure (*E*)-**6**. The yields of (*E*)-**5** and (*E*)-**6** were determined to be 20% and 38%, respectively.

(E,1'R,2'S*,4'R*,7'S*)-4-(2',5',5'-Trimethyl-3'-oxatricyclo[5.1.0.0^{2,4}]oct-4'-yl)-3-buten-2-one* ((*E*)-**6**). B.p. 80°/0.03 Torr. UV (0.189 mg in 10 ml): 231 (8900). UV (2.2 mg in 2 ml): 329 (32), end absorption to 390. IR: 3092*w*, 3003*m*, 2960*s*, 2920*m*, 2870*m*, 2850*m*, 1695*s*, 1675*s*, 1624*s*, 1465*m*, 1450*m*, 1435*m*, 1420*m*, 1400*m*, 1373*m*, 1361*m* sh, 1355*s*, 1295*m*, 1278*s*, 1245*s*, 1203*m*, 1165*m*, 1153*m*, 1138*w*, 1098*w*, 1070*w*, 1038*w*, 1019*m*, 981*m*, 965*w* sh, 930*w*, 912*w*, 890*w*, 880*w*, 859*w*, 835*w*. ^{1}H–NMR (100 MHz, CCl_4): 0.50–0.70 (*m*, 2 H) and 0.75–1.34 (*m*, 2 H, H–C(1'), H–C(7'), 2 H–C(8')); 0.88, 1.17, 1.25 (3*s*, CH_3–C(2'), 2 CH_3–C(5')); 1.70 (*AB*-

system, J = 14, δ_A = 1.48, split into *d*, J = 2.5, δ_B = 1.92, split into *d*, J = 4, 2 H–C(6')); 2.15 (*s*, 3 H–C(1)); 6.45 (*AB*-system, J = 15, δ_A = 6.14, δ_B = 6.76, H–C(3), H–C(4)). ^{13}C-NMR: 19.8, 28.0, 28.1, 28.8 (4*q*, 4 CH_3); 9.6 (*t*, C(8')); 34.1 (*t*, C(6')); 11.3, 15.0 (2*d*, C(1'), C(7')); 132.8, 141.6 (2*d*, C(3), C(4)); 32.9 (*s*, C(5')); 68.2, 70.1 (2*s*, C(2'), C(4')); 197.2 (*s*, C(2)). MS: 220 (1, M^+, $C_{14}H_{20}O_2$), 177 (17), 149 (11), 125 (11), *123* (100), 121 (29), 109 (15), 55 (11), 43 (56), 41 (19). Anal. calc. for $C_{14}H_{20}O_2$ (220.30): C 76.33, H 9.15; found: C 76.22, H 9.22.

2. Photolysis Experiments. – 2.1. *Irradiation of* (E)-**5** *at* λ = *254 nm.* – 2.1.1. *In THF.* A solution of (*E*)-**5** (1.180 g, 5.36 mmol) in THF (120 ml) containing *ca.* 50 mg of Na_2CO_3 was irradiated (quartz, lamp *A*, 96% conversion). Chromatography (SiO_2, Et_2O/pentane 1:2) yielded several fractions. The following product distribution was determined (^{1}H-NMR and GC): **9** (15%), **10** (5%), **11** (23%), **12** (12%).

1,6,6-Trimethyl-10-oxatricyclo[5.2.1.0^{2,4}]dec-7-en-9-ylmethyl ketone (**9**). 80% pure. IR: 3060*w*, 2960*s*, 2925*s*, 2910*s*, 2862*m*, 1700*s*, 1635*m*, 1448*m*, 1372*s*, 1350*s*, 1308*m*, 1205*m*, 1177*s*, 1159*s*, 1117*m*, 1092*m*, 1073*m*, 1045*m*, 1035*m*, 937*m*, 882*m*, 870*m*. ^{1}H-NMR: 0.05–2.47 (*m*, H–C(2), 2 H–C(3), H–C(4), 2 H–C(5)); 1.04, 1.18 (2*s*, 2 CH_3–C(6)); 1.65 (*s*, CH_3–C(1)); 2.24 (*s*, CH_3CO); 3.99 (*d*, J = 0.5, H–C(9)); 5.24 (*d*, J = 0.5, H–C(8)). MS: (17, M^+, $C_{14}H_{20}O_2$), 177 (48), 149 (21), 136 (58), 135 (23), 123 (72), 121 (41), 109 (51), 107 (26), 93 (32), 91 (24), 79 (29), 77 (23), 69 (21), 55 (21), *43* (100), 41 (39).

4-(5',5'-Dimethyl-2'-methyliden-3'-oxabicyclo[5.1.0]oct-4'-yliden)-2-butanone (**10**). B.p. 90°/0.03 Torr. UV (0.354 mg in 10 ml pentane): 213 (8600). UV (2.244 mg in 2 ml pentane): 281 (100), end absorption to 330. IR: 3120*w*, 3080*w*, 3005*m*, 2965*s*, 2925*m*, 2862*m*, 1720*s*, 1702*s*, 1675*m*, 1667*m*, 1635*s*, 1468*w*, 1458*m*, 1450*m*, 1418*w*, 1385*m*, 1353*s*, 1335*m*, 1308*m*, 1265*w*, 1210*s*, 1195*m*, 1182*m*, 1171*m*, 1155*s*, 1115*s*, 1089*m*, 1060*m*, 1052*m*, 1033*m*, 1021*w*, 973*w*, 955*w*. ^{1}H-NMR: 1.08, 1.24 (2*s*, 2 CH_3–C(5')); 0.40–2.32 (*m*, H–C(1'), 2 H–C(6'), H–C(7'), 2 H–C(8')); 2.18 (*s*, 3 H–C(1)); 3.35 (*d*, J = 7, broadened, 2 H–C(3)); 4.15, 4.52 (2*d*, J = 2, CH_2=C(2)); 5.21 (*t*, J = 7, H–C(4)). MS: 220 (5, M^+, $C_{14}H_{20}O_2$), 177 (56), 136 (10), 123 (26), 121 (15), 109 (10), 107 (19), 95 (10), 93 (19), 91 (17), 81 (13), 79 (72), 77 (30), 69 (27), 67 (11), 55 (56), 53 (17), *43* (100), 41 (39). Anal. calc. for $C_{14}H_{20}O_2$ (220.30): C 76.33, H 9.15; found: C 76.19, H 9.21.

(3E)-5-Isopropyliden-7-methyl-6-oxa-3,7,10-undecatrien-2-one (**11**). B.p. 90°/0.03 Torr. UV (0.148 mg in 10 ml): 288 (17000). UV (2.462 mg in 2 ml): end absorption to 390. IR: 3080*w*, 3055*w*, 3000*m*, 2990*m*, 2928*m* sh, 2950*m*, 2920*m*, 2880*m*, 2850*w*, 1690*s*, 1668*s*, 1635*s*, 1621*s*, 1590*s*, 1440*m*, 1430*m*, 1379*s*, 1365*s*, 1330*m*, 1305*m*, 1295*s*, 1260*s*, 1195*s*, 1168*s*, 1112*m*, 1070*w*, 1035*w*, 982*m* sh, 970*s*, 953*m*, 910*s*. ^{1}H-NMR (300 MHz): 1.62–1.63 (*m*, CH_3–C(7)); 1.81, 1.95 (2*m*, $w_{1/2}$ = 2, 2 CH_3–C=C(5)); 2.26 (*s*, 3 H–C(1)); 2.93 (*ddm*, J_1 = 7.2, J_2 = 6.2, 2 H–C(9)); 4.47 (*tq*, J_1 = 7.2, J_2 = 1.0, H–C(8)); 4.95–4.97 and 4.98–5.00 (2*m*, H–C(11)); 5.08 (*ddt*, J_1 = 17.0, J_2 = 1.9, J_3 = 1.9, H–C(11)); 5.88 (*ddt*, J_1 = 17.0, J_2 = 10.0, J_3 = 6.2, H–C(10)); 6.86 (*AB*-system, J = 15.2, δ_A = 6.28, δ_B = 7.45, H–C(3), H–C(4)). ^{13}C-NMR: 17.4, 19.3, 28.6 (4*q*, 2 at 19.3, 4 CH_3); 29.0 (*t*, C(9)); 114.0 (*t*, C(11)); 103.3 (*d*, C(8)); 124.9, 134.8, 137.5 (3*d*, C(3), C(4), C(10); 134.5, 143.1, 149.6 (3*s*, 2 CH_3–*C*=*C*(5), C(7)); 198.2 (*s*, C(2)). MS: 220 (7, M^+, $C_{14}H_{20}O_2$); 177 (42), 149 (13), 136 (12), 125 (21), 123 (35), 109 (15), 81 (12), 79 (17), 55 (11), 53 (14), *43* (100), 41 (24). Anal. calc. for $C_{14}H_{20}O_2$ (220.30): C 76.33, H 9.15; found: C 76.34, H 9.06.

Methyl 2-[2'-methyl-2'-(5''-methyl-2''-furyl)propyl]cyclopropyl ketone (**12**). B.p. 80°/0.04 Torr. UV (0.209 mg in 10 ml): 218 (10200). UV (2.361 mg in 2 ml): 275 (200), end absorption to 380. IR: 3105*w*, 3080*w*, 3030*w*, 3000*m*, 2962*s*, 2920*s*, 2868*m*, 1692*s*, 1610*w*, 1560*w*, 1552*w*, 1538*w*, 1460*m*, 1448*m*, 1433*m*, 1422*m*, 1380*s*, 1362*m*, 1348*m*, 1296*w*, 1219*m*, 1190*m*, 1163*s*, 1138*m*, 1115*m*, 1095*w*, 1075*w*, 1068*w*, 1048*w*, 1019*m*, 988*w*, 950*m*, 935*m*, 905*m*, 852*m*. ^{1}H-NMR: 0.76–2.35 (*m*, H–C(1), H–C(2), 2 H–C(1'), 2 H–C(3); 1.20, 1.24 (2*s*, CH_3–C(2'), 3 H–C(3')); 2.20, 2.24 (2*s*, CH_3CO, CH_3–C(5'')); 5.80 (*s*, H–C(3''), H–C(4'')). ^{13}C–NMR (20 MHz): 13.5, 26.9, 32.1 (4*q*, 2 at 26.9, 4 CH_3); 14.8 (*t*, C(3)); 37.9 (*t*, C(1')); 21.8, 25.9 (2*d*, C(1), C(2)); 104.0, 105.5 (2*d*, C(3''), C(4'')); 36.1 (*s*, C(2')); 150.1, 160.9 (2*s*, C(2''), C(5'')); 207.1 (*s*, CO). MS: 220 (7, M^+, $C_{14}H_{20}O_2$), *123* (100), 43 (25). Anal. calc. for $C_{14}H_{20}O_2$ (220.30): C 76.33, H 9.15; found: C 76.30, H 9.00.

2.1.2. *In MeCN.* A solution of (*E*)-**5** (1.067 g, 4.85 mmol) in MeCN (100 ml) was irradiated and worked up as described in *Sect. 2.1.1.* The following product distribution was determined: **9** (16%), **10** (12%), **11** (3%), **12** (10%).

2.1.3. *Capillary GC Analysis of the Irradiation of* (E)-**5.** Solutions of (*E*)-**5** (0.018M) in *a*) hexane, *b*) THF and *c*) MeCN were irradiated with hexadecane as an internal standard in a merry-go-round (lamp *A*). After 75 min the following product distributions were determined (GC): *a*) 81% conversion: (*Z*)-**5** (13%), **9** (9%), **10** (1%), **11** (9%); *b*) 72% conversion: (*Z*)-**5** (11%), **9** (11%), **10** (1%), **11** (20%); *c*) 70% conversion: (*Z*)-**5** (10%), **9** (18%), **10** (3%), **11** (3%).

2.2. *Irradiation of* (E)-**6** *at* λ = *254 nm.* 2.2.1. *In THF.* A solution of (*E*)-**6** (2.180 g, 9.91 mmol) in THF (150 ml) was irradiated (quartz, lamp *A*, 87% conversion). Chromatography (SiO_2, Et_2O/pentane 1:2) yielded

several fractions. The following product distribution was determined (^{1}H–NMR and GC): **9** (10%), **10** (2%), **11** (15%), **12** (19%).

2.2.2. *Capillary GC Analysis of the Irradiation of* (E)-**6.** Solutions of (*E*)-**6** (0.0154M) in *a*) hexane; *b*) THF and *c*) MeCN were irradiated as described in *Sect. 2.1.3.* The following product distributions were determined (capillary GC): *a*) 62% conversion: (*Z*)-**6** (11%), **9** (5%), **10** (0.5%), **11** (7%); *b*) 61% conversion: (*Z*)-**6** (10%), **9** (8%), **10** (1%), **11** (11%) and *c*) 68% conversion: (*Z*)-**6** (12%), **9** (13%), **10** (1%), **11** (2%).

2.3. *Irradiation of* (E)-**5** *at* $\lambda \geq 347$ *nm.* A solution of (*E*)-**5** (760 mg, 3.45 mmol) in MeCN (200 ml) was irradiated ($Pb(NO_3)_2$/KBr filter [19], lamp *B*, 82% conversion). Chromatography (SiO_2, Et_2O/pentane 1:1 to 2:1) of the photolysis mixture yielded fractions; the following product distribution was determined (^{1}H-NMR and GC): (*E*)-**13** (8%), (*Z*)-**13** (8%), **14** (18%) and **15** (8%).

*(*E,*1′*R*,*3′*S*,*6′*R**)-4-(3′,4′,4′-Trimethyl-2′-oxobicyclo[4.1.0]hept-3′-yl)-3-buten-2-one* ((*E*)-**13**). UV (0.370 mg in 25 ml): 217 (7900), 240 sh (5200); UV (1.262 mg in 2 ml): 289 (170), 296 (170), end absorption to 380. IR: 3080*w*, 3010*m*, 2990*m* sh, 2970*s*, 2960*s*, 2940*m*, 2925*m*, 2870*m*, 1685*s*, 1608*s*, 1468*m*, 1450*m*, 1438*m*, 1420*m*, 1390*m*, 1369*s*, 1355*s*, 1348*s*, 1321*w*, 1312*w*, 1290*m*, 1270*m*, 1250*s*, 1195*m*, 1175*m*, 1170*m* sh, 1110*m*, 1095*w*, 1088*w*, 1038*w*, 1018*m*, 985*s*, 980*m* sh, 968*m*, 930*m*, 910*s*, 835*m*. ^{1}H-NMR: 0.80–2.07 (*m*, H–C(1′), 2 H–C(5′), H–C(6′), 2 H–C(7′)); 0.96, 1.05, 1.18 (3*s*, CH_3–C(3′), 2 CH_3–C(4′)); 2.23 (*s*, 3 H–C(1)); 6.52 (*AB*-system, $J = 16$, $\delta_A = 6.02$, $\delta_B = 7.02$, H–C(3), H–C(4)). ^{13}C-NMR: 18.3, 24.5, 28.5 (3*q*, 2 at 24.5, 4 CH_3); 19.8 (*t*, C(7′)); 36.0 (*t*, C(5′)); 16.0, 23.5 (2*d*, C(1′), C(6′)); 131.0, 147.3 (2*d*, C(3), C(4)); 41.5, 56.1 (2*s*, C(3′), C(4′)); 197.1, 209.3 (2*s*, C(2), C(2′)). MS: 220 (1, M^+, $C_{14}H_{20}O_2$), 177 (12), *123* (100), 95 (15), 93 (10), 55 (13), 53 (10), 43 (42), 41 (17).

(*Z*)-**13**. B.p. 140°/0.04 Torr. UV (0.447 mg in 20 ml): 215 sh (4400); UV (2.137 mg in 5 ml): 280 sh (390), end absorption to 390. IR: 3090*w*, 3020*m*, 2975*s*, 2962*s*, 2940*m*, 2920*m*, 2875*m*, 1705*s*, 1690*s*, 1600*w*, 1468*m*, 1451*m*, 1411*m*, 1390*m*, 1370*s*, 1350*s*, 1263*w*, 1248*m*, 1175*s*, 1103*m*, 1037*w*, 1022*w*, 969*m*, 943*w*, 928*w*, 920*w*, 890*w*, 835*m*. ^{1}H-NMR: 0.80–2.35 (*m*, H–C(1′), 2 H–C(5′), H–C(6′), 2 H–C(7′)); 0.97 (6 H), 1.15 (3 H), (2*s*, CH_3–C(3′), 2 CH_3–C(4′)); 2.18 (*s*, 3 H–C(1)); 6.10 (*AB*-system, $J = 12$, $\delta_A = 6.01$, $\delta_B = 6.19$, H–C(3), H–C(4)). ^{13}C-NMR (20 MHz): 17.4, 23.7, 24.0, 30.7 (4*q*, 4 CH_3), 19.1 (*t*, C(7′)); 35.6 (*t*, C(5′)); 17.4, 25.7 (2*d*, C(1′), C(6′)); 129.5, 141.8 (2*d*, C(3), C(4)); 44.1, 55.4 (2*s*, C(3′), C(4′)); 199.0, 207.1 (2*s*, C(2), C(2′)). MS: 220 (1, M^+, $C_{14}H_{20}O_2$), 177 (10), *123* (100), 109 (10), 95 (17), 93 (12), 55 (16), 53 (12), 43 (51), 41 (21).

*(1*R*,*2*R*,*4*R**)-1,6,6-Trimethyl-10-oxatricyclo[5.3.0.0^{2,4}]dec-7-en-9-ylmethyl ketone* (**14**). UV (1.294 mg in 2 ml): 299 (140), end absorption to 360. IR: 3070*w*, 3000*s*, 2960*s*, 2922*s*, 2910*s*, 2857*s*, 1713*s*, 1642*w*, 1455*m*, 1413*m*, 1389*m*, 1365*s*, 1350*s*, 1298*w*, 1272*m*, 1216*m* sh, 1208*m*, 1180*m*, 1145*m*, 1139*s*, 1110*s*, 1098*s*, 1090*s*, 1084*s*, 1047*s*, 1025*m*, 990*w*, 970*w*, 950*w*, 935*w*, 905*w*, 885*m*, 880*m* sh, 868*m*, 835*m*. ^{1}H-NMR: 0.10–0.75 (*m*, 2 H), 0.95–2.15 (*m*, 4 H) (H–C(2), 2 H–C(3), H–C(4), 2 H–C(5)); 1.10, 1.15, 1.62 (3*s*, 2 CH_3–C(6), CH_3–C(1)); 2.20 (*s*, CH_3CO); 5.17 (*AB*-system, $J = 2$, $\delta_A = 4.92$, $\delta_B = 5.42$, H–C(8), H–C(9)). ^{13}C-NMR (20 MHz): 25.6, 30.1, 31.4 (4*q*, 2 at 31.4, 4 CH_3); 7.7 (*t*, C(3)); 37.3 (*t*, C(5)); 11.8, 22.7 (2*d*, C(2), C(4)); 89.5 (*d*, C(9)); 116.9 (*d*, C(8)); 32.7 (*s*, C(6)); 91.8 (*s*, C(1)); 153.3 (*s*, C(7)); 209.8 (*s*, C=O). MS: 220 (4, M^+, $C_{14}H_{20}O_2$), 177 (71), 135 (10), 133 (10), 123 (18), 121 (48), 119 (14), 109 (11), 107 (24), 105 (20), *95* (100), 93 (32), 91 (34), 81 (12), 79 (20), 77 (22), 69 (20), 67 (17), 55 (17), 53 (13), 43 (87), 41 (37).

*(1*R*,*2*R*,*4*R**)-1,6,6-Trimethyl-10-oxatricyclo[5.3.0.0^{2,4}]dec-7-en-9-one* (**15**). M.p. 87° (pentane). UV (0.104 mg in 10 ml): 210 (12400); UV (1.529 mg in 2 ml): end absorption to 380. IR: 3078*w*, 3010*m*, 2970*s*, 2930*m*, 2860*m*, 1750*s*, 1630*m*, 1460*m*, 1390*m*, 1370*m*, 1365*m*, 1349*w*, 1339*w*, 1278*m*, 1249*s*, 1225*w*, 1210*m*, 1195*s*, 1180*m*, 1148*m*, 1132*m*, 1110*m*, 1098*w*, 1080*m*, 1041*m*, 1030*m*, 1018*w*, 952*s*, 911*w*, 895*w*, 881*w*, 861*s*, 835*w*. ^{1}H-NMR: 0.05–2.30 (*m*, H–C(2), 2 H–C(3), H–C(4), 2 H–C(5)); 1.25 (2*s*, 2 CH_3–C(6)); 1.70 (*s*, CH_3–C(1)); 5.65 (*s*, H–C(8)). ^{13}C-NMR: 26.9, 30.2, 30.7 (3*q*, 3 CH_3); 7.3 (*t*, C(3)); 37.4 (*t*, C(5)); 11.5, 21.7 (2*d*, C(2), C(4)); 114.4 (*d*, C(8)); 33.7 (*s*, C(6)); 88.8 (*s*, C(1)); 172.0 (*s*, C(7)); 181.6 (*s*, C(9)). MS: 192 (23, M^+, $C_{12}H_{16}O_2$), 177 (31), 151 (55), 150 (22), 123 (31), 122 (14), 121 (70), 110 (17), 109 (30), 107 (45), 105 (35), 95 (48), 93 (36), 91 (41), 79 (37), 77 (29), 67 (67), 65 (22), 55 (22), 53 (25), 51 (23), *43* (100), 41 (72). Anal. calc. for $C_{12}H_{16}O_2$ (192.26): C 74.97, H 8.39; found: C 74.80, H 8.37.

2.4. *Irradiation of* (E)-**6** *at* $\lambda \geq 347$ *nm.* A solution of (*E*)-**6** (2.409 g, 10.95 mmol) in MeCN (240 ml) was irradiated (94% conversion) and worked up as described in *Sect. 2.3.* The following product distribution was determined: **12** (2%), (*E*)-**16** (14%), (*Z*)-**16** (20%), **17** (14%) and **18** (9%).

*(*E,*1′*R*,*3′*R*,*6′*R**)-4-(3′,4′,4′-Trimethyl-2′-oxobicyclo[4.1.0]hept-3′-yl)-3-buten-2-one* ((*E*)-**16**). M.p. 115–7° (Et_2O/pentane). UV (0.446 mg in 25 ml): 214 (12000). UV (1.972 mg in 3 ml): 293 (146), 303 (176), 311 (186), 322 (151), 334 (87), end absorption to 390. IR: 3090*w*, 3050*w*, 3020*m*, 2982*s*, 2930*s*, 2888*m*, 1700*s* sh, 1675*s*, 1620*s*, 1610*s*, 1455*m*, 1425*m*, 1389*m*, 1365*s*, 1351*s*, 1315*w*, 1291*m*, 1245*s*, 1235*s* sh, 1178*s*, 1110*w*, 1090*w*, 1015*w*, 980*m*, 972*m*, 955*m* sh, 939*m*, 921*m*, 892*w*. ^{1}H-NMR: 0.80, 1.07, 1.15 (3*s*, 2 CH_3–C(4′), CH_3–C(3′));

0.75–1.95 (*m*, H–C(1'), 2 H–C(5'), H–C(6'), 2 H–C(7')); 2.27 (*s*, 3 H–C(1)); 6.53 (*AB*-system, $J = 15$, $\delta_A = 6.04$, $\delta_B = 7.02$, H–C(3), H–C(4)). ^{13}C-NMR: 16.5, 25.0, 26.0, 27.1 (4*q*, 4 CH_3); 18.5 (*t*, C(7')); 35.3 (*t*, C(5')); 14.9, 22.3 (2*d*, C(1'), C(6')); 131.7, 148.9 (2*d*, C(3), C(4)); 41.1 (*s*, C(4')); 56.5 (*s*, C(3')); 179.9, 211.5 (2*s*, C(2), C(2')). MS: 220 (2, M^+, $C_{14}H_{20}O_2$), 177 (17), *123* (100), 95 (16), 93 (10), 43 (27), 41 (10). Anal. calc. for $C_{14}H_{20}O_2$ (220.30): C 76.33, H 9.15; found: C 76.29, H 9.10.

(*Z*)-**16.** B.p. 100°/0.03 Torr. UV (0.552 mg in 25 ml): 218 (4900). UV (2.136 mg in 2 ml): 293 (130), end absorption to 380. IR: 3080*w*, 3010*m*, 2962*s*, 2930*m*, 2875*m*, 1695*s*, 1615*m*, 1465*m*, 1455*m*, 1420*m* sh, 1409*m*, 1389*m*, 1370*m*, 1350*s*, 1285*w*, 1268*w*, 1255*w*, 1231*w*, 1215*w*, 1175*s*, 1145*w*, 1111*w*, 1090*w*, 1022*w*, 1012*w*, 972*m*, 940*w*, 926*m*. ^{1}H-NMR: 0.91, 1.15, 1.22 (3*s*, 2 CH_3–C(4'), CH_3–C(3')); 0.67–2.40 (*m*, H–C(1'), 2 H–C(5'), H–C(6'), 2 H–C(7')); 2.22 (*s*, 3 H–C(1)); 5.96 (*AB*-system, $J = 13$, $\delta_A = 5.68$, $\delta_B = 6.24$, H–C(3), H–C(4)). ^{13}C-NMR: 20.6, 25.1, 25.7, 30.9 (4*q*, 4 CH_3); 17.3 (*t*, C(7')); 35.1 (*t*, C(5')); 13.2, 21.4 (2*d*, C(1'), C(6')); 129.8, 141.3 (2*d*, C(3), C(4)); 40.7 (*s*, C(4')); 56.3 (*s*, C(3')); 199.3, 209.4 (2*s*, C(2), C(2')). MS: 220 (2, M^+, $C_{14}H_{20}O_2$), 177 (20), 124 (10), *123* (100), 121 (11), 109 (11), 95 (23), 93 (13), 55 (12), 43 (41), 41 (15). Anal. calc. for $C_{14}H_{20}O_2$ (220.30): C 76.33, H 9.15; found: C 76.13, H 8.96.

(1R,2S*,4S*)-1,6,6-Trimethyl-10-oxatricyclo[5.3.0.0^{2,4}]dec-7-en-9-ylmethyl ketone* (**17**). B.p. 80°/0.03 Torr. UV (5.238 mg in 5 ml): 298 (130), end absorption to 340. IR: 3070*w*, 3000*s* sh, 2955*s*, 2930*s*, 2860*s*, 1708*s*, 1455*m*, 1412*m*, 1380*m* sh, 1370*m* sh, 1360*s*, 1350*s*, 1338*s* sh, 1315*w*, 1300*w*, 1290*w*, 1260*w*, 1205*m*, 1193*m*, 1175*m*, 1165*m* sh, 1110*s*, 1088*s*, 1030*m*, 1022*m*, 1005*m*, 990*w*, 950*w*, 935*w*, 900*w*, 880*m*. ^{1}H-NMR: 0.20–0.48 (*m*, 1 H), 0.60–2.05 (*m*, 5 H) (H–C(2), 2 H–C(3), H–C(4), 2 H–C(5)); 1.05, 1.20, 1.28 (3*s*, CH_3–C(1), 2 CH_3–C(6)); 2.24 (*s*, CH_3CO); 5.27 (*AB*-system, $J = 2$, $\delta_A = 5.07$, $\delta_B = 5.47$ (H–C(8), H–C(9)). ^{13}C-NMR (20 MHz): 25.6, 27.0, 30.8, 31.5 (4*q*, 4 CH_3); 11.5 (*t*, C(3)); 39.0 (*t*, C(5)); 8.2, 22.2 (2*d*, C(2), C(4)); 90.4 (*d*, C(9)); 115.2 (*d*, C(8)); 34.8 (*s*, C(6)); 89.3 (*s*, C(1)); 156.8 (*s*, C(7)); 209.1 (*s*, C=O). MS: 220 (1, M^+, $C_{14}H_{20}O_2$); 178 (11), 177 (80), 121 (39), *95* (100), 93 (16), 91 (15), 69 (19), 43 (28), 41 (14).

(1R,2S*,4S*)-1,6,6-Trimethyl-10-oxatricyclo[5.3.0.0^{2,4}]dec-7-en-9-one* (**18**). M.p. 82–3° (Et_2O/hexane). UV (0.228 mg in 20 ml MeCN): 211 (14000). UV (1.109 mg in 2 ml MeCN): end absorption to 270. IR: 3070*w*, 3000*m*, 2960*s*, 2935*s*, 2900*m* sh, 2862*m*, 1750*s* br., 1628*m*, 1458*m*, 1442*m*, 1375*m*, 1362*m*, 1340*m*, 1231*s*, 1210*m*, 1186*m*, 1170*m*, 1165*m*, 1150*m*, 1108*m*, 1068*w*, 1032*m* sh, 1025*m*, 1005*w*, 995*w*, 953*s*, 940*m*, 928*w*, 903*m*, 892*m*, 873*m*, 858*m*. ^{1}H-NMR: 0.35–0.62, 0.70–1.45 and 1.80–2.25 (3*m*, H–C(2), 2 H–C(3), H–C(4), 2 H–C(5)); 1.16, 1.30, 1.35 (3*s*, CH_3–C(1), 2 CH_3–C(6)); 5.71 (*s*, H–C(8)). ^{13}C-NMR: 24.5, 29.2, 30.5 (3*q*, 3 CH_3); 11.3 (*t*, C(3)); 38.3 (*t*, C(5)); 7.6, 18.3 (2*d*, C(2), C(4)); 112.3 (*d*, C(8)); 35.8 (*s*, C(6)); 85.5 (*s*, C(1)); 172.5 (*s*, C(7)); 184.8 (*s*, C(9)). MS: 192 (11, M^+, $C_{12}H_{16}O_2$), 177 (29), 164 (55), 151 (35), 149 (60), 135 (16), 123 (38), 122 (14), 121 (63), 110 (16), 109 (48), 107 (28), 105 (23), 95 (32), 93 (30), 91 (31), 79 (29), 77 (20), 67 (51), 65 (15), 55 (15), 53 (16), 51 (14), *43* (100), 41 (41). Anal. calc. for $C_{12}H_{16}O_2$ (192.26): C 74.97, H 8.39; found: C 75.25, H 8.73.

3. Additional Experiments. 3.1. *Hydratization of* **9.** A solution of **9** (70 mg, 0.28 mmol) in THF (3 ml) was stirred with H_2O (1 ml) and oxalic acid (5 mg) for 24 h. After workup and chromatography (SiO_2; Et_2O/pentane 2:1) crystalline **20** (31 mg, 46%) was obtained.

7-Hydroxy-1,6,6-trimethyl-10-oxatricyclo[5.2.1.0^{2,4}]dec-9-yl-methyl ketone (**20**). M.p. 90–91° (Et_2O/hexane). UV (5.500 mg in 5 ml CH_3CN): 276 (37), end absorption to 350. IR: 3600*m*, 3460*w* br., 3080*w*, 2990*s* sh, 2970*s*, 2920*s*, 2890*s*, 2870*m*, 2850*m*, 1713*s*, 1455*m*, 1395*m*, 1368*s* sh, 1353*s*, 1280*m* sh, 1260*m*, 1188*m*, 1161*s* sh, 1151*s*, 1120*s*, 1075*s*, 1045*s*, 1030*s*, 985*m*, 950*m*, 910*m*, 878*w*, 848*w*. ^{1}H-NMR (300 MHz): 0.39 (*ddd*, $J_1 = 9.6$, $J_2 = 8.4$, $J_3 = 3.8$, 1 H), 0.54–0.67 (*m*, 2 H) and 0.85–0.91 (*m*, 2 H) (H–C(2), 2 H–C(3), H–C(4)); 0.93, 1.07 (2*s*, 2 CH_3–C(6)); 1.62 (*s*, CH_3–C(1)); 1.88 (*dd*, $J_1 = 13.9$, $J_2 = 9.6$, H–C(8)); 1.93 (*AB*-system, $J = 15.4$, $\delta_A = 1.83$, split into *d*, $J = 3.0$, $\delta_B = 2.04$, split into *d*, $J = 4.4$, 2 H–C(5)); 2.26 (*s*, CH_3CO); 2.30 (*s*, OH); 2.92 (*dd*, $J_1 = 13.9$, $J_2 = 10.7$, H–C(8)); 3.34 *dd*, $J_1 = 10.7$, $J_2 = 9.6$, H–C(9)). ^{13}C-NMR: 22.7, 27.9, 30.8 (4*q*, 2 at 27.9, 4 CH_3); 3.5 (*t*, C(3)); 35.7, 37.2 (2*t*, C(5), C(8)); 15.8, 21.5 (2*d*, C(2), C(4)); 60.6 (*d*, C(9)); 43.3 (*s*, C(6)); 82.9 (*s*, C(1)); 108.6 (*s*, C(7)); 206.3 (*s*, CO). MS: 238 (5, M^+, $C_{14}H_{22}O_3$), 123 (11), 109 (10), 99 (21), 93 (12), 82 (16), 81 (28), 71 (20), 69 (19), 55 (15), *43* (100), 41 (26). Anal. calc. for $C_{14}H_{22}O_3$ (238.32): C 70.56, H 9.30; found: C 70.46, H 9.47.

3.2. *Hydrolysis of* **10.** A solution of a mixture (2 g) obtained from the photolysis of (*E*)-**5**, which consisted according to GC of (*Z*)-**5** (18%), **9** (43%) and **10** (22%) in THF (50 ml) was stirred with H_2O (25 ml) and oxalic acid (250 mg) for 6 h. Workup and chromatography gave **12** (90 mg, 25%), **20** (530 mg, 62%) and **21** (311 mg, 71%).

7-(2'-Acetylcyclopropyl)-6,6-dimethyl-2,5-heptanedione (**21**). UV (1.708 mg in 2 ml CH_3CN): 281 (110), end absorption to 380. IR: 3080*w*, 3030*w*, 3000*m*, 2965*m*, 2925*m*, 2870*w*, 1717*s*, 1695*s*, 1467*m*, 1448*m*, 1431*m*, 1420*m*, 1418*m*, 1395*s*, 1381*s*, 1363*s*, 1350*s*, 1217*w*, 1165*s*, 1120*w*, 1080*m*, 1050*w*, 1022*w*, 989*m*, 962*w*, 955*w*, 948*w*,

910*s*, 855*w*. ^{1}H-NMR: 0.75–2.15 (*m*, 2 H–C(7), H–C(1'), H–C(2'), 2 H–C(3')); 1.13, 1.16 (2*s*, 2 CH_3–C(6)); 2.20, 2.26 (2*s*, 3 H–C(1), 3 H–C(2")); 2.52–2.92 (*m*, 2 H–C(3), 2 H–C(4)). ^{13}C-NMR: 24.4, 24.6, 29.9, 32.1 (4*q*, 4 *C*H_3); 15.0 (*t*, C(3')); 31.1, 35.7, 36.8 (3*t*, C(3), C(4), C(7)); 21.1, 25.7 (2*d*, C(1'), C(2')); 47.5 (*s*, C(6)); 206.9, 207.0, 213.8 (3*s*, C(2), C(5), C(1")). MS: 238 (1, M^+, $C_{14}H_{22}O_3$), 99 (64), 81 (19), 71 (15), 59 (10), *43* (100), 41 (12).

3.3. *Oxidation of* **14.** A solution of **14** (70 mg, 0.32 mmol) in Et_2O (5 ml) was stirred with Na_2CO_3 (20 mg) under O_2 for 2 days. Filtration over *Celite* yielded pure **15** (46 mg, 75%).

3.4. *Oxidation of* **17.** A solution of a mixture (83 mg), which contained according to ^{1}H-NMR **12** (60%) and **17** (40%) in Et_2O (5 ml) was stirred with Na_2CO_3 (20 mg) under O_2. After filtration over *Celite* a mixture was obtained, which consisted of **18** (50%) and **12** (30%) (^{1}H-NMR and GC).

3.5. *Photolysis of (*E*)-***6*** in MeOH.* A solution of (*E*)-**6** (228 mg, 1.04 mmol) in MeOH (10 ml) was irradiated in the presence of Na_2CO_3 (50 mg) (quartz, lamp *A*, 92% conversion). After chromatography (SiO_2, Et_2O/pentane 1:1 to 2:1) the following product distribution was determined (^{1}H-NMR and GC): **12** (6%), **21** (22%).

3.6. *Stern-Volmer analysis.* – 3.6.1. *Determination of the Lifetime* τ *of the Ylide Derived from (*E*)-***5*** as a Function of the MeOH-Concentration.* To samples of a MeCN *(UVASOL, Merck)* solution of (*E*)-**5**, which had an absorbance of *ca.* 1 at 265 nm were added various amounts of MeOH and the lifetimes τ of the ylide were determined by the laser flash technique [10] as given in *Table 2*. The plot of τ^{-1} *vs.* [MeOH] yielded a straight line with an intercept of $0.94 \pm 0.15 \cdot 10^5 s^{-1}$ and a slope of $1.4 \pm 0.2 \cdot 10^5 s^{-1} M^{-1}$.

Table 2. *Lifetimes* τ *of the Ylide Derived from (*E*)-***5*** as Function of the MeOH-Concentration*

[MeOH] [M]	τ (μs)	[MeOH] [M]	τ (μs)
0.123	8.14	1.289	2.53
0.245	5.88	1.399	2.07
0.365	5.26	1.509	1.86
0.485	4.68	1.617	1.92
0.603	4.62	1.724	1.71
0.720	3.97	1.831	1.45
0.836	3.20	1.936	1.49
0.951	2.74	2.041	1.18
1.064	2.63	2.144	1.46
1.177	2.57	2.247	1.43

3.6.2. *Determination of the Relative Quantum Yields of* **9** *and* **11** *as a Function of the MeOH-Concentration.* To aliquots (10 ml) of a 6.3 mM MeCN solution of (*E*)-**5** and hexadecane as an internal standard for GC-analysis and Na_2CO_3 (*ca.* 20 mg) were given 0, 20, 40, 60, 80, 100, 120 and 140 μl MeOH and the resulting solutions were irradiated in a merry-go-round (quartz, lamp *A*). After 45 min of irradiation (58% conversion in all samples) the fraction of Φ_0/Φ was determined by GC-analysis for **9** and **11**. Φ_0 was taken as the product yield (%) at [MeOH] = 0 and Φ was taken as yield (%) at the various MeOH-concentrations. The values for Φ_0/Φ are listed in *Tables 3* and *4*. The plot of Φ_0/Φ *vs.* [MeOH] yielded straight lines for **9** and **11** with a slope $1.2 \pm 0.1 M^{-1}$ and $17 \pm 2 M^{-1}$, respectively.

Table 3. *Relative Quantum Yields* Φ_0/Φ *of* **9** *as Function of the MeOH-Concentration*

[MeOH] [M]	Φ_0/Φ	[MeOH] [M]	Φ_0/Φ
0	1.00	0.198	1.29
0.049	1.10	0.247	1.37
0.099	1.22	0.296	1.47
0.148	1.22	0.346	1.47

Table 4. *Relative Quantum Yields* Φ_0/Φ *of* **11** *as Function of the MeOH-Concentration*

[MeOH] [M]	Φ_0/Φ
0	1.00
0.049	1.87
0.099	2.73

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