158. Photochemical Reactions

129th Communication[1])

Photochemistry of a Conjugated Diepoxydiene: Product Formation *via* Carbonyl Ylide and Carbene Intermediates with Participation of Neighbouring Epoxy Functions[2])

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In memoriam Hans Heusser (1917–1982)

(8.VI.83)

Summary

On singlet excitation ($\lambda = 254$ nm, acetonitrile) the diepoxydiene (*E*)-**7** undergoes photocleavage to the carbonyl ylide **VII** and the carbenes **X** and **XI**. The carbonyl ylide **VII** rearranges to the thermally labile dioxabicyclo[3.2.1]octene **20** or fragments *via* **VIII** to the aldehyde **9** and propyne. The carbene **X**, showing behaviour typical of vinyl carbenes, undergoes addition to the adjacent double bond furnishing the cyclopropene **11**. The carbene **XI**, however, undergoes an insertion reaction into the neighbouring oxirane C,C-bond leading to the oxetene (*E*)-**21** which can be isolated at −78°, but at room temperature is rapidly transformed to the aldehyde **10**. On triplet excitation (acetone, $\lambda > 280$ nm), however, (*E*)-**7** shows the typical behaviour of epoxydienes, undergoing C,O-cleavage of the oxirane and isomerization to **22**, **23** and (*E*/*Z*)-**24**.

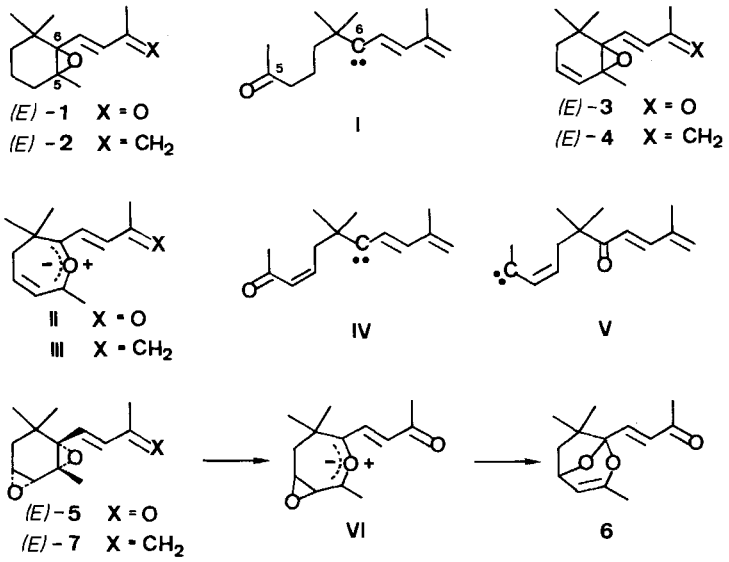
1. Introduction. – To get deeper insight into the mechanisms of the reactions found on photolysis of α,β-unsaturated γ,δ-epoxyketones, we investigated the corresponding epoxydienes. Comparison of the results showed that, in general, ylide formation is favoured on $^1\pi,\pi^*$-excitation of the epoxyenones, whereas carbene formation is more efficient on $^1\pi,\pi^*$-excitation of the corresponding epoxydienes. Thus, it was found, *e.g.*, that irradiation ($\lambda = 254$ nm) of the epoxyenone (*E*)-**1** caused isomerization *via* ylide and carbene intermediates [3], while, on singlet

[1]) 128th Communication, see [1].

[2]) Presented in part by *B.F.* at the IXth IUPAC Symposium on Photochemistry, July 25–30, 1982, Pau (France) [2] and by *N.B.* at the Herbstversammlung der Schweizerischen Chemischen Gesellschaft, October 15, 1982, Bern.

excitation, the epoxydiene (*E*)-**2** exclusively underwent cyclopropene formation *via* the vinyl C(6)-carbene **I** (s. *Scheme 1*) [4][3]). Furthermore, irradiation ($\lambda = 254$ nm) of (*E*)-**3** led exclusively to products of the ylide intermediate **II** [6], while the corresponding epoxytriene (*E*)-**4** produced apart from products of the ylide **III** those of the two isomeric vinyl carbene intermediates **IV** and **V** [7] (s. *Scheme 1*).

Scheme 1



Recently, we have shown that $^1\pi,\pi^*$-excitation ($\lambda = 254$ nm) of the diepoxyenone (*E*)-**5** induces as a main process cleavage of the C(5),C(6) bond of the oxirane leading to the ylide **VI**, which undergoes subsequent 1,4-oxygen migration to produce the thermally unstable acetal **6** (s. *Scheme 1*) [1] [8]. On the other hand, product formation *via* the C(6)-carbene intermediate was observed only to a small extent.

In the present investigation, the photolysis of the diepoxydiene (*E*)-**7** [1] *(Scheme 1)* was studied. This diepoxydiene was thought to be a suitable model to delineate the interaction of carbonyl-ylide and carbene centers with an adjacent oxirane function. The reaction of the oxirane with the expected carbene would be particularly interesting, since previous attempts to produce a carbene next to an oxirane proved to be unsuccessful [9].

2. Photolyses. – 2.1. *Singlet Excitation of* (E)-**7** *at Room Temperature.* Photolysis of a *ca.* 0.05 M solution of (*E*)-**7** in CH_3CN ($\lambda = 254$ nm, 92% conversion) gave the following products (s. *Scheme 2*)[4])[5]): (*Z*)-**7** (2%), (*E*)-**8** (3%), (*Z*)-**8** (3%), **9** (3%),

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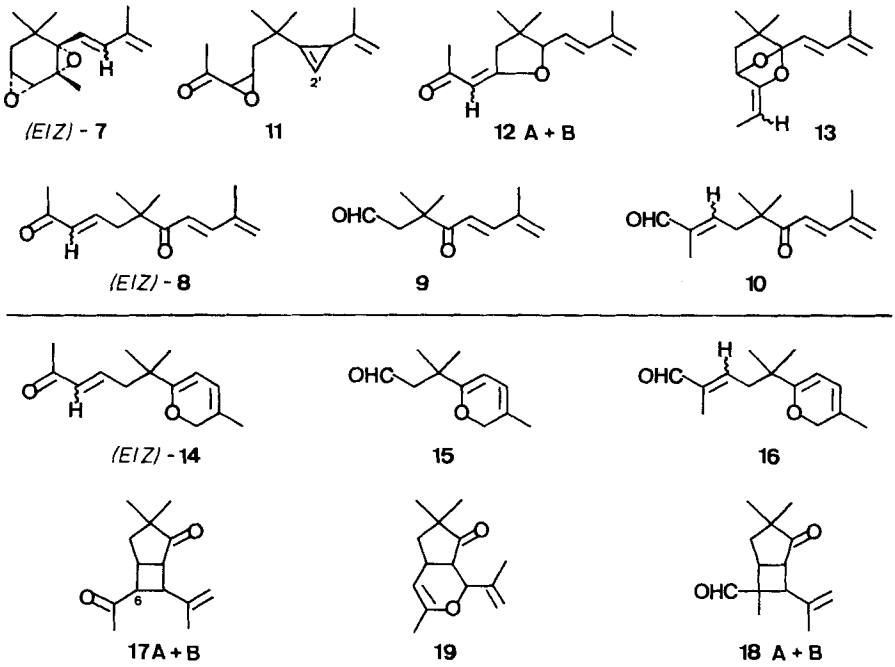
[3]) Numbering according to the carotinoid nomenclature [5] is used.

[4]) Yields were determined by ^{1}H-NMR analysis of the fractions obtained after chromatography on SiO_2.

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

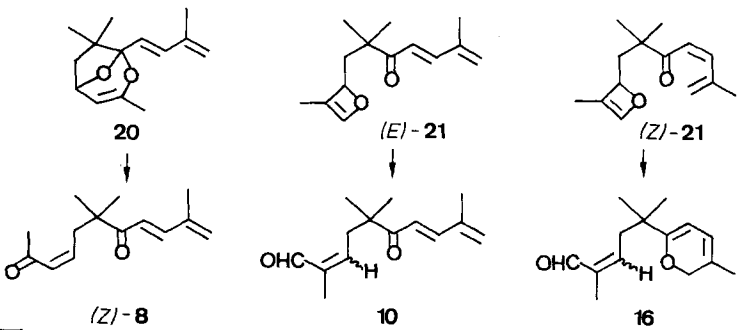
Scheme 2



10 (4%), **11** (10%), **12A** (2%), **12B** (2%), **13** (2%), (*E*)-**14** (1%), (*Z*)-**14** (5%), **15**[6]) (2%), **16** (4%), **17A** (5%), **17B** (2%), **18A** (8%), **18B** (3%), and **19** (2%).

2.2. *Singlet Excitation of* (E)-**7** *at* $-78°$. Photolysis of a THF solution of (*E*)-**7** ($\lambda = 254$ nm) and chromatography at $-78°$ yielded two non-polar fractions. According to NMR analysis, one fraction contained **20**, from which (*Z*)-**8** was obtained in quantitative yield on warming the NMR samples to ambient temperature. Rechromatography of the other fraction ($-78°$) produced a 2:1 mixture of the oxetenes (*E*)- and (*Z*)-**21**, which afforded the aldehydes **10** and **16** after warming to room temperature *(Scheme 3)*.

Scheme 3

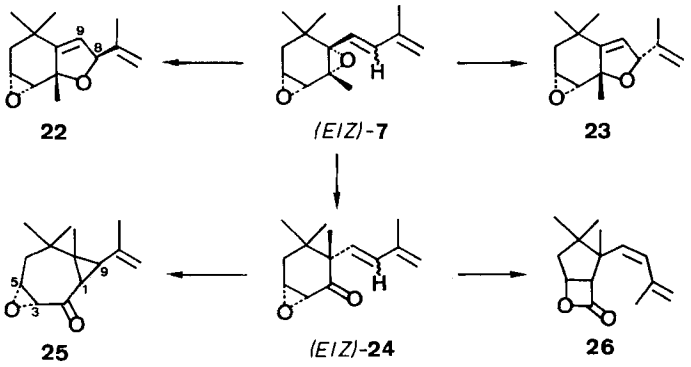


[6]) Compound **15** was identified in a mixture with the pyrans (*E*/*Z*)-**14** and **16** by the *t* at 9.75 ppm in the ^{1}H-NMR spectrum, but could not be isolated in pure form.

2.3. *Irradiation of* (E)-**8**. Preparative photolysis of a *ca.* 0.03 M solution of (*E*)-**8** in CH_3CN ($\lambda = 254$ nm, 88% conversion) gave (*Z*)-**8** (1%), (*E*)-**14** (9%), (*Z*)-**14** (1%), **17A** (20%), and **17B** (2%)[4][5]) (s. *Scheme 2*).

2.4. *Triplet Excitation of* (E)-**7**. Photolysis of a *ca.* 0.045 M solution of (*E*)-**7** in acetone ($\lambda > 280$ nm, 98% conversion) gave (*Z*)-**7** (1%), **22** (24%), **23** (5%), (*E*)-**24** (2%), (*Z*)-**24** (3%), **25** (1%), and **26** (4%)[4][7]) (*Scheme 4*).

Scheme 4



2.5. *Triplet Excitation of* (E/Z)-**24**. Photolysis of a 2:3 mixture of (*E*)-**24** and (*Z*)-**24** in acetone ($\lambda > 280$ nm, 97% conversion) gave, according to GC analysis using nonadecane as an internal standard, **25** (9%), **26** (9%), and 65% of nonvolatile products (s. *Scheme 4*).

3. Structure of the Products. – As analogues of most of the products obtained here were already described in previous work from our laboratory, only the most relevant spectral data are discussed herein; full data and assignment of the NMR signals is presented in the *Exper. Part.*

Dienones (E)- *and* (Z)-**8** *(Scheme 2).* Their structure follows from comparison of the NMR spectra with those of the corresponding triketones [8]. The presence of a dienone substructure can be deduced, in particular, from the UV maximum at 264 ($\varepsilon = 18100$) and 269 nm ($\varepsilon = 20400$) for (*E*)- and (*Z*)-**8**, respectively.

Aldehyde **9** *(Scheme 2).* The MS shows a molecular peak at *m/z* 180 indicating the molecular formula $C_{11}H_{16}O_2$. The spectral evidence for the dienone moiety includes a UV band at 266 nm ($\varepsilon = 17300$) and IR bands at 1680 and 1590 cm^{-1}. The aldehyde group is evidenced by a *t* in the ^{1}H-NMR spectrum at 9.75 ppm showing a vicinal coupling constant of $J = 2$ Hz, which is typical for aliphatic aldehydes, as well as by the IR bands at 1722, 2730, and 2820 cm^{-1}.

α,β-Unsaturated Aldehyde **10** *(Scheme 2).* The UV maxima at 265 ($\varepsilon = 15800$) and 226 nm ($\varepsilon = 14000$) are indicative for the dienone and the α,β-unsaturated aldehyde chromophore. The IR bands at 2710 and 2820 cm^{-1} are characteristic of an aldehyde group; in the ^{1}H-NMR spectrum the *s* of the aldehyde H-atom appears at 9.4 ppm.

Cyclopropene **11** *(Scheme 2).* The structure of **11**, which was obtained as a mixture of diastereomers, was easily deduced from its spectral data by comparing them with those of previously isolated compounds of the same type (s. *e.g.* [4] [7]). Moreover, direct spectroscopic proof for the cyclopropene

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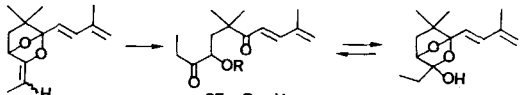
[7]) The same product distribution was found on GC analysis of the photolysis mixture using nonadecane as an internal standard.

moiety was obtained by measurement of the $^1H,^{13}C(2')$-coupling constant of 226 Hz, which is characteristic of cyclopropenes [10a].

Keto-enol Ethers **12A + B** *(Scheme 2).* The spectral evidence for the isomer **12A** includes a UV maximum at 227 nm and an *AB*-system at 5.97 ppm ($J = 15.7$ Hz) in the ^{1}H-NMR spectrum, proving the *trans*-diene moiety. One part of this *AB*-system is split into a *d* by coupling with a H-atom geminal to an oxygen function (*d* at 4.39 ppm, $J = 7.8$ Hz). The IR band at 1680 cm^{-1} as well as the UV absorption at 267 nm account for an enone chromophore, β-substituted by an alkoxy substituent [10b]. The H-atom of the enone moiety appears as a *s* at 5.81 ppm. On treatment with aqueous acid, the enol ether **12B**, whose spectral data correspond to that of **12A**, undergoes isomerization to **12A** (s. *Exper. Part*).

Bicyclic Acetal **13** *(Scheme 5).* The UV maximum at 228 nm ($\varepsilon = 26\,140$) signifies a conjugated diene, which is also evidenced in the NMR spectra. Furthermore, the ^{1}H-NMR spectrum includes a *q* at 4.58 ppm, indicating the shielded olefinic H-atom of the enol ether moiety, coupling with the methyl group at 1.57 ppm ($J = 7$ Hz). The presence of the acetal function is derived especially from the *s* at 112.8 ppm in the ^{13}C-NMR spectrum. To obtain further proof for structure **13**, the acetal was hydrolyzed (THF, H_2O, oxalic acid) to give an equilibrium mixture of **27** and **28**. Acetylation of this mixture gave a single acyclic dienone **29**, whose structure follows conclusively from the spectral data (s. *Exper. Part, Scheme 5*).

Scheme 5



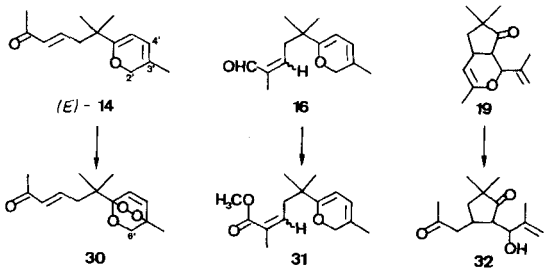
13 **27** R = H; **29** R = Ac **28**

*2H-Pyrans (E/Z)-***14** *and* **16** *(Scheme 6).* The spectroscopic evidence for the pyran moiety in the three isomers include: a UV maximum at *ca.* 280 nm (ε *ca.* 4000) and an *AB*-system in the ^{1}H-NMR spectrum at *ca.* 5.3 ppm ($J = 5$ to 6 Hz). The signal of the olefinic H-atom in the 4'-position shows a fine structure due to allylic coupling with CH_3–C(3') and the 2 H–C(2').

Moreover, the pyran (*E*)-**14** was converted to its endoperoxide **30** (51%) by reaction with singlet oxygen *(Scheme 6).* The ^{1}H-NMR spectrum of the latter compound shows an *AB*-system for the 2 H–C(6') at 3.72 ppm with a coupling constant of $J = 9$ Hz, characteristic of a CH_2-group bearing an electronegative substituent. The olefinic H-atoms of the trioxabicyclooctene moiety appear as an independent *AB*-system (6.55 ppm, $J = 8$ Hz).

The α,β-unsaturated aldehyde **16** was transformed to the corresponding methyl ester **31** *(Scheme 6)* by treatment with NaCN and MnO_2 in CH_3OH [11].

Scheme 6



(*E*) - **14** **16** **19**

30 **31** **32**

Bicyclo[3.2.0]heptanones **17A + B** *and* **18A + B** *(Scheme 2).* The IR bands of these four compounds at 1735 cm^{-1} prove the presence of a cyclopentanone. Compounds **17A** and **17B** exhibit an additional IR band at 1710 cm^{-1} and in the ^{1}H-NMR spectrum a *s* at 2.09 ppm, indicating a methyl ketone moiety. Most of the structural evidence, however, stems from the 300-MHz-^{1}H-NMR spectra in which every individual H-atom was assigned conclusively; the couplings are in agreement with the proposed

structure (s. *Exper. Part*). Moreover, isomer **17A** was treated with base furnishing **17B**, thus showing that the two compounds are epimers at C(6). On the other hand, the IR bands at 2820, 2720, and 1720 cm^{-1} of **18A** and **18B** signify the aldehyde function, which is also evidenced in the ^{1}H-NMR spectrum by *s* at 9.7 and 9.6 ppm for **18A** and **18B**, respectively.

Bicyclic Enol Ether **19** *(Scheme 6).* The main structural features are derived from the spectral data. In particular, the IR bands at 1745 and 1660 cm^{-1} signify the cyclopentanone and the enol ether moiety, respectively. The latter is also evidenced by a *d* (98.6 ppm) and a *s* (152.0 ppm) in the ^{13}C-NMR spectrum. To obtain further proof for the enol ether, **19** was hydrolyzed, furnishing the monocyclic hydroxyketone **32** *(Scheme 6).* The latter shows IR bands at 3500, 1745, and 1715 cm^{-1} for the hydroxy and the two carbonyl functions, respectively; in the ^{1}H-NMR spectrum the *s* at 2.12 ppm signifies the methyl ketone.

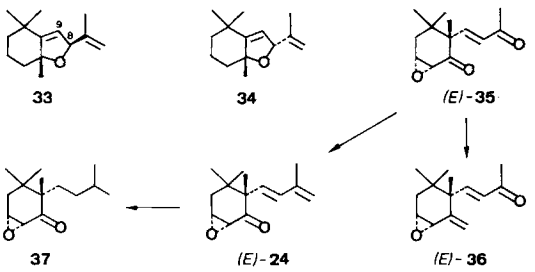
Dioxabicyclo[3.2.1]octene **20** *(Scheme 3).* The structure of this compound is based on comparison of its NMR spectra with those of the corresponding enone **6** *(Scheme 1).* Particularly, the ^{13}C-NMR signals for the 2,8-dioxabicyclo[3.2.1]octene moiety are almost identical in both compounds [1].

Oxetenes (E)- *and* (Z)-**21** *(Scheme 3).* The structure of these compounds was derived from the spectral data of their 2:1 mixture, which was obtained on chromatography at $-78°$. The dienone moiety is evidenced by the UV maximum at 263 nm as well as by the *AB*-system in the ^{1}H-NMR spectrum at 6.97 ($J = 15.0$ Hz) and 6.36 ppm ($J = 12.9$ Hz) for (*E*)- and (*Z*)-**21**, respectively. The oxetene substructure is confirmed by the NMR data. Thus, in the ^{13}C-NMR spectrum the *d* at 90.4 and 90.5 ppm, respectively, are indicative of tertiary C-atoms adjacent to an O-atom in four-membered ring ethers. The two olefinic C-atoms of the oxetene moiety exhibit a *d* and a *s* at 146.9 and 122.1 ppm, respectively, confirming the enol ether functionality. In the ^{1}H-NMR spectrum the olefinic H-atom of the oxetene appears as a *m* at 6.47 ppm, in accordance with reported ^{1}H-NMR data for oxetenes [12]. On warming the ^{1}H-NMR samples to room temperature, the 2:1 mixture of (*E*)- and (*Z*)-**21** was converted quantitatively to a 2:1 mixture of the aldehydes **10** and **16**.

Dihydrofurans **22** *and* **23** *(Scheme 4).* The structure of these compounds, and in particular the assignment of their relative configuration, was derived by comparison of their ^{1}H-NMR spectra with those of compounds **33** and **34** *(Scheme 7)* [13]. In particular, the spectra of **22** and **23** are characterized by the same pattern for the H-atoms at C(8) and C(9) as **33** and **34**, respectively.

Cyclohexanones (E)- *and* (Z)-**24** *(Scheme 4).* The structure was deduced by comparison of their spectra with those of the corresponding enones (*cf.* (*E*)-**35**). Furthermore, reaction of (*E*)-**35** with methylenetriphenylphosphorane gave (*E*)-**24** and (*E*)-**36**; catalytic hydrogenation (Pd/C) of a mixture of (*E*)- and (*Z*)-**24** led to **37** *(Scheme 7).*

Scheme 7

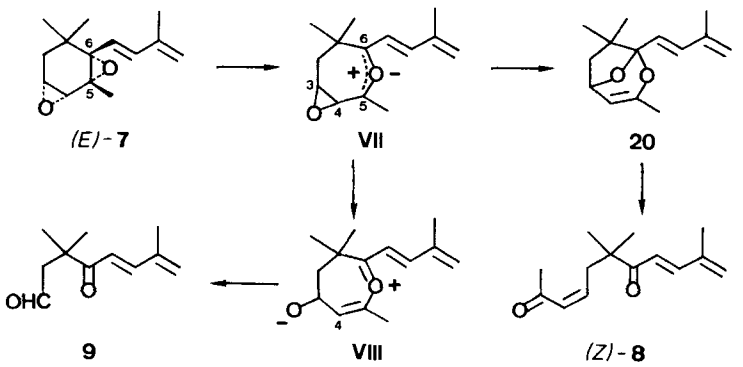


2-Oxatricyclo[6.1.0.0^{3,5}]nonane derivative **25** *(Scheme 4).* The proposal for this structure is based on the spectral data. In particular, the ^{1}H-NMR spectrum shows an *AB*-system at 2.57 ppm ($J = 10$ Hz) which was assigned to H–C(1) and H–C(9). The signals of H–C(9) at 2.30 ppm are broadened due to allylic coupling with the methylidene H-atoms. Moreover, the *m* at 3.07–3.31 ppm shows the characteristic pattern of H–C(3) and H–C(5) of the oxirane function. The carbonyl group shows an IR band at 1708 cm^{-1}.

β-Lactone **26** *(Scheme 4).* The structural features of this compound are evidenced by its spectral data. In particular, the β-lactone moiety is signified by an IR band at 1830 cm^{-1}, a *s* at 170.9 ppm in the ^{13}C-NMR spectrum and the characteristic elimination of CO_2 in the MS. The diene moiety shows a UV absorption at 217 nm ($\varepsilon = 1400$), indicating a (*Z*)-configuration, which is also evidenced by the coupling constant of 12.8 Hz of the *AB*-system at 5.74 ppm in the ^1H-NMR spectrum.

4. Discussion. – On singlet excitation ($\lambda = 254$ nm), the diepoxydiene (*E*)-**7** undergoes cleavage to the ylide **VII**, followed by a 1,4-oxygen migration from C(4) to C(6) leading to compound **20** (s. *Scheme 8*). Thus, (*E*)-**7** shows a reaction sequence analogous to the one observed previously on $^1\pi,\pi^*$-excitation of the corresponding diepoxyenone (*E*)-**5** (s. *Scheme 1* and [1]). As in the case of the corresponding enone, the dioxabicyclo[3.2.1]octene **20** is thermally unstable at room temperature, undergoing electrocyclic ring opening to (*Z*)-**8**[8]).

Scheme 8



However, to a larger extent the diene (*E*)-**7** undergoes transformations which do not have precedent in the photolysis of the enone (*E*)-**5**. Thus, the oxirane function in ylide **VII** cleaves to give the dipolar intermediate **VIII**, the positive charge of which is presumably stabilized by the diene side chain. Subsequent fragmentation of **VIII** leads to the aldehyde **9** and propyne[9])[10]).

In addition to product formation *via* the carbonyl ylide **VII**, the diepoxydiene (*E*)-**7** shows photoisomerization involving carbene intermediates. Thus, evidence for the intermediacy of the vinyl carbene **X** is provided by the formation of the cyclopropene **11** (s. *Scheme 10*).

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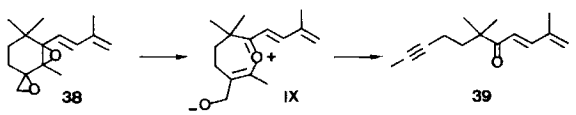
[8]) For a discussion of the reactivity of **20** see [1].

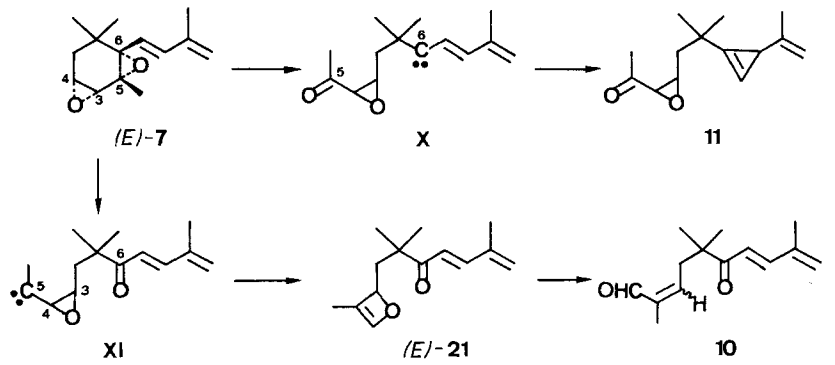
[9]) An analogous reaction sequence was observed on photolysis of **38** → **IX** → **39** [14].

Scheme 9



[10]) This transformation involving a dienone as leaving group represents a novel type of the *Eschenmoser* fragmentation [15].

Scheme 10



The photocleavage of the 5,6-epoxy function in (*E*)-**7** also furnishes the alternative carbene intermediate **XI**. Subsequent migration of the C,C-bond of the oxirane adjacent to the carbene center from C(4) to C(5) leads to the oxetene (*E*)-**21**. This process represents a previously unobserved carbene insertion into an oxirane in the α-position leading to an oxetene. Thus, an oxirane adjacent to a carbenic center follows in its reactivity the carbocyclic analog, since a cyclopropylcarbene is known to rearrange to a cyclobutene [16]. An isomeric oxetene arising from carbene insertion into the oxirane C(4),O-bond was not detected. This result is in agreement with findings in [17] that β-alkoxy substituents enhance the migration of C, C-bonds to the carbene center.

The oxetene (*E*)-**21** could only be isolated at $-78°$ since, as expected, it is thermally labile and rearranges at room temperature to the α,β-unsaturated aldehyde **10** (*Scheme 10*)[11]).

Besides the aforementioned primary photoproducts derived from ylide and carbene intermediates, compounds **12A**, **12B** and **13** (s. *Scheme 2*) were isolated in low yield. A reaction mechanism for these transformations cannot yet be given, further experiments are in progress.

Compounds (*E*/*Z*)-**8**, **9**, **10** and (*E*)-**21** (*Schemes 2* and *3*) contain a dienone chromophore with a strong UV absorption at *ca.* 260 nm, which makes them prone to undergo secondary photoreactions. Thus, (*E*/*Z*)-isomerization of the α,β-dienone double bond leads to the (*Z*)-isomers, which, in a thermal reaction, cyclize to the 2*H*-pyran derivatives (*E*/*Z*)-**14**, **15**, and **16**, respectively (s. *Scheme 2*)[12]). Additionally, (*E*/*Z*)-**8** and **10** undergo photochemical, intramolecular [2+2]-cycloadditions furnishing **17A**+**B** and **18A**+**B**, respectively. The bicyclic enol ether **19** is formally the product of a *Diels-Alder* reaction of an isomer of structure **8**. Since **19** could not be detected on photolysis of (*E*)-**8**, it seems reasonable that it is a product of (*Z*)-**8**[13]).

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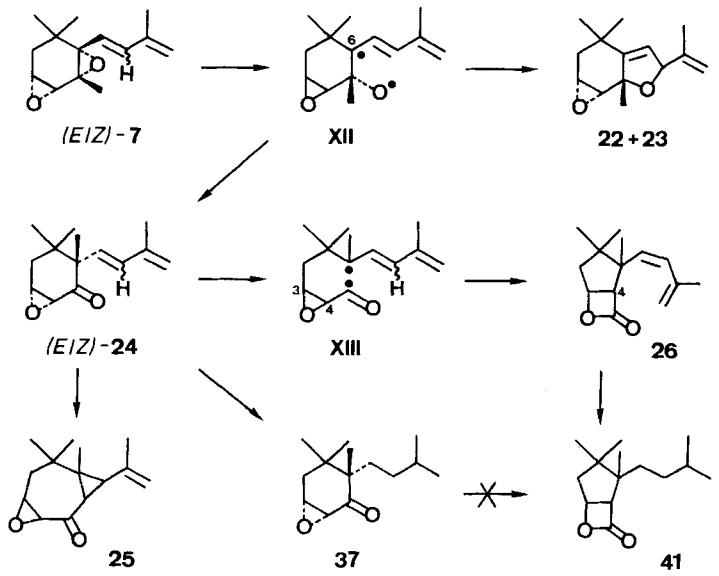
[11]) For other examples of the thermal isomerization of oxetenes see *e.g.* [12] [18].

[12]) For a recent publication on the isomerization of dienones to 2*H*-pyrans see [19].

[13]) Due to the availability of only small amounts of (*Z*)-**8**, this hypothesis could not be proven.

On triplet sensitization ($\lambda > 280$ nm, acetone), the diepoxydiene (*E*)-**7** shows the typical behaviour of epoxydienes[14]) undergoing C(6),O-cleavage to **XII** and stabilization to compounds **22**, **23**, and (*E*/*Z*)-**24** (s. *Scheme 11*).

Scheme 11



Compound (*E*)-**24** exhibits the typical reactivity of homoconjugated carbonyl compounds and, as could be demonstrated by further irradiation, undergoes an oxa-di-π-methane rearrangement furnishing **25**. In addition, (*E*)-**24** shows a novel type of photoisomerization leading to the bicyclic β-lactone **26**. The formation of the latter is presumably due to initial α-cleavage of **24** to the stabilized diradical **XIII**, which apparently undergoes C(4),O-cleavage and subsequent ring closure to **26** (s. *Scheme 11*). The diene side chain seems to be essential for this transformation, since it was shown that the photolysis of **37**, the tetrahydro derivative of **24**, does not lead to the corresponding β-lactone **41** *(Scheme 11)*. Therefore, we assume that the diene must stabilize the diradical **XIII** and/or serve as an energy acceptor.

Conclusion. – On triplet sensitization of the diepoxydiene (*E*)-**7**, the same types of photoproducts were formed as on $^1n,\pi^*$-excitation of the corresponding enone (*E*)-**5**, involving initial cleavage of the C(6),O-bond of the epoxide. In both systems, there was primarily no reaction of the additional oxirane with the diradical or dipolar intermediates. The interaction of this epoxy function is substantial on $^1\pi,\pi^*$-excitation of (*E*)-**5** and (*E*)-**7**, however. Both compounds undergo cleavage to the ylide intermediates **VI** and **VII**, respectively, followed by subsequent rearrangement to **6** and **20**. However, due to the electron donating effect of the diene side chain, only the ylide **VII** opens to the dipolar intermediate **VIII**, which fragments to **9**

[14]) Compare *e.g.* (*E*)-**2** *(Scheme 1)* [13].

and propyne. In contrast to the photolysis of the epoxyenone (*E*)-**5**, where product formation *via* the ylide intermediate **VI** was by far the main process, the epoxydiene (*E*)-**7** undergoes reactions involving ylide and carbene intermediates to an equal extent. Thereby, the most interesting finding is the *insertion reaction of the carbene center in* **XI** *into the C, C-bond of the neighbouring oxirane,* leading to the oxetenes (*E*/*Z*)-**21**.

This work was supported by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung* and *Ciba-Geigy, Ltd.*, Basle. The authors are very grateful to Drs. *E. Rüegg, E. Widmer,* and *M. Schlageter, F. Hoffmann-La Roche & Co., Ltd.*, Basle, for the generous gift of 3,4-didehydro-β-ionone used in this study. We are indebted to the following people for their help: Miss *B. Brandenberg,* Mr. *F. Bangerter,* Mr. *F. Fehr* and Mr. *M. Langenauer* (NMR), Mrs. *L. Golgowsky* and Prof. *J. Seibl* (MS) and Mr. *D. Manser* (elemental analysis).

Experimental Part

General. See [20] except as noted below. Analytical gas chromatography was performed using a 25 m × 0.33 mm *Ucon 50 HB 5100* capillary column. Column chromatographies were carried out on silica gel (SiO_2) *60 Merck,* 0.040–0.063 mm, 230–400 mesh ASTM. Analytically pure samples were obtained, in general, after repeated column chromatography on SiO_2; in some cases further purification was necessary on HPLC (*Du Pont Instruments* Model *830,* UV detector), using a 25 cm × 23.6 mm SiO_2 column, or by prep. GC. ^{1}H-NMR spectra were taken in $CDCl_3$ solution on a *Bruker-WP-80/CW* instrument (80 MHz) exceptions are noted below.

1. Photolysis Experiments. – 1.1. *Irradiation of* (E)-**7** *at* $\lambda = 254$ *nm.* – 1.1.1. *At Room Temperature.* A solution of (*E*)-**7** [1] (5.071 g, 23 mmol) in MeCN (430 ml) was irradiated (quartz, lamp *A*, 92% conversion). Chromatography on SiO_2 (Et_2O/pentane 1:3 to 1:0) yielded several fractions from which the following product distribution was determined by ^{1}H-NMR and GC analysis: (*Z*)-**7** (2%), (*E*)-**8** (3%) [1], (*Z*)-**8** (3%), **9** (3%), **10** (4%), **11** (10%), **12A** (2%), **12B** (2%), **13** (2%), (*E*)-**14** (1%), (*Z*)-**14** (5%), **15** (2%), **16** (4%), **17A** (5%), **17B** (2%), **18A** (8%), **18B** (3%), and **19** (2%). *(Z,1'R*,2'S*,3'S*,4'S*)-1-(1',2':3',4'-diepoxy-2',6',6'-trimethyl-1'-cyclohexyl)-3-methyl-1,3-butadiene* ((*Z*)-**7**). B.p. 80°/0.02 Torr. UV (0.116 mg in 10 ml of EtOH): 232 (9700). IR: 3080*w*, 3000*s*, 2962*s*, 2922*s*, 2870*m*, 1595*w*, 1465*m* sh, 1460*m* sh, 1450*m*, 1435*m*, 1385*m* sh, 1379*m*, 1365*m*, 1320*w*, 1280*w*, 1260*w*, 1155*w*, 1120*w*, 1110*w*, 1078*m*, 1060*w*, 1028*m* sh, 1018*m*, 990*w*, 965*w*, 940*m*, 912*m*, 900*m*, 892*s*, 880*w*, 852*w*. ^{1}H-NMR: 0.97, 1.20 (2 *s*, 2 H_3C–C(6')); 1.42 (*s*, H_3C–C(2')); 1.48–1.62 (*m*, 2 H–C(5')); 1.82 (*m*, $w_{1/2} = 3.5$, H_3C–C(3)); 2.80–3.12 (*m*, H–C(3'), H–C(4')); 4.88 (*m*, $w_{1/2} = 4$, 2 H–C(4)); 6.75 (*AB*-system, $J = 13$, $\delta_A = 5.40$, $\delta_B = 6.10$, *B*-part broadened, H–C(1), H–C(2)). MS: 220 (5, M^+, $C_{14}H_{20}O_2$), 137 (21), 136 (21), 135 (11), 125 (28), 123 (29), 121 (24), 109 (13), 107 (21), 105 (27), 96 (15), *95* (100), 93 (24), 91 (28), 83 (18), 79 (18), 77 (20), 67 (50), 55 (16), 53 (13), 43 (92), 41 (38).

(3Z,8E)-6,6,10-Trimethyl-3,8,10-undecatrien-2,7-dione ((**Z**)-**8**). UV (0.1056 mg in 10 ml of MeCN): 230 (1100), 269 (20400). UV (1.389 mg in 2 ml of MeCN): 334 (140), end absorption to 390. IR: 3095*w*, 3060*w*, 3025*w*, 2970*s*, 2930*m*, 2895*m*, 2875*m*, 1815*w*, 1687*s*, 1612*s*, 1590*s*, 1463*m*, 1447*m*, 1437*m*, 1415*m*, 1385*m*, 1375*m*, 1367*m*, 1352*m*, 1318*m*, 1282*w*, 1266*m*, 1250*m*, 1178*s*, 1075*s*, 1035*m*, 1024*m*, 982*s*, 908*s*, 882*w*, 860*m*. ^{1}H-NMR: 1.21 (*s*, 2 H_3C–C(6)); 1.92 (*s*, $w_{1/2} = 2$, H_3C–C(10)); 2.28 (*s*, 3 H–C(1)); 2.96 (*d*, $J = 7$, 2 H–C(5)); 5.40 (*m*, $w_{1/2} = 4$, 2 H–C(11)); 6.06 (*AB*-system, $J = 11.5$, $\delta_A = 5.92$, split into *d*, $J = 7$, H–C(4), $\delta_B = 6.20$, br., H–C(3)); 6.92 (*AB*-system, $J = 15$, $\delta_A = 6.49$, $\delta_B = 7.35$, H–C(8), H–C(9)): MS: 220 (17, M^+, $C_{14}H_{20}O_2$), 177 (11), 105 (28), 95 (21), *93* (100), 92 (27), 91 (20), 77 (18), 43 (41), 41 (16).

3,3,7-Trimethyl-4-oxo-5,7-octadienal (**9**). UV (0.189 mg in 20 ml): 266 (17300). UV (1.844 mg in 2 ml): 340 (70), end absorption to 390. IR: 3090*w*, 3060*w* sh, 2970*s*, 2930*m*, 2900*m* sh, 2870*w*, 2820*w*, 2730*w*, 1722*s*, 1685*s* sh, 1680*s*, 1610*m*, 1590*s*, 1462*m*, 1455*m* sh, 1450*m* sh, 1435*w*, 1380*m* sh, 1375*m*, 1365*m*, 1320*m*, 1310*m* sh, 1282*m*, 1268*m*, 1252*m*, 1170*w*, 1075*s*, 1035*w*, 1015*w*, 980*m*, 910*m*, 860*w*. ^{1}H-NMR: 1.30 (*s*, 2 H_3C–C(3)); 1.92 (*m*, $w_{1/2} = 2$, H_3C–C(7)); 2.60 (*d*, $J = 2$, 2 H–C(2)); 5.42 (*m*, $w_{1/2} = 4$, 2 H–C(8)); 6.95 (*AB*-system, $J = 16$, $\delta_A = 6.50$, $\delta_B = 7.40$, H–C(5), H–C(6)); 9.75 (*t*, $J = 2$, H–C(1)). MS: 180 (2, M^+, $C_{11}H_{16}O_2$), 138 (6), 96 (10), *95* (100), 67 (44), 41 (27).

(7E)-2,5,5,9-Tetramethyl-6-oxo-2,7,9-decatrienal (**10**). UV (0.510 mg in 25 ml): 226 (14000), 265 (15800). UV (1.300 mg in 2 ml): 330 (90), end absorption to 390. IR: 3090*w*, 3060*w*, 2970*s*, 2930*s*, 2870*m*, 2820*m*, 2765*w*, 2710*w*, 1820*w*, 1685*s* sh, 1680*s*, 1640*s*, 1610*s*, 1590*s*, 1462*m*, 1458*m* sh, 1450*m* sh, 1435*m*, 1400*m*, 1388*m*, 1375*m*, 1360*m*, 1319*m*, 1284*m*, 1260*s*, 1228*w* sh, 1210*m*, 1160*w*, 1135*w*, 1080*m* sh, 1055*s*, 1022*m*, 1005*m*, 980*s*, 908*s*, 855*m*. ^{1}H-NMR: 1.27 (*s*, 2 H_3C–C(5)); 1.78, 1.95 (2 *m*, $w_{1/2}$ = 3, H_3C–C(2), H_3C–C(9)); 2.62 (*d*, *J* = 7, 2 H–C(4)); 5.45 (*m*, $w_{1/2}$ = 4, 2 H–C(10)); 6.45 (*t*, *J* = 7, with fine structure, overlapping with signal at 6.42, H–C(3)); 6.95 (*AB*-system, *J* = 15, δ_A = 6.50, δ_B = 7.40, H–C(7), H–C(8)); 9.40 (*s*, H–C(1)). ^{13}C-NMR: 9.5, 18.2 (2 *q*, H_3C–C(2), H_3C–C(9)); 24.5 (2 *q*, 2 H_3C–C(5)); 38.4 (*t*, C(4)); 125.9 (*t*, C(10)); 120.5, 146.4, 150.1 (3 *d*, C(3), C(7), C(8)); 195.0 (*d*, C(1)); 46.9 (*s*, C(5)); 140.7, 141.0 (2 *s*, C(2), C(9)); 202.9 (*s*, C(6)). MS: 220 (6, M^+, $C_{14}H_{20}O_2$), 191 (23), 119 (42), 108 (10), *107* (100), 91 (22), 41 (10).

3,4-Epoxy-6-methyl-6-(3'-isopropenyl-1'-cyclopropen-1'-yl)-2-heptanone (**11**; *mixture of diastereomers*). B.p. 100°/0.03 Torr. UV (4.782 mg in 5 ml): end absorption to 400. IR: 3130*w*, 3080*m*, 2970*s*, 2930*s*, 2915*s*, 2870*m*, 1760*m*, 1725*s*, 1710*s*, 1635*m*, 1465*m*, 1448*s*, 1430*s* sh, 1420*s*, 1385*s*, 1370*s* sh, 1362*s*, 1320*w*, 1310*w*, 1290*w*, 1275*w* sh, 1252*m*, 1220*m*, 1179*m*, 1158*m*, 1125*w*, 1095*w*, 1040*m*, 1025*m*, 965*m*, 940*m*, 905*m* sh, 900*m*, 868*s*. ^{1}H-NMR: 1.18, 1.20, 1.22, 1.28 (4 *s*, 6 H, 3 H–C(7), H_3C–C(6)); 1.40–1.95 (*m*, H–C(3'), 2 H–C(5)); 1.52 (*m*, $w_{1/2}$ = 2.5, CH_3C=CH_2); 2.25 (*s*, 3 H–C(1)); 3.15–3.60 (*m*, H–C(3), H–C(4)); 4.70, 4.75 (2 *m*, $w_{1/2}$ = 4, CH_3C=CH_2); 6.65 (*d*, *J* = 1, H–C(2')). ^{13}C-NMR (75 MHz; signals of major diastereomer are given only): 19.9, 26.1, 26.7, 28.3 (4 *q*, 4 CH_3); 38.4 (*t*, C(5)); 107.6 (*t*, CH_3C=CH_2); 25.8–28.3 (4 overlapping signals, one presumably *d*, C(3')); 55.8, 57.8 (2 *d*, C(3), C(4)); 101.6 (*d*, C(2')); 34.4 (*s*, C(6)); 130.7, 149.8 (2 *s*, C(1'), CH_3C=CH_2); 203.8 (*s*, C(2)). MS: 220 (8, M^+, $C_{14}H_{20}O_2$), 147 (18), 133 (13), 125 (14), 122 (13), *121* (100), 120 (17), 119 (37), 117 (14), 107 (38), 106 (17), 105 (78), 96 (11), 95 (50), 93 (24), 91 (49), 85 (14), 79 (35), 77 (38), 67 (22), 65 (14), 55 (25), 53 (18), 51 (12), 43 (92), 41 (48).

$C_{14}H_{20}O_2$ (220.30) Calc. C 76.32 H 9.15% Found C 76.37 H 9.02%

1-[5'-((E)-3''-Methyl-1'',3''-butadien-1''-yl)-4',4'-dimethyl-1'-oxa-2'-cyclopentyliden]-2-propanone; isomer **12A**. UV (0.123 mg in 10 ml of EtOH): 227 (16400), 267 (17800). UV (1.129 mg in 2 ml of EtOH): end absorption to 360. IR: 3090*w*, 3060*w*, 2965*s*, 2935*m*, 2900*m* sh, 2878*m*, 1755*w*, 1705*w* sh, 1680*s*, 1600*s* br., 1465*m*, 1455*w*, 1435*w*, 1423*m*, 1390*m*, 1370*s*, 1355*m*, 1275*m*, 1265*m*, 1245*w*, 1162*m* sh, 1146*s*, 1121*s*, 1028*w*, 1014*w*, 992*m*, 958*s*, 932*w*, 908*m*, 892*m*, 852*m*. ^{1}H-NMR (300 MHz): 0.92, 1.12 (2 *s*, 2 H_3C–C(4')); 1.87 (*s*, H_3C–C(3'')); 2.13 (*s*, 3 H–C(3)); 3.00 (*AB*-system, *J* = 18.1, δ_A = 2.78, split into *d*, *J* = 1.8, δ_B = 3.23, split into *d*, *J* = 0.98, 2 H–C(3')); 4.39 (*d*, *J* = 7.8, H–C(5')); 5.05–5.06 (*m*, 2 H–C(4'')); 5.97 (*AB*-system, *J* = 15.7, δ_A = 5.57, split into *d*, *J* = 7.8, H–C(1''), δ_B = 6.38, H–C(2'')); 5.81 (*s*, H–C(1)). ^{13}C-NMR (75 MHz): 18.4, 21.9, 24.9, 31.3 (4 *q*, 4 CH_3); 46.2 (*t*, C(3')); 118.3 (*t*, C(4'')); 91.5 (*d*, C(5')); 99.6 (*d*, C(1)); 123.2, 137.2 (2 *d*, C(1''), C(2'')); 41.3 (*s*, C(4')); 175.2 (*s*, C(2')); 197.7 (*s*, C(2)). MS: 220 (16, M^+, $C_{14}H_{20}O_2$), 205 (16), 178 (13), 177 (47), 136 (28), 135 (14), 125 (19), 122 (16), *121* (100), 109 (32), 107 (41), 105 (20), 95 (22), 93 (55), 91 (30), 85 (54), 81 (19), 79 (26), 77 (25), 69 (22), 67 (14), 55 (19), 53 (16), 43 (72), 41 (37).

Isomer **12B**. UV (0.267 mg in 25 ml of EtOH): 227 (20600), 264 (12150). UV (2.168 mg in 5 ml of EtOH): end absorption to 370. IR: 3082*w*, 3040*w*, 2962*s*, 2925*m*, 2895*m* sh, 2870*m*, 1735*w*, 1668*s*, 1618*s*, 1461*m*, 1452*m*, 1435*m*, 1382*s*, 1368*m*, 1355*m*, 1328*s*, 1308*m* sh, 1282*m*, 1276*m*, 1250*w*, 1221*m*, 1175*m*, 1163*m*, 1138*m*, 1088*w*, 1045*w*, 1027*m*, 1005*m*, 990*m*, 968*s*, 937*w*, 895*s*. ^{1}H-NMR: 1.04 (*s*, 2 H_3C–C(4')); 1.88 (*m*, $w_{1/2}$ = 3, H_3C–C(3'')); 2.00 (*s*, 3 H–C(3)); 2.54 (*AB*-system, *J* = 14, δ_A = 2.34, split into *d*, *J* = 1.5, δ_B = 2.74, 2 H–C(3')); 4.31 (*d*, *J* = 7, H–C(5')); 5.06 (*m*, $w_{1/2}$ = 4, 2 H–C(4'')); 5.34 (*m*, $w_{1/2}$ = 3, H–C(1)); 6.02 (*AB*-system, *J* = 15, δ_A = 5.72, split into *d*, *J* = 7, H–C(1''), δ_B = 6.32, H–C(2'')). ^{13}C-NMR: 18.5, 22.9, 23.8, 25.7 (4 *q*, 4 CH_3); 56.0 (*t*, C(3')); 118.1 (*t*, C(4'')); 94.1 (*d*, C(5')); 109.6 (*d*, C(1)); 124.1, 136.4 (2 *d*, C(1''), C(2'')); 39.6 (*s*, C(4')); 140.9 (*s*, C(3'')); 172.6 (*s*, C(2')); 198.7 (*s*, C(2)). MS: 220 (23, M^+, $C_{14}H_{20}O_2$), 205 (17), 179 (19), 177 (35), 163 (17), 159 (22), 138 (15), 137 (26), 135 (22), 121 (42), 119 (14), 107 (22), 105 (17), 95 (17), 93 (28), 91 (30), 85 (14), 79 (19), 77 (25), 55 (15), *43* (100), 41 (34).

1-((E)-3'-Methyl-1',3'-butadien-1'-yl)-3-ethylidene-6,6-dimethyl-2,7-dioxabicyclo[2.2.1]heptane (**13**). UV (0.150 mg in 25 ml): 228 (26140). IR: 3090*m*, 3025*m*, 2965*s*, 2940*s*, 2930*s*, 2895*m*, 2870*s*, 1800*w*, 1712*s*, 1650*m*, 1614*s*, 1468*m*, 1460*m*, 1449*s*, 1440*m*, 1388*s*, 1380*m*, 1368*s*, 1360*s*, 1311*s*, 1295*s*, 1285*m*, 1279*m*, 1245*m*, 1210*m*, 1185*s*, 1166*s*, 1109*s*, 1075*s*, 1038*s*, 1009*s*, 989*s*, 971*s*, 960*s*, 942*s*, 920*s*, 897*s*,

868*m*, 834*m*. ^{1}H-NMR: 0.98, 1.11 (2 *s*, 2 H_3C–C(6)); 1.42–1.97 (*m*, 2 H–C(5)); 1.57 (*d*, *J* = 7, CH_3CH=C(3)); 1.88 (*m*, $w_{1/2}$ = 3, H_3C–C(3′)); 4.58 (*q*, *J* = 7, CH_3CH=C(3)); 5.02–5.20 (*m*, 2 H–C(4′). H–C(4)); 6.25 (*AB*-system, *J* = 16, δ_A = 5.78, δ_B = 6.73, H–C(1′), H–C(2′)). ^{13}C-NMR: 11.4, 18.2, 23.2, 28.0 (4 *q*, 4 CH_3); 43.4 (*t*, C(5)); 119.0 (*t*, C(4′)); 75.5 (*d*, C(4)); 87.0 (*d*, CH_3CH=C(3)); 118.7, 137.2 (2 *d*, H–C(1′), H–C(2′)); 45.8 (*s*, C(6)); 112.8 (*s*, C(1)); 140.8 (*s*, C(3′)); 153.1 (*s*, C(3)). MS: 220 (26, M^+, $C_{14}H_{20}O_2$), 164 (25), 122 (11), 121 (32), 107 (31), 105 (14), 96 (10), *95* (100), 93 (19), 91 (15), 79 (10), 77 (10), 67 (28), 55 (12), 43 (12), 41 (32).

*(*E*)-6-Methyl-6-(3′-methyl-2′*H*-pyran-6′-yl)-3-hepten-2-one ((*E*)-***14***).* UV (0.477 mg in 25 ml): 217 (15200), 281 (4500). IR: 3090*w*, 3040*w*, 2965*s*, 2922*m*, 2910*m*, 2880*m*, 2875*m*, 2815*m*, 2740*w*, 1695*m* sh, 1672*s*, 1625*s*, 1610*m*, 1460*m*, 1445*m*, 1435*m*, 1425*m* sh, 1385*m*, 1360*s*, 1330*w*, 1280*m*, 1265*m* sh, 1250*s*, 1190*m*, 1178*m*, 1102*s*, 1082*m* sh, 1070*w* sh, 1052*w*, 1035*w*, 1012*w*, 980*s*, 955*m*, 935*w* sh, 905*m*. ^{1}H-NMR: 1.12 (*s*, H_3C–C(6), 3 H–C(7)); 1.70 (*m*, $w_{1/2}$ = 4, H_3C–C(3′)); 2.25 (*s*, 3 H–C(1)); 2.35 (*d*, *J* = 7, 2 H–C(5)); 4.41 (*m*, $w_{1/2}$ = 3.2, 2 H–C(2′)); 5.32 (*AB*-system, *J* = 6, δ_A = 5.05, H–C(5′). δ_B = 5.60, split into *m*, H–C(4′)); 6.38 (*AB*-system, *J* = 16, δ_A = 6.02, broadened, H–C(3), δ_B = 6.75, split into *t*, *J* = 7, H–C(4)). MS: 220 (14, M^+, $C_{14}H_{20}O_2$), 177 (29), 137 (15), 136 (28), 123 (24), 121 (13), 105 (39), 95 (13), *93* (100), 92 (22), 91 (18), 77 (16), 43 (40), 41 (11).

*(*Z*)-6-Methyl-6-(3′-methyl-2′*H*-pyran-6′-yl)-3-hepten-2-one ((*Z*)-***14***).* UV (0.195 mg in 20 ml): 225 (15000), 280 (5680). UV (1.324 mg in 2 ml): end absorption to 390. IR: 3090*w*, 3042*w*, 3025*m*, 2970*s*, 2930*s*, 2915*s*, 2880*m*, 2860*m*, 2820*m*, 2760*w*, 2740*w*, 1693*s*, 1665*s*, 1610*s*, 1448*m*, 1535*m*, 1413*s*, 1382*m*, 1350*s*, 1302*m*, 1288*m*, 1280*m*, 1240*w*, 1179*s*, 1141*m*, 1102*s*, 1052*m*, 1038*m*, 1017*m*, 985*m*, 970*m*, 960*m*, 906*m*, 858*w*. ^{1}H-NMR: 1.10 (*s*, 3 H–C(7), H_3C–C(6)); 2.70 (*m*, $w_{1/2}$ = 4, H_3C–C(3′)); 2.20 (*s*, 3 H–C(1)); 2.75 (*d*, *J* = 6, 2 H–C(5)); 4.40 (*m*, $w_{1/2}$ = 3.6, 2 H–C(2′)); 5.33 (*AB*-system, *J* = 5, δ_A = 5.05, H–C(5′). δ_B = 5.60, split into *m*, H–C(4′)); 6.12 (*AB*-system, *J* = 11, δ_A = 6.05, split into *t*, *J* = 6, H–C(4), δ_B = 6.20, H–C(3)). MS: 220 (7, M^+, $C_{14}H_{20}O_2$), 125 (15), *123* (100), 109 (13), 95 (22), 93 (24), 43 (85), 41 (17).

6-Acetyl-7-isopropenyl-3,3-dimethylbicyclo[3.2.0]heptan-2-one, isomer **17A**. B.p. 100°/0.02 Torr. IR: 3082*w*, 2963*m*, 2930*m*, 2900*w* sh, 2868*m*, 1735*s*, 1709*s*, 1638*w*, 1462*m*, 1452*m*, 1439*w* sh, 1430*w* sh, 1420*w* sh, 1382*m*, 1375*m* sh, 1360*m*, 1342*w* sh, 1311*w*, 1288*w*, 1238*w*, 1228*w*, 1175*m* sh, 1162*m*, 1130*w* sh, 1105*w*, 1090*m*, 1022*w*, 952*w*, 900*s*. ^{1}H-NMR (300 MHz): 1.03, 1.19 (2 *s*, 2 H_3C–C(3)); 1.70 (*m*, $w_{1/2}$ = 3, CH_3C=CH_2); 1.97 (*AB*-system, *J* = 13.6, δ_A = 1.75, split into *d*, *J* = 6.2, δ_B = 2.20, split into *d*, *J* = 8.8, 2 H–C(4)); 2.09 (*s*, CH_3CO); 3.00–3.40 (*m*, H–C(1), H–C(5), H–C(6), H–C(7)); 4.89, 4.97 (2 *m*, $w_{1/2}$ = 4.5, CH_3C=CH_2). ^{13}C-NMR (contaminated with *ca.* 20% of isomer **17B**): 21.2, 23.9, 25.6, 30.2 (4 *q*, 4 CH_3); 42.3 (*t*, C(4)); 113.5 (*t*, CH_3C=CH_2); 29.6, 45.7, 46.2, 56.3 (4 *d*, C(1), C(5), C(6), C(7)); 48.7 (*s*, C(3)); 142.2 (*s*, CH_3C=CH_2); 208.0, 221.9 (2 *s*, C(2), CH_3CO). MS: 220 (8, M^+, $C_{14}H_{20}O_2$), 178 (12), 177 (36), 167 (15), 163 (11), 149 (10), 137 (19), 136 (32), 121 (25), 110 (27), 109 (18), 107 (18), 105 (16), 96 (13), *95* (100), 93 (53), 92 (12), 91 (21), 84 (15), 77 (19), 67 (28), 43 (75), 41 (34).

Isomer **17B**. B.p. 100°/0.03 Torr. UV (4.241 mg in 5 ml of EtOH): 265 sh (220), end absorption to 390. IR: 3082*m*, 2960*s*, 2935*s*, 2900*m* sh, 2870*m*, 1735*s*, 1710*s*, 1645*m*, 1462*s* sh, 1452*s*, 1438*m* sh, 1420*m* sh, 1382*s*, 1362*s*, 1352*s*, 1312*m*, 1298*m*, 1250*m*, 1192*s*, 1172*s*, 1125*s*, 1095*s*, 1039*w*, 1020*w*, 965*w* sh, 950*w*, 940*w*, 930*w* sh, 890*s*, 870*w*. ^{1}H-NMR (300 MHz): 0.97, 1.12 (2 *s*, 2 H_3C–C(3)); 1.82 (*AB*-system, *J* = 13.5, δ_A = 1.65, split into *d*, *J* = 8.6, δ_B = 1.98, split into *d*, *J* = 8.4, 2 H–C(4)); 1.72 (*m*, CH_3=CH_2); 2.10 (*s*, CH_3CO); 2.83 (*d*×*d*, *J* = 8.6, 7.6, H–C(6)); 3.05 (*d*×*d*×*d*×*d*, *J* = 9.1, 8.6, 8.4, 7.6, H–C(5)); 3.19 (*d*×*d*, *J* = 9.3, 9.1, H–C(7)); 3.35 (*d*×*d*, *J* = 9.3, 8.6, H–C(1)); 4.75, 4.83 (2 *m*, $w_{1/2}$ = 4, CH_3C=CH_2). MS: 220 (3, M^+, $C_{14}H_{20}O_2$), 177 (31), 137 (18), 136 (32), 121 (22), 110 (29), 109 (15), 107 (16), 105 (14), 96 (10), *95* (100), 93 (51), 92 (12), 91 (18), 77 (18), 67 (29), 43 (80), 41 (38).

$C_{14}H_{20}O_2$ (220.30) Calc. C 76.32 H 9.15% Found C 76.04 H 9.02%

7-Isopropenyl-3,3,6-trimethyl-2-oxobicyclo[3.2.0]heptan-6-carbaldehyde, isomer **18A**. B.p. 70°/0.02 Torr. UV (2.075 mg in 2 ml): 295 (61), end absorption to 380. IR: 3082*w*, 2962*s*, 2930*m*, 2870*m*, 2820*w*, 2720*m*, 1735*s*, 1720*s*, 1645*w*, 1455*m*, 1445*m* sh, 1400*w*, 1380*m*, 1362*w*, 1305*w*, 1242*w*, 1230*w* sh, 1210*w*, 1189*w* sh, 1169*w*, 1160*w*, 1150*w*, 1120*w*, 1090*m*, 933*w*, 920*w*, 896*m*. ^{1}H-NMR (300 MHz): 1.04, 1.19, 1.28 (3 *s*, 2 H_3C–C(3), H_3C–C(6)); 1.67 (*m*, $w_{1/2}$ = 3, CH_3C=CH_2); 2.02 (*d*, *J* = 8.8, 2 H–C(4)); 2.84 (*d*, *J* = 8.2, H–C(7), and *d*×*t*, *J* = 8.8, 8.4. H–C(5)); 3.29 (*d*×*d*, *J* = 8.4, 8.2, H–C(1)); 4.90, 4.92 (2 *m*, $w_{1/2}$ = 4.5, CH_3C=CH_2); 9.74 (*s*, CHO). ^{13}C-NMR (20 MHz): 16.5, 21.6, 23.1, 25.0 (4 *q*, 4 CH_3);

36.7 (*t*, C(4)); 112.0 (*t*, $CH_3C{=}CH_2$); 31.8, 44.4, 52.4 (3 *d*, C(1), C(5), C(7)); 203.7 (*d*, CHO); 48.7, 52.7 (2 *s*, C(3), C(6)); 141.2 (*s*, $CH_3C{=}CH_2$); 220.2 (*s*, C(2)). MS: 220 (13, M^+, $C_{14}H_{20}O_2$), 191 (12), 137 (48), 136 (25), 125 (19), 123 (17), 121 (28), 119 (14), 111 (12), 109 (29), 107 (51), 105 (18), 96 (19), *95* (100), 93 (30), 91 (33), 83 (13), 81 (12), 79 (20), 77 (20), 67 (43), 65 (11), 55 (22), 53 (14), 43 (56), 41 (45).

$C_{14}H_{20}O_2$ (220.30) Calc. C 76.32 H 9.15% Found C 76.41 H 9.27%

Isomer **18B**. M.p. 68° (pentane). UV (1.068 mg in 2 ml): 265 (270), end absorption to 350. IR: 3082*w*, 2960*s*, 2930*m*, 2900*m*, 2882*m*, 2795*w*, 2700*w*, 1735*s*, 1720*s*, 1690*w*, 1648*w*, 1462*m* sh, 1452*m*, 1382*m*, 1378*m* sh, 1365*m*, 1300*w*, 1250*w*, 1210*w*, 1188*w*, 1150*w*, 1130*w*, 1095*m*, 1088*m*, 955*w*, 932*w*, 920*w*, 895*m*. ^{1}H-NMR (300 MHz): 0.97, 1.12, 1.26 (3 *s*, 2 H_3C–C(3), H_3C–C(6)); 1.59 (*m*, $w_{1/2}$ = 4, $CH_3C{=}CH_2$); 1.87 (*AB*-system, J = 13.6, δ_A = 1.77, split into *d*, J = 8.8, δ_B = 1.98, split into *d*, J = 8.0, 2 H–C(4)); 2.53 (*d*×*d*×*d*, J = 8.8, 8.2, 8.0, H–C(5)); 3.15 (*d*×*d*, J = 9.1, 8.2, H–C(1)); 3.32 (*d*, J = 9.1, H–C(7)); 4.93, 5.01 (2 *m*, $w_{1/2}$ = 4, $CH_3C{=}CH_2$); 9.60 (*s*, CHO). ^{13}C-NMR: 16.5, 21.8, 22.9, 24.8 (4 *q*, 4 CH_3); 37.4 (*t*, C(4)); 112.4 (*t*, $CH_3C{=}CH_2$); 38.5, 42.8, 43.9 (3 *d*, C(1), C(5), C(7)); 203.4 (*d*, CHO); 48.9, 51.8 (2 *s*, C(3), C(6)); 141.6 (*s*, $CH_3C{=}CH_2$); 220.4 (*s*, C(2)). MS: 220 (23, M^+, $C_{14}H_{20}O_2$), 191 (19), 177 (11), 137 (64), 136 (33), 125 (26), 121 (31), 119 (15), 109 (21), 107 (52), 105 (20), 96 (15), *95* (100), 93 (34), 91 (28), 83 (12), 81 (11), 79 (17), 77 (18), 69 (13), 67 (33), 55 (22), 53 (12), 43 (35), 41 (43).

$C_{14}H_{20}O_2$ (220.30) Calc. C 76.32 H 9.15% Found C 76.30 H 9.09%

2-Isopropenyl-4,8,8-trimethyl-3-oxabicyclo[4.3.0]non-4-en-9-one (**19**). B.p. 70–80°/0.005 Torr. UV (2.114 mg in 2 ml): end absorption to 400. IR: 3085*w*, 3060*w*, 2960*s*, 2930*s*, 2900*m*, 2870*s*, 2840*w* sh, 1745*s*, 1660*s*, 1468*m*, 1460*m*, 1448*m*, 1435*m*, 1380*s*, 1365*s*, 1352*s*, 1330*m*, 1318*w*, 1302*m*, 1277*m*, 1258*m*, 1240*w*, 1215*m*, 1190*s*, 1160*m*, 1118*m*, 1091*m*, 1060*s*, 1040*m*, 1022*s*, 1010*m* sh, 980*m*, 962*s*, 950*w*, 910*s*, 891*m*, 862*w*. 849*m*. ^{1}H-NMR: 1.10, 1.12 (2 *s*, 2 H_3C–C(8)); 1.75, 1.81 (2 *m*, $w_{1/2}$ = 4, H_3C–C(4), $CH_3C{=}CH_2$); 0.80–2.70 (*m*, H–C(1), H–C(6), 2 H–C(7)); 4.52 (*d*, J = 9) and 4.70 (*s*, H–C(2), H–C(5)); 5.10 (*m*, $w_{1/2}$ = 4, $CH_3C{=}CH_2$). ^{13}C-NMR: 17.3, 19.9, 24.7, 26.7 (4 *q*, 4 CH_3); 42.0 (*t*, C(7)); 116.0 (*t*, $CH_3C{=}CH_2$); 33.0, 53.1 (2 *d*, C(1), C(6)); 81.2 (*d*, C(2)); 98.6 (*d*, C(5)); 47.1 (*s*, C(8)); 142.2, 152.0 (2 *s*, C(4), $CH_3C{=}CH_2$); 215.6 (*s*, C(9)). MS: 220 (23, M^+, $C_{14}H_{20}O_2$), 177 (32), 121 (14), 107 (10), 105 (44), 95 (25), 94 (14), *93* (100), 92 (22), 91 (23), 77 (21), 43 (49), 41 (23).

1.1.2. *At −78°*. A solution of (*E*)-**7** (1.972 g, 8.5 mmol) in dry THF (120 ml) was irradiated at −78° (quartz, lamp *A* air-cooled) with stirring, employing an external dry ice/2-propanol cooling bath. The reaction was followed by ^{1}H-NMR of aliquots of the photolysis mixture. After 10 h of irradiation, the solvent was removed under light vacuum at −10°. The residue was chromatographed on SiO_2 (Et_2O/pentane 1:1) which was cooled with dry ice, and the fractions were kept cold in a basin containing dry ice. A fraction was collected which contained **20**. Another fraction was chromatographed (Et_2O/pentane 2:3) by the same procedure, and a sample was obtained which contained a 2:1 mixture of (*E*)- and (*Z*)-**21** according to ^{1}H-NMR. *1-(3′,7′,7′-Trimethyl-2′,8′-dioxabicyclo[3.2.1]oct-3′-en-1′-yl)-3-methyl-1,3-butadiene* (**20**; *ca.* 70% pure). ^{1}H-NMR (300 MHz, −50°, [D_8]THF): 0.87, 1.17 (2 *s*, 2 H_3C–C(7′)); 1.64, 1.73 (2 *s*, H_3C–C(3), H_3C–C(3′)); 2.08–2.27 (*m*, 2 H–C(6′)); 4.30–4.38 (*m*, H–C(5′)); 4.90–4.91 (*m*, H–C(4′)); 5.03 (*s*, 2 H–C(4)); 6.12 (*AB*-system, J = 16, δ_A = 5.67, δ_B = 6.57, H–C(1), H–C(2)). ^{13}C-NMR (75 MHz, −50°, [D_8]THF): 20.1, 20.3, 27.0, 32.2 (4 *q*, 4 CH_3); 53.4 (*t*, C(6′)); 119.5 (*t*, C(4)); 74.8 (*d*, C(5′)); 103.9 (*d*, C(4′)); 127.6, 135.0 (2 *d*, C(1), C(2)); 51.9 (*s*, C(7′)); 110.4 (*s*, C(1′)); 143.5 (*s*, C(3)); 51.9 (*s*, C(7′)); 110.4 (*s*, C(1′)); 143.5 (*s*, C(3)); 150.5 (*s*, C(3′)).

1-(3′-Methyloxeten-4′-yl)-2,2,6-trimethyl-4,6-heptadien-3-one ((*E*/*Z*)-**21**; (*E*/*Z*)-mixture *ca.* 3:2). UV (pentane): 263. ^{1}H-NMR (300 MHz; −30°, $CDCl_3$): signals which can be assigned to the (*E*)-isomer: 1.26, 1.29 (2 *s*, 2 H_3C–C(2)); 1.69 (*m*, $w_{1/2}$ = 2, H_3C–C(3′)); 1.94 (*s*, H_3C–C(6)); 1.82–1.91, 2.16–2.21 (2 *m*, 2 H–C(1)); 5.18 (br. *s*, H–C(4′)); 5.21 (*s*, 2 H–C(7)); 6.47 (br. *s*, H–C(2′)); 6.97 (*AB*-system, J = 15, δ_A = 6.54, δ_B = 7.39, H–C(4), H–C(5)). Signals which can be assigned to the (*Z*)-isomer: 1.26, 1.27 (2 *s*, 2 H_3C–C(2)); 1.69 (*m*, $w_{1/2}$ = 2, H_3C–C(3′)); 1.82 (*s*, H_3C–C(6)); 1.82–1.91, 2.16–2.21 (2 *m*, 2 H–C(1)); 5.21 (signal overlapping with the signal of 2 H–C(7) of the (*E*)-isomer, H–C(4′)); 5.43, 5.46 (2 *s*, 2 H–C(7)); 6.36 (*AB*-system, J = 12.9, δ_A = 6.31, δ_B = 6.41, H–C(4), H–C(5)); 6.47 (*m*, H–C(2′)). ^{13}C-NMR (75 MHz, −30°, $CDCl_3$): Signals which can be assigned to the (*E*)-isomer: 9.1 (*q*, H_3C–C(3′)); 18.4 (*q*, H_3C–C(6)); 24.0, 24.8 (2 *s*, 2 H_3C–C(2)); 41.9 (*t*, 2 H–C(1)); 126.0 (*t*, C(7)); 90.5 (*d*, C(4′)); 120.6 (*d*, C(4)); 145.5 (*d*, C(5)); 146.9 (*d*, C(2′)); 45.6 (*s*, C(2)); 122.1 (*s*, C(3′));

140.5 (*s*, C(6)); 204.0 (*s*, C(3)). Signals which can be assigned to the (*Z*)-isomer: 9.1 (*q*, H_3C–C(3′)); 20.9 (*q*, H_3C–C(6)); 24.6, 25.3 (2 *q*, 2 H_3C–C(2)); 42.1 (*t*, C(1)); 90.4 (*d*, C(4′)); 124.8 (*d*, C(4)); 141.3 (*d*, C(5)); 146.9 (*d*, C(2′)); 46.3 (*s*, C(2)); 122.1 (*s*, C(3′)); 141.3 (*s*, C(6)); 208.2 (*s*, C(3)).

1.2. *Irradiation of* (E)-**8** *at* $\lambda = 254$ *nm.* A solution of (*E*)-**8** [1] (1.490 g, 6.8 mmol) in MeCN (200 ml) was irradiated (quartz, lamp *A*, 88% conversion). Chromatography on SiO_2 (Et_2O/pentane 1:2 to 1:1) and subsequent ^{1}H-NMR analysis of the fractions gave the following product distribution: (*Z*)-**8** (1%), (*E*)-**14** (9%), (*Z*)-**14** (1%), **17A** (20%), and **17B** (2%).

1.3. *Triplet Excitation of* (E)-7. A solution of (*E*)-7 [1] (5.80 g, 26 mmol) in acetone (580 ml) was irradiated ($Pb(NO_3)_2$/KBr filter [21], lamp *B*, 98% conversion). Chromatography on SiO_2 (Et_2O/pentane 1:2) and GC and ^{1}H-NMR analysis of the fractions gave the following product distribution: (*Z*)-7 (1%), **22** (24%), **23** (5%), (*E*)-**24** (2%), (*Z*)-**24** (3%), **25** (1%), and **26** (4%). *(4*R**,5*R**,6*S**,8*S**)-4,5-Epoxy-8-isopropenyl-2,2,6-trimethyl-7-oxabicyclo[4.3.0]non-9-ene* (**22**). B.p. 90°/0.02 Torr. UV (1.630 mg in 25 ml): end absorption to 230. IR: 3080*m*, 2980*s* sh, 2970*s*, 2930*s*, 2910*s* sh, 2885*s*, 2860*s* sh, 1738*w*, 1655*m*, 1650*m* sh, 1465*m* sh, 1460*m*, 1450*s*, 1430*m*, 1383*m*, 1370*s*, 1365*m* sh, 1342*m*, 1310*m*, 1292*m*, 1280*m* sh, 1275*m*, 1242*m*, 1210*m*, 1188*w*, 1163*w*, 1145*m*, 1100*s*, 1074*m*, 1051*s*, 1038*m*, 1010*s*, 990*s*, 962*w*, 950*m*, 938*m*, 920*m*, 902*s*, 875*s*, 851*m*, 838*m*. ^{1}H-NMR: 1.12, 1.25 (2 *s*, 2 H_3C–C(2)); 1.50 (*s*, H_3C–C(6)); 1.75 (*m*, $w_{1/2} = 3$, $CH_3C{=}CH_2$); 1.90 (*m*, $w_{1/2} = 3$, 2 H–C(3)); 3.12–3.35 (*m*, H–C(4), H–C(5)); 4.82, 5.00, 5.12 (3 *m*, $w_{1/2} = 5$, $CH_3C{=}CH_2$, H–C(8)); 5.45 (*d*, $J = 2$, H–C(9)). ^{13}C-NMR (20 MHz): 18.1, 25.5, 30.8, 31.4 (4 *q*, 4 CH_3); 38.1 (*t*, C(3)); 110.7 (*t*, $CH_3C{=}CH_2$); 52.3, 58.1 (2 *d*, C(4), C(5)); 87.6 (*d*, C(8)); 121.1 (*d*, C(9)); 31.6 (*s*, C(2)); 88.1 (*s*, C(6)); 145.6, 148.5 (2 *s*, C(1), $CH_3C{=}CH_2$). MS: 220 (48, M^+, $C_{14}H_{20}O_2$), 205 (66), 191 (17), 179 (20), 164 (33), 163 (35), 149 (33), 136 (36), 135 (30), 123 (19), 122 (18), 121 (74), 119 (41), 107 (32), 105 (32), 95 (84), 93 (28), 91 (43), 79 (26), 77 (31), *69* (100), 67 (16), 65 (16), 55 (23), 53 (19), 43 (90), 41 (84).

*(4*R**,5*R**,6*S**,8*R**)-4,5-Epoxy-8-isopropenyl-2,2,6-trimethyl-7-oxabicyclo[4.3.0]non-9-ene* (**23**). B.p. 60°/0.02 Torr. IR: 3080*m*, 2980*s* sh, 2962*s*, 2925*s*, 2862*m*, 2850*m*, 1655*m*, 1465*m*, 1460*m*, 1445*m*, 1430*m*, 1383*m*, 1368*s*, 1361*m*, 1342*w*, 1308*m*, 1292*w*, 1270*m*, 1241*m*, 1212*m*, 1188*w*, 1142*m*, 1108*m* sh, 1095*s*, 1073*m*, 1051*m*, 1042*m*, 1012*s*, 990*s*, 962*w*, 950*m*, 938*w*, 920*m*, 901*s*, 874*m*, 850*m*, 838*m*. ^{1}H-NMR: 1.13, 1.21, 1.42 (3 *s*, H_3C–C(2), 2 H_3C–C(6)); 1.73 (*m*, $w_{1/2} = 3$, $CH_3C{=}CH_2$); 1.91 (*m*, $w_{1/2} = 4$, 2 H–C(5)); 3.22 (*m*, $w_{1/2} = 3.5$, H–C(3), H–C(4)); 4.86, 5.01 (2 *m*, $w_{1/3} = 5$, $CH_3C{=}CH_2$); 5.14, 5.28 (2 *s*, H–C(8), H–C(9)). MS: 220 (27, M^+, $C_{14}H_{20}O_2$), 205 (42), 195 (74), 179 (24), 177 (20), 149 (34), 137 (14), 136 (17), 135 (29), 123 (19), 122 (15), 121 (60), 119 (20), 109 (20), 107 (34), 105 (27), 95 (75), 93 (23), 91 (32), 81 (15), 79 (23), 77 (22), 69 (50), 67 (20), 55 (20), *43* (100), 41 (57).

$C_{14}H_{20}O_2$ (220.30) Calc. C 76.32 H 9.15% Found C 76.15 H 9.15%

*(E,2*R**,5*S**,6*S**)-5,6-Epoxy-2,3,3-trimethyl-2-(3′-methyl-1′,3′-butadien-1′-yl)cyclohexanone* ((E)-**24**). B.p. 90°/0.04 Torr. UV (0.2908 mg in 25 ml): 232 (19700). UV (1.619 mg in 5 ml): 311 (600), 319 (560), end absorption to 360. IR: 3092*w*, 2998*m* sh, 2978*s*, 2960*s*, 2940*s*, 2900*m* sh, 2880*m*, 2860*w* sh, 1709*s*, 1602*m*, 1464*m*, 1450*m*, 1437*m*, 1400*m*, 1395*m*, 1370*s*, 1342*m*, 1325*w*, 1312*w*, 1265*m*, 1250*m*, 1245*m* sh, 1210*w*, 1185*w*, 1135*w*, 1104*w*, 1032*m*, 1020*w*, 980*m*, 975*m*, 962*m*, 930*w*, 908*m*, 890*s*, 857*w*. ^{1}H-NMR: 0.95, 0.97, 1.20 (3 *s*, 2 H_3C–C(3), H_3C–C(2)); 1.90 (*s*, $w_{1/2} = 3$, H_3C–C(3′)); 2.06 (*AB*-system, $J = 15$, $\delta_A = 1.76$, split into *d*, $J = 5$, partly overlapping with signal at 1.90, $\delta_B = 2.37$ broadened, 2 H–C(4)); 3.41 (*AB*-system, $J = 4$, $\delta_A = 3.30$, H–C(6), $\delta_B = 3.52$, split into *d*, $J = 5$, H–C(5)); 4.95 (*m*, $w_{1/2} = 3.6$, 2 H–C(4′)); 6.10 (*s*, H–C(1′), H–C(2′)). MS: 220 (32, M^+, $C_{14}H_{20}O_2$), 123 (25), *122* (100), 121 (28), 107 (39), 105 (15), 98 (25), 95 (21), 94 (43), 93 (25), 91 (19), 79 (34), 77 (16), 69 (10), 67 (11), 55 (12), 41 (25), 39 (10).

$C_{14}H_{20}O_2$ (220.30) Calc. C 76.32 H 9.15% Found C 76.23 H 9.20%

*(Z,2*R**,5*S**,6*S**)-5,6-Epoxy-2,3,3-trimethyl-2-(3′-methyl-1′,3′-butadien-1′-yl)cyclohexanone* ((Z)-**24**; contamined with *ca.* 15% of (*E*)-**24**): B.p. 85°/0.02 Torr. IR: 3084*w*, 3010*m* sh, 2995*s* sh, 2980*s*, 2965*s*, 2940*s*, 2920*m*, 2880*m*, 2850*w* sh, 1703*s*, 1630*w*, 1465*m*, 1450*m*, 1438*m*, 1400*m*, 1395*m*, 1370*s*, 1340*m*, 1252*m*, 1240*m*, 1028*m*, 902*m*. ^{1}H-NMR: 0.85, 0.98, 1.15 (3 *s*, 2 H_3C–C(3), H_3C–C(2)); 1.76 (*m*, $w_{1/2} = 3$, H_3C–C(3′)); 2.01 (*AB*-system, $J = 15$, $\delta_A = 1.68$, split into *d*, $J = 5.5$, $\delta_B = 2.35$, broadened, 2 H–C(4)); 3.38 (*AB*-system, $J = 4$, $\delta_A = 3.32$, H–C(6), $\delta_B = 3.45$, split into *d*, $J = 5.5$, H–C(5)); 4.67, 4.86 (2 *m*, $w_{1/2} = 4$, 2 H–C(4′)); 5.72 (*AB*-system, $J = 12$, $\delta_A = 5.62$, $\delta_B = 5.83$, broadened, H–C(1′), H–C(2′)). MS: 220 (23, M^+, $C_{14}H_{20}O_2$), 205 (14), 136 (15), 135 (16), 123 (42), *122* (100),

121 (40), 107 (57), 105 (26), 98 (30), 95 (29), 94 (55), 93 (39), 91 (36), 79 (57), 77 (30), 69 (21), 67 (19), 55 (21), 43 (35), 41 (53).

$C_{14}H_{20}O_2$ (220.30) Calc. C 76.32 H 9.15% Found C 76.23 H 9.03%

9-Isopropenyl-7,7,8-trimethyl-4-oxatricyclo[6.1.0.0^{3,5}]nonan-2-one (**25**). B.p. 110°/0.03 Torr. UV (0.8742 mg in 2 ml): 292 (95), end absorption to 390. IR: 3080*w*, 2990*m* sh, 2970*s*, 2940*m*, 2915*m*, 2895*m*, 1730*m* sh, 1708*s*, 1642*w*, 1459*m*, 1451*m*, 1435*w*, 1407*w*, 1382*m*, 1370*m*, 1350*w*, 1328*w*, 1296*w*, 1244*w*, 1217*w*, 1175*w*, 1161*w*, 1146*m*, 1095*w*, 1076*w*, 975*w*, 905*m*, 895*s*, 873*w*. ^{1}H-NMR: 0.82, 0.98, 1.15 (3 *s*, 2 H_3C–C(7), H_3C–C(8)); 1.81 (*s*, $w_{1/2}$ = 4, 3 H–C(3′)); 2.00–2.40 (*m*, 2 H–C(6)); 2.57 (*AB*-system, J = 10, δ_A = 2.30, broadened, H–C(9), δ_B = 2.85, H–C(1)); 3.07–3.31 (*m*, H–C(3), H–C(5)); 4.84 (*m*, $w_{1/2}$ = 4, 2 H–C(1′)). MS: 220 (20, M^+, $C_{14}H_{20}O_2$), 192 (22), 177 (63), 149 (15), 136 (33), 135 (20), 125 (21), 123 (18), 122 (61), 121 (78), 119 (21), 109 (21), 108 (20), 107 (53), 105 (41), 98 (16), 95 (35), 94 (80), 93 (76), 91 (64), 81 (20), 79 (89), 77 (61), 69 (22), 68 (15), 67 (32), 65 (23), 55 (39), 53 (40), 51 (20), 43 (27), *41* (100).

$C_{14}H_{20}O_2$ (220.30) Calc. C 76.32 H 9.15% Found C 76.40 H 9.22%

2-((Z)-3′-Methyl-1′,3′-butadien-1′-yl)-2,3,3-trimethyl-6-oxabicyclo[3.2.0]heptan-7-one (**26**). B.p. 80°/0.02 Torr. UV (0.314 mg in 5 ml): 217 (1400). UV (1.915 mg in 2 ml): absorption to 380. IR: 3082*w*, 2965*m*, 2940*m*, 2870*m*, 1830*s*, 1755*w*, 1705*w*, 1625*w*, 1460*m*, 1448*m*, 1435*m* sh, 1390*m*, 1375*m*, 1325*m*, 1310*m*, 1280*m*, 1230*m*, 1178*m*, 1160*m*, 1128*m*, 1100*m*, 1090*m* sh, 1065*w* sh, 1020*m*, 1005*m*, 962*w*, 939*w*, 917*m*, 892*m*, 880*w*, 840*m*. ^{1}H-NMR (300 MHz): 1.02, 1.08, 1.18 (3 *s*, H_3C–C(2), 2 H_3C–C(3)); 1.89 (*m*, $w_{1/2}$ = 3, H_3C–C(3′)); 1.99 (*AB*-system, J = 15.5, δ_A = 1.89, split into *d*, J = 5.1, δ_B = 2.10, 2 H–C(4)); 4.08 (*d*, J = 4.4, H–C(1)); 4.91 (*d*×*d*, J = 4.4, 5.1, H–C(5)); 4.90–4.96 (*m*, 2 H–C(4′)); 5.74 (*AB*-system, J = 12.8, δ_A = 5.53, δ_B = 5.94, broadened, H–C(1′), H–C(2′)). ^{13}C-NMR (20 MHz): 23.6, 25.1, 25.2, 27.9 (4 *q*, 4 CH_3); 42.9 (*t*, C(4)); 113.7 (*t*, C(4′)); 65.9 (*d*, C(1)); 76.7 (*d*, C(5)); 128.4, 133.4 (2 *d*, C(1′), C(2′)); 44.9, 51.3 (2 *s*, C(2), C(3)); 144.3 (*s*, C(3′)); 170.9 (*s*, C(7)). MS: 220 (10, M^+, $C_{14}H_{20}O_2$), 176 (11), 161 (33), 159 (11), 137 (16), 136 (32), 135 (47), 133 (39), 125 (11), 122 (10), 121 (36), 120 (26), 119 (37), 109 (28), 108 (49), *107* (100), 106 (24), 105 (61), 95 (29), 94 (29), 93 (73), 92 (12), 91 (70), 81 (11), 79 (34), 77 (29), 69 (21), 67 (16), 65 (16), 57 (13), 55 (30), 53 (16), 43 (25), 41 (50).

1.4. *Triplet Excitation of (E/Z)-***24**. A solution of (*E*)- and (*Z*)-**24** (18 mg, 0.08 mmol, ratio 3:2) in acetone (5 ml) was irradiated ($Pb(NO_3)_2$/KBr filter [21], lamp *B*) with nonadecane as an internal standard, and the reaction was periodically checked by capillary GC. After 97% conversion of (*E*/*Z*)-**24**, GC analysis showed **25** (9%) and **26** (9%) as the only volatile products.

1.5. *Triplet Excitation of* **37**. A solution of **37** (35 mg, 0.159 mmol) in acetone (5 ml) was irradiated ($Pb(NO_3)_2$/KBr filter [21], lamp *B*), and the reaction was followed by capillary GC. The formation of compound **41** could not be observed.

2. Additional Experiments. – 2.1. *Acid-catalyzed Isomerization of* **12B** *to* **12A**. A solution of **12B** (13 mg, 0.06 mmol) in H_2O (1 ml)/THF (5 ml)/acetone (0.5 ml) was stirred with oxalic acid (10 mg) for 2 days. Workup of the mixture yielded pure **12A** according to ^{1}H-NMR.

2.2. *Hydrolysis of* **13**. A solution of **13** (32 mg, 0.14 mmol) in THF (10 ml) was stirred with H_2O (5 ml) and oxalic acid (10 mg) for 3 h. Workup and subsequent chromatography (SiO_2, Et_2O/pentane 1:3 to 1:1) yielded 20 mg of a product, which consisted according to ^{1}H-NMR of an equilibrium mixture **27**/**28**.

2.3. *Acetylation of the equilibrium mixture* **27**/**28**. A solution of **27**/**28** (23 mg, 0.10 mmol) was stirred with pyridine (5 ml) and Ac_2O (0.2 ml, 1.96 mmol) for 12 h. Workup and chromatography (SiO_2, Et_2O/pentane 1:1) yielded *3,7-dioxo-6,6,10-trimethyl-8,10-undecadien-4-yl acetate* (**29**; 25 mg, 89%). UV (0.241 mg in 25 ml of EtOH): 270 (18500). UV (1.332 mg in 2 ml of EtOH): end absorption to 390. IR: 3085*w*, 3060*s*, 2970*m*, 2940*m*, 2880*w*, 1820*w*, 1747*s*, 1735*s*, 1685*s*, 1613*m*, 1592*s*, 1469*m*, 1458*m*, 1450*m*, 1437*m*, 1410*w*, 1389*m*, 1370*s*, 1320*m*, 1270*m* sh, 1260*m* sh, 1255*m*, 1230*s*, 1072*s*, 1045*m*, 1022*m*, 978*m*, 940*w*, 905*m*, 855*w*. ^{1}H-NMR (300 MHz): 1.06 (*t*, J = 7.3, 3 H–C(1)); 1.20, 1.23 (2 *s*, 2 H_3C–C(6)); 1.92 (*m*, $w_{1/2}$ = 3, H_3C–C(10)); 1.99 (*s*, CH_3COO); 2.01–2.05 (*m*, 2 H–C(5)); 2.49–2.55 (*m*, 2 H–C(2)); 5.18 (*d*×*d*, J = 8, 4.5, H–C(4)); 5.40, 5.42 (2 *m*, $w_{1/2}$ = 4, 2 H–C(11)); 6.92 (*AB*-system, J = 15.5, δ_A = 6.49, δ_B = 7.36, H–C(8), H–C(9)). MS: 280 (1, M^+, $C_{16}H_{24}O_4$), 224 (10), 223 (11), 181 (31), 138 (14), 125 (66), 123 (13), 97 (25), 96 (15), *95* (100), 93 (10), 85 (11), 67 (39), 57 (38), 55 (17), 43 (72), 41 (38).

2.4. *Photooxygenation of* (E)-**14**. A solution of (*E*)-**14** (60 mg, 0.27 mmol) in CH_2Cl_2 (15 ml) was photooxygenated by bubbling O_2 through the solution and by irradiation with visible light with *Sensitox* as photosensitizer. After 12 h, the product was chromatographed (SiO_2, Et_2O/pentane 1:1 to 2:1) to yield *(E)-6-methyl-6-(1'-methyl-2',3',5'-trioxabicyclo[2.2.2]oct-7'-en-4'-yl)-3-hepten-2-one* (**30**; 35 mg, 51%). UV (0.445 mg in 25 ml): 219 (12900). UV (1.601 mg in 2 ml): 323 (33), end absorption to 380. IR: 3055*w*, 3040*w*, 2970*m*, 2932*m*, 2870*m*, 1692*m*, 1670*s*, 1622*s*, 1458*m*, 1442*m*, 1425*m* sh, 1388*m* sh, 1379*s*, 1365*m* sh, 1355*s*, 1250*s*, 1225*m*, 1212*w*, 1180*m*, 1137*s*, 1100*m*, 1061*s*, 1021*m*, 980*s*, 940*s*, 906*s*, 881*m*, 870*m*. ^{1}H-NMR: 1.07 (*s*, 3 H–C(7), H_3C–C(6)); 1.35 (*s*, H_3C–C(1')); 2.24 (*s*, 3 H–C(1)); 2.41 (*d*, J=8, 2 H–C(5)); 3.72 (*AB*-system, J=9, δ_A=3.43, δ_B=4.10, 2 H–C(6')); 6.52 (*AB*-system, J=16, δ_A=6.20. broadened, H–C(3), δ_B=6.85, split into *t*, J=8, H–C(4)); 6.55 (*AB*-system, J=8, δ_A=6,42, δ_B=6,68, H–C(7'), H–C(8')). MS: 177 (12, $M^+ - O_2 - COCH_3$); 135 (19), 125 (54), 123 (13), 109 (15), 107 (15), 99 (10), 98 (14), 95 (29), 86 (34), 84 (54), 83 (17), 82 (10), 81 (12), 71 (12), 69 (12), 55 (21), 47 (10), *43* (100), 41 (23).

2.5. *Oxidation of* **16** *to* **31**. A solution of a mixture (407 mg) which contained, according to ^{1}H-NMR, the pyrans **16** (*ca.* 30%), **15** (*ca.* 30%) and (*Z*)-**14** (*ca.* 30%) in MeOH (30 ml) was stirred with NaCN (500 mg), MnO_2 (2.6 g) and HOAc (150 µl) for 5 h. Filtration over *Celite*, workup and chromatography (SiO_2, Et_2O/pentane 1:3) yielded a fraction which contained *methyl 2,5-dimethyl-5-(3'-methyl-2'H-pyran-6'-yl)-2-hexenoate* (**31**; 93 mg). UV (0.370 mg in 25 ml): 215 (11600), 282 (3650). UV (1.110 mg in 2 ml): end absorption to 380. IR: 3090*w*, 3040*w*, 2960*s*, 2950*s*, 2920*m*, 2910*m* sh, 2870*m*, 2850*m*, 2810*m*, 2740*w*, 1720*s* sh, 1710*s*, 1662*w*, 1648*m*, 1610*m*, 1460*m* sh, 1435*m* sh, 1432*m*, 1382*m*, 1360*m*, 1350*m*, 1302*m*, 1270*s* sh, 1255*s*, 1198*m* sh, 1190*m*, 1150*m*, 1112*s* sh, 1100*s*, 1082*m*, 1055*m*, 1035*w*, 1020*w* sh, 989*w*, 950*w*, 935*w*, 907*s*. ^{1}H-NMR: 1.10 (*s*, 3 H–C(6), H_3C–C(5)); 1.68, 1.83 (2 *m*, $w_{1/2}$=4, H_3C–C(2), H_3C–C(3')); 2.28 (*d*, J=7.5, 2 H–C(4)); 3.72 (*s*, CH_3O); 4.40 (*m*, $w_{1/2}$=3.6, 2 H–C(2')); 5.31 (*AB*-system, J=5.5, δ_A=5.03, H–C(5'), δ_B=5.59, split into *m*, H–C(4')); 6.75 (*t*, J=7.5, split into *m*, H–C(3)). MS: 250 (13, M^+, $C_{15}H_{22}O_3$), 138 (12), *137* (100), 136 (45), 123 (88), 121 (14), 119 (13), 118 (22), 117 (23), 109 (31), 107 (39), 96 (14), 95 (78), 93 (18), 91 (24), 81 (17), 79 (20), 77 (23), 67 (61), 65 (16), 59 (20), 55 (33), 53 (28), 43 (97), 41 (79), 39 (44).

2.6. *Isomerization of* **17A** *to* **17B**. A mixture (54 mg) which contained according to ^{1}H-NMR analysis **17A** (70%) and **12A** (30%) was stirred in Et_2O (10 ml) with NaOMe (10 mg) for 5 days. Chromatography (SiO_2, dimethoxyethane/pentane 1:10) of the mixture yielded unchanged **12A** (7 mg) and **17B** (27 mg, 71%).

2.7. *Hydrolysis of* **19**. A solution of **19** (38 mg, 0.17 mmol) in THF (10 ml) was stirred with H_2O (1 ml) and oxalic acid (10 mg) for 12 h. Workup yielded *5-(1''-hydroxy-2''-methyl-2''-propen-1''-yl)-2,2-dimethyl-4-(2'-oxopropyl)cyclopentanone* (**32**; 31 mg, 77%), m.p. 68–70°. UV (1.687 mg in 2 ml of EtOH): 293 (68). IR: 3620*w*, 3500*w* br., 3090*w*, 2960*s*, 2928*m*, 2862*m*, 1735*s*, 1715*s*, 1648*w*, 1415*m*, 1405*m*, 1380*m*, 1368*m*, 1298*w*, 1265*w*, 1240*m* sh, 1230*m*, 1192*w*, 1255*m*, 1125*m*, 1108*m*, 1071*m*, 1048*m*, 990*w*, 930*w*, 903*m*. ^{1}H-NMR: 1.03, 1.08 (2 *s*, 2 H_3C–C(2)); 1.73 (*m*, $w_{1/2}$=4, H_3C–C(2'')); 2.12 (*s*, 3 H–C(3')); 1.77–3.00 (*m*, H–C(5), H–C(4), 2 H–C(3), 2 H–C(1'), OH); 4.52 (*m*, $w_{1/2}$=10, H–C(1'')); 4.94, 5.14 (2 *m*, $w_{1/2}$=4, 2 H–C(3'')). MS: 220 (10, $M^+ - H_2O$), 168 (18), 153 (11), 111 (47), 93 (10), 83 (21), 82 (20), 70 (26), 56 (18), 55 (13), *43* (100), 41 (54).

$C_{14}H_{22}O_3$ (238.32) Calc. C 70.56 H 9.30% Found C 70.15 H 9.15%

2.8. Wittig *Olefination of* (E)-**35**. To a solution of (*E*)-**35** (159 mg, 5.2 mmol) in dry Et_2O (20 ml) was added a *ca.* 0.2 M etheral solution of methylidenetriphenylphosphorane. Chromatography (SiO_2, Et_2O/pentane 1:2) of the mixture yielded (*E*)-**24** (16 mg, 18%), (*E*)-**35** (70 mg), and (*E*)-**36** (26 mg, 29%)[5]. *(E,1'R*,3'S*,4'S*)-4-(3',4'-Epoxy-1',6',6'-trimethyl-2'-methylidene-1'-cyclohexyl)-3-buten-2-one* (**36**). B.p. 90°/0.02 Torr. UV (0.065 mg in 5 ml): 220 (14900). UV (1.358 mg in 2 ml): 326 (44), end absorption to 380. IR: 3095*w*, 3085*w*, 2975*s*, 2930*m*, 2880*w*, 1696*m*, 1675*s*, 1618*s*, 1466*m*, 1450*m*, 1425*m*, 1391*s*, 1369*s*, 1355*s*, 1341*w*, 1324*m*, 1302*w*, 1280*m*, 1253*s*, 1220*w*, 1180*m*, 1165*w*, 1145*w*, 1120*w*, 1105*w*, 1050*w*, 1015*w*, 995*m*, 970*m*, 915*s* sh, 910*s*, 888*w*. ^{1}H-NMR: 0.90, 0.95, 1.21 (3 *s*, H_3C–C(1'), 2 H_3C–C(6')); 1.91 (*AB*-system, J=16, δ_A=1.74, split into *d*, J=4, δ_B=2.07, broadened, 2 H–C(5')); 2.28 (*s*, 3 H–C(1)); 3.32–3.50 (*m*, H–C(4')); 3.59 (*d*, J=4, H–C(3')); 5.27, 5.51 (2 *s*, H_2C=C(2')); 6.63 (*AB*-system, J=16, δ_A=6.01, δ_B=7.25, H–C(3), H–C(4)). MS: 220 (2, M^+, $C_{14}H_{20}O_2$), *122* (100), 107 (18), 43 (35).

$C_{14}H_{20}O_2$ (220.30) Calc. C 76.32 H 9.15% Found C 76.30 H 9.18%

2.9. *Hydrogenation of* (E/Z)-**24**. A solution of (*E*)-**24** (20%) and (*Z*)-**24** (80%) (76 mg, 0.34 mmol) in EtOH (10 ml) was stirred with 10% Pd/C under H_2 for 3 h. Filtration and chromatography (SiO_2, Et_2O/pentane 1:3) afforded pure *(2R*,5S*,6S*)-5,6-epoxy-2,3,3-trimethyl-2-(3'-methyl-1'-butyl)cyclohexanone* (**37**; 60 mg, 79%), b.p. 75°/0.02 Torr. UV (1.855 mg in 2 ml): 307 (40), end absorption to 380. IR: 2980*s*, 2958*s*, 2930*s*, 2870*s*, 1700*s*, 1462*m*, 1455*m*, 1435*w*, 1398*m*, 1395*m*, 1383*m*, 1362*m*, 1358*m*, 1345*m*, 1322*w*, 1280*w*, 1265*w*, 1240*w*, 1215*w*, 1168*w*, 1158*w*, 1125*m*, 1110*w* sh, 1095*w*, 1030*m*, 1020*w* sh, 981*w*, 955*w*, 915*w*, 900*w*, 879*w*. ^{1}H-NMR: 0.75–1.10 (*m*, 2 H_3C–C(3), H_3C–C(2), 3 H–C(4'), H_3C–C(3')); 0.75–2.30 (*m*, 2 H–C(1'), 2 H–C(2'), H–C(3')); 2.04 (*AB*-system, $J = 16$, $\delta_A = 1.66$, split into *d*, $J = 5$, $\delta_B = 2.42$, broadened, 2 H–C(4)); 3.35 (*AB*-system, $J = 4$, $\delta_A = 3.21$, H–C(6), $\delta_B = 3.49$, split into *d*, $J = 5$, H–C(5)). ^{13}C-NMR: 15.5, 22.5, 23.9, 26.0 (5 *q*, 2 at 22.5, 5 CH_3); 31.6, 34.0, 35.9 (3 *t*, C(4), C(1'), C(2')); 28.7 (*d*, C(3')); 54.9, 56.0 (2 *d*, C(5), C(6)); 42.5, 53.3 (2 *s*, C(2), C(3)); 210.9 (*s*, C(1)). MS: 224 (< 1, M^+, $C_{14}H_{24}O_2$), 154 (58), 139 (35), 111 (11), 109 (11), *98* (100), 97 (14), 95 (10), 84 (19), 83 (35), 69 (41), 57 (19), 56 (14), 54 (35), 43 (24), 41 (44).

$C_{14}H_{24}O_2$ (224.33) Calc. C 74.95 H 10.78% Found C 74.99 H 10.65%

Hydrogenation of **26**. A solution of **26** (8 mg, 0.036 mmol) in Et_2O (3 ml) was stirred with 10% Pd/C under H_2 for 5 h. Filtration over *Celite* and removal of the solvent yielded *2-(3'-methyl-1'-butyl)-2,3,3-trimethyl-6-oxabicyclo[3.2.0]heptan-7-one* (**41**; 7.7 mg, 96%). IR: 2960*s*, 2930*m*, 2870*m*, 1832*s*, 1818*s*, 1700*w*, 1468*m*, 1430*w* sh, 1392*w*, 1385*w* sh, 1378*m*, 1368*m*, 1325*w*, 1310*w*, 1285*w*, 1240*w*, 1200*w*, 1180*w*, 1170*w* sh, 1130*m*, 1098*m*, 1021*w*, 1010*m*, 1005*m*, 958*w*, 950*w* sh, 945*w* sh, 918*w*, 906*w*, 870*w*. ^{1}H-NMR (300 MHz): 0.85, 0.97, 1.14 (3 *s*, H_3C–C(2), 2 H_3C–C(3)); 0.91, 0.94 (2 *d*, $J = 6.6$, H_3C–C(3'), 3 H–C(4')); 1.19–1.74 (*m*, 2 H–C(1'), 2 H–C(2'), H–C(3')); 2.01 (*AB*-system, $J = 15.7$, $\delta_A = 1.92$, split into *d*, $J = 4.9$, $\delta_B = 2.10$, 2 H–C(4)); 3.56 (*d*, $J = 4.4$, H–C(1)); 4.88 (*d*×*d*, $J = 4.4$, 4.9, H–C(5)). MS: 180 (3, $M^+ - 44$), 165 (10), 139 (31), 110 (11), *109* (100), 96 (15), 95 (18), 81 (26), 69 (23), 67 (13), 55 (17), 43 (14), 41 (21).

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