92. Photochemical Reactions

136th Communication[1])

Photochemistry of Conjugated Epoxyenones and Dienes of the Ionone Series: Influence of a Neighboring Spiro-oxirane Function

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Summary

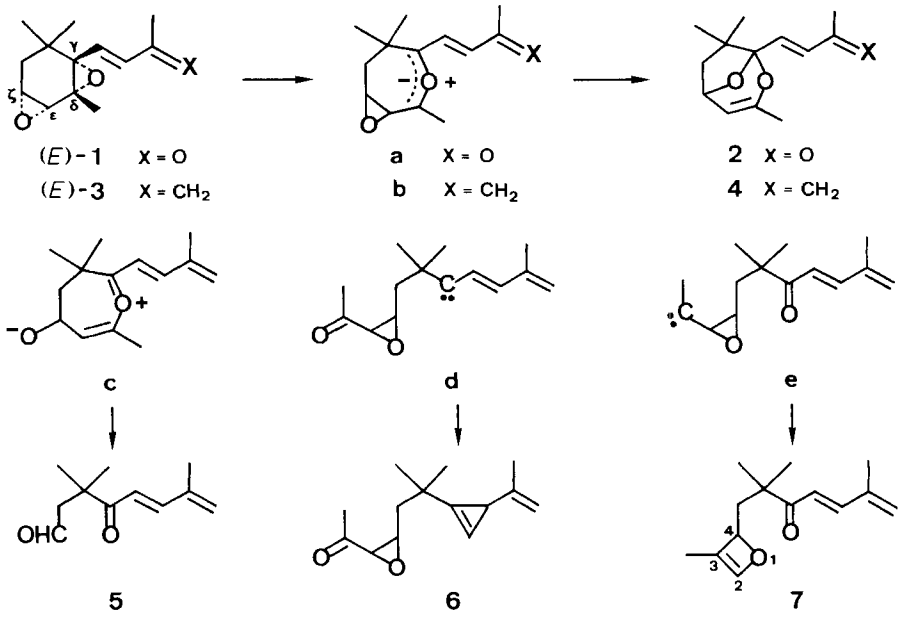
The preparation and photolyses of the diepoxyenones (*E*)-**8** and (*E*)-**9** as well as the diepoxydiene (*E*)-**10** are described. On $^1\pi,\pi^*$-excitation (λ = 254 nm), the diastereoisomeric diepoxyenones (*E*)-**8** and (*E*)-**9** undergo isomerization *via* the ylide intermediate **f** and the carbene intermediate **g** leading to the primary photoproducts **17A** and **18–21** *(Scheme 8)*. On $^1n,\pi^*$-excitation ($\lambda > 347$ nm), (*E*)-**8** shows behaviour typical of epoxyenones undergoing C(γ),O-bond cleavage of the oxirane and isomerization to compounds **22**, (*E*/*Z*)-**23** and (*E*)-**24** *(Scheme 10)*. On singlet excitation, the diepoxydiene (*E*)-**10** is cleaved to the carbonyl ylide **j** and the carbenes **l** and **m** *(Scheme 11)*. The carbonyl ylide **j** fragments *via* the dipolar intermediate **k** to the acetylenic dienone (*E*)-**31**. The carbene **l**, showing behaviour typical of vinyl carbenes, furnishes the cyclopropene **30**. The alternative carbene **m**, however, undergoes an insertion reaction into the neighboring oxirane C,C-bond leading to the proposed but not isolated oxetene **43**, which is further transformed to the products **33A** + **B** by an intramolecular cycloaddition.

1. Introduction. It has been shown that the diepoxyenone (*E*)-**1** on $^1\pi,\pi^*$-excitation (λ = 254 nm) is cleaved to the ylide intermediate **a,** which undergoes subsequent 1,4-O migration leading to the dioxabicyclooctene **2** as the major photoproduct [2] (see *Scheme 1*). Singlet excitation of the corresponding diene (*E*)-**3** induces the analogous reaction sequence ((*E*)-**3**→**b**→**4**). However, to a larger extent (*E*)-**3** undergoes transformations *via* the dipolar intermediate **c** and the carbene intermediates **d** and **e** leading to compounds **5–7** [3] (see *Scheme 1*).

In the present investigation, the photolyses of the diepoxyenones (*E*)-**8** and (*E*)-**9** and the diepoxydiene (*E*)-**10** (see *Scheme 2*) were studied. Of particular interest was the

[1]) 135th Communication, see [1].

Scheme 1



influence of the spiro-oxirane function on the reaction of ylide intermediates, since a rearrangement analogous to **a**→**2** seemed unlikely due to the formation of a highly strained product.

2. Preparation of the Diepoxides (*E*)-8, (*E*)-9, (*E*)-10 and (*E*)-11. The diepoxyenones (*E*)-**8** and (*E*)-**9** were synthesized from the epoxyenones (*E*)-**12** [4] and (*E*)-**13** [5]. Epoxidation of (*E*)-**12** with *m*-chloroperbenzoic acid produced both diastereoisomers (*E*)-**8** and (*E*)-**9** in 21% yield each, whereas reaction of (*E*)-**13** with (dodecyl-

Scheme 2

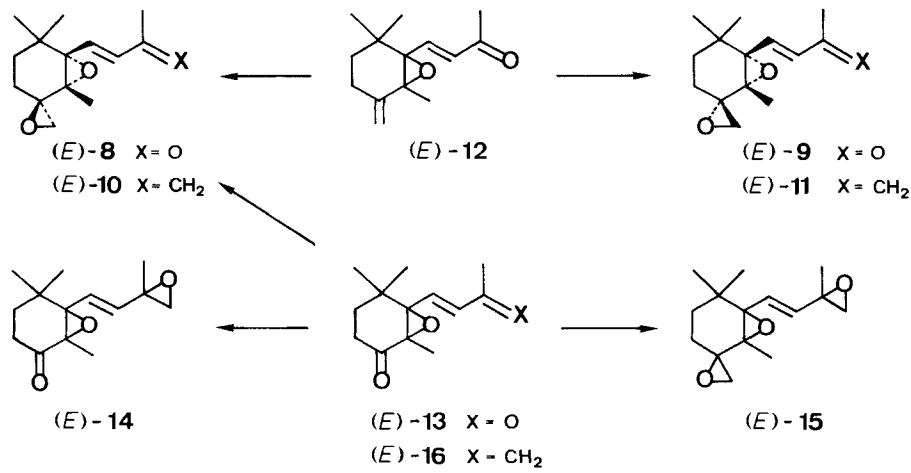


Table. *Results of the Photolyses of* (E)-**8** *and* (E)-**9**[a])

Substrate	λ [nm]	Solvent	Conversion [%]	Product Distribution [%][b])																
				(Z)-**8**[c])	(E)-**9**	**17A**	**18**[d])	**19**	**20**	**21**	**22**[e])	(E)-**23**	(Z)-**23**	(E)-**24**	**25A**	**26**	**27**	**28**	**29**	Unknown Products
(E)-**8**	254	MeCN	95	14	2	*ca.* 1	4	1	10	9	–	5	–	–	2	1	–	2	–	2
(E)-**8**	254	pentane	91	15	9	–	1	–	12	15	–	*ca.* 1	–	–	1	1	–	4	–	4
(E)-**8**	254	Et_2O	74	8	19	–	–	–	12	13	–	2	–	–	–	–	–	28	–	3
(E)-**8**	254	Et_2O[f])	81	29	2	*ca.* 1	5	1	5	4	–	–	–	–	–	2	–	2	–	5
(E)-**8**	> 347	MeCN	83	–	–	–	–	–	–	–	–	17	21	2	–	–	5	5	3	2
(E)-**9**	254	MeCN	92	–	–	*ca.* 1	–	2	5	5	–	–	–	–	3	3	–	2	–	–

[a]) At r.t., unless otherwise stated.

[b]) Based on converted starting material.

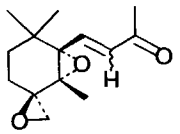
[c]) The epoxyenone (Z)-**8** could not be isolated in pure form, since on rechromatography it rearranged to the furan **28**. The ^{1}H-NMR spectrum of mixed fractions containing (Z)-**8** showed an *AB*-system at 6.13 ppm (J = 12 Hz; δ_A = 5.98 ppm, δ_B = 6.29 ppm).

[d]) Compound **18** could only be isolated in a 3:7 mixture with (E)-**8**; it was identified in the ^{1}H-NMR spectrum on the basis of the characteristic signals [4] at 4.17 and 5.10 ppm.

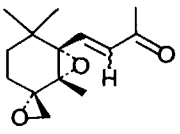
[e]) The dihydrofuran **22** could not be isolated; presumably it was oxidized to the lactone **29**.

[f]) At −60°.

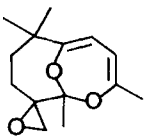
methylsulfonio)methanide [6] led to only one diastereoisomer ((*E*)-**8**) in 40% yield along with a mixture of presumably the alternative diepoxide (*E*)-**14** and the triepoxide (*E*)-**15** in varying ratios (39% combined yield). Toluene was found to be the solvent of choice in this reaction producing the highest yield of (*E*)-**8**. *Wittig* reaction of (*E*)-**8** and (*E*)-**9** gave the corresponding diepoxydienes (*E*)-**10** and (*E*)-**11** in 93 and 77% yield, respectively. Compound (*E*)-**10** was also obtained by reaction of the epoxyketone (*E*)-**16** [7] with (dodecylmethylsulfonio)methanide in 90% yield.



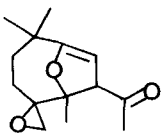
(*E*/*Z*)-**8**



(*E*/*Z*)-**9**



17A+B



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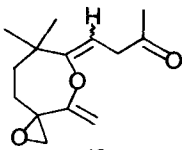

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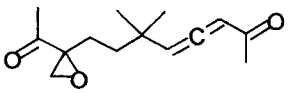

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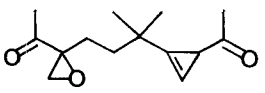

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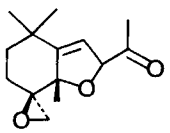

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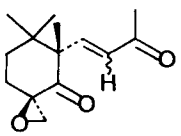
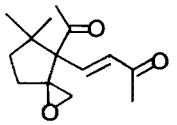
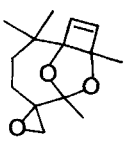


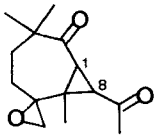
(*E*/*Z*)-**23**



(*E*)-**24**



25 A+B



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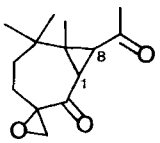

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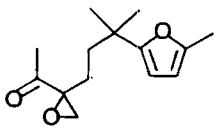

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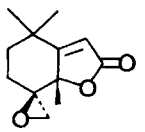

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3. Photolyses. 3.1. *Irradiation of* (E)-*8 and* (E)-*9*. The products obtained are shown below and the results of the photolyses are summarized in the *Table*.

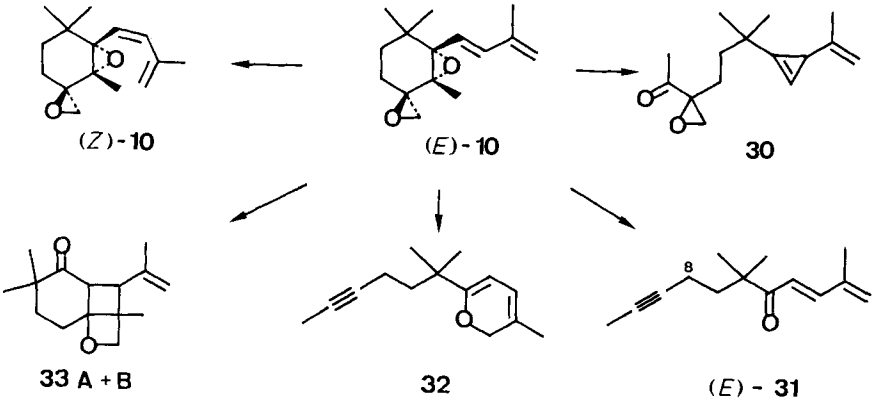
3.2. *Photolyses of* **17A** *and* **17B**. Irradiation (λ = 254 nm) of *ca.* 0.05M MeCN solutions of **17A** and **17B** produced **25A** and **25B** in 42 and 26% yield, respectively.

3.3. *Photolysis of* (E)-**23**. Irradiation ($\lambda > 280$ nm) of a *ca.* 0.4M CD_3CN solution of (*E*)-**23** gave (*Z*)-**23** and **27** in 20 and 9% yield[2]) (89% conversion), respectively.

3.4. *Singlet Excitation of* (E)-**10**. 3.4.1. *In MeCN at room temperature*. Photolysis of a *ca.* 0.04M solution of (*E*)-**10** in MeCN (λ = 254 nm, 72% conversion) gave[2]) (*Z*)-**10** (7%), **30** (25%), (*E*)-**31** (4%), **32** (3%), **33A** (5%), and **33B** (3%) (*Scheme 3*).

[2]) Based on converted starting material.

Scheme 3

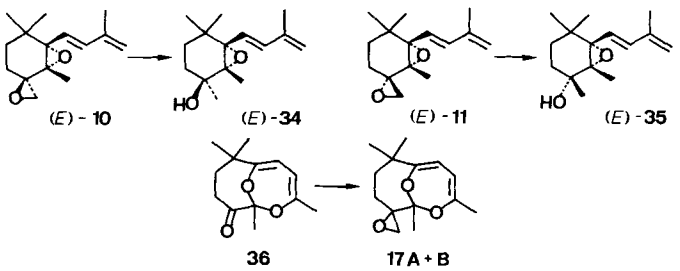


3.4.2. *In Et_2O at −60°.* Photolysis of a *ca.* 0.02M solution of (*E*)-**10** in Et_2O (λ = 254 nm, 73% conversion) gave[2]) (*Z*)-**10** (6%), **30** (17%), (*E*)-**31** (17%), and **33A** (4%).

4. Structure of the Compounds. As analogs of most of the products obtained here were already described in previous publications from our laboratory, only the most relevant spectral data are discussed herein: full data and assignment of the NMR signals are presented in the *Exper. Part.*

Diepoxyenones (E)-**8** *and* (E)-**9** (see *Scheme 2*). Their structures are evidenced by the spectral data. In particular, the ^{1}H-NMR spectrum shows an *AB*-system (*J* = 5 Hz) centered at 2.59 ppm for (*E*)-**8** and at 2.62 ppm for (*E*)-**9** for the spiro-oxirane CH_2-group, which is also evidenced in the ^{13}C-NMR by a *t* at 52.0 and 51.5 ppm for (*E*)-**8** and (*E*)-**9**, respectively. The configuration of (*E*)-**8** and (*E*)-**9** was proven by reaction of the corresponding epoxydienes (*E*)-**10** and (*E*)-**11** with $LiEt_3BH$ [8] leading to the known hydroxy compounds (*E*)-**34** and (*E*)-**35**, respectively (see *Scheme 4*) [9].

Scheme 4



Tricyclic Acetal **17A**. The reaction of the analogous acetal **36** (obtained on photolysis of (*E*)-**13**, $\lambda > 347$ nm) [5] with (dodecylmethylsulfonio)methanide [6] gave in moderate yields the product **17A** (9%) together with the diastereoisomer **17B** (18%). The structures of **17A** + **B** follow conclusively by comparison of their spectral data (see *Exper. Part*) with that of **36**. The configuration, however, could not be assigned (see also *Chap. 5*).

Dihydrofuran **18**. This compound could not be isolated in pure form. Evidence for its structure stems only from the ^{1}H-NMR spectrum of a 3:7 mixture of **18** and (*E*)-**8** showing two broad *s* at 4.17 and 5.10 ppm, which are characteristic for the H-atom in *α*-position to the carbonyl group and the enol ether H-atom [4].

Divinyl Ether **19**. The *s* and the *t* at 56.8 and 54.8 ppm, respectively, in the ^{13}C-NMR spectrum and the *AB*-system at 2.60 ppm (*J* = 5 Hz) in the ^{1}H-NMR spectrum indicate that the spiro-oxirane moiety is intact. The methylidene group is evidenced by a *s* and a *t* at 160 and 88 ppm, respectively, in the ^{13}C-NMR spectrum and by signals at 4.34 and 4.43 ppm in the ^{1}H-NMR spectrum. Finally, an IR band at 1720 cm^{-1} and a *s* (2.10 ppm), a *d* (3.17 ppm, *J* = 7 Hz), and a *t* (5.27 ppm, *J* = 7 Hz) in the ^{1}H-NMR spectrum are characteristic of the keto side chain.

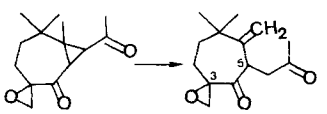
Compounds **20**, **21**, *(*E/Z*)*-**23**, *(*E*)*-**24**, **28**, *and* **29**. The NMR spectra indicate that the oxirane moiety is intact in these compounds and has spectral characteristics similar to those described for the aforementioned compounds. The structures become fully evident after comparison of the spectral data with those of the corresponding compounds obtained on photolysis of 5,6-epoxy-5,6-dihydro-β-ionone [10].

Tetracyclic Acetals **25A** + **B**. The structures of **25A** + **B**, which are photoproducts of the tricyclic acetals **17A** + **B**, are evidenced by comparison of the spectra with those of the corresponding compound bearing a methylidene group in place of the spiro-oxirane function [11]. Instead of the methylidene signals in the NMR spectra, **25A** and **25B** show for the oxirane moiety an *AB*-system (J = 5 Hz) centred at 2.71 and 2.69 ppm, respectively, in the ^{1}H-NMR spectrum, and in the ^{13}C-NMR spectrum of **25A** a *t* at 51.7 ppm and a *s* at 65.7 ppm.

Bicyclo[5.1.0]octan-2-one **26**. The structure of **26** was also mainly determined by comparison of the spectral data with that of the corresponding compound bearing a methylidene group in place of a spiro-oxirane function [4]. Instead of the methylidene signals, **26** shows for the oxirane moiety in the ^{1}H-NMR spectrum an *AB*-system (2.63 ppm, J = 4 Hz), and in the ^{13}C-NMR spectrum a *s* (60.1 ppm) and a *t* (53.3 ppm).

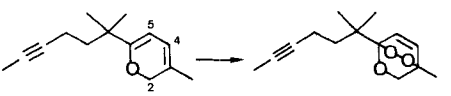
Bicyclo[5.1.0]octan-2-one **27**. The structure of this compound is based on the fact that it was formed on photolysis of *(E/Z)*-**23** *via* an oxa-di-π-methane rearrangement [12][13]. The spectral data of **27** are similar to that of **26**; however, the ^{13}C-NMR signal of the C-atom bearing the geminal CH_3-groups is shifted 10 ppm upfield in the spectrum of **27** (*s* at 38.1 ppm) in comparison to that of **26** (*s* at 48.1 ppm) indicating that the *gem*-dimethyl group of the former is not in α-position to a C=O group. Furthermore, on thermolysis at 200°, **27** undergoes a known reaction [14], namely a 1,5-homosigmatropic H-shift with cleavage of the cyclopropane ring, leading to the *methylidene-cycloheptanone* **37** (see *Scheme 5*). The structure of the latter was derived from the spectral data. The two saturated C=O groups are evidenced by ^{13}C-NMR signals at 208.6 and 204.8 ppm as well as by the strong IR band at 1715 cm^{-1}. As signals of the spiro-oxirane moiety, the ^{13}C-NMR spectrum of **37** shows a *s* and a *t* at 63.5 and 54.7 ppm, respectively, and in the ^{1}H-NMR an *AB*-system at 2.78 ppm (J = 5 Hz). The methylidene group is evidenced in the ^{13}C-NMR spectrum by a *s* (153.0 ppm) and a *t* (115.3 ppm) as well as in the ^{1}H-NMR spectrum by a *s* (4.97 ppm) and a *d* (5.28 ppm, J = 1.6 Hz) showing allylic coupling with H–C(5). The latter appears at 3.67 ppm as *ddd* exhibiting coupling with the 2H–C(1') (J = 11.5 and 4.0 Hz), and the 2H–C(1') show an *AB*-system centered at 2.84 ppm with a geminal coupling constant J = 13 Hz.

Scheme 5



27 37

Scheme 6



32 38

Cyclopropene **30** (see *Scheme 3*). The structure of this compound was confirmed by comparison of the spectral data with that of **6** [3] (see *Scheme 1*).

*Acetylenic Dienone (*E*)*-**31**. The structure was deduced from the spectral data. The elemental analysis and a molecular peak m/z 204 in the MS prove the molecular formula $C_{14}H_{20}O$. The conjugated dienone moiety is evidenced by a UV maximum at 262 nm (ε = 18600), a strong IR band at 1675 cm^{-1}, an *AB*-system (6.90 ppm, J = 16 Hz) as well as a *m* (5.38 ppm, 2H) in the ^{1}H-NMR spectrum, and a *t* (125.1 ppm), 2*d* (121.1 and 145.2 ppm), and 2*s* (140.9 and 203.4 ppm) in the ^{13}C-NMR spectrum. The methylacetylene moiety exhibits in the ^{13}C-NMR spectrum 2*s* (76.0 and 78.9 ppm) and a *q* (3.4 ppm) and in the ^{1}H-NMR spectrum a *t* (J = 3 Hz) at 1.70 ppm indicating a long-range coupling with the 2H–C(8).

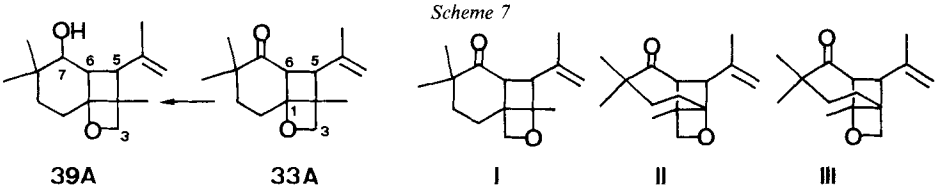
*Acetylenic 2*H*-Pyran* **32**. As characteristic signals the ^{1}H-NMR spectrum shows an *AB*-system at 5.30 ppm (J = 6 Hz) of H–C(4) and H–C(5). The signal of H–C(4) is further split to a *m* due to allylic coupling with the olefinic CH_3-group and the 2H–C(2), which appear as a broad signal at 4.40 ppm. These spectral characteristics are almost identical to those of a 2*H*-pyran previously obtained on photolysis of (*E*)-**3** [3].

Since compound **32** is labile, it could not be obtained in pure form, and was, therefore, converted to the endoperoxide **38** by reaction with $^1O_2$ (see *Scheme 6*). The trioxabicyclooctene moiety was confirmed by comparison of the NMR data with that of an analog derived from (*E*)-**3** [3]. The methylacetylene moiety demonstrated spectral characteristics similar to those described for (*E*)-**31**.

2-Oxatricyclo[4.4.0.0^{1,4}]decanones **33A** + **B**. The proposal for these structures is based on the spectroscopic data. Most of the evidence that **33A** and **33B** are diastereoisomers rather than constitutional isomers stems

from the MS of both compounds showing the same fragmentation pattern, only the intensities of the peaks being different. Characteristic peaks in the MS are *m/z* 206 (loss of CO) and 178 (loss of $(CH_3)_2C{=}CH_2$). The saturated C=O function is evidenced by IR bands at 1700 and 1710 cm^{-1} for **33A** and **33B**, respectively. Comparison of the NMR data of **33A** and **33B** also suggests that these two compounds are diastereoisomers. The oxetane moiety is characterized most distinctively by the ^{13}C-NMR spectra showing *t*'s for C(3) at 75.1 ppm (**33A**) and 81.0 ppm (**33B**). The *s* of C(1) is shifted even further downfield because of strain due to the fusion with the cyclobutane and the cyclohexane rings and appears at 91.5 and 100.4 ppm for **33A** and **33B**, respectively. The ^{1}H-NMR spectra show *AB*-systems for the 2H–C(3) at 4.42 ppm (J = 7 Hz, **33A**) and 4.45 ppm (J = 5 Hz, **33B**). One H–C(3) of the isomer **33A** shows a long-range coupling (J = 1 Hz) to H–C(5), which allows us to assign the H–C(5) as *exo* relative to the oxabicyclohexane system, and thus the isopropenyl group is *endo*. This coupling also makes the hypothetical isomers **I** and **II** as possible structures of **33A** less plausible. Structure **III** remains still possible according to the spectral data, but it is not favorable for mechanistic reasons (see *Chap. 5*). In the ^{1}H-NMR spectra of **33A** and **33B**, as characteristic signals of H–C(5) and H–C(6), *AB*-systems appear which are further split by allylic and long-range coupling in the case of **33A** and by allylic coupling in the case of **33B**. The absence of a long-range coupling in **33B** would suggest an *exo*-configuration of the isopropenyl group relative to the oxabicyclohexane system, however, the H–C(5),H–C(6) coupling constants (J = 7 Hz, **33A**; J = 10 Hz, **33B**) do not allow the assignment of the relative configuration at C(6).

Scheme 7



39A **33A** **I** **II** **III**

Further evidence for the structure of **33A** was obtained by reduction with $LiEt_3BH$ leading to **39A** (see *Scheme 7*). The 300-MHz-^{1}H-NMR spectrum of **39A** shows the same spectral characteristics as **33A**, including the long-range coupling (J = 1.3 Hz) between H–C(3) and H–C(5). The H–C(6) is now coupled with H–C(7) (J = 7.2 Hz) as well as with H–C(5), which confirms the position of the OH-group in **39A**, and thus the position of the C=O function in **33A**.

5. Discussion. $^1\pi,\pi^*$-Excitation (λ = 254 nm) of the diepoxyenones (*E*)-**8** and (*E*)-**9** leads to the (*Z*)-isomers[3]) and (*via* C(γ),C(δ)-bond cleavage of the oxirane) to formation of the same type of products as obtained on photolyses of analogous epoxyenones in the ionone series. The finding that the diastereoisomeric epoxyenones produce identical photoproducts (**17A**, and **18**[4])–**21**) proves that $^1\pi,\pi^*$-excitation of (*E*)-**8** and (*E*)-**9** leads to the common intermediates ylide **f** and carbene **g** (see *Scheme 8*). In particular, the formation of the bicyclic acetal **17A** and its secondary photoproduct **25A**[5]) as the only diastereosiomers[6]) on irradiation of the epoxyenones (*E*)-**8** and (*E*)-**9** proves that on $^1\pi,\pi^*$*-excitation,* **17A** *is a product of the ylide intermediate* **f**. On the other hand, it was shown previously [15] that on $^1n,\pi^*$*-excitation* (λ > 347 nm) of optically pure epoxyenone of structure (*E*)-**13**, the bicyclic acetal **36** is produced in optically active form, and thus *not* via *an ylide intermediate.*

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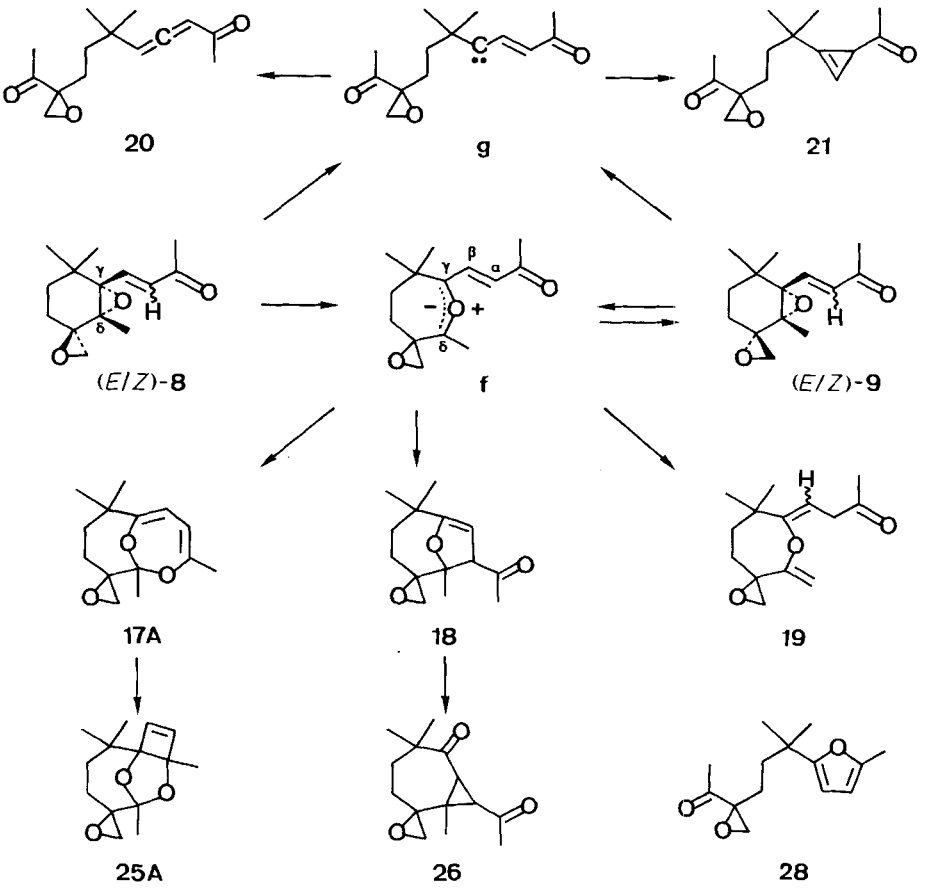
[3]) The epoxyenones (*Z*)-**8** and (*Z*)-**9** could not be isolated in pure form, since on chromatography they rearranged to the furan **28**. For a mechanistic discussion of the (*Z*)-epoxyenone→furan isomerization see [5] [16].

[4]) The unstable dihydrofuran **18** was detected on $^1\pi,\pi^*$-excitation of (*E*)-**8**, but it could not be isolated in pure form. Further evidence for the formation of **18** from (*E*)-**8** and (*E*)-**9** stems, however, from the isolation of **26**, which is a known type of photoproduct of such dihydrofurans [4].

[5]) For a transformation analogous to **17A**→**25A**, see [11].

[6]) The absence of **17B** and **25B** was demonstrated by comparison of the photoproducts with authentic material (see *Chap. 3* and *4*).

Scheme 8



In addition to the electrocyclic reaction of the ylide intermediate **f** involving the whole enone side chain (**f**→**17A**), **f** undergoes electrocyclization with the α,β-double bond (**f**→**18**)[7]), a 1,6-sigmatropic H-shift (**f**→**19**)[8]), and ring closure to the epoxide (**f**→(*E*)-**9**).

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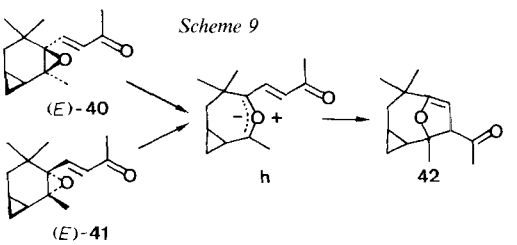
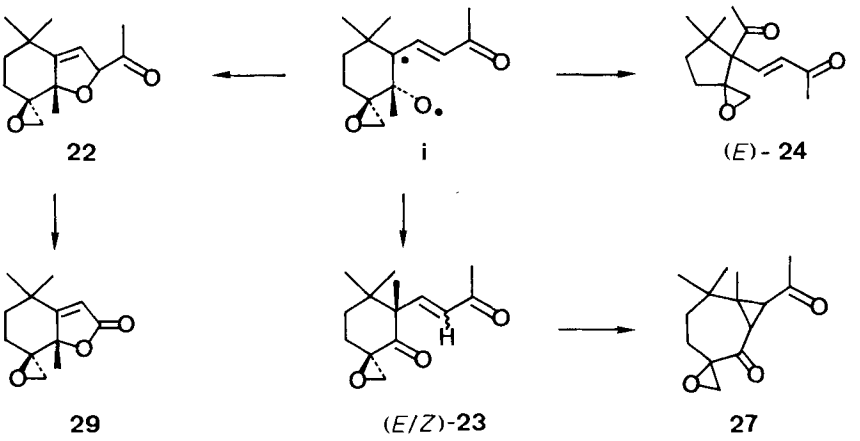
[7]) Concerning the mechanism of the formation of a dihydrofuran analogous to **18**, proof for the intermediacy of a carbonyl ylide was given by laser-flash photolysis and by kinetic measurements [17] ((*E*)-**40** and (*E*)-**41**→**h**→**42**)

Scheme 9



[8]) It may not be excluded that **19** is formed by a 1,5-homosigmatropic H-shift from (*E*)-**8** and (*E*)-**9**.

Scheme 10



Whereas the formation of the ylide products markedly depends on the solvent polarity and the temperature (see *Table*), the yields and ratios of the carbene products **20** and **21**, which are the main products of the 254-nm irradiation of (*E*)-**8** and (*E*)-**9**, are more or less constant for the photolysis of (*E*)-**8** in MeCN, pentane, and Et_2O (at r.t.). On $^1n,\pi^*$-excitation ($\lambda > 347$ nm), (*E*)-**8**[9]) shows behaviour typical of epoxyenones [2] [10], undergoing C(γ),O-bond cleavage of the oxirane ((*E*)-**8**→**i**) and the formation of the compounds **22**[10]), (*E*/*Z*)-**23**, and (*E*)-**24** (see *Scheme 10*). Compound (*E*)-**23** exhibits the typical reactivity of homoconjugated carbonyl compounds [12] [13] and, as was demonstrated by $^1n,\pi^*$-excitation, undergoes an oxa-di-π-methane rearrangement furnishing **27**.

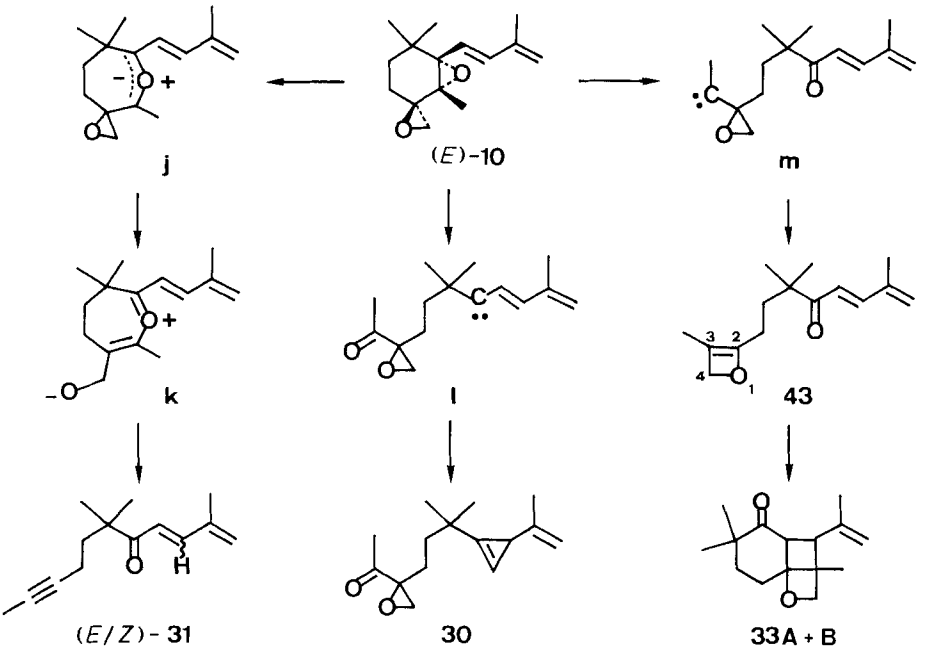
On singlet excitation ($\lambda = 254$ nm), the diepoxydiene (*E*)-**10** is transformed *via* the ylide **j** to the dipolar intermediate **k**. Subsequent fragmentation with loss of CH_2O leads to the acetylenic dienone (*E*)-**31** (see *Scheme 11*). An analogous transformation was found previously ((*E*)-**3**→**b**→**c**→**5**, see *Scheme 1*). These conversions represent a type of *Eschenmoser* fragmentation [18] with a dienone as leaving group. Under the irradiation conditions, the dienone (*E*)-**31** isomerizes to (*Z*)-**31**, which cyclizes in a thermal reaction [19] to the 2*H*-pyran **32**.

As is characteristic of epoxydienes, (*E*)-**10** shows photoisomerization *via* carbene intermediates. Thus, the cyclopropene **30** is formed *via* the vinyl carbene **l** (see *Scheme 11*). Evidence for the intermediacy of the alternative carbene **m** is provided by the isolation of the compounds **33A** + **B**. They may be formed by carbene insertion into the neighboring C,C-oxirane bond in **m** leading to the oxetene **43** (see *Scheme 11*). This process finds precedence in the isomerization of (*E*)-**3**→**e**→**7** [3] (see *Scheme 1*). Whereas compound **7** undergoes C(4),O-bond cleavage of the oxetene and ring opening to an α,β-unsaturated aldehyde very rapidly above 0°, the oxetene **43**, apparently, is long-

[9]) Due to the availability of only small amounts of (*E*)-**9**, its photolysis on $^1n,\pi^*$-excitation was not investigated.

[10]) The dihydrofuran **22** could not be detected, presumably it was oxidized to the lactone **29** (for a discussion see [10]).

Scheme 11



lived enough to undergo cycloaddition to the dienone α,β-double bond leading to **33A + B**. While this difference in the stability of **7** and **43** may at first seem surprising, it is keeping with a previous observation by *Friedrich et al.* [20] that the cleavage of oxetenes is accelerated by an alkyl substituent at the C(4)-atom. Indeed, compound **7** has an alkyl group at C(4) of the oxetene moiety, whereas **43** bears only substituents at the oxetene double bond, thus explaining its increased stability.

6. Conclusion. Whereas on $^1\pi,\pi^*$-excitation, the diepoxyenone (*E*)-**1** undergoes as main process cleavage of the C(γ),C(δ)-bond to the ylide intermediate **a** and subsequent 1,4-O migration of the second oxirane moiety leading to compound **2** as major photoproduct, *on irradiation of* (E)-**8** *and* (E)-**9**, *participation of the spirooxirane group is not observed.* Instead of the rearrangement analogous to **a**→**2**, which would lead to a highly strained product, the ylide **f** reacts to compounds (*E*)-**9**, **17A**, **18**, and **19**. The main photoprocess, however, is cleavage to the carbene intermediate **g** leading to the compounds **20** and **21**.

An interaction of the spiro-oxirane moiety is observed on singlet excitation of the diepoxydiene (E)-**10**. Analogous to the process **b**→**c** (see *Scheme 1*) the ylide **j** undergoes cleavage to a dipolar intermediate **k**, which fragments to (*E*)-**31** and CH_2O (see *Scheme 11*). As with the diepoxyenones (*E*)-**8** and (*E*)-**9**, the rearrangement corresponding to **b**→**4** (see *Scheme 1*) does not occur with the diepoxydiene (*E*)-**10**. Finally, again in analogy to the formation of the cyclopropene **6** and the oxetene **7** (see *Scheme 1*), compounds **30** and **43** are formed *via* the two carbene intermediates **l** and **m**, respectively.

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. 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 [21], except as noted below. Analytical gas chromatography was performed using a 25 m × 0.33 mm *Ucon 50 HB 5100* glass capillary. Column chromatography was carried out on silica gel *60 Merck*, 0.040–0.063 mm, 230–400 mesh ASTM (SiO_2 *A*), or *Merck* silica gel HF_{254}, 0.010–0.040 mm, (SiO_2 *B*). Analytically pure samples were obtained, in general, after repeated column chromatography on SiO_2; in some cases further purification was necessary with an HPLC (*Du Pont Instruments*, Model *830*, UV detector), using a 25 cm × 23.6 mm SiO_2 column. In general, ^{1}H-NMR spectra were taken in $CDCl_3$ solutions on a *Varian-HA-100* instrument (100 MHz) or, exceptionally (as indicated below), on a *Bruker-WP-80-CW* (80 MHz) or *WM-300* (300 MHz) instrument. *Filter solution A* ($Pb(NO_3)_2$/KBr), see [22].

1. Preparation of the Diepoxyenones (*E*)-8 and (*E*)-9 and the Diepoxydienes (*E*)-10 and (*E*)-11. 1.1. *Epoxidation of* (E)-**12.** A solution of (*E*)-**12** [4] (2.42 g, 11.0 mmol) and *m*-chloroperbenzoic acid (90%; 4.2 g, 220 mmol) in CH_2Cl_2 (10 ml) was stirred with sat. $NaHCO_3$ (10 ml) at r.t. for 3 h. The mixture was worked up in Et_2O, washed with 1N NaOH and 5% aq. Na_2SO_3, and chromatographed (SiO_2 *A*, Et_2O/hexane 2:1) yielding (*E*)-**8** (533 mg, 21%) and (*E*)-**9** (537 mg, 21%). *(*E*,1'R*,2'S*,3'S*)-4-(1',2'-Epoxy-3',3'-epoxymethano-2',6',6'-trimethyl-1'-cyclohexyl)-3-buten-2-one* ((*E*)-**8**). B.p. 150°/0.1 Torr. UV (1.12 mg in 50 ml): 229 (12200). UV (2.48 mg in 2 ml): 331 (41). IR: 3045*w*, 3000*m*, 2965*s*, 2940*s*, 2870*m*, 1703*s*, 1700*s*, 1680*s*, 1630*s*, 1450*m*, 1425*m*, 1390*m*, 1380*m*, 1358*s*, 1305*m*, 1290*m*, 1265*s*, 1250*s*, 1170*m*, 1155*w*, 1142*w*, 1095*m*, 1078*w*, 1043*w*, 1025*w*, 1010*m*, 985*s*, 945*s*, 932*w*, 910*w*, 880*m*, 855*m*. ^{1}H-NMR (CCl_4): 0.84, 0.95, 1.24 (3*s*, CH_3–C(2'), $2CH_3$–C(6')); 0.8–2.0 (*m*, 2H–C(4'), 2H–C(5')); 2.16 (*s*, 3H–C(1)); 2.62 (*AB*, J = 5, δ_A = 2.45, δ_B = 2.78, *B*-part br., CH_2–C(3')); 6.50 (*AB*, J = 16, δ_A = 6.13, δ_B = 6.87, H–C(3), H–C(4)). ^{13}C-NMR: 12.9, 24.7, 26.2, 27.9 (4*q*, C(1), CH_3–C(2'), $2CH_3$–C(6')); 26.2, 33.2 (2*t*, C(4'), C(5')); 52.0 (*t*, CH_2–C(3')); 133.3, 141.0 (2*d*, C(3), C(4)); 33.8 (*s*, C(6')); 55.7, 66.9, 71.6 (3*s*, C(1'), C(2'), C(3')); 196.8 (*s*, C(2)). MS: 236 (< 1, M^+, $C_{14}H_{20}O_3$), 163 (10), *123* (100), 91 (10), 55 (12), 53 (11), 43 (99), 41 (24). Anal. calc. for $C_{14}H_{20}O_3$ (236.31): C 71.16, H 8.53; found C 71.08, H 8.48.

*(*E*,1'R*,2'S*,3'R*)-4-(1',2'-Epoxy-3',3'-epoxymethano-2',6',6'-trimethyl-1'-cyclohexyl)-3-buten-2-one* ((*E*)-**9**). M.p. 78–79° (from hexane). UV (0.115 mg in 10 ml): 227 (12500). UV (5.236 mg in 5 ml): 330 (45). IR: 2995*m*, 2960*s*, 2940*s*, 2870*w*, 1690*s*, 1673*s*, 1625*s*, 1460*m*, 1450*m*, 1430*w*, 1388*m*, 1378*m*, 1363*s*, 1360*s*, 1305*m*, 1285*m*, 1265*s*, 1252*s*, 1172*m*, 1150*w*, 1095*m*, 1078*w*, 1040*w*, 1022*w*, 1008*w*, 985*s*, 935*m*, 908*w*, 890*w*, 880*w*, 870*w*, 860*w*, 835*w*. ^{1}H-NMR (CCl_4): 0.91, 0.97, 1.15 (3*s*, CH_3–C(2'), $2CH_3$–C(6')); 1.1–1.9 (*m*, 2H–C(4'), 2H–C(5')); 2.16 (*s*, 3H–C(1)); 2.59 (*AB*, J = 5, δ_A = 2.42, δ_B = 2.76, CH_2–C(3')); 6.52 (*AB*, J = 15, δ_A = 6.21, δ_B = 6.83, H–C(3), H–C(4)). ^{13}C-NMR: 13.5, 25.6, 25.8, 28.2 (4*q*, C(1), CH_3–C(2'), $2CH_3$–C(6')); 26.7, 34.5 (2*t*, C(4'), C(5')); 51.5 (*t*, CH_2–C(3')); 132.9, 140.9 (2*d*, C(3), C(4)); 33.7 (*s*, C(6')); 57.6, 65.4, 71.5 (3*s*, C(1'), C(2'), C(3')); 197.2 (*s*, C(2)). MS: 236 (< 1, M^+, $C_{14}H_{20}O_3$), 124 (9), *123* (100), 55 (5), 53 (5), 43 (36). Anal. calc. for $C_{14}H_{20}O_3$ (236.31): C 71.16, H 8.53; found: C 71.00, H 8.46.

1.2. *Reaction of* (E)-**13** *with (Dodecylmethylsulfonio)methanide.* Analogous to the method described in [6], a solution of (*E*)-**13** [5] (8.06 g, 36.3 mmol) in toluene (40 ml) was stirred mechanically with a suspension of dodecyldimethylsulfonium chloride (14.1 g, 62.3 mmol) and 17N NaOH (20 ml) at r.t. for 90 min. The mixture was worked up in Et_2O and chromatographed (Et_2O/hexane 2:1) affording recovered (*E*)-**13** (1.14 g), (*E*)-**8** (3.40 g, 40%), and (*E*)-**14**/(*E*)-**15** (3.32 g, 39%)[11]). *(*E*)-3,4-Epoxy-1-(1',2'-epoxy-3',3'-epoxymethano-2',6',6'-trimethyl-1'-cyclohexyl)-3-methyl-1-butene* ((*E*)-**15**). M.p. 38–43°, B.p. 135°/0.08 Torr. IR: 3040*w*, 2965*s*, 2940*s*, 2865*w*, 1445*m*, 1388*m*, 1380*m*, 1365*m*, 1340*w*, 1300*w*, 1270*w*, 1238*w*, 1140*w*, 1092*w*, 1068*w*, 990*w*, 973*s*, 942*m*, 910*w*, 885*m* (br.), 852*m* (br.), 680*w*, 605*w*. ^{1}H-NMR (CCl_4, mixture of diastereoisomers) 0.85, 0.87, 0.92, 0.93, 1.14, 1.16, 1.38, (7*s*, CH_3–C(3), CH_3–C(2'), $2CH_3$–C(6')); 1.00–1.90 (*m*, 2H–C(4'), 2H–C(5')); 2.58 (*AB*, J = 6, δ_A = 2.52 (br.), δ_B = 2.64) and 2.59 (*AB*, J = 5, δ_A = 2.43, δ_B = 2.76 (br.), 2H–C(4), CH_2–C(3')); 5.69 (*AB*, J = 17, δ_A = 5.48, δ_B = 5.90, H–C(1), H–C(2)). MS: 250 (1, M^+, $C_{15}H_{22}O_3$), 163 (26), 135 (16), 121 (17), 109 (18), 107 (19), 105 (18), 95 (34), 93 (18), 91 (26), 83 (17), 79 (17), 77 (20), 69 (27), 67 (25), 55 (39), 53 (30), *43* (100), 41 (44). Anal. calc. for $C_{15}H_{22}O_3$ (250.33): C 71.97, H 8.86; found: C 71.68, H 8.77.

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[11]) The mixture (*E*)-**14**/(*E*)-**15** could not be separated. Only compound (*E*)-**15** could be obtained in pure form by reaction of (*E*)-**13** with a large excess of (docecylmethylsulfonio)methanide.

1.3. *Transformation of (*E*)-***8*** and (*E*)-***9*** to (*E*)-***10*** and (*E*)-***11*** resp.* a) To a solution of (*E*)-**8** (146 mg, 0.62 mmol) in abs. Et_2O (2 ml) was added under Ar a *ca.* 0.15M solution of methylidenetriphenylphosphorane in Et_2O (5 ml). After 5 min, the reaction was quenched with H_2O, worked up, and chromatographed (SiO_2 *B*; hexane/EtOAc gradient, 0→8% EtOAc) giving (*E*)-**10** (134 mg, 93%). b) Analogous treatment of (*E*)-**9** (119 mg, 0.50 mmol) yielded (*E*)-**11** (91 mg, 77%). *(*E*,1′R*,2′S*,3′S*)-1-(1′,2′-Epoxy-3′,3′-epoxymethano-2′,6′,6′-trimethyl-1′-cyclohexyl)-3-methyl-1,3-butadiene* ((*E*)-**10**; 85% pure). B.p. 100°/0.05 Torr. UV (0.189 mg in 25 ml): 236 (24800). IR: 3080*w*, 3040*w*, 2990*m* (sh), 2960*s*, 2940*s*, 2865*m*, 1800*w*, 1640*w*, 1610*m*, 1480*w*, 1450*m*, 1385*m*, 1378*m*, 1363*m*, 1333*w*, 1313*w*, 1252*m*, 1143*w*, 1092*m*, 1078*m*, 1040*w*, 1023*w*, 1008*w*, 990*m*, 973*s*, 940*w*, 930*m*, 890*s*, 853*m*, 820*w*. ^{1}H-NMR: 0.93, 0.97, 1,17 (3*s*, CH_3–C(2′), $2CH_3$–C(6′)); 1.84 (*m*, $w_{½}$ = 3, CH_3–C(3)); 1.10–2.10 (*m*, 2H–C(4′), 2H–C(5′)); 2.71 (*AB*, *J* = 5, δ_A = 2.55, δ_B = 2.88, split into *d*, *J* = 1, CH_2–C(3′)); 4.96 (*m*, $w_{½}$ = 4, 2H–C(4)); 6.03 (*AB*, *J* = 16, δ_A = 5.80, δ_B = 6.27, H–C(1), H–C(2)). ^{13}C-NMR: 13.0, 18.6, 24.9, 26.2 (4*q*, CH_3–C(3), CH_3–C(2′), $2CH_3$–C(6′)); 26.4, 33.3 (2*t*, C(4′), C(5′)); 52.1 (*t*, CH_2–C(3′)); 117.0 (*t*, C(4)); 124.0, 136.3 (2*d*, C(1), C(2)); 33.9 (*s*, C(6)); 56.1, 66.5, 72.0 (3*s*, C(1′), C(2′), C(3′)); 140.8 (*s*, C(3)). MS: 234 (3, M^+, $C_{15}H_{22}O_2$), 163 (57), 133 (21), 123 (31), 121 (32), 119 (28), 107 (33), 105 (88), 95 (27), 93 (21), 91 (36), 79 (25), 77 (25), 69 (27), 67 (29), 55 (25), *43* (100), 41 (61). Anal. calc. for $C_{15}H_{22}O_2$ (234.33): C 76.88, H 9.46; found C 76.77, H 9.64.

*(*E*,1′R*,2′S*,3′R*)-1-(1′,2′-Epoxy-3′,3′-epoxymethano-2′,6′,6′-trimethyl-1′-cyclohexyl)-3-methyl-1,3-butadiene* ((*E*)-**11**). ^{1}H-NMR (80 MHz): 1.01, 1.01, 1.13 (3*s*, CH_3–C(2′), $2CH_3$–C(6′)); 0.7–2.0 (*m*, 2H–C(4′), 2H–C(5′)); 1.85 (*s*, CH_3–C(3)); 2.73 (*AB*, *J* = 5, δ_A = 2.53, δ_B = 2.93, CH_2–C(3′)); 4.97 (*m*, $w_{½}$ = 4, 2H–C(4)); 6.05 (*AB*, *J* = 18, δ_A = 5.78, δ_B = 6.32, H–C(1), H–C(2)).

1.4. *Reaction of (*E*)-***16*** with (Dodecylmethylsulfonio)methanide.* A solution of (*E*)-**16** [7] (4.16 g, 18.7 mmol) in toluene (15 ml) was stirred mechanically with dodecylmethylsulfonium chloride (8.4 g, 37.2 mmol) and 17N NaOH (10 ml) overnight. Work-up in Et_2O and chromatography (SiO_2 *B*; hexane/EtOAc gradient, 0→5% EtOAc) gave (*E*)-**10** (3.95 g, 90%).

2. Photolysis Experiments. 2.1. *Photolyses of (*E*)-***8***.* 2.1.1. *At λ > 254 nm.* 2.1.1.1. *In MeCN.* A solution of (*E*)-**8** (4.15 g, 17.6 mmol) in MeCN (400 ml) was irradiated (lamp *A*, quartz; 95% conversion). Chromatography (550 g of SiO_2*A*; Et_2O/hexane 1:1 (2.5 l), Et_2O (2 l), Et_2O/MeOH 9:1 (1.5 l)) gave mixed fractions. From their GC and ^{1}H-NMR analysis, the following product yields were determined: (*Z*)-**8** (14%), (*E*)-**9** (2%), **17A** (*ca.* 1%), **18** (4%), **19** (1%), **20** (10%), **21** (9%), (*E*)-**23** (5%), **25A** (2%), **26** (1%), **28** (2%), and 2 compounds of unknown structure (*ca.* 1% each). Anal. samples of the following compounds were obtained by HPLC: (*E*)-**9** (Et_2O/pentane 7:13), **19** (Et_2O/pentane 1:9), (*E*)-**23** (EtOAc/hexane 7:13), **25A** (Et_2O/pentane 1:19), **26** (EtOAc/pentane 1:9), and **28** (EtO/pentane 1:9). *(*Z*,1′R*,2′S*,3′S*)-4-(1′,2′-Epoxy-3′,3′-epoxymethano-2′,6′,6′-trimethyl-1′-cyclohexyl)-3-buten-2-one* ((*Z*)-**8**). Characteristic ^{1}H-NMR signals (80 MHz) of a sample contaminated with *ca.* 50% of (*E*)-**8**: 2.71 (*AB*, *J* = 5, δ_A = 2.55, δ_B = 2.87, CH_2–C(3′)); 6.13 (*AB*, *J* = 12, δ_A = 5.98, δ_B = 6.29, H–C(3), H–C(4)).

10,10-Epoxymethano-1,3,7,7-tetramethyl-2,11-dioxabicyclo[4.4.1]undeca-3,5-diene, isomer **A** (**17A**). B.p. 140°/0.05 Torr. UV (0.289 mg in 10 ml): 259 (8300). IR: 3030*w* sh, 2940*s*, 2920*s*, 2875*m*, 2850*w*, 1720*w*, 1655*m* (sh), 1638*s*, 1465*w* (sh), 1458*w* (sh), 1445*m*, 1438*m*, 1430*m*, 1377*s*, 1355*s*, 1333*w*, 1280*w*, 1170*s*, 1150*m*, 1115*m* (sh), 1110*m*, 1087*m*, 1070*m*, 1018*m*, 990*w*, 962*w*, 950*m*, 940*m*, 920*w*, 860*m*, 845*m*. ^{1}H-NMR (80 MHz, 80% pure): 1.14, 1.21 (2*s*, $2CH_3$–C(7)); 1.63, 1.85 (2*s*, CH_3–C(1), CH_3–C(3)); 0.75–2.5 (*m*, 2H–C(8), 2H–C(9)); 2.50 (*AB*, *J* = 6, δ_A = 2.36, δ_B = 2.64, CH_2–C(10)); 5.01 (*AB*, *J* = 6, δ_A = 4.65, δ_B = 5.38, H–C(4), H–C(5)). MS: 236 (9, M^+, $C_{14}H_{20}O_3$), 124 (10), *123* (100), 99 (7), 95 (5), 43 (39), 41 (8). Anal. calc. for $C_{14}H_{20}O_3$ (236.31): C 71.16, H 8.53; found C 70.96, H 8.67.

4-(7′,7′-Dimethyl-4′-methylidene-1′,5′-dioxaspiro[2.6]non-6′-ylidene)-2-butanone (**19**). B.p. 135°/0.08 Torr. UV (2.014 mg in 5 ml): 280 (105). IR: 3045*w*, 2965*s*, 2950*m*, 2930*m*, 2870*w*, 1720*s*, 1670*w*, 1642*s*, 1475*m*, 1445*m*, 1390*m*, 1355*s*, 1335*m*, 1280*s*, 1225*w*, 1185*w*, 1158*s*, 1115*s*, 1060*m*, 1020*w*, 945*w*, 930*w*, 868*m*, 845*m*. ^{1}H-NMR: 1.15 (*s*, $2CH_3$–C(7′)); 1.0–2.4 (*m*, 2H–C(8′), 2H–C(9′)); 2.10 (*s*, 3H–C(1)); 2.60 (*AB*, *J* = 5, δ_A = 2.56, δ_B = 2.64, *A*-part with fine structure, 2H–C(2′)); 3.17 (br. *d*, *J* = 7, 2H–C(3)); 4.34, 4.43 (2*m* with fine structure, CH_2=C(4′)); 5.27 (*t*, *J* = 7, H–C(4)). ^{13}C-NMR: 25.7, 27.5, 29.6 (3*q*, C(1), $2CH_3$–C(7′)); 30.9, 39.8, 39.9 (3*t*, C(3), C(8′), C(9′)); 54.8 (*t*, C(3′)); 88.3 (*t*, CH_2=C(4′)); 107.1 (*d*, C(4)); 38.9 (*s*, C(7′)); 56.8 (*s*, C(3′)); 159.7, 160.3 (2*s*, C(4′), C(6′)); 206.3 (*s*, C(2)). MS: 236 (3, M^+, $C_{14}H_{20}O_3$), 193 (45), 133 (17), 123 (13), 119 (13), 109 (10), 107 (20), 105 (17), 98 (24), 97 (10), 81 (13), 79 (20), 77 (12), 69 (28), 67 (17), 55 (54), 53 (11), *43* (100), 41 (31). Anal. calc. for $C_{14}H_{20}O_3$ (236.31): C 71.16, H 8.53; found: C 70.89, H 8.71.

9,9-Epoxymethano-6,6-dimethyl-3,4-undecadien-2,10-dione (**20**). B.p. 170°/0.08 Torr. UV (0.212 mg in 5 ml): 219 (7150). UV (4.19 mg in 5 ml): 280 (sh, 120), end absorption to 350. IR: 3045*w*, 2962*s*, 2925*m*, 2870*w*, 1945*s*, 1710*s*, 1685*s*, 1680*s*, 1470*w*, 1455*w*, 1420*m*, 1357*s*, 1317*w*, 1272*w*, 1230*s*, 1160*w*, 1093*w*, 1018*w*, 993*w*, 958*w*,

920*w*, 882*m*, 872*m*. ^{1}H-NMR: 1.09, 1.10 (2*s*, $2CH_3$–C(6)); 0.8–2.3 (*m*, 2H–C(7), 2H–C(8)); 1.99, 2.19 (2*s*, 3H–C(1), 3H–C(11)); 2.91 (*AB*, J = 5, δ_A = 2.85, δ_B = 2.96, CH_2–C(9)); 5.65 (*AB*, J = 6, δ_A = 5.54, δ_B = 5.77, H–C(3), H–C(5)). ^{13}C-NMR: 23.3, 26.1, 27.3, 27.3 (4*q*, C(1), C(11), $2CH_3$–C(6)); 25.5, 37.3 (2*t*, C(7), C(8)); 50.7 (*t*, CH_2–C(9)); 99.2, 104.7 (2*d*, C(3), C(5)); 35.4 (*s*, C(6)); 62.3 (*s*, C(9)); 198.0, 206.9, 211.5 (3*s*, C(2), C(4), C(10)). MS: 236 (< 1, M^+, $C_{14}H_{20}O_3$), 221 (3), 163 (3), 137 (4), 123 (16), 109 (5), 95 (6), 79 (8), *43* (100), 41 (9). Anal. calc. for $C_{14}H_{20}O_3$ (236.31): C 71.16, H 8.53; found C 71.09, H 8.57.

3,3-Epoxymethano-6-methyl-6-(3'-acetyl-1'-cyclopropen-1'-yl)-2-heptanone (**21**; *ca.* 3:2 mixture of 2 diastereoisomers). B.p. 130°/0.03 Torr. UV (1.688 mg in 5 ml of MeCN): 284 (155). IR: ($CHCl_3$): 3145*w*, 3035*w*, 2990*m* (sh), 2960*s*, 2940*m*, 2870*w*, 1788*w*, 1708*s*, 1675*s*, 1610*w*, 1465*m*, 1450*m*, 1418*w*, 1387*m*, 1360*s*, 1318*w*, 1238*m* (br.), 1182*m*, 1150*m*, 1092*m*, 1065*w*, 1028*w*, 950*m*, 920*w*, 878*w*. ^{1}H-NMR (80 MHz): 1.10, 1.14 (2*s*, 3H–C(7), CH_3–C(6)); 0.6–2.7 (*m*, 2H–C(4), 2H–C(5)); 2.37 (*m*, $w_{½}$ = 4, H–C(3')); 2.89 (*AB*, J = 5, δ_A = 2.86, δ_B = 2.92, CH_2–C(3)); 6.33 (*m*, $w_{½}$ = 3, H–C(2')). ^{13}C-NMR (*ca.* 80% pure): 23.7, 25.5, 25.7, 25.9 (4*q*, C(1), C(7), CH_3–C(6), CH_3CO–C(3')); 34.6, 35.4 (2*t*, C(4), C(5)); 51.0 (*t*, CH_2–C(3)); 30.0, 30.1 (2*d*, C(3') of 2 isomers); 94.8 (*d*, C(2')); 26.4 (*s*, C(6)); 62.5 (*s*, C(3)); 123.8 (*s*, C(1')); 207.3, 213.0 (2*s*, C(2), *C*O–C(3')). MS: 236 (1, M^+, $C_{14}H_{20}O_3$), 193 (46), 123 (31), 93 (10), 91 (14), 79 (12), 77 (11), *43* (100), 41 (14). Anal calc. for $C_{14}H_{20}O_3$ (236.31): C 71.16, H 8.53; found C 71.28, H 8.36.

(E)-4-(5',5'-Epoxymethano-1',2',2'-trimethyl-6'-oxo-1'-cyclohexyl)-3-buten-2-one ((*E*)-**23**). M.p. 75–76.5° (Et_2O/hexane). UV (0.097 mg in 10 ml of MeCN): 228 (10700). UV (0.904 mg in 2 ml of MeCN): 301 (543). IR: 3045*w*, 2980*m*, 2960*m*, 2940*m*, 2870*w*, 1725*s*, 1700*s*, 1680*s*, 1610*s*, 1465*w*, 1450*w*, 1395*w*, 1370*m*, 1355*m*, 1295*m*, 1268*m*, 1250*m*, 1185*w*, 1010*m*, 983*m*, 970*m*, 930*w*, 880*w*. ^{1}H-NMR[12]): 1.00, 1,00, 1.23 (3*s*, CH_3–C(1'), $2CH_3$–C(6')); 1.5–2.5 (*m*, 2H–C(4'), 2H–C(5')); 2.22 (*s*, 3H–C(1)); 2.76 (*AB*, J = 6, δ_A = 2.69, δ_B = 2.83, CH_2–C(3')); 6.59 (*AB*, J = 16, δ_A = 6.02, δ_B = 7.16, H–C(3), H–C(4)). ^{13}C-NMR[12]): 15.2, 23.7, 25.0, 27.9 (4*q*, C(1), CH_3–C(1'), $2CH_3$–C(6')); 28.4, 34.2 (2*t*, C(4'), C(5')); 55.9 (*t*, CH_2–C(3')); 131.4, 145.8 (2*d*, C(3), C(4)); 39.8 (*s*, C(6')); 58.6, 59.8 (2*s*, C(1'), C(3')); 196.9, 205.9 (2*s*, C(2), C(2')): MS: 236 (2, M^+, $C_{14}H_{20}O_3$), 193 (21), 137 (15), 125 (40), 123 (22), 122 (16), 109 (24), 107 (21), 97 (48), 96 (34), 95 (30), 81 (13), 79 (18), 69 (35), 67 (14), 55 (20), 53 (16), *43* (100), 41 (31). Anal. calc. for $C_{14}H_{20}O_3$ (236.31): C 71.16, H 8.53; found: C 71.05, H 8.59.

7,7-Epoxymethano-4,6,10,10-tetramethyl-5,11-dioxatricyclo[4.4.1.0^{1,4}]undec-2-ene, isomer A (**25A**). B.p. 135°/0.08 Torr. IR: 3040*w* (sh), 2980*m* (sh), 2960*s* (sh), 2950*s*, 2930*s*, 2870*m*, 2860*m*, 1700*w*, 1470*w* (sh), 1442*m*, 1387*w*, 1370*s*, 1290*m*, 1180*m*, 1160*s*, 1147*s*, 1115*m*, 1097*m*, 1050*m*, 1030*m*, 993*s*, 968*m*, 940*m*, 893*m*, 880*m*, 865*m*, 845*w*, 825*w*. ^{1}H-NMR: 0.98, 1.13, 1.27, 1.62 (4*s*, CH_3–C(4), CH_3–C(6), $2CH_3$–C(10)); 1.0–2.6 (*m*, 2H–C(8), 2H–C(9)); 2.71 (*AB*, J = 5, δ_A = 2.63, δ_B = 2.80, *B*-part split into *d*, J = 2, CH_2–C(7)); 6.44 (*s*, H–C(2), H–C(3)). ^{13}C-NMR: 20.6, 22.4, 25.1, 25.5 (4*q*, CH_3–C(4), CH_3–C(6), $2CH_3$–C(10)); 31.0, 36.5 (2*t*, C(8), C(9)); 51.7 (*t*, CH_2–C(7)); 139.5, 146.5 (2*d*, C(2), C(3)); 35.8 (*s*, C(10)); 65.7 (*s*, C(7)); 88.8, 98.6 (2*s*, C(1), C(4)); 116.1 (*s*, C(6)). MS: 236 (< 1, M^+, $C_{14}H_{20}O_3$), 124 (13), *123* (100), 121 (11), 109 (12), 95 (15), 44 (15), 43 (79). Anal. calc. for $C_{14}H_{20}O_3$ (236.31): C 71.16, H 8.53; found: C 71.02, H 8.61.

8-Acetyl-6,6-epoxymethano-3,3,7-trimethylbicyclo[5.1.0]octan-2-one (**26**). B.p. 130°/0.08 Torr. UV (0.584 mg in 2 ml): 281 (178). IR: 3030*w*, 2970*m*, 2935*m*, 2865*w*, 1710*s* (sh), 1692*s*, 1610*w*, 1460*w* (sh), 1450*w*, 1383*m*, 1360*s*, 1322*m*, 1272*w*, 1172*m*, 1118*w*, 1080*w*, 1060*w*, 1040*w*, 1014*w*, 978*m*, 948*w*, 915*w*, 900*w*, 885*w*, 870*w*, 850*w*. ^{1}H-NMR (80 MHz; 90% pure): 1.13, 1.13, 1.17 (3*s*, $2CH_3$–C(3), CH_3–C(7)); 2.26 (*s*, CH_3CO); 1.50–2.20 (*m*, 2H–C(4), 2H–C(5)); 2.63 (*AB*, J = 4, δ_A = 2.55, δ_B = 2.70, CH_2–C(6)); 2.95 (*AB*, J = 8, δ_A = 2.73, δ_B = 3.18, H–C(1), H–C(8)). ^{13}C-NMR: 19.1, 23.8, 26.4, 31.9 (4*q*, $2CH_3$–C(3), CH_3–C(7), CH_3–CO); 34.7, 38.4 (2*t*, C(4), C(5)); 53.5 (*t*, CH_2–C(6)); 39.2, 44.0 (2*d*, C(1), C(8)); 34.0 (*s*, C(7)); 48.1 (*s*, C(3)); 60.1 (*s*, C(6)); 201.6, 205.1 (2*s*, C(2), CH_3CO). MS: 236 (8, M^+, $C_{14}H_{20}O_3$), 206 (21), 175 (16), 163 (21), 133 (15), 122 (29), 109 (14), 108 (41), 107 (15), 91 (15), 79 (18), 77 (19), 53 (11), *43* (100), 41 (29). Anal. calc. for $C_{14}H_{20}O_3$ (236.31): C 71.16, H 8.53; found C 71.07, H 8.43.

3,3-Epoxymethano-6-methyl-6-(5'-methyl-2'-furyl)-2-heptanone (**28**). B.p. 140°/0.08 Torr. UV (0.039 mg in 10 ml): 216 (sh, 13800). UV (4.020 mg in 5 ml): 279 (50). IR: 3110*w*, 3045*w*, 2975*s*, 2922*m*, 2865*w*, 1713*s*, 1610*w*, 1560*w* (br.), 1450*w*, 1425*w* (br.), 1382*w*, 1360*s*, 1320*w*, 1260*w* (br.), 1220*m*, 1195*w*, 1180*w*, 1150*w* (br.), 1120*w* (br.), 1090*w*, 1020*s*, 960*w*, 940*m*, 885*w*, 845*w* (br.). ^{1}H-NMR: 1,18 (*s*, CH_3–C(6), 3H–C(7)); 1.1–2.0 (*m*, 2H–C(4), 2H–C(5)); 1.96, 2.20 (2*s*, 3H–C(1), CH_3–C(5')); 2.80 (*AB*, J = 5, δ_A = 2.75, δ_B = 2.85, CH_2–C(3)); 5.78 (*m* with fine structure, H–C(3'), H–C(4')). ^{13}C-NMR: 13.5 (*q*, CH_3–C(5')); 23.7, 26.6, 26.8 (3*q*, C(1), CH_3–C(6), C(7)); 25.7, 36.5 (2*t*, C(4), C(5)); 50.7 (*t*, CH_2–C(3)); 104.2, 105.5 (2*d*, C(3'), C(4')); 35.2 (*s*, C(6)); 62.7 (*s*, C(3)); 150.1, 160.2 (2*s*, C(2'), C(5')); 207.2 (*s*, C(2)). MS: 236 (7, M^+, $C_{14}H_{20}O_3$), *123* (100), 43 (28). Anal. calc. for $C_{14}H_{20}O_3$ (236.31): C 71.16, H 8.53; found: C 71.04, H 8.43.

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[12]) For the sake of a better comparison, the numbering of the cyclohexane moiety is the same as in (*E*)-**8**.

2.1.1.2. *In Pentane.* A solution of (*E*)-**8** (497 mg, 2.11 mmol) in pentane (150 ml) was irradiated (lamp *A*, quartz; 91% conversion) and the mixture chromatographed (20 g of SiO_2 *A*; Et_2O/hexane 1:1 (250 ml), Et_2O (250 ml)). By GC and ^{1}H-NMR of the mixed fractions, the following product distribution was determined: (*Z*)-**8** (15%), (*E*)-**9** (9%), **18** (1%), **20** (12%), **21** (15%), (*E*)-**23** (*ca.* 1%), **25A** (1%), **26** (1%), **28** (4%), and a compound of unknown structure (4%).

2.1.1.3. *In Et_2O at r.t.* A solution of (*E*)-**8** (861 mg, 3.65 mmol) in Et_2O (150 ml) was irradiated (lamp *A*, quartz; 74% conversion) and the mixture chromatographed (SiO_2 *B*, EtOAc/hexane gradient, 0→50% EtOAc). By GC and ^{1}H-NMR of the mixed fractions, the following product distribution was determined: (*Z*)-**8** (8%), (*E*)-**9** (19%), **20** (12%), **21** (13%), (*E*)-**23** (2%), **28** (28%), and a compound of unknown structure (3%).

2.1.1.4. *In Et_2O at −60°.* A solution of (*E*)-**8** (805 mg, 3.14 mmol) in Et_2O (200 ml) was irradiated (lamp *A* (air cooled), quartz; 81% conversion) at −60° and the mixture chromatographed (75 g of SiO_2 *A*; Et_2O/hexane 1:1 (500 ml), Et_2O (500 ml)). By GC and ^{1}H-NMR of the fractions, the following product distribution was determined: (*Z*)-**8** (29%), (*E*)-**9** (2%), **17A** (*ca.* 1%), **18** (5%), **19** (1%), **20** (5%), **21** (4%), **26** (2%), **28** (2%), and 2 compounds of unknown structure (4 and 1%, resp.).

2.1.2. *At $\lambda > 347$ nm in MeCN.* A solution of (*E*)-**8** (2.9 g, 12.3 mmol) in MeCN (300 ml) was irradiated (lamp *B*, filter *A*; 83% conversion) and the mixture chromatographed on SiO_2 *A* with various solvent systems to yield the following products: (*E*)-**23** (17%), (*Z*)-**23** (21%), (*E*)-**24** (2%), **27** (5%), **28** (5%), **29** (3%), and a compound of unknown structure (2%). Anal. samples of the following compounds were obtained by HPLC: (*E*)-**24** and **29** (Et_2O/pentane 1:3), **27** (EtOAc/pentane 1:4). *(Z)-4-(5',5'-Epoxymethano-1',2',2'-trimethyl-6'-oxo-1'-cyclohexyl)-3-buten-2-one* ((*Z*)-**23**). M.p. 63–65° (Et_2O/hexane). UV (0.222 mg in 10 ml): 222 (3100). UV (4.67 mg in 5 ml): 300 (144). IR: 3050*w* (sh), 2960*s*, 2940*s*, 2870*m*, 1710*s*, 1703*s*, 1610*m* (br.), 460*m* (br)., 1450*m*, 1430*m*, 1410*m*, 1395*m*, 1370*m*, 1355*m*, 1285*w*, 1268*w*, 1253*w*, 1180*w*, 1140*s*, 1102*w*, 1008*m*, 975*m*, 930*w*, 923*w*, 893*w*, 850*w*. ^{1}H-NMR[12]) (300 MHz): 0.97, 1.10, 1.23 (3*s*, CH_3–C(1'), $2CH_3$–C(6')); 1.62 (*ddd*, J = 14, 6, 4, H_{eq}–C(5')); 1.79 (*ddd*, J = 14, 5, 4, H_{eq}–C(4')); 2.03 (*ddd*, J = 14, 12, 5, H_{ax}–C(5')); 2.17 (*s*, 3H–C(1)); 2.21 (*dddd*, J = 14, 12, 6, 1, H_{ax}–C(4')); 2.79 (*AB*, J = 6, δ_A = 2.72, δ_B = 2.87 (split into *d*, J = 1), CH_2–C(3')); 6.17 (*AB*, J = 13, δ_A = 6.14, δ_B = 6.20, H–C(3), H–C(4)). ^{13}C-NMR[12]): 15.5, 22.7, 24.3, 30.9 (4*q*, C(1), CH_3–C(1'), $2CH_3$–C(6')); 29.3, 33.9 (2*t*, C(4'), C(5')); 54.4 (*t*, CH_2–C(3')); 130.4, 141.9 (2*d*, C(3), C(4)); 58.5, 59.5 (2*s*, C(1'), C(3')); 199.1, 203.5 (2*s*, C(2); C(2')). MS: 236 (10, M^+, $C_{14}H_{20}O_3$), 193 (19), 165 (17), 137 (43), 135 (16), 125 (63), 124 (16), 123 (31), 122 (32), 112 (19), 109 (42), 107 (31), 97 (63), 96 (51), 95 (43), 93 (19), 91 (19), 81 (18), 79 (26), 77 (18), 69 (44), 67 (16), 55 (24), 53 (18), *43* (100), 41 (41). Anal. calc. for $C_{14}H_{20}O_3$ (236.31): C 71.16, H 8.53; found: C 71.20, H 8.43.

(E)-4-(1'-Acetyl-2',2'-epoxymethano-5',5'-dimethyl-1'-cyclopentyl)-3-buten-2-one ((*E*)-**24**; 80% pure). IR: 2940*m* (br.), 2870w, 1690s, 1670s, 1610s, 1460w, 1420w (br.), 1355*s*, 1290*w*, 1175*m*, 980*w*, 900*w*. ^{1}H-NMR (80 MHz): 1.14, 1.16 (2*s*, $2CH_3$–C(5')); 0.8–2.5 (*m*, 2H–C(3'), 2H–C(4')); 2.13, 2.27 (2*s*, 3H–C(1), CH_3CO); 2.76 (*AB*, J = 4, δ_A = 2.62, δ_B = 2.90, CH_2–C(2')); 6.51 (*AB*, J = 16, δ_A = 6.27, δ_B = 6.75 H–C(3), H–C(4)). ^{13}C-NMR: 24.7, 25.9, 27.3, 30.9 (4*q*, C(1), CH_3CO, $2CH_3$–C(5')); 30.3, 36.8 (2*t*, C(3'), C(4')); 48.4 (*t*, CH_2–C(2')); 132.9, 141.6 (2*d*, C(3), C(4)); 47.9 (*s*, C(5')); 66.5, 67.8 (2*s*, C(1'), C(2')); 197.6, 207.1 (2*s*, CH_3–*C*O, C(1)). MS: 236 (< 1, M^+, $C_{14}H_{20}O_3$), 124 (15), *123* (100), 121 (12), 109 (15), 95 (17), 93 (10), 91 (10), 67 (10), 55 (12), 53 (16), 43 (99), 41 (19).

8-Acetyl-3,3-epoxymethano-6,6,7-trimethylbicyclo[5.1.0]octan-2-one (**27**). M.p. 110–111° (EtOAc/hexane). IR: 3050*w* (sh), 3030*w* (sh), 2980*m*, 2960*w*, 2930*w*, 1735*s*, 1710*s*, 1465*m*, 1430*w*, 1390*m*, 1370*w*, 1355*m*, 1320*m*, 1280*m*, 1260*w* (br.), 1205*m*, 1178*m*, 1150*w*, 1135*w*, 1100*w*, 1075*w*, 1060*w*, 950*w*, 915*w*, 873*w*. ^{1}H-NMR (300 MHz): 0.87, 1.14, 1.18 (3*s*, 2 CH_3–C(6), CH_3–C(7)); 1.29–1.43 (*m*, 2H), 2.22–2.31 (*m*, 1H), 2.70–2.81 (*m*, 1H), (together 2H–C(4), 2H–C(5)); 2.30 (*s*, CH_3CO); 2.58, 3.45 (2*d*, J = 8.7, H–C(1), H–C(8)); 2.66, 3.11 (2*d*, J = 6.6, CH_2–C(3)). ^{13}C-NMR: 20.3, 22.9, 27.7, 30.9 (4*q*, $2CH_3$–C(6), CH_3–C(7), CH_3CO); 30.2, 39.8 (2*t*, C(4), C(5)); 54.0 (*t*, CH_2–C(3)); 36.4, 45.5 (2*d*, C(1), C(8)); 37.8, 38.1 (2*s*, C(6), C(7)); 60.0 (*s*, C(3)); 199.1, 201.7 (2*s*, C(2), CH_3CO). MS: 236 (2, M^+, $C_{14}H_{20}O_3$), 125 (11), 123 (19), 121 (12), 109 (19), 107 (19), 105 (11), 98 (19), 97 (32), 96 (23), 95 (32), 93 (14), 91 (13), 83 (16), 81 (18), 79 (17), 77 (11), 69 (22), 67 (21), 57 (12), 55 (34), 53 (13), *43* (100), 41 (35). Anal. calc. for $C_{14}H_{20}O_3$ (236.31): C 71.16, H 8.53; found: C 70.73, H 8.55.

5,5-Epoxymethano-2,2,6-trimethyl-7-oxabicyclo[4.3.2]non-9-en-8-one (**29**). M.p. 98–102° (Et_2O/hexane). UV (0.159 mg in 5 ml): 213 (11350). IR: 3060*w*, 2990*w*, 2970*m*, 2940*m*, 2870*w*, 2850*w*, 1762*s*, 1723*m*, 1630*m*, 1460*w* (br.), 1385*w*, 1372*m*, 1355*w*, 1260*w*, 1232*m*, 1190*w*, 1150*w*, 1135*w*, 1110*w*, 1100*w*, 1085*w*, 1037*w*, 993*w* (br.), 965*m*, 947*m*, 927*w*, 913*w*, 890*w*, 876*m*, 862*m*. ^{1}H-NMR: 1.30 (6H), 1.64 (3H) (2*s*, $2CH_3$–C(2), CH_3–C(6)); 1.2–2.5 (*m*, 2H–C(3), 2H–C(4)); 2.76 (*AB*, J = 5, δ_A = 2.49, δ_B = 3.03 split into *d*, J = 2, CH_2–C(5)); 5.67 (*s*, H–C(9)). ^{13}C-NMR: 21.9, 24.3, 29.4 (3*q*, $2CH_3$–C(2), CH_3–C(6)); 27.9, 38.7 (2*t*, C(3), C(4)); 50.9 (*t*, CH_2–C(5)); 113.4 (*d*, C(9)); 35.9 (*s*, C(2)); 64.8 (*s*, C(5)); 85.4 (*s*, C(6)); 171.4 (*s*, C(1)); 180.6 (*s*, C(8)): MS: 208

(4, M^+, $C_{12}H_{16}O_3$), 193 (17), 165 (25), 151 (18), 150 (18), 149 (14), 137 (13), 135 (29), 123 (31), 121 (11), 119 (10), 109 (30), 107 (27), 105 (17), 95 (35), 93 (16), 91 (40), 81 (13), 79 (19), 77 (21), 67 (33), 65 (19), 55 (13), 53 (21), 52 (12), 51 (26), *43* (100), 42 (14), 41 (55). Anal. calc. for $C_{12}H_{16}O_3$ (208.25): C 69.21, H 7.74; found: C 69.34, H 7.76.

2.2. *Photolysis of (*E*)-***9*** at λ = 254 nm in MeCN.* A solution of (*E*)-**9** (520 mg, 2.20 mmol) in MeCN (50 ml) was irradiated (lamp *A*, quartz; 92% conversion), and the mixture chromatographed (75 g of SiO_2 *A*; Et_2O/hexane 2:1). By GC and ^{1}H-NMR of the fractions, the following product distribution was determined: **17A** (*ca.* 1%), **19** (2%), **20** (5%), **21** (5%), **25A** (3%), **26** (3%), **28** (2%), and 2 compounds of unknown structure (3 and 5%, resp.).

2.3. *Photolyses of (*E*)-***10***.* 2.3.1. *Singlet Excitation* (λ = 254 nm. 2.3.1.1. *In MeCN at r.t.* A solution of (*E*)-**10** (2.42 g, 10.3 mmol) in MeCN (250 ml) was irradiated (lamp *A*, quartz, 72% conversion) and the mixture chromatographed (160 g of SiO_2 *A*; Et_2O/hexane 1:9 (1 l) and 3:7 (1 l)). By GC and ^{1}H-NMR of the fractions, the following product distribution was determined: (*Z*)-**10**[13]) (7%), **30** (25%), (*E*)-**31** (4%), **32** (3%), **33A** (5%), and **33B** (3%). Anal. samples of **33A** and **33B** were obtained by HPLC (Et_2O/hexane 1:4). *(Z,1'R*,2'S*,3'S*)-1-(1',2'-Epoxy-3',3'-epoxymethano-2',6',6'-trimethyl-1'-cyclohexyl)-3-methyl-1,3-butadiene* ((*Z*)-**10**). Characteristic ^{1}H–NMR signals (80 MHz) of a *ca.* 2:1 mixture of (*E*)- and (*Z*)-**10**: 5.80 (*AB*, *J* = 13, δ_A = 5.50, δ_B = 6.10, H–C(1), H–C(2)).

3,3-Epoxymethano-6-(3'-isopropenylcyclopropen-1'-yl)-6-methyl-2-heptanone (**30**). B.p. 130°/0.1 Torr. IR: 3070*w*, 2960*s*, 2920*s*, 2865*m*, 1765*m*, 1708*s*, 1630*m*, 1468*m* (sh), 1448*m*, 1425*m*, 1382*m* (sh), 1360*s*, 1315*w*, 1260*w* (br.), 1145*w*, 1092*m*, 1022*w*, 965*m*, 875*s*. ^{1}H-NMR (*ca.* 80% pure): 1.11, 1.12 (2*s*, 3H–C(7), CH_3–C(6)); 1.48 (*m*, $w_{1/2}$ = 3, CH_2=C–CH_3); 1.98 (*s*, 3H–C(1)); 0.8–2.0 (*m*, 2H–C(4), 2H–C(5)); 2.16 (*d*, *J* = 2, H–C(3')); 2.86 (*AB*, *J* = 5, δ_A = 2.82, δ_B = 2.91, CH_2–C(3)); 4.66, 4.73 (2*m*, $w_{1/2}$ = 4, CH_2=C–CH_3); 6.53 (*m*, $w_{1/2}$ = 3, H–C(2')). ^{13}C-NMR: 20.0, 23.6, 25.8, 26.4 (4*q*, C(1), C(7), CH_3–C(6), CH_2=C–CH_3); 25.6, 35.8 (2*t*, C(4), C(5)); 50.8 (*t*, CH_2–C(3)); 107.2 (*t*, CH_2=C–CH_3); 25.8 (*d*, C(3')); 100.3 (*d*, C(2')); 34.5 (*s*, C(6)); 62.6 (*s*, C(3)); 131.4, 150.2 (2*s*, C(1'), CH_2=C–CH_3); 206.9 (*s*, C(2)). MS: 234 (3, M^+, $C_{15}H_{22}O_2$), 122 (14), 121 (80), 120 (10), 119 (34), 107 (17), 105 (44), 95 (11), 93 (18), 91 (32), 79 (22), 77 (22), 69 (13), 67 (12), 55 (19), 53 (12), *43* (100), 41 (38).

2,6,6-Trimethylundeca-1,3-dien-9-yn-5-one ((*E*)-**31**). B.p. 140°/0.04 Torr. UV (0.542 mg in 50 ml): 262 (18600). IR: 3080*w*, 2960*s*, 2940*m*, 2920*m*, 2860*w*, 1675*s*, 1610*s*, 1590*s*, 1465*w*, 1450*m*, 1440*w*, 1388*w*, 1375*w*, 1368*w*, 1320*w*, 1267*m*, 1070*s*, 1020*w*, 980*m*, 910*m*, 860*w*. ^{1}H-NMR: 1.12 (*s*, 2CH_3–C(6)); 1.70 (*t*, *J* = 3, 3H–C(11)); 1.90 (*m*, $w_{1/2}$ = 4, CH_3–C(2)); 1.00–2.15 (*m*, 2H–C(7), 2H–C(8)); 5.38 (*m*, $w_{1/2}$ = 6, 2H–C(1)); 6.90 (*AB*, *J* = 16, δ_A = 6.48, δ_B = 7.32, H–C(3), H–C(4)). ^{13}C-NMR: 3.4 (*q*, C(11)); 18.2 (*q*, CH_3–C(2)); 24.1 (*q*, 2CH_3–C(6)); 14.5 (*t*, C(8)); 39.2 (*t*, C(7)); 125.1 (*t*, C(1)); 121.1 (*d*, C(4)); 145.2 (*d*, C(3)); 46.3 (*s*, C(6)); 76.0, 78.9 (2*s*, C(9), C(10)); 140.9 (*s*, C(2)); 203.4 (*s*, C(5)). MS: 204 (< 1, M^+, $C_{14}H_{20}O$), 148 (13), 138 (36), 123 (26), 120 (13), 109 (16), 105 (13), 96 (24), 95 (93), 91 (10), 81 (22), 79 (11), 69 (13), *67* (100), 65 (11), 55 (29), 53 (24), 43 (26), 41 (62). Anal. calc. for $C_{14}H_{20}O$ (204.30): C 82.30, H 9.87; found: C 82.15, H 9.72.

*3-Methyl-6-(2'-methyl-5'-heptyn-2'-yl)-2*H*-pyran* (**32**). ^{1}H-NMR (80 MHz; *ca.* 50% pure): 1.05 (*s*, CH_3–C(2'), 3H–C(1')); 1.75 (*m*, $w_{1/2}$ = 7, CH_3–C(3), 3H–C(7')); 4.40 (*s*, $w_{1/2}$ = 4, 2H–C(2)); 5.30 (*AB*, *J* = 6, δ_A = 5.02, H–C(5), δ_B = 5.58, split into *m*, H–C(4)).

5-Isopropenyl-4,8,8-trimethyl-2-oxatricyclo[4.4.0.0^{1,4}]decan-7-one, isomer A (**33A**). B.p. 120°/0.05 Torr. IR: 3080*w*, 2950*s*, 2930*s*, 2875*s*, 1700*s*, 1645*m*, 1468*m*, 1450*s*, 1385*m*, 1380*m*, 1366*m*, 1350*w*, 1330*w*, 1300*m*, 1165*w*, 1100*m*, 1040*w*, 1010*w*, 955*s*, 930*w*, 892*s*, 850*w*, 815*w*. ^{1}H-NMR (80 MHz): 1.06, 1.09, 1.27 (3*s*, CH_3–C(4), 2CH_3–C(8)); 1.65 (*m*, $w_{1/2}$ = 3, CH_2=C–CH_3); 0.9–2.3 (*m*, 2H–C(9), 2H–C(10)); 3.09 (*AB*, *J* = 7, δ_A = 2.77 (br.), $w_{1/2}$ = 6, δ_B = 3.41, H–C(5), H–C(6)); 4.42 (*AB*, *J* = 7, δ_A = 4.26, split into *d*, *J* = 1, δ_B = 4.58, 2H–C(3)); 4.95, 5.04 (2*m*, $w_{1/2}$ = 5, CH_2=C–CH_3). ^{13}C-NMR: 19.1, 21.6, 23.0, 24.7 (4*q*, CH_3–C(4), 2CH_3–C(8), CH_2=C–CH_3); 24.7, 34.1 (2*t*, C(9), C(10)); 75.1 (*t*, C(3)); 111.5 (*t*, CH_2=C–CH_3); 52.1, 53.6 (2*d*, C(5), C(6)); 43.5, 46.1 (2*s*, C(4), C(8)); 91.5 (*s*, C(1)); 142.9 (*s*, CH_2=C–CH_3); 215.3 (*s*, C(7)). MS: 234 (< 1, M^+, $C_{15}H_{22}O_2$), 206 (4), 178 (34), 163 (48), 150 (68), 135 (91), 109 (23), 107 (28), *95* (100), 93 (32), 91 (25), 79 (27), 77 (24), 69 (24), 67 (53), 55 (41), 43 (27), 41 (85).

Isomer B (**33B**). IR: 3080*w*, 2960*s*, 2930*s*, 2870*s*, 1710*s*, 1640*w*, 1465*m*, 1450*s*, 1385*m*, 1373*m*, 1367*m*, 1328*m*, 1310*m*, 1150*w*, 1112*w*, 1065*w*, 980*w*, 955*s*, 890*s*, 850*m*. ^{1}H-NMR (80 MHz): 1.05, 1.10, 1.24 (3 *s*, CH_3–C(4), 2CH_3–C(8)); 1.73 (*s*, CH_2=C–CH_3); 1.00–2.20 (*m*, 2H–C(9), 2H–C(10)); 3.68 (*AB*, *J* = 10, δ_A = 3.60, δ_B = 3.76, H–C(5), H–C(6)); 4.45 (*AB*, *J* = 5, δ_A = 4.34, δ_B = 4.56, 2H–C(3)); 4.66, 4.98 (2 *m*,

[13]) Compound (*Z*)-**10** could not be isolated in pure form. A *ca.* 2:1 mixture of (*E*)- and (*Z*)-**10** was obtained on triplet sensitization of (*E*)-**10** (λ > 280 nm, acetone; see *Section 2.3.2*).

$w_{1/2}$ = 5, CH_2=C–CH_3). ^{13}C-NMR: 11.3, 23.0, 24.8, 26.2 (4*q*, CH_3–C(4), 2CH_3–C(8), CH_2=C–CH_3); 28.4, 37.5 (2 *t*, C(9), C(10)); 81.0 (*t*, C(3)); 110.7 (*t*, CH_2=C–CH_3); 51.1, 54.6 (2*d*, C(5), C(6)); 45.5, 52.3 (2*s*, C(4), C(8)); 100.4 (*s*, C(1)); 143.2 (*s*, CH_2=C–CH_3); 209.6 (*s*, C(7)). MS: 234 (7, M^+, $C_{15}H_{22}O_2$), 206 (4), 178 (37), 163 (54), 150 (63), 135 (93), 121 (21), 109 (24), 107 (33), 105 (25), 95 (95), 93 (37), 91 (36), 79 (32), 77 (31), 69 (26), 67 (58), 55 (46), 53 (26), 43 (31), *41* (100).

2.3.1.2. *In Et_2O at −60°*. A solution of (*E*)-**10** (612 mg, 2.62 mmol) in Et_2O (150 ml) was irradiated (lamp *A*, air cooled; quartz; 73% conversion) at −60°. After evaporation of the solvent, the mixture was filtered through SiO_2 *A* (washing with Et_2O) to remove polar impurities and then chromatographed (75 g of SiO_2 *A*, Et_2O/hexane 1:5 (500 ml)→1:1 (500 ml)). By GC and ^{1}H-NMR of the fractions, the following product distribution was determined: (*Z*)-**10** (6%), **30** (17%), (*E*)-**31** (17%), and **33A** (4%).

2.3.2. *Triplet Excitation* ($\lambda > 280$ nm, acetone). A solution of (*E*)-**10** (269 mg, 1.15 mmol) in acetone (10 ml) was irradiated (lamp *B*, *Pyrex*) under cooling with ice/H_2O. After 30 min, GC showed a *ca.* 2:1 mixture of (*E*)- and (*Z*)-**10**. After a further 30 min of irradiation, the ratio was the same (^{1}H-NMR).

2.4. *Photolysis of* **17A** *and* **17B**. a) A solution of **17A** (98 mg, 0.415 mmol) in MeCN (10 ml) was irradiated (lamp *A*, quartz; *ca.* 100% conversion) and chromatographed (SiO_2 *B*; EtOAc/hexane gradient, 0→5% EtOAc) yielding **25A** (41 mg, 42%). b) A solution of **17B** (38 mg, 0.161 mmol) in MeCN (10 ml) was irradiated and chromatographed (as described for **17A**) affording *7,7-epoxymethano-4,6,10,10-tetramethyl-5,11-dioxatricyclo[4.4.1.0^{1,4}]undec-2-ene, isomer B* (**25B**; 10 mg, 26%)). ^{1}H-NMR (80 MHz): 1.02, 1.11, 1.37, 1.80 (4 *s*, CH_3–C(4), CH_3–C(6), 2CH_3–C(10)); 0.8–2.6 (*m*, 2H–C(8), 2H–C(9)); 2.69 (*AB*, J = 5, δ_A = 2.57, δ_B = 2.81, CH_2–C(7)); 6.51 (*AB*, J = 3, δ_A = 6.48, δ_B = 6.54, H–C(2), H–C(3)).

2.5. *Photolysis of* (E)-**23**. A solution of (*E*)-**23** (46 mg, 0.194 mmol) in CD_3CN (0.5 ml) was irradiated (lamp *B*, *Pyrex*; 89% conversion). Chromatography (SiO_2 *B*; EtOAc/hexane gradient, 0→20% EtOAc) gave (*Z*)-**23** (8 mg, 20%) and a 1:1 mixture (7 mg; ^{1}H-NMR) of **27** (9%) and an unknown compound (9%).

3. Additional Experiments. 3.1. *Reaction of* (E)-**10** *and* (E)-**11** *with LiBHEt$_3$*. a) A solution of (*E*)-**10** (27 mg, 0.115 mmol) in THF (1 ml) was treated with a 1M solution of $LiBHEt_3$ in THF (0.75 ml, 0.75mmol) under Ar. After 5 min, H_2O (5 ml) and H_2O_2 (30%; 1 ml) were added, and the mixture was worked up with Et_2O to yield (*E*)-**34** [8] (21 mg, 78%). b) Analogous treatment of a solution of (*E*)-**11** (91 mg, 0.389 mmol) in THF (2 ml) afforded (*E*)-**35** [8] (64 mg, 70%).

3.2. *Preparation of* **17A** + **B** *by Reaction of* **36** *with (Dodecylmethylsulfonio)methanide*. A solution of **36** [5] (1.07 g, 4.83 mmol) in toluene (4 ml) was stirred mechanically with a suspension of dodecylmethylsulfonium chloride (10 g, 44.3 mmol) and 17N NaOH at 85° for 2 h. The mixture was worked up in Et_2O and chromatographed (SiO_2 *B*; hexane/EtOAc gradient, 0→2% EtOAc) to yield **17A** (102 mg, 9%), **17B** (214 mg, 18%), and recovered starting material **36** (145 mg). *10,10-Epoxymethano-1,3,7,7-tetramethyl-2,11-dioxabicyclo-[4.4.1.]undeca-3,5-diene, isomer* **B** (**17B**). M.p. 81–82° (from hexane). UV (0.341 mg in 10 ml): 280 (8900). IR: 3050*w*, 2940*s* (sh), 2920*s*, 2875*m*, 1720*w*, 1635*s*, 1575*w*, 1445*m*, 1375*s*, 1355*s*, 1278*m*, 1175*s*, 1148*m*, 1112*s*, 1070*s*, 1015*m*, 992*w*, 960*w*, 940*m*, 882*w*, 865*m*, 852*m*. ^{1}H-NMR: 1.08, 1.18 (2*s*, 2CH_3–C(7)); 1.64, 1.82 (2*s*, CH_3–C(1), CH_3–C(3)); 1.00–2.50 (*m*, 2H–C(8), 2H–C(9)); 2.73 (*AB*, J = 5, δ_A = 2.55, δ_B = 2.91, *B*-part split into *d*, J = 1.5, CH_2–C(10)); 4.95 (*AB*, J = 6, δ_A = 4.63 (br.) δ_B = 5.27, H–C(4), H–C(5)). ^{13}C-NMR: 22.6, 23.1, 24.2, 27.1 (4*q*, CH_3–C(1), CH_3–C(3), 2CH_3–C(7)); 30.0, 44.5, 50.0 (3*t*, C(8), C(9), CH_2–C(10)); 96.3 108.3 (2*d*, C(4), C(5)); 38.1 (*s*, C(7)); 60.9 (*s*, C(10)); 109.5 (*s*, C(1)); 153.7, 161.6 (2*s*, C(3), C(6)). MS: 236 (8, M^+, $C_{14}H_{20}O_3$), 124 (9), *123* (100), 122 (9), 43 (37). Anal. calc. for $C_{14}H_{20}O_3$ (236.31): C 71.16, H 8.53; found: C 71.04, H 8.57.

3.3. *Thermolysis of* **27**. In a bulb tube, **27** (34 mg, 0.144 mmol) was heated to 200° at 760 Torr under Ar. After 30 min, the mixture was distilled (190°, 0.08 Torr) to yield **37** (29 mg, 90% pure; 77%), which was further purified on HPLC (Et_2O/pentane 1:3; 50 bar) to leave pure. *7,7-Dimethyl-6-methylidene-5-(2'-oxo-1'-propyl)-1-oxaspiro[2.6]nonan-4-one* (**37**; 8 mg). B.p. 190°/0.08 Torr. UV (5 mg in 5 ml MeCN): 280 (88). IR: 3050*w*, 2960*m*, 2925*m*, 2875*w*, 1715*s*, 1630*w*, 1480*w*, 1460*w*, 1433*w*, 1385*w*, 1365*w*, 1355*w*, 1252*w*, 1162*w*, 1140*w*, 1080*w*, 920*m*. ^{1}H-NMR (300 MHz): 1.19, 1.22 (2*s*, 2CH_3–C(7)); 1.50–1.70, 1.85–2.05 (2*m*, 2H–C(8), 2H–C(9)); 2.20 (*s*, 3H–C(3')); 2.78 (*AB*, J = 5, δ_A = 2.74, δ_B = 2.82, 2H–C(2)); 2.84 (*AB*, J = 13, δ_A = 2.73, split into *d*, J = 11.5, δ_B = 2.96, split into *d*, J = 4, 2H–C(1')); 3.67 (*ddd*, J = 11.5, 4, 1.6, H–C(5)); 4.97 (*s*, H–C=C(6)); 5.28 (*d*, J = 1.6, H–C=C(6)). ^{13}C-NMR (80% pure): 25.7, 28.3 (tentatively assigned as *q*), 31.1 (3*q*, 2CH_3–C(7), C(3')); 31.1, 36.2, 46.0 (3*t*, C(8), C(9), C(1')); 54.7 (*t*, C(2)); 115.3 (*t*, CH_2=C(6)); 48.7 (*d*, C(5)); 39.8 (*s*, C(7)); 63.5 (*s*, C(3)); 153.0 (*s*, C(6)); 204.8, 208.6 (2*s*, C(4), C(2')). MS: 236 (2, M^+, $C_{14}H_{20}O_3$), 179 (12), 163 (12), 149 (13), 137 (16), 135 (10), 124 (26), 123 (69), 121 (16), 109 (20), 107 (15), 105 (11), 97 (11), 95 (29), 93 (18), 91 (15), 81 (14), 79 (19), 77 (12), 69 (16), 67 (16), 55 (21), 53 (11), *43* (100), 41 (26). Anal. calc. for $C_{14}H_{20}O_3$ (236.31): C 71.16, H 8.53; found: C 71.25, H 8.36.

3.4. *Reaction of* **32** *with* $^1O_2$. O_2 was bubbled through a stirred suspension of *Sensitox I* (40 mg) in a solution of **32** (46 mg, 0.197 mmol) in CH_2Cl_2 (10 ml) while irradiating (lamp *B*, $Na_2Cr_2O_7$ filter) for 30 min. The mixture was then filtered through SiO_2 (eluting with Et_2O) and the solvent evaporated to give *1-methyl-4-(2'-methyl-5'-heptyn-2'-yl)-2,3,5-trioxabicyclo[2.2.2]oct-7-ene* (**38**; 38 mg, 71%). IR: 2960*m* (sh), 2935*s*, 2875*m*, 2860*w*, 1458*w*, 1380*m*, 1370*w*, 1130*m*, 1097*w*, 1065*s*, 1025*m*, 978*w*, 940*s*, 930*s*, 908*m*, 880*w*, 870*w* (sh). ^{1}H-NMR: 1.00 (*s*, 3H–C(1'), CH_3–C(2')); 1.32 (*s*, CH_3–C(1)); 1.74 (*m*, $w_{1/2}$ = 6, 3H–C(7')); 1.00–1.80 (*m*, 2H–C(3')); 2.05–2.30 (*m*, 2H–C(4')); 3.73 (*AB*, *J* = 8, δ_A = 3.39, δ_B = 4.08, 2H–C(6)); 6.52 (*AB*, *J* = 8 δ_A = 6.40, δ_B = 6.65, H–C(7), H–C(8)). ^{13}C-NMR: 3.4 (*q*, C(7')); 17.4, 21.4, 21.4 (3*q*, CH_3–C(1), C(1'), CH_3–C(2')); 14.1 (*t*, C(4')); 36.8 (*t*, C(3')); 69.8 (*t*, C(6)); 131.2, 132.4 (2*d*, C(7), C(8)); 38.5 (*s*, C(2')); 72.6, 75.3, 79.6 (3*s*, C(1), C(6'), C(5')); 101.0 (*s*, C(4)). MS: 236 (1, M^+, $C_{14}H_{18}O_3$), 204 (1), 163 (19), 123 (12), 109 (22), 107 (10), 98 (25), 95 (31), 93 (21), 91 (24), 83 (11), 82 (22), 81 (17), 79 (15), 77 (17), 70 (10), 69 (21), 67 (48), 57 (13), 56 (22), 55 (41), 53 (29), 44 (49), *43* (100), 42 (11), 41 (77).

3.5. *Reduction of* **33A** *with LiBHEt*$_3$. A 1M solution of $LiBHEt_3$ in THF (0.5 ml, 0.6 mmol) was added to a solution of **33A** (3 mg, 0.013 mmol) in THF (*ca.* 1 ml) at 0° with stirring. After 15 min at r.t., H_2O (3 ml) and H_2O_2 (30%, 3 ml) were added, and after 5 min, the mixture was worked up with Et_2O and chromatographed (SiO_2 *B*; hexane/EtOAc gradient, 0→5% EtOAc) affording *5-isopropenyl-4,8,8-trimethyl-2-oxatricyclo[4.4.0.0^{1,4}]decan-7-ol* (**39A**; 3 mg, *ca.* 100%). ^{1}H-NMR (300 MHz): 0.90, 0.96, 1.24 (3*s*, CH_3–C(4), $2CH_3$–C(8)); 1.64 (*m*, $w_{1/2}$ = 4, CH_2=C–CH_3); 1.10–1.17 (1 H), 1.50–1.58 (2 H), 2.03–2.12 (1H) (3 *m*, 2H–C(9), 2H–C(10)); 1.54 (*s*, OH); 2.94 (*dd*, $J_1 = J_2$ = 7.3, H–C(6)); 3.11 (*d*, *J* = 7.3, br., $w_{1/2}$ = 4, H–C(5)); 3.53 (*dd*, *J* = 4.0, 7.3, H–C(7)); 4.25 (*dd*, *J* = 6.2, 1.3, H_{exo}–C(3)); 4.50 (*d*, *J* = 6.2, H_{endo}–C(3)); 4.88, 5.00 (2*m*, $w_{1/2}$ = 5, CH_2=C–CH_3).

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