162. Photochemical Reactions

146th Communication[1])

Photochemistry of Conjugated Methano-Epoxydienes: Participation of the Neighboring Cyclopropane Ring in Product Formation *via* Carbonyl Ylide and Carbene Intermediates

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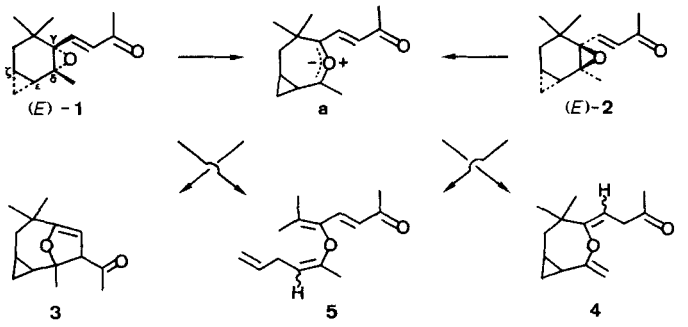
On singlet excitation (λ = 254 nm, THF, pentane or hexane), the diastereoisomeric methano-epoxydienes (*E*)-**6** and (*E*)-**7** undergo interconversion and yield the products **8**–**11**. The main process is the cleavage of the oxirane ring to the vinyl carbene intermediate **e** which undergoes addition to the adjacent double bond furnishing the cyclopropene **8**. The alternative carbene intermediate **f** is evidenced by the formation of the cyclobutene **10**. For the fragmentation leading to **11**, the carbene **f** as well as the dipolar species **h** are considered as possible intermediates. On triplet sensitization (acetone, $\lambda > 280$ nm), (*E*)-**7** shows behavior typical of epoxydienes, undergoing fission of the C–O bond of the oxirane ring and isomerization to the compounds **13**, **14** and (*E*/*Z*)-**15**.

1. Introduction. – Previously, we have shown that, on π,π^*-excitation of the methano-epoxyenones (*E*)-**1** and (*E*)-**2**, the main reaction is cleavage of the C–C bond of the oxirane ring leading to the carbonyl-ylide intermediate **a** *(Scheme 1)* [2]. The latter is transformed to compounds **3** and **4**, it does not, however, undergo ring closure to the epoxides (*E*)-**1** and (*E*)-**2**. As an additional product, which is most likely not formed *via* the ylide **a**, the acyclic compound **5** was obtained. On the other hand, products arising *via*

Scheme 1



[1]) 145th Communication: [1].

[2]) Taken in part from the Ph. D. thesis of *N.B.*, Diss. ETHZ No. 7422 (1983).

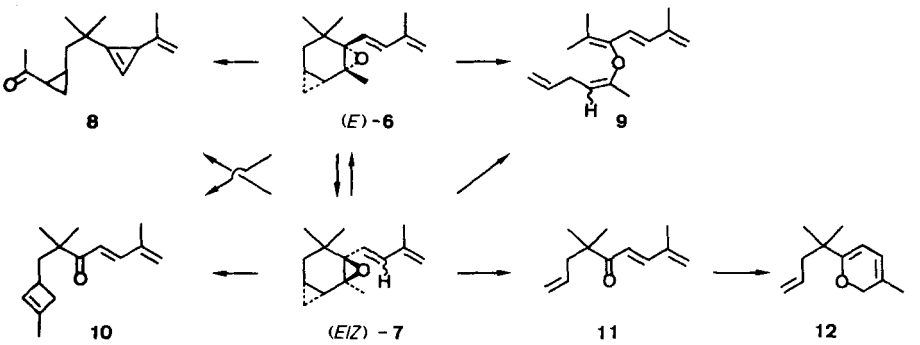
a carbene intermediate, which were normally formed on π,π^*-excitation of epoxyenones [3] [4] could not be detected. Since epoxydienes are known to undergo preferentially isomerizations *via* carbene intermediates [5] [6], the behavior of the epoxydienes (*E*)-**6** and (*E*)-**7**[3] *(Scheme 2)* was investigated. In particular, it was expected that the results of the singlet excitation of (*E*)-**6** and (*E*)-**7** could give some information on the reactivity of a photochemically generated carbene next to the cyclopropane.

Table. *Results of the Singlet Excitation of* (E)-**6** *and* (E)-**7** *(λ = 254 nm)*

Substrate	Solvent	Conversion [%]	Product Distribution [%][a]							
			(*E*)-**6**	(*E*)-**7**	(*Z*)-**7**	**8**	**9**	**10**	**11**	**12**
(*E*)-**6**	Hexane	73	–	13	–	44	10	3	–	–
(*E*)-**6**	THF	68	–	10	–	41	16	3	–	–
(*E*)-**7**	Pentane	70	2	–	11	28	–	–	4	4
(*E*)-**7**	THF	68	2	–	8	24	3	2	7	6

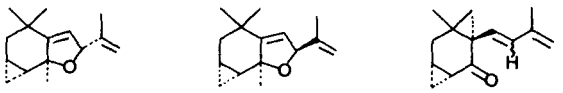
[a]) Yields were determined after chromatography on SiO_2 by ^{1}H-NMR and GC analysis of the fractions and are based on converted starting material.

Scheme 2



2. Photolyses. – 2.1. *Singlet Excitation of* (E)-**6** *and* (E)-**7** (λ = 254 mm). The results are given in the *Table* and the photoproducts are depicted in *Scheme 2*.

2.2. *Triplet-Sensitized Excitation of* (E)-**7** (λ > 280 mm, acetone, 87% conversion) gave (*Z*)-**7** (3%), **13** (5%), **14** (3%), (*E*)-**15** (7%), and (*Z*)-**15** (20%).

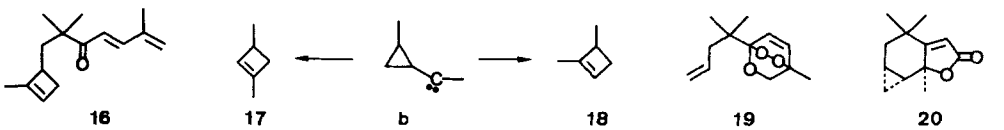


3. Structures of the Photoproducts. – *Epoxydiene* (Z)-**7**, *Cyclopropene* **8**, and *Divinyl Ether* **9** *(Scheme 2)*. The structures of these compounds were assigned by comparison of their spectral data (see *Exper. Part*) with those of analogous compounds previously obtained [2] [5] [6]. Furthermore, **9** was obtained from the corresponding ketone **5** *(Scheme 1)* by reaction with methylidenetriphenylphosphorane.

[3]) Compounds (*E*)-**6** and (*E*)-**7** were obtained by reaction of (*E*)-**1** and (*E*)-**2** with methylidenetriphenylphosphorane in 97 and 91% yield.

Cyclobutene **10** *(Scheme 2)*. The dienone moiety is evidenced, in particular, by the UV maximum at $\lambda = 262$ nm ($\varepsilon = 20000$) and the IR bands at 1680, 1611, and 1591 cm^{-1}. In the ^{1}H-NMR spectrum, the diastereotopic H-atoms of the CH_2 group neighboring the cyclobutene ring give rise to an *AB* system ($\delta = 1.73$ ppm, $J = 14$ Hz) which is further split to 2*d* ($J = 7.5$ and 7.0 Hz, resp.) by coupling with the cyclobutene H–C(3') (*m*, 1.90–1.97 ppm). In the ^{13}C-NMR spectrum, a *s* (144.5 ppm), 2*d* (35.9 and 132.3 ppm), and a *t* (40.1 or 44.6 ppm) were assigned to the cyclobutene moiety. However, the position of the CH_3 group at the cyclobutene double bond could not be determined on the basis of the spectral data; therefore, as alternative structure, the isomeric cyclobutene **16** *(Scheme 3)* had to be considered. Due to the availability of only small amounts of **10**, unfortunately, a chemical transformation proving the structure (*e.g.* thermal cleavage of the cyclobutene moiety to a cyclobutadiene) could not be performed. Therefore, the positions of the cyclobutene substituents were tentatively assigned on the basis of the known regioselectivity of the carbene-insertion reaction into cyclopropanes. Thus, from carbene **b** *(Scheme 3)*, as predominant product, **17** was formed by migration of the less substituted bond of the cyclopropane ring (**17**/**18** *ca.* 95:5) [7].

Scheme 3



Dienone **11** *and 2*H*-Pyran* **12** *(Scheme 2)*. The structure of **11** is assigned unequivocally from the spectral data (see *Exper. Part*). It was observed previously, that 2*H*-pyrans of type **12** are rather labile [6]. Therefore, **12** was transformed by reaction with $^1O_2$ to the more stable endoperoxide **19** *(Scheme 3)* which showed spectral data (see *Exper. Part*) analogous to a similar compound [6].

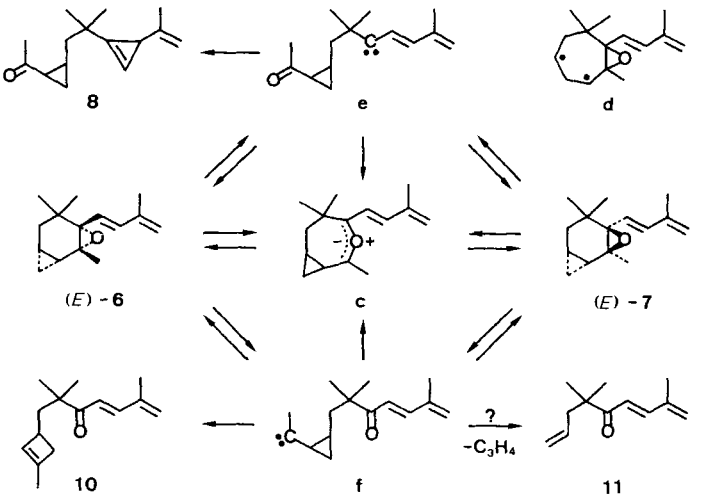
Dihydrofurans **13** *and* **14**, *and Cyclohexanones* (E/Z)-**15**. Their structure and relative configuration were assigned by comparison of the spectral data with that of previously obtained analogs, either which an oxirane instead of the cyclopropane [6] or without a cyclopropane moiety [5]. Finally, the diastereoisomeric dihydrofurans **13** and **14** were transformed to the lactone **20** *(Scheme 3)* by oxidation with NiO_2 [8].

4. Discussion. – Comparison of the products of the π,π^*-excitation ($\lambda = 254$ nm) of (*E*)-**1** and (*E*)-**2** with that of the singlet excitation ($\lambda = 254$ nm) of (*E*)-**6** and (*E*)-**7** shows only the acyclic divinyl ethers **5** *(Scheme 1)* and **9** *(Scheme 2)* as common product types. Like the formation of **5**, that of **9** depends on the solvent (see [2] and the *Table*). Therefore, it is assumed that the formation of both products involves the same mechanism, the details of which is still open for discussion [2]. On the other hand, it is most surprising that the epoxydienes (*E*)-**6** and (*E*)-**7** undergo interconversion, which could not be observed with the corresponding epoxyenones (*E*)-**1** and (*E*)-**2**. It was shown previously, that the interconversion of diastereoisomeric epoxides occurs *via* cleavage of the C–C bond of the oxirane ring [9] [10]. Therefore, the carbonyl ylide **c** *(Scheme 4)* would be a plausible intermediate for the interconversion of (*E*)-**6** and (*E*)-**7**. However, by laser flash photolysis of (*E*)-**6** or by photolysis at 77 K, a transient absorption corresponding to **c** could not be detected. This finding indicates that, if the ylide **c** was formed, its lifetime would be beyond the time resolution of the laser system (*ca.* 20 ns)[4]). Another possibility for the interconversion of the diastereoisomeric epoxydienes, which cannot be excluded, may involve the diradical intermediate **d** *(Scheme 4)* arising from C–C cleavage of the cyclopropane ring[5]). Since, on singlet excitation of epoxydienes in general, the formation of carbene intermediates prevails over the generation of carbonyl ylides [5] [6], a further possibility for the interconversion of (*E*)-**6** and (*E*)-**7** is *via* the

[4]) The ylide **a**, derived from (*E*)-**1**, was shown to be rather long-lived (2.7 μs in Et_2O and 10 μs in MeCN) as compared to ylides formed from analogous epoxyenones in the ionone series [11].

[5]) For the photolytic interconversion of diastereoisomeric vinylcyclopropanes, see [12].

Scheme 4



carbenes **e** and **f**, respectively *(Scheme 4)*. Thus, the two carbene intermediates could undergo a cycloaddition to the carbonyl group giving back both diastereoisomeric epoxydienes (*E*)-**6** and (*E*)-**7**, either directly or *via* the carbonyl-ylide intermediate **c**, finally undergoing rapid ring closure to the oxiranes[6]).

As it is typical of epoxydienes, the main reaction of singlet excitation of (*E*)-**6** and (*E*)-**7** is cleavage to the vinyl-carbene intermediate **e** *(Scheme 4)*, which reacts to the cyclopropene **8** (see the *Table*). Sound evidence for the intermediacy of the alternative carbene **f** is the formation of the cyclobutene **10**, which arises by insertion of the carbene center into the adjacent, less substituted cyclopropane C–C bond (see above). As well as this ring enlargement of α-cyclopropyl carbenes which is ubiquitous, in some cases, fragmentation to an ethylene and an acetylene moiety is known to take place[7]). Therefore, it could be assumed that **f** is also the precursor of **11**, formed by fragmentation with loss of propyne; **12** is then a secondary product of **11**. However, the fragmentation product **11** is only formed from (*E*)-**7**, whereas the cyclobutene **10** arises from either (*E*)-**6** or (*E*)-**7**[8]). These findings could indicate that **10** and **11** may not arise from the same carbene intermediate **f**, otherwise these products would be formed in the same ratio. As a feasible hypothesis for this behavior of (*E*)-**6** and (*E*)-**7**, the formation of the carbene **f** in a singlet and a triplet state could be considered, both states showing different reactivity[9]). Furthermore, on the basis of models, the difference in reactivity of (*E*)-**6** and (*E*)-**7** could also be explained by two different conformers of **f**. Thus, it could be assumed that from (*E*)-**7**, the carbene **f** is formed in a conformation, prone to undergo fragmentation to **11**. On the

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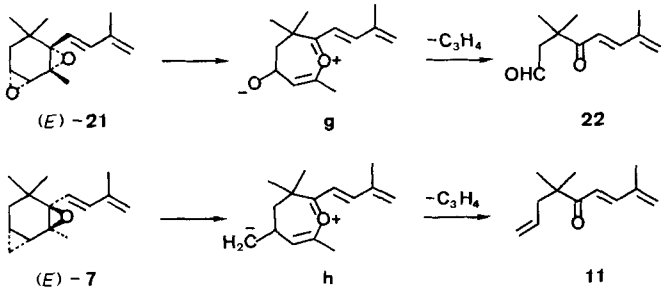
[6]) It was shown previously that the reaction of carbenes with carbonyl compounds led to oxiranes [13] or to carbonyl ylides [14–16].

[7]) For reviews on the reactivity of α-cyclopropyl carbenes, see [17] [18]; for a theoretical interpretation, see [19].

[8]) The diastereoisomeric methano-epoxydienes being interconvertible, it was necessary to follow the course of the reaction (λ = 254 nm, THF) and determine the yield of **10** by extrapolation to a conversion of 0%. By this method, it was shown that **10** is formed in 8% yield from (*E*)-**6** and in 3% yield from (*E*)-**7** (GC).

[9]) For discussions of α-cyclopropyl-carbene rearrangements and fragmentations considering singlet and triplet states of carbenes, see *e.g.* [20] [21].

Scheme 5

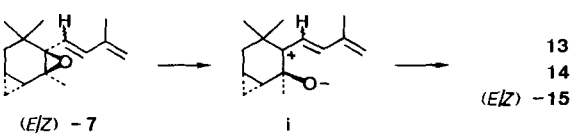


other hand, by subsequent rotation around the C–C bond between the carbene center and the cyclopropyl moiety, a second conformer of **f** could arise, which would be directly formed from (*E*)-**6** undergoing insertion into the adjacent cyclopropane ring (**f**→**10**). In the latter case, it would have to be assumed that the carbene-insertion reaction is apparently faster than the bond rotation.

Finally, it may well be possible, that only **10** arises from a carbene intermediate, and fragmentation to **11** occurs *via* a different mechanism. It is noteworthy that a process which is related to the transformation of (*E*)-**7**→**11** was found on photolysis of the diepoxydiene (*E*)-**21**. Thus, in addition to rearrangements *via* carbonyl-ylide and carbene intermediates, (*E*)-**21** undergoes fragmentation to the keto-aldehyde **22** and propyne, presumably *via* the dipolar intermediate **g** *(Scheme 5)* [6]. In analogy to this transformation, it may be suggested that (*E*)-**7** is cleaved to the dipolar intermediate **h**. Subsequent fragmentation with loss of propyne would lead to **11**[10]). Support for this latter mechanism and an explanation for the different reactivity of (*E*)-**6** and (*E*)-**7** may be obtained by the inspection of models. Only (*E*)-**7** seems to fulfil the stereoelectronic requirements – namely the *trans*-antiparallel arrangement of the oxirane C–C bond and the adjacent, less substituted cyclopropane C–C bond – which may be necessary for a straightforward cleavage leading to **h**. On the basis of the present results, neither one of the above discussed mechanisms for the formation of **11** may be favored and further investigations will be necessary to provide conclusive evidence.

Concluding the discussion, it may be noted that on triplet sensitization ($\lambda > 280$ nm, acetone), (*E*)-**7** shows behavior typical of epoxydienes [5] [6] undergoing cleavage of the C–O bond of the oxirane to **i** and formation of the known types of compounds **13**, **14** and (*E*/*Z*)-**15** *(Scheme 6)*.

Scheme 6



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

[10]) A similar fragmentation of α-cyclopropyl-tosylhydrazones passing through a non-carbenoid intermediate was reported by *Ohloff* and *Pickenhagen* [22].

Experimental Part

General. See [23], except as noted below. Anal. GC was performed using a 25 m × 0.33 mm *Ucon HB-5100* glass capillary. Column chromatographies (CC) were carried out on silica gel (SiO_2) 60 *Merck*, 0.040–0.063 mm, 230–400 mesh ASTM. Anal. pure samples were obtained, in general, after repeated CC, in some cases further purification was necessary on HPLC (*Du Pont Instruments Model 830*, UV detector), using a 25 cm × 23.6 mm SiO_2 column, or by prep. GC. ^{1}H-NMR spectra were taken in $CDCl_3$ soln. on a *Bruker-WP-80/CW* instrument (80 MHz) or exceptionally (as noted below) on a *Bruker WM-300* instrument (300 MHz).

1. Preparations of (*E*)-6 and (*E*)-7. *a*) A soln. of methylidenetriphenylphosphorane (*ca.* 0.2M) in THF was added dropwise to a soln. of (*E*)-**1** [2] (3.22 g, 14.6 mmol) in Et_2O (100 ml) until all starting material was consumed (TLC control). The mixture was diluted with pentane (*ca.* 600 ml) and filtered through SiO_2. Removal of the solvents and distillation of the residue (70°/0.03 Torr) yielded (*E*)-**6** (3.11 g, 97%). *b*) Analogous treatment of (*E*)-**2** [2] (4.57 g, 20.8 mmol) afforded (*E*)-**7** (4.11 g, 91%).

(E,1'RS,2'RS,4'SR,7'SR)-1-(2',5',5'-Trimethyl-3'-oxatricyclo[5.1.0.0^{2,4}]oct-4'yl)-3-methyl-1,3-butadiene ((*E*)-**6**). B.p. 65°/0.04 Torr. UV (0.0944 mg in 10 ml): 236 (25,000). IR: 3080*m*, 3010*s*, 3000*s*, 2960*s*, 2938*s*, 2920*s*, 2900*m* (sh), 2869*s*, 2850*m*, 1780*w* (br.), 1605*s*, 1467*m*, 1455*m*, 1450*s*, 1434*m*, 1388*s*, 1372*s*, 1361*s*, 1312*w*, 1288*w*, 1259*m*, 1200*w*, 1180*m*, 1172*w* (sh), 1137*m*, 1106*w*, 1093*w* (sh), 1084*m*, 1050*m*, 1031*m*, 1028*m*, 1005*w* (sh), 970*s*, 952*m*, 944*m*, 919*w*, 903*s*, 888*s*, 871*m*, 845*m*. ^{1}H-NMR: 0.82, 1.15, 1.35 (3*s*, CH_3–C(2'), 2 CH_3–C(5')); 0.30–0.50 (1 H) and 0.50–2.37 (5 H) (2*m*, H–C(1'), 2 H–C(6'), H–C(7'), 2 H–C(8')); 1.88 (*m*, $w_{1/2}$ = 2, CH_3–C(3)), 4.96 (*m*, $w_{1/2}$ = 2.5, 2 H–C(4)); 6.04 (*AB* system, J = 16, δ_A = 5.80, δ_B = 6.28, H–C(1), H–C(2)). ^{13}C-NMR: 18.6, 20.0, 23.5, 27.0 (4*q*, 4 CH_3); 9.8 (*t*, C(8')); 35.7 (*t*, C(6')); 116.2 (*t*, C(4)); 4.9, 13.1 (2*d*, C(1'), C(7')); 123.9, 135.2 (2*d*, C(1), C(2)); 35,4 (*s*, C(5')); 63.4, 70.5 (2*s*, C(2'), C(4')); 141.0 (*s*, C(3)). MS: 218 (11, M^+, $C_{15}H_{22}O$), 203 (22), 177 (16), 175 (12), 162 (36), 161 (26), 159 (11), 147 (40), 145 (20), 135 (15), 134 (15), 133 (25), 131 (10), 123 (36), 121 (45), 120 (18), 119 (90), 117 (13), 109 (12), 108 (15), 107 (46), 106 (26), *105* (100), 95 (24), 93 (35), 91 (55), 81 (23), 80 (11), 79 (38), 77 (35), 69 (15), 67 (35), 65 (19), 57 (11), 55 (33), 53 (22), 51 (12), 43 (61), 41 (86), 39 (36). Anal. calc. for $C_{15}H_{22}O$ (218.33): C 82.52, H 10.16; found: C 82.99, H 10.03.

(E,1'RS,2'SR,4'RS,7'SR)-1-(2',5',5'-Trimethyl-3'-oxatricyclo[5.1.0.0^{2,4}]oct-4'-yl)-3-methyl-1,3-butadiene ((*E*)-**7**). B.p. 75°/0.04 Torr. UV (0.707 mg in 50 ml): 232 (23,000). IR: 3085*m*, 3005*s*, 2962*s*, 2934*s*, 2920*s*, 2875*m*, 2850*m*, 1780*w* (br.), 1606*m*, 1466*m*, 1449*m*, 1435*m*, 1400*m*, 1380*m* (sh), 1373*m*, 1362*m*, 1343*w*, 1312*w*, 1288*w*, 1255*w*, 1244*w*, 1204*m*, 1195*w*, 1155*w*, 1140*w*, 1099*w*, 1072*w*, 1038*w*, 1018*m*, 998*w*, 972*s*, 925*w*, 913*m*, 890*s*, 847*w*, 835*w*. ^{1}H-NMR: 0.52–2.35 (*m*, H–C(1'), 2 H–C(6'), H–C(7'), 2 H–C(8')); 0.97, 1.17, 1.36 (3*s*, CH_3–C(2'), 2 CH_3–C(5')); 1.88 (*m*, $w_{1/2}$ = 2.5, CH_3–C(3)); 5.20 (*m*, $w_{1/2}$ = 2.5, 2 H–C(4)); 6.04 (*AB* system, J = 16, δ_A = 5.76, δ_B = 6.32, H–C(1), H–C(2)). ^{13}C-NMR: 18.6, 20.0, 28.1, 28.9 (4*q*, 4 CH_3); 9.6 (*t*, C(8')); 34.3 (*t*, C(6')); 116.5 (*t*, C(4)); 11.5, 15.4 (2*d*, C(1'), C(7')); 127.5, 135.9 (2*d*, C(1), C(2)); 33.2 (*s*, C(5')); 67.4, 70.2 (2*s*, C(2'), C(4')); 140.8 (*s*, C(3)). MS: 218 (6, M^+, $C_{15}H_{22}O$), 203 (15), 177 (12), 162 (25), 161 (22), 147 (33), 145 (16), 135 (11), 134 (15), 133 (22), 123 (25), 121 (40), 120 (16), 119 (86), 117 (12), 108 (13), 107 (42), 106 (25), *105* (100), 95 (21), 93 (35), 92 (15), 91 (60), 81 (20), 80 (11), 79 (41), 78 (10), 77 (36), 69 (14), 67 (31), 65 (19), 55 (32). Anal. calc. for $C_{15}H_{22}O$ (218.33): C 82.52, H 10.16; found: C 82.28, H 10.34.

2. Photolysis Experiments. – 2.1. *Irradiation of* (E)-**6** *at* λ = 254 nm. – 2.1.1. *In Hexane.* A soln. of (*E*)-**6** (2.36 g, 10.8 mmol) in hexane (200 ml) was irradiated (Hg low-pressure lamp [23], quartz; 73% conversion). CC (Et_2O/hexane 1:10) afforded several fractions from which the following product distribution was determined (GC, ^{1}H-NMR)[11]): (*E*)-**7** (13%), **8** (44%), **9** (10%), and **10** (3%).

2-{[2'-(3"-Isopropenyl-1"-cyclopropenyl)-2'-methyl]propyl}cyclopropyl Methyl Ketone (**8**). B.p. 100°/0.1 Torr. UV (0.316 mg in 10 ml): 235 sh (2700). UV (0.570 mg in 5 ml): end absorption to 380. IR: 3078*m*, 3030*w*, 3000*m*, 2965*s*, 2910*s*, 2870*m*, 1765*m*, 1700*s* (sh), 1695*s*, 1631*m*, 1465*m*, 1458*m*, 1448*m*, 1435*m* (br.), 1395*s*, 1381*s*, 1370*m*, 1361*m*, 1349*m*, 1320*w*, 1291*w*, 1280*w*, 1245*w*, 1208*w*, 1165*s*, 1125*w*, 1095*w*, 1080*w*, 1070*w*, 1049*w*, 1023*m*, 990*m*, 970*m*, 965*m*, 955*m*, 914*m*, 896*w*, 873*s*. ^{1}H-NMR: 1.12 (*s*, 3 H–C(3'), CH_3–C(2')); 0.80–2.20 (*m*, H–C(1), H–C(2), 2 H–C(3), 2 H–C(1')); 1.51 (*m*, $w_{1/2}$ = 3, CH_3C=CH_2); 2.24 (*d*, J = 1.5, H–C(3")); 2.26 (*s*, CH_3CO); 4.70, 4.76 (2*m*, $w_{1/2}$ = 5, CH_2=CCH_3); 6.55 (*d*, J = 1.5, H–C(2")). ^{13}C-NMR (mixture of two diastereoisomers): 25.7–26.4 (several unresolved signals); 20.0, 32.1 (2*q*, 2 CH_3); 14.9, 15.1 (2*t*, C(3)); 36.9, 37.0, (2*t*, C(1')); 107.2 (*t*, CH_2=CCH_3); 21.4 (*d*, C(1)); 100.1 (*d*, C(2")); 35.4 (*s*, C(2')); 131.9, 150.2 (2*s*, C(1"), CH_2=CCH_3); 206.5 (*s*, CO). MS: 218 (8, M^+, $C_{15}H_{22}O$); 160 (11), 147 (25), 145 (39), 133 (24), 122 (10), 121 (86), 120 (14), 119 (47), 117 (11), 107

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

(24), 106 (14), 105 (66), 93 (22), 91 (48), 81 (15), 79 (27), 77 (30), 71 (17), 67 (11), 65 (12), 55 (24), 53 (18), *43* (100), 41 (44), 39 (25). Anal. calc. for $C_{15}H_{22}O$ (218.33): C 82.52, H 10.16; found: C 82.48, H 10.27.

(3E)-5-Isopropylidene-2,7-dimethyl-6-oxa-1,3,7,10-undecatetraene (**9**). B.p. 70°/0.03 Torr. UV (0.225 mg in 25 ml): 274 (28,000). IR: 3080*m*, 3060*m*, 2980*m* (sh), 2972*m*, 2940*m* (sh), 2918*s*, 2850*m*, 1775*w* (br.), 1678*m*, 1635*m*, 1615*w*, 1588*w*, 1450*m*, 1432*m*, 1376*s*, 1329*m*, 1315*m*, 1305*m*, 1295*m*, 1262*s*, 1233*m*, 1190*s*, 1158*m*, 1112*m*, 1070*m*, 1020*w*, 990*m*, 970*m*, 960*s*, 909*s*, 888*s*, 952*w*. ^{1}H-NMR: 1.67, 1.75, 1.83 and 1.90 (4*m*, $w_{1/2} \approx 2.5$, CH_3–C(2), 2 CH_3–C=C(5), CH_3–C(7)); 2.97 (*dd*, $J_1 = 7$, $J_2 \approx 7$, with fine structure, 2 H–C(9)); 4.43 (br. *t*, $J = 7$, H–C(8)); 4.87–5.13, 5.17–5.27 (2*m*, 2 H–C(11)); 5.00 (*m*, $w_{1/2} = 3$, partially overlapping with *m* at 4.87–5.13, 2 H–C(1)); 5.65–6.20 (*m*, H–C(10)); 6.15 (*s*, H–C(3), H–C(4)). ^{13}C-NMR (75 MHz; +1 drop of Et_3N): 17.5, 18.6, 18.7 (4*q*, presumably 2*q* overlapping at 18.6, 4 CH_3); 29.1 (*t*, C(9)); 113.8, 117.1 (2*t*, C(1), C(11)); 102.3 (*d*, C(8)); 121.4, 130.5, 137.8 (3*d*, C(3), C(4), C(10)); 123.3 (*s*, *C*=C(5)); 141.8, 143.8, 150.3 (3*s*, C(2), C(5), C(7)). MS: 218 (18, M^+, $C_{15}H_{22}O$), 177 (11), 147 (14), 133 (13), 123 (39), 121 (47), 119 (27), 109 (12), 107 (28), 106 (30), *105* (100), 95 (21), 93 (26), 91 (38), 81 (18), 79 (36), 77 (32), 69 (10), 67 (22), 65 (11), 55 (22), 53 (24), 43 (69), 41 (63), 39 (31). Anal. calc. for $C_{15}H_{22}O$ (218.33): C 82.52, H 10.16; found: C 82.50, H 10.20.

1-(3'-Methyl-2'-cyclobutenyl)-2,2,6-trimethyl-4,6-heptadien-3-one (**10**). B.p. 75°/0.03 Torr. UV (0.359 mg in 25 ml): 262 (20000). UV (1.114 mg in 5 ml): 340 (70), end absorption to 390. IR: 3085*w*, 3060*w*, 3035*w*, 2962*s*, 2930*s*, 2910*s*, 2870*m*, 2850*m*, 2830*m*, 1813*w*, 1680*s*, 1636*m*, 1611*s*, 1591*s*, 1467*m*, 1445m (sh), 1440*m*, (sh), 1435*m*, 1382*m*, 1372*m*, 1363*m*, 1349*w*, 1320*m*, 1310*w* (sh), 1277*m*, 1265*m*, 1250*s*, 1182*w*, 1100*w* (sh), 1095*m*, 1062*s*, 1022*w*, 1018*w*, 1010*w*, 981*s*, 935*w*, 905*s*, 890*w*, 878*w*, 859*m*, 845*w*. ^{1}H-NMR (300 MHz): 1.16 (*s*, 2 CH_3–C(2)); 1.64 (*m*, $w_{1/2} = 4$, CH_3–C(3')); 1.73 (*AB* system, $J = 14$, $\delta_A = 1.70$, split into *d*, $J = 7.5$, $\delta_B = 1.76$, split into *d*, $J = 7.0$, 2 H–C(1)); 1.91 (*m*, $w_{1/2} = 3$, CH_3–C(6)); 1.90–1.97 (*m*, H–C(1')); 2.50–2.62 (*m*, 2 H–C(4')); 5.35, 5.39 (2*m*, $w_{1/2} = 5$, 2 H–C(7)); 5.64 (*m*, $w_{1/2} = 4.5$, H–C(2')); 6.92 (*AB* system, $J = 15.4$, $\delta_A = 6.52$, $\delta_B = 7.31$, H–C(4), H–C(5)). ^{13}C-NMR: (75 MHz; *ca.* 90% pure): 16.7 (*q*, *C*H_3–C(3')); 18.2 (*q*, *C*H_3–C(6)); 24.2, 24.6, (2*q*, 2 *C*H_3–C(2)); 40.1, 44.6 (2*t*, C(1), C(4')); 124.7 (*t*, C(7)); 35.9 (*d*, C(1')); 121.5 (*d*, C(4)); 132.3 (*d*, C(2')); 144.8 (*d*, C(5)); 47.0 (*s*, C(2)); 140.9 (*s*, C(6)); 144.5 (*s*, C(3')); 204.5 (*s*, C(3)). MS: 218 (32, M^+, $C_{15}H_{22}O$), 203 (11), 175 (14), 147 (6), 137 (25), 135 (12), 134 (33), 133 (16), 123 (65), 122 (11), 121 (12), 120 (10), 119 (58), 109 (17), 108 (13), 107 (34), 106 (12), 105 (37), 96 (18), *95* (100), 93 (34), 92 (19), 91 (36) 81 (84), 79 (27), 77 (27), 69 (14), 67 (62), 65 (18), 55 (31), 53 (23), 43 (33), 41 (90), 39 (38). Anal. calc. for $C_{15}H_{22}O$ (218.33): C 82.52, H 10.16; found: C 82.51 H 10.24.

2.1.2. *In THF.* A soln. of (*E*)-**6** (990 mg, 4.54 mmol) in THF (90 ml) was irradiated and worked up as described in *Sect. 2.1.1* (68% conversion); the following product distribution was determined[11]): (*E*)-**7** (10%), **8** (41%), **9** (16%), and **10** (3%).

2.2. *Irradiation of (*E*)-***7*** at λ = 254 nm.* – 2.2.1. *In Pentane.* A soln. of (*E*)-**7** (1.47 g, 6.72 mmol) in pentane (100 ml) was irradiated and worked up as described in *Sect. 2.1.1* (70% conversion); the following product distribution was determined[11]): (*E*)-**6** (2%), (*Z*)-**7** (11%), **8** (28%), **11** (4%), and **12** (4%).

(Z,1'RS,2'SR,4'RS,7'SR)-1-(2',5',5'-Trimethyl-3'-oxabicyclo[5.1.0.0^{2,4}]oct-4'-yl)-3-methyl-1,3-butadiene ((*Z*)-**7**). B.p. 70°/0.04 Torr. UV (0.518 mg in 25 ml): 231 (11000). IR: 3080*m*, 3000*s*, 2963*s*, 2940*s*, 2920*s*, 2870*m*, 2850*m*, 1630*w*, 1595*w*, 1465*m*, 1435*m*, 1415*s*, 1400*m*, 1382*m*, 1372*s*, 1361*m*, 1342*w*, 1284*w*, 1235*w*, 1205*w*, 1195*w*, 1155*w*, 1103*w*, 1098*w*, 1071*m*, 1038*m*, 1025*m* (sh), 1018*m*, 995*w*, 925*m*, 890*s*, 872*m*, (sh), 831*w*. ^{1}H-NMR: 0.50–2.32 (*m*, H–C(1'), 2 H–C(6'), H–C(7'), 2 H–C(8')); 1.05, 1.12, 1.41 (3*s*, CH_3–C(2'), 2CH_3–C(5')); 1.92 (*m*, $w_{1/2} = 3.8$, CH_3–C(3)); 5.02 (*m*, $w_{1/2} = 4.5$, 2 H–C(4)); 5.74 (*AB* system, $J = 13$, $\delta_A = 5.42$, $\delta_B = 6.06$, H–C(1), H–C(2)). MS: 218 (6, M^+, $C_{15}H_{22}O$), 177 (13), 175 (28), 162 (31), 161 (29), 147 (48), 145 (18), 135 (14), 134 (11), 133 (26), 123 (32), 121 (47), 120 (16), 119 (75), 109 (13), 108 (16), 107 (49), 106 (26), *105* (100), 95 (28), 93 (39), 92 (14), 91 (56), 81 (40), 80 (14), 79 (41), 77 (36), 71 (10), 69 (18), 67 (34), 65 (18), 55 (37), 53 (25), 51 (11), 43 (68), 41 (83), 39 (38).

(E)-2,6,6-Trimethyl-1,3,8-nonatrien-5-one (**11**). B.p. 50°/0.03 Torr. UV (0.332 mg in 50 ml): 262 (28,000). IR: 3078*m*, 3000*m* (sh), 2960*s*, 2920*s*, 2870*m*, 2850*m* (sh), 1812*w*, 1678*s*, 1636*m*, 1608*s*, 1590*s*, 1462*s*, 1447*s*, 1434*m*, 1400*w*, 1380*m*, 1371*m*, 1361*m*, 1339*w*, 1318*m*, 1285*w*, 1260*s*, 1250*s*, 1201*w*, 1192*w*, 1152*w*, 1139*w*, 1088*m*, 1065*s*, 1049*s*, 1019*m*, 975*w*, 915*s*, 907*s*, 890*s*, 857*m*, 834*w*. ^{1}H-NMR: (300 MHz): 1.16 (*s*, 2 CH_3–C(6)); 1.91 (*dd*, $J_1 = 1.3$, $J_2 = 0.8$, CH_3–C(2)); 2.31 (*dt*, $J_1 = 7.4$, $J_2 = 1.1$, 2 H–C(7)); 4.99–5.02 and 5.05–5.06 (2*m*, 2 H–C(9)); 5.37 and 5.40 (2*m*, $w_{1/2} = 4.2$, 2 H–C(1)); 5.62–5.76 (*m*, H–C(8)); 6.92 (*AB* system, $J = 15.4$, $\delta_A = 6.51$, $\delta_B = 7.33$, H–C(3), H–C(4)). ^{13}C-NMR (75 MHz, contaminated with 15% of (*E*)-**7**, sample contained 1 drop of Et_3N): 18.2 (*q* *C*H_3–C(2)); 24.0 (*q* 2 *C*H_3–C(6)); 43.9 (*t*, C(7)); 117,8 (*t*, C(9)); 124.9 (*t*, C(1)); 121.2, 134.1 (*d*, C(8)); 145.2 (*d*, C(3)); 46,4 (*s*, C(6)); 141.0 (*s*, C(2)); 203.5 (*s*, C(5)). MS: 178 (14, M^+, $C_{12}H_{18}O$), 96 (21), *95* (100), 94 (10), 83 (16), 67 (51), 55 (48), 41 (49), 39 (22).

2.2.2. *In THF.* A soln. of (*E*)-**7** (2.72 g, 12.5 mmol) in THF (200 ml) was irradiated in the presence of a spatula tip full of Na_2CO_3 and worked up as described in *Sect. 2.1.1* (68% conversion); the following product distribution was determined[11]): (*E*)-**6** (2%), (*Z*)-**7** (8%), **8** (24%), **9** (3%), **10** (2%), **11** (7%), and **12** (6%).

2.3. *Triplet Sensitized Excitation of (*E*)-***7*** (λ > 280 nm, Acetone).* A soln. of (*E*)-**7** (1.05 g, 4.8 mmol) in acetone (180 ml) was irradiated (125W Hg medium-pressure lamp [23]; 87% conversion). CC (hexane/Et_2O 10:1) gave several fractions from which the following product distribution was determined (GC, ^{1}H-NMR)[11]. (*Z*)-**7** (3%), **13** (5%), **14** (3%), (*E*)-**15** (7%), and (*Z*)-**15** (20%).

*(1*RS*,2*SR*,4*SR*,9*SR*)-1,6,6-Trimethyl-9-isopropenyl-10-oxatricyclo[5.3.0.0^{2,4}]dec-7-ene* (**13**). IR: 3070*w*, 3002*m*, 2955*s*, 2915*s*, 2900*m* (sh), 2860*m*, 1653*w*, 1645*w*, 1450*m*, 1380*m*, 1370*m*, 1362*m*, 1337*w*, 1290*w*, 1276*w*, 1264*w*, 1208*w*, 1192*w*, 1179*w*, 1170*w*, 1165*m*, 1118*s*, 1085*m*, 1075*s*, 1060*m*, 1045*m*, 1031*m*, 1023*m*, 1005*m*, 990*m*, 935*m*, 900*s*, 889*m*, 848*w*. ^{1}H-NMR: 0.15–0.42 (1 H) and 0.50–2.00 (5 H) (2*m*, H–C(2), 2 H–C(3), H–C(4), 2 H–C(5)); 1.00 (3 H), 1.17 (6 H), (2*s*, CH_3–C(1), 2 CH_3–C(6)); 1.70 (*m*, $w_{½}$ = 3, 3 H–C(3′)); 4.75, 4.92, 5.10 (3*m*, $w_{½}$ = 4.5, H–C(9), 2 H–C(1′)); 5.32 (*d*, *J* = 2, H–C(8)). MS: 218 (24, M^+, $C_{15}H_{22}O$), 204 (16), *203* (100), 177 (26), 175 (25), 163 (10, 162 (24), 161 (18), 159 (10), 149 (39), 148 (12), 147 (30), 145 (12), 136 (17), 135 (22), 134 (12), 133 (28), 123 (14), 121 (53), 120 (13), 119 (47), 117 (12), 107 (41), 105 (45), 95 (58), 93 (36), 91 (50), 81 (16), 79 (28), 77 (32), 69 (28), 67 (17), 65 (13), 55 (20), 53 (15), 43 (60), 41 (61), 39 (32).

*(1*RS*,2*SR*,4*SR*,9*RS*)-1,6,6-Trimethyl-9-isopropenyl-10-oxatricyclo[5.3.0.0^{2,4}]dec-7-ene* (**14**). IR: 3070*m*, 3003*m*, 2960*s*, 2927*s*, 2900*m*, 2860*s*, 2840*m*, 1651*m* (sh), 1649*m*, 1459*s*, 1455*s*, 1442*m*, 1435*m* (sh), 1430*m* (sh), 1390*w*, 1380*m*, 1363*s*, 1339*m*, 1315*w*, 1304*m*, 1290*w*, 1265*m*, 1215*w*, 1205*w*, 1191*w*, 1180*m*, 1164*m*, 1117*s*, 1085*m*, 1072*s*, 1061*m*, 1031*s*, 1020*s*, 1005*s*, 990*s*, 950*w*, 940*m*, 900*s*, 880*m*, 848*m*, 834*w*. ^{1}H-NMR: 0.13–0.37 (1 H) and 0.47–2.05 (5 H) (2*m*, H–C(2), 2 H–C(3), H–C(4), 2 H–C(5)); 1.00 (3 H), 1.13 (6 H), (2*s*, CH_3–C(1), 2 CH_3–C(6)); 1.65 (*m*, $w_{½}$ = 3, 3 H–C(3′)); 4.80, 4.96 (2*m*, $w_{½}$ = 4.5); 5.12, 5.23 (2*m*, $w_{½}$ = 3, 2 H–C(1′), H–C(8), H–C(9)). MS: 218 (16, M^+, $C_{15}H_{22}O$), 204 (16), *203* (100), 177 (14), 175 (11), 162 (13), 161 (11), 148 (23), 147 (21), 136 (12), 135 (15), 133 (18), 121 (36), 119 (25), 107 (27), 105 (26), 95 (41), 93 (24), 91 (36), 81 (11), 79 (19), 77 (22), 69 (20), 67 (11), 55 (16), 53 (13), 41 (46), 39 (23).

*(*E*,1*RS*,3*SR*,6*RS*)-3-(3′-Methyl-1′,3′-butadienyl)-3,4,4-trimethylbicyclo[4.1.0]heptan-2-one* ((*E*)-**15**). M.p. 67–70° (hexane). IR: 3080*w*, 3015*m*, 2970*s*, 2960*s*, 2940*s*, 2920*s*, 2870*m*, 1760*w* (br.), 1695*s* (sh), 1690*s* (sh), 1680*s*, 1603*m*, 1462*m*, 1450*m*, 1435*m*, 1395*w*, 1385*m*, 1370*s*, 1365*m*, 1348*m*, 1328*w*, 1311*w*, 1285*w*, 1275*w*, 1250*m*, 1230*w*, 1210*w*, 1190*w*, 1178*m*, 1155*w*, 1108*w*, 1092*w*, 1085*w*, 1021*w*, 1002*w*, 965*s*, 940*w*, 920*m*, 905*m*, 892*s*, 870*w*. ^{1}H-NMR: 0.86, 1.02, 1.15 (3*s*, CH_3–C(3), 2 CH_3–C(4)); 0.95–2.12 (*m*, H–C(1), 2 H–C(5), H–C(6), 2 H–C(7)); 1.87 (*m*, $w_{½}$ = 3, CH_3–C(3′)); 4.94 (*m*, $w_{½}$ = 3, 2 H–C(4′)); 6.02 (*AB* system, *J* = 16, δ_A = 5.85, δ_B = 6.18, H–C(1′), H–C(2′)). MS: 218 (13, M^+, $C_{15}H_{22}O$), 149 (10), 136 (27), 122 (12), *121* (100), 119 (13), 105 (20), 93 (12), 91 (16), 86 (13), 84 (20), 79 (14), 77 (13), 55 (10), 41 (16), 39 (12).

*(*Z*,1*RS*,3*SR*,6*RS*)-3-(3′-Methyl-1′,3′-butadienyl)-3,4,4-trimethylbicyclo[4.1.0]heptan-2-one* ((*Z*)-**15**). B.p. 90°/0.04 Torr. UV (0.562 mg in 25 ml): 225 sh (5000). UV (2.870 mg in 5 ml): 287 (140), 296 (180), 306 (190), 315 (155), 328 (70), end absorption to 360. IR: 3093*w*, 3005*s*, 2970*s*, 2940*s*, 2910*s*, 2870*m*, 1700*s*, 1683*s*, 1621*w*, 1462*m*, 1448*s*, 1435*m*, 1392*m*, 1383*m*, 1367*s*, 1348*s*, 1326*m*, 1268*w*, 1244*m*, 1235*m*, 1205*w*, 1189*w*, 1179*m*, 1163*w*, 1138*w*, 1108*m*, 1085*m*, 1021*m*, 1003*m*, 970*m*, 953*m*, 939*w*, 922*m*, 903*s*, 893*s*, 870*w*. ^{1}H-NMR: 0.81, 1.03, 1.20 (3*s*, CH_3–C(3), 2 CH_3–C(4)); 0.75–2.25 (*m*, H–C(1), 2 H–C(5), H–C(6), 2 H–C(7)); 1.78 (*m*, $w_{½}$ = 3.5, CH_3–C(3′)); 4.76, 4.88 (2*m*, $w_{½}$ = 5, 2 H–C(4′)); 5.77 (*AB* system, *J* = 13, δ_A = 5.53, δ_B = 6.02, broad, $w_{½}$ = 4, H–C(2′), H–C(1′)). ^{13}C-NMR (75 MHz): 16.2, 23.6, 26.5 (*q*, 2 at 26.5, 4 CH_3); 14.0 (*t*, C(7)); 34.6 (*t*, C(5)); 114.6 (*t*, C(4′)); 12.9, 21.8 (2*d*, C(1), C(6)); 129.9, 133.7 (2*d*, C(1′), C(2′)); 38.9 (*s*, C(4)); 57.4 (*s*, C(3′)); 141.4 (*s*, C(3′)); 210.3 (*s*, C(2)). MS: 218 (9, M^+, $C_{15}H_{22}O$), 149 (12), 136 (32), 122 (13), *121* (100), 119 (12), 107 (11), 105 (19), 95 (11), 93 (12), 91 (15), 79 (14), 77 (13), 55 (15), 53 (10), 41 (24), 39 (13).

3. Additional Experiments. – 3.1. *Transformation of* **5** *into* **9**. A soln. of methylidenetriphenylphosphorane (*ca.* 0.2M) in THF was added dropwise to a soln. of **5** [2] (118 mg, 0.54 mmol) in abs. THF (5 ml) until all starting material was consumed (TLC control). The mixture was diluted with pentane (*ca.* 100 ml), worked up and chromatographed (Et_2O/pentane 1: 10) affording **9** (88 mg, 75%).

3.2. *Photooxygenation of* **12**. A soln. of a chromatography fraction (520 mg) containing **12** (*ca.* 20%) in CH_2Cl_2 (30 ml) was photooxygenated by bubbling O_2 through the soln. while irradiating (Hg medium-pressure lamp [23]; $Na_2Cr_2O_7$ filter) in the presence of *Sensitox I* (catalytic amount). After 24 h, the mixture was filtered through *Celite* and chromatographed (Et_2O/hexane 1:20) yielding **19** (62 mg, *ca.* 50%).

4-Methyl-1-(1′,1′-dimethyl-3′-butenyl)-5,6,7-trioxabicyclo[2.2.2]oct-2-ene (**19**). B.p. 60°/0.03 Torr. IR: 3075*w*, 3060*w*, 3030*w*, 2980*s*, 2930*s*, 2910*s*, 2870*s*, 2850*m*, 2830*w*, 2810*w* (sh), 1638*m*, 1625*w*, 1465*m*, 1458*m*, 1442*m*, 1437*m*, 1425*w* (sh), 1420*w* (sh), 1385*m* (sh), 1379*s*, 1365*m*, 1353*w*, 1322*w*, 1270*w*, 1255*w*, 1227*w*, 1195*w*, 1165*w*, 1138*m*, 1130*s*, 1100*w*, 1062*s*, 1026*m*, 996*m*, 980*m*, 950*w* (sh), 942*s*, 931*m*, 918*m*, 880*m*, 870*m*. ^{1}H-NMR (300 MHz): 1.02 (*s*, 2 CH_3–C(1′)); 1.36 (*s*, CH_3–C(4)); 2.22–2.25 (*m*, 2 H–C(2′)); 3.78 (*AB* system, *J* = 8.8, δ_A = 3.44, δ_B = 4.12, 2 H–C(8)); 5.03 (*dm*, *J* = 6.2, H–C(4′)); 5.07 (br. *s*, H–C(4′)); 5.72–5.92 (*m*, H–C(3′)); 6.57

(*AB* system, $J = 8.6$, $\delta_A = 6.44$, $\delta_B = 6.70$, H–C(2), H–C(3)). ^{13}C-NMR (75 MHz): 17.5, 21.5, 21.6 (3*q*, 3 CH_3); 41.0 (*t*, C(2')); 69.9 (*t*, C(8)); 117.9 (*t*, C(4')); 131.3, 132.3, 134.6 (3*d*, C(2), C(3), C(3')); 38.8 (*s*, C(1')); 72.7 (*s*, C(4)); 101.1 (*s*, C(1)). MS: 210 (5, M^+, $C_{12}H_{18}O_3$), 153 (20), 139 (14), 135 (32), 128 (27), 123 (12), 107 (12), 99 (20), 98 (32), 97 (11), 95 (15), 85 (16), 84 (14), 83 (60), 82 (22), 81 (26), 79 (14), 77 (10), 71 (22), 70 (10), 69 (23), 67 (29), 57 (11), 56 (12), 55 (100), 53 (23), 44 (23), 43 (97), 42 (13), 41 (94), 40 (10), 39 (49). Anal. calc. for $C_{12}H_{18}O_3$ (210.26): C 68.55, H 8.63; found: C 68.40, H 8.63.

3.3. *Oxidation of* **13** *and* **14** *to* **20.** *a*) A soln. of **13** (3.3 mg, 0.015 mmol) in Et_2O (2 ml) was stirred at r.t. in the presence of NiO_2 (300 mg, *ca.* 3 mmol) for 1 week. Filtration through *Celite* afforded a mixture (3.4 mg) containing (^{1}H-NMR and GC) **13** (20%), and **20** [2] (65%). *b*) Analogous treatment of **14** (11 mg, 0.05 mmol) gave a mixture (10 mg) of **14** (24%), and **20** [2] (50%).

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