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233. Photochemical Reactions

127th Communication[1])

Photochemistry of Epoxy-enones: Intramolecular Trapping of a Carbonyl Ylide[2])

by **Shigeru Ohta, Bruno Frei** and **Oskar Jeger**

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

Dedicated to Prof. *T. Reichstein* on the occasion of his 85th birthday

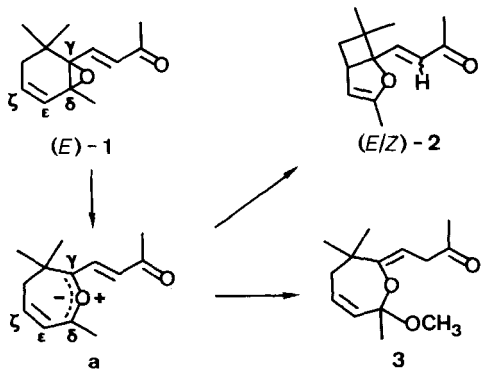
(6.X.82)

Summary

On $^1n,\pi^*$-excitation 5,6-epoxy-2-hydroxy-5,6-dihydro-β-ionone ((*E*)-**4**) shows the typical behaviour of α,β-unsaturated γ,δ-epoxy ketones undergoing primarily C(γ), O-cleavage of the oxiran. However, $^1\pi,\pi^*$-excitation of (*E*)-**4** leads to enol ether **10** which is formed by intramolecular insertion of the hydroxyl group of the ylide **c**.

1. Introduction. - In previous reports carbonyl ylides have been postulated as intermediates in the photoisomerization of α,β-unsaturated γ,δ-epoxy ketones[3]).

Scheme 1



[1]) 126th Communication, see [1].
[2]) Presented in part at the IXth IUPAC Symposium on Photochemistry, July 25–30 1982, Pau, France.
[3]) For a recent paper in this series see [2].

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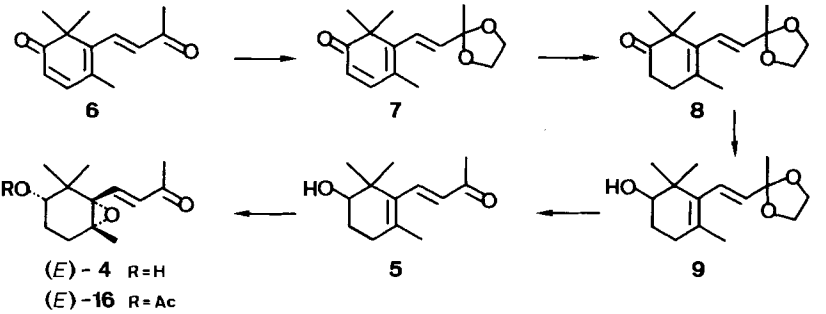
Thus *e.g.* $^1n,\pi^*$- or $^1\pi,\pi^*$-excitation of (*E*)-**1** in pentane causes C(γ),C(δ)-cleavage leading to ylide intermediate **a**, which undergoes stabilization to (*E*/*Z*)-**2** through internal electrocyclic ring closure *(Scheme 1)*. On photolysis of (*E*)-**1** in methanol, the acetal **3** is formed (besides (*E*/*Z*)-**2**), presumably by addition of the solvent to the ylide **a** [3].

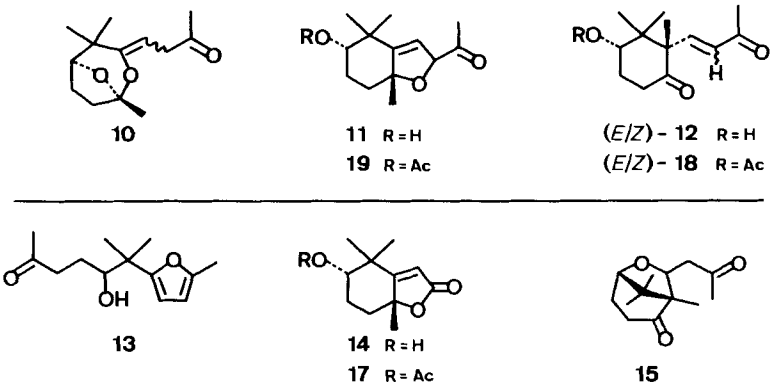
We investigated the photochemistry of (*E*)-**4** *(Scheme 2)* with the object of trapping a carbonyl ylide of type **a** by an *intramolecular* reaction involving a OH-group situated in a 'strategic position' on the cyclohexane ring.

Scheme 2



2. Preparation of (*E*)-*4*. – Epoxydation of 2-hydroxy-β-ionone (**5**) [4][4]) by the method of *Sharpless & Michaelson* [6] (*t*-BuOOH, VO(acac)$_2$, benzene), which is known to give *syn*-epoxy alcohols, afforded (*E*)-**4** in 80% yield. Compound **5** was prepared by a slight modification of the synthesis of *Tsukida et al.* [4] *(Scheme 2)*. Monoacetal **7** which was obtained selectively from the diketone **6** [4] (ethylene glycol, *p*-TsOH, benzene, reflux) in 86% yield, was reduced with lithium trimethoxy-aluminum hydride/CuBr in THF [7] affording **8** (78%). Reduction of **8**→**9** with $NaBH_4$ and acetal cleavage (*Dowex* 50, H^+-form, acetone) gave **5** [4] in 91% yield.

Scheme 3



[4]) In compounds named as ionone derivatives, numbering of the carotinoid nomenclature [5] is used.

3. Photolyses. – 3.1. *Irradiation of* (E)-**4**. The products obtained are shown in *Scheme 3* and the results of the photolyses are summarized in the *Table.*

Table. *Results of the photolyses of* (*E*)-**4**

λ [nm]	Solvent	Conversion [%]	Product distribution [%][a]						
			(*Z*)-**4**	**10**[b]	**11**	(*E*)-**12**[c]	**13**[d]	**14**[e]	**15**[c]
254[f]	CH_3CN	75	~2	16	17	–	–	5	–
254[g]	CH_3CN	66	–	55	10	–	–	–	–
⩾347[f]	CH_3CN	78	6	–	33	–	~3	–	22
⩾347[h]	CD_3CN	90	–	–	40	20	–	–	10
⩾347[h][i]	CD_3CN	90	–	–	42	4	–	–	32

[a]) Yields are based on amount of converted starting material. [b]) Enol ether **10** is extremely unstable and could be recovered only in low yield after chromatography on SiO_2 or *Florisil.* [c]) Compounds (*E*/*Z*)-**12** could not be isolated, since they cyclized spontaneously to **15**. The (*E*)-isomer of **12** could be identified in the ^{1}H-NMR. spectrum ($CDCl_3$) of the photolysis mixture on the basis of the characteristic signals of an *AB*-system at 6.73 ppm ($J = 16$ Hz, $\delta_A = 7.53$, $\delta_B = 5.93$ ppm). These signals disappeared after base treatment (see *Exper. Part*) and were replaced by signals corresponding to **15**. [d]) Furan derivative **13** is formed by acid-catalyzed rearrangement of (*Z*)-**4**. For a mechanistic interpretation of the isomerization of (*Z*)-epoxy-enones to furans see [8]. [e]) Lactone **14** is formed by the auto-oxidation of dihydrofuran derivative **11** (see *Exper. Part* and [9]). [f]) Preparative scale, yields are determined after chromatography on SiO_2 by ^{1}H-NMR. analysis of the fractions. [g]) Analytical scale, yields determined by GC. analysis using eicosane as an internal standard. [h]) Analytical scale, yields are determined by ^{1}H-NMR. analysis of the reaction mixture using bis(trimethylsilyl)acetylene as an internal standard. [i]) After treatment of the photolysis mixture with *ca.* 1 mg of Na_2CO_3 for 10 min.

3.2. *Irradiation of acetate* (E)-**16** *(Scheme 2).* Photolysis of a *ca.* 0.01 M solution of (*E*)-**16** in CH_3CN (91% conversion) at $\lambda \geqslant 347$ nm gave the following products: **17**[5]) (30%), (*E*)-**18** (25%) and (*Z*)-**18** (21%) *(Scheme 3).*

4. Structure of the compounds. – *Epoxy-enones* (E)- *and* (Z)-**4**. The spectral evidence for (*E*)-**4** includes in the ^{1}H-NMR. spectrum an *AB*-system at 6.47 ppm ($J = 15$ Hz) for the two olefinic H-atoms, three *s* for the CH_3-groups of the cyclohexane ring at 1.02, 1.12 and 1.14 ppm, a *s* for the methyl ketone at 2.16 ppm and a *m* at 3.00–3.25 ppm corresponding to the H-atom geminal to the OH-group.

Significant signals in the ^{13}C-NMR. spectrum are two *s* at 66.7 and 72.2 ppm of the C-atoms of the oxiran ring. As expected for the enone system, the UV. spectrum includes a π,π^*-band at 230 nm ($\varepsilon = 11900$) and the IR. spectrum shows a strong band at 1680 cm^{-1}.

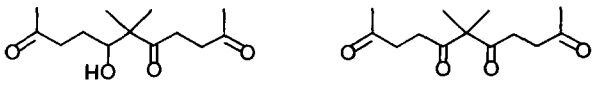
The structure of (*Z*)-**4** followed from comparison of its spectra with those of the (*E*)-isomer. In the ^{1}H-NMR. spectrum the *AB*-system at 6.11 ppm shows the characteristic coupling constant of $J = 12$ Hz.

Enol-ether **10**. The structure of **10** was ascertained primarily from spectral data. In particular, the IR. band at 1675 cm^{-1} indicates an enol-ether system. This is also evident in the ^{13}C-NMR. spectrum by a *s* (158.4 ppm) and a *d* (98.5 ppm), and in the ^{1}H-NMR. spectrum the *t* at 4.75 ppm ($J = 7$ Hz) corresponds to the olefinic H-atom. Furthermore, the methyl acetal moiety is indicated in the ^{13}C-NMR. spectrum by a *s* at 107.3 ppm as well as in the ^{1}H-NMR. spectrum by a *s* at 1.58 ppm. Decisive evidence for the structure of **10** was obtained by acidic hydrolysis (aq. 1N HCl, ether) leading to the aliphatic hydroxy-trione **20** *(Scheme 4).* Finally, PCC-oxidation [10] of the latter afforded the symmetrical tetraone **21** which shows only seven signals in the ^{13}C-NMR. spectrum (see *Exper. Part*).

Compounds **11–14**, **17** *and* **18**. The proposed structure of these compounds are supported by comparison of their spectral data with those of analogous compounds obtained from the photolysis

[5]) Dihydrofuran derivative **19** could not be isolated (see also *Footnote e* in the *Table*).

Scheme 4



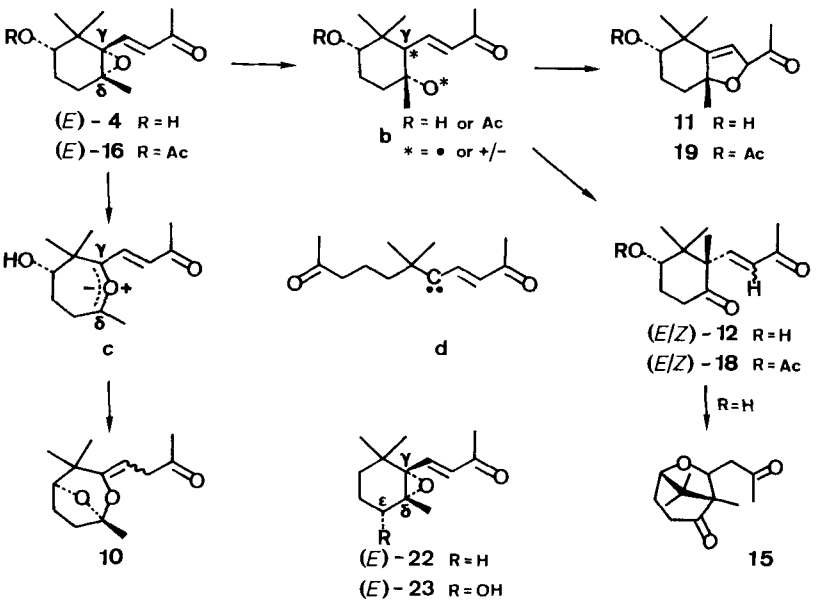
20 **21**

of (*E*)-**22** [9] *(Scheme 5)*. The configuration of compounds **12** and **18** could be assigned on the basis that (*E*)-**12** cyclizes to **15**[6]) (see also footnote c to the *Table*), a process which is only possible if the OH-group and the enone side-chain are in *cis*-relation[7]).

Bicyclic diketone **15**. The main structural features of **15** are evidenced by spectral data. In particular, the IR. bands at 1720 and 1710 cm^{-1} indicate two carbonyl functions. The ^{13}C-NMR. spectrum includes two *d* at 79.5 and 83.6 ppm for the bridge-head C-atoms. Corresponding signals in the ^1H-NMR. spectrum are the *m* at 3.89 ppm and the $d \times d$ at 4.26 ppm ($J_1 = 4$, $J_2 = 8$ Hz) for both H-atoms geminal to the ether function.

5. Discussion. – The photolysis of the epoxy-enone (*E*)-**4** shows a strong dependence of product formation upon the mode of excitation. Thus, on $^1n,\pi^*$-excitation (*E*)-**4** selectively undergoes C(*γ*),O-cleavage leading to intermediate **b** followed by stabilization to compounds **11** and (*E*/*Z*)-**12**, respectively *(Scheme 5)*. An interaction of the OH-function could not be detected, except for the non-photochemical transformation of (*E*/*Z*)-**12** into **15** by 1,4-addition of the hydroxyl onto the enone.

Scheme 5



[6]) Experiments to convert the acetates (*E*)- and (*Z*)-**18**, respectively, to **15** by treatment with aq. base failed due to the instability of the latter compound.

[7]) An analogous intramolecular *Michael* addition has been described by *Kaiser & Lamparsky* for 2-hydroxy-*α*-ionone[4]) [11].

Acetate (*E*)-**16** shows a corresponding behaviour on $^1n,\pi^*$-excitation, leading to the acetates (*E*/*Z*)-**18** and **19**.

However, on $^1\pi,\pi^*$-excitation of (*E*)-**4** a profound change of the photochemical picture is observed. The irradiation of (*E*)-**4** now leads to the acetal **10** as the main product. Its formation is presumably due to rapid intramolecular trapping of ylide intermediate **c** by the OH-group. Products derived from a possible carbene intermediate of type **d**, as they are formed under *analogous* conditions of irradiation from (*E*)-**22** [9], could not be detected.

An enormous difference is observed, when the results of this study are compared with those involving isomer (*E*)-**23**, where the OH-group is in ε-position. Thus, in contrast to (*E*)-**4**, $^1\pi,\pi^*$-excitation of (*E*)-**23** does not lead to products arising from intramolecular insertion of the OH-group in an ylide intermediate. Instead, products arising from a carbene intermediate of type **d** are obtained. However, in the case of (*E*)-**23** the OH-group is observed to have quite a different influence: both modes of excitation cause C(γ),O-cleavage of the epoxide, followed by a H-transfer from the OH-group to the former oxiran O-atom. This main process leads to a 1,4-diradical, which is stabilized by cleavage of the C(δ),C(ε)-bond [12].

On the basis of these results, it is evident that the course of the photorearrangement of ring-hydroxylated α,β-unsaturated γ,δ-epoxy ketones of the ionone series is directed, to a substantial extent, by the position of the OH-group.

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Experimental Part

General. See [13] except as noted below. Melting points (m.p.) were determined in capillary tubes using a *Büchi* melting point apparatus and are uncorrected. Analytical gas-chromatography (GC.) was performed using a 20 m × 0.36 mm *Ucon 50 HB 5100* capillary column. All UV. spectra were taken in CH_3CN-solution. *Filter solution A* see [14].

1. Preparation of (*E*)-*4*. – 1.1. *Monoacetal* **7**. A solution of 2.76 g (13.5 mmol) of **6** [4], 1.00 g (16.5 mmol) of ethylene glycol and 52 mg (0.3 mmol) *p*-toluenesulfonic acid in 150 ml of benzene was refluxed with a *Dean-Stark* apparatus. After 2.5 h, 250 mg (4.1 mmol) of ethylene glycol was added, and the solution was refluxed for another 3 h. The solvent was evaporated and the residue chromatographed on SiO_2 (ether/hexane 2:1) to give 2.87 g (86%) of **7**.

(E)-5-(3',3'-Ethylendioxy-1'-butenyl)-4,6,6-trimethyl-2,4-cyclohexadien-1-one (**7**). B.p. 95°/0.01 Torr. – UV. (0.222 mg in 10 ml): 228 (6370), 330 (7260). – IR.: 3040*w*, 2990*m*, 2930*m*, 2880*m*, 1665*s*, 1650*m S*, 1630*m*, 1560*w*, 1550*w*, 1540*w*, 1460*w*, 1445*w*, 1405*w*, 1375*m*, 1355*w*, 1340*w*, 1275*m*, 1215*m S*, 1205*s*, 1180*m*, 1160*m*, 1105*m*, 1090*m*, 1045*s*, 975*w*, 950*w*, 870*m*. – ^{1}H-NMR.: 1.15 (*s*, 2 H_3C–C(6)); 1.42 (*s*, 3 H–C(4')); 1.96 (*s*, H_3C–C(4)); 3.70–4.04 (*m*, OCH_2CH_2O); 5.87 (*AB*-system, J = 16, δ_A = 5.52, δ_B = 6.21, H–C(1'), H–C(2')); 6.31 (*AB*-system, J = 10, δ_A = 5.85, δ_B = 6.77, H–C(2), H–C(3)). – ^{13}C-NMR.: 19.6, 24.8, 25.1 (4 *qa*, 2 *qa* at 25.1, 4 CH_3); 64.3 (*t*, OCH_2CH_2O); 123.0, 125.1, 136.5, 146.7 (4 *d*, C(2), C(3), C(1'), C(2')); 48.4 (*s*, C(6)); 106.8 (*s*, C(3')); 123.6, 148.8 (2 *s*, C(4), C(5)); 204.4 (*s*, C(1)). – MS.: 248 (19, M^+, $C_{15}H_{20}O_3$), 233 (31), 206 (10), 205 (67), 161 (30), 148 (18), 133 (30), 119 (12), 117 (10), 115 (10), 113 (10), 105 (18), 100 (17), 91 (21), *87* (100), 77 (12), 43 (62), 41 (15).

$C_{15}H_{20}O_3$ (248.31) Calc. C 72.55 H 8.12% Found C 72.56 H 8.05%

1.2. *Reduction of* **7**. A solution of 14.3 g (112 mmol) of lithium trimethoxyaluminum hydride [7] in 140 ml of dry THF was added dropwise to a suspension of 8.04 g (56 mmol) CuBr in 42 ml of dry THF maintained at -10 to $-15°$. After 30 min, the suspension was cooled to $-20°$, a solution of 3.47 g (14 mmol) of **7** in 20 ml of THF was added dropwise and stirred at -15 to $-20°$ for 1.5 h. The mixture was poured into sat. aq. NH_4Cl-solution, worked up with ether and chromatographed on SiO_2 (ether/hexane 1:1) to give 2.72 g (78%) of **8**.

(E)-3-(3',3'-Ethylendioxy-1'-butenyl)-2,2,4-trimethyl-3-cyclohexen-1-one (**8**). B.p. 105°/0.01 Torr. – UV. (0.407 mg in 10 ml): 233 (4910). – UV. (15.6 mg in 5 ml): 299*s* (34) end absorption to 325. – IR.: 2980*s*, 2930*s*, 2910*m S*, 2880*s*, 1715*s*, 1460*m*, 1440*m*, 1420*w*, 1370*m*, 1355*m*, 1300*w*, 1285*w*, 1270*w*, 1210*s*, 1170*m*, 1140*m*, 1100*m*, 1040*s*, 975*m*, 945*w*, 880*w S*, 860*m*. – ^{1}H-NMR.: 1.08 (*s*, 2 H_3C–C(2)); 1.40 (*s*, 3 H–C(4')); 1.75 (*s*, H_3C–C(4)); 2.34–2.52 (*m*, 2 H–C(6), 2 H–C(5)); 3.74–3.98 (*m*, OCH_2CH_2O); 5.70 (*AB*-system, $J = 16$, $\delta_A = 5.36$, $\delta_B = 6.04$ broadened, H–C(1'), H–C(2')). – ^{13}C-NMR.: 21.0, 24.9, 25.2 (4 *qa*, 2 *qa* at 24.9, 4 CH_3); 31.8, 35.9 (2 *t*, C(5), C(6)); 64.6 (*t*, OCH_2CH_2O); 126.4, 135.8 (2 *d*, C(1'), C(2')); 46.7 (*s*, C(2)); 107.4 (*s*, C(3')); 128.9, 135.8 (2 *s*, C(4), C(3)); 214.5 (*s*, C(1)). – MS.: 250 (11, M^+, $C_{15}H_{22}O_3$), 236 (16), *235* (100), 193 (11), 163 (14), 121 (17), 105 (15), 100 (22), 99 (12), 93 (10), 91 (20), 87 (71), 79 (11), 77 (14), 55 (13), 43 (50), 41 (16).

$C_{15}H_{22}O_3$ (250.33) Calc. C 71.97 H 8.86% Found C 71.80 H 8.81%

1.3. *Reduction of* **8**. To a solution of 1.32 g (5.3 mmol) of **8** in 20 ml of abs. ethanol at 0° was added dropwise a solution of 230 mg (6.1 mmol) of $NaBH_4$ in 50 ml of abs. ethanol. After stirring for 1 h, water was added, and the mixture was worked up with ether affording 1.30 g (98%) of **9**. An analytical sample of **9** was obtained by KR.-distillation (115°/0.01 Torr).

(E)-4-(5'-Hydroxy-2',6',6'-trimethyl-1'-cyclohexen-1'-yl)-3-buten-2-one ethylene acetal (**9**). B.p. 115°/0.01 Torr. – UV. (0.590 mg in 10 ml): 234 (5400). – IR.: 3630*w*, 3500 br. *w*, 2970*m*, 2940*m*, 2910*m*, 2880*m*, 2840*w*, 1460*w*, 1445*w*, 1430*w*, 1375*m*, 1360*w*, 1210*s*, 1140*w*, 1100*m*, 1065*w*, 1040*s*, 1005*w*, 975*m*, 945*w*, 865*w*. – ^{1}H-NMR.: 0.92, 0.98 (2 *s*, 2 H_3C–C(6')); 1.38 (*s*, 3 H–C(1)); 1.61 (*s*, H_3C–C(2')); 1.54–1.80 (*m*, 3 H, 2 H–C(4'), OH); 2.04 (*t*, $J = 6$, 2 H–C(3')); 3.38 (*d* × *d*, $J_1 = 5$, $J_2 = 8$, H–C(5')); 3.70–3.92 (*m*, OCH_2CH_2O); 5.64 (*AB*-system, $J = 16$, $\delta_A = 5.24$, $\delta_B = 6.04$ broadened, H–C(3), H–C(4)). – ^{13}C-NMR.: 21.0, 21.7, 25.2, 26.5 (4 *qa*, 4 CH_3); 26.5, 30.1 (2 *t*, C(3'), C(4')); 64.4 (*t*, OCH_2CH_2O); 75.2 (*d*, C(5')); 127.7, 134.4 (2 *d*, C(3), C(4)); 39.0 (*s*, C(6')); 107.6 (*s*, C(2)); 127.9, 135.2 (2 *s*, C(1'), C(2')). – MS.: 252 (19, M^+, $C_{15}H_{24}O_3$), 238 (16), *237* (100), 219 (32), 193 (15), 175 (11), 147 (19), 137 (11), 133 (18), 121 (13), 107 (14), 105 (24), 100 (15), 99 (10), 93 (11), 91 (19), 87 (74), 79 (14), 77 (18), 73 (11), 55 (12), 43 (57), 41 (17).

$C_{15}H_{24}O_3$ (252.34) Calc. C 71.39 H 9.59% Found C 71.25 H 9.60%

1.4. *Hydrolysis of the acetal* **9**. A mixture of 1.30 g (5.2 mmol) of **9** and 50 mg of activated *Dowex 50* (H^+-form) in 30 ml of acetone was stirred for 1 h. After filtration and evaporation of the solvent 1.00 g (93%) of **5** [4] were obtained.

1.5. *Epoxydation of* **5**. A solution of 3.0 g (30 mmol) of *t*-butylhydroperoxide in 45 ml of benzene was added dropwise to a solution of 3.02 g (14.5 mmol) of **5** and 48 mg (0.19 mmol) of $VO(acac)_2$ in 45 ml of benzene cooled in an ice bath. The mixture was stirred for 2 h at RT., treated with sat. aq. Fe(II)SO_4-solution, worked up with ether and chromatographed on SiO_2 (ether) to give 2.60 g (80%) of *(E)*-**4**.

(3E,1'R,2'S*,5'R*)-4-(5'-Hydroxy-2',6',6'-trimethyl-1',2'-epoxy-1'-cyclohexyl)-3-buten-2-one* ((*E*)-**4**). M.p. 57.9–57.5° (hexane). – UV. (0.196 mg in 10 ml): 230 (11900). – UV. (23.2 mg in 5 ml): 322 (47) end absorption to 390. – IR.: 3620*w*, 3520*s*, 3010*m S*, 2970*s*, 2940*s*, 2910*s S*, 2880*m*, 1700*s*, 1680*s*, 1630*s*, 1465*m*, 1450*s*, 1435*m*, 1415*s*, 1380*s*, 1360*s*, 1295*s*, 1285*s S*, 1260*s*, 1250*s*, 1235*m S*, 1205*m*, 1180*s*, 1170*s S*, 1085*s*, 1055*s*, 1020*s*, 980*s*, 940*s*, 910*w*, 900*w*, 890*w*, 875*m*, 865*m*, 850*w*. – ^{1}H-NMR.: 1.02, 1.12, 1.14 (3 *s*, 2 H_3C–C(6'), H_3C–C(2')); 1.52–2.32 (*m*, 2 H–C(3'), 2 H–C(4')); 2.16 (*s*, 3 H–C(1)); 2.45–2.65 (*m*, HO–C(5')); 3.00–3.25 (*m*, H–C(5')); 6.47 (*AB*-system, $J = 15$, $\delta_A = 6.16$, $\delta_B = 6.78$, H–C(3), H–C(4)). – ^{13}C-NMR.: 20.5, 21.2, 25.2, 28.1 (4 *qa*, 4 CH_3); 24.0, 26.4 (2 *t*, C(3'), C(4')); 75.4 (*d*, C(5')); 132.8, 141.0 (2 *d*, C(3), C(4)); 37.2 (*s*, C(6')); 66.7, 72.2 (2 *s*, C(1'), C(2')); 197.2 (*s*, C(2)). – MS.: 224 (1, M^+, $C_{13}H_{20}O_3$), 165 (19), 125 (15), 124 (20), *123* (100), 109 (49), 101 (16), 98 (13), 83 (13), 81 (10), 55 (19), 43 (99), 41 (21).

$C_{13}H_{20}O_3$ (224.29) Calc. C 69.61 H 8.99% Found C 69.96 H 8.84%

1.6. *Acetylation of* (*E*)-**4**. To a solution of 250 mg (1.1 mmol) of (*E*)-**4** in 3 ml of dry pyridine was added dropwise 3 ml of acetic anhydride in an ice bath. The mixture was stirred for 5 h at RT., treated with sat. aq. Cu(II)SO_4-solution and worked up with ether. Chromatography on SiO_2 (hexane/ether 1:2) afforded 267 mg (90%) of (*E*)-**16**.

*(1'*E,*1*R**,3*R**,4*S**)-[3-(3'-Oxo-1'-butenyl)-3,4-epoxy-2,2,4-trimethylcyclohexyl] acetate* ((*E*)-**16**). M.p. 92.5–93.5° (hexane). – UV. (0.190 mg in 10 ml): 229 (11700). – UV. (15.8 mg in 5 ml): 322 (49) end absorption to 390. – IR.: 3000*w S*, 2980*m*, 2930*w*, 2880*w*, 1745*s*, 1700*m*, 1680*m*, 1625*m*, 1470*w*, 1450*w*, 1430*w*, 1380*m*, 1315*m*, 1310*m S*, 1290*m*, 1240*s*, 1205*w*, 1190*w*, 1170*w*, 1105*w*, 1050*m*, 1030*m*, 1015*m*, 1000*m S*, 990*m*, 950*w*, 910*w*, 890*w*. – ^{1}H-NMR.: 0.93, 1.06, 1.12 (3 *s*, 2 H_3C–C(2), H_3C–C(4)); 1.36–2.14 (*m*, 2 H–C(5), 2 H–C(6)); 1.96 (*s*, H_3C–COO); 2.16 (*s*, 3 H–C(4')); 4.25–4.45 (*m*, H–C(1)); 6.49 (*AB*-system, J = 16, δ_A = 6.16, δ_B = 6.82, H–C(1'), H–C(2')). – ^{13}C-NMR.: 17.7, 19.6, 21.1, 25.9, 28.2 (5 *qa*, 5 CH_3); 21.9, 30.1 (2 *t*, C(5), C(6)); 76.8 (*d*, C(1)); 132.6, 141.9 (2 *d*, C(1'), C(2')); 37.3 (*s*, C(2)); 65.9, 69.4 (2 *s*, C(3), C(4)); 170.5 (*s*, H_3C–COO); 197.1 (*s*, C(3')). – MS.: 266 (< 1, M^+, $C_{15}H_{22}O_4$); 223 (1), 165 (6), 163 (6), 124 (11), *123* (100), 109 (14), 43 (61).

$C_{15}H_{22}O_4$ (266.33) Calc. C 67.65 H 8.33% Found C 67.65 H 8.29%

2. Photolysis experiments. – 2.1. *Irradiation of* (E)-**4**. – 2.1.1. *At* λ = *254 nm*. 2.1.1.1. A solution of 800 mg (3.6 mmol) of (*E*)-**4** in 200 ml of CH_3CN was irradiated (quartz, lamp *A*, 75% conversion). The products and yields[8]) determined by ^{1}H-NMR. analysis of the fractions obtained from chromatography on SiO_2 (hexane/ether 1:2) were: *ca.* 2% (*Z*)-**4**, 16% **10**, 17% **11** and 5% **14**[9]).

*(3Z,1'*R**,2'*S**,5'*R**)-4-(5'-Hydroxy-2',6',6'-trimethyl-1',2'-epoxy-1'-cyclohexyl)-3-buten-2-one* ((*Z*)-**4**). – IR.: 3620*w*, 3510*m*, 3000*m S*, 2970*s*, 2940*s*, 2870*m*, 1720*s*, 1700*s*, 1680*m*, 1615*m S*, 1600*s*, 1460*m*, 1455*m*, 1435*m*, 1410*s*, 1385*m*, 1375*m*, 1370*s*, 1355*s*, 1275 br. *w*, 1230*m*, 1205*m*, 1175*s*, 1130*s*, 1075*m*, 1055*s*, 1020*s*, 1010*m*, 980*m*, 960*m*, 945*m*, 900*w*, 880*w*, 870*w*, 855*w*. – ^{1}H-NMR. (80 MHz, $CDCl_3$): 1.03 (3 H); 1.19 (6 H, 2 *s*, H_3C–C(2'), 2 H_3C–C(6')); 1.40–2.40 (*m*, 5 H, 2 H–C(3'), 2 H–C(4'), OH); 2.25 (*s*, 3 H–C(1)); 3.25–3.50 (*m*, H–C(5')); 6.11 (*AB*-system, J = 12, δ_A = 5.93, δ_B = 6.29, H–C(3), H–C(4)). – MS.: 224 (1, M^+, $C_{13}H_{20}O_3$), 206 (11), 124 (42), *123* (100), 109 (17), 83 (15), 43 (29).

4-(1',4',4'-Trimethyl-2',8'-dioxabicyclo[3.2.1]octan-3'-ylidene)-2-butanone (**10**). – IR.: 2990*s*, 2960*s*, 2870*m*, 1720*s*, 1675*m*, 1460*m*, 1440*m*, 1390*s*, 1355*m*, 1345*s*, 1320*m*, 1310*m S*, 1280*m*, 1260*w*, 1230*w*, 1205*m*, 1180*s*, 1170*s*, 1150*s*, 1110*m*, 1080*m*, 1050*s*, 1025*m*, 1005*m*, 980*m*, 940*s*, 895*s*, 835*m*. – ^{1}H-NMR. (80 MHz, $CDCl_3$): 1.03, 1.34 (2 *s*, 2 H_3C–C(4')); 1.58 (*s*, H_3C–C(1')); 2.15 (*s*, 3 H–C(1)); 1.65–2.10 (*m*, 2 H–C(6'), 2 H–C(7')); 3.13 (*d*, J = 7, 2 H–C(3)); 3.80–4.00 (*m*, H–C(5')); 4.75 (*t*, J = 7, H–C(4)). – ^{13}C-NMR.: 22.3, 23.1, 27.2, 29.4 (4 *qa*, 4 CH_3); 24.9, 35.2, 39.7 (3 *t*, C(3), C(6'), C(7')); 84.9 (*d*, C(5')); 98.5 (*d*, C(4)); 38.0 (*s*, C(4')); 107.3 (*s*, C(1')); 158.4 (*s*, C(3')); 207.5 (*s*, C(2)). – MS.: 224 (2, M^+, $C_{13}H_{20}O_3$), 142 (18), 111 (12), 109 (17), 83 (13), 71 (12), 69 (10), 55 (58), *43* (100), 41 (19).

*(3*R**,6*S**)-(3-Hydroxy-2,2,6-trimethyl-7-oxabicyclo[4.3.0]non-9-en-8-yl)methyl ketone* (**11**). – IR.: 3510*w*, 3400*w S*, 2960*s*, 2940*s*, 2870*m S*, 1715*s S*, 1705*s*, 1680*m*, 1625*m*, 1445*m*, 1410*m*, 1395*m*, 1375*m*, 1365*m*, 1355*m*, 1295*m*, 1275*m*, 1260*m*, 1245*m*, 1175*m*, 1155*m*, 1080*m*, 1050*m*, 1015*m*, 975*m*, 935*m*, 915*m*. – ^{1}H-NMR. (80 MHz, $CDCl_3$, 80% pure): 1.15, 1.23 (2 *s*, 2 H_3C–C(2)); 1.53 (*s*, H_3C–C(6)); 2.23 (*s*, H_3C–CO): 1.50–2.10 (*m*, 2 H–C(4), 2 H–C(5), HO–C(3)); 3.53 (*m*, $w_{1/2}$ = 5, H–C(3)); 5.26 (*AB*-system, J = 3, δ_A = 5.03, δ_B = 5.48, H–C(8), H–C(9)). – ^{13}C-NMR. (signals of the spectrum of a *ca.* 1:1 mixture of **11** and **14** which can be assigned to **11**): 25.2, 25.4, 25.5, 27.7 (4 *qa*, 4 CH_3), 27.3, 34.5 (2 *t*, C(4), C(5)); 75.4 (*d*, C(3)); 88.8 (*d*, C(8)); 117.8 (*d*, C(9)); 39.8 (*s*, C(2)); 89.5 (*s*, C(6)); 151.8 (*s*, C(1)); 210.0 (*s*, C=O). – MS.: 224 (2, M^+, $C_{13}H_{20}O_3$), 182 (10), 181 (55), 165 (19), 163 (22), 140 (10), 135 (13), 133 (11), 123 (12), 121 (16), 109 (11), 107 (14), *95* (100), 93 (12), 91 (10), 67 (10), 43 (58), 41 (14).

*(3*R**,6*S**)-3-Hydroxy-2,2,6-trimethyl-7-oxabicyclo[4.3.0]non-9-en-8-one* (**14**). M.p. 136.5–137.0° (ether). – IR. ($CHCl_3$): 3610*w*, 3460*w*, 3040*w*, 3000*m*, 2970*m*, 2940*m*, 2880*w*, 1740*s*, 1630*m*, 1480*w S*, 1460*w*, 1440*w S*, 1390*w*, 1380*m*, 1370*w S*, 1350*w*, 1330*w*, 1315*w*, 1260*m*, 1150*m*, 1135*w*, 1110*w*, 1050*w*, 1030*m*, 1020*m*, 1000*m*, 970*s*, 935*m*, 880*w*, 865*m*. – ^{1}H-NMR. ($CDCl_3$): 1.20, 1.29 (2 *s*, 2 H_3C–C(2)); 1.53 (*s*, H_3C–C(6)); 1.74–2.10 (*m*, 2 H–C(4), 2 H–C(5)); 2.27 (*m*, HO–C(3)); 3.68 (*m*, $w_{1/2}$ = 6, H–C(3)); 5.68 (*s*, H–C(9)). – ^{13}C-NMR.: 24.2, 24.6 (3 *qa*, 2 *qa* at 24.6, 3 CH_3); 26.6, 33.5 (2 *t*, C(4), C(5)); 75.9 (*d*, C(3)); 115.3

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[8]) Based on amount of converted starting material.

[9]) Analytical samples of the photolysis products were obtained by repeated chromatography on SiO_2.

(*d*, C(9)); 41.4 (*s*, C(2)); 87.2 (*s*, C(6)); 172.3, 180.4 (2 *s*, C(1), C(8)). – MS.: 196 (66, M^+, $C_{11}H_{16}O_3$), 178 (28), 168 (24), 163 (26), 153 (72), 140 (88), 139 (45), 135 (47), 133 (81), 125 (22), 121 (20), 119 (23), 111 (23), 110 (17), 109 (20), 107 (64), 95 (19), 93 (28), 91 (33), 81 (17), 79 (21), 67 (43), 55 (22), *43* (100), 41 (42).

$C_{11}H_{16}O_3$ (196.24) Calc. C 67.32 H 8.22% Found C 67.16 H 8.15%

2.1.1.2. A solution of 15 mg (0.067 mmol) of (*E*)-**4** and 5 mg (0.018 mmol) of eicosane as an internal standard in 10 ml of CH_3CN was irradiated (quartz, lamp *A*, 66% conversion). The product yields[8]) as estimated by GC. analysis were: 55% **10** and 10% **11**.

2.1.2. *At* $\lambda \geqslant 347$ *nm.* – 2.1.2.1. *In* CH_3CN. A solution of 400 mg (1.8 mmol) of (*E*)-**4** in 150 ml of CH_3CN was irradiated (filter *A*, lamp *B*, 78% conversion). The product yields[8]) determined by ^{1}H-NMR. analysis of the fractions obtained from chromatography on SiO_2 (hexane/ether 1:2) were: 6% (*Z*)-**4**, 33% **11**, *ca.* 3% **13** and 22% **15**[9]).

5-Hydroxy-6-methyl-6-(5'-methyl-2'-furyl)-2-heptanone (**13**). – IR.: 3600*m*, 3440 br. *s*, 3100*w*, 2980*s*, 2940*s*, 2880*s*, 1765*m*, 1710*s*, 1610*m*, 1560*m S*, 1550*m*, 1540*m S*, 1460*s*, 1450*s*, 1380*s*, 1360*s*, 1280*s*, 1260*s*, 1220*s*, 1160*s*, 1110*s*, 1080*s*, 1050*s*, 1020*s*, 940*s*, 905*s*, 870*m*. – ^{1}H-NMR. (80 MHz, $CDCl_3$): 1.25 (*s*, H_3C–C(6), 3 H–C(7)); 2.13, 2.25 (2 *s*, 3 H–C(1), H_3C–C(5')); 1.4–1.9 (*m*, 2 H–C(4), HO–C(5)); 2.60 (*m* with *t*-character, 2 H–C(3)); 3.50 ($d \times d$, $J_1 = 10$, $J_2 = 2.5$, H–C(5)); 5.75–6.10 (*m* with *AB*-character, $J = 3$, $\delta_A = 5.83$, $\delta_B = 5.93$, H–C(3'), H–C(4')). – MS.: 224 (< 1, M^+, $C_{13}H_{20}O_3$), 209 (2), 206 (6), 135 (2), 125 (33), 124 (55), *123* (100), 109 (20), 83 (18), 43 (30).

1,8,8-Trimethyl-7-(2'-oxo-1'-propyl)-6-oxabicyclo[3.2.1]octan-2-one (**15**). M.p. 58.5–59.0° (pentane). – IR.: 2970*s*, 2950*m*, 2880*m*, 1720*s*, 1710*s*, 1630*w*, 1450*m*, 1410*m*, 1400*m*, 1380*m*, 1370*m*, 1355*m*, 1345*m S*, 1300*w*, 1275*w*, 1260*w*, 1245*w*, 1180*m*, 1160*m*, 1095*w*, 1080*m*, 1055*m*, 1025*m*, 975*m*, 940*w*, 920*m*. – ^{1}H-NMR.: 0.83 (*s*, 2 H_3C–C(8)); 1.11 (*s*, H_3C–C(1)); 2.10 (*s*, 3 H–C(3')); 1.70–2.35 (*m*, 2 H–C(3), 2 H–C(4), 2 H–C(1')); 3.89 (*m*, $w_{1/2} = 7$, H–C(5)); 4.26 ($d \times d$, $J_1 = 4$, $J_2 = 8$, H–C(7)). – ^{13}C-NMR.: 9.0, 19.6, 22.6, 30.7 (4 *qa*, 4 CH_3); 26.3, 35.0, 44.3 (3 *t*, C(3), C(4), C(1')); 79.5, 83.6 (2 *d*, C(5), C(7)); 45.3 (*s*, C(8)); 61.2 (*s*, C(1)); 205.8, 211.3 (2 *s*, C(2), C(2')). – MS.: 224 (8, M^+, $C_{13}H_{20}O_3$), 181 (14), 167 (20), 166 (21), 141 (23), 139 (20), 138 (13), 125 (19), 123 (32), 121 (16), 114 (21), 111 (14), 110 (26), 109 (20), 107 (11), 98 (12), 97 (13), 96 (28), 95 (20), 85 (34), 83 (11), 82 (15), 81 (18), 69 (29), *67* (20), 55 (23), 53 (10), *43* (100).

$C_{13}H_{20}O_3$ (224.29) Calc. C 69.61 H 8.99% Found C 69.47 H 8.99%

2.1.2.2. *In* CD_3CN *followed by base-treatment of the reaction mixture.* A solution of 40 mg (0.18 mmol) of (*E*)-**4** and 2 mg (0.01 mmol) of bis(trimethylsilyl)acetylene as an internal standard in 0.5 ml of CD_3CN was irradiated in a pyrex NMR. tube (filter *A*, lamp *B*, 90% conversion). The product yields estimated by ^{1}H-NMR. analysis were: 40% **11**, 20% (*E*)-**12** and 10% **15**. After stirring the photolysis mixture with *ca.* 1 mg of Na_2CO_3 for 10 min followed by filtration of the mixture, the product yields were: 42% **11**, 4% (*E*)-**12** and 32% **15**.

2.2. *Irradiation of* (*E*)-**16** *at* $\lambda \geqslant 347$ *nm.* A solution of 240 mg (1.1 mmol) of (*E*)-**16** in 150 ml of CH_3CN was irradiated (filter *A*, lamp *B*, 91% conversion). The product yields[8]) determined by ^{1}H-NMR.-analysis of the fractions obtained from chromatography on SiO_2 (hexane/ether 3:2) were: 30% **17**, 25% (*E*)-**18** and 21% (*Z*)-**18**[9]).

(3R,6S*)-[2,2,6-Trimethyl-8-oxo-7-oxabicyclo[4.3.0]non-9-en-3-yl] acetate* (**17**). M.p. 149–150° (ether). – IR. ($CHCl_3$): 3030*w*, 2990*w*, 2940*w*, 2870*w*, 2850*w S*, 1735*s*, 1630*w*, 1475*w*, 1465*w S*, 1450*w*, 1435*w S*, 1390*w*, 1375*m*, 1345*w*, 1335*w*, 1170*w*, 1155*w*, 1125*w*, 1110*m*, 1055*w*, 1020*m*, 995*m*, 975*m*, 965*m*, 955*w*, 945*w*, 930*w*, 900*w*, 880*w*, 860*m*. – ^{1}H-NMR.: 1.19, 1.28 (2 *s*, 2 H_3C–C(2)); 1.53 (*s*, H_3C–C(6)); 1.96 (*s*, H_3C–COO); 1.80–2.18 (*m*, 2 H–C(4), 2 H–C(5)); 4.74–4.88 (*m*, H–C(3)); 5.58 (*s*, H–C(9)). – MS.: 196 (78, $M^+ - 42$), 178 (12), 163 (10), 153 (24), 149 (11), 140 (32), 139 (11), 135 (17), 133 (28), 107 (17), 91 (10), 67 (17), *43* (100), 41 (21).

$C_{13}H_{18}O_4$ (238.27) Calc. C 65.53 H 7.61% Found C 65.47 H 7.71%

(1'E,1R,3R*)-[3-(3'-Oxo-1'-butenyl)-2,2,3-trimethyl-4-oxocyclohexyl] acetate* ((*E*)-**18**). B.p. 110°/0.03 Torr. – UV. (0.214 mg in 10 ml): 217 (11100). – IR.: 2980*m S*, 2970*m*, 2950*m S*, 2880*w*, 1740*s*, 1715*s*, 1700*m*, 1680*m*, 1610*m*, 1455 br. *w*, 1425*w*, 1395*w*, 1375*m*, 1360*m*, 1310*w S*, 1295*w*, 1230*s*, 1175*m*, 1150*w*, 1055*w*, 1040*m*, 1030*m*, 1020*m*, 990*w*, 945*w*, 935*w*, 910*m*. – ^{1}H-NMR. (90% pure): 0.88, 0.98, 1.18 (3 *s*, 2 H_3C–C(2), H_3C–C(3)); 2.06, 2.17 (2 *s*, 3 H–C(4'), H_3C–COO); 1.80–2.70 (*m*, 2 H–C(5),

2 H–C(6)); 4.95 ($d \times d$, $J_1 = 4$, $J_2 = 6$, H–C(1)); 6.59 (*AB*-system, $J = 16$, $\delta_A = 5.86$, $\delta_B = 7.32$, H–C(1'), H–C(2')). – MS.: 266 (1, M^+, $C_{15}H_{22}O_4$), 224 (28), 196 (13), 181 (23), 163 (10), 149 (14), 140 (13), 139 (97), 135 (11), 123 (20), 121 (24), 109 (11), 98 (26), 97 (28), *43* (100).

(1'Z,1R,3R*)-[3-(3'-Oxo-1'-butenyl)-2,2,3-trimethyl-4-oxocyclohexyl] acetate* ((*Z*)-**18**). B.p. 105°/0.03 Torr. – UV. (0.467 mg in 10 ml): 218 (6090). – IR.: 3030*w S*, 2980*m*, 2950*m*, 2880*w*, 1735*s*, 1720*s*, 1700*s*, 1680*m*, 1630*w S*, 1615*w S*, 1610*m*, 1465*m S*, 1455*m*, 1430*m*, 1390*m*, 1370*s*, 1355*m*, 1320*w*, 1300*w*, 1240*s*, 1175*s*, 1080*m*, 1060*m*, 1025*s*, 965*m*, 945*w*, 900*w*, 890*w*. – ^{1}H-NMR. (*ca.* 80% pure): 0.92 (*s*, 2 H_3C–C(2)); 1.36 (*s*, H_3C–C(3)); 2.00, 2.11 (2 *s*, 3 H–C(4'), H_3C–COO); 1.80–2.60 (*m*, 2 H–C(5), 2 H–C(6)); 5.01 ($d \times d$, $J_1 = 4$, $J_2 = 8$, H–C(1)); 6.02 (*AB*-system, $J = 13$, $\delta_A = 5.93$, $\delta_B = 6.11$, H–C(1'), H–C(2')). – MS.: 266 (2, M^+, $C_{15}H_{22}O_4$), 224 (20), 196 (18), 181 (22), 163 (13), 149 (16), 140 (13), 139 (70), 135 (18), 125 (10), 123 (20), 122 (13), 121 (22), 109 (14), 107 (11), 97 (23), 96 (33), 95 (15), *43* (100), 41 (16).

3. Additional experiments. – 3.1. *Oxidation of* **11**. A solution of 100 mg (0.45 mmol) of **11** in 5 ml of ether was stirred under O_2 for 3 h. Chromatography of the mixture on SiO_2 afforded 75 mg (84%) of **14**.

3.2. *Transformation of* **10** *into* **21**. – 3.2.1. *Hydrolysis of* **10**. To a solution of 55 mg (0.25 mmol) of **10** in 20 ml of ether was added 5 ml of aq. 1N HCl. After stirring for 3 h at RT., sat. aq. $NaHCO_3$ was added, and the mixture was worked up in ether to give 47 mg (79%) of *7-hydroxy-6,6-dimethylundecan-2,5,10-trione* (**20**) (*ca.* 80% pure) which was oxidized without further purification.

3.2.2. *Oxidation of* **20**. A solution of 47 mg (0.19 mmol) of **20** in 6 ml of dry CH_2Cl_2 was added dropwise to a mixture of 200 mg (0.93 mmol) of PCC [10] in 6 ml of dry CH_2Cl_2. After stirring for 6 h, the mixture was worked up by filtration through *Celite* and chromatographed on SiO_2 to give 15 mg (34%) of **21**.

6,6-Dimethylundecan-2,5,7,10-tetraone (**21**). – UV. (1.618 mg in 2 ml): 283 (157). – IR.: 2990*w S*, 2970*m*, 2930*m S*, 2910*m*, 2870*w S*, 2850*w S*, 1715*s*, 1700*s*, 1465*m*, 1455*m S*, 1395*m*, 1385*m S*, 1365*s*, 1355*s*, 1305 br. *w*, 1225*w S*, 1200*w S*, 1180*m*, 1160*m*, 1090*m*, 1070*m*, 1015*m S*, 1005*m S*, 995*m*, 970*w*, 950*w S*. – ^{1}H-NMR.: 1.32 (*s*, 2 H_3C–C(6)); 2.10 (*s*, 3 H–C(1), 3 H–C(11)); 2.57 (*s*, 2 H–C(3), 2 H–C(4), 2 H–C(8), 2 H–C(9)). – ^{13}C-NMR.: 21.6, 29.8 (2 *qa*, 2 H_3C–C(6), C(1), C(11)); 32.2, 37.0 (2 *t*, C(3), C(4), C(8), C(9)); 61.8 (*s*, C(6)); 207.0, 208.5 (2 *s*, C(2), C(5), C(7), C(10)). – MS.: 240 (< 1, M^+, $C_{13}H_{20}O_4$), 142 (25), 105 (12), *99* (100), 71 (20), 43 (45).

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