# 101. Photochemical Reactions

144th Communication[1])

## Photochemistry of 5,6-Epoxy-1,3-dienes in the Ionone Series: Influence of a Methoxy Group in Position 7

by **Urs Goldener**[2]), **Bruno Frei**, and **Oskar Jeger***

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

(15.III.85)

On triplet excitation ($\lambda > 280$ nm, acetone), the epoxydiene (*E*)-**5** undergoes initial cleavage of the C(5)–O bond of the oxirane and subsequent cleavage of the C(6)–C(7) bond leading to the diradical intermediate **e** which reacts by recombination furnishing the cyclic compounds (*E*/*Z*)-**6**, (*E*/*Z*)-**7**, **8**, and **9**. Alternatively, a H-shift leads to the aliphatic methyl-enol ether **10** which undergoes a photochemical [2 + 2]-cycloaddition to compounds **12** and **13**, the main products on triplet excitation of (*E*)-**5**. On singlet excitation ($\lambda = 254$ nm, MeCN), (*E*)-**5** undergoes cleavage to the carbene intermediates **f** and **g**. The vinyl carbene **f** reacts with the adjacent double bond furnishing the cyclopropene **14** as the main product. From the carbene intermediate **g**, the methyl-enol ether **15** arises by carbene insertion into the neighboring C–H bond. Furthermore, the diastereomer of the starting material, the epoxydiene (*E*)-**16**, and compounds **17A** + **B** are formed *via* the ylide intermediate **h**. Finally, the cyclobutene **18** is the product of an electrocyclic reaction of the diene side chain.

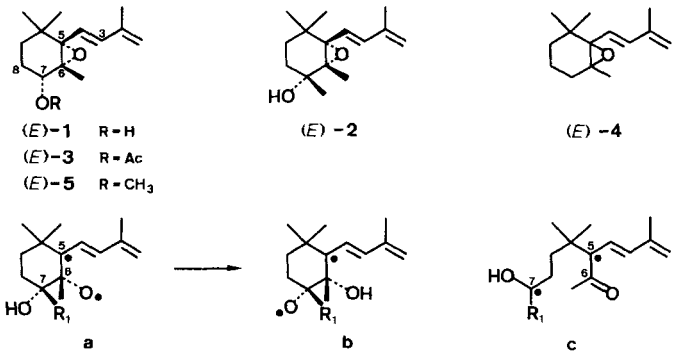
**1. Introduction.** – In previous papers, we have shown that triplet excitation ($\lambda > 280$ nm, acetone) of the 5,6-epoxy-7-hydroxy-1,3-dienes (*E*)-**1** and (*E*)-**2** gave rise to initial cleavage of the C(5)–O bond of the oxirane followed by product formation *via* cleavage of the C(6)–C(7) bond [1] [2]. On the other hand, the acetate (*E*)-**3** [2] showed a photochemical behavior analogous to that of the C(7)-unsubstituted epoxydiene (*E*)-**4**, which did not undergo the aforementioned isomerizations [3]. Therefore, it was proposed that product formation *via* scission of the C(6)–C(7) bond on photolysis of (*E*)-**1** and (*E*)-**2** may require a H-shift from the OH group at C(7) to the former epoxide O-atom (**a**→**b**, *Scheme 1*), a mechanism obviously not compatible in the cases of (*E*)-**3** and (*E*)-**4**. The results of the triplet excitation of (*E*)-**2**, however, suggested that, alternatively to an initial H-transfer (**a**→**b**), direct cleavage of the C(6)–C(7) bond of **a** could furnish a more stable diradical (**c**, *Scheme 1*)[3]), which subsequently reacted to various products [1]. Hence, it was assumed that the lack of cleavage of the C(6)–C(7) bond on photolysis of (*E*)-**3** and (*E*)-**4** was due to less effective stabilization of the diradical intermediates of type **c**, either

[1]) 143rd Communication: [1].

[2]) Taken in part from the Ph.D. thesis of *U.G.*

[3]) Numbering of the centers analogous to that of (*E*)-**1** and **a**.

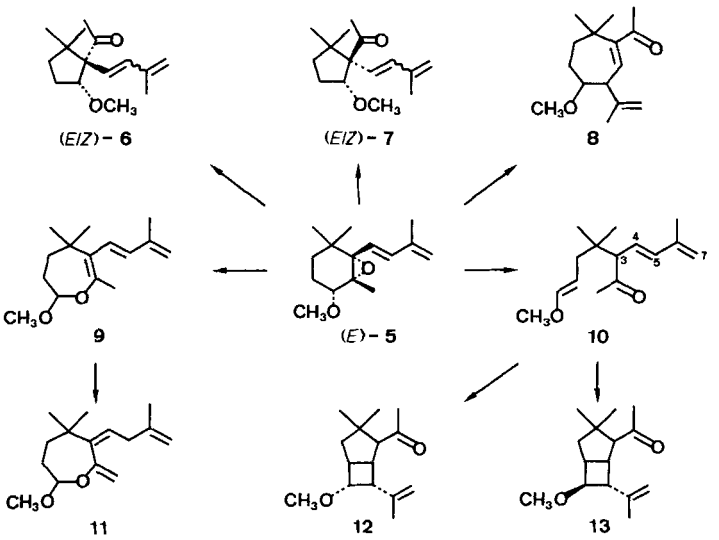
*Scheme 1*




in the presence of an AcO group or in the absence of an O function at C(7), respectively. To test this hypothesis, the methyl ether (*E*)-**5**[4]) was investigated, since the degree of stabilization of radical intermediates by alkoxy and OH groups is known to be similar, but superior to that by carbonyloxy groups [4] [5].

**2. Photolysis Experiments.** – 2.1. *Triplet excitation of* (E)-**5** ($\lambda > 280$ nm, acetone, 92% conversion) gave the following product distribution[5]): (*E*)-**6** (4%), (*Z*)-**6** (6%), (*E*)-**7** (1%), (*Z*)-**7** (1%), **8** (3%), **9** (2%), **10** (7%), **11** (2%), **12** (18%), **13** (13%), and intractable material.

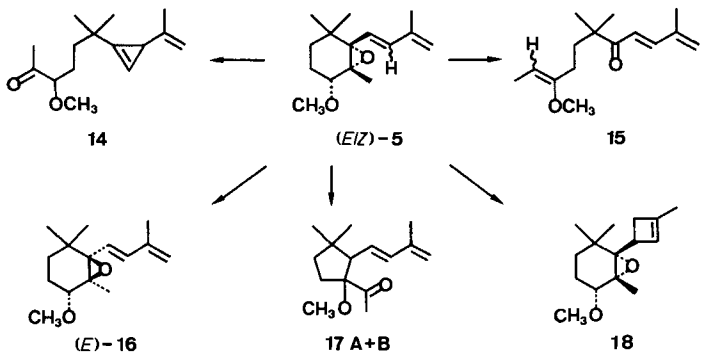
*Scheme 2*




[4]) Compound (*E*)-**5** was obtained in 95% yield by reaction of (*E*)-**1** [2] with NaH/MeI in DME.

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

*Scheme 3*




2.2. *Singlet excitation of* (E)-**5** ($\lambda$ = 254 nm, MeCN, 83% conversion) afforded the following products[5]: (*Z*)-**5** (6%), **14** (20%), **15** (1%), (*E*)-**16** (3%), **17A** (4%), **17B** (6%), **18** (2%), and intractable material[6])[7][8]).

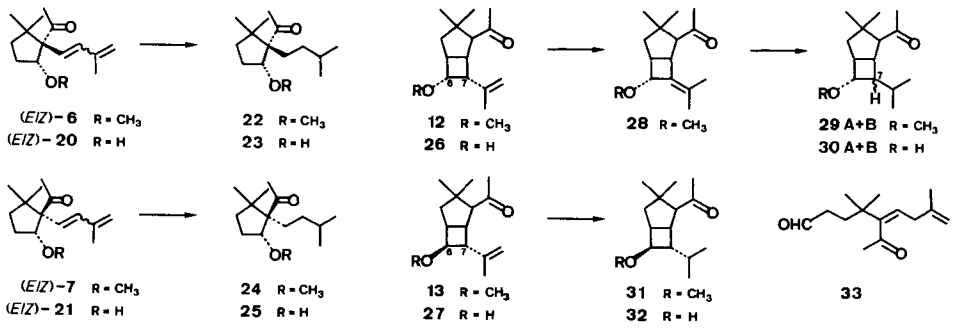
2.3. *Triplet excitation of* **9** ($\lambda$ > 280 nm, acetone) gave **11** in quantitative yield (*Scheme 2*).

2.4. *Triplet excitation of* **10** ($\lambda$ > 280 nm, acetone) gave **12** (33%) and **13** (19%; *Scheme 2*).

**3. Structure of the Photoproducts.** – The structures of all new compounds were deduced from their spectral data. Compounds (*E*/*Z*)-**6**, (*E*/*Z*)-**7**, **8**, **12**, **13**, **14**, (*E*)-**16**, **17A** + **B**, and **18** are analogs of the products obtained from the photolysis of (*E*)-**1** [2] [6]. Therefore, only the most relevant spectral data of the new types of products are discussed here together with the chemical transformations which confirmed the assigned structures.

*Cyclopentylmethyl Ketones* (E/Z)-**6** *and* (E/Z)-**7** (*Scheme 4*). To assign the stereochemistry, (*E*/*Z*)-**6** and (*E*/*Z*)-**7** were correlated with the alcohols (*E*/*Z*)-**20** and (*E*/*Z*)-**21**, respectively, which were obtained previously on photolysis of (*E*)-**1** [2]. Thus, catalytic hydrogenation (Pd/C) of (*E*/*Z*)-**6** led to the methoxy compound **22** which

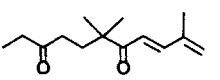
*Scheme 4*




---

[6]) In this paper, the terms **A** and **B** are generally used for the description of diastereomers whose stereochemistry was not assigned conclusively.

[7]) When the chromatography of the photolysis mixture was not carried out in the presence of $Et_3N$, instead of the enol ether **15**, its hydrolysis product **19** [6], was isolated.



**19**

[8]) $^1$H-NMR (300 MHz) analysis of the photolysis mixture showed a similar product distribution.

was also obtained by catalytic hydrogenation of (*E*/*Z*)-**20** and subsequent reaction of the alcohol **23** [2] with $Me_3OBF_4$ according to [7] in 88% yield. Analogously, compound **24** was obtained by hydrogenation of (*E*/*Z*)-**7** as well as by hydrogenation of (*E*/*Z*)-**21** furnishing **25** [2], followed by reaction of the latter with $Me_3OBF_4$. Furthermore, **22** was cleaved by reaction with $Me_3SiI$ [8] leading to the alcohol **23** in moderate yield (22%).

*Acetals* **9** *and* **11**. Compound **11**, which was obtained on photolysis of **9** *(Scheme 2)*, was hydrolyzed to the aliphatic keto-aldehyde **33** *(Scheme 4)*.

*Enolether* **10** *(Scheme 2)*. In particular, the diene and the methyl-enol ether moieties are evidenced by their characteristic $^1$H-NMR signals: 2*m* at 4.94 and 4.96 ppm of 2H–C(7), a *dd* at 5.64 ppm of H–C(4) which is coupled with H–C(5) (*d* at 6.18 ppm, $J$ = 15.6 Hz) and H–C(3) (*d* at 3.11 ppm, $J$ = 10.0 Hz), a *dt* at 4.70 ppm, and a *d* at 6.20 ppm with $J$ = 12.5 Hz which is characteristic for *trans*-enol-ethers [9]. On photolysis ($\lambda > 280$ nm, acetone) **10** was transformed to the bicyclo[3.2.0]heptyl methyl ketones **12** and **13** in 52% combined yield *(Scheme 2)*.

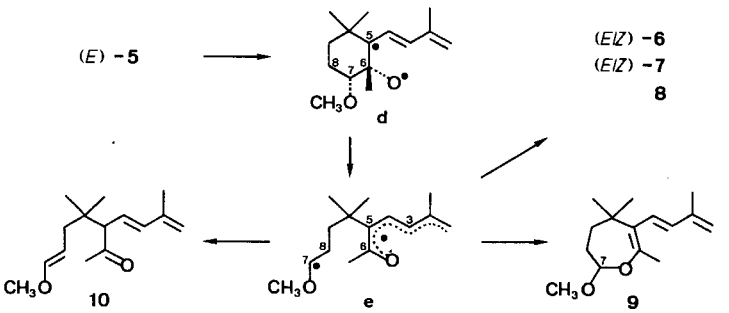
*Bicyclo[3.2.0]heptyl Methyl Ketones* **12** *and* **13** *(Scheme 4)*. The structures and, in particular, the relative configuration at C(6) and C(7) of **12** and **13** was assigned by correlation with the alcohols **26** and **27** [2]. Thus, catalytic hydrogenation (Pd/$BaSO_4$) of **26** gave the double-bond isomer of the starting material (**28**) and, in addition, the two reduced diastereomeric products **29A** and **29B**[6]), presumably epimers at C(7). Hydrogenation (Pd/C) of **28** led to **29A** and **29B** which were also obtained by catalytic hydrogenation of **26** and subsequent reaction of the alcohols **30A** and **30B** with $Me_3OBF_4$. Likewise, compound **31**, the hydrogenation product of **13**, was obtained from the alcohol **27** *via* **32** *(Scheme 4)*.

*Enolether* **15** *(Scheme 3)*. On chromatography with $SiO_2$, which was not treated with $Et_3N$, compound **15** was hydrolyzed to the known ketodienone **19**.

The *cyclobutene* **18** *(Scheme 3)* was cleaved to the epoxydiene (*E*)-**5** on thermolysis at 115° in toluene.

**4. Discussion.** – Compounds (*E*/*Z*)-**6**, (*E*/*Z*)-**7**, **8**, **12**, and **13** *(Scheme 3)* formed on triplet excitation of (*E*)-**5** are analogs of the products previously obtained on photolysis of (*E*)-**1** [2]. On the other hand, compounds **9**, **10**, and **11** are new types of photoproducts in this series. As postulated previously for (*E*)-**1** and (*E*)-**2** [1] [2], (*E*)-**5** undergoes cleavage of the C(5)–O bond of the oxirane, leading to the intermediate **d** *(Scheme 5)*, followed by scission of the C(6)–C(7) bond furnishing the biradical intermediate **e**, which is stabilized by the MeO group *(Scheme 5)*. Cyclization by bond formation between C(5)

*Scheme 5*



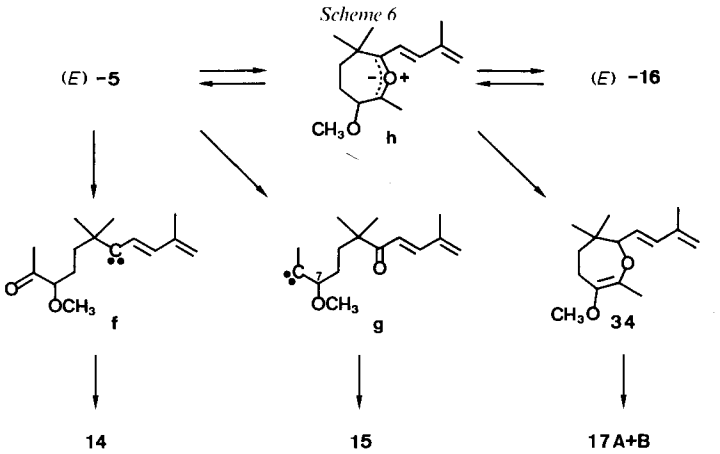

and C(7) or between C(3) and C(7)[3]) leads to products (*E*/*Z*)-**6**, (*E*/*Z*)-**7** and **8**, respectively. Alternatively, ring closure between C(7) and the O-atom at C(6) furnishes the acetal **9** which may undergo a 1,5-H-shift leading to **11**, as was shown on photolysis of **9** *(Scheme 2)*. Furthermore, by a H-shift – formally from C(8) to C(5) – the methyl-enol ether **10** was formed. Analogously to the corresponding enol intermediates, which were postulated on triplet excitation of the OH compounds (*E*)-**1** and (*E*)-**2** [1] [2] *(Scheme 1)*, **10** undergoes a photochemical [2 + 2]-cycloaddition leading to **12** and **13**, the main products of the photolysis of (*E*)-**5** (see *Sect. 2.4.*).

As expected, on singlet excitation ($\lambda = 254$ nm, MeCN), (*E*)-**5** shows photoisomerizations *via* carbene and ylide intermediates. As on photolysis of (*E*)-**2** *(Scheme 1)*, the cyclopropene **14** *(Scheme 3)* is formed as the main product *via* the vinyl carbene **f** *(Scheme 6)*. Evidence for the alternative carbene intermediate **g** is provided by the isolation of **15** *(Scheme 3)* which may be formed by carbene insertion into the adjacent C(7)–H bond in **g**[3]). However, the low yield (1%) of **15** was surprising, since on photolysis of (*E*)-**1**, secondary products of the postulated enol corresponding to **15** were obtained in more than 30% combined yield [6]. On the other hand, on photolysis of (*E*)-**5**, compounds **14**, (*E*)-**16**, **17A** + **B**, and **18** were isolated in yields similar to the corresponding hydroxy compounds on singlet excitation of (*E*)-**1**. Therefore, it may be assumed that the low yield of **15** is due to some unspecific photochemical or thermal secondary reactions.

Analogously to the 7-hydroxy-epoxydiene (*E*)-**1**, the 7-methoxy compound (*E*)-**5** also shows product formation *via* an ylide intermediate. Thus, cleavage of the C(5)–C(6) bond of the oxirane leads to **h** *(Scheme 6)* which undergoes a ring closure to the diastereomeric expoxydiene (*E*)-**16**. In addition, compounds **17A** + **B** are presumably formed by an initial 1,4-H-shift in **h** leading to the postulated enol ether **34**, followed by a photochemical ring contraction of the latter[9]).

Furthermore, (*Z*)-**5** is obtained by (*E*/*Z*)-isomerization, and the cyclobutene **18** by an electrolytic reaction of the diene side chain *(Scheme 2)*.

*Scheme 6*




**Conclusion.** – On triplet excitation, the methoxy-epoxydiene (*E*)-**5** shows photochemical behavior analogous to that of the hydroxy-epoxydiene (*E*)-**1**. Both compounds undergo product formation involving cleavage of the C(5)–O bond of the oxirane followed by scission of the C(6)–C(7) bond. On the other hand, the latter process was not observed on triplet excitation of the corresponding acetate (*E*)-**3** [2] *(Scheme 1)*. These results demonstrate that the cleavage of the C(6)–C(7) bond is promoted by substituents at C(7), which stabilize the diradical intermediate of type **e** *(Scheme 5)*. The previously proposed H-transfer (**a**→**b**, *Scheme 1*) followed by fragmentation of a 1,4-diradical seems, therefore, less probable.

[9]) For a transformation analogous to **34**→**17A** + **B**, see [10]. It has also to be considered, however, that **17A** + **B** may result from a carbene C,H insertion of the postulated intermediate **f**.

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).

## Experimental Part

*General.* See [1] [10]. All $^1$H-NMR spectra were taken in $CDCl_3$ or exceptionally (as indicated below) in $C_6D_6$ solns. on a *Bruker WM-300* (300 MHz) instrument. Catalytic hydrogenations were carried out, in general, according to *Procedure I*: a suspension of Pd/C (5%, 10 mg) in EtOH (*ca.* 1 ml) was stirred under $H_2$ for 1 h. Then a soln. of the olefin (10–50 mg) in EtOH (0.5–1 ml) was added. The mixture was stirred under $H_2$ until the starting material was consumed (TLC, GC), filtered through *Celite* and the solvent was evaporated. Analytical pure samples of the hydrogenated compounds were obtained, in general, by column chromatography. *Transformations of Alcohols to Methyl Ethers (Procedure II)* [7]. To a soln. of $Me_3OBF_4$ (5 equiv.) and 1,8-bis(dimethylamino)naphthalene (5.2 equiv.) in $CH_2Cl_2$ (*ca.* 3M soln.) was added a soln. of the alcohol (1 equiv.) in $CH_2Cl_2$ (0.5–1 ml) and the mixture was stirred at r.t. until the starting material was consumed (TLC). The mixture was diluted with $Et_2O$ ( 5 ml), washed with HCl (1M) and NaCl (sat.), dried ($MgSO_4$) and evaporated under reduced pressure. Analytical pure samples of the methyl ethers were obtained, in general, by column chromatography.

**1. Preparation of (*E*)-5.** – To a suspension of NaH (0.836 g, 35 mmol; prepared from NaH dispersion (55%, 1.52 g) by washing it twice with pentane (20 ml)) in abs. DME (30 ml) was added dropwise a soln. of (*E*)-**1** (6.67 g, 30 mmol) and MeI (4.5 ml, 48.5 mmol) in abs. DME (30 ml) over 30 min. After stirring the mixture at r.t. for 3 h, NaH (0.1 g, 4.2 mmol) and MeI (1 ml, 10.8 mmol) was added and stirring continued for 2 h. Then the mixture was concentrated and the residue dissolved in $Et_2O$ and filtered. Distillation (110–120°) afforded (*E*)-**5** (6.71 g, 95%).

*(E,1'RS,2'RS,3'SR)-1-(1',2'-Epoxy-3'-methoxy-2',6',6'-trimethyl-1-cyclohexyl)-3-methyl-1,3-butadiene* ((*E*)-**5**). UV (0.544 mg in 25 ml): 232 (25600). IR: 3080*w*, 3030*w*, 2960*s*, 2930*s*, 2900*s* (sh), 2860*m*, 2850*m* (sh), 2815*m*, 1605*m*, 1460*m*, 1445*s*, 1435*m*, 1375*m*, 1360*m*, 1310*w*, 1250*w*, 1240*w*, 1190*m*, 1150*w*, 1100*s*, 1070*m*, 1045*m*, 1020*m*, 970*s*, 890*s*. $^1$H-NMR: 0.95, 1.04 (2*s*, 2 $CH_3$–C(6')); 1.03–1.10 (*m*, H–C(5')); 1.25 (*s*, $CH_3$–C(2')); 1.46–1.70 (*m*, 2H–C(4'), H–C(5')); 1.85 (*m*, $w_{1/2}$ = 2.5, $CH_3$–C(3)); 3.4–3.5 (*m*, H–C(3')); 3.41 (*s*, $CH_3O$); 4.98 (*m*, $w_{1/2}$ = 5, 2H–C(4)); 6.05 (*AB*-system, *J* = 15.7, $\delta_A$ = 5.79, $\delta_B$ = 6.31, H–C(1), H–C(2)). $^{13}$C-NMR (25 MHz): 17.5, 18.6, 24.9, 27.0 (4*q*, $CH_3$–C(3), $CH_3$–C(2'), 2 $CH_3$–C(6')); 56.6 (*q*, $CH_3O$); 22.0, 34.1 (2*t*, C(4'), C(5')); 116.7 (*t*, C(4)); 79.4 (*d*, C(3')); 124.6, 135.9 (2*d*, C(1), C(2)); 33.4 (*s*, C(6')); 66.0, 70.8 (2*s*, C(1'), C(2')); 141.0 (*s*, C(3)). MS: 236 (16, $M^+$, $C_{15}H_{24}O_2$), 221 (27), 165 (17), 163 (15), 161 (28), 147 (19), 138 (17), 137 (19), 135 (16), 133 (20), *123* (100), 122 (23), 121 (31), 119 (27), 107 (43), 106 (16), 105 (46), 95 (23), 93 (28), 91 (36), 85 (20), 81 (23), 79 (25), 77 (24), 71 (18), 69 (19), 67 (27), 55 (34), 53 (19), 43 (98), 41 (66). Anal. calc. for $C_{15}H_{24}O_2$ (236.36): C 76.23, H 10.24; found: C 76.37, H 10.06.

**2. Photolysis Experiments.** – 2.1. *Triplet Excitation of (E)-5.* A soln. of (*E*)-**5** (2.0 g, 8.46 mmol) in acetone (180 ml) was irradiated (*Pyrex* lamp B, *ca.* 90% conversion) in the presence of $Na_2CO_3$. Chromatography of the photolysis mixture ($SiO_2$ + 0.3% $Et_3N$; hexane/$Et_2O$ 10:1) gave mixed fractions, from which the following product distribution was determined ($^1$H-NMR, GC)[5]): (*E*)-**6** (4%), (*Z*)-**6** (6%), (*E*)-**7** (1%), (*Z*)-**7** (1%), **8** (3%), **9** (2%), **10** (7%), **11** (2%), **12** (18%), **13** (13%), and intractable material.

*(E,1RS,5SR)-5-Methoxy-2,2-dimethyl-1-(3'-methyl-1',3'-butadienyl)cyclopentyl Methyl Ketone* ((*E*)-**6**). UV (0.368 mg in 25 ml): 234 (22600). IR: 3080*w*, 3030*w* (sh), 2960*s*, 2940*s*, 2910*m* (sh), 2870*m*, 1705*s*, 1635*w*, 1605*w*, 1460*m*, 1435*m*, 1415*m*, 1380*m*, 1360*m*, 1345*s*, 1310*w*, 1230*m*, 1195*m*, 1155*m*, 1135*m*, 1105*s*, 1090*s*, 975*m*, 890*s*. $^1$H-NMR: 0.91, 1.10 (2*s*, 2 $CH_3$–C(2)); 1.40–1.46 (*m*, H–C(3)); 1.88 (*m*, $w_{1/2}$ = 2.5, $CH_3$–C(3')); 1.80–1.95 (*m*, H–C(3), H–C(4)); 2.07 (*s*, $CH_3CO$); 2.06–2.18 (*m*, H–C(4)); 3.29 (*s*, $CH_3O$); 4.08 (*dd*, $J_1$ = 8.0, $J_2$ = 4.6, H–C(5)); 4.97, 5.00 (2*m*, $w_{1/2} \approx 4$, 2H–C(4')); 5.94 (*AB*-system, *J* = 16.3, $\delta_A$ = 5.68, $\delta_B$ = 6.21, H–C(1'), H–C(2')). $^{13}$C-NMR (75 MHz): 18.6, 24.4, 27.2, 31.6 (4*q*, $CH_3CO$, 2 $CH_3$–C(2), $CH_3$–C(3')); 56.9 (*q*, $CH_3O$); 27.4, 37.9 (2*t*, C(3), C(4)); 116.4 (*t*, C(4')); 87.0 (*d*, C(5)); 129.5, 133.5 (2*d*, C(1'), C(2')); 44.7 (*s*, C(2)); 69.0 (*s*, C(1)); 141.6 (*s*, C(3')); 209.1 (*s*, CO). MS: 236 (2, $M^+$, $C_{15}H_{24}O_2$), 165 (10), 162 (56), 161 (21), 147 (78), 123 (24), 119 (32), 107 (27), 106 (75), 105 (55), 93 (19), 91 (44), 79 (19), 77 (18), 55 (24), *43* (100), 41 (32). Anal. calc. for $C_{15}H_{24}O_2$ (236.36): C 76.23, H 10.24; found: C 76.32, H 10.27.

(*Z*)-**6**. UV (0.702 mg in 25 ml): end absorption to 400. IR: 3080*w*, 2960*s*, 2930*s*, 2870*m*, 2820*m*, 1705*s*, 1650*w*, 1620*w*, 1460*m*, 1435*m*, 1420*w* (sh), 1380*m*, 1365*m*, 1360*m*, 1345*s*, 1230*m*, 1195*m*, 1175*m*, 1130*m*, 1105*s*, 1085*m*, 895*m*. $^1$H-NMR: 1.01, 1.11 (2*s*, 2 $CH_3$–C(2)); 1.50 (*ddd*, $J_1$ = 11.8, $J_2$ = 10.0, $J_3$ = 5.9, H–C(3)); 1.83 (*m*, $w_{1/2}$ = 3.5, $CH_3$–C(3')); 1.68–1.95 (*m*, H–C(3), H–C(4)); 2.11 (*s*, $CH_3CO$); 2.02–2.13 (*m*, H–C(4)); 3.16 (*s*, $CH_3O$); 4.23 (*dd*,

$J_1$ = 7.9, $J_2$ = 4.8, H–C(5)); 4.83, 4.90 (2*m*, $w_{1/2} \approx 5$, 2H–C(4')); 5.65 (*AB*-system, $J$ = 13.1, $\delta_A$ = 5.30, $\delta_B$ = 6.00, H–C(1'), H–C(2')). $^{13}$C-NMR (75 MHz): 23.2, 24.4, 27.9, 31.7 (4*q*, $CH_3CO$, 2 $CH_3$–C(2), $CH_3$–C(3')); 56.1 (*q*, $CH_3O$); 27.2, 38.3 (2*t*, C(3), C(4)); 114.1 (*t*, C(4')); 86.7 (*d*, C(5)); 128.7, 132.5 (2*d*, C(1'), C(2')); 45.0 (*s*, C(2)); 69.9 (*s*, C(1)); 140.6 (*s*, C(3')); 208.8 (*s*, CO). MS: 236 (1, $M^+$, $C_{15}H_{24}O_2$), 162 (20), 147 (69), 123 (18), 119 (31), 107 (22), 106 (69), 105 (53), 93 (17), 91 (48), 79 (20), 77 (20), 55 (23), *43* (100), 41 (36). Anal. calc. for $C_{15}H_{24}O_2$ (236.36): C 76.23, H 10.24; found: C 76.36, H 10.26.

(E,*1*RS,*5*RS)-*5-Methoxy-2,2-dimethyl-1-(3'-methyl-1',3'-butadienyl)cyclopentyl Methyl Ketone* ((*E*)-**7**). *Ca.* 80% pure. UV (0.429 mg in 25 ml): 233 (*ca.* 20000). *IR*: 3080*w*, 2965*s*, 2870*m*, 2820*w*, 1695*s*, 1600*w*, 1460*m*, 1450*m*, 1430*m*, 1380*m*, 1350*s*, 1200*m*, 1130*m*, 1095*s*, 970*m*, 885*s*. $^1$H-NMR: 0.93, 1.11 (2*s*, 2$CH_3$–C(2)); 1.43 (*ddd*, $J_1$ = 12.6, $J_2$ = 9.2, $J_3$ = 3.2, H–C(3)); 1.58–1.83 (*m*, H–C(3), H–C(4)); 1.87 (*m*, $w_{1/2}$ = 3, $CH_3$–C(3')); 2.18 (*s*, $CH_3CO$); 2.15–2.30 (*m*, H–C(4)); 3.33 (*s*, $CH_3O$); 4.31 (*dd*, $J_1$ = 9.1, $J_2$ = 6.5, H–C(5)); 4.93, 4.95 (2*m*, $w_{1/2} \approx 4$, 2H–C(4')); 5.87 (*AB*-system, $J$ = 16.5, $\delta_A$ = 5.71, $\delta_B$ = 6.03, H–C(1'), H–C(2')). $^{13}$C-NMR (75 MHz): 18.5, 25.6, 26.1, 29.3 (4*q*, $CH_3CO$, 2$CH_3$–C(2), $CH_3$–C(3')); 57.5 (*q*, $CH_3O$); 26.4, 37.3 (2*t*, C(3), C(4)); 116.3 (*t*, C(4')); 83.9 (*d*, C(5)); 125.9, 135.6 (2*d*, C(1'), C(2')); 44.4 (*s*, C(2)); 69.0 (*s*, C(1)); 141.6 (*s*, C(3')); 209.5 (*s*, CO). MS: 236 (2, $M^+$, $C_{15}H_{24}O_2$), 176 (20), 165 (29), 162 (16), 161 (42), 147 (26), 135 (15), 123 (36), 121 (17), 119 (19), 107 (26), 106 (16), 105 (30), 81 (23), 71 (21), *43* (100), 41 (19). Anal. calc. for $C_{15}H_{24}O_2$ (236.36): C 76.23, H 10.24; found: C 76.02, H 10.29.

(*Z*)-**7**. UV (1.248 mg in 25 ml): 225 (6700). IR: 3080*w*, 2950*s*, 2870*m*, 2810*w*, 1690*s*, 1630*w*, 1460*m*, 1435*m*, 1385*w*, 1370*m*, 1350*s*, 1240*w*, 1190*m*, 1165*m*, 1130*m*, 1090*s*, 1050*w*, 925*w*, 890*m*. $^1$H-NMR: 0.88, 1.14 (2*s*, 2$CH_3$–C(2)); 1.42–1.90 (*m*, 2H–C(3), H–C(4)); 1.75 (*m*, $w_{1/2}$ = 2.5, $CH_3$–C(3')); 2.07 (*s*, $CH_3CO$); 2.14–2.21 (*m*, H–C(4)); 3.28 (*s*, $CH_3O$); 4.40 (*dd*, $J_1$ = 8.4, $J_2$ = 6.0, H–C(5)); 4.78, 4.99 (2*m*, $w_{1/2} \approx 5$, 2H–C(4')); 5.76 (*AB*-system, $J$ = 12.6, $\delta_A$ = 5.48, $\delta_B$ = 6.04, H–C(1'), H–C(2')). $^{13}$C-NMR (75 MHz): 23.0, 25.0, 26.3, 30.1 (4*q*, $CH_3CO$, 2$CH_3$–C(2), $CH_3$–C(3')); 56.9 (*q*, $CH_3O$); 27.3, 37.1 (2*t*, C(3), C(4)); 114.5 (*t*, C(4')); 83.4 (*d*, C(5)); 126.4, 134.3 (2*d*, C(1'), C(2')); 44.5 (*s*, C(2)); 69.5 (*s*, C(1)); 140.7 (*s*, C(3')); 209.0 (*s*, CO). MS: 236 (2, $M^+$, $C_{15}H_{24}O_2$), 176 (12), 165 (26), 161 (24), 147 (26), 123 (27), 119 (16), 107 (20), 105 (31), 91 (19), 55 (15), *43* (100), 41 (26).

*3-Isopropenyl-4-methoxy-7,7-dimethyl-1-cycloheptenyl Methyl Ketone* (**8**). *Ca.* 90% pure. UV (0.536 mg in 25 ml): 228 (*ca.* 8000). IR: 3080*w*, 2960*s*, 2930*s*, 2870*m* (sh), 2820*m*, 1680*s*, 1640*m*, 1615*w* (sh), 1460*m* (br.), 1370*m*, 1360*m*, 1345*m*, 1305*w*, 1275*w*, 1235*m*, 1220*m*, 1210*m*, 1185*m*, 1160*w*, 1095*s*, 970*w*, 895*s*. $^1$H-NMR: 1.14, 1.28 (2*s*, 2$CH_3$–C(7)); 1.43 (*ddd*, $J_1$ = 14.0, $J_2$ = 6.4, $J_3$ = 4.3, H–C(6)); 1.88 (*m*, $w_{1/2}$ = 3, $CH_3$–C=$CH_2$); 1.7–2.0 (*m*, 2H–C(5), H–C(6)); 2.28 (*s*, $CH_3CO$); 3.26–3.30 (*m*, H–C(3)); 3.31 (*s*, $CH_3O$); 3.59 (*ddd*, $J_1$ = 6.6, $J_2$ = 5.3, $J_3$ = 2.4, H–C(4)); 4.88, 4.92 (2*m*, $w_{1/2} \approx 4$, $CH_2$=C–$CH_3$); 6.07 (*d*, $J$ = 5.5, H–C(2)). $^{13}$C-NMR (75 MHz): 22.6, 26.7, 28.9, 29.8 (4*q*, 2$CH_3$–C(7), $CH_3CO$, $CH_3$–C=$CH_2$); 56.3 (*q*, $CH_3O$); 27.5, 36.8 (2*t*, C(5), C(6)); 112.7 (*t*, $CH_2$=C–$CH_3$); 48.8 (*d*, C(3)); 80.6 (*d*, C(4)); 134.3 (*d*, C(2)); 38.4 (*s*, C(7)); 146.3, 151.9 (2*s*, C(1), $CH_2$=*C*–$CH_3$); 204.0 (*s*, CO). MS: 236 (1, $M^+$, $C_{15}H_{24}O_2$), 176 (11), 165 (26), 161 (30), 147 (17), 123 (25), 121 (15), 119 (10), 107 (19), 105 (17), 91 (12), 81 (12), 71 (15), 55 (11), *43* (100), 41 (21).

*1-(4'-Methoxy-2',7',7'-trimethyl-3'-oxa-1'-cycloheptenyl)-3-methyl-1,3-butadiene* (**9**). *Ca.* 80% pure. UV (0.419 mg in 25 ml): 225 (11100), 255 (sh, 6300). IR: 3080*w*, 2955*s*, 2930*s* (sh), 2905*s* (sh), 2865*m*, 1640*m* (sh), 1620*m*, 1465*m*, 1445*s*, 1435*m* (sh), 1385*m*, 1370*m*, 1360*m*, 1280*m*, 1240*m*, 1195*s*, 1170*m*, 1150*s*, 1130*s*, 1075*s*, 1045*s*, 1020*s*, 1015*s*, 965*s*, 920*w*, 905*m*, 885*s*. $^1$H-NMR ($C_6D_6$): 1.03, 1.09 (2*s*, 2$CH_3$–C(7')); 1.39 (*ddd*, $J_1$ = 13.7, $J_2$ = 7.8, $J_3$ = 3.9, H–C(6')); 1.60–2.22 (*m*, 2H–C(5'), H–C(6')); 1.79, 1.93 (2*m*, $w_{1/2}$ = 3, $CH_3$–C(3), $CH_3$–C(2')); 3.31 (*s*, $CH_3O$); 4.51 (*dd*, $J_1$ = 9.0, $J_2$ = 4.2, H–C(4')); 4.93, 4.96 (2*m*, $w_{1/2} \approx 5$, 2H–C(4)); 6.14 (*AB*-system, $J$ = 15.8, $\delta_A$ = 6.08, $\delta_B$ = 6.20, H–C(1), H–C(2)). $^{13}$C-NMR (75 MHz, $C_6D_6$): 18.7, 20.6, 29.3, 29.6 (4*q*, $CH_3$–C(3), $CH_3$–C(2'), 2$CH_3$–C(7')); 55.8 (*q*, $CH_3O$); 31.7, 37.1 (2*t*, C(5'), C(6')); 115.7 (*t*, C(4)); 106.3 (*d*, C(4')); 128.4, 136.6 (2*d*, C(1), C(2)); 38.2 (*s*, C(7')); 110.6 (*s*, C(1')); 142.4, 147.2 (2*s*, C(3), C(2')). MS: 236 (2, $M^+$, $C_{15}H_{24}O_2$), 165 (34), 161 (16), 147 (17), 123 (26), 121 (18), 119 (13), 107 (23), 105 (27), 95 (11), 93 (11), 91 (19), 81 (15), 79 (12), 77 (13), 71 (33), 69 (10), 55 (17), *43* (100), 41 (31).

*(4*E,*4'*E*)-3-(1',1'-Dimethyl-4'-methoxy-3'-butenyl)-6-methyl-4,6-heptadien-2-one* (**10**). *Ca.* 90% pure. UV (0.375 mg in 25 ml): 233 (22500), 300 (800). IR: 3080*w*, 3060*w*, 3040*w*, 2990*m* (sh), 2960*s*, 2930*s*, 2900*m* (sh), 2830*m*, 1780*w* (br.), 1710*s*, 1665*m*, 1645*s*, 1605*w*, 1460*m* (sh), 1450*m*, 1435*m*, 1380*m*, 1365*m*, 1350*s*, 1255*m*, 1210*s*, 1175*m* (sh), 1150*m*, 1130*m*, 970*m*, 940*s*, 890*s*. $^1$H-NMR: 0.93, 0.96 (2*s*, 2$CH_3$–C(1')); 1.84 (*m*, $w_{1/2}$ = 4, $CH_3$–C(6)); 1.81–2.00 (*m*, 2H–C(2')); 2.14 (*s*, 3H–C(1)); 3.11 (*d*, $J$ = 10.0, H–C(3)); 3.53 (*s*, $CH_3O$); 4.70 (*dt*, $J_1$ = 12.5, $J_2$ = 7.9, H–C(3')); 4.94, 4.96 (2*m*, $w_{1/2}$ = 6, 2H–C(7)); 5.64 (*dd*, $J_1$ = 15.6, $J_2$ = 10.0, H–C(4)); 6.18 (*d*, $J$ = 15.6, H–C(5)); 6.20 (*d*, $J$ = 12.5, H–C(4')). $^{13}$C-NMR (75 MHz): 18.6, 24.5, 24.7, 32.2 (4*q*, C(1), $CH_3$–C(6), 2$CH_3$–C(1')); 56.0 (*q*, $CH_3O$); 38.9 (*t*, C(2')); 116.3 (*t*, C(7)); 64.4 (*d*, C(3)); 98.3 (*d*, C(3')); 125.8, 137.2 (2*d*, C(4), C(5)); 149.0 (*d*, C(4')); 37.5 (*s*, C(1')); 141.6 (*s*, C(6)); 209.7 (*s*, CO). MS: 236 (2, $M^+$, $C_{16}H_{24}O_2$), 161 (25), 148 (24), 123 (14), 113 (26), 112 (43), 109 (12), 107 (22), 91 (13), 81 (57), 79 (11), *71* (100), 55 (12), 43 (81), 41 (41).

*4-(7',7'-Dimethyl-4'-methoxy-2'-methyliden-3'-oxacycloheptylidene)-2-methyl-1-butene* (**11**). UV (0.467 mg in 25 ml): 231 (sh, 4700). IR: 3115*w*, 3080*w*, 2960*s*, 2930*s*, 2910*s*, 2870*m*, 2840*m*, 1645*m*, 1620*s*, 1465*m* (sh), 1455*m* (sh), 1445*s*, 1380*s*, 1370*m*, 1345*m*, 1320*m*, 1280*w*, 1240*s*, 1235*s*, 1210*s*, 1195*s*, 1165*s*, 1150*s*, 1135*s*, 1070*s*, 1040*s*, 1025*s*, 1005*s*, 925*m* (br.), 890*s*. $^1$H-NMR: 1.10, 1.17 (2*s*, 2CH$_3$–C(7')); 1.34 (*ddd*, $J_1$ = 12.8, $J_2$ = 8.5, $J_3$ = 4.9, H–C(6')); 1.65–1.95 (*m*, H–C(6'), 2H–C(5')); 1.73 (*m*, $w_{½}$ = 3, CH$_3$–C(2)); 2.89 (*dd*, $J_1$ = 15.9, $J_2$ = 7.0) and 2.97 (*dd*, $J_1$ = 15.9, $J_2$ = 8.0, 2H–C(3)); 3.41 (*s*, CH$_3$O); 3.96, 4.56 (2*s*, CH$_2$=C(2')); 4.65, 4.73 (2*m*, $w_{½} \approx 6$, 2H–C(1)); 4.69 (*dd*, $J_1$ = 7.7, $J_2$ = 3.1, H–C(4')); 5.60 (*dd*, $J_1$ = 8.0, $J_2$ = 7.0, H–C(4)). $^{13}$C-NMR (75 MHz): 23.0, 27.9, 28.2 (3*q*, CH$_3$–C(2), 2CH$_3$–C(7')); 56.0 (*q*, CH$_3$O); 31.7, 38.1, 38.6 (3*t*, C(3), C(5'), C(6')); 92.4 (*t*, CH$_2$=C(2')); 110.1 (*t*, C(1)); 102.8 (*d*, C(4')); 125.9 (*d*, C(4)); 37.4 (*s*, C(7')); 145.0, 145.5, 154.7 (3*s*, C(2), C(1'), C(2')). MS: 236 (1, $M^+$, C$_{15}$H$_{24}$O$_2$), 166 (13), 165 (100), 147 (14), 123 (21), 121 (13), 119 (12), 109 (12), 107 (18), 105 (22), 95 (10), 93 (10), 91 (25), 81 (17), 79 (14), 77 (14), 71 (52), 69 (13), 55 (20), 53 (11), 44 (10), 43 (62), 41 (38).

*(6*RS,7RS*)-7-Isopropenyl-6-methoxy-3,3-dimethyl-2-bicyclo[3.2.0]heptyl Methyl Ketone* (**12**). B.p. 90°/0.07 Torr. IR: 3080*w*, 2950*s*, 2925*s*, 2870*m*, 2820*s*, 1705*s*, 1640*w* (br.), 1455*m*, 1445*m*, 1415*w*, 1365*s*, 1350*s*, 1280*w*, 1240*w*, 1200*m* (br.), 1175*m*, 1125*s*, 1105*s*, 1050*w*, 1000*w* (br.), 890*m*. $^1$H-NMR: 0.80, 1.29 (2*s*, 2CH$_3$–C(3)); 1.63 (*dd*, $J_1$ = 14, $J_2$ = 8, H–C(4)); 1.81 (*m*, $w_{½}$ = 3, CH$_3$–C=CH$_2$); 1.85 (*dd*, overlapping with *m* at 1.81, $J_1$ = 14, $J_2$ = 8.5, H–C(4)); 2.12 (*s*, CH$_3$–CO); 2.58 (*d*, *J* = 7.6, H–C(2)); 2.57–2.72, 2.85–2.95, 3.18–3.25 (3*m*, H–C(1), H–C(5), H–C(7)); 3.22 (*s*, CH$_3$O), 3.75 (*dd*, $J_1$ = 7.5, $J_2$ = 3.5, H–C(6)); 4.80, 4.89 (2*m*, $w_{½} \approx 5$, CH$_2$=C–CH$_3$). $^{13}$C-NMR (75 MHz): 22.2, 23.4, 28.4, 31.7 (4*q*, 2CH$_3$–C(3), CH$_3$–C=CH$_2$, CH$_3$CO); 51.2 (*q*, CH$_3$O); 48.8 (*t*, C(4)); 111.3 (*t*, CH$_2$=C–CH$_3$); 40.9, 42.1, 56.0 (3*d*, C(1), C(2), C(5)); 69.6, 83.2 (2*d*, C(6), C(7)); 48.6 (*s*, C(3)); 143.6 (*s*, CH$_2$=C–CH$_3$); 208.7 (*s*, CO). MS: 236 (1, $M^+$, C$_{15}$H$_{24}$O$_2$), 221 (11), 204 (10), 161 (45), 149 (24), 148 (75), 123 (21), 113 (18), 112 (28), 107 (24), 105 (19), 99 (22), 98 (60), 91 (16), 83 (29), 81 (57), *71* (100), 55 (20), 43 (94), 41 (40). Anal. calc. for C$_{15}$H$_{24}$O$_2$ (236.36): C 76.23, H 10.24; found: C 76.14, H 10.24.

*(6*RS,7SR*)-3,3-Dimethyl-7-isopropenyl-6-methoxy-2-bicyclo[3.2.0]heptyl Methyl Ketone* (**13**). *Ca.* 90% pure. IR: 3080*w*, 2960*s*, 2930*s* (sh), 2870*m*, 2820*w*, 1705*s*, 1640*w*, 1460*m*, 1450*m*, 1440*m*, 1390*m*, 1370*m*, 1350*s*, 1290*w*, 1275*w*, 1205*s*, 1170*m*, 1150*m*, 1120*s*, 1065*m*, 985*w*, 890*m*. $^1$H-NMR: 0.76, 1.36 (2*s*, 2CH$_3$–C(3)); 1.55 (*dd*, $J_1$ = 12.7, $J_2$ = 7.7, H–C(4)); 1.68 (*s*, CH$_3$–C=CH$_2$); 2.02 (*dd*, $J_1$ = 12.7, $J_2$ = 9.9, H–C(4)); 2.13 (*s*, CH$_3$CO); 2.50 (*dd*, $J_1$ = $J_2$ = 7.2, H–C(7)); 2.64 (*d*, *J* = 4.5, H–C(2)); 2.73–2.90 (*m*, H–C(1), H–C(5)); 3.21 (*s*, CH$_3$O); 3.65 (*dd*, $J_1$ = $J_2$ = 7.2, H–C(6)); 4.71 (*m*, $w_{½}$ = 4, CH$_2$=C–CH$_3$). $^{13}$C-NMR (75 MHz): 20.6, 23.6, 28.8, 31.5 (*q*, 2CH$_3$–C(3), CH$_3$–C=CH$_2$, CH$_3$CO); 55.8 (*q*, CH$_3$O); 42.1 (*t*, C(4)); 108.8 (*t*, CH$_2$=C–CH$_3$); 37.9, 39.2, 57.5 (3*d*, C(1), C(2), C(5)); 71.2, 75.2 (2*d*, C(6), C(7)); 47.7 (*s*, C(3)); 145.3 (*s*, CH$_2$=C–CH$_3$); 208.6 (*s*, CO). MS: 236 (1, $M^+$, C$_{15}$H$_{24}$O$_2$), 204 (13), 161 (36), 149 (18), 148 (53), 123 (20), 113 (16), 112 (21), 107 (23), 105 (15), 99 (20), 98 (73), 91 (17), 83 (30), 81 (40), 71 (75), 55 (23), 53 (15), *43* (100), 41 (41).

2.2. *Singlet Excitation of* (E)-**5**. A soln. of (*E*)-**5** (2.00 g, 8.46 mmol) in MeCN was irradiated (quartz, lamp *A*, 85% conversion) in the presence of anh. $Na_2CO_3$ (50 mg). Chromatography of the photolysis mixture ($SiO_2$ + 0.3% $Et_3N$; $CH_2Cl_2$/hexane/acetone 50:50:1) gave mixed fractions, from which the following product distribution was determined ($^1$H-NMR, GC)[5]: (*Z*)-**5** (6%), **14** (20%), **15** (1%), (*E*)-**16** (3%), (*E*)-**17A** (4%), (*E*)-**17B** (6%), **18** (2%), and intractable material.

*6-(3'-Isopropenyl-1'-cyclopropenyl)-3-methoxy-6-methyl-2-heptanone* (**14**, mixture of two diastereomers). IR: 3075*w*, 2960*s*, 2930*s*, 2910*s* (sh), 2865*m* (sh), 2820*m*, 1760*w*, 1715*s*, 1630*w*, 1465*m* (sh), 1455*m* (sh), 1450*m*, 1430*w*, 1380*w*, 1370*m*, 1360*m*, 1350*m*, 1210*w* (br.), 1105*s*, 1020*w*, 960*w*, 870*m*. $^1$H-NMR (300 MHz): 1.11, 1.12 (2*s*, CH$_3$–C(6), 3H–C(7)); 1.38–2.00 (*m*, 2H–C(4), 2H–C(5)); 1.49 (*s*, CH$_3$–C=CH$_2$); 2.12–2.17 (*m*, H–C(3')); 2.14 (*s*, 3H–C(1)); 3.35 (*s*, CH$_3$O); 3.51 (*m*, with *t* character, H–C(3)); 4.67, 4.75 (2*m*, $w_{½} \approx 6$, CH$_2$=C–CH$_3$); 6.54 (*m*, $w_{½}$ = 4, H–C(2')). $^{13}$C-NMR (75 MHz): 20.0, 25.1 (2*q*, 2CH$_3$); 25.8–27.1 (several unresolved signals, presumably 2*q*, 1*t*, 1*d*): 57.9 (*q*, CH$_3$O); 36.2, 36.3 (2*t*, of 2 diastereomers, C(4)); 107.1 (*t*, CH$_2$=C–CH$_3$); 87.6, 100.2 (2*d*, C(3), C(2')); 34.6 (*s*, C(6)); 131.4, 150.3 (2*s*, C(1'), CH$_2$=C–CH$_3$); 210.8 (*s*, C(2)). MS: 236 (3, $M^+$, C$_{15}$H$_{24}$O$_2$), 193 (19), 161 (30), 155 (20), 148 (16), 139 (18), 138 (18), 137 (19), 135 (23), 133 (39), 123 (30), 121 (78), 119 (40), 109 (15), 107 (58), 105 (59), 95 (20), 93 (39), 91 (38), 88 (18), 69 (39), 67 (18), 59 (16), 55 (37), 53 (16), 45 (15), *43* (100), 41 (54). Anal. calc. for C$_{15}$H$_{24}$O$_2$ (236.36): C 76.23, H 10.24; found: C 76.06, H 10.02.

*(3*E*)-9-Methoxy-2,6,6-trimethyl-1,3,9-undecatrien-5-one* ((*E*)-**15**; *ca.* 1:1 mixture with **17A**). $^1$H-NMR: 1.17 (*s*, 2CH$_3$–C(6)); 1.53 (*d*, *J* = 6.8, 3H–C(11)); 1.5–2.2 (*m*, 2H–C(7), 2H–C(8)); 1.91 (*m*, $w_{½}$ = 6, CH$_3$–C(2)); 3.42 (*s*, CH$_3$O); 4.32 (*q*, *J* = 6.8, H–C(10)); 5.35, 5.39 (2*m*, $w_{½}$ = 4, 2H–C(1)); 6.95 (*AB*-system, *J* = 15.4, $\delta_A$ = 6.55, $\delta_B$ = 7.35, H–C(3), H–C(4)). $^{13}$C-NMR (75 MHz): 11.4, 18.2 (2*q*, CH$_3$–C(2), C(11)); 24.2 (2*q*, 2CH$_3$–C(6)); 53.8 (*q*, CH$_3$O); 25.6, 37.5 (2*t*, C(7), C(8)); 124.8 (*t*, C(1)); 89.9 (*d*, C(10)); 121.2, 145.0 (2*d*, C(3), C(4)); 46.4 (*s*, C(6)); 140.9 (*s*, C(2)); 156.9 (*s*, C(9)); 203.7 (*s*, C(5)).

*(*E,*1'*RS,*2'*SR,*3'*RS*)-1-(1',2'-Epoxy-3'-methoxy-2',6',6'-trimethylcyclohexyl)-3-methyl-1,3-butadiene* ((*E*)-**16**). UV (0.385 mg in 25 ml): 230 (19500). IR: 3080*w*, 3035*w*, 2960*s*, 2920*s*, 2860*m*, 2820*m*, 1740*w*, 1710*w*, 1605*w*,

1455*m*, 1445*m*, 1435*m*, 1375*m*, 1360*m*, 1330*w*, 1310*w*, 1255*w*, 1240*w*, 1205*w*, 1190*m*, 1155*w*, 1095*s*, 1040*m*, 975*s*, 930*m*, 905*m*, 890*s*. $^1$H-NMR: 0.93, 1.08 (2*s*, 2CH$_3$–C(6')); 1.21 (*s*, CH$_3$–C(2')); 1.23–1.34 (*m*, H–C(5')); 1.35–1.58 (*m*, H–C(4'), H–C(5')); 1.70–1.81 (*m*, H–C(4')); 1.84 (*m*, $w_{1/2}$ = 5, CH$_3$–C(3)); 3.38 (*s*, CH$_3$O); 3.43 (*dd*, $J_1$ = 6.1, $J_2$ = 5.0, H–C(3')); 4.96 (*m*, $w_{1/2}$ = 6, 2H–C(4)); 6.04 (*AB*-system, $J$ = 15.7, $\delta_A$ = 5.82, $\delta_B$ = 6.26, H–C(1), H–C(2)). $^{13}$C-NMR (75 MHz): 16.5, 18.6, 25.1, 26.9 (4*q*, CH$_3$–C(3), CH$_3$–C(2'), 2CH$_3$–C(6')); 57.5 (*q*, CH$_3$O); 21.9, 31.5 (2*t*, C(4'), C(5')); 116.5 (*t*, C(4)); 89.9 (*d*, C(3')); 125.2, 135.4 (2*d*, C(1), C(2)); 33.3 (*s*, C(6')); 66.5, 71.6 (2*s*, C(1'), (2')); 141.0 (*s*, C(3)). MS: 236 (8, $M^+$, $C_{15}H_{24}O_2$), 221 (14), 161 (17), 138 (15), 137 (16), *123* (100), 122 (15), 121 (21), 119 (15), 107 (25), 105 (26), 98 (17), 95 (22), 93 (17), 91 (16), 85 (28), 67 (15), 55 (20), 43 (52), 41 (30).

*(*E*)-3,3-Dimethyl-1-methoxy-2-(3'-methyl-1',3'-butadienyl)cyclopentyl Methyl Ketone* ((*E*)-**17A**). UV (0.256 mg in 25 ml): 228 (23700), 234 (25800), 242 (16800). IR: 3080*w*, 3040*w*, 2950*s*, 2860*m*, 2820*m*, 1705*s*, 1605*w*, 1450*m*, 1430*m*, 1380*w*, 1360*m*, 1350*m*, 1310*w*, 1190*m*, 1160*w*, 1130*w*, 1085*s*, 1070*m*, 1045*m*, 970*m*, 905*w*, 885*m*, 870*w*. $^1$H-NMR: 0.92, 0.95 (2*s*, 2CH$_3$–C(3)); 1.49–1.68 (*m*, 2H–C(4)); 1.90 (*m*, $w_{1/2}$ = 3, CH$_3$–C(3')); 1.86–1.96 (*m*, H–C(2), H–C(5)); 2.08 (*s*, CH$_3$CO); 2.36 (*ddd*, $J_1$ = 13.7, $J_2$ = 8.5, $J_3$ = 5.2, H–C(5)); 3.17 (*s*, CH$_3$O); 4.90, 4.91 (2*m*, $w_{1/2} \approx 5$, 2H–C(4')); 5.86 (*dd*, $J_1$ = 15.8, $J_2$ = 9.8, H–C(1')); 6.06 (*d*, $J$ = 15.8, H–C(2')). $^{13}$C-NMR (75 MHz): 18.9, 23.9, 26.1, 28.9 (4*q*, *C*H$_3$CO, 2*C*H$_3$–C(3), *C*H$_3$–C(3')); 52.5 (*q*, *C*H$_3$O); 28.2, 40.0 (2*t*, C(4), C(5)); 115.3 (*t*, C(4')); 62.9 (*d*, C(2)); 126.2, 135.8 (2*d*, C(1'), C(2')); 43.7 (*s*, C(3)); 95.6 (*s*, C(1)); 142.0 (*s*, C(3')); 212.4 (*s*, CO). MS: 236 ( < 1, $M^+$, $C_{15}H_{24}O_2$), 204 (39), *193* (100), 163 (44), 161 (72), 137 (57), 135 (35), 123 (19), 121 (21), 119 (29), 107 (39), 105 (98), 99 (16), 93 (27), 91 (33), 85 (40), 81 (20), 79 (30), 77 (25), 69 (24), 55 (23), 53 (16), 45 (30), 43 (26), 41 (40). Anal. calc. for $C_{15}H_{24}O_2$ (236.36): C 76.23, H 10.24; found: C 76.07, H 10.20.

*Isomer B* (**17B**). UV (0.338 mg in 25 ml): 232 (24500), 228 (23600). IR: 3080*w*, 3020*w*, 2950*s*, 2860*m*, 2820*w*, 1710*s*, 1605*w*, 1455*m* (br.), 1435*w*, 1385*w*, 1365*m*, 1350*m*, 1310*w*, 1265*w*, 1230*w*, 1200*w*, 1155*w*, 1125*m*, 1070*s*, 1035*w*, 975*m*, 890*m*. $^1$H-NMR: 0.82, 1.03 (2*s*, 2CH$_3$–C(3)); 1.54–1.65 (*m*, 2H–C(4)); 1.78 (*m*, $w_{1/2}$ = 3, CH$_3$–C(3')); 1.86 (*ddd*, $J_1$ = 14.3, $J_2$ = 6.5, $J_3$ = 3.5, H–C(5)); 2.09 (*s*, CH$_3$CO); 2.34 (*ddd*, $J_1$ = 14.3, $J_2$ = 10.8, $J_3$ = 8.2, H–C(5)); 2.36 (*d*, $J$ = 11.0, H–C(2)); 3.18 (*s*, CH$_3$O); 4.90 (*m*, $w_{1/2}$ = 5, 2H–C(4')); 5.27 (*dd*, $J_1$ = 15.4, $J_2$ = 11.0, H–C(1')); 6.13 (*d*, $J$ = 15.4, H–C(2')). $^{13}$C-NMR (75 MHz): 18.8, 23.6, 26.9, 29.7 (4*q*, *C*H$_3$CO, 2*C*H$_3$–C(3), *C*H$_3$–C(3')); 52.6 (*q*, CH$_3$O); 27.5, 39.3 (2*t*, C(4), C(5)); 115.6 (*t*, C(4')); 64.4 (*d*, C(2)); 126.6, 136.0 (2*d*, C(1'), C(2')); 43.2 (*s*, C(3)); 97.7 (*s*, C(1)); 141.6 (*s*, C(3')); 211.7 (*s*, CO). MS: 236 (2, $M^+$, $C_{15}H_{24}O_2$), 194 (14), *193* (100), 163 (16), 161 (63), 137 (41), 135 (27), 123 (21), 121 (23), 119 (27), 107 (38), 105 (77), 93 (28), 91 (31), 85 (35), 81 (20), 79 (25), 77 (21), 69 (21), 55 (21), 45 (23), 43 (64), 41 (35). Anal. calc. for $C_{15}H_{24}O_2$ (236.36): C 76.23, H 10.24; found: C 76.07, H 10.33.

*(1'*RS,2'RS,3'SR*)-3-(1',2'-Epoxy-3'-methoxy-2',6',6'-trimethylcyclohexyl)-1-methyl-1-cyclobutene* (**18**). IR: 3040*w*, 2960*s*, 2935*s*, 2910*s*, 2870*s*, 2850*m*, 2820*m*, 1635*w*, 1460*m* (sh), 1450*m*, 1440*m*, 1380*m*, 1370*m*, 1360m, 1270*w* (br.), 1190*m*, 1155*w*, 1100*s*, 1070*m* (sh), 1050*m*, 990*m*, 955*w*, 895*w*. $^1$H-NMR: 0.88–0.97 (*m*, H–C(5')); 1.07, 1.09 (2*s*, 2CH$_3$–C(6')); 1.44 (*s*, CH$_3$–C(2')); 1.46–1.62 (*m*, 2H–C(4'), H–C(5')); 1.67 (*m*, $w_{1/2}$ = 5, CH$_3$–C(1)); 2.47–2.59 (*m*, 2H–C(4)); 3.07–3.11 (*m*, H–C(3)); 3.38 (*s*, CH$_3$O); 3.33–3.40 (*m*, H–C(3')); 5.74 (*m*, H–C(2)). $^{13}$C-NMR (75 MHz): 16.6, 18.5, 24.3, 25.4 (4*q*, *C*H$_3$–C(1), *C*H$_3$–C(2'), 2*C*H$_3$–C(6')); 56.6 (*q*, *C*H$_3$O); 21.6, 35.6, 37.6 (3*t*, C(4), C(4'), C(5')); 42.3 (*d*, C(3)); 80.0 (*d*, C(3')); 130.3 (*d*, C(2)); 34.7 (*s*, C(6')); 65.0, 68.8 (2*s*, C(1'), C(2')); 144.3 (*s*, C(1)). MS: 236 (7, $M^+$, $C_{15}H_{24}O_2$), 221 (20), 161 (21), 138 (20), 137 (18), 133 (19), *123* (100), 122 (20), 121 (29), 119 (22), 107 (36), 105 (37), 95 (21), 93 (24), 91 (26), 85 (23), 81 (15), 79 (17), 77 (17), 69 (17), 67 (21), 55 (28), 53 (15), 43 (66).

2.3. *Triplet Excitation of* **9**. A soln. of **9** (30 mg, 0.13 mmol) in ($D_6$)acetone was irradiated (*Pyrex* NMR tube, lamp *B*) for 6 h. $^1$H-NMR analysis indicated quantitative conversion of **9** to **11**.

2.4. *Triplet Excitation of* **10**. A soln. of **10** (74 mg, 0.31 mmol) in acetone (10 ml) was irradiated for 2 h (*Pyrex*, lamp *B*, *ca.* 100% conversion). Chromatography (hexane/AcOEt 17:3) afforded **12** (24 mg, 33%) and **13** (14 mg, 19%).

**3. Additional Experiments.** – 3.1. *Preparation of* **22**. – 3.1.1. *From* (E/Z)-**6**. Catalytic hydrogenation of a mixture (2:1) of (*E*/*Z*)-**6** (72 mg, 0.31 mmol) according to *Procedure I* for 24 h afforded **22** (72 mg, 98%).

*(1*RS,5SR*)-2,2-Dimethyl-5-methoxy-1-(3'-methylbutyl)cyclopentyl Methyl Ketone* (**22**). *Ca.* 90% pure. IR: 2950*s*, 2930*s*, 2870*s*, 2820*w*, 1690*s*, 1460*m* (br.), 1380*m*, 1360*m*, 1350*m*, 1195*m*, 1130*m*, 1105*m*, 1090*m*. $^1$H-NMR: 0.89, 0.90 (2*d*, $J$ = 6.6, 3H–C(4'), CH$_3$–C(3')); 1.01, 1.03 (2*s*, 2CH$_3$–C(2)); 1.1–2.1 (*m*, 2H–C(3), 2H–C(4), 2H–C(1'), 2H–C(2'), H–C(3')); 2.15 (*s*, CH$_3$CO); 3.26 (*s*, CH$_3$O); 3.73 (*dd*, $J_1$ = 7.5, $J_2$ = 3.7, H–C(5)). $^{13}$C-NMR (75 MHz): 22.5, 26.3, 27.1, 31.6 (5*q*, 2 at 22.5, 2*C*H$_3$–C(2), *C*H$_3$CO, C(4'), *C*H$_3$–C(3')); 56.9 (*q*, CH$_3$O); 27.3, 32.4, 34.7, 38.8 (4*t*, C(3), C(4), C(1'), C(2')); 29.2 (*d*, C(3')); 89.8 (*d*, C(5)); 44.2, 66.5 (2*s*, C(1), C(2)); 211.1 (*s*, CO). MS: 240 (1, $M^+$, $C_{15}H_{28}O_2$), 171 (17), 169 (62), 151 (15), 149 (15), 113 (46), 109 (25), 96 (19), 95 (83), 83 (17), 81 (22), 69 (36), 55 (22), *43* (100), 41 (38).

3.1.2. *From* **23**. The alcohol **23** [2] (48 mg, 0.21 mmol) was treated according to *Procedure II* (reaction time 1 h) yielding **22** (51 mg, 88%).

3.2. *Preparation of* **24**. – 3.3.1. *From* (E)- *and* (Z)-**7**. Catalytic hydrogenation of (*E*)-**7** (30 mg, 0.13 mmol) and (*Z*)-**7** (45 mg, 0.19 mmol) according to *Procedure I* for 24 h afforded **24** (25 mg (86%) and 39 mg (85%) resp.).

*(1RS,5RS)-2,2-Dimethyl-1-(3'-methylbutyl)-5-methoxycyclopentyl Methyl Ketone* (**24**). IR: 2950*s*, 2930*s* (sh), 2900*s* (sh), 2865*s*, 2815*m*, 1685*s*, 1460*s*, 1385*m*, 1365*m*, 1350*s*, 1250*w*, 1190*m*, 1170*m*, 1150*m*, 1110*m*, 1090*s*, 965*w*. $^1$H-NMR: 0.88, 0.89 (2*d*, $J_1 = J_2 = 6.6$, $CH_3$–C(3'), 3H–C(4')); 0.91, 1.06 (2*s*, 2$CH_3$–C(2)); 1.18–1.82 (*m*, 2H–C(3), H–C(4), 2H–C(1'), 2H–C(2'), H–C(3')); 2.06–2.16 (*m*, H–C(4)); 2.12 (*s*, $CH_3CO$); 3.24 (*s*, $CH_3O$); 4.04 (*dd*, $J_1 = 7.6$, $J_2 = 3.9$, H–C(5)). $^{13}$C-NMR (75 MHz): 22.6, 25.5, 26.7, 29.3 (5*q*, 2 at 22.6, 2$CH_3$–C(2), $CH_3$–C(3'), C(4'), $CH_3CO$); 57.0 (*q*, $CH_3O$); 26.4, 28.6, 35.0, 38.4 (4*t*, C(3), C(4), C(1'), C(2')); 29.2 (*d*, C(3')); 84.5 (*d*, C(5)); 43.9 (*s*, C(2)); 67.6 (*s*, C(1)); 212.9 (*s*, CO). MS: 240 (1, $M^+$, $C_{15}H_{28}O_2$), 171 (12), 170 (14), *169* (100), 113 (54), 109 (23), 95 (28), 83 (16), 72 (18), 69 (25), 55 (16), 43 (71), 41 (23). Anal. calc. for $C_{15}H_{28}O_2$ (240.40): C 74.95, H 11.74; found: C 74.82, H 11.79.

3.2.2. *From* **25**. The alcohol **25** [2] (42 mg, 0.19 mmol) was treated according to *Procedure II* (reaction time 5 h) yielding **24** (43 mg, 95%).

3.3. *Preparation of* **29A** *and* **29B**. – 3.3.1. *Catalytic hydrogenation of* **12** (200 mg, 0.85 mmol) according to *Procedure I* with Pd/$BaSO_4$ for 2 h and chromatography of the mixture ($CH_2Cl_2$/acetone/hexane 59:1:40) afforded **28** (85 mg, 42%), **29A** (26 mg, 13%), and **29B** (16 mg, 8%).

*3,3-Dimethyl-7-isopropylidene-6-methoxy-bicyclo[3.2.0]hept-2-yl Methyl Ketone* (**28**). IR: 2950*s*, 2920*s*, 2870*m*, 2845*m*, 2810*m*, 1700*s*, 1460*m*, 1445*m*, 1385*w*, 1370*s*, 1350*m*, 1280*w*, 1225*m*, 1195*m*, 1165*m*, 1140*m*, 1120*m*, 1090*s*. $^1$H-NMR: 0.79, 1.23 (2*s*, 2$CH_3$–C(3)); 1.46, 1.65 (2*s*, $(CH_3)_2$–C=C(7)); 1.53 (*dd*, $J_1 = 12.8$, $J_2 = 7.3$, H–C(4)); 1.90 (*dd*, $J_1 = 12.8$, $J_2 = 8.7$, H–C(4)); 2.17 (*s*, $CH_3CO$); 2.57–2.66 (*m*, H–C(5)); 2.64 (*d*, $J = 7.2$, H–C(2)); 3.26 (*s*, $CH_3O$); 3.68–3.77 (*m*, H–C(1)); 4.07 (*m*, $w_{1/2} = 8$, H–C(6)). $^{13}$C-NMR (75 MHz): 19.0, 19.2, 23.5, 28.3, 32.0 (5*q*, 2$CH_3$–C(3), $(CH_3)_2$–C=C(7), $CH_3CO$); 54.5 (*q*, $CH_3O$); 48.3 (*t*, C(4)); 40.5, 45.2, 68.2 (3*d*, C(1), C(2), C(5)); 84.9 (*d*, C(6)); 48.9 (*s*, C(3)); 131.1, 134.3 (2*s*, C(7), $(CH_3)_2C$=C(7)); 209.2 (*s*, CO). MS: 236 (31, $M^+$, $C_{15}H_{24}O_2$), 221 (38), 204 (15), 193 (29), 189 (19), 180 (46), 165 (24), 161 (49), 149 (21), 148 (31), 147 (17), 137 (54), 123 (29), 119 (33), 107 (19), 105 (33), 99 (29), 95 (25), 91 (29), 83 (37), 79 (19), 77 (19), 69 (17), 67 (20), 55 (30), 53 (17), *43* (100), 41 (46).

*3,3-Dimethyl-7-isopropyl-6-methoxybicyclo[3.2.0]hept-2-yl Methyl Ketone, Isomer A* (**29A**). IR: 2950*s*, 2920*s*, 2860*s*, 2820*m*, 1705*s*, 1460*m*, 1380*m*, 1365*s*, 1355*s*, 1210*m*, 1180*m*, 1165*m*, 1145*m*, 1105*s*, 1055*w*, 1000*w* (br.). $^1$H-NMR: 0.75 (*d*, $J = 6.3$, 3H–C(1')); 0.75, 1.28 (2*s*, 2$CH_3$–C(3)); 0.87 (*d*, $J = 6.2$, 3H–C(3')); 1.58 (*dd*, $J_1 = 12.6$, $J_2 = 8.5$, H–C(4)); 1.74–1.91 (*m*, H–C(4), H–C(7), H–C(2')); 2.13 (*s*, $CH_3CO$); 2.48–2.58 (*m*, H–C(5)); 2.58 (*d*, $J = 7.6$, H–C(2)); 2.85–2.93 (*m*, H–C(1)); 3.22 (*s*, $CH_3O$); 3.58 (*dd*, $J_1 = 7.0$, $J_2 = 2.5$, H–C(6)). $^{13}$C-NMR (75 MHz): 19.8, 21.5, 23.5, 28.5, 32.0 (5*q*, $CH_3CO$, 2$CH_3$–C(3), C(1'), C(3')); 55.6 (*q*, $CH_3O$); 48.5 (*t*, C(4)); 27.4 (*d*, C(2')); 41.4, 42.7, 52.9, 70.5 (4*d*, C(1), C(2), C(5), C(7)); 81.8 (*d*, C(6)); 49.2 (*s*, C(3)); 209.0 (*s*, CO). MS: 238 (1, $M^+$, $C_{15}H_{26}O_2$), 126 (10), 113 (13), *112* (100), 100 (54), 95 (10), 85 (71), 71 (43), 55 (11), 43 (51), 41 (19).

*Isomer B* (**29B**). IR: 2950*s*, 2920*s*, 2895*s*, 2870*s*, 2820*m*, 1705*s*, 1460*m*, 1385*m*, 1365*s*, 1350*m*, 1300*w* (br.), 1260*w*, 1205*m*, 1190*m*, 1175*m*, 1160*m*, 1140*m*, 1120*s*, 1090*m*, 1045*w*, 995*m*. $^1$H-NMR: 0.67, 0.88 (2*d*, $J = 6.5$, 3H–C(1'), 3H–C(3')); 0.77, 1.23 (2*s*, 2$CH_3$–C(3)); 1.48 (*dd*, $J_1 = 13.0$, $J_2 = 5.5$, H–C(4)); 1.51–1.64 (*m*, H–C(2')); 1.76–1.82 (*m*, H–C(7)); 1.89 (*dd*, $J_1 = 13.0$, $J_2 = 8.7$, H–C(4)); 2.17 (*s*, $CH_3CO$); 2.37–2.42 (*m*, H–C(5)); 2.69 (*d*, $J = 9.9$, H–C(2)); 3.21 (*s*, $CH_3O$); 3.15–3.23 (*m*, H–C(1), H–C(6)). $^{13}$C-NMR (75 MHz): 19.9, 20.8, 23.8, 28.5, 32.2 (5*q*, $CH_3CO$, 2$CH_3$–C(3), C(1'), C(3')); 55.3 (*q*, $CH_3O$); 49.5 (*t*, C(4)); 29.3 (*d*, C(2')); 38.3, 41.0, 48.3, 62.6 (4*d*, C(1), C(2), C(5), C(7)); 89.3 (*d*, C(6)); 48.6 (*s*, C(3)); 209.6 (*s*, CO). MS: 238 (1, $M^+$, $C_{15}H_{26}O_2$), 112 (91), 100 (81), 95 (10), *85* (100), 71 (34), 43 (40), 41 (11).

3.3.2. *Catalytic hydrogenation of* **28** (82 mg, 0.35 mmol) according to *Procedure I* for 48 h gave after chromatography **29A** (20 mg, 24%) and **29B** (15 mg, 18%).

3.3.3. *Catalytic hydrogenation of* **26** [2] (200 mg, 0.90 mmol) according to *Procedure I* for 24 h afforded after chromatography (hexane/$Et_2O$ 1:4) **30A** (58 mg, 29%) and **30B** (26 mg, 13%).

*3,3-Dimethyl-6-hydroxy-7-isopropylbicyclo[3.2.0]hept-2-yl Methyl Ketone, Isomer A* (**30A**). *Ca.* 80% pure. IR: 3620*w*, 3600–3300*w*, 2950*s*, 2920*s* (sh), 2860*s*, 1700*s*, 1460*m*, 1385*m*, 1365*s*, 1355*m*, 1290*w*, 1200*m*, 1175*m*, 1160*m*, 1075*m*, 1030*w*. $^1$H-NMR: 0.73, 1.29 (2*s*, 2$CH_3$–C(3)); 0.77, 0.89 (*d*, $J = 6.4$, 3H–C(1'), 3H–C(3')); 1.5–1.9 (*m*, OH, 2H–C(4), H–C(7), H–C(2')); 2.13 (*s*, $CH_3CO$); 2.40–2.55 (*m*, H–C(5)); 2.61 (*d*, $J = 6.1$, H–C(2)); 2.92–3.00 (*m*, H–C(1)); 4.08 (*dd*, $J_1 = 6.5$, $J_2 = 2.0$, H–C(6)). $^{13}$C-NMR (75 MHz): 19.6, 21.3, 23.4, 27.2, 28.5 (5*q*, $CH_3CO$, 2$CH_3$–C(3), C(1'), C(3')); 48.2 (*t*, C(4)); 26.9 (*d*, C(2')); 42.7, 49.1, 54.2 (3*d*, C(1), C(2), C(5)); 70.7, 72.8 (2*d*, C(6), C(7)); 49.2 (*s*, C(3)); 209.7 (*s*, CO). MS: 224 (4, $M^+$, $C_{14}H_{24}O_2$), 165 (14), 163 (13), 139 (30),

*126* (100), 125 (25), 123 (18), 111 (22), 109 (44), 107 (17), 99 (55), 98 (75), 95 (65), 93 (15), 83 (22), 81 (20), 71 (40), 69 (60), 67 (18), 57 (27), 55 (20), 43 (90), 41 (20).

*Isomer B* (**30B**). IR ($CHCl_3$): 3600*m*, 3560–3300*w*, 2950*s*, 2920*s*, 2890*s*, 2865*s*, 1695*s*, 1615*w*, 1460*m*, 1385*m*, 1365*s*, 1350*m* (sh), 1295*m*, 1160*m*, 1100*m*, 1070*s*. $^1$H-NMR: 0.68, 0.93 (2*d*, $J$ = 6.3, 3H–C(1'), 3H–C(3')); 0.76, 1.22 (2*s*, $2CH_3$–C(3)); 1.51 (*dd*, $J_1$ = 13.0, $J_2$ = 4.9, H–C(4)); 1.50–1.65 (*m*, H–C(2')); 1.64–1.74 (*m*, H–C(7)); 1.87 (*dd*, $J_1$ = 13.0, $J_2$ = 8.7, H–C(4)); 1.9–2.0 (*m*, OH), 2.17 (*s*, $CH_3CO$); 2.34–2.48 (*m*, H–C(5)); 2.68 (*d*, $J$ = 10.0, H–C(2)); 3.11–3.21 (*m*, H–C(1)); 3.61 (*dd*, $J_1 = J_2 \approx 6$, H–C(6)). MS: 224 (3, $M^+$, $C_{14}H_{24}O_2$), 163 (10), 139 (15), 126 (95), 111 (22), 99 (22), 98 (70), 95 (67), 71 (46), 69 (50), 57 (20), 55 (18), *43* (100), 41 (23).

3.3.4. *Transformation of* **30A** *to* **29A**, *and* **30B** *to* **29B**. *a)* Reaction of **30A** (40 mg, 0.18 mmol) according to *Procedure II* for 16 h yielded **29A**. *b)* Analogously, reaction of **30B** (25 mg, 0.11 mmol) for 3 h gave **29B** (26 mg, 93%).

3.4. *Preparation of* **31**. – 3.4.1. *Catalytic hydrogenation of* **13** (28 mg, 0.12 mmol) according to *Procedure I* for 4 h afforded **31** (26 mg, 92%).

*(6*RS,7SR*)-3,3-Dimethyl-7-isopropyl-6-methoxybicyclo[3.2.0]hept-2-yl Methyl Ketone* (**31**). IR: 2955*s*, 2925*s*, 2890*s*, 2865*s*, 2820*m*, 1700*s*, 1460*s*, 1380*m*, 1365*s*, 1355*m*, 1215*m*, 1195*m*, 1180*m*, 1160*m*, 1120*s*, 1100*m* (sh), 1060*m*, 1020*w*, 980*w*. $^1$H-NMR (300 MHz): 0.74, 1.34 (2*s*, $2CH_3$–C(3)); 0.74 (*d*, $J$ = 6.5) and 0.87 (*d*, $J$ = 6.3, 3H–C(1'), 3H–C(3')); 1.35–1.58 (*m*, H–C(4), H–C(7), H–C(2')); 1.98 (*dd*, $J_1$ = 12.5, $J_2$ = 10.2, H–C(4)); 2.13 (*s*, $CH_3CO$); 2.42–2.50 (*m*, H–C(1)); 2.61 (*d*, $J$ = 4.8, H–C(2)); 2.74–2.87 (*m*, H–C(5)); 3.18 (*s*, $CH_3O$); 3.43 (*dd*, $J_1 = J_2$ = 6.4, H–C(6)). $^{13}$C-NMR (75 MHz): 19.8, 20.1, 23.7, 28.8, 31.8 (5*q*, $CH_3CO$, $2CH_3$–C(3), C(1'), C(3')); 55.7 (*q*, $CH_3O$); 42.1 (*t*, C(4)); 32.6, 38.3, 38.8, 59.0 (4*d*, C(1), C(2), C(5), C(2')); 71.7, 76.0 (2*d*, C(6), C(7)); 47.8 (*s*, C(3)); 209.1 (*s*, CO). MS: 238 ( < 1, $M^+$, $C_{15}H_{26}O_2$), 126 (11), 113 (15), *112* (100), 100 (62), 95 (12), 85 (90), 81 (12), 71 (45), 55 (15), 43 (62), 41 (24).

3.4.2. *Catalytic hydrogenation of* **27** (200 mg, 0.90 mmol) according to *Procedure I* for 16 h yielded **32** (124 mg, 61%).

*(6*RS,7RS*)-3,3-Dimethyl-6-hydroxy-7-isopropylbicyclo[3.2.0]hept-2-yl Methyl Ketone* (**32**). IR: 3610*m*, 3600–3250*w*, 2950*s*, 2920*s*, 2880*m*, 2860*s*, 1705*s*, 1460*m*, 1385*m*, 1365*s*, 1355*m*, 1295*w*, 1225*w*, 1180*m*, 1115*m*, 1070*w*, 1040*m*, 1010*w*, 905*m*. $^1$H-NMR: 0.74, 1.36 (2*s*, $2CH_3$–C(3)); 0.75, 0.91 (2*d*, $J \approx 6.3$, 3H–C(1'), 3H–C(3')); 1.45–1.60 (*m*, H–C(4), H–C(7), H–C(2')); 1.95–2.06 (*m*, OH); 2.00 (*dd*, $J_1$ = 12.3, $J_2$ = 10.4, H–C(4)); 2.13 (*s*, $CH_3CO$); 2.35–2.45 (*m*, H–C(5)); 2.62 (*d*, $J$ = 4.6, H–C(2)); 2.78–2.92 (*m*, H–C(1)); 3.89 (*dd*, $J_1 = J_2$ = 6.4, H–C(6)). $^{13}$C-NMR (75 MHz): 19.9, 20.1, 23.6, 28.8, 31.8 (5*q*, $CH_3CO$, $2CH_3$–C(3), C(1'), C(3')); 42.4 (*t*, C(4)); 32.8, 38.2, 41.3, 61.9 (4*d*, C(1), C(2), C(5), C(2')); 68.0, 71.7 (2*d*, C(6), C(7)); 47.9 (*s*, C(3)); 209.7 (*s*, CO). MS: 224 (3, $M^+$, $C_{14}H_{24}O_2$), 139 (18), 125 (58), 111 (17), 99 (35), 98 (28), 95 (46), 84 (21), 71 (26), 69 (44), 57 (16), 55 (20), *43* (100), 41 (24).

3.4.3. *Transformation of* **32** *into* **31**. Reaction of **32** (70 mg, 0.31 mmol) according to *Procedure II* for 3 h afforded **31** (70 mg, 89%).

3.5. *Hydrolysis of* **11**. A soln. of **11** (32 mg, 0.13 mmol) and oxalic acid (*ca.* 20 mg) in ($D_8$)THF (0.5 ml) and $D_2O$ (3 drops) was kept at r.t. for 2*d* until the hydrolysis of **11** was complete ($^1$H-NMR), the mixture was diluted with $Et_2O$ (5 ml) and worked up yielding **33** (24 mg, 80%).

*5-Acetyl-4,4,8-trimethyl-5,8-nonadienal* (**33**). IR: 3080*w*, 2960*s*, 2930*m*, 2910*m*, 2870*m*, 2810*w*, 2715*w*, 1725*s*, 1690*s*, 1645*w*, 1470*w*, 1445*w*, 1385*m*, 1370*m*, 1350*m*, 1250*m*, 1215*w*, 1170*m*, 1080*w*, 1000*w*, 980*w*, 890*s*. $^1$H-NMR: 1.10 (*s*, $2CH_3$–C(4)); 1.68–1.80 (*m*, 2H–C(3)); 1.72 (*m*, $w_{1/2}$ = 3, $CH_3$–C(8)); 2.26 (*s*, $CH_3CO$); 2.41 (*dt*, $J_1$ = 1.7, $J_2$ = 7.9, 2H–C(2)); 2.64 (*d*, $J$ = 7.8, 2H–C(7)); 4.70, 4.79 (2*m*, $w_{1/2}$ = 5, 2H–C(9)); 5.38 (*t*, $J$ = 7.8, H–C(6)); 9.76 (*t*, $J$ = 1.7, H–C(1)).

## REFERENCES


[1] U. Goldener, M.E. Scheller, P. Mathies, B. Frei, O. Jeger, *Helv. Chim. Acta* **1985**, *68*, 635.
[2] B. Frei, O. Jeger, N. Nakamura, H.R. Wolf, *Tetrahedron* **1981**, *37*, 3339.
[3] A.P. Alder, H.R. Wolf, O. Jeger, *Helv. Chim. Acta* **1978**, *61*, 2681.
[4] H.E. O'Neal, S.W. Benson, in 'Free Radicals', Ed. J.K. Kochi, J. Wiley, New York, 1973, Vol. II, p. 275.
[5] K.W. Egger, A.T. Cocks, *Helv. Chim. Acta* **1973**, *56*, 1516.
[6] G. de Weck, N. Nakamura, K. Tsutsumi, H.R. Wolf, B. Frei, O. Jeger, *Helv. Chim. Acta* **1983**, *66*, 2236.
[7] M. Diem, D. Burow, J. Fry, *J. Org. Chem.* **1977**, *42*, 1801.
[8] M.V. Bhatt, S.U. Kulkarni, *Synthesis* **1983**, 249.
[9] E. Taskinen, P. Liukas, *Acta Chem. Scand. Ser. B* **1974**, *28*, 114.
[10] A.P. Alder, H.R. Wolf, O. Jeger, *Helv. Chim. Acta* **1980**, *63*, 1833.