73. Photochemical Reactions

143rd Communication[1])

Photochemistry of 5,6-Epoxy-1,3-dienes in the Ionone Series. Influence of a Hydroxy Group in the 7-Position

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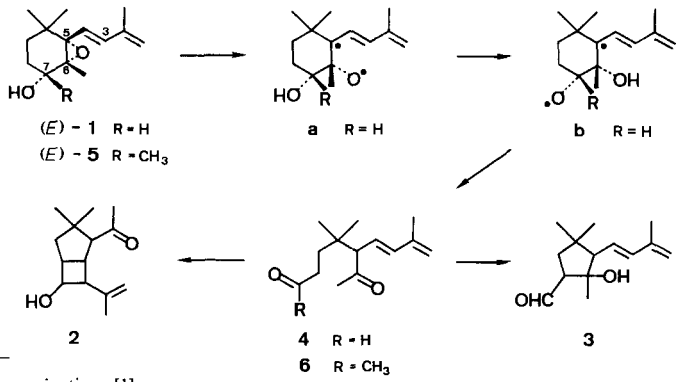
The synthesis and photolyses of the epoxydiene (*E*)-**5** are described. On triplet excitation ($\lambda > 280$ nm, acetone), (*E*)-**5** undergoes initial cleavage of the C(5)–O bond leading to the intermediate **c**. Presumably an H-shift (**c**→**e**) followed by the fragmentation of the 1,4-diradical **e** leads (*via* the enol **37**) to the diketones (*E*)-**6** and (*Z*)-**12**. Alternatively, cleavage of the C(6)–C(7) bond of **c** furnishes the diradical intermediate **d** which reacts by recombination leading to (*E*)-**13A** + **B**, **16**, and **17A** + **B**, or by an H-shift to the enol intermediate **38**. The latter undergoes an aldol-type reaction to (*E*/*Z*)-**14A** + **B** and (*E*/*Z*)-**15A** + **B**, as well as a photochemical [2 + 2]-cycloaddition to **18**. On singlet excitation (λ = 254 nm, MeCN), (*E*)-**5** undergoes photocleavage to the carbene intermediates **f** and **g**. The vinyl carbene **f** reacts with the adjacent double bond furnishing the cyclopropene **22** as the main product. From the carbene intermediate **g**, compounds **23**, **24**, and **25** arise by carbene insertion into the neighboring C–C or C–H bond. Furthermore, the diastereomer of the starting material, the epoxydiene (*E*)-**20**, is formed *via* the ylide intermediate **h**.

1. Introduction. – It was shown previously that triplet excitation (acetone, $\lambda > 280$ nm) of the 5,6-epoxy-7-hydroxy-1,3-diene (*E*)-**1** led to the compounds **2** and **3** which were new types of photoproducts in the series of conjugated epoxydienes derived from β-ionone [2]. The formation of **2** and **3** was assumed to involve cleavage of the C(5)–O bond

Scheme 1



[1]) 142nd Communication: [1].

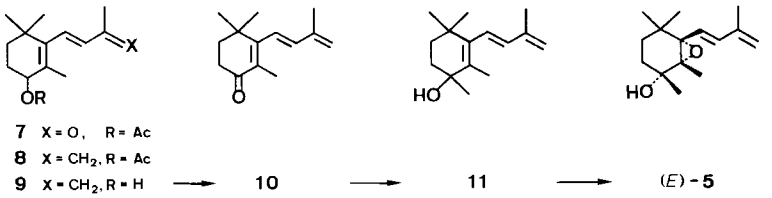
[2]) Taken in part from the planned Ph. D. thesis of *U. G.*

[3]) The X-ray analysis was carried out by this author.

of the oxirane followed by a H-shift from the OH group (**a**→**b**) and subsequent 1,4-diradical fragmentation leading to the postulated aldehyde **4** *(Scheme 1)*. To gain evidence for the proposed mechanism, the photochemistry of the tertiary alcohol **5** was investigated. Thus, it was expected that, instead of the presumably unstable aldehyde **4** which was not detected, the corresponding diketone **6** could be isolated and its photochemical behavior examined.

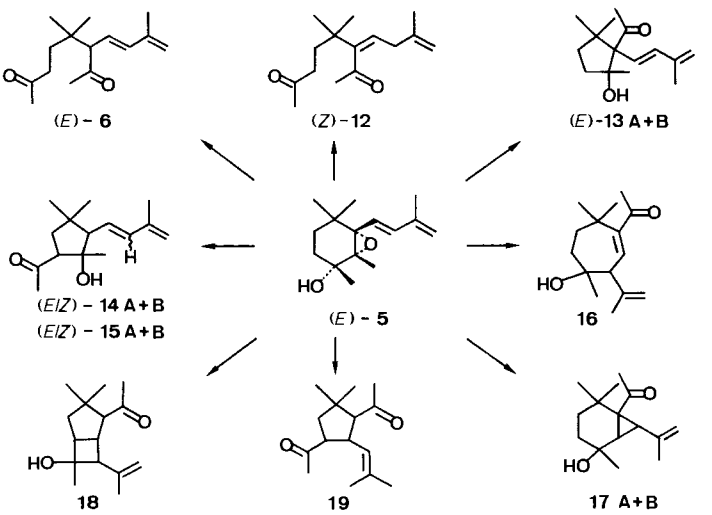
2. Preparation of the Epoxydiene (*E*)-5. – The synthesis of (*E*)-**5** was achieved as depicted in *Scheme 2*. Reaction of 4-acetoxy-β-ionone (**7**) [3][4]) with methylidenetriphenylphosphorane in Et_2O afforded the triene **8** (99%). Reduction of **8** with $LiAlH_4$ (97%) and oxidation of the trienol **9** with MnO_2 in hexane led to the trienone **10** (89%). Reaction of **10** with MeLi afforded the alcohol **11** (92%), which was subsequently epoxidized by the method of *Sharpless et al.* [5] leading stereoselectively to the epoxydiene (*E*)-**5** (85%) with *cis*-relation of the OH with the epoxy function.

Scheme 2



3. Photolyses. – 3.1. *Triplet excitation of* (E)-**5** ($\lambda > 280$ nm, acetone, 77% conversion) gave the following product distribution: (*E*)-**6** (2%), (*Z*)-**12** (20%), (*E*)-**13A** (2%), (*E*)-**13B** (4%), (*E*)-**14A** (10%), (*Z*)-**14A** (7%), (*E*)-**14B** (*ca.* 1%), (*E*)-**15A** (5%), (*Z*)-

Scheme 3

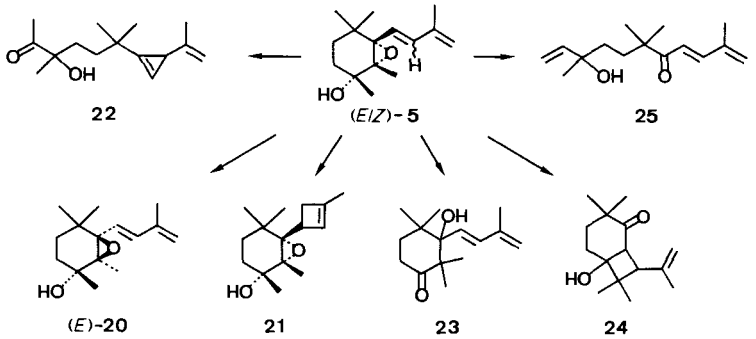


[4]) Numbering of the carotinoid nomenclature is used [4].

15A (1%), (*E*)-**15B** (2%), **16** (1%), **17A** (3%), **17B** (1%), **18** (1%), and **19** (*ca.* 1%) (*Scheme 3*)[5]).

3.2. *Singlet excitation of* (E)-**5** (λ = 254 nm, MeCN, 72% conversion) afforded (*Z*)-**5** (6%), (*E*)-**20** (4%), **21** (6%), **22** (45%), **23** (1%), **24** (1%), and **25** (1%) (*Scheme 4*).

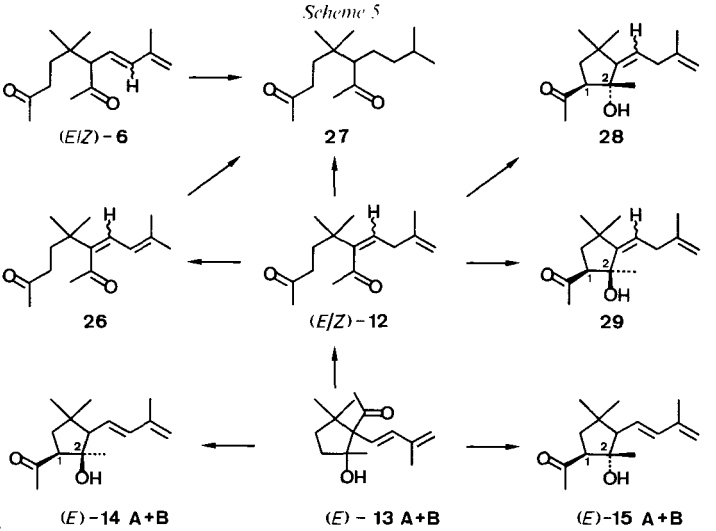
Scheme 4



4. Structure and Reactivity of the Photoproducts. – The structures of all new compounds were deduced from their spectral data. Compounds (*E*)-**13A + B**, (*E/Z*)-**14A + B**, (*E/Z*)-**15A + B**, **18**, **19**, (*E*)-**20**, **21**, **22**, and **23** are analogs of the products obtained by 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. For full spectral data and the NMR assignments see *Exper. Part.*

2,7-Octandiones (E)-**6** *and* (E/Z)-**12.** While the configuration around the C(1')=C(2') bond of (*E*)-**6** is evidenced by the ^{1}H-NMR coupling constant J = 15 Hz, the configuration around the C(3)=C(1') bond of

Scheme 5



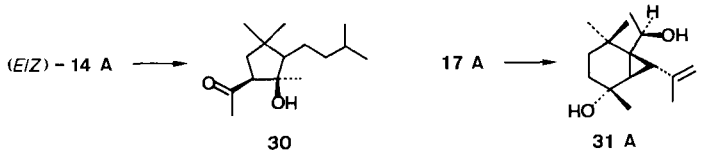
[5]) In this paper, the terms **A** and **B** are generally used for the description of diastereomeric compounds whose stereochemistry was not assigned conclusively.

(*E*/*Z*)-**12** was assigned by comparison of the chemical shift of H–C(1') (5.25 ppm) of (*Z*)-**12** with that of its photoisomer (*E*)-**12** (5.77 ppm), indicating that, as expected, in (*E*)-**12**, H–C(1') is deshielded due to an anisotropy effect of the Ac group. Furthermore, catalytic hydrogenation of (*E*)-**6** and (*Z*)-**12** led to the saturated diketone **27**. Of particular interest is the behavior of compound (*Z*)-**12** on treatment with base. Thus, on reaction with NaOMe, (*Z*)-**12** underwent an aldol reaction leading to the cyclopentanols **28** and **29** in a ratio of *ca.* 3:1 *(Scheme 5)*. Treatment of compound **28** under the same conditions gave again a *ca.* 5:1 mixture of **28**/**29**. Due to the availability of only small amounts of (*E*)-**6**, its reaction with base could not be investigated. On the other hand, it is noteworthy that treatment of compound (*E*)-**13A** with NaOMe induces a sequence of *retro*-aldol and aldol reactions leading to a mixture of compounds (*E*)-**14A** + **B** and (*E*)-**15A** + **B**. Furthermore, irradiation ($\lambda > 280$ nm) of (*E*)-**13A** induced (*E*)/(*Z*)-isomerization and γ-H-abstraction leading to (*Z*)-**12**; on photolysis of (*E*)-**13B**, compound (*E*)-**6** was obtained in addition to (*Z*)-**12**.

Cyclopentanols (*E*/*Z*)-**14A** + **B**, (*E*/*Z*)-**15A** + **B**, **28**, and **29**. The relative stereochemistry at C(1) and C(2) was assigned by measurement of their IR spectra at different concentrations. Thus, even dilute solutions of compounds (*E*)-**14A** + **B** and **29** show broad IR bands in the region of 3500–3400 cm^{-1}, characteristic of associated OH groups, evidencing an intramolecular H-bridge between the OH and the carbonyl of the Ac group; therefore, OH and Ac groups must be in *cis*-relation. On the other hand, the IR spectra of dilute solutions of compounds (*E*)-**15A** + **B** and **28** show only sharp bands in the region of 3600–3500 cm^{-1} of the free OH stretching vibration. In agreement with this stereochemical assignment, the IR bands of the carbonyl group of the former compounds with intramolecular H-bonding appear at 1695 cm^{-1} and that of the latter at 1710 cm^{-1}.

Compounds (*E*/*Z*)-**14A** could not be separated, therefore a 3:1 mixture was hydrogenated (Pd/C) leading to compound **30** in 90% yield *(Scheme 6)*.

Scheme 6



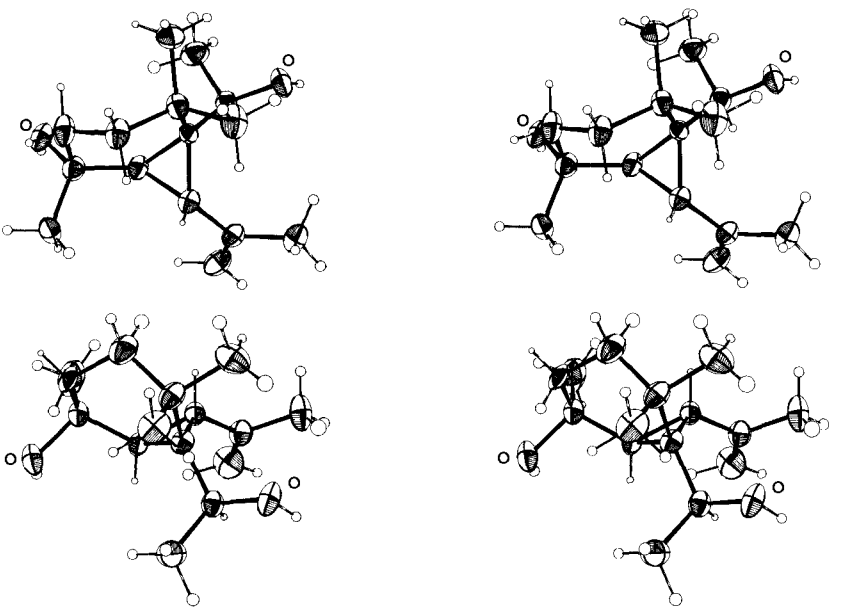


Figure. *Stereoscopic view of the two molecules* **31A** *in the asymmetric unit drawn by ORTEP* [7] *with thermal vibration ellipsoids at the 50% probability level*

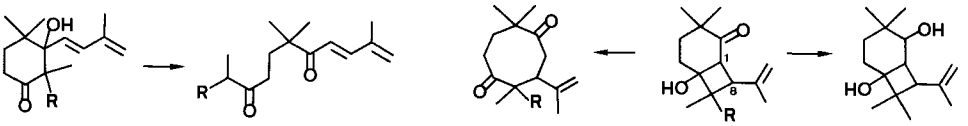
Bicyclic Compounds **17A + B**. Their structures could not be derived unequivocally from the spectral data. To prove the proposed structure and, in particular, to assign the stereochemistry, compound **17A** was reduced with $NaBH_4$ to the diols **31A + B**. The crystalline compound **31A** *(Scheme 6)* was subjected to X-ray analysis.

X-Ray Analysis of **31A**. Monoclinic space group $P2_1/n$, a = 13.294, b = 13.029, c = 17.602 Å, β = 105.32°, Z = 8, d(calc) = 1.077 g/cm^3. Intensity measurements were made at room temperature with a *SYNTEX* $P2_1$ diffractometer (graphite monochromator, MoK radiation, λ = 0.7107 Å, 3236 independent reflexions with $\theta < 22.5°$). The structure was solved by direct methods with SHELX 76 [8] and refined by full-matrix least-squares analysis using 1728 reflexions ($I > 3\sigma(I)$) with experimental weights (SHELX 76 [8], XRAY-72 [9]). H-atoms were located at an intermediate stage and included in the refinement with isotropic vibrational parameters (other atoms anisotropic), final R was 0.041 (R_w = 0.038)[6]).

The cyclobutene **21** *(Scheme 4)* was cleaved to epoxydiene (*E*)-**5** on thermolysis at 120°.

β-Hydroxyketone **23**. On treatment with NaOMe, **23** was transformed to the acyclic diketone **32**, in analogy to the previously reported reaction of **33**→**34** [6] *(Scheme 7)*.

Scheme 7



23 R = CH_3 **33** R = H **32** R = CH_3 **34** R = H **35** R = CH_3 **41** R = H **24** R = CH_3 **40** R = H **36**

The structure of the *bicyclic β-hydroxyketone* **24** was deduced from the spectral data (see *Exper. Part*). On treatment with NaOMe, **24** was transformed to the 1,5-cyclooctandione **35** proving the β-hydroxyketone moiety. Furthermore, on reduction of the ketone **24** with $NaBH_4$, the diol **36** was isolated *(Scheme 7)*, whose ^{1}H-NMR spectrum (300 MHz) shows the expected coupling pattern of H–C(1), H–C(2) and H–C(8) (see *Exper. Part*)[7]).

5. Discussion. – On triplet excitation ($\lambda > 280$ nm, acetone) of (*E*)-**5**, in addition to the known types of photoproducts ((*E*)-**13A + B**, (*E*/*Z*)-**14A + B**, (*E*/*Z*)-**15A + B**, **16**, **17A + B**, **18**, and **19**), the acyclic diketones (*E*)-**6** and (*Z*)-**12** were obtained. As postulated previously [2] [10], compounds (*E*)-**13A + B**, **16**, and **17A + B** are presumably formed by initial cleavage of the C(5)–O bond of the oxirane ((*E*)-**5**→**c**) followed by cleavage of the C(6)–C(7) bond (**c**→**d**) and subsequent bond formation between C(5) and C(7) (**d**→(*E*)-**13A + B**), between C(3) and C(7) (**d**→**16**), and between C(4) and C(7) as well as C(3) and C(5) (**d**→**17A + B**, *Scheme 8*)[8]).

On the other hand, (*E*)-**6** and (*Z*)-**12** could be formed *via* the trienol **37** *(Scheme 8)* arising from **c** by a H-transfer (**c**→**e**) and subsequent cleavage of the 1,4-diradical **e**[9]). With the isolation of the diketone (*E*)-**6** it became possible to examine, whether compounds (*E*/*Z*)-**14A + B**, (*E*/*Z*)-**15A + B**, and **18** are secondary photoproducts of the former, as was previously postulated for the formation of the related compounds **2** and **3** from the corresponding aldehyde **4** which could not be detected [2] *(Scheme 1)*. Triplet excitation of (*E*)-**6** ($\lambda > 280$ nm, acetone) led only to (*E*)/(*Z*)-isomerization; the formation of products (*E*/*Z*)-**14A + B**, (*E*/*Z*)-**15A + B**, and **18** was, however, not observed. Similarly, on triplet excitation, (*Z*)-**12** underwent (*E*)/(*Z*)-isomerization leading to (*E*)-

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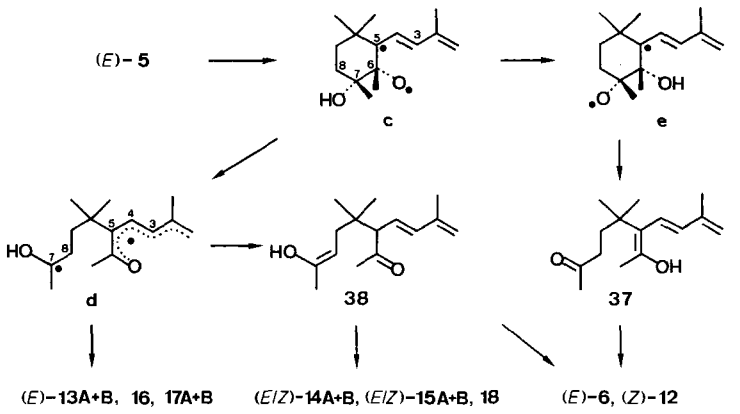
[6]) Atomic parameters have been deposited with the *Cambridge Crystallographic Data Centre*, Lensfield Road, Cambridge C2B 1EW, England.

[7]) For better comparison of the NMR data, for compound **36** numbering analogous to that of **24** was chosen.

[8]) Numbering of the centers was chosen as in (*E*)-**5** *(Scheme 1)* and **c** *(Scheme 8)*.

[9]) It may not be ruled out that (*E*)-**6** and (*Z*)-**12** could simply be secondary products of (*E*)-**13A + B** as was shown on photolyses of the two latter compounds *(Scheme 5)*.

Scheme 8



12 and, additionally, compound **26** was formed by γ-H-abstraction. On the basis of these findings, an alternative reaction mechanism was considered. Thus, it may be assumed that the intermediate **d** undergoes a H-shift formally from C(8) to C(5) leading to the enol **38**[8])[10]). The latter would undergo either an aldol-type reaction to (*E*/*Z*)-**14A** + **B** and (*E*/*Z*)-**15A** + **B** or a photochemical [2 + 2]-cycloaddition to **18**[11]). Furthermore, the enol intermediate **38** also has to be considered as a precursor of (*E*)-**6**. In connection with the transformation of **38** to (*E*/*Z*)-**14A** + **B** and (*E*/*Z*)-**15A** + **B**, it is noteworthy that on treatment with NaOMe, (*Z*)-**12** underwent an aldol reaction furnishing the related compounds **28** and **29** *(Scheme 5)*. Due to the availability of only small amounts of (*E*)-**6**, its reaction with NaOMe was unfortunately not investigated. However, it was of interest that (*E*)-**14A** + **B** and (*E*)-**15A** + **B** were obtained on treatment of (*E*)-**13A** with NaOMe, presumably *via* (*E*)-**6** as an intermediate.

As is characteristic for epoxydienes, on singlet excitation (λ = 254 nm) (*E*)-**5** shows photoisomerization *via* carbene intermediates. Thus, as main product, the cyclopropene **22** is formed *via* the vinyl carbene **f** *(Scheme 9)*. Evidence for the intermediacy of the alternative carbene **g** is provided by the isolation of the products **23**–**25** *(Scheme 4)*. Compounds **23** and **24** may be formed *via* the enol **39** which arises from carbene insertion into the neighboring C(7)–CH_3 bond in **g**[8])[12]). An intramolecular aldol-type reaction of **39** could subsequently lead to **23**. The latter process finds precedence in the formation of the corresponding cyclohexanone **33** *(Scheme 7)* on singlet excitation of (*E*)-**1** [6]. On the other hand, a [2 + 2]-cycloaddition of the enol double bond to the α,β-double bond of the dienone moiety of **39** could furnish the bicyclic compound **24**. An analogous process was postulated previously on singlet excitation of (*E*)-**1** leading to compound **40** *(Scheme 7)*

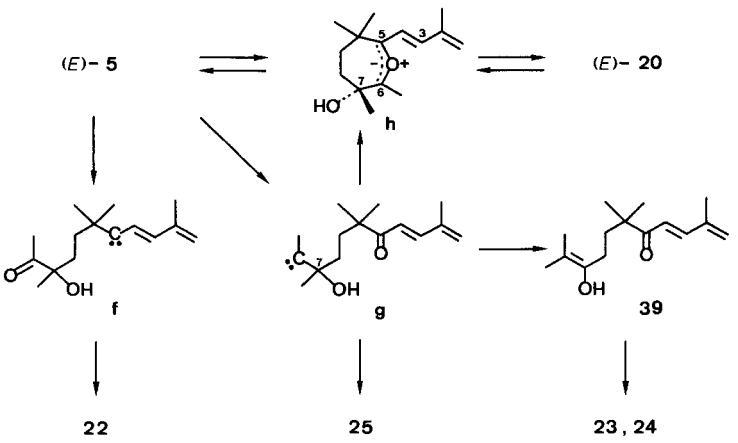
[10]) As will be shown in the following paper [11], on photolysis of the methyl ether of (*E*)-**1**, the methyl enolether corresponding to **38** was isolated.

[11]) In contrast to the photolysis of (*E*)-**1** producing two diastereomers of structure **2**, on triplet excitation of (*E*)-**5**, **18** was obtained as the only diastereomer. Presumably a diastereomer of **18** was transformed to compound **19** *(Scheme 3)* in analogy to the previously observed preferential thermal cleavage of one of the diastereomers of **2** [2].

[12]) As will be shown in the following paper [11], on photolysis of the methyl ether of (*E*)-**1**, the methyl enolether corresponding to **39** was isolated.

which could not be detected, however, since it presumably underwent spontaneous *retro*-aldol reaction to the cyclooctanedione **41** *(Scheme 7)* [6][13]). It is of interest that the yields of **23** and **24** are minute (1% each), whereas on photolysis of (*E*)-**1**, the corresponding compounds **33** and **41** were obtained in 31% and 3% yield, respectively. It is well-documented that in carbenes CH_3 groups migrate less efficiently than H-atoms [12]. Therefore, the carbene insertion **g**→**39** is an unfavorable process and, in competition, a carbene insertion into the C–H bond of the neighboring CH_3 group occurred leading to the allylic alcohol **25** in 1% yield *(Scheme 4)*. However, the dominant photoreaction of (*E*)-**5** was the formation of the carbene intermediate **f** furnishing the cyclopropene **22** in 45% yield, whereas on photolysis of (*E*)-**1**, the cyclopropene corresponding to **22** was obtained in 18% yield. The difference of the relative yields of products arising from the carbene intermediates of type **f** and **g** on photolysis of (*E*)-**1** and (*E*)-**5** finds an explanation, if the carbene **g** would preferentially escape to the ylide intermediate **h**, instead of undergoing the unfavorable transformations **g**→**25** or **39**, respectively. Subsequently, the ylide **h**, which alternatively could also arise directly from C–C bond cleavage of singlet-excited (*E*)-**5**, may close to the starting material or to the diastereomeric epoxydiene (*E*)-**20**.

Scheme 9



Furthermore, the cyclobutene **21** was obtained *(Scheme 4)*, by an electrocyclic reaction of the diene side chain.

Conclusion. – The isolation of (*E*)-**6** and (*Z*)-**12** on triplet excitation of (*E*)-**5** and the investigation of their photochemical behavior allows to draw some mechanistic conclusions on the formation of (*E*/*Z*)-**14A** + **B**, (*E*/*Z*)-**15A** + **B**, and **18** and their analogs, obtained on photolysis of (*E*)-**1** [2]. On the other hand, on singlet excitation of (*E*)-**5**, a marked effect of the CH_3 group at C(7) on the reactivity of the carbene **g** is documented.

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), Mr. *D. Manser* (elemental analysis), Mr. *H. U. Hediger* (IR) and Prof. *W. Petter*, Institut für Kristallographie und Petrographie der ETHZ (X-ray).

[13]) Analogously, **24** underwent a *retro*-aldol reaction leading to **35** on treatment with NaOMe *(Scheme 7)*.

Experimental Part

General. See [13], except as noted below. Anal. GC was performed using a 25 m × 0.33 mm *Ucon HB-5100* glass capillary. Column chromatographies were carried out on silica gel (SiO_2) 60 *Merck*, 0.040–0.063 mm, 230–400 mesh ASTM according to [14]. Analytically pure samples were obtained, in general, after repeated column chromatography, 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 CCl_4 solns. on a *Varian HA-100* instrument (100 MHz) or exceptionally (as indicated below), on a *Bruker WP-80/CW* (80 MHz) or a *WM-300* (300 MHz) instrument in $CDCl_3$ solns.

1. Preparation of the Epoxydiene (*E*)-5. – 1.1. *Transformation of the Dienone* 7 *into the Triene* **8**. A soln. of methylidenetriphenylphosphorane (*ca.* 0.24M) in Et_2O was added dropwise *via* a canula to a soln. of **7** [3] (29.0 g, 0.116 mol) in abs. Et_2O (500 ml) at 0° under Ar until all starting material was consumed (TLC control). The mixture was diluted with pentane (500 ml) and filtered through SiO_2. Evaporation of the solvents afforded **8** (28.8 g, 99%).

*(*E*)-2,4,4-Trimethyl-3-(3'-methyl-1',3'-butadienyl)-2-cyclohexenyl Acetate* (**8**). B.p. 100°/0.05 Torr. UV (0.073 mg in 10 ml): 237 (12900). UV (1.1675 mg in 2 ml): end absorption to 320. IR: 3090*w*, 3010*w* (sh), 2960*s*, 2940*s*, 2920*s* (sh), 2860*m*, 1735*s* (sh), 1732*s*, 1605*m*, 1470*m* (sh), 1460*m* (sh), 1450*s*, 1440*m*, 1370*s*, 1345*w*, 1315*w*, 1245*s*, 1180*m*, 1150*w*, 1125*w*, 1080*w*, 1015*s*, 995*m*, 970*s*, 960*s*, 925*w*, 890*s*, 865*w*. ^{1}H-NMR: 0.99, 1.04 (2*s*, 2 CH_3–C(4)); 1.62 (*s*, CH_3–C(2)); 1.86 (*s*, CH_3–C(3')); 1.96 (*s*, CH_3CO_2); 1.2–2.2 (*m*, 2H–C(5), 2H–C(6)); 4.88 (*m*, $w_{1/2}$ = 3, 2H–C(4')); 5.10 (*t*, *J* = 4, H–C(1)); 6.01 (*AB* system, *J* = 16, δ_A = 5.92, δ_B = 6.10, H–C(1'), H–C(2')). MS: 248 (6, M^+, $C_{16}H_{24}O_2$), 206 (9), 188 (16), 174 (13), 173 (83), 147 (11), 145 (32), 143 (11), 133 (27), 132 (58), 131 (33), 129 (17), 128 (16), 121 (14), 119 (27), 117 (27), 115 (21), 107 (18), 105 (39), 95 (13), 91 (57), 81 (12), 79 (24), 78 (11), 77 (34), 69 (11), 67 (16), 65 (18), 55 (22), 53 (20), *43* (100). Anal. calc. for $C_{16}H_{24}O_2$ (248.37): C 77.38, H 9.74; found: C 77.49, H 9.87.

1.2. *Transformation of* **8** *into the Alcohol* **9**. A soln. of **8** (28.8 g, 0.116 mol) in abs. Et_2O (100 ml) was added at 0° to a suspension of $LiAlH_4$ (8.8 g, 0.232 mol) in abs. Et_2O (1000 ml) over a 30 min period. The mixture ws stirred for 3 h at r.t. and worked up by adding *Celite* and sat. aq. $(NH_4)_2SO_4$. Filtration through $MgSO_4$ and *Celite*, evaporation of the solvent and distillation (135°/0.06 Torr) yielded **9** (23.2 g, 97%).

*(*E*)-2,4,4-Trimethyl-3-(3'-methyl-1',3'-butadienyl)-2-cyclohexen-1-ol* (**9**). B.p. 135°/0.06 Torr. UV (0.376 mg in 25 ml): 238 (11500), 250 sh (11400). IR: 3620*m*, 3480*w* (br.), 3090*w*, 2960*s*, 2930*s*, 2860*s*, 1630*w*, 1600*m*, 1450*s*, 1440*s*, 1375*s*, 1360*s*, 1310*w*, 1200*w* (br.), 1170*w*, 1030*s*, 1015*s* (sh), 995*s*, 970*s*, 890*s*. ^{1}H-NMR: 0.96, 0.99 (2*s*, 2 CH_3–C(4)); 1.48 (*s*, OH); 1.73 (*s*, CH_3–C(2)); 1.84 (*m*, $w_{1/2}$ = 3, CH_3–C(3')); 1.2–2.1 (*m*, 2H–C(5), 2H–C(6)); 3.84 (*dd*, $J_1 = J_2$ = 5, H–C(1)); 4.85 (*m*, $w_{1/2}$ = 3, 2H–C(4')); 5.98 (*AB* system, *J* = 16, δ_A = 5.87, δ_B = 6.07, H–C(1'), H–C(2')). MS: *206* (100, M^+, $C_{14}H_{22}O$), 191 (63), 173 (35), 163 (15), 150 (40), 147 (12), 145 (20), 135 (59), 133 (18), 132 (16), 131 (24), 123 (15), 121 (27), 119 (19), 117 (14), 109 (22), 108 (19), 107 (49), 105 (29), 95 (18), 94 (12), 93 (27), 91 (37), 81 (16), 79 (19), 77 (19), 69 (14), 67 (11), 55 (18), 53 (10), 43 (24).

1.3. *Oxidation of* **9** *to* **10**. Five portions of **9** (3.3 g, 15.9 mmol) in hexane (300 ml) and MnO_2 were stirred vigorously for 15 h at r.t. The mixtures were filtered through *Celite*, the solvent evaporated and the residue distilled (106°/0.06 Torr) affording **10** (14.4 g, 89%).

*(*E*)-2,4,4-Trimethyl-3-(3'-methyl-1',3'-butadienyl)-2-cyclohexen-1-one* (**10**). B.p. 106°/0.06 Torr. UV (0.181 mg in 20 ml): 221 (19000), 226 (19900), 281 (17700). UV (4.857 mg in 5 ml): end absorption to 400. IR: 3080*w*, 2960*s*, 2920*s*, 2860*m*, 1660*s* (br.), 1600*m* (br.), 1470*m* (sh), 1460*m* (sh), 1450*m*, 1440*m*, 1420*m*, 1375*m*, 1360*m*, 1350*s*, 1330*s*, 1310*m*, 1300*m*, 1275*w*, 1230*w*, 1195*s*, 1140*w*, 1090*m*, 1025*m* (br.), 965*s*, 890*s*. ^{1}H-NMR: 1.15 (*s*, 2 CH_3–C(4)); 1.74 (*s*, CH_3–C(2)); 1.90 (*m*, $w_{1/2}$ = 4, CH_3–C(3')); 1.70–1.95 (*m*, 2H–C(5)); 2.29–2.48 (*m*, with *t* character, *J* = 6.5, 2H–C(6)); 5.00 (*m*, $w_{1/2}$ = 7, 2H–C(4')); 6.16 (*AB* system, *J* = 16, δ_A = 6.06 H–C(2'), δ_B = 6.26 H–C(1')). ^{13}C-NMR: 13.5, 18.2, 27.5, (4*q*, 2*q* at 27.5, 2 *C*H_3–C(4), *C*H_3–C(2), *C*H_3–C(3')); 34.3, 37.4 (2*t*, C(5), C(6)); 118.5 (*t*, C(4')); 125.3, 138.7 (2*d*, C(1'), C(2')); 35.6 (*s*, C(4)), 129.9, 141.4, 160.6 (3*s*, C(2), C(3), C(3')); 198.6 (*s*, C(1)). MS: 205 (17), *204* (100, M^+, $C_{14}H_{20}O$), 189 (52), 171 (17), 164 (17), 163 (69), 161 (30), 150 (13), 148 (57), 147 (42), 145 (10), 136 (10), 135 (19), 134 (15), *133* (100), 131 (13), 122 (14), 121 (34), 120 (18), 119 (70), 117 (11), 115 (12), 107 (29), 106 (26), 105 (67), 93 (21), 91 (59), 79 (25), 77 (33), 69 (15), 67 (11), 65 (21), 55 (37), 53 (21), 51 (14), 43 (49).

1.4. *Reaction of* **10** *with MeLi.* A soln. of MeLi in Et_2O (1.6M, 64 ml, 102.4 mmol) was added at −10° to a soln. of **10** (14.4 g, 70.5 mmol) in abs. Et_2O (500 ml) over a 90 min period. The mixture was allowed to warm up to r.t., worked up with sat. aq. NH_4Cl and chromatographed (Et_2O/hexane 1:2) affording **11** (12.5 g, 81%) and starting material (**10**, 2.3 g). The latter was treated with MeLi as described before yielding **11** (1.64 g, 11%; total yield of **11**: 92%).

*(*E*)-1,2,4,4-Tetramethyl-3-(3'-methyl-1',3'-butadienyl)-2-cyclohexen-1-ol* (**11**). B.p. 107°/0.07 Torr. UV (0.663 mg in 20 ml): 229 (5900), 252 sh (4400), end absorption to 300. IR: 3610*m*, 3480*w* (br.), 3080*w*, 2960*s*, 2880*s*,

2810*w*, 1670*w* (br.), 1600*m*, 1450*s*, 1435*s*, 1420*s*, 1380*m*, 1360*m*, 1340*m*, 1310*m*, 1290*s*, 1245*s*, 1165*m*, 1070*m*, 1025*w* (br.), 970*s*, 925*m*, 870*s*, 690*s*. ^{1}H-NMR: 0.93, 1.01 (2*s*, 2 CH_3–C(4)); 1.08 (*s*, OH); 1.21 (*s*, CH_3–C(1)); 1.68 (*s*, CH_3–C(2)); 1.3–1.8 (*m*, 2H–C(5), 2H–C(6)); 1.84 (*s*, CH_3–C(3′)); 4.86 (*m*, with fine structure, $w_{1/2}$ = 4, 2H–C(4′)); 5.97 (*s*, H–C(1′), H–C(2′)).^{13}C-NMR: 15.2, 18.8, 27.7, 28.7 (5*q*, 2*q* at 28.7, CH_3–C(1), CH_3–C(2), 2 CH_3–C(4), CH_3–C(3′)); 36.0 (2*t*, C(5), C(6)); 115.8 (*t*, C(4′)); 127.5, 136.6 (2*d*, C(1′), C(2′)); 34.8 (*s*, C(4)); 71.4 (*s*, C(1)); 133.1, 139.6 (2*s*, C(2), C(3)); 142.2 (*s*, C(3′)). MS: 220 (5, M^+, $C_{15}H_{24}O$), 203 (13), 202 (74), 188 (15), *187* (100), 172 (22), 160 (11), 159 (68), 158 (15), 157 (27), 147 (21), 146 (56), 145, (92), 144 (14), 143 (21), 142 (14), 141 (14), 133 (25), 132 (12), 131 (60), 130 (13), 129 (21), 128 (20), 121 (17), 119 (41), 117 (20), 115 (21), 107 (24), 106 (13), 105 (57), 95 (34), 93 (18), 91 (45), 81 (17), 79 (20), 77 (32), 69 (32), 67 (16), 65 (16), 57 (11), 55 (21), 53 (19), 51 (10), 43 (24). Anal. calc. for $C_{15}H_{24}O$ (220.36): C 81.76, H 10.98; found: C 81.62, H 10.84.

1.5. *Epoxidation of* **11**. To a soln. of **11** (14.3 g, 65.0 mmol) in benzene (1000 ml) and $VO(acac)_2$ (270 mg, 1.02 mmol), which was cooled in an ice/NaCl bath, a soln. of *t*-BuOOH (12.3 g, 110 mmol) in benzene (200 ml was added over a 45 min period. The mixture was allowed to come to r.t. and after *ca.* 2 h, it was worked up in Et_2O (400 ml) with sat. aq. $FeSO_4$. Filtration over SiO_2 (Et_2O/hexane 2:3) and distillation (110°/0.01 Torr) gave (*E*)-**5** (13.0 g, 85%).

(E,1RS,2RS,3SR)-2,3-Epoxy-1,2,4,4-tetramethyl-3-(3′-methyl-1′,3′-butadienyl)-1-cyclohexanol ((*E*)-**5**). M.p. 71–72°. UV (0.247 mg in 20 ml): 231 (27500). IR: 3590*w*, 3570*m*, 3490*w* (br.), 3080*w*, 3040*w*, 2970*s*, 2940*s*, 2870*m*, 1785*w* (br.), 1610*m*, 1470*m* (sh), 1460*m* (sh), 1450*s*, 1440*s* (sh), 1380*s*, 1365*s*, 1345*m*, 1320*s*, 1315*m*, 1255*m*, 1240*m*, 1205*w*, 1180*m*, 1160*m*, 1140*m* (sh), 1130*m*, 1075*s*, 1060*s*, 1045*m*, 1020*m*, 975*s*, 955*m*, 930*s*, 890*s*. ^{1}H-NMR: 0.92, 1.02 (2*s*, 2 CH_3–C(4)); 1.13, 1.18 (2*s*, CH_3–C(1), CH_3–C(2)); 1.25–1.70 (*m*, 2H–C(5), 2H–C(6)); 1.81 (*m*, $w_{1/2}$ = 3, CH_3–C(3′)); 2.09 (*s*, OH); 4.93 (*m*, $w_{1/2}$ = 5, 2H–C(4′)); 5.94 (*AB* system, J = 16, δ_A = 5.67 H–C(2′), δ_B = 6.20 H–C(1′)). ^{13}C-NMR: 14.4, 18.5, 25.2, 25.4, 26.6 (5*q*, CH_3–C(1), CH_3–C(2), 2 CH_3–C(4), CH_3–C(3′)); 33.7, 34.3 (2*t*, C(5), C(6)); 116.7 (*t*, C(4′)); 124.4, 135.7 (2*d*, C(1′), C(2′)); 33.1 (*s*, C(4)); 70.3, 74.3 (3*s*, 2*s* at 70.3, C(1), C(2), C(3)); 140.7 (*s*, C(3′)). MS: 236 (2, M^+, $C_{15}H_{24}O_2$), 193 (10), 165 (14), 139 (22), 138 (88), 135 (10), 133 (11), *123* (100), 121 (16), 107 (15), 105 (11), 98 (13), 95 (21), 91 (11), 85 (14), 43 (63). Anal. calc. for $C_{15}H_{24}O_2$ (236.36): C 76.23, H 10.24; found: C 76.15, H 10.31.

2. Photolysis Experiments. – 2.1. *Triplet Excitation of (E)-***5** (λ > 280 nm, acetone). A soln. of (*E*)-**5** (1.9 g, 8.05 mmol) in acetone (180 ml) was irradiated for 2 h under Ar (lamp *B*, *Pyrex*, 77% conversion). Chromatography of the photolysis mixture (SiO_2, hexane/Et_2O gradient O→80% Et_2O) afforded several fractions from which the following product distribution was determined (GC, ^{1}H-NMR)[14]: (*E*)-**6** (2%), (*Z*)-**12** (20%), (*E*)-**13A** (2%), (*E*)-**13B** (4%), (*E*)-**14A** (10%), (*Z*)-**14A** (7%), (*E*)-**14B** (*ca.* 1%), (*E*)-**15A** (5%), (*Z*)-**15A** (1%), (*E*)-**15B** (2%), **16** (1%), **17A** (3%), **17B** (1%), **18** (1%), **19** (*ca.* 1%), and two compounds of unknown structure in 1 and 3% yield, respectively.

(E)-4,4-Dimethyl-3-(3′-methyl-1′,3′-butadienyl)-2,7-octanedione ((*E*)-**6**). *Ca.* 90% pure. UV (0.250 mg in 25 ml): 233 (22900), 240 sh (18000). UV (1.934 mg in 2 ml): end absorption to 340. IR: 3080*w*, 2960*s*, 2920*s*, 2870*m*, 2850*m* (sh), 1780*w* (br.), 1715*s* (sh), 1710*s*, 1640*w*, 1605*w*, 1450*m*, 1435*m*, 1420*m* (sh), 1385*m*, 1365*s*, 1350*s*, 1290*m* (br.), 1235*m* (br.), 1155*s*, 970*m*, 890*s*. ^{1}H-NMR: 0.88, 0.91 (2*s*, 2 CH_3–C(4)); 1.14–1.68 (*m*, 2H–C(5)); 1.83 (*m*, $w_{1/2}$ = 2, CH_3–C(3′)); 2.02, 2.05 (2*s*, 3H–C(8), 3H–C(1)); 1.91–2.40 (*m*, 2H–C(6)); 2.95 (*d*, J = 10, H–C(3)); 4.88 (*m*, $w_{1/2}$ = 3, 2H–C(4′)); 5.54 (*dd*, J_1 = 10, J_2 = 15, H–C(1′)); 6.10 (*d*, J = 15, H–C(2′)). ^{13}C-NMR (75 MHz): 18.6, 24.3, 24.3, 29.8, 32.2 (5*q*, C(1), 2 CH_3–C(5), CH_3–C(3′), C(7)); 33.9, 38.3 (2*t*, C(5), C(6)); 116.5 (*t*, C(4′)), 65.0 (*d*, C(3)); 125.4, 137.2 (2*d*, C(1′)), C(2′)), 36.4 (*s*, C(4)); 141.3 (*s*, C(3′)); 208.1, 209.0 (2*s*, C(2), C(7)). MS: 236 (1, M^+, $C_{15}H_{24}O_2$), 135 (18), 113 (29), 109 (14), 107 (14), 95 (14), 81 (24), *43* (100), 41 (10).

(Z)-4,4-Dimethyl-3-(3′-methyl-3′-butenylidene)-2,7-octanedione ((*Z*)-**12**). B.p. 124°/0.07 Torr. UV (0.172 mg in 10 ml): 226 (2500). UV (1.94 mg in 2 ml): end absorption to 350. IR: 3080*w*, 2970*s*, 2940*s*, 2880*m*, 1720*s*, 1695*s*, 1650*m*, 1450*m* (br.), 1390*m*, 1370*s*, 1350*s*, 1290*w* (br.), 1180*m*, 1080*w*, 960*w*, 930*w*, 895*s*. ^{1}H-NMR: 1.05 (*s*, 2 CH_3–C(4)); 1.46–1.80 (*m*, 2H–C(5)); 1.71 (*m*, $w_{1/2}$ = 3, CH_3–C(3′)); 2.04 (*s*, 3H–C(8)); 2.16 (*s*, 3H–C(1)); 2.10–2.38 (*m*, 2H–C(6)); 2.58 (*d*, J = 8, broadened to *m*, $w_{1/2}$ = 3, 2H–C(2′)); 4.60–4.78 (*m*, 2H–C(4′)); 5.25 (*t*, J = 8, H–C(1′)). ^{13}C-NMR: 22.2, 27.1, 29.3, 33.0 (5*q*, 2*q* at 27.1, C(1), 2 CH_3–C(5), C(8), CH_3–C(3′)); 34.6, 37.0, 39.0 (3*t*, C(5), C(6), C(2′)); 110.8 (*t*, C(4′)); 122.5 (*d*, C(1′)); 36.9 (*s*, C(4)); 143.3, 150.6 (2*s*, C(3), C(3′)); 207.5, 207.7 (2*s*, C(2), C(7)). MS: 236 (< 1, M^+, $C_{15}H_{24}O_2$), 165 (10), 147 (21), 123 (22), 113 (10), 107 (10), *43* (100), 41 (10). Anal. calc. for $C_{15}H_{24}O_2$ (236.36): 76.23, H 10.24; found: C 76.27, H 10.15.

(E)-2-Hydroxy-2,5,5-trimethyl-1-(3′-methyl-1′,3′-butadienyl)cyclopentyl Methyl Ketone, Isomer A ((*E*)-**13A**). M.p. 65–69°. UV (0.297 mg in 20 ml): 233 (20400). UV (2.26 mg in 2 ml): end absorption to 330. IR: 3530*m*, 3080*w*,

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

2960*s*, 2940*s*, 2880*m*, 1720*m*, 1685*s*, 1605*w*, 1460*m*, 1450*m*, 1440*m*, 1390*m*, 1370*s*, 1355*s*, 1305*m*, 1245*w*, 1220*m*, 1185*m*, 1165*m*, 1110*w*, 1060*w*, 975*m*, 935*m*, 905*m*, 890*m*. ^{1}H-NMR: 1.12, 1.22, 1.28 (3*s*, CH_3–C(2), 2 CH_3–C(5)); 1.50–2.10 (*m*, 2H–C(3), 2H–C(4)); 1.81 (*m*, $w_{1/2}$ = 4, CH_3–C(3')); 2.09 (*s*, CH_3–CO); 3.76 (*d*, *J* = 2, OH); 4.88 (*m*, $w_{1/2}$ = 4, 2H–C(4')); 5.66 (*AB* system, *J* = 16, δ_A = 5.55, δ_B = 5.77, H–C(1'), H–C(2')). ^{13}C-NMR: 18.4, 27.3, 28.1, 29.4, 30.2 (5*q*, CH_3–CO, CH_3–C(2), 2 CH_3–C(5), CH_3–C(3')); 37.6, 39.7 (2*t*, C(3), C(4)); 116.9 (*t*, C(4')); 129.9, 134.5 (2*d*, C(1'), C(2')); 44.1 (*s*, C(5)); 72.8 (*s*, C(1)); 85.7 (*s*, C(2)); 141.2 (*s*, C(3')); 214.1 (*s*, CO). MS: 236 (< 1, M^+, $C_{15}H_{24}O_2$), 175, (16), 165 (18), 147 (46), 135 (15), 123 (38), 121 (14), 119 (11), 113 (23), 107 (17), 105 (13), 95 (13), 91 (12), 81 (15), *43* (100), 41 (15).

Isomer B ((*E*)-**13B**). *Ca.* 70% pure. UV (0.11 mg in 10 ml): 235 (*ca.* 10000). UV (1.646 mg in 2 ml): end absorption to 340. IR: 3590*w*, 3080*w*, 2960*s*, 2940*s*, 2870*m*, 1700*s*, 1600*w*, 1460*m*, 1450*m*, 1160*m*, 890*m*. ^{1}H-NMR (80 MHz): 1.04, 1.24, 1.38 (3*s*, CH_3–C(2), 2 CH_3–C(5)); 1.50–2.20 (*m*, 2H–C(3), 2H–C(4)); 1.94 (*s*, CH_3–C(3')); 2.11 (*s*, CH_3–CO); 5.00 (*m*, $w_{1/2}$ = 6, 2H–C(4')); 6.15 (*AB* system, *J* = 17, δ_A = 5.90, δ_B = 6.40, H–C(1'), H–C(2')): MS: 236 (5, M^+, $C_{15}H_{24}O_2$), 175 (15), 165 (14), 147 (19), 135 (11), 123 (23), 113 (12), 107 (13), 95 (13), 81 (14), 55 (10), *43* (100), 41 (14).

*(*E,*1*RS,*2*RS*)-2-Hydroxy-2,4,4-trimethyl-3-(3'-methyl-1'3'-butadienyl)cyclopentyl Methyl Ketone, Isomer A* ((*E*)-**14A**). UV (0.118 mg in 10 ml): 228 (22200), 233 (23400), 240 sh (15200). UV (1.574 mg in 2 ml): 276 sh (310) end absorption to 360. IR: 3500*m* br., 3080*w*, 3040*w*, 2960*s*, 2930*s*, 2870*s*, 1695*s*, 1610*m*, 1450*s*, 1435*m*, 1385*s* (sh), 1370*s*, 1320*w*, 1290*w*, 1250*w*, 1185*m* (sh), 1170*s*, 1130*w*, 1105*m*, 1075*w*, 975*s*, 945*w*, 885*s*. ^{1}H-NMR: (300 MHz): 1.02, 1.05 (2*s*, 2 CH_3–C(4)); 1.19 (*s*, CH_3–C(2)); 1.83 (*d*, broadened to *m*, $w_{1/2}$ = 3, *J* = 10.5, H–C(3)); 1.87–2.02 (*m*, 2H–C(5)); 1.89 (*m*, $w_{1/2}$ = 3, CH_3–C(3')); 2.19 (*s*, CH_3–CO); 2.80 (*dd*, J_1 = 12, J_2 = 10.5, H–C(1)); 3.59 (*d*, *J* = 1, OH); 4.90 (*m*, $w_{1/2}$ = 3, 2H–C(4')); 5.79 (*dd*, J_1 = 10.5, J_2 = 15, H–C(1')); 6.11 (*d*, J = 15, H–C(2')). MS: 236 (< 1, M^+, $C_{15}H_{24}O_2$), 175 (38), 123 (17), 113 (44), 107 (18), 95 (14), 93 (14), 91 (15), 81 (14), 79 (10), 71 (17), 55 (10), *43* (100), 41 (20).

Isomer B ((*E*)-**14B**). UV (0.180 mg in 10 ml): 227 (14800), 232 (15300). UV (1.644 mg in 2 ml): end absorption to 350. IR: 3590*w*, 3500*m* (br.), 3080*w*, 3020*w* (sh), 2960*s*, 2930*s*, 2900*s*, 2870*s*, 1780*w*, 1695*s*, 1640*w*, 1605*m*, 1450*s*, 1435*m*, 1415*m*, 1370*s*, 1360*s*, 1300*m*, 1245*m* (br.), 1180*m*, 1160*m*, 1115*s*, 1075*m*, 970*s*, 930*m*, 905*m*, 885*s*. ^{1}H-NMR: 0.88, 1.03 (2*s*, 2 CH_3–C(4)); 1.29 (*s*, CH_3–C(2)); 1.2–2.3 (*m*, H–C(3), 2*H*–C(5)); 1.84 (*m*, $w_{1/2}$ = 4, CH_3–C(3')); 2.18 (*s*, CH_3–CO); 2.87 (*dd*, J_1 = 11, J_2 = 7, H–C(1)); 3.02 (*m*, $w_{1/2}$ = 3, OH); 4.89 (*m*, $w_{1/2}$ = 4, 2H–C(4')); 5.42 (*dd*, J_1 = 16, J_2 = 10, H–C(1')); 6.14 (*d*, *J* = 16, H–C(2')). MS: 236 (1, M^+, $C_{15}H_{24}O_2$), 218 (16), 175 (55), 155 (14), 123 (23), 113 (61), 107 (22), 95 (18), 93 (17), 91 (14), 81 (16), 79 (10), 77 (11), 71 (20), 55 (11), *43* (100), 41 (19).

*(*Z,*1*RS,*2*RS*)-2-Hydroxy-2,4,4-trimethyl-3-(3'-methyl-1',3'-butadienyl)cyclopentyl Methyl Ketone, Isomer A* ((*Z*)-**14A**). NMR signals assigned from the spectrum of a 7:3 mixture of (*E*)- and (*Z*)-**14A**: ^{1}H-NMR (100 MHz, $CDCl_3$): 1.02, 1.07 (2*s*, 2 CH_3–C(4)); 1.19 (*s*, CH_3–C(2)); 1.70–2.10 (*m*, H–C(5), 2H–C(3)); 1.86 (*m*, $w_{1/2}$ = 3, CH_3–C(3')); 2.16 (*s*, CH_3–CO); 2.56 (*d*, *J* = 10.5, presumably part of *dd*, H–C(1)); 3.53 (*m*, $w_{1/2}$ = 3, OH); 4.82 (*m*, $w_{1/2}$ = 6, 2H–C(4')); 5.55 (*dd*, J_1 = J_2 = 11, H–C(1')); 6.12 (*d*, *J* = 11, H–C(2')). ^{13}C-NMR: 43.8 (*t*, C(5)); 114.6 (*t*, C(4')); 57.3 (*d*, C(3)); 58.9 (*d*, C(1)); 126.4, 134.4 (2*d*, C(1'), C(2')); 82.7 (*s*, C(2)); 141.8 (*s*, C(3')).

*(*E,*1*RS,*2*SR*)-2-Hydroxy-2,4,4-trimethyl-3-(3'-methyl-1',3'-butadienyl)cyclopentyl Methyl Ketone, Isomer A* ((*E*)-**15A**). UV (0.124 mg in 10 ml): 228 (17200), 234 (17600). UV (2.28 mg in 2 ml): end absorption to 350. IR: 3590*m*, 3500*w* (br.), 3080*w*, 3030*w* (sh), 2950*s*, 2870*s*, 1780*w*, 1705*s*, 1640*w*, 1605*m*, 1455*s*, 1435*m*, 1370*s*, 1360*s*, 1310*m*, 1285*m*, 1265*m*, 1245*m*, 1190*s*, 1170*m*, 1145*m*, 1115*m*, 1085*s*, 975*s*, 950*m*, 935*m*, 890*s*. ^{1}H-NMR (80 MHz): 0.96, 1.04, 1.12 (3*s*, CH_3–C(2), 2 CH_3–C(4)); 1.33–1.93 (*m*, H–C(3), 2H–C(5)); 1.89 (*s*, CH_3–C(3')); 1.96 (*s*, OH); 2.26 (*s*, CH_3–CO); 3.29 (*dd*, J_1 = 11, J_2 = 8, H–C(1)); 4.95 (*m*, $w_{1/2}$ = 3, 2H–C(4')); 5.61 (*dd*, J_1 = 16, J_2 = 9, H–C(1')); 6.19 (*d*, *J* = 16, H–C(2')). MS: 236 (1, M^+, $C_{15}H_{24}O_2$), 218 (14), 175 (50), 155 (12), 123 (23), 113 (52), 107 (17), 95 (15), 93 (15), 91 (12), 81 (16), 71 (18), 44 (17), 43 (100), 41 (16).

Isomer B ((*E*)-**15B**, 90% pure). UV (1.0 mg in 100 ml) 229 (20200), 234 (21000). UV (5 mg in 5 ml): end absorption to 360. IR: 3600*w*, 3080*w*, 2980*s*, 2960*s* (sh), 2930*s*, 2900*s* (sh), 2870*s*, 2810*w*, 1710*s*, 1605*w*, 1455*m*, 1445*m*, 1385*s*, 1350*m*, 1285*w*, 1245*w*, 1220*w*, 1180*m*, 1155*m*, 1120*s*, 1080*m*, 975*m*, 940*w*, 910*m*, 890*m*. ^{1}H-NMR (80 MHz): 0.96 (3H), 1.05 (6H), (2*s*, CH_3–C(2), 2 CH_3–C(4)); 1.46–2.14 (*m*, H–C(3), 2H–C(5)); 1.88 (*s*, CH_3–C(3')); 2.25 (*s*, CH_3–CO); 2.36 (*s*, OH); 3.06 (*dd*, J_1 = 11, J_2 = 9, H–C(1)); 4.95 (*m*, $w_{1/2}$ = 3, 2H–C(4')); 5.54 (*dd*, J_1 = 15, J_2 = 10, H–C(1')); 6.20 (*d*, *J* = 15, H–C(2')). MS: 236 (1, M^+, $C_{15}H_{24}O_2$), 218 (13), 175 (57), 155 (15), 123 (29), 121 (12), 113 (62), 109 (10), 107 (21), 95 (21), 93 (18), 91 (14), 81 (21), 79 (10), 71 (24), 69 (12), 55 (15), *43* (100), 41 (22).

*(*Z,*1*RS,*2*SR*)-2-Hydroxy-2,4,4-trimethyl-3-(3'-methyl-1',3'-butadienyl)cyclopentyl Methyl Ketone, Isomer A* ((*Z*)-**15A**). *Ca.* 80% pure. IR: 3590*m*, 3490*w* (br.), 3080*w*, 3010*m* (sh), 2960*s*, 2940*s*, 2870*s*, 1710*s*, 1630*w*, 1600*w*, 1450*m*, 1370*s*, 1360*s*, 1310*m*, 1285*m*, 1245*m*, 1185*s*, 1170*m*, 1120*s*, 1095*s*, 1075*m*, 955*w*, 935*w*, 895*s*, 880*m* (sh). ^{1}H-NMR (80 MHz): 0.98, 1.04, 1.11 (3*s*, CH_3–C(2), 2 CH_3–C(4)); 1.10–2.00 (*m*, 2H–C(5)); 1.85 (*m*, $w_{1/2}$ = 4,

CH_3–C(3')); 2.24 (*s*, CH_3–CO); 2.68 (*d*, J = 11, H–C(3)); 3.28 (*dd*, J_1 = 11, J_2 = 8, H–C(1)); 4.90 (*m*, $w_{½}$ = 5, 2H–C(4')); 5.40 (*dd*, $J_1 = J_2$ = 11, H–C(1')); 6.23 (*d*, J = 11, broadened to *m*, $w_{½}$ = 3, H–C(2')). MS: 236 (1, M^+, $C_{15}H_{24}O_2$), 175 (46), 155 (11), 123 (26), 121 (12), 113 (49), 107 (17), 95 (16), 93 (16), 91 (13), 81 (18), 71 (20), 55 (11), *43* (100), 41 (20).

4-Hydroxy-3-isopropenyl-4,7,7-trimethyl-1-cycloheptenyl Methyl Ketone (**16**). UV (0.468 mg in 10 ml): 232 (5200). UV (1.624 mg in 2 ml): end absorption to 360. IR: 3610*w*, 3570*w*, 3500*w* (br.), 3080*w*, 2960*s*, 2930*s*, 2870*m*, 1685*s*, 1680*s*, 1645*m*, 1615*w* (sh), 1480*m* (sh), 1460*m* (sh), 1450*s*, 1435*m*, 1370*s*, 1360*s*, 1350*s*, 1315*m*, 1275*m*, 1240*s*, 1225*s*, 1200*m*, 1175*m*, 1160*m*, 1080*s*, 1050*w* (sh), 1020*w* (br.), 955*w*, 930*m*, 900*s*, 845*w*. ^{1}H-NMR: 1.04, 1.10 (2*s*, 2 CH_3–C(7)); 1.28 (*s*, CH_3–C(4)); 1.30–2.15 (*m*, 2H–C(5), 2H–C(6), OH); 1.89 (*m*, $w_{½}$ = 3, CH_3–C(2')); 2.16 (*s*, CH_3–CO); 3.40 (*d*, J = 6, H–C(3)); 4.87, 5.03 (2*m*, $w_{½}$ = 4, 2H–C(1')); 6.01 (*d*, J = 6, H–C(2)). ^{13}C-NMR (75 MHz): 23.2, 25.9, 28.0, 28.6, 30.0 (5*q*, CH_3–CO, C(3'), CH_3–C(4), 2 CH_3–C(7)); 37.9, 39.0 (2*t*, C(5), C(6)); 115.6 (*t*, C(1')); 53.9 (*d*, C(3)); 133.4 (*d*, C(2)); 27.0 (*s*, C(7)); 74.6 (*s*, C(4)); 145.1, 151.8 (2*s*, C(1), C(2')); 204.0 (*s*, CO). MS: 236 (< 1, M^+, $C_{15}H_{24}O_2$), 175 (16), 165 (15), 147 (29), 135 (11), 123 (30), 121 (11), 113 (12), 107 (14), 105 (10), 95 (11), 91 (11), 81 (11), 55 (11), *43* (100), 41 (16).

(1RS,5RS,6RS,7SR)-5-Hydroxy-7-isopropenyl-2,2,5-trimethylbicyclo[4.1.0]heptyl Methyl Ketone, Isomer A (**17A**). IR: 3600*w*, 3420*m* (br.), 3080*w*, 2960*s*, 2930*s*, 2860*m*, 1690*s*, 1640*m*, 1625*w*, 1460*s* (sh), 1450*s*, 1435*m* (sh), 1385*m*, 1370*s*, 1350*s*, 1270*m*, 1200*m* (br.), 1175*m*, 1160*m*, 1105*m*, 1080*m*, 1035*m*, 930*m*, 890*s*. ^{1}H-NMR (300 MHz): 0.9–1.5 (*m*, 2H–C(3), 2H–C(4), OH); 1.13, 1.25, 1.28 (3*s*, 2 CH_3–C(2), CH_3–C(5)); 1.31 (*d*, J = 7.1, H–C(6)); 1.77 (*m*, $w_{½}$ = 3, CH_3–C=CH_2); 1.94 (*d*, J = 7, H–C(7)); 2.05 (*s*, CH_3–CO); 4.62, 4.75 (2*m*, $w_{½}$ = 4, CH_2=C–CH_3). ^{13}C-NMR (75 MHz, *ca.* 80% pure): 23.2, 27.8, 28.7, 28.8, 32.2 (5*q*, 2 CH_3–C(2), CH_3–C(5), CH_3–C=CH_2, CH_3–CO); 33.5, 35.2 (2*t*, C(3), C(4)); 110.1 (*t*, CH_2=C–CH_2); 31.7, 35.0 (2*d*, C(6), C(7)); 30.1, (*s*, C(2)); 50.5 (*s*, C(1)); 68.3 (*s*, C(5)); 141.7 (*s*, CH_2=*C*–CH_3); 208.2 (*s*, CO). MS: 236 (1, M^+, $C_{15}H_{24}O_2$), 175 (12), 165 (20), 161 (13), 147 (15), 135 (15), 133 (11), 123 (20), 121 (10), 119 (18), 115 (15), 113 (12), 111 (19), 109 (14), 107 (11), 105 (16), 95 (17), 93 (14), 91 (18), 81 (12), 79 (13), 77 (14), 69 (11), 67 (10), 55 (18), 53 (12), *43* (100), 41 (17). Anal. calc. for $C_{15}H_{24}O_2$ (236.36): C 76.23, H 10.24; found: C 76.07, H 10.38.

Isomer B (**17B**). IR: 3610*w*, 3480*w* (br.), 3080*w*, 2960*s*, 2930*s*, 2860*m*, 1695*s*, 1640*m*, 1460*m* (sh), 1450*m*, 1370*s*, 1360*s*, 1350*s*, 1270*m*, 1200*m* (sh), 1190*m*, 1170*m*, 1090*m*, 1075*m*, 970*w*, 930*w*, 890*s*. ^{1}H-NMR (300 MHz): 1.05–1.11 (*m*, H–C(3)); 1.02, 1.31 (2*s*, 2 CH_3–C(2)); 1.38–1.49 (*m*, H–C(3), 2H–C(4), OH); 1.52 (*s*, CH_3–C(5)); 1.75 (*d*, J = 6.7, H–C(6)); 1.80 (*m*, $w_{½}$ = 3, CH_3–C=CH_2); 1.98 (*d*, J = 6.7, H–C(7)); 2.04 (*s*, CH_3–CO); 4.57, 4.73 (2*m*, $w_{½} \approx 5$, CH_2=C–CH_3). ^{13}C-NMR (75 MHz, *ca.* 80% pure): 23.3, 26.1, 29.4, 31.4, 33.4 (5*q*, 2 CH_3–C(2), CH_3–C(5), CH_3–C=CH_2, CH_3–CO); 33.8, 33.9 (2*t*, C(3), C(4)); 109.7 (*t*, CH_2=C–CH_3); 31.8, 34.5 (2*d*, C(6), C(7)); 30.6 (*s*, C(2)); 51.8 (*s*, C(1)); 67.0 (*s*, C(5)); 142.1 (*s*, CH_2=*C*–CH_3); 207.1 (*s*, CO). MS: 236 (1, M^+, $C_{15}H_{24}O_2$), 165 (21), 123 (21), 107 (10), 55 (11), *43* (100), 41 (18).

6-Hydroxy-7-isopropenyl-3,3,6-trimethylbicyclo[3.2.0]hept-2-yl Methyl Ketone (**18**). M.p. 69–71°. IR: 3600*w*, 3480*w* (br.), 3080*w*, 2955*s*, 2860*m*, 1695*s*, 1640*w*, 1450*m* (br.), 1385*m*, 1365*s*, 1350*m*, 1305*w* (br.), 1275*w*, 1200*s*, 1165*m*, 1125*w*, 1060*w*, 1025*w*, 940*w*, 905*w*, 890*m*. ^{1}H-NMR (300 MHz): 0.77, 1.19, 1.38 (3*s*, 2 CH_3–C(3), CH_3–C(6)); 1.62 (*dd*, J_1 = 13, J_2 = 8, H–C(4)); 1.72 (*s*, CH_3–C=CH_2); 1.86 (*s*, OH); 1.99 (*dd*, J_1 = 13, J_2 = 10, H–C(4)); 2.14 (*s*, CH_3–CO), 2.43–2.52 (*m*, H–C(5)); 2.54 (*d*, J = 8, H–C(7)); 2.61 (*d*, J = 4, H–C(2)); 2.80 (*ddd*, $J_1 = J_2$ = 8, J_3 = 4, H–C(1)); 4.59, 4.80 (2*m*, $w_{½} \approx 5$, CH_2=C–CH_3). ^{13}C-NMR (75 MHz): 22.5, 23.7, 24.1, 29.0, 31.4 (5*q*, 2 CH_3–C(3), CH_3–C(6), CH_3–C=CH_2, CH_3–CO); 43.7 (*t*, C(4)); 110.0 (*t*, CH_2=C–CH_3); 35.6, 48.3 (2*d*, C(1), C(5)); 62.2, 70.5 (2*d*, C(2), C(7)); 48.1 (*s*, C(3)); 71.3 (*s*, C(6)); 143.4 (*s*, CH_2=*C*–CH_3); 209.1 (*s*, CO). MS: 236 (1, M^+, $C_{15}H_{24}O_2$), 175 (11), 165 (14), 123 (15), 109 (10), 107 (12), 99 (17), 98 (16), 95 (16), 91 (10), 83 (27), 81 (24), 71 (19), 55 (13), *43* (100), 41 (18). Anal. calc. for $C_{15}H_{24}O_2$ (236.36): C 76.23, H 10.24; found: C 76.36, H 10.29.

3-Acetyl-4,4-dimethyl-2-(2'-methyl-1'-propenyl)-cyclopentyl Methyl Ketone (**19**). IR: 2960*s*, 2860*m*, 1705*s*, 1455*m*, 1445*m*, 1435*m*, 1415*m*, 1385*m*, 1370*m*, 1350*s*, 1285*w*, 1220*w*, 1190*w*, 1170*m*, 1155*m*. ^{1}H-NMR (300 MHz, *ca.* 90% pure): 0.87, 1.30 (2*s*, 2 CH_3–C(4)); 1.51 (*dd*, J_1 = 13, J_2 = 7, H–C(5)); 1.63, 1.67 (2*s*, 3H–C(3'), CH_3–C(2')); 2.00, 2.10 (2*s*, CH_3–CO–C(1), CH_3–CO–C(3)); 2.09 (*dd*, J_1 = 13, J_2 = 10, H–C(5)); 2.64 (*d*, J = 9, H–C(3)); 3.27 (*ddd*, $J_1 = J_2$ = 10, J_3 = 7, H–C(1)); 3.75 (*ddd*, $J_1 = J_2$ = 10, J_3 = 9, H–C(2)); 4.80 (*d*, J = 10, H–C(1')). ^{13}C-NMR (75 MHz): 18.0, 24.2, 25.7, 29.5, 31.3, 32.5 (6*q*, 2 CH_3–C(4), CH_3–CO–C(1), CH_3–CO–C(3), CH_3–C(2'), C(3')); 44.1 (*t*, C(5)); 41.9, 52.6, 68.4 (3*d*, C(1), C(2), C(3)); 124.4 (*d*, C(1')); 29.7 (*s*, C(4)); 133.9 (*s*, C(2')); 208.6, 210.1 (2*s*, 2 CO). MS: 236 (11, M^+, $C_{15}H_{24}O_2$), 165 (29), 123 (13), 99 (11), 95 (14), 81 (11), 57 (14), 55 (11) *43* (100), 41 (23).

2.2. *Irradiation of (E)-***5** *at 254 nm.* A soln. of (*E*)-**5** (2.0 g, 8.47 mmol) in MeCN (sat. with Ar; 180 ml) was irradiated for 32 h (lamp *A*, quartz, 72% conversion). Chromatography (SiO_2, Et_2O/hexane 3:2) of the mixture

gave several fractions, from which the following product distribution was determined (GC and ^{1}H-NMR)[14]: (*Z*)-**5** (6%), (*E*)-**20** (4%), **21** (6%), **22** (45%), **23** (1%), **24** (1%), and **25** (1%).

*(Z,1*RS,*2*RS,*3*SR*)-2,3-Epoxy-1,2,4,4-tetramethyl-3-(3'-methyl-1',3'-butadienyl)-1-cyclohexanol* ((*Z*)-**5**). *Ca.* 80% pure. UV (0.054 mg in 10 ml): 232 (10800). IR: 3570*w*, 3490*w* (br.), 3080*w*, 2970*s*, 2940*s*, 2870*m*, 1640*w*, 1595*w*, 1475*m* (sh), 1470*m* (sh), 1450*s*, 1380*s*, 1370*s*, 1365*s*, 1345*m*, 1325*s*, 1280*w* (br.), 1240*m*, 1180*m*, 1160*m*, 1145*w*, 1110*m*, 1075*s*, 1060*m*, 1045*m*, 1020*m*, 1010*m*, (sh), 970*m*, 955*m*, 935*s*, 910*s*, 895*s*. ^{1}H-NMR (80 MHz): 1.08 (6H), 1.30 (6H) (2*s*, CH_3–C(1), CH_3–C(2), 2 CH_3–C(4)); 1.90 (*m*, $w_{1/2}$ = 3, CH_3–C(3')): 1.10–2.25 (*m*, 2H–C(5), 2H–C(6)); 2.38 (*m*, $w_{1/2}$ = 4, OH); 5.01 (*m*, $w_{1/2}$ = 6, 2H–C(4')); 5.74 (*AB* system, *J* = 13, δ_A = 5.44, δ_B = 6.04, H–C(1'), H–C(2')). MS: 236 (1, M^+, $C_{15}H_{24}O_2$), 139 (11), 138 (40), 135 (13), 133 (11), 123 (72), 121 (20), 119 (12), 107 (19), 105 (15), 95 (21), 93 (13), 91 (18), 85 (12), 79 (12), 77 (15), 69 (11), 67 (15), 55 (17), 53 (11), *43* (100), 41 (36).

*(E,1*RS,*2*SR,*2*RS)-2,3-Epoxy-1,2,4,4-tetramethyl-3-(3'methyl-1',3'-butadienyl)-1-cyclohexanol* ((*E*)-**20**). *Ca.* 90% pure. UV (0.132 mg in 10 ml): 231 (21900). IR: 3620*m*, 3500*w* (br.), 3090*w*, 3040*w*, 2970*s*, 2930*s*, 2870*s*, 1785*w* (br.), 1680*w* (br.), 1610*m*, 1470*m* (sh), 1460*m* (sh), 1450*s*, 1440*m*, 1380*m*, 1370*s*, 1360*s*, 1345*w*, 1315*m*, 1255*w*, 1245*w*, 1185*m*, 1170*m*, 1125*m*, 1095*m*, 1075*m*, 1060*m*, 1040*m*, 1025*m*, 975*m*, 955*w*, 935*m*, 905*s*, 890*s*. ^{1}H-NMR (100 MHz, $CDCl_3$): 0.91, 1.09 (2*s*, 2 CH_3–C(4)); 1.19, 1.30 (2*s*, CH_3–C(1), CH_3–C(2)); 1.30–1.90 (*m*, 2H–C(5), 2H–C(6)); 1.61 (*s*, OH); 1.83 (*m*, $w_{1/2}$ = 3, CH_3–C(3')); 4,95 (*m*, $w_{1/2}$ = 3, 2H–C(4')); 6.01 (*AB* system, *J* = 16, δ_A = 5.78, δ_B = 6.24, H–C(1'), H–C(2')). ^{13}C-NMR: 14.0, 18.6, 25.2, 25.6, 26.7 (5*q*, CH_3–C(1), CH_3–C(2), 2 CH_3–C(4), CH_3–C(3')); 32.7, 33.8 (2*t*, C(5), C(6)); 116.6 (*t*, C(4')); 125.3, 135.7 (2*d*, C(1'), C(2')); 33.4 (*s*, C(4)); 69.2, 70.9, 72.6 (3*s*, C(1), C(2), C(3)); 141.1 (*s*, C(3')). MS: 236 (< 1, M^+, $C_{15}H_{24}O_2$), 139 (18), 138 (69), 133 (11), 124 (10), *123* (100), 119 (11), 107 (17), 105 (17), 98 (11), 95 (27), 93 (13), 91 (19), 85 (14), 79 (13), 77 (15), 69 (11), 67 (21), 57 (11), 53 (10), 44 (13), 43 (89), 41 (40). Anal. calc. for $C_{15}H_{24}O_2$ (236.36): C 76.23, H 10.24; found: C 76.24, H 10.08.

*(1*RS,*2*RS,*3*SR*)-2,3-Epoxy-1,2,4,4-tetramethyl-3-(3'-methyl-2'-cyclobutenyl)-1-cyclohexanol* (**21**). *Ca.* 80% pure. IR: 3590*w*, 3570*w*, 3480*w* (br.), 3050*w*, 2970*s*, 2940*s*, 2920*s*, 2870*s*, 1640*w*, 1450*s* (br.), 1385*s*, 1365*s*, 1345*m*, 1320*m*, 1275*w* (br.), 1240*m*, 1180*m*, 1160*m*, 1130*m* (sh), 1075*m* (sh), 1065*s*, 1020*m*, 965*m* (sh), 955*m*, 930*s*, 900*m*. ^{1}H-NMR (80 MHz): 1.14 (6H), 1.34, 1.49 (3*s*, CH_3–C(1), CH_3–C(2), 2 CH_3–C(4)); 1.75 (*m*, $w_{1/2}$ = 7, CH_3–C(3')); 1.00–2.70 (*m*, 2H–C(5), 2H–C(6), 2H–C(4'), OH); 2.53 (*m*, $w_{1/2}$ = 9, H–C(1')); 5.86 (*m*, $w_{1/2}$ = 5, H–C(2')). MS: 236 (1, M^+, $C_{15}H_{24}O_2$), 139 (12), 138 (45), 133 (10), 123 (74), 121 (15), 119 (11), 109 (10), 107 (17), 105 (16), 95 (22), 93 (12), 91 (19), 85 (14), 79 (13), 77 (15), 69 (11), 67 (18), 55 (18), 53 (11), *43* (100), 41 (39).

3-Hydroxy-6-(3'-isopropenyl-1'-cyclopropenyl)-3,6-dimethyl-2-heptanone (**22**). *Ca.* 90% pure. UV (3.462 mg in 2 ml): end absorption to 350. IR: 3490*m*, 3080*w*, 2970*s*, 2935*m*, 2920*m*, 2870*w*, 1765*w*, 1710*s*, 1635*w*, 1470*m*, 1460*m* (sh), 1450*m*, 1430*m*, 1385*m*, 1370*m*, 1360*m*, 1320*w*, 1285*w*, 1265*w*, 1220*w* (br.), 1170*m* (br.), 1100*m*, 1025*w*, 960*m*, 875*s*. ^{1}H-NMR (100 MHz, $CDCl_3$): 1.10 (*m*, $w_{1/2}$ = 4, 3H–C(7), CH_3–C(6)); 1.34 (*s*, CH_3–C(3)); 1.48 (*m*, $w_{1/2}$ = 3, CH_3–C=CH_2); 1.10–2.00 (*m*, 2H–C(4), 2H–C(5)); 2.13 (*m*, H–C(3') overlapping with *s* at 2.16); 2.16 (*s*, 3H–C(1)); 3.76 (*m*, $w_{1/2}$ = 2, OH); 4.66, 4.76 (2*m*, $w_{1/2}$ = 4, CH_2=C–CH_3); 6.51 (*d*, *J* = 2, H–C(2')). ^{13}C-NMR: 20.1, 23.6, 25.3, 26.3, 26.8 (5*q*, C(1), CH_3–C(2), CH_3–C(6), C(7), CH_3–C=CH_2); 25.9, 34.5 (2*t*, C(4), C(5)); 107.2 (*t*, CH_2=C–CH_3); 25.4 (*d*, C(3')); 100.2 (*d*, C(2')); 34.5 (*s*, C(6)); 78.6 (*s*, C(3)); 131.5, 150.4 (2*s*, C(1'), CH_2=*C*–CH_3); 212.2 (*s*, C(2)). MS: 236 (3, M^+, $C_{15}H_{24}O_2$), 138 (14), 135 (39), 133 (26), 123 (21), 121 (47), 119 (24), 107 (31), 105 (24), 95 (16), 93 (25), 91 (24), 88 (11), 81 (11), 79 (16), 77 (17), 71 (11), 69 (13), 55 (17), *43* (100), 41 (25). Anal. calc. for $C_{15}H_{24}O_2$ (236.36): C 76.23, H 10.24; found: C 76.06, H 10.17.

(E)-3-Hydroxy-2,2,4,4-tetramethyl-3-(3'-methyl-1',3'-butadienyl)cyclohexanone (**23**). M.p. 82–85°. UV (0.092 mg in 10 ml): 226 sh (15700), 232 (17200), 240 sh (11600). UV (1.77 mg in 2 ml): end absorption to 360. IR: 3620*w*, 3090*w*, 2970*s*, 2930*s*, 2870*m*, 1785*w* (br.), 1710*s*, 1610*m*, 1595*w*, 1460*m* (sh), 1450*m*, 1440*m*, 1385*s*, 1370*m*, 1345*w*, 1325*m*, 1315*m*, 1270*m*, 1200*w*, 1180*w*, 1115*w*, 1075*m*, 1045*w*, 1010*m*, 980*m*, 960*m*, 895*s*. ^{1}H-NMR (300 MHz): 0.98, 1.05, 1.24, 1.25 (4*s*, 2 CH_3–C(2), 2 CH_3–C(4)); 1.60 (*ddd*, J_1 = 13.5, J_2 = 6, J_3 = 5, H–C(5)); 1.61 (*s*, OH), 1.87 (*m*, $w_{1/2}$ = 3, CH_3–C(3')); 2.09 (*ddd*, J_1 = 13.5, J_2 = 11.5, J_3 = 5, H–C(5)); 2.44 (*ddd*, J_1 = 15, J_2 = J_3 = 5, H–C(6)); 2.72 (*ddd*, J_1 = 15, J_2 = 11.5, J_3 = 6, H–C(6)); 5.03 (*m*, $w_{1/2} \approx 4$, 2H–C(4')); 6.11 (*AB* system, *J* = 16, δ_A = 5.89, δ_B = 6.33, H–C(1'), H–C(2')). ^{13}C-NMR (75 MHz; *ca.* 80% pure): 18.8, 21.1, 24.4, 26.0, 26.5 (5*q*, 2 CH_3–C(2), 2 CH_3–C(4), CH_3–C(3')); 34.9, 35.9 (2*t*, C(5), C(6)); 116.9 (*t*, C(4')); 129.1, 132.9 (2*d*, C(1'), C(2')); 38.8, 53.5 (2*s*, C(2), C(4)); 82.9 (*s*, C(3)); 141.4 (*s*, C(3')); 215.4 (*s*, CO). MS: 236 (4, M^+, $C_{15}H_{24}O_2$), 141 (54), 138 (12), 123 (37), 96 (18), 95 (68), 81 (10), 71, (68), 69 (23), 67 (35), 55 (21), *43* (100), 41 (63).

6-Hydroxy-8-(isopropenyl)-3,3,7,7-tetramethylbicyclo[4.2.0]octan-2-one (**24**).UV (0.564 mg in 2 ml MeCN): 300 (73). IR ($CHCl_3$): 3600*w*, 2960*s*, 2930*s*, 2860*m*, 1690*s*, 1645*w*, 1455*m* (br.), 1385*m*, 1375*m*, 1300*w* (br.), 1145*m* (br.), 1120*w* (br.), 1080*w*, (sh), 1070*m*, 1020*m*, 970*w*, 900*m*. ^{1}H-NMR (300 MHz): 0.93, 1.12, 1.16, 1.17 (4*s*, 2 CH_3–C(3), 2 CH_3–C(7)); 1.6–1.8 (*m*, 2H–C(4), OH); 1.68 (*m*, CH_3–C=CH_2); 1.98–2.22 (*m*, 2H–C(5)); 2.32 (*d*,

J_1 = 10, H–C(8)); 2.86 (*dd*, J_1 = 10, J_2 = 1.5, H–C(1)); 4.93, 5.00 (2*m*, $w_{1/2} \approx 4$, CH_2=C–CH_3). ^{13}C-NMR (75 MHz): 17.3, 23.0, 23.2, 26.8 (5*q*, 2*q* at 26.8, 2 CH_3–C(3), 2 CH_3–C(7), CH_3–C=CH_2); 27.2, 34.4 (2*t*, C(4), C(5)); 111.8 (*t*, CH_2=C–CH_3); 50.7, 53.5 (2*d*, C(1), C(8)); 43.7, 45.0 (2*s*, C(3), C(7)); 75.4 (*s*, C(6)); 141.8 (*s*, CH_2–C=CH_2); 216.0 (*s*, CO). MS: 236 (0.4, M^+, $C_{15}H_{24}O_2$), 141 (37), 123 (14), *96* (100), 95 (12), 81 (48), 67 (13), 55 (10), 43 (12), 41 (24). Anal. calc. for $C_{15}H_{24}O_2$ (236.36): C 76.23, H 10.24; found: C 76.27, H 10.17.

*(*E*)-9-Hydroxy-2,6,6,9-tetramethyl-1,3,10-undecatrien-5-one* (**25**). UV (0.42 mg in 25 ml MeCN): 266 (15300). IR: 3610*w*, 3500*w* (br.), 3080*w*, 3060*w*, 2960*s*, 2940*s*, 2930*s*, 2860*m*, 1815*w* (br.), 1680*s*, 1610*s*, 1590*s*, 1465*m*, 1450*m*, 1435*m*, 1410*m*, 1385*m*, 1370*m* (sh), 1365*m*, 1330*m* (sh), 1320*m*, 1270*m*, 1250*m*, 1180*m* (br.), 1090*m* (sh), 1065*s*, 1020*m*, 980*m*, 920*s*, 905*s*, 860*w*. ^{1}H-NMR (100 MHz, $CDCl_3$): 0.8–2.4 (*m*, 2H–C(7), 2H–C(8), OH); 1,12 (*s*, 2 CH_3–C(6)); 1.24 (*s*, CH_3–C(9)); 1.89 (*m*, $w_{1/2}$ = 3, CH_3–C(2)); 5.02 (*dd*, J_1 = 11, J_2 = 2.5, H–C(11)); 5.16 (*dd*, J_1 = 18, J_2 = 2.5, H–C(11)); 5.38 (*m*, $w_{1/2}$ = 6, 2H–C(1)); 5.84 (*dd*, J_1 = 18, J_2 = 11, H–C(10)); 6.90 (*AB*-system, J = 16, δ_A = 6.48, δ_B = 7.32, H–C(3), H–C(4)). ^{13}C-NMR (75 MHz; *ca.* 90% pure): 18.2, 24.3, 24.4, 27.9 (4*q*, 2 CH_3–C(6), CH_3–C(2), CH_3–C(9)); 33.6, 37.0 (2*t*, C(7), C(8)); 111.9, 125.1 (2*t*, C(1), C(11)); 121.1, 144.7, 145.3 (3*d*, C(3), C(4), C(10)); 46.2 (*s*, C(6)), 72.9 (*s*, C(9)), 140.8 (*s*, C(2)), 204.4 (*s*, C(5)). MS: 236 (1, M^+, $C_{15}H_{24}O_2$), 165 (10), 138 (18), 124 (13), 123 (81), 109 (15), 96 (20), 95 (62), 81 (58), 79 (13), 71 (28), 69 (17), 68 (22), 67 (48), 57 (12), 55 (31), 53 (12), *43* (100), 41 (69).

2.3. *Triplet Excitation of (*E*)-***6***.* A soln. of (*E*)-**6** (100 mg, 0.42 mmol) in acetone (10 ml) was irradiated for 25 h (lamp *B*, *Pyrex*, 50% conversion) furnishing (*Z*)-**6** (24 mg, 47%)[14]) as the only product.

*(*Z*)-4,4-Dimethyl-3-(3'-methyl-1',3'-butadienyl)-2,7-octanedion* ((*Z*)-**6**). UV (0.317 mg in 25 ml): 234 (8000). IR: 3080*w*, 2960*s*, 2940*m*, 2875*w*, 1715*s* (br.), 1630*w*, 1460*m* (sh), 1445*m*, 1415*m*, 1385*m*, 1365*s*, 1350*s*, 1290*w*, 1155*m*, 890*m*. ^{1}H-NMR (80 MHz): 0.95, 0.97 (2*s*, 2 CH_3–C(4)); 1.0–2.6 (*m*, 2H–C(6), 2H–C(5)); 1.85 (*m*, $w_{1/2}$ = 2, CH_3–C(3')); 2.14, 2.17 (2*s*, 3H–C(1), 3H–C(8)); 3.66 (*d*, J = 11, H–C(3)); 4.84, 5.03 (2*m*, $w_{1/2}$ = 3, 2H–C(4')); 5.56 (*dd*, J_1 = J_2 = 11, H–C(1')); 6.10 (*d*, J = 11, H–C(2')). MS: 236 (2, M^+, $C_{15}H_{24}O_2$), 175 (12), 135 (13), 123 (14), 113 (24), 107 (13), 95 (14), 81 (16), *43* (100).

2.4. *Photolyses of (*Z*)-***12***.* *a*) A soln. of (*Z*)-**12** (84 mg, 0.36 mmol) in acetone (8 ml) was irradiated for 6 h (lamp *B*, *Pyrex*) furnishing (*E*)-**12**/(*Z*)-**12** 1:2 (^{1}H-NMR, GC). *b*) A soln. of (*Z*)-**12** (123 mg, 0.52 mmol) in pentane was irradiated under the same conditions. After 6 h, GC analysis indicated (*E*)-**12**/(*Z*)-**12** 1:2. After 45 h, chromatography (DME/Et_2O/pentane 1:3:30) of the mixture afforded (*E*)-**12**/(*Z*)-**12** (1:2 mixture, *ca.* 25 mg), **26** (10 mg, 8%), and intractable material.

*(*E*)-4,4-Dimethyl-3-(3'-methyl-3'-butenylidene)-2,7-octanedione* ((*E*)-**12**). ^{1}H-NMR (80 MHz) signals of (*E*)-**12**/(*Z*)-**12** 1:2, which can be assigned to (*E*)-**12**: 1.20 (*s*, 2 CH_3–C(4)); 1.78 (*m*, $w_{1/2}$ = 3, CH_3–C(3')); 2.16, 2.29 (2*s*, 3H–C(8), 3H–C(1)); 3.00 (br. *d*, J = 7, H–C(2')); 5.77 (*t*, J = 7, H–C(1')).

4,4-Dimethyl-3-(3'-methyl-2'-butenylidene)-2,7-octanedione (**26**). UV (0.0902 mg in 25 ml): 269 (15000), end absorption to 400. IR: 3070*w* (sh), 2960*s*, 2920*s*, 1715*s*, 1680*s* (sh), 1675*s*, 1630*m*, 1470*m* (sh), 1460*m* (sh), 1440*m*, 1415*m* (sh), 1380*m* (sh), 1370*m* (sh), 1350*s*, 1280*w* (sh), 1245*s*, 1190*m*, 1170*m*, 1050*w* br., 885*w*, 845*w*. ^{1}H-NMR (80 MHz): 1.23 (*s*, 2 CH_3–C(4)); 0.8–2.70 (*m*, 2H–C(6), 2H–C(5)); 1.83, 1.90 (2*s*, 3H–C(4'), CH_3–C(3')); 2.12, 2.32 (2*s*, 3H–C(8), 3H–C(1)); 6.48 (*AB*-system, J = 12, δ_A = 6.32, δ_B = 6.65, H–C(1'), H–C(2')). MS: 236 (3, M^+, $C_{15}H_{24}O_2$), 221 (16), 175 (12), 165 (16), 135 (14), 123 (29), 121 (10), 119 (14), 107 (17), 95 (11), 91 (16), 79 (10), 69 (10), 55 (11), *43* (100), 41 (18).

2.5. *Triplet Excitation of (*E*)-***13A*** and (*E*)-***13B***.* *a*) A soln. of (*E*)-**13A** (100 mg, 0.42 mmol) in acetone (10 ml) was irradiated for 3 h (lamp *B*, *Pyrex*, 70% conversion) affording (*Z*)-**12** (9%), (*Z*)-**13A** (20%), a compound of unknown structure (6%), and intractable material (^{1}H-NMR, GC). *b*) Irradiation of a soln. to (*E*)-**13B** (*ca.* 60% pure; 110 mg) for 6 h as in *a* (90% conversion) gave (*E*)-**6** (15%), (*Z*)-**12** (20%), a compound of unknown structure (10%), and intractable material.

*(*Z*)-2-Hydroxy-2,5,5-trimethyl-1-(3'-methyl-1',3'-butadienyl)cyclopentyl Methyl Ketone. Isomer A* ((*Z*)-**13A**). ^{1}H-NMR (80 MHz) signals of (*E*)-**13A**/(*Z*)-**13A** 7:3, which can be assigned to (*Z*)-**13A**: 2.06 (*s*, CH_3CO); 4.80 (*m*, $w_{1/2} \approx 5$, 2H–C(4')); 6.62 (*AB*-system, J = 13, δ_A = 6.33, δ_B = 6.91, overlapping with *AB*-system of (*E*)-**13A**, H–C(1'), H–C(2')).

3. Additional Experiments. – 3.1. *Catalytic Hydrogenation of (*E*)-***6*** and (*Z*)-***12***.* *a*) A soln. of (*E*)-**6** (12.4 mg, 0.05 mmol) in EtOH (5 ml) and a spatula tip full of Pd/C (10%) was stirred under H_2 for 2.5 h. Filtration through *Celite* and removal of the solvent afforded **27** (11.4 mg, 90%). *b*) Analogously, hydrogenation of (*Z*)-**12** (18.4 mg, 0.08 mmol) yielded **27** (17.6 mg, 94%). *c*) Hydrogenation of **26** (6.2 mg, 0.026 mmol) under similar conditions yielded **27** (4.2 mg, 67%).

4,4-Dimethyl-3-(3'-methylbutyl)-2,7-octanedione (**27**). UV (1.622 mg in 2 ml): 283 (75), end absorption to 340. IR: 2960*s*, 2940*s*, 2900*m*, 2870*m*, 1720*s*, 1715*s*, 1465*m*, 1455*m* (sh), 1415*w*, 1390*m*, 1370*s*, 1355*s*, 1295*w* (br.),

1160*m*, 910*w*. ^{1}H-NMR: 0.85 (*s*, 2 CH_3–C(4)); 0.86 (*d*, *J* = 6, CH_3–C(3'), 3H–C(4')); 0.90–1.80 (*m*, 2H–C(5), 2H–C(1'), 2H–C(2'), H–C(3')); 2.05, 2.06 (2*s*, 3H–C(8), 3H–C(1)); 2.10–2.40 (*m*, 2H–C(6), H–C(3)). MS: 240 (< 1, M^+, $C_{15}H_{28}O_2$), 128 (13), 113 (23), 110 (16), 99 (13), 95 (15), 84 (21), 83 (14), 71 (25), 69 (24), 56 (26), 55 (22), *43* (100), 41 (31).

3.2. *Reaction of (*Z*)-***12*** and* ***28*** *with Base. a)* A soln. of (*Z*)-**12** (50 mg, 0.21 mmol) and NaOMe (140 mg, 2.59 mmol) in abs. MeOH (10 ml) was stirred at r.t. for 2 h. The mixture was diluted with Et_2O, worked up with sat. aq. $(NH_4)_2SO_4$ and purified by chromatography (Et_2O/hexane 1:1) affording **28** (34.4 mg, 69%) and **29** (12.1 mg, 24%). *b)* Analogous treatment of a soln. of **28** (20 mg, 0.09 mmol) in MeOH (5 ml) with NaOMe (56 mg, 1.04 mmol) gave a 84:16 mixture of **28** and **29** (GC).

*(1*RS,2SR*)-2-Hydroxy-2,4,4-trimethyl-3-(3'-methyl-3'-butenylidene)cyclopentyl Methyl Ketone* (**28**). M.p. 71°. UV (2.174 mg in 2 ml): 228 (148), 243 (104), 251 (92), 260 (72), 285 (41), end absorption to 360. IR: 3600*w*, 3080*w*, 2960*s*, 2930*m*, 2870*m*, 1710*s*, 1645*w*, 1460*m*, 1445*m* (sh), 1430*m* (sh), 1365*s*, 1310*w*, 1290*w*, 1255*w*, 1230*m*, 1190*m*, 1130*m*, 1090*m*, 1040*w*, 1000*w*, 970*w*, 930*m*, 890*s*. ^{1}H-NMR: 1.10 (6H), 1.17 (3H) (2*s*, CH_3–C(2), 2 CH_3–C(4)); 1.40–2.00 (*m*, 2H–C(5)); 1.75 (*s*, CH_3–C(3')); 2.23 (*s*, CH_3–CO); 2.30 (*s*, OH); 2.70–3.30 (*m*, H–C(1), 2H–C(2')); 4.60–4.77 (*m*, 2H–C(4')); 5.31 (*t*, *J* = 8, H–C(1')). ^{13}C-NMR: 23.1, 23.2, 30.9, 31.2, 32.1, (5*q*, CH_3–C(2), 2 CH_3–C(4), CH_3–C(3'), CH_3–CO); 34.8, 38.5 (2*t*, C(5), C(2')); 109.8 (*t*, C(4')); 62.3 (*d*, C(1)); 121.8 (*d*, C(1')); 38.8 (*s*, C(4)); 81.6 (*s*, C(2)); 146.1, 157.0 (2*s*, C(3), C(3')); 210.0 (*s*, CO), MS: 236 (< 1, M^+, $C_{15}H_{24}O_2$), 218 (12), 203 (10), 181 (13), 176 (16), *175* (100), 151 (13), 147 (11), 133 (18), 123 (22), 121 (12), 119 (18), 109 (12), 107 (13), 105 (12), 95 (13), 93 (10), 91 (15), 81 (14), 77 (12), 71 (14), 69 (21), 67 (10), 57 (13), 55 (21), 43 (80), 41 (25). Anal. calc. for $C_{15}H_{24}O_2$ (236.36): C 76.23, H 10.24; found: C 75.93, H 10.18.

*(1*RS,2RS*)-2-Hydroxy-2,4,4-trimethyl-3-(3'-methyl-3'-butenylidene)cyclopentyl Methyl Ketone* (**29**). *Ca.* 90% pure. UV (1.835 mg in 2 ml): end absorption to 380. IR: 3590*w*, 3500*w* (br.), 3075*w*, 2960*s*, 2930*s*, 2860*m*, 1695*s*, 1645*w*, 1450*m* (br.), 1370*s*, 1355*s*, 1260*w*, 1175*s*, 1120*w* (br.), 1085*m*, 1050*w*, 885*s*. ^{1}H-NMR: 1.02, 1.11 (2*s*, 2 CH_3–C(4)); 1.40–2.10 (*m*, 2H–C(5)); 1.50 (*s*, CH_3–C(2)); 1.71 (*m*, $w_{1/2}$ = 3, CH_3–C(3')); 2.12 (*s*, CH_3–CO); 2.78 (*dd*, J_1 = 9,5, J_2 = 8, H–C(1)); 2.94 (*s*, OH); 2.98 (*d*, *J* = 8, 2H–C(2')); 4.61 (*m*, $w_{1/2}$ = 8, 2H–C(4')); 5.20 (*t*, *J* = 8, H–C(1')). MS: 236 (< 1, M^+, $C_{15}H_{24}O_2$), 176 (15), *175* (100), 133 (15), 123 (17), 119 (15), 91 (10), 69 (13), 55 (13), 43 (69), 41 (17).

3.3. *Reaction of (*E*)-***13A*** with Base.* A soln. of (*E*)-**13A** (36 mg, 0.15 mmol) and NaOMe (103 mg, 1.91 mmol) in abs. MeOH (7 ml) was stirred at r.t. for 3 h. The mixture was diluted with Et_2O, worked up with sat. aq. $(NH_4)_2SO_4$ and purified by chromatography (Et_2O/hexane 1:4) affording (*E*)-**14A** (7.9 mg, 22%), (*E*)-**14B** (4.3 mg, 12%), (*E*)-**15A** (5.8 mg, 16%), and (*E*)-**15B** (1.9 mg, 5%).

3.4. *Reaction of (*E/Z*)-***14A*** with Base.* A mixture of (*E*/*Z*)-**14A** (3:1, 77 mg, 0.33 mmol) and NaOMe (220 mg, 4.1 mmol) was stirred at r.t. for 3 h. The mixture was diluted with Et_2O and worked up with sat. aq. $(NH_4)_2SO_4$ soln. Column chromatography (Et_2O/pentane 1:1) and HPLC (Et_2O/pentane 1:3, p = 55 atm) afforded (*E*/*Z*)-**14A** (3:1, 28.4 mg, 37%), (*E*)-**14B** (5.1 mg, 7%), (*E*)-**15A** (9.5 mg, 12%), (*E*)-**15B** (3.6 mg, 5%), and (*Z*)-**15A** + **B** (5.4 mg, 7%).

3.5. *Catalytic Hydrogenation of a (*E/Z*)-***14A***.* A mixture of (*E*/*Z*)-**14A** (3:1; 52 mg, 0.22 mmol) in EtOH (20 ml) and a spatula tip full of Pd/C (10%) was stirred under H_2 for 3 h. Filtration through *Celite* and removal of the solvent gave **30** (47 mg, 90%).

*(1*RS,2RS*)-2-Hydroxy-2,4,4-trimethyl-3-(3'-methylbutyl)cyclopentyl Methyl Ketone* (**30**). UV (1.454 mg in 2 ml): 285 (40), end absorption to 330. IR: 3510*m* (br.), 2960*s*, 2930*s*, 2900*s*, 2870*s*, 1695*s*, 1465*s* (sh), 1460*s*, 1450*m* (sh), 1420*m*, 1385*s*, 1370*s*, 1340*m*, 1330*m*, 1290*w*, 1250*w* (br.), 1195*m*, 1170*s*, 1135*w*, 1105*w*, 1070*w* (br.), 940*w*, 910*m*, 865*w*. ^{1}H-NMR (100 MHz, $CDCl_3$): 0.88 (*d*, *J* = 6, CH_3–C(3'), 3H–C(4')); 1.06 (*s*, 2 CH_3–C(4)); 1.24 (*s*, CH_3–C(2)); 1.00–1.90 (*m*, H–C(3), 2H–C(5), 2H–C(1'), 2H–C(2'), H–C(3')); 2.13 (*s*, CH_3–CO); 2.73 (*dd*, $J_1 = J_2$ = 10, H–C(1)); 3.49 (*m*, $w_{1/2}$ = 5, OH). ^{13}C-NMR: 22.4, 22.9, 26.3, 28.7, 31.3, 33.3 (6*q*, CH_3–CO, CH_3–C(2), 2 CH_3–C(4), CH_3–C(3'), C(4')); 22.0, 39.0, 44.9 (3*t*, C(5), C(1'), C(2')); 25.9 (*d*, C(3')); 58.3, 59.2 (2*d*, C(1), C(3)); 39.1 (*s*, C(4)); 82.5 (*s*, C(2)); 214.2 (*s*, CO). MS: 240 (< 1, M^+, $C_{15}H_{28}O_2$), 113 (34), *112* (100), 109 (12), 102 (31), 99 (41), 71 (35), 69 (24), 57 (14), 56 (12), 55 (13), 43 (87), 41 (24).

3.6. *Reduction of* **17A** *with $LiAlH_4$.* To a suspension of $LiAlH_4$ (80 mg, 2.10 mmol) in abs. Et_2O (10 ml) cooled to −10°, a soln. of **17A** (130 mg, 0.55 mmol) in 1 ml abs. Et_2O was added dropwise. After stirring the mixture for 1 h, it was worked up with sat. aq. $(NH_4)_2SO_4$ and purified by chromatography (Et_2O/AcOEt 3:1) affording **31A** (35.8 mg, 27%) and **31B** (30.2 mg, 23%).

*(1*RS,2RS,6RS,7SR,1'RS*)-6-(1'-Hydroxyethyl)-7-isopropenyl-2,5,5-trimethylbicyclo[4.1.0]heptan-2-ol* (**31A**). M.p. 118–121° (from CH_2Cl_2). IR ($CHCl_3$): 3600*m*, 3450*m* (br.), 3080*w*, 2960*s*, 2930*s*, 2860*s*, 1635*m*, 1445*s*, 1370*s*, 1340*m*, 1315*m*, 1145*s*, 1075*s* (br.), 1035*m*, 990*w*, 955*w*, 915*m*, 980*s*. ^{1}H-NMR (300 MHz): 1.00–1.23 (*m*, 2H–C(3), 2H–C(4)); 1.20, 1.26 (2*s*, 2 CH_3–C(5)); 1.35 (*s*, CH_3–C(2)); 1.38 (*d*, *J* = 7, 3H–C(2')); 1.43–1.49 (*m*,

H–C(1), H–C(7)); 1.5–1.9 (*m*, 2OH), 1.88 (*m*, $w_{1/2}$ = 3, CH_3–C=CH_2), 3.49 (*q*, *J* = 7, H–C(1')); 4.76, 4.91 (2*m*, $w_{1/2}$ = 5, CH_2=C–CH_3). ^{13}C-NMR (75 MHz): 23.5, 24.0, 27.6, 29.1, 31.4 (5*q*, CH_3–C(2), 2 CH_3–C(5), CH_3–C=CH_2, C(2')); 34.9, 36.4 (2*t*, C(3), C(4)); 112.0 (*t*, CH_2=C–CH_3); 33.7, 35.6 (2*d*, C(1), C(7)); 71.2 (*d*, C(1')); 32.2, 39.3 (2*s*, C(5), C(6)); 69.0 (*s*, C(2)); 143.4 (*s*, CH_2=C–CH_3). MS: 238 (1, M^+, $C_{15}H_{26}O_2$), 177 (18), 161 (21), 149 (22), 125 (27), 123 (15), 122 (19), 121 (52), 119 (23), 111 (29), 109 (26), 108 (32), 107 (56), 105 (21), 99 (42), 95 (32), 93 (37), 91 (22), 81 (18), 79 (16), 69 (22), 55 (24), 45 (15), *43* (100), 41 (29).

(1RS,2RS,6RS,7SR,1'SR)-6-(1'-Hydroxyethyl)-7-isopropenyl-2,5,5-trimethylbicyclo[4.1.0]heptan-2-ol (**31B**). IR ($CHCl_3$): 3650*w* (br.), 3590*m*, 3380*s* (br.), 3070*w*, 2960*s*, 2930*s*, 2860*s*, 1640*m*, 1450*s*, 1370*s*, 1345*m*, 1320*m*, 1155*s*, 1090*s*, 1075*s*, 1035*m*, 1010*m*, 985*w*, 955*w*, 920*m*, 890*s*. ^{1}H-NMR (300 MHz): 1.15, 1.23 (2*s*, 2 CH_3–C(5)); 1.37 (*s*, CH_3–C(2)); 1.33 (*d*, *J* = 7, 3H–C(2')); 1.04–1.85 (*m*, H–C(1), 2H–C(3), 2H–C(4), H–C(7)); 1.81 (*m*, $w_{1/2}$ = 3, CH_3–C=CH_2); 2.0–4.3 (*m*, 2OH), 3.28 (*q*, *J* = 7, H–C(1')); 4.74, 4.85 (2*m*, $w_{1/2} \approx 5$, CH_2=C–CH_3). MS: 238 (< 1, M^+, $C_{15}H_{26}O_2$), 161 (18), 149 (18), 125 (20), 123 (15), 122 (25), 121 (45), 119 (19), 111 (24), 109 (26), 108 (21), 107 (54), 105 (18), 99 (51), 95 (30), 93 (32), 91 (19), 81 (18), 69 (20), 55 (23), 45 (15), *43* (100), 41 (28).

3.7. *Thermal Transformation of* **21** *into* (E)-**5**. A soln. of **21** (10 mg, 0.04 mmol) in (D_8)toluene (0.5 ml) was heated to 120° for 1 h. ^{1}H-NMR analysis indicated (*E*)-**5** as the only product.

3.8. *Transformation of* **23** *into* **32**. A soln. of **23** (10 mg, 0.04 mmol) and NaOMe (9 mg, 0.2 mmol) in abs. MeOH (0.3 ml) was stirred at r.t. for 1 h. The mixture was diluted with Et_2O and worked up with sat. aq. $(NH_4)_2SO_4$ affording **32** (6 mg, 60%).

(E)-2,6,6,10-Tetramethyl-8,10-undecadien-3,7-dione (**32**). 90% pure. UV (0.247 mg in 25 ml): 263 (12400). UV (0.520 mg in 2 ml): end absorption to 380. IR: 3090*w*, 2970*s*, 2930*s*, 2870*m*, 1820*w* (br.), 1715*s*, 1685*s*, 1615*m*, 1595*s*, 1470*m*, 1460*m* (sh), 1450*m* (sh), 1440*m*, 1410*w*, 1385*m*, 1370*m*, 1320*w* (br.), 1260*m*, 1080*m*, 1060*m*, 1020*m* (br.), 985*m*, 910*m*, 895*m*, 860*w*. ^{1}H-NMR (300 MHz): 1.06 (*d*, *J* = 7, 3H–C(1), CH_3–C(2)); 1.17 (*s*, 2 CH_3–C(6)); 1.82–1.88 (*m*, 2H–C(5)); 1.90 (*m*, $w_{1/2}$ = 3, CH_3–C(10)); 2.31–2.38 (*m*, 2H–C(4)); 2.56 (*sept.*, *J* = 7, H–C(2)); 5.38, 5.41 (2*m*, $w_{1/2}$ = 3, 2H–C(11)); 6.93 (*AB*-system, *J* = 16, δ_A = 6.50, δ_B = 7.35, H–C(8), H–C(9)). MS: 236 (3, M^+, $C_{15}H_{24}O_2$), 141 (55), 123 (27), 98 (10), 96 (13), 95 (49), 71 (67), 69 (24), 67 (27), 55 (24), *43* (100), 41 (54).

3.9. *Transformation of* **24** *into* **35**. Treatment of **24** (*ca.* 3 mg) with NaOMe (9 mg) in abs. MeOH (0.3 ml) and workup as described in *Sect. 3.8* afforded **35** (1.3 mg).

3-Isopropenyl-2,2,6,6-tetramethyl-1,5-cyclooctandione (**35**). IR: 3080*w*, 2980*m* (sh), 2960*m*, 2920*m*, 2870*w*, 2850*w*, 1705*s*, 1700*s* (sh), 1695*s* (sh), 1635*w*, 1470*m* (sh), 1460*m*, 1450*m* (sh), 1430*w*, 1385*w*, 1375*w*, 1360*w*, 1290*w* (br.), 1240*w* (br.), 1145*w* (sh), 1140*w*, 1050*m*, 1020*w*, 900*m*, 880*w*. ^{1}H-NMR (300 MHz): 1.04, 1.13, 1.19, 1.31 (4*s*, 2 CH_3–C(2), 2 CH_3–C(6)); 1.78 (*ddd*, J_1 = 14.5, J_2 = 5.9, J_3 = 4.5, H–C(7)); 1.82 (*m*, $w_{1/2}$ = 3, CH_3–C=CH_2); 2.12 (*dd*, J_1 = 12.8, J_2 = 2.6, H–C(3)); 2.32 (*ddd*, J_1 = 14.5, J_2 = 12.0, J_3 = 4.0, H–C(7)); 2.50 (*ddd*, J_1 = 13.0, J_2 = 12.0, J_3 = 4.5, H–C(8)); 2.72 (*ddd*, J_1 = 13.0, J_2 = 5.9, J_3 = 4.0, H–C(8)); 2.85 (*dd*, J_1 = 12.8, J_2 = 2.6, H–C(4)); 3.12 (*dd*, J_1 = J_2 = 12.8, H–C(4)); 4.79, 5.00, (2*m*, $w_{1/2}$ = 4, CH_2=C–CH_3). ^{13}C-NMR (75 MHz): 18.3, 22.0, 23.9, 26.6, 27.1 (5*q*, 2 CH_3–C(2), 2 CH_3–C(6), CH_3–C=CH_2); 36.0, 36.7, 40.5 (3*t*, C(4), C(7), C(8)); 115.2 (*t*, CH_2=C–CH_3); 51.6 (*d*, C(3)); 47.5, 50.6 (2*s*, C(2), C(6)); 144.8 (*s*, CH_2–C=CH_2); 215.4, 216.1 (2*s*, C(1), C(5)). MS: 236 (2, M^+, $C_{15}H_{24}O_2$), 180 (10), 140 (16), *96* (100), 95 (18), 81 (23), 70 (20), 67 (14), 55 (13), 43 (10), 41 (28). Anal. calc. for $C_{15}H_{24}O_2$ (236.36): C 76.23, H 10.24; found: C 76.21, H 10.24.

3.10. *Reduction of* **24**. A soln. of **24** (20 mg, 0.08 mmol) and $NaBH_4$ (12 mg, 0.31 mmol) in MeOH (1 ml) was stirred at 0° for 6 h. The mixture was worked up in Et_2O and purified by chromatography (Et_2O/hexane/pentane 8:2:1) to give **36** (8 mg, 40%).

7-Isopropenyl-4,4,8,8-tetramethylbicyclo[4.2.0]octan-1,5-diol (**36**). IR ($CHCl_3$): 3600*m*, 3450*w* (br.), 3080*w*, 2960*s*, 2920*s*, 2870*s*, 1640*m*, 1460*m* (sh), 1450*m*, 1435*m* (sh), 1395*m*, 1380*m*, 1375*m* (sh), 1365*m*, 1315*w* (br.), 1070*m*, 1050*m*, 1020*m*, 995*m*, 970*m*, 900*s*. ^{1}H-NMR (300 MHz): 0.87, 0.99, 1.01, 1.12 (4*s*, 2 CH_3–C(4), 2 CH_3–C(8)); 1.20–1.65 (*m*, 2H–C(3), H–C(2), 2OH); 1.70 (*s*, CH_3–C=CH_2); 1.90–2.08 (*m*, H–C(2)); 2.24 (br., *d*, *J* = 11, H–C(7)); 2.61 (*ddd*, J_1 = 11, J_2 = 7, J_3 = 2, H–C(6)); 3.64 (br., *d*, *J* = 7, H–C(5)); 4.88, 4.91 (2*m*, CH_2=C–CH_3). MS: 238 (< 1, M^+, $C_{15}H_{26}O_2$), 141 (20), 125 (40), 123 (15), 121 (11), 111 (12), 109 (13), 107 (22), 97 (69), *96* (100), 95 (21), 93 (16), 86 (93), 85 (17), 83 (14), 81 (97), 79 (21), 77 (17), 71 (40), 69 (20), 67 (39), 57 (14), 55 (30), 53 (18), 43 (43), 41 (60).

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