102. Photochemical Reactions

150th Communication[1])

Wavelength Dependence of the Photochemistry of 7-Methyl-β-ionone

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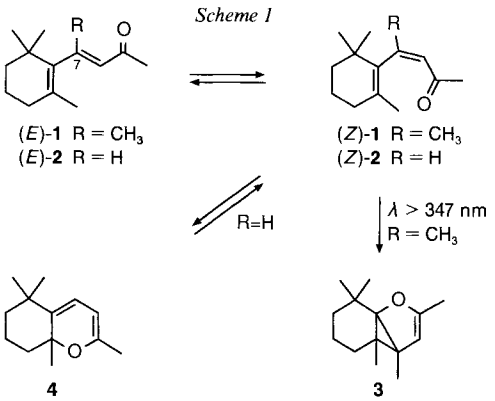
In memoriam Edgar Lederer

(2.VI.89)

The wavelength dependence of the photolysis of 7-methyl-β-ionone ((*E*)-**1**) was investigated. Irradiation of (*E*)-**1** with light of $\lambda > 347$ nm leads primarily to (*E*/*Z*)-isomerization followed by transformation to the tricyclic enol ether **3** as the only secondary photoproduct. On photolysis of (*E*)-**1** with light of shorter wavelength ($\lambda > 280$ nm or $\lambda = 254$ nm), however, a series of other products was formed *via a)* photocyclization of the dienone chromophore (→ **5**), *b)* photo-enolization (→ **8**), and *c)* a 1,5-sigmatropic H-shift (→ (*E*/*Z*)-**7**). For the structure elucidation of the new products, 7-[^{13}C]methyl-β-ionone ((*E*)-[7-*methyl*-^{13}C]-**1**) was prepared and irradiated furnishing the corresponding ^{13}C-labelled photoproducts.

1. Introduction. – In a previous paper on the photolysis of 7-methyl-β-ionone ((*E*)-**1**) [3], we have already shown that the presence of a Me group at C(7)[5]) of the chromophore of β-ionone gives rise to a dramatic change of the photochemical behavior of (*E*)-**1** in comparison to that of β-ionone ((*E*)-**2**) itself *(Scheme 1)*. Thus, photolysis of (*E*)-**1**

Scheme 1



[1]) 149th Communication: [1].

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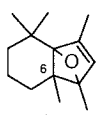
[5]) Numbering according to the carotenoid nomenclature [4].

($\lambda > 347$ nm) causes rapid (E/Z)-isomerization and subsequent formation of **3** [3]. In contrast to (Z)-β-ionone ((Z)-**2**), which could be detected only below $-50°$ [5], due to thermal (as well as photochemical) reaction to the pyran **4** [5], the 7-methyl analog (Z)-**1** is stable at r.t. [3]. This thermal stability is a result of the steric interaction of the 7-Me group and the Me groups of the cyclohexene ring, preventing a planar conformation for the dienone chromophore. However, (Z)-**1** is photo-isomerized to the tricyclic compound **3** [3]. In the present paper, we describe the results of further photolyses of (E)-**1** at wavelengths $\lambda > 280$ nm and $\lambda = 254$ nm, in comparison with the photolysis at $\lambda > 347$ nm.

2. Photolyses. – The results of the photolyses of (E)-**1** are given in the *Table*.



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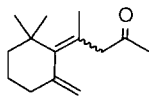
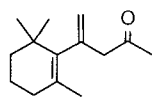


(*E/Z*)-**7**



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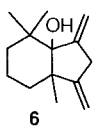

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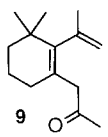

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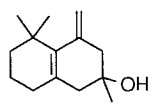

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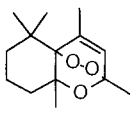
Table. *Results of the Photolyses of* (E)-**1**

λ	Conversion	Product Distribution [%][a][b]								
[nm]	[%]	(Z)-**1**[c]	**3**	**5**	**6**	(E)-**7**[c]	(Z)-**7**[c]	**8**[c]	**9**[c]	**10**
> 347 [3]	99	26	66	–	–	–	–	–	–	–
> 280[d][e]	96	16	17	22	5	1	15	1	1	4
254[d][e]	88	20	1	6	5	–	1	14	9	14

[a]) Yields were determined, after chromatography on SiO_2, by ^{1}H-NMR of the fractions and are based on converted starting material.

[b]) If O_2 was not excluded from the photolysis mixture, in addition, 5–10% of photo-oxidation products of (E)-**1** have been obtained (**11** [6], **12** [7], and **13**).



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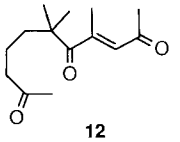

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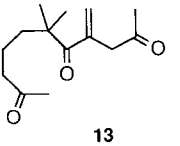

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[c]) Isolated and fully characterized as the corresponding acetates (see *Scheme 4* and *Exper. Part*).

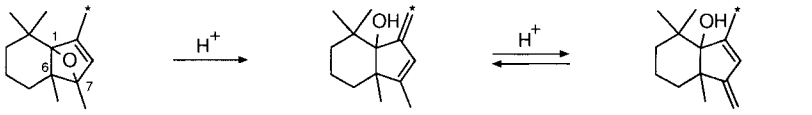
[d]) In the presence of traces of acid, in addition to the photoproducts, the alcohols **14** and **15** (see *Scheme 2*) have been isolated in up to 20% yield.

[e]) *Ca.* 0.05M soln. in MeCN.

3. Structure of the Products. – The structures of all new photoproducts were deduced from their spectral data. Only the most relevant spectral data are discussed below, together with the decisive chemical transformations which confirmed the assignments. For full spectral data and the NMR assignments, see *Exper. Part*.

Oxatricyclo[5.2.1.0^{1,6}]decene **5** (*Scheme 2*). Characteristic signals in the ^{13}C-NMR spectrum are in particular a *d* (137.0 ppm) and an *s* (150.4 ppm) corresponding to the

Scheme 2



5 **14** **15**

* *ca.* 10% ^{13}C-labelled

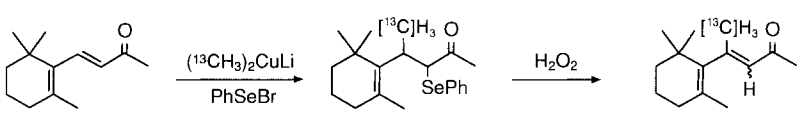
C=C bond, and 3*s* (84.7, 78.4, and 64.2 ppm) of the bridgehead C-atoms and C(6). Acid treatment of **5** (HCl/Et_2O) rapidly furnished the dienol **14** (94%) which, upon longer treatment, is further isomerized to **15** *(Scheme 2)*. This isomerization is reversible; thus, treatment of **15** under the same conditions led to the same equilibrium mixture as obtained from **14** (*ca.* 1:3 mixture **14**/**15**; *Scheme 2*). Both dienols show characteristic UV maxima at 237 nm (ε = 11200) and 236 nm (ε = 10400), respectively, and very similar NMR spectra. On the basis of these spectral data, the structures of **14** and **15** could not be assigned conclusively. Therefore, 7-[^{13}C]methyl-β-ionone ((*E*)-[7-*methyl*-^{13}C]-**1**)[6]) was prepared and irradiated to furnish the corresponding ^{13}C-labelled photoproducts. Thus, acid-catalyzed cleavage of [9-*methyl*-^{13}C]-**5** gave [9-*methylidene*-^{13}C]-**14** which isomerized to the thermodynamically more stable [9-*methyl*-^{13}C]-**15**. The configuration of compounds **5**, **14**, and **15**, however, could not be assigned on the basis of the spectral data.

Bicyclo[4.3.0]nonanol **6**. Its structure was assigned by comparison of the spectral data with those of the corresponding conjugated dienols **14** and **15** *(Scheme 2)*. In particular, the ^{1}H- and ^{13}C-NMR spectra of **6** show signals of only 3 Me groups, and signals corresponding to CH_2=C and 2 H–C(8) (see *Exper. Part*).

Dienones (E)-**7**, (Z)-**7**, **8**, *and* **9** *(Scheme 4)*. Due to their instability, in particular the acid sensitivity of (*Z*)-**7**, the compounds could not be isolated in pure form and were, therefore, reduced with $LiAlH_4$ and transformed to the stable acetates (*E*)-**17**, (*Z*)-**17**, **18**, and **19** which could be purified and characterized (see *Scheme 4*). Again these acetates show very similar NMR spectra. The assignment of the structures was achieved by photolysis of (*E*)-[7-*methyl*-^{13}C]-**1** furnishing the ^{13}C-labelled photoproducts which were converted into the corresponding acetates. Thus, the *t* at 133.9 ppm in the ^{13}C-NMR established the structure of **18**. Furthermore, on T sensitization of the four acetates, only (*E*)-**17** and (*Z*)-**17** underwent rapid interconversion leading to a 1:1 mixture, whereas **18** and **19** were stable under the same conditions. This finding allows to assign the structure of the *retro*-γ-ionol derivatives (*E*/*Z*)-**17**. The configuration around the double bonds of the ketones (*E*/*Z*)-**7** (and, thus, the acetates (*E*/*Z*)-**17**) was established by acid treatment of (*E*)-**7** and (*Z*)-**7**. The (*Z*)-isomer underwent cyclization to the dienol **10**, which could

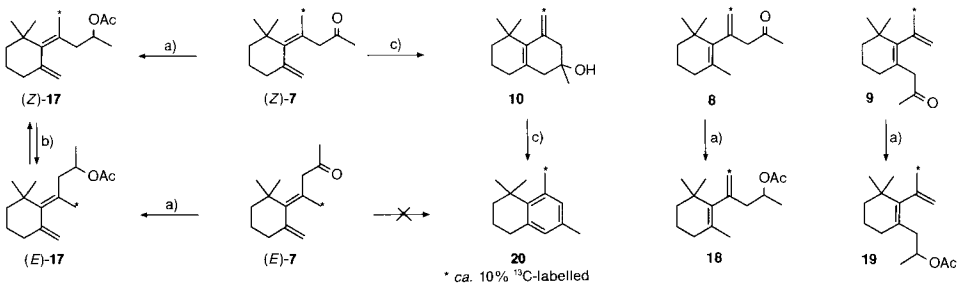
[6]) 7-[^{13}C]methyl-β-ionone ((*E*)-[7-*methyl*-^{13}C]-**1**) was prepared *via* **16** analogous to the procedure described in [3] using $^{13}CH_3I$ [8], and the labelled material was diluted with 90% unlabelled (*E*)-**1**.

Scheme 3



(*E*)-**2** **16** (*E*/*Z*)-[7-*methyl*-^{13}C]-**1**

Scheme 4

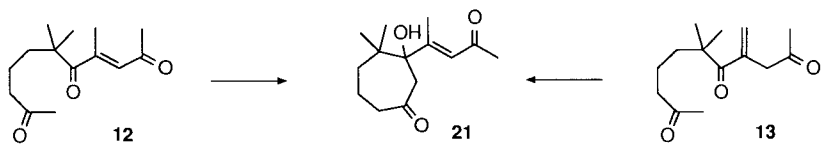


a) 1. $LiAlH_4/Et_2O$, 2. Ac_2O/pyridine; b) $\lambda > 280$ nm/acetone; c) HCl/Et_2O.

be isolated and reacted further to **20**[7]) (see *Scheme 4*), whereas (*E*)-**7** was stable under the same conditions.

Aliphatic Triones **12** *and* **13** *(Scheme 5)*. The structure of the oxidation product **13** (see *Footnote b* in the *Table*) was derived by comparison of the NMR spectra with those of the known isomer **12** [7]. Furthermore, on reaction with NaOMe in MeOH, **12** and **13** cyclized to the hydroxy-ketone **21** *(Scheme 5)*, whose structure was assigned unequivocally on the basis of the spectral data (see *Exper. Part*).

Scheme 5



4. Discussion. – As described in [3], irradiation of (*E*)-**1** with light of $\lambda > 347$ nm causes primarily rapid (*E*/*Z*)-isomerization followed by transformation to the tricyclic enol ether **3** as the only secondary photoproduct. On photolysis of (*E*)-**1** with light of shorter wavelength ($\lambda > 280$ nm or $\lambda = 254$ nm), however, a series of other products is formed in competition with **3** (see *Table*).

Formally, compounds **3** and **5** could be formed *via* the same intermediate **a**, since both are products of bond formation between C(6) and the O-atom of the C=O group (see *Scheme 6*). The finding, however, that on photolysis of (*E*)-**1** with light of $\lambda > 347$ nm, **5** is not formed, while **3** is the main product, indicates that they are formed *via* different processes[8]). Thus, **3** arises *via* a [π2a + π4s] cycloaddition [3], whereas **5** may be formed *via* the intermediate **a** *(Scheme 6)*.

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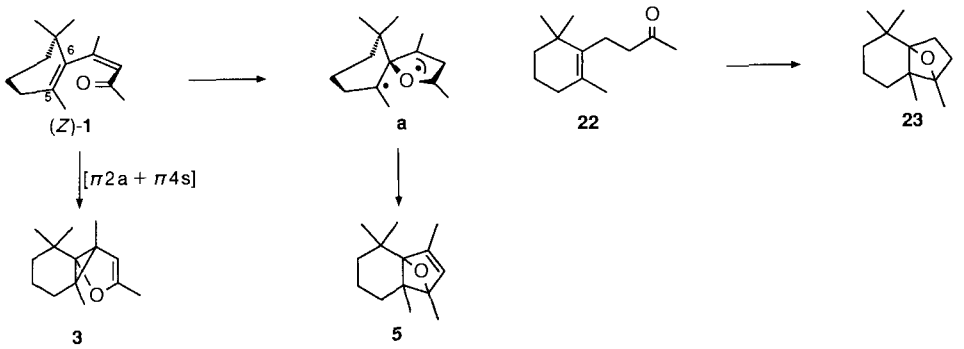
[7]) A transformation analogous to (*Z*)-**7** → **20** was reported by *Ramamurthy* and *Liu* [9] on photolysis of (*E*)-3,4-didehydro-β-ionone. The primary product corresponding to **10** was, however, not detected.

[8]) Compound **3** has no UV absorption above 260 nm and, thus, is most unlikely to be transformed to **5** upon irradiation with light of wavelength $\lambda > 280$ nm. It was shown, however, that, on irradiation with $\lambda = 254$ nm, **3** is photochemically transformed to (*Z*)-**1**, and **14** (a hydrolysis product of **5**).

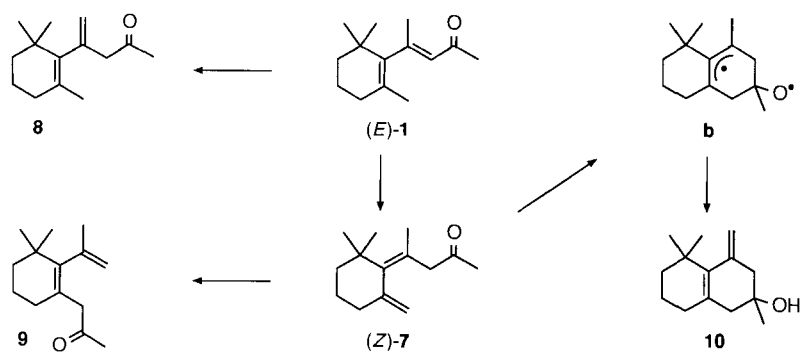
Scheme 6



A transformation analogous to (*E*/*Z*)-**1** → **5** was observed on photolysis of 7,8-dihydro-β-ionone (**22**) leading to **23** [10] *(Scheme 6)*; for conjugated dienones, however, the photo-isomerization (*E*/*Z*)-**1** → **5** seems to be a novel type of reaction.

On π,π*-excitation (λ = 254 nm) of (*E*/*Z*)-**1**, compound **8** is formed as main product by photo-enolization [11], a process typical for enones with γ-H atoms *(Scheme 7)*.

Scheme 7

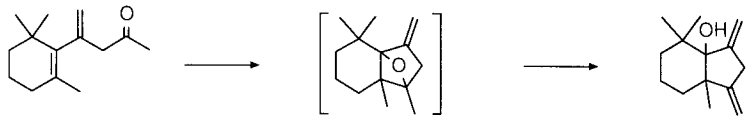


The dienone (*Z*)-**7** is the product of a [1,5]-sigmatropic rearrangement *via* an excited singlet state, as shown for β-ionone [5]. It subsequently undergoes (*Z*/*E*)-isomerization to (*E*)-**7** (see (*E*/*Z*)-isomerization of the corresponding acetates (*E*)- and (*Z*)-**17**, *Scheme 4*). The low yield of (*E*/*Z*)-**7** on irradiation with light of λ = 254 nm is due to various competitive processes and secondary reactions. Thus, (*Z*)-**7** undergoes photochemical or acid-catalyzed cyclization ((*Z*)-**7** → **b** → **10**, see *Schemes 4* and *7*)[7][9]). Another secondary photoreaction of (*E*/*Z*)-**7** is a 1,5-acyl shift furnishing the dienone **9**. On photolysis of *retro*-α-ionone, an analogous photo-isomerization was observed together with a 1,3-acyl shift [12]. On photolysis of (*E*)-**1**, however, the product arising from a 1,3-acyl shift in (*E*/*Z*)-**7** was not detected, presumably due to steric hindrance at C(6)[5]).

[9]) Alternatively, **10** could also be formed from **8** *via* an ε-H abstraction. Since **8** could not be isolated in pure form, this hypothesis could, however, not be verified.

On photolysis of (*E*)-**1** with light of wavelength $\lambda > 280$ nm or $\lambda = 254$ nm, the bicyclic dienol **6** was obtained in low yield. It is probably formed by photocyclization of **8** → **24** and acid-catalyzed cleavage to **6** *(Scheme 8)*, analogous to the transformation of (*Z*)-**1** → **5** → **14** (see *Schemes 2* and *6*)[10]).

Scheme 8



8 **24** **6**

Conclusion. – On photolysis of (*E*)-**1** with short-wavelength light ($\lambda > 280$ nm or $\lambda = 254$ nm), in competition with **3**, a series of other products is formed *via* photocyclization of the dienone chromophore (→ **5**), photo-enolization (→ **8**), and a 1,5-sigmatropic H-shift (→ (*E*/*Z*)-**7**). While the two latter processes are known photoreactions of 2,4-dienones, the photocyclization to **5** is a new process type. It most likely occurs due to the presence of the 7-Me substituent, which has a marked influence of the ground-state conformation of the dienone chromophore.

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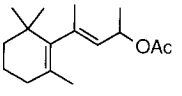
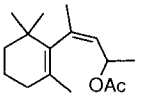
Experimental Part

General. See [13] except as noted below. Column chromatography (CC) was carried out on silica gel *60 Merck* 0.040–0.063 mm, 230–400 mesh ASTM (SiO_2) according to [14] (flash chromatography). Anal. pure samples were obtained, in general, after repeated CC 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 in $CDCl_3$ solns. on a *Bruker WP-80 CW* (80 MHz) or *WM-300* (300 MHz), or a *Varian EM-390* (90 MHz) instrument.

1. Photolyses. – 1.1. *Photolyses of (*E*)-7-Methyl-β-ionone* ((*E*)-**1**). 1.1.1. *With Light of* $\lambda > 280$ *nm.* A soln. of (*E*)-**1** (2.70 g, 13.1 mmol) in MeCN (270 ml) was irradiated in arrangement *II* under exclusion of O_2 (lamp *B*, conversion 96%). CC of the photolysis mixture (SiO_2, Et_2O/pentane 1:4 to 1:1) yielded **3** [3] (464 mg, 17%), **5** (589 mg, 22%), **6** (140 mg, 5%), and **10** (107 mg, 4%) in pure fractions as well as one mixed fraction (1.207 g, 45%). Reduction of this mixture with $LiAlH_4$, followed by acetylation (Ac_2O/pyridine) and HPLC (SiO_2, $p = 35$ bar, flow = 33 ml/min, $\lambda_{DET} = 235$ nm, Et_2O/hexane 1:67) afforded (*E*)-**17** (20 mg, 1%), (*Z*)-**17** (486 mg, 15%), **18** (20 mg, 1%), **19** (28 mg, 1%), (*E*)-**25** (119 mg, 4%), (*Z*)-**25A**[11]) (255 mg, 8%), and (*Z*)-**25B**[11]) (258 mg, 8%).



(*E*)-**25**



(*Z*)-**25A** + **B**

[10]) Compound **6** was not formed on treatment of either **14** or **15** with acid (see *Scheme 2*).

[11]) The terms **A** and **B** refer to isolated conformers whose configurations could not be assigned.

2,2,6,7,9-Pentamethyl-10-oxatricyclo[5.2.1.0^{1,6}]dec-8-ene (**5**). B.p. 60°/0.01 Torr. IR: 3030*w*, 2950*s*, 2920*s*, 2850*s*, 2800*w*, 2660*w*, 1620*w*, 1460*m* (sh), 1445*m*, 1435*m* (sh), 1380*m*, 1365*s*, 1305*w*, 1295*m*, 1250*w*, 1240*w*, 1220*w*, 1160*w*, 1125*m*, 1085*w*, 1050*m*, 965*w*, 905*w*, 885*m*, 860*m*. ^{1}H-NMR (80 MHz): 0.88, 1.02 (2 CH_3–C(2)); 1.21 (*s*, CH_3–C(6)); 1.48 (*s*, CH_3–C(7)); 1.89 (*d*, J = 1.5, CH_3–C(9)); 0.9–2.1 (*m*, 2 H–C(3), 2 H–C(4), 2 H–C(5)); 6.17 (*q*, J = 1.5, H–C(8)). ^{13}C-NMR (20 MHz): 17.5 (*q*, enhanced signal due to *ca.* 10% ^{13}C-labelling, CH_3–C(9)); 18.4, 25.2, 27.8, 28.2 (4*q*, 4 CH_3); 17.2, 35.8, 36.7 (3*t*, C(3), C(4), C(5)); 31.1 (*s*, C(2)); 64.2 (*s*, C(6)); 78.4 (*s*, C(7)); 84.7 (*s*, C(1)); 137.0 (*d*, C(8)); 150.4 (*s*, C(9)). MS: 206 (5, M^+, $C_{14}H_{22}O$), 192 (5), 191 (21), 148 (15), 135 (18), 133 (12), 121 (9), 107 (9), 84 (81), 69 (29), *56* (100), 55 (39), 43 (23), 42 (27), 41 (57).

2,2,6-Trimethyl-7,9-di(methylidene)bicyclo[4.3.0]nonan-1-ol (**6**). B.p. 60°/0.02 Torr. UV (0.365 mg in 25 ml of MeCN): end absorption to 360. IR: 3640*w* (sh), 3610*m*, 3450*w* (br.), 3080*w*, 2980*s*, 2950*s* (sh), 2940*s* (sh), 2920*s*, 2870*m*, 1665*m*, 1635*m*, 1480*w*, 1455*m*, 1440*m*, 1425*m*, 1405*m*, 1380*m*, 1375*s*, 1360*m*, 1320*m*, 1280*w*, 1235*s*, 1215*m*, 1175*w*, 1090*m*, 1080*m*, 1055*w*, 990*w*, 970*m*, 955*w*, 950*m*, 910*w*, 905*m* (sh), 890*s*, 880*m*, 850*w*. ^{1}H-NMR (80 MHz): 0.92, 1.25, 1.31 (3*s*, 3 CH_3); 1.64 (*m*, $w_{½}$ = 3, OH); 0.8–2.4 (*m*, 2 H–C(3), 2 H–C(4), 2 H–C(5)); 2.62 (*AB*, J = 16, δ_A = 2.42, $w_{½}$ = 6, δ_B = 2.84, $w_{½}$ = 8, 2 H–C(8)); 4.84 (1 H), 4.92 (2 H), 5.14 (1 H) (3*m*, $w_{½} \approx 6$, CH_2=C(7), CH_2=C(9)). ^{13}C-NMR (20 MHz): 25.1, 28.3, 28.4 (3*q*, 3 CH_3); 23.2, 34.8, 37.3 (3*t*, C(3), C(4), C(5)); 37.4 (*s*, C(2)); 47.3 (*t*, C(8)); 68.2, 76.3 (2*s*, C(1), C(6)); 109.3 (*t*, CH_2=C(7)); 110.9 (*t*, CH_2=C(9), enhanced signal due to *ca.* 10% ^{13}C-labelling); 145.3, 148.6 (2*s*, C(7), C(9)). MS: 206 (2, M^+, $C_{14}H_{22}O$), 191 (17), 188 (16), 173 (22), 163 (14), 149 (17), 135 (11), 133 (37), 121 (16), 119 (10), 107 (33), 105 (23), 95 (15), 93 (20), 91 (29), 79 (17), 77 (16), 69 (27), 55 (15), *43* (100), 41 (31). Anal. calc. for $C_{14}H_{22}O$: C 81.50, H 10.75; found: 81.40, 10.64.

(E)-4-(2′,2′-Dimethyl-6′-methylidenecyclohexylidene)pentan-2-one ((*E*)-**7**, containing *ca.* 40% **9**). ^{1}H-NMR (90 MHz): 1.18 (*s*, 2 CH_3); 1.73 (*s*, 3 H–C(5)); 2.16 (*s*, 3 H–C(1)); 3.40 (*s*, 2 H–C(3)); 4.59 (*m*, $w_{½}$ = 5, 1 H, CH_2=C(6′)); 4.99 (*m*, $w_{½}$ = 5, 1 H, CH_2=C(6′)).

(E)-3-(2′,2′-Dimethyl-6′-methylidenecyclohexylidene)-1-methylbutyl Acetate ((*E*)-**17**). B.p. 65°/0.02 Torr. IR: 3065*w*, 2970*m*, 2925*s*, 2860*m*, 1730*s*, 1715*m* (sh), 1695*w* (sh), 1620*w*, 1475*w* (sh), 1465*w* (sh), 1455*w* (sh), 1440*m*, 1365*s*, 1240*s*, 1195*w* (sh), 1120*m*, 1105*w* (sh), 1060*m*, 1015*w*, 950*w*, 895*m*. ^{1}H-NMR (300 MHz): 1.22 (*s*, broadened, $w_{½}$ = 1.5, 2 CH_3–C(2′)); 1.24 (*d*, J = 6.5, CH_3–C(1)); 1.34–1.41 (*m*, 2 H–C(3′)); 1.54–1.68 (*m*, 2 H–C(4′)); 1.74 (*s*, 3 H–C(4)); 2.01 (*s*, CH_3COO); 2.17 (*tm*, J = 7.0 $w_{½}$ = 3, 2 H–C(5′)); 2.55 (*AB*, J = 14.0; δ_A = 2.38, *A*-part split to *dm*, J = 5.5, $w_{½}$ = 5; δ_B = 2.72, *B*-part split to *dm*, J = 8.5, $w_{½}$ = 5; 2 H–C(2)); 4.45 (*dm*, J = 3.0, $w_{½}$ = 2, 1 H, CH_2=C(6′)); 4.93 (*dt*, J = 3.0, 1.5, 1 H, CH_2=C(6′)); 5.19 (*qdd*, J = 6.5, 8.5, 6.0, H–C(1)). ^{13}C-NMR (75 MHz): 20.2, 21.3, 29.4 (3*q*, 2*q* overlapping at 29.4, 4 CH_3); 23.2 (*q*, enhanced signal due to *ca.* 10% ^{13}C-labelling, C(4)); 21.5, 34.6 (2*t*, C(3′), C(4′)); 38.8 (*s*, C(2′)); 40.9, 42.7 (2*t*, C(5′), C(2)); 69.9 (*d*, C(1)); 113.1 (*t*, CH_2=C(6′)), 124.4, 145.5, 149.3 (3*s*, C(1′), C(6′), C(3)); 170.4 (*s*, C=O).

(Z)-4-(2′,2′-Dimethyl-6′-methylidenecyclohexylidene)pentan-2-one ((*Z*)-**7**, containing 10% (*E*)-**1** and 55% (*Z*)-**1**). ^{1}H-NMR (80 MHz): 1.23 (*s*, 2 CH_3–C(2′)); 1.82 (*s*, 3 H–C(5)); 2.06 (*s*, 3 H–C(1)); 3.30 (*s*, 2 H–C(3)); 4.5 (*dm*, J = 3, $w_{½}$ = 2, 1 H, CH_2=C(6′)); 4.82 (*m*, $w_{½}$ = 7, 1 H, CH_2=C(6′)).

(Z)-3-(2′,2′-Dimethyl-6′-methylidenecyclohexylidene)-1-methylbutyl Acetate ((*Z*)-**17**). B.p. 65°/0.02 Torr. UV (0.150 mg in 10 ml of MeCN): 228 (3200), end absorption to 260. IR: 3065*w*, 2975*m*, 2940*m*, 2860*m*, 1730*s*, 1625*w*, 1445*m* (br.), 1365*m*, 1240*s*, 1125*w*, 1060*m*, 1010*w*, 950*w*, 895*m*. ^{1}H-NMR (300 MHz): 1.14 (*d*, J = 6.5, CH_3–C(1)); 1.17, 1.19 (2*s*, broadened, $w_{½}$ = 6, 2 CH_3–C(2′)); 1.24–1.40 (*m*, 2 H–C(3′)); 1.55–1.68 (*m*, 2 H–C(4′)); 1.83 (*s*, 3 H–C(4)); 2.00 (*s*, CH_3COO); 2.21 (*m*, *t*-like, $w_{½}$ = 16, 2 H–C(5′)); 2.12–2.48, 2.48–2.76 (2*m*, 2 H–C(2)); 4.56 (*dm*, J = 3, $w_{½}$ = 3, 1 H, CH_2=C(6′)); 4.90 (*dt*, J = 3, 1.5, 1 H, CH_2=C(6′)); 5.07 (*qdd*, J = 6.5, 7.2, 7, H–C(1)). ^{13}C-NMR (20 MHz): 19.5 (*q*, enhanced signal due to *ca.* 10% ^{13}C-labelling, C(4)); 20.8, 27.5, 27.6 (3*q*, 1*q* overlapped by other signals, 4 CH_3); 20.6, 34.1 (2*t*, C(3′), C(4′)); 38.4 (*s*, C(2′)); 42.1, 44.0 (2*t*, C(2), C(5′)); 69.1 (*d*, C(1)); 112.5 (*t*, CH_2=C(6′)); 124.4, 145.5, 148.6 (3*s*, C(1′), C(6′), C(3)); 169.7 (*s*, C=O). MS: 190 (22, $[M - AcOH]^+$, $C_{14}H_{22}$), 176 (26), *175* (100), 147 (16), 134 (16), 133 (19), 121 (18), 120 (13), 119 (24), 107 (15), 105 (29), 91 (15), 69 (15), 43 (61), 41 (21).

4-(2′,6′,6′-Trimethylcyclohex-1′-enyl)pent-4-en-2-one (**8**, containing *ca.* 30% of **9**). ^{1}H-NMR (80 MHz): 1.02 (*s*, 2 CH_3–C(6′)); 1.57 (*m*, $w_{½}$ = 3, CH_3–C(2′)); 2.22 (*s*, 3 H–C(1)); 3.17 (*m*, $w_{½}$ = 3.5, 2 H–C(3)); 4.81 (*m*, $w_{½}$ = 4, H–C(5)); 5.10 (*m*, $w_{½}$ = 4, H–C(5)).

1-Methyl-3-(2′,6′,6′-trimethylcyclohex-1′-enyl)but-3-enyl Acetate (**18**). B.p. 65°/0.02 Torr. UV (0.345 mg in 25 ml of MeCN): end absorption to 250. IR: 3075*w*, 2970*m*, 2925*m*, 2910*m*, 2865*w*, 2850*w* (sh), 2830*w*, 1730*s*, 1620*w*, 1455*m*, 1445*m* (sh), 1435*w* (sh), 1425*w*, 1370*s*, 1240*s*, 1170*w*, 1130*m*, 1050*m*, 1010*w*, 955*w*, 940*w*, 900*w*. ^{1}H-NMR (300 MHz): 0.99 (*s*, broadened, $w_{½}$ = 2, CH_3–C(6′)); 1.01 (*s*, broadened, $w_{½}$ = 3, CH_3–C(6′)); 1.27 (*d*, J = 6.5, CH_3–C(1)); 1.40–1.46 (*m*, 2 H–C(5′)); 1.54 (*m*, $w_{½}$ = 3, CH_3–C(2′)); 1.58–1.68 (*m*, 2 H–C(4′)); 1.95 (*m*, $w_{½}$ = 16, *t*-like, 2 H–C(3′)); 2.00 (*s*, CH_3COO); 2.33 (*AB*, J = 16.0; δ_A = 2.24, *A*-part split to *dm*, J = 5.0, $w_{½}$ = 5; δ_B = 2.42, *B*-part split to *dm*, J = 8.0, $w_{½}$ = 6; 2 H–C(2)); 4.65 (*m*, $w_{½}$ = 5.0, H–C(4)); 5.01 (*m*, $w_{½}$ = 5.0,

H–C(4)); 5.14 (*m*, $w_{1/2}$ = 23, H–C(1)). ^{13}C-NMR (20 MHz): 20.2, 20.7, 21.0, 29.0 (5*q*, 2*q* overlapping, 5 CH_3); 19.0, 31.6 (2*t*, C(4'), C(5')); 33.7 (*s*, C(6')); 39.8, 43.5 (2*t*, C(2), C(3')); 68.8 (*d*, C(1)); 133.9 (*t*, C(4), enhanced signal due to *ca.* 10% ^{13}C-labelling); 127.3, 141.0, 144.8 (3*s*, C(1'), C(2'), C(4')); 170.3 (*s*, C=O). MS: 250 (1, M^+, $C_{16}H_{26}O_2$), 191 (14), 190 (42), 176 (27), 175 (99), 161 (12), 149 (17), 148 (61), 147 (24), 135 (16), 134 (48), 133 (50), 123 (11), 122 (10), 121 (24), 120 (23), 119 (51), 107 (27), 106 (13), 105 (46), 95 (15), 93 (22), 92 (13), 91 (29), 81 (19), 69 (22), 55 (25), *43* (100), 41 (36).

1-[3',3'-Dimethyl-2'-(1''-methylethenyl)cyclohex-1'-enyl]propan-2-one (**9**, containing *ca.* 70% **8**). ^{1}H-NMR (80 MHz): 1.05 (*s*, 2 CH_3–C(3')); 1.81 (*m*, $w_{1/2}$ = 3, CH_3–C(1'')); 2.08 (*s*, 3 H–C(3)); 3.04 (*m*, $w_{1/2}$ = 3, 2 H–C(1)); 4.59 (*m*, $w_{1/2}$ = 6, H–C(2'')); 5.05 (*m*, $w_{1/2}$ = 6, H–C(2'')).

2-[3',3'-Dimethyl-2'-(1''-methylethenyl)cyclohex-1'-enyl]-1-methylethyl Acetate (**19**). B.p. 65°/0.02 Torr. UV (0.666 mg in 25 ml of MeCN): end absorption to 245. IR: 3075*w*, 2960*m*, 2930*m*, 2910*m* (sh), 2860*m*, 2845*w*, 1730*s*, 1615*w*, 1465*w* (sh), 1455*m*, 1445*m*, 1430*m* (sh), 1375*m* (sh), 1370*s*, 1355*m* (sh), 1240*s*, 1320*m*, 1055*m*, 1035*w* (sh), 1015*w*, 950*w*, 900*m*. ^{1}H-NMR (300 MHz): 0.99, 1.00 (2*s*, 2 CH_3–C(3')); 1.16 (*d*, *J* = 6.3, CH_3–C(1)); 1.38–1.48 (*m*, 2 H–C(4')); 1.56–1.68 (*m*, 2 H–C(5')); 1.83 (*dd*, *J* = 1.4, 0.9, CH_3–C(1'')); 1.80–2.10 (*m*, 2 H–C(6')); 1.99 (*s*, CH_3COO); 2.19 (*AB*, *J* = 13.5; δ_A = 2.09, *A*-part split to *dm*, *J* = 6.0, $w_{1/2}$ = 2.5; δ_B = 2.29, *B*-part split to *dm*, *J* = 8.0, $w_{1/2}$ = 5; 2 H–C(2)); 4.52 (*dq*, *J* = 2.8, 0.9, H–C(2'')); 5.03 (*dq*, *J* = 2.8, 1.4, H–C(2'')); 5.09 (*qdd*, *J* = 6.3, 6, 8.0, H–C(1)). ^{13}C-NMR (20 MHz): 19.7, 21.0, 28.8 (3*q*, 2*q* overlapping, 4 CH_3); 25.7 (*q*, enhanced signal due to *ca.* 10% ^{13}C-labelling, CH_3–C(1'')); 19.0, 29.1 (2*t*, C(4'), C(5')); 34.0 (*s*, C(3')); 39.4, 40.7 (2*t*, C(2), C(6')); 69.5 (*d*, C(1)); 114.9 (*t*, C(2'')); 126.2, 144.1, 144.5 (3*s*, C(1'), C(2'), C(1'')); 170.2 (*s*, C=O). MS: 250 (0.4, M^+, $C_{16}H_{26}O_2$), 191 (10), 190 (32), 176 (26), *175* (100), 161 (14), 147 (17), 134 (15), 133 (17), 121 (19), 120 (11), 119 (28), 107 (16), 105 (31), 91 (16), 69 (14), 55 (15), 43 (69), 41 (23).

3,7,7-Trimethyl-5-methylidenebicyclo[4.4.0]dec-1(6)-en-3-ol (**10**). UV (0.471 mg in 25 ml of MeCN): 241 (12700), end absorption to 270. IR: 3610*w*, 3570*w*, 3480*w* (br.), 3110*w*, 2960*s*, 2930*s*, 2910*s*, 2870*s*, 2850*m* (sh), 2810*m*, 1755*m*, 1615*m*, 1455*m*, 1435*m*, 1425*m*, 1415*m* (sh), 1380*m*, 1370*m*, 1360*m*, 1315*m*, 1280*m*, 1260*m*, 1120*m*, 1095*m* (sh), 1080*m*, 1020*w*, 915*m*, 890*m*. ^{1}H-NMR (90 MHz): 1.20, 1.23, 1.28 (3*s*, CH_3–C(3), 2 CH_3–C(7)); 1.2–1.9 (*m*, 2 H–C(8), 2 H–C(9)); 1.85–2.15 (*m*, 2 H–C(10), OH); 2.18, 2.30 (2*m*, $w_{1/2}$ = 6, 2 H–C(2), 2 H–C(4)); 5.00, 5.20 (2*m*, $w_{1/2}$ = 4, 2 H–C=C(5)). ^{13}C-NMR (25 MHz): 28.0, 29.2, 29.2 (3*q*, 3 CH_3); 18.5, 32.4 (2*t*, C(8), C(9)); 33.5 (*s*, C(7)); 43.9, 47.4, 50.0 (3*t*, C(2), C(4), C(10)); 68.6 (*s*, C(3)); 113.0 (*t*, CH_2=C(5)); 133.3, 135.3, 140.4 (3*s*, C(1), C(5), C(6)). MS: 206 (43, M^+, $C_{14}H_{22}O$), 191 (30), 189 (17), 188 (64), 174 (13), 173 (56), 163 (27), 160 (11), 159 (20), 150 (11), 149 (28), 148 (21), 147 (15), 145 (16), 135 (16), 134 (13), 133 (62), 132 (12), 131 (14), 121 (22), 119 (17), 107 (48), 105 (27), 95 (18), 93 (25), 91 (32), 77 (18), 69 (24), 55 (15), *43* (100), 41 (28).

(E)-1-Methyl-3-(2',6',6'-trimethylcyclohex-1'-enyl)but-2-enyl Acetate ((*E*)-**25**). ^{1}H-NMR (80 MHz): 0.98 (*s*, 2 CH_3–C(6')); 1.30 (*d*, *J* = 7, CH_3–C(1)); 1.48 (*s*, CH_3–C(2')); 1.80 (*d*, *J* = 1.5, 3 H–C(4)); 2.00 (*s*, CH_3CO); 0.8–2.1 (*m*, 2 H–C(3'), 2 H–C(4'), 2 H–C(5')); 5.22 (*AB*, *J* = 8, δ_A = 4.92, *A*-part split to *q*, *J* = 1.5, H–C(2); δ_B = 5.52, *B*-part split to *q*, *J* = 7, H–C(1)).

(Z)-1-Methyl-3-(2',6',6'-trimethylcyclohex-1'-enyl)but-2-enyl Acetate, Conformer A ((*Z*)-**25A**). ^{1}H-NMR (80 MHz, *ca.* 80% pure): 0.90, 1.02 (2*s*, 2 CH_3–C(6')); 1.22 (*d*, *J* = 6, CH_3–C(1)); 1.48 (*s*, CH_3–C(2')); 1.82 (*d*, *J* = 1.5, 3 H–C(4)); 1.98 (*s*, CH_3CO); 0.8–2.1 (*m*, 2 H–C(3'), 2 H–C(4'), 2 H–C(5')); 5.27 (*AB*, *J* = 10, δ_A = 5.15, *A*-part split to *q*, *J* = 6, H–C(1); δ_B = 5.39, *B*-part split to *m*, $w_{1/2}$ = 4, H–C(2)).

Conformer B ((*Z*)-**25B**). ^{1}H-NMR (80 MHz, *ca.* 80% pure): 0.93, 1.03 (2*s*, 2 CH_3–C(6')); 1.21 (*d*, *J* = 6, CH_3–C(1)); 1.41 (*s*, CH_3–C(2')); 1.82 (*s*, 3 H–C(4)); 1.95 (*s*, CH_3CO); 0.8–2.1 (*m*, 2 H–C(3'), 2 H–C(4'), 2 H–C(5')); 5.0–5.5 (*m*, H–C(1), H–C(2)).

1.1.2. *With Light of* λ = *254 nm.* A soln. of (*E*)-**1** (1.40 g, 6.79 mmol) in MeCN (140 ml) was irradiated in arrangement *I* (lamp *A*, conversion 87%). During irradiation, Ar was bubbled through the reaction soln.[12]). CC of the photolysis mixture (SiO_2, Et_2O/pentane 1:4 to 1:1) yielded **3** (12 mg, 1%), **5** (77 mg, 6%), **6** (60 mg, 5%), and **10** (167 mg, 14%) in pure fractions, as well as a mixed fraction (880 mg, 72%). Reduction of this mixture with $LiAlH_4$, followed by acetylation (Ac_2O/pyridine) and HPLC (SiO_2, *p* = 35 bar, flow = 33 ml/min, λ_{DET} = 235 nm, Et_2O/hexane 1:67), afforded (*Z*)-**17** (15 mg, 1%) **18** (208 mg, 14%), **19** (126 mg, 9%), (*E*)-**25** (176 mg, 12%), (*Z*)-**25A** (153 mg, 10%), and (*Z*)-**25B** (153 mg, 10%).

6,6-Dimethyl-4-methylideneundeca-2,5,10-trione (**13**). ^{1}H-NMR (80 MHz, 80% pure): 1.28 (*s*, 2 CH_3–C(6)); 2.13, 2.19 (2*s*, 3 H–C(1), 3 H–C(11)); 0.8–2.3 (*m*, 2 H–C(7), 2 H–C(8)); 2.3–2.6 (*m*, 2 H–C(9)); 3.38 (*m*, $w_{1/2}$ = 3, 2 H–C(3)); 5.72, 5.97 (2*m*, $w_{1/2}$ = 2, CH_2=C(4)).

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[12]) In photolyses, which were protected from O_2 only by an Ar balloon, additionally the products **11** [6] (*ca.* 6%), **12** [7] (*ca.* 3%) and **13** (*ca.* 3%) were isolated.

1.2. *Sensitized Photolysis of (Z)-***17**. A soln. of (*Z*)-**17** (124 mg, 0.50 mmol) in acetone (15 ml) was irradiated in arrangement *III* (*Pyrex*, lamp *B*, 1 h). HPLC of the photolysis mixture (SiO_2, $p = 35$ bar, flow = 33 ml/min $\lambda_{DET} = 235$ nm, Et_2O/hexane 1:67) afforded (*Z*)-**17** (60 mg, 48%) and (*E*)-**17** (56 mg, 45%)[13]).

2. Additional Experiments. – 2.1. *Acid-Catalyzed Transformations.* 2.1.1. *Treatment of* **5** *with Acid.* A soln. of **5** (160 mg, 0.78 mmol) in Et_2O (10 ml) was acidified by bubbling HCl gas (*ca.* 5 bubbles), and stirred for 5 min, at r.t. Workup yielded **14** (150 mg, 94%).

2,2,6,7-Tetramethyl-9-methylidenebicyclo[4.3.0]non-7-en-1-ol (**14**). B.p. 90°/0.02 Torr. UV (0.180 mg in 10 ml of pentane): 237 (11200), end absorption to 275. IR: 3610*w*, 3080*w*, 3040*w*, 3010*w*, 2960*s*, 2940*s* (sh), 2920*s*, 2910*s*, 2865*s*, 2850*m*, 1655*s*, 1650*m* (sh), 1590*s*, 1470*m*, 1455*m*, 1445*m*, 1430*m*, 1385*m*, 1370*m*, 1360*m*, 1275*m*, 1185*s*, 1150*m*, 1110*w*, 1065*m*, 1000*m*, 965*w*, 940*w*, 910*m*, 880*s*, 850*s*. ^{1}H-NMR (300 MHz): 1.01, 1.21 (2*s*, 2 CH_3–C(2)); 1.30 (*s*, CH_3–C(6)); 0.9–2.0 (*m*, 2 H–C(3), 2 H–C(4), 2 H–C(5), OH); 1.99 (*m*, $w_{1/2} = 4$, CH_3–C(7)); 4.42, 4.45 (2*m*, $w_{1/2} = 4$, CH_2=C(9)); 6.15 (*m*, $w_{1/2} = 5$, H–C(8)). ^{13}C-NMR (75 MHz): 17.4, 26.6, 28.6, 28.7 (4*q*, 4 CH_3); 18.7, 39.6, 39.9 (3*t*, C(3), C(4), C(5)); 35.2 (*s*, C(2)); 67.9, 73.9 (2*s*, C(1), C(6)); 94.4 (*t*, CH_2=C(9)); 133.2 (*d*, C(8)); 152.6, 157.3 (2*s*, C(7), C(9)). ^{13}C-NMR (20 MHz, mixture with 50% **15**): 94.7 (*t*, CH_2=C(9), enhanced signal due to *ca.* 10% ^{13}C-labelling). MS: 206 (19, M^+, $C_{14}H_{22}O$), 191 (11), 173 (7), 149 (17), *135* (100), 133 (75), 123 (13), 124 (30), 121 (48), 120 (14), 119 (19), 109 (17), 107 (48), 105 (34), 93 (23), 91 (28), 79 (22), 43 (69), 41 (29). Anal. calc. for $C_{14}H_{22}O$: C 81.50, H 10.75; found: C 81.33, H 10.82.

2.1.2. *Treatment of* **14** *and* **15** *with Acid.* A soln. of **14** (102 mg, 0.50 mmol) in Et_2O (15 ml) was acidified, by adding Et_2O saturated with HCl (1 ml), and stirred at r.t. for 12 h. Workup and CC (SiO_2, DME/hexane 1:9) afforded **14** (27 mg, 26%) and **15** (71 mg, 70%). The analogous transformation of **15** (82 mg, 0.37 mmol) in Et_2O (10 ml) afforded **14** (19 mg, 23%) and **15** (56 mg, 68%).

2,2,6,9-Tetramethyl-7-methylidenebicyclo[4.3.0]non-8-en-1-ol (**15**). B.p. 80°/0.01 Torr. UV (0.391 mg in 25 ml of MeCN): 236 (10400), end absorption to 275. IR: 3600*m*, 3480*m* (br.), 3080*w*, 3045*w*, 3010*w*, 2960*s*, 2950*s*, 2925*s*, 2910*s* (sh), 2865*s*, 2850*m*, 1655*m*, 1650*m* (sh), 1590*s*, 1465*w*, 1455*m* (sh), 1450*s*, 1430*m*, 1380*m*, 1370*s*, 1360*s*, 1310*m*, 1270*m*, 1215*w*, 1190*m*, 1150*m*, 1125*m* (sh), 1115*m*, 1070*m*, 1020*w*, 1005*m*, 965*w*, 950*m*, 910*s*, 875*m*, 860*s*, 845*m*. ^{1}H-NMR (80 MHz): 0.85, 1.12 (2*s*, 2 CH_3–C(2)); 1.37 (*s*, CH_3–C(6)); 1.86 (*m*, $w_{1/2} = 3$, CH_3–C(9)); 0.8–2.2 (*m*, 2 H–C(3), 2 H–C(4), 2 H–C(5), OH); 4.52, 4.57 (2*s*, CH_2=C(7)); 6.09 (*m*, $w_{1/2} = 5$, H–C(8)). ^{13}C-NMR (20 MHz, *ca.* 85% pure): 16.9 (*q*, CH_3–C(9), enhanced signal due to *ca.* 10% ^{13}C-labelling); 27.8, 29.0, 29.4 (3*q*, 3 CH_3); 18.3, 38.3, 39.0 (3*t*, C(3), C(4), C(5)); 35.0 (*s*, C(2)); 67.3 (*s*, C(6)); 73.2 (*s*, C(1)); 96.5 (*t*, CH_2=C(7)); 133.0 (*d*, C(8)); 150.4, 158.3 (2*s*, C(7), C(9)). MS: 206 (20, M^+, $C_{14}H_{22}O$), 191 (7), 149 (18), 148 (84), 136 (16), *135* (100), 133 (66), 122 (35), 121 (48), 119 (20), 107 (45), 105 (32), 93 (22), 91 (29), 79 (23), 77 (25), 69 (24), 43 (93), 41 (40).

2.1.3. *Treatment of (Z)-7 with Acid.* A soln. of (*Z*)-**7** (52 mg, 0.25 mmol) was acidified by bubbling HCl gas (*ca.* 30 s) through the soln., and stirring for 1 h at r.t. Workup gave **20** (41 mg, *ca.* 70%, > 80% pure).

1,2,3,4-Tetrahydro-1,1,6,8-tetramethylnaphthalene (**20**). B.p. 50°/0.01 Torr. UV (1.966 mg in 10 ml of MeCN): 270 (470), 275 (sh, 390), 279 (370), end absorption to 350. IR: 2990*s*, 2950*s* (sh), 2910*s*, 2860*s*, 2710*w*, 2650*w*, 1610*m*, 1560*w*, 1455 (br.), 1435*m* (sh), 1385*m*, 1375*m*, 1360*m*, 1335*w*, 1285*w*, 1265*w*, 1260*w*, 1220*w*, 1200*w*, 1180*w*, 1160*w*, 1120*w*, 1080*w*, 1060*m*, 1030*w* (br.), 975*w*, 940*w*, 900*w*, 895*w*, 855*s*, 840*m*. ^{1}H-NMR (80 MHz): 1.37 (*s*, 2 CH_3–C(1)); 2.22, 2.47 (2*s*, CH_3–C(6), CH_3–C(8)); 0.8–2.0 (*m*, 2 H–C(2), 2 H–C(3)); 2.76 (*m*, $w_{1/2} = 14$, 2 H–C(4)); 6.80 (*m*, $w_{1/2} = 5$, H–C(5), H–C(7)). ^{13}C-NMR (20 MHz): 20.4, 23.4, 29.4, 29.4 (4*q*, 4 CH_3); 19.7, 32.5, 44.1 (3*t*, C(2), C(3), C(4)); 34.5 (*s*, C(1)); 128.4, 131.5 (2*d*, C(5), C(7)); 134.5, 136.9, 137.3, 140.4 (4*s*, C(4a), C(7), C(8), C(8a)). MS: 188 (23, M^+, $C_{14}H_{20}$), 174 (14), *173* (100), 158 (7), 145 (6). Anal. calc. for $C_{14}H_{20}$: C 89.29, H 10.71; found: C 89.16, H 10.67.

2.1.4. *Treatment of* **10** *with Acid.* A soln. of **10** (110 mg, 0.53 mmol) in Et_2O (30 ml) was acidified with 3 drops of conc. HCl and stirred for 2 h at r.t. Workup and CC (SiO_2, Et_2O/hexane 1:9) afforded **20** (41 mg, 41%).

2.2. *Base-Catalyzed Transformations.* 2.2.1. *Treatment of* **13** *with Base.* To a soln. of **13** (68 mg, 0.29 mmol) in MeOH (3 ml), NaOMe (60 mg, 1.11 mmol) was added and the resulting suspension was stirred for 2 h at r.t. Workup and CC (SiO_2, Et_2O/pentane 4:1) afforded **21** (18 mg, 26%).

3-Hydroxy-4,4-dimethyl-3-(1-methyl-3-oxobut-1-enyl)cycloheptanone (**21**). B.p. 130°/0.02 Torr. UV (0.555 mg in 25 ml of MeCN): 223 (11400). UV (3.803 mg in 2 ml of MeCN): 275 (100), 322 (60), end absorption to 360. IR: 3600*w*, 3450*w* (br.), 2960*m*, 2905*w* (sh), 2885*w* (sh), 1715*s*, 1700*s*, 1615*m*, 1465*w* (br.), 1435*w*, 1405*w*, 1385*w*, 1370*m*, 1360*m* (sh), 1300*w*, 1260*w* (br.), 1200*w*, 1110*w* (br.), 1010*w*, 850*w*. ^{1}H-NMR (300 MHz): 1.00, 1.03 (2*s*, 2 CH_3–C(4)); 1.15–1.45 (*m*, 2 H–C(5)); 1.52–1.70 (*m*, 2 H–C(6)); 2.12 (*s*, 3 H–C(4′)); 2.16 (*d*, $J = 1.5$, CH_3–C(1′)); 2.40 (*t*, $J = 7.0$, 2 H–C(7)); 2.66 (*AB*, $J = 18.0$, $\delta_A = 2.30$, $\delta_B = 2.83$, 2 H–C(2)); 5.94 (*q*, $J = 1.5$, H–C(2′)), OH

[13]) Under these conditions, compounds **18** and **19** were photostable.

signal probably overlapped with signals at 2.12 and 2.16. ^{13}C-NMR (25 MHz): 17.3, 22.2, 22.4, 30.0 (4*q*, 4 CH_3); 18.6, 37.2, 44.3, 49.4 (4*t*, C(5), C(6), C(7), C(2)); 40.5 (*s*, C(4)); 85.4 (*s*, C(3)); 133.0 (*d*, C(2')); 179.5 (*s*, C(1')); 205.7, 209.1 (2*s*, C(1), C(3')). MS: 238 (1, $M^{+\cdot}$, $C_{14}H_{22}O_3$), 153 (3), 128 (13), *112* (100), 111 (13), 109 (40), 71 (11), 69 (41), 43 (50). Anal. calc. for $C_{14}H_{22}O_3$: C 70.55, H 9.31; found: 70.41, 9.39.

2.2.2. *Treatment of* **12** *with Base.* To a soln. of **12** (51 mg, 0.21 mmol) in MeOH (7 ml), NaOMe (*ca.* 5 mg) was added and the resulting mixture was stirred for 2 h at r.t. Workup and CC (SiO_2, Et_2O/pentane 10:1) yielded **21** (28 mg, 55%).

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