120. Thermal Reactions of Epoxyenones and Epoxydienes in the Ionone Series

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Dedicated to Prof. *Hans H. Günthard*

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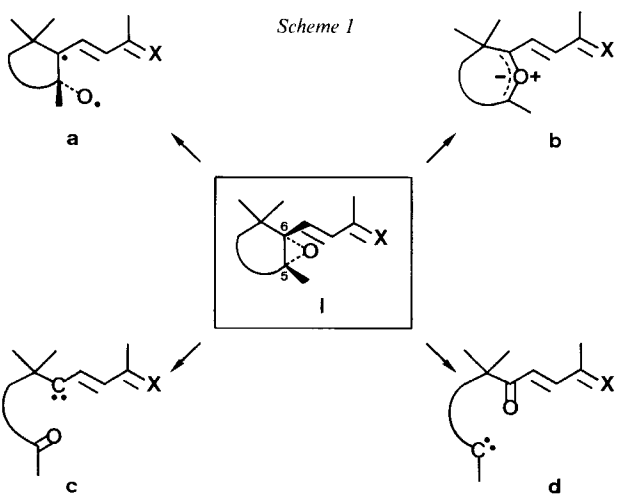
On flash vacuum thermolysis at temperatures between 390 and 585°, the epoxyenones **1**–**9** and the epoxydienes **10**–**12** undergo various types of reactions involving C–C and/or C–O bond cleavage in the oxirane ring. Thus, the compounds **1**, **4**–**9**, **11**, and **12** were transformed to the divinyl ethers **13**, **20**, **21**, **24**, **25**, **29**, and **38** by a reversible [1,5] homosigmatropic H-shift. On thermolysis of the epoxides **1**–**12**, several products formed *via* carbonyl-ylide intermediates were also isolated. The extent of the formation of ylide products is clearly related to the conjugating ability of the functional groups neighboring the oxirane. Thus, the epoxides **3**, **5**, and **7**–**10**, bearing a C(3)=C(4) bond, a 5-oxo function, a 3,4-epoxy or a 3,4-methano group, preferentially underwent reactions *via* a carbonyl-ylide intermediate. As a further reaction pathway, the epoxides **1**–**12** undergo cleavage of the C–O bonds of the oxirane, which, however, is presumably an acid-catalyzed rather than a thermal reaction.

1. Introduction. – For several years, the photolysis of α,β-unsaturated γ,δ-epoxyketones and the corresponding epoxydienes has been extensively investigated in our laboratory[2]). From these studies, it has been disclosed that, in general, on $^1n,\pi^*$-excitation or triplet sensitization, substrates of type **I** (X=O or X=CH_2) undergo (*E*)/(*Z*)-isomeriza-

Scheme 1



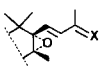
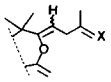
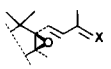
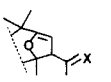
[1]) Taken in part from the Ph. D. thesis of *N. B.*, Diss. ETHZ, No. 7422 (1983).

[2]) For a recent paper, see [1]; for a review, see [2].

tion and/or product formation *via* C(6)–O bond cleavage of the oxirane (**I**→**a**)[3]). Selective $^1\pi,\pi^*$-excitation, however, leads to reactions which include cleavage of the C(5)–C(6) bond of the oxirane, leading to ylide and carbene intermediates of type **b**, **c**, and **d** *(Scheme 1)*, which react further in various ways to form different isolable products [2].

It is well-known that the thermolysis of epoxides gives rise to the formation of products *via* C–O and/or C–C bond cleavage of the oxirane [4] [5]. Therefore, it was of interest for us to test, if the thermolyses of the epoxyenones **1**–**9** and the epoxydienes **10**–**12** in the ionone series (see the *Table*), whose photochemical behavior was carefully investigated [2], would lead to the same types of products and, thereby, allow a comparison of thermal and photochemical reaction mechanisms.

Table. *Product Distributions of the*

	Epoxide				Product distribution[a])		
	No.	X	Temp. [°C]	Conv. [%]			
I					II	III	IV
	**1**	O	585°	41	**13** (78%)	–	–
			560°[b])	48	**13** (63%)	–	–
			560°[c])	83	**13** (14%)	–	–
	**2**	O	520°	85	–	**16** (7%)	–
	**3**	O	325°	30	–	–	–
			560°	100	–	–	–
	**4**[e])	O	455°	63	**20** (57%)	–	–
	**5**	O	520°	94	**21** (7%)	–	**22A** (6%)[f]) **22B** (14%)[f])
	**6**[e])	O	520°	94	**24** (10%)	–	–
	**7**	O	450°	89	**25** (52%)	**26** (14%)	–
			450°[c])	67	**25** (37%)	**26** (5%)	–
	10	CH_2	440°	80	–	**32** (5%)	–
			400°[c])	47	–	–	–
	**8**	O	520°	85	**29** (45%)	**9** (5%)	–
			520°[c])	100	–	–	–
	11	CH_2	520°	76	**38** (15%)	**12** (12%)	–
			390°[c])	88	–	–	–
	**9**	O	520°	88	**29** (37%)	**8** (13%)	–
			520°[c])	50	–	–	–
	12	CH_2	520°	77	**38** (12%)	**11** (24%)	–
			390°[c])	93	–	–	–

[a]) Yields were determined in general by GC and ^{1}H-NMR (80 MHz) analysis of the thermolysis mixture, and are based on the amount of converted starting material.

[b]) Thermolysis carried out in a tube conditioned with edta without silylation.

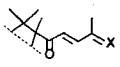
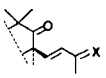
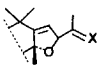
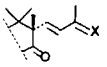
[c]) Thermolysis carried out in an untreated tube.

[3]) For the ionone derivatives, numbering according to the carotenoid nomenclature [3] is used.

2. Results and Discussion. – The epoxides **1–12** were subjected to flash vacuum thermolysis (FVT) [5] [6] to avoid intermolecular reactions. The results are given in the *Table*.

Initial experiments showed that the yields of products formed *via* C–O bond cleavage of the oxirane depends on the glass surface of the thermolysis tube. Thus, thermolysis of 5,6-epoxy-5,6-dihydro-β-ionone (**1**) through an untreated quartz or *Pyrex* tube filled with quartz-rings gave, in addition to compounds **13** and **14**, the diketone **15**. As **15** was the major product formed upon treatment of **1** with $BF_3 \cdot Et_2O$ in benzene solution [7], it appeared that on thermolysis of **1**, **15** was formed by an acid-catalyzed rearrangement on the glass surface. Therefore, the tube and packing were treated with aqueous ethylenediaminetetraacetate (edta) solution according to the method of *Baldwin et al.* [8] followed by silylation of the surface with bis(trimethylsilyl)acetamide[4]). Indeed, the formation of **15** was greatly diminished, although to a lesser extent, even when the silylation step was omitted. The reaction

Flash Vacuum Thermolyses of **1–12**

 V	 VI	 VII	 VIII	Other Ylide products	Other Products	Secondary Products
15 (2%)	–	–	–	–	–	**14** (5%)
15 (8%)	–	–	–	–	–	–
15 (36%)	–	–	–	–	–	**14** (12%)
–	–	–	–	–	–	**17** (31%)
–	–	–	–	**18** (28%)[d])	–	–
–	–	–	–	–	–	**19** (36%)[d])
–	–	–	–	–	–	–
–	–	–	–	–	**23** (9%)	–
–	–	–	–	–	**14** (16%)	–
–	–	–	–	–	–	**28A** (7%), **28B** (18%)[f])
–	–	–	–	**27** (3%)	–	**28A** (7%), **28B** (18%)[f])
–	–	**33** (5%)	**34** (3%)	–	**35** (3%)	**36** (11%), **37** (29%)
–	–	**33** (7%)	**34** (5%)	–	–	**36** (18%), **37** (19%)
–	**30** (7%)	–	–	–	–	–
–	**30** (53%)[d])	–	–	–	–	–
39 (12%)	**40** (1%)	**41** (6%)	–	–	–	–
39 (29%)[d])	–	–	–	–	–	–
–	**31** (7%)	–	–	–	–	–
–	**31** (40%)	–	–	–	**30** (20%)	–
39 (9%)	–	–	–	–	**40** (9%), **41** (5%)	–
–	–	–	–	–	**40** (55%)	–

[d]) Isolated yields.

[e]) Due to the low amount of epoxyenone available, only the main products could be isolated.

[f]) The terms **A** and **B** are generally used for the description of diastereomers whose configuration was not assigned conclusively.

[4]) Silylation of the reactor on thermolysis of acid-sensitive compounds was previously used in the group of Prof. *P. Schiess*, University of Basle (private communication; see also [9]), and by *Meyer* and *de Meijere* [10].

1→**15**, however, could never be completely suppressed. To distinguish between the acid-catalyzed processes and the thermal reactions, the compounds **1** and **7**–**12**, which gave rise to product formation *via* C–O bond cleavage, were thermolyzed in a silylated tube as well as in an untreated one.

With the exception of **3** and **10**, thermolysis of the epoxides of type **I** gave rise to the formation of divinyl ethers of type **II** (see *Table*)[5]). This process could occur by two alternative mechanisms: a [1,5] homosigmatropic H-shift or an initial cleavage of the C(5)–C(6) bond of the oxirane to the ylide **b** followed by a [1,6] H-shift. The thermal transformation (D_5)-**1**[6])→(D_5)-**13** was shown to be approximately 1.8 times slower than **1**→**13** (see *Exper. Part*). This result indicates that a [1,5] homosigmatropic H-shift is the rate-determining step in the thermal rearrangement of **1**. This view is supported by the fact that, on thermolysis, the divinyl ethers **13** (giving rise to 61% of **1**) and **29** (leading to 44% of **8** and 21% of **9**) undergo the reverse [1,5] homosigmatropic H-shifts. As a side reaction, **13** was transformed to its double-bond isomer **14**, involving a surface-catalyzed process. The divinyl ether **44** *(Scheme 3)*, formed on thermolysis of the epoxyenone **2** with an OH group at C(2) was not isolated; however, **16** and **17** are presumably consecutive products of **44**. Thus, the diastereoisomeric epoxyenone **16** may be formed analogously to the transformation **8**→**29**→**9**, whereas the aldehyde **17** probably arises from a retro-ene raction of **44**.

As expected, thermolysis **1**–**12** gave rise to product formation *via* carbonyl ylides of type **b** *(Scheme 1)*. The most noted reaction of carbonyl ylides is ring closure to epoxides and, indeed, thermolysis of compounds **2** and **7**–**12** led to interconversion of diastereomeric oxiranes (see *Table*). This ring closure of carbonyl-ylide intermediates would go unnoticed with the epoxyenones **1** and **3**–**5** in their racemic form. Since the thermolyses of compounds **7**–**9**, **11**, and **12** also produce divinyl ethers of type **II**, which were shown to revert thermally to the epoxides (see above), it can not be proven, whether the interconversion of the diastereomeric epoxides occurs exclusively *via* the divinyl ethers or also *via* the ylide intermediates. The aforementioned hypothesis that on thermolysis of **2**, the diastereomeric epoxyenone **16** may be formed *via* compound **44** rather than *via* the carbonyl-ylide intermediate **e**, may be supported by the previous finding [13] that on photolysis (λ = 254 nm, MeCN) of **2**, the bicyclic acetal **45** (55%; *Scheme 3*) was obtained as an intramolecular-trapping product of **e**. Compound **45** could not be detected on thermolysis of **2**, however.

On the other hand, thermolysis of the epoxides **3**, **5**, **7**, and **10** led to products which are clearly derived from carbonyl-ylide intermediates. Thus, on thermolysis of **3** at 325°, the dihydrofuran **18** was isolated as the only product. The latter compound is also a photoproduct of **3** [14] and arises in both cases from electrocyclic ring closure of the ylide **f** *(Scheme 5)*, which has been trapped with MeOH and also detected by laser-flash

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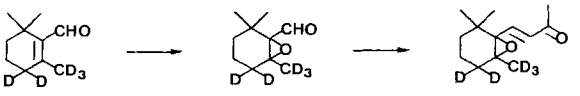
[5]) As reported previously by *Crandall* and *Watkins* [11], thermolysis of 3,4-epoxycycloheptene gives rise to ring opening and a H-shift leading to 3-oxa-1,4-cyclooctadiene.

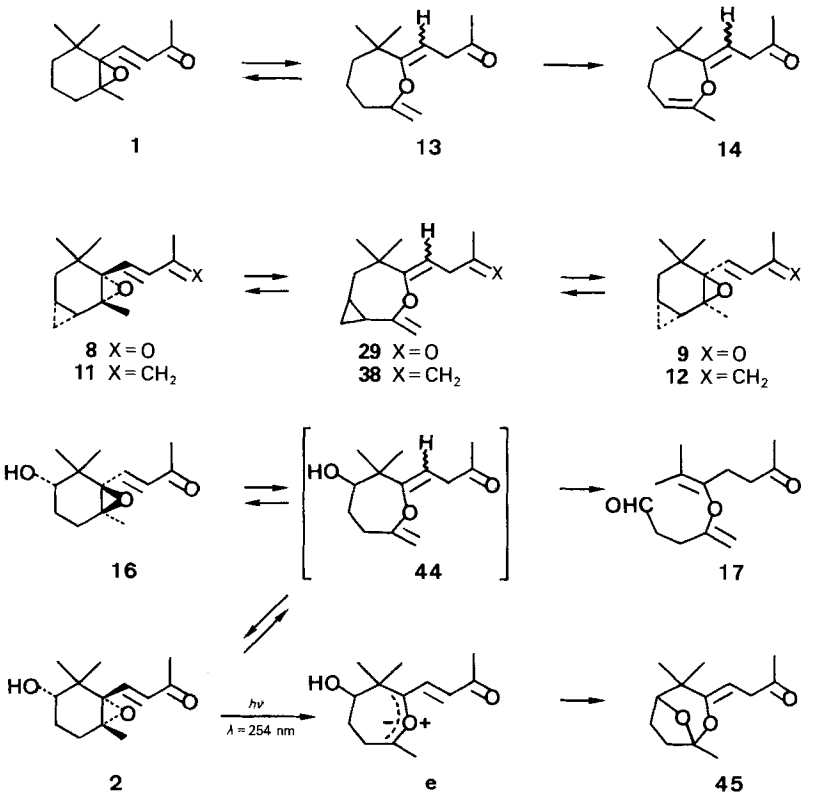
[6]) Compound (D_5)-**1** was synthesized from (D_5)-cyclocitral (**42**) [12] as shown in *Scheme 2*.

Scheme 2



42 **43** (D_5)-**1**

Scheme 3



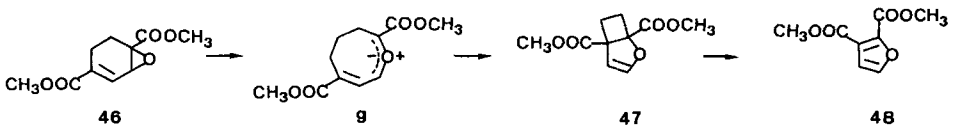
photolysis [15]. The transformation **3**→**18** is reversible at 325°, as was shown by thermolysis of **18** leading to a mixture **3**/**19** *(Scheme 5)*. The fragmentation product **19** was isolated as the only compound on thermolysis of **3** at 560° (see *Table*)[7]).

Thermolysis of the epoxide **4**, bearing a methylidene group at C(4) instead of an endocyclic double bond as **3**, gave rise to the formation of the divinyl ether **20** *(Scheme 5)*; however, products formed *via* an ylide intermediate were not detected.

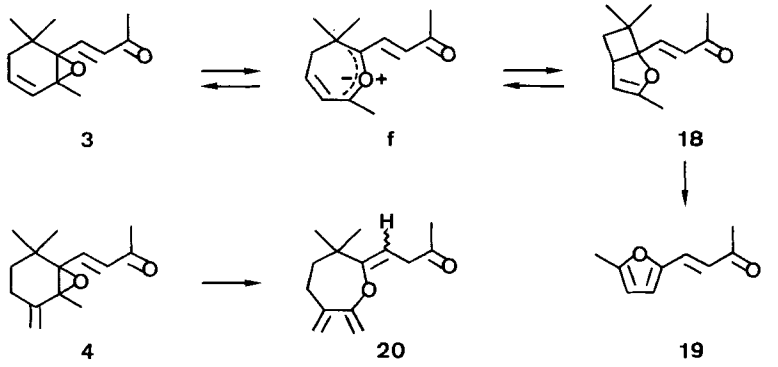
Other ylide-derived products are the two diastereomeric dihydrofurans **22A** + **B** obtained on thermolysis of the 4-oxo-β-ionone-5,6-epoxide **5** *(Scheme 6)*. These isomers arise from the ylide intermediate **h** by electrocyclic ring closure with the double bond of the enone side chain. Evidence for **h** was also obtained by thermolysis of optically pure

[7]) The carbonyl-ylide intermediate **g** has been suggested by *Eberbach* and *Carre* [16] to explain the formation of the furan diester **48** as a product of the thermolysis of the epoxide **46**. Analogously to **f**→**18**, **g** was assumed to undergo an electrocyclic reaction to **47** as a primary product.

Scheme 4

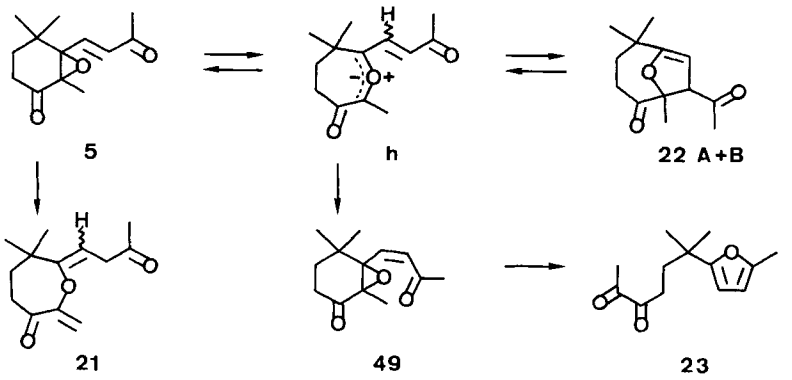


Scheme 5



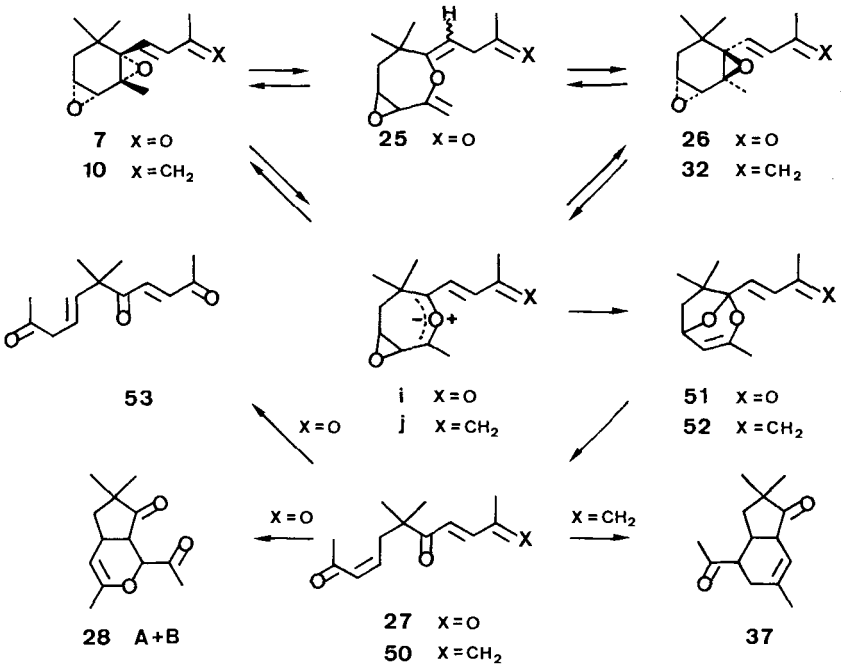
epoxyenone (−)-**5** ($[\alpha]_D = -131°$ [17]). At 455°, the recovered starting material (63%) as well as the products **22A** (6%) and **22B** (10%) were racemic. On thermolysis of (−)-**5** at 390°, 95% of the starting material was recovered with an optical purity of only *ca.* 25% ($[\alpha]_D = -34°$). The dihydrofurans **22A** + **B** could also undergo ring opening leading to ylides as shown by thermolysis of **22B** at 520° giving the epoxyenone **5** (21%) in addition to **22A** (*ca.* 20%) and the furan **23** (6%; *Scheme 6*). As was shown previously, furans of type **23** may arise from thermal reaction of (*Z*)-epoxyenones [18]. Therefore, on thermolysis of **22B**, the formation of **23** *via* the postulated (*Z*)-epoxyenone **49** indicates that opening of the dihydrofuran ring of **22B** is not stereoselective leading to an (*E*)/(*Z*)-mixture of the ylide **h**, which undergoes ring closure to afford the (*E*)- and (*Z*)-epoxyenones **5** and **49**, respectively. It cannot be excluded, however, that surface-catalyzed epimerization **22B**→**22A** takes place before the ring opening to the ylide.

Scheme 6



Another type of transformation proceeding *via* an ylide intermediate was observed on thermolysis of the epoxyenone **7** and the corresponding epoxydiene **10** leading – *via* the aliphatic compounds **27** and **50** – to the secondary products of their intramolecular *Diels-Alder* reaction, **28A** + **B** and **37**, respectively. As shown on photolysis ($\lambda = 254$ nm) of **7** and **10**, the dioxabicyclooctenones **51** and **52** arising from a 1,4-oxygen-shift in the ylide intermediate **i** and **j**, respectively, are thermally unstable and undergo cleavage to

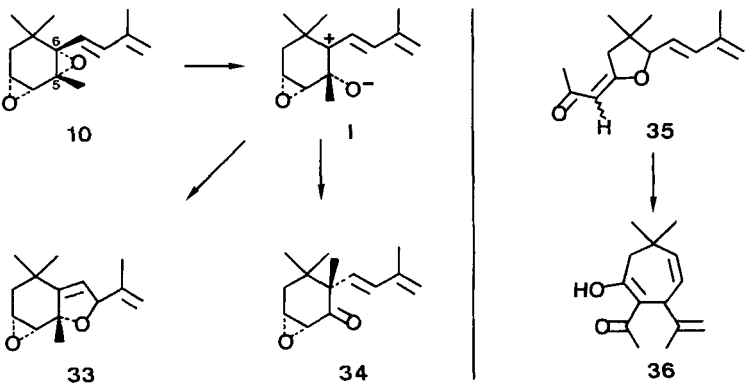
Scheme 7



compounds **27** and **50** already at r.t. *(Scheme 7)* [19]. Compound **27** was thermolyzed separately at 400° furnishing the *Diels-Alder* products **28A + B** (15% each) along with the product of a [1,5] sigmatropic H-shift followed by tautomerization, the triketone **53**, which had been obtained previously on distillation of **27** at 140° [20]. The diketone **50** was not detected on thermolysis of **10** and, due to the low yield of **50** on photolysis of **10**, its thermal behavior was not investigated.

In the thermolysis of **10**, compounds **33** and **34** (see *Table* and *Scheme 8*) were formed as further products *via* C–O bond cleavage of the oxirane, together with compounds **35**

Scheme 8

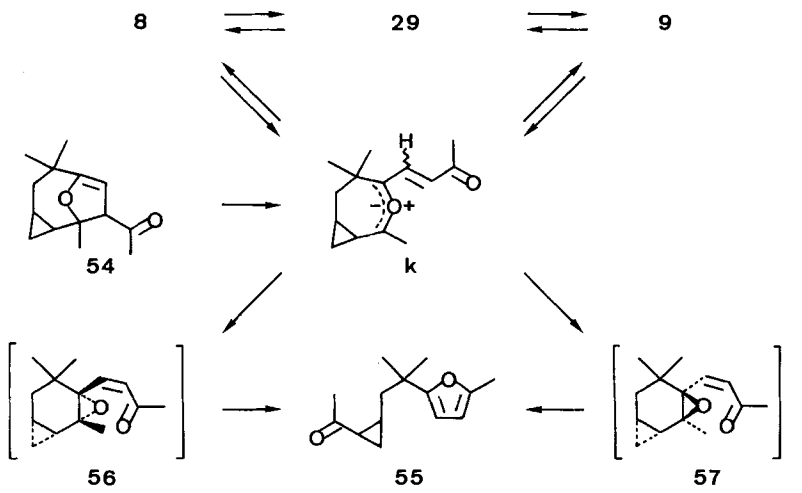


and **36**. Further, it could be shown by thermolysis of the vinyl allyl ether **35** that the cycloheptadienol **36** is formed by a *Claisen* rearrangement of the former. The origin of **35**, which was also formed from the photolysis of **10** [21], could not yet be satisfactorily explained.

In contrast to the diepoxide **7**, thermolysis of the spirocyclic diepoxide **6** ($C_{14}H_{20}O_3$) led only to the isomer **24**, arising from the [1,5] homosigmatropic H-shift, and, surprisingly, to **14** ($C_{13}H_{20}O_2$, *Scheme 3*), a formal decarbonylation product of **6**, for whose formation no satisfactory mechanism can be proposed so far.

As already mentioned, thermolysis of the methanoepoxyenones **8** and **9** leads to interconversion of the two diastereomers either *via* the divinyl ether **29** and, in addition, possibly *via* the ylide intermediate **k** *(Scheme 9)*: Analogous behavior is observed with the corresponding epoxydienes **11** and **12** producing the divinyl ether **38** (see *Table*). Photolysis of **8** and **9** does not give rise to mutual interconversion of **8** and **9**, but to formation of **29**; however, the tricyclic compound **54** *(Scheme 9)* was obtained as an additional product [22]. Since the latter was not detected on thermolysis of **8** and **9**, it was of interest to investigate its thermal behavior. At 520°, compounds **8** (5%), **9** (1%), **29** (5%), and **55** (32%) were obtained. Hence, **54** shows behavior analogous to that of **22B** *(Scheme 6)* undergoing non-stereospecific cleavage to an (*E*)/(*Z*)-mixture of the ylide **k** which undergoes ring closure yielding the (*E*)-epoxyenones **8** and **9** and their (*Z*)-isomers

Scheme 9

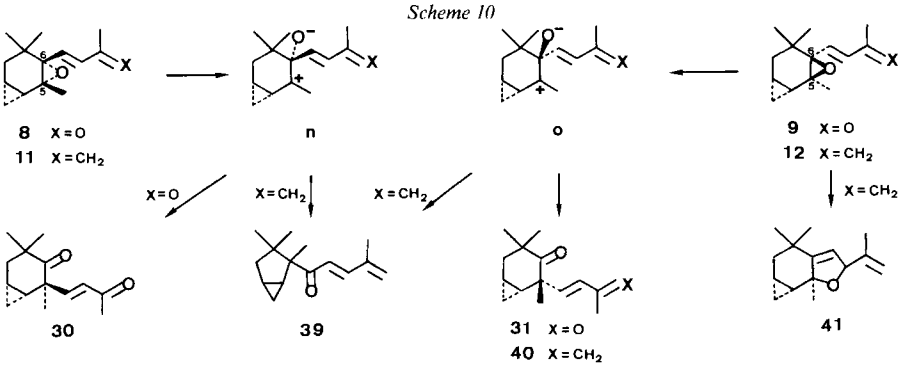


56 and **57**, respectively *(Scheme 9)*. Under the reaction conditions, **56** and **57** subsequently reacted to the furan **55**. On thermolysis of **54** at 390°, under conditions at which the epoxyenones **8** and **9** are stable, compounds **8** (11%), **9** (1%), and **55** (58%) were obtained; the divinyl ether **29** was, however, not detected. This finding further supports the above hypothesis that on thermolysis, the divinyl ethers of type **II** are formed by a [1,5] homosigmatropic H-shift and not *via* an ylide intermediate.

On thermolysis of the epoxides **8**–**12**, the C–O bond cleavage was also observed. Thus, compounds **33**, **34**, and **41** were formed by cleavage of the C(6)–O bond, whereas

compounds **30**, **31**, **39**, and **40** were formed by cleavage of the C(5)–O bond (see *Table* and *Schemes 8* and *10*). It is noteworthy that the thermal reactions of the cyclopropylepoxydienes **11** and **12** in untreated tubes required much lower temperatures (see *Table*). Comparison of the results of the thermolyses of **8**–**12** in silylated and untreated tubes clearly shows that epoxides substituted with electron-donating diene or cyclopropyl groups are particularly sensitive to the acidic surface sites, which cannot be completely suppressed by silylation of the glass surface. That the reactions involving cleavage of the C–O bond of the oxirane are surface-catalyzed was shown by thermolysis through untreated tubes. The thermolysis of **8**, *e.g.* through untreated *Pyrex* or quartz tubes, induced cleavage of the C(5)–O bond and migration of the enone side chain leading to compound **30** *(Scheme 10)* in 53% yield, but the divinyl ether **29** *(Scheme 9)* and the diastereomeric epoxide **9** were not formed. Under the same conditions, the diastereomeric epoxyenone **9** gave a mixture of compounds **30** and **31** in 20 and 40% yield, respectively. Thermolysis of the epoxydiene **10** on untreated glass resulted in only a small increase of the amounts of compounds **33** and **34** (see *Table* and *Scheme 8*). This finding indicates that the transformation **10**→**50**→**37** *(Scheme 7)* can also be surface-catalyzed, in analogy to the *Lewis*-acid-catalyzed formation of the (*E*)-isomer of **50** in solution [19]. Whereas the diepoxydiene **10** additionally underwent C(6)–O bond cleavage of the oxirane leading to **33** and **34**, thermolysis of **11** and **12** under acidic conditions did not involve this type of process. Instead, **11** and **12** selectively underwent cleavage of the oxirane C(5)–O bond adjacent to the cyclopropyl function leading to the dipolar intermediates **n** and **o**, respectively. The latters react by ring contraction (**n** or **o**→**39**) or by migration of the diene side chain (**o**→**40**; *Scheme 10*). The rapid ring opening of cyclopropylmethyl to homoallyl radicals, a useful mechanistic probe for the detection of radical intermediates [23], would intervene, if **n** and **o** were radical intermediates. Thus, the isolation of products **30**, **31**, **39**, and **40** is a feasible proof for an ionic mechanism. Finally, in the

Scheme 10

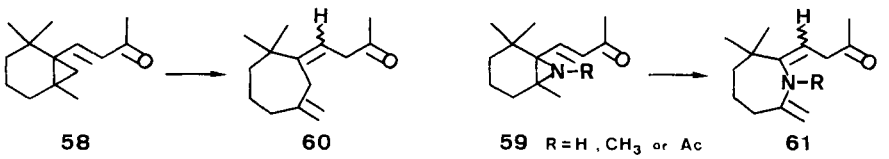


formation of compounds **33**, **34** *(Scheme 8)*, and **41** *(Scheme 10)*, which are also products of the triplet excitation of **10** [21] and **12** [24], respectively, the intermediacy of biradicals has not been disproved, although an acid-catalyzed reaction seems to be most likely.

Conclusion. – On thermolysis, the epoxyenones **1**–**9** and the epoxydienes **10**–**12** were transformed to compounds of type **II**–**VIII** *via* C–C or C–O bond cleavage of the

oxirane. With the exception of **V** and **VI**, products of these types have also been observed on photolysis of some of the epoxides. The formation of the same kind of products, however, does not necessarily imply the same mechanisms. Thus, the divinyl ethers **13** and **29**, which are also photoproducts of **1** and **8** or **9**, respectively, [25] [22] were shown to be products of a thermal [1,5] homosigmatropic H-shift, but on photolysis, they presumably arise from a 1,6-H-shift *via* carbonyl ylides [22]. It is noteworthy that the thermal reactions of epoxides in the ionone series leading to divinyl ethers of type **II** is paralleled by the transformation of 5,6-methano-5,6-dihydro-β-ionone (**58**) [26] and 5,6-epimino-5,6-dihydro-β-ionone (**59**) and its derivatives to their corresponding monocyclic isomers **60** and **61**, respectively *(Scheme 11)*[8]).

Scheme 11



58 **60** **59** R=H, CH_3 or Ac **61**

A general photochemical reaction which is observed on $^1\pi,\pi^*$-excitation of the epoxyenones **1–9** is the cleavage of the C–C bond of the oxirane leading to carbonyl ylides [15]. As shown above, several products which may be formed *via* carbonyl-ylide intermediates were isolated also on thermolysis of the epoxides **1–12**. The results demonstrate that the extent of the formation of ylide products is clearly related to the conjugating ability of the groups neighboring the epoxy function. For example, the double bond in the epoxyenone **3** and the carbonyl group in **5** have a strongly accelerating effect on the epoxide ring opening, and the oxirane and cyclopropane in **7** and **8** or **9**, respectively, a somewhat smaller one. On thermolysis of compounds **1**, **2**, **4**, and **6**, products of an ylide intermediate have not been detected within the limits of our experiments. Also thermolysis of optically active epoxyenone (–)-**1** (455°, 12% conversion) did not give rise to racemization, whereas, at the same temperature, the 4-oxo-epoxyenone (–)-**5** showed 37% conversion to products, and the recovered epoxyenone was completely racemic.

In contrast to their photochemical reactions, thermolysis of **1–12** does not give rise to formation of carbene products [15]. Finally, **1–12** undergo thermal cleavage of the C–O bonds of the oxirane, which was also observed on their photolyses. As shown above, this thermal cleavage of the C–O bond is presumably acid-catalyzed.

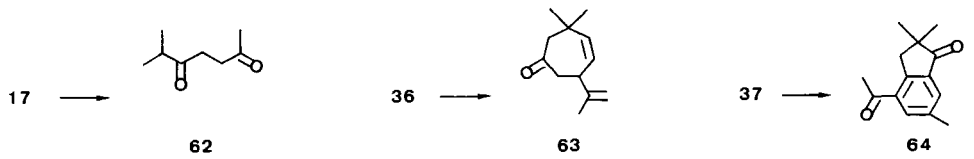
3. Structure of the New Products. – The structures of all new compounds were deduced from their spectral data. Since most of the compounds obtained here were known or are analogs of known products, previously obtained on photolyses of the epoxides **1–12**, only the most relevant spectral data are discussed here together with the chemical transformations which confirmed the assigned structures. For full spectral data and the NMR assignments, see *Exper. Part.*

Divinyl Ethers **13**, **20**, **21**, **24** [28], **25**, **29** [22], *and* **38**. The enol-ether moieties are evidenced by IR bands between 1630–1700 cm^{-1}, by ^{1}H-NMR signals of the methylidene group between 4–5 ppm and of the H-atom of the trisubstituted double bond between 5.0–5.5 ppm, and by a *t* (85–100 ppm), a *d* (100–110 ppm), and 2*s* (150–160 ppm) in the ^{13}C-NMR spectra. Finally, the carbonyl compound **29** [22] was transformed by a *Wittig* reaction to the corresponding olefin **38**.

The *divinyl ether* **17** was hydrolyzed (aq. CH_3COOH) to the known diketone **62** [7] *(Scheme 12)*.

[8]) Private communication by *E. P. Müller*, University of Innsbruck, see [27].

Scheme 12



The *enol-β-diketone* **36** was transformed to the cycloheptenone **63** by reaction with KOH *(Scheme 12)* (for analogous reactions of 2-acetyl-cycloalkanones, see [29]).

The *acetylbicyclo[4.3.0]nonenone* **37** *(Scheme 12)* was converted to the indanone compound **64** by reaction with *N*-bromo-succinimide followed by elimination of HBr with Li_2CO_3/LiF/DMF [30].

Bicyclo[4.1.0]heptan-3-ones **30** *and* **31** *(Scheme 10).* The marked differences in the positions of the UV maxima (**30**: 237 nm, **31**: 209 nm) and the *AB* systems of the olefinic H-atoms (**30**: 7.25 ppm, **31**: 6.56 ppm) in the ^{1}H-NMR spectra indicate a conjugation of the enone and the cyclopropane ring in **30** and allow the assignment of the configuration, since inspection of models showed that only in **30**, conjugation of the enone with the *Walsh* orbitals of the cyclopropane moiety is possible.

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Experimental Part

General. See [31], except as noted below. Anal. gas chromatography (GC) 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). 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 $CDCl_3$ solns. on a *Bruker WP-80-CW* (80 MHz) instrument or, exceptionally (as indicated below) on a *Bruker WM-300* (300 MHz) or a *Varian HA-100* (100 MHz) instrument.

Treatment of the Thermolyses Tube. The tube and packing were treated with HCl (conc. aq.) and NH_3/edta (aq.) as described in [8]; 30 min before thermolysis of the substrate, bis(trimethylsilyl)acetamide was passed through the hot oven. Some effort was made to avoid air entering the thermolysis tube when it was hot. After *ca.* 10 thermolyses, the tube and fresh packing were treated again as above.

Description of the Thermolyses Procedure. The oven, tube, packing, and procedure were copied from *Karpf* and *Dreiding* [32]. The substances to be thermolyzed were evaporated by means of a heating tape (50–100°) from a boat placed in the thermolysis tube at the mouth of the oven. The vapors were swept through the oven by a N_2 stream (8 ml/min) into a trap cooled by liq. N_2. The system was evacuated to 0.04 Torr throughout. After the thermolysis, the system was filled with N_2 and the trap warmed to r.t. Unless otherwise stated, the thermolyses were carried out in treated tubes, and the yields were determined by GC and ^{1}H-NMR (80 MHz) analysis of the thermolysis mixture and are based on the amount of converted starting material.

1. Thermolyses of the Epoxides 1–12. – 1.1. *(E)-4-(1',2'-Epoxy-2',6',6'-trimethylcyclohexyl)-3-buten-2-one* (**1**). – 1.1.1. *Racemic Epoxyenone* (±)-**1**. *a*) Thermolysis of (±)-**1** (325 mg, 1.56 mmol) at 585° in a silylated tube (conversion 41%) yielded a mixture of **13** (78%), **14** [25] (5%), and **15** [7] (2%), according to GC and ^{1}H-NMR. Several batches were combined and chromatographed (AcOEt/hexane 1:9) and the products finally purified by HPLC (AcOEt/hexane 1:33). *b*) Thermolysis of (±)-**1** at 560° in a tube conditioned with edta without silylation (conversion 48%) afforded a mixture of **13** (63%) and **15** (8%). *c*) Thermolysis of (±)-**1** in an untreated tube (conversion 83%) gave a mixture of **13** (14%), **14** (12%), and **15** (36%).

4-(7',7'-Dimethyl-3'-methylidene-2'-oxacycloheptylidene)-2-butanone (**13**). IR: 3115*w*, 2960*s*, 2925*s*, 2865*w*, 1755*w*, 1715*s*, 1672*w*, 1630*m*, 1470*w*, 1445*w*, 1430*w*, 1385*m*, 1353*s*, 1342*m*, 1299*w*, 1265*m*, 1230*m*, 1215*m*, 1155*m*, 1115*s*, 1065*w*, 1022*w*, 980*w*, 960*w*. ^{1}H-NMR: 1.14 (*s*, 2 CH_3–C(7')); 2.15 (*s*, 3H–C(1)); 1.2–2.3 (*m*, 2H–C(4'), 2H–C(5'), 2H–C(6')); 3.22 (*d*, J = 6, 2H–C(3)); 4.00, 4.30 (2*s*, CH_2=C(3')); 5.23 (*t*, J = 6, H–C(4)). ^{13}C-NMR: 26.8 (*q*, 2 CH_3–C(3')); 29.5 (*q*, C(1)); 24.1, 30.9 (2*t*, C(5'), C(6')); 40.1, 42.5 (2*t*, C(4'), C(3)); 87.9 (*t*, CH_2=C(3')); 105.5 (*d*, C(4)); 38.7 (*s*, C(7')); 160.3, 161.5 (2*s*, C(1'), C(3')); 206.2 (*s*, C(2)). MS: 208 (5, M^+, $C_{13}H_{20}O_2$), 165 (36), 123 (14), 109 (11), 107 (41), 99 (11), 95 (18), 81 (12), 79 (11), 69 (21), 67 (20), 55 (20), *43* (100), 41 (25).

1.1.2. *(–)-***1**. Thermolysis of (–)-**1** [34] ($[\alpha]_D$ = –92° (*c* = 1.0, $CHCl_3$); 27 mg, 0.13 mmol) at 455° led to a mixture (25 mg) of (–)-**1** (88%) and **13** (10%); the mixture was chromatographed (12 g SiO_2, AcOEt/hexane 1:4) to yield (–)-**1** (17 mg; $[\alpha]_D$ = –92° (*c* = 1.0, $CHCl_3$)).

1.1.3. *[2'-methyl-$^2H_3$,3',3'-$^2H_2$]-4-(1',2'-Epoxy-2',6',6'-trimethylcyclohexal)-3-buten-2-one* ((D$_5$)-**1**). *a*) *At 520°*. The epoxyenones **1** and (D$_5$)-**1** (5 mg each) were thermolyzed separately and consecutively three times each. GC indicated the following yields: **1** (37.9, 40.4, 40.5; mean = 39.6%), **13** (45.4, 41.0, 44.1; mean = 43.5%); (D$_5$)-**1** (58.0, 55.2; mean = 56.6%), (D$_5$)-**13** (35.8, 32.0; mean = 33.9).

b) *At 455°*. Compounds **1** and (D$_5$)-**1** (5 mg each) were thermolyzed separately and consecutively three times each. GC indicated the following yields: **1** (85.4, 86.7, 86.3%; mean = 86.1%), **13** (13.2, 11.2, 10.2; mean = 11.5%); (D$_5$)-**1** (92.1, 92.7, 93.5; mean = 92.8%); (D$_5$)-**13** (6.6, 5.9, 6.4; mean = 6.3%). From this experiment, the ratios of the conversions **1**/(D$_5$)-**1** and the product yields **13**/(D$_5$)-**13** were determined to be 1.9 and 1.8, resp.

1.2. *(E,1'RS,3'RS,6'SR)-4-(1',6'-Epoxy-3'-hydroxy-2',2',6'-trimethylcyclohexyl)-3-buten-2-one* (**2**). The epoxyenone **2** (470 mg, 2.10 mmol) was thermolyzed at 520° (conversion 85%). The mixture was chromatographed (75 g SiO_2, AcOEt/hexane 2:3→4:1) to produce fractions containing the following compounds (^{1}H-NMR and GC): **16** (7%) and **17** (32%). The epoxyenones **2** and **16** were separated by further chromatography (acetone/CH_2Cl_2 1:20).

(E,1'RS,3'SR,6'SR)-4-(1',6'-Epoxy-3'-hydroxy-2',2',6'-trimethylcyclohexyl)-3-buten-2-one (**16**). IR: 3640*w*, 3510*w* (br.), 2960*s*, 2930*s*, 2870*w*, 1695*s*, 1675*s*, 1623*s*, 1456*w*, 1443*w*, 1430*w*, 1420*w*, 1378*m*, 1355*s*, 1291*m*, 1248*m*, 1170*w*, 1116*w*, 1040*m*, 1010*m*, 983*m*, 940*w*, 910*w*, 888*w*, 868*w*. ^{1}H-NMR: 1.03, 1.13, 1.15 (3*s*, CH_3–C(6'), 2 CH_3–C(2')); 1.0–2.1 (*m*, 2H–C(5'), 2H–C(4')); 1.92 (*s*, OH); 2.29 (*s*, 3H–C(1)); 3.61 (*dd*, J_1 = 5, J_2 = 8, H–C(3')); 6.66 (*AB* system, J = 16, δ_A = 6.28, δ_B = 7.03, H–C(3), H–C(4)). ^{13}C-NMR: 18.9, 20.5, 22.8, 28.2 (4*q*, C(1), CH_3–C(6'), 2 CH_3–C(2')); 24.9, 28.0 (2*t*, C(5'), C(4')); 71.4 (*d*, C(3')); 132.5, 142.2 (2*d*, C(3), C(4)); 38.0 (*s*, C(2')); 65.5, 71.9 (2*s*, C(1'), C(6')); 197.7 (*s*, C(2)). MS: 224 (< 1, M^+, $C_{13}H_{20}O_3$), 165 (15), 125 (12), 124 (21), *123* (100), 109 (42), 101 (17), 98 (14), 83 (13), 55 (17), 43 (98), 41 (17).

4-Methylidene-5-oxa-9-oxo-6-isopropylidenedecanal (**17**). IR: 3115*w*, 2970*w* (br.), 2915*m*, 2875*w*, 2815*w*, 2720*w*, 1718*s*, 1660*w*, 1628*m*, 1435*m*, 1382*w*, 1358*m*, 1288*w*, 1270*m*, 1242*m*, 1197*w*, 1182*m*, 1160*m*, 1146*m*, 1115*m*, 1040*w*. ^{1}H-NMR: 1.52, 1.70 (2*s*, 2 CH_3–C=C(6)); 2.14 (*s*, 3H–C(10)); 2.3–2.8 (*m*, 2H–C(2), 2H–C(3), 2H–C(7), 2H–C(8)); 3.94 (*m*, $w_{1/2}$ = 6, CH_2=C(4)); 9.80 (*m*, $w_{1/2}$ = 4, H–C(1)). ^{13}C-NMR: 17.4, 18.4, 29.9 (3*q*, 2 CH_3–C=C(6), C(10)); 22.4, 27.1 (2*t*, C(3), C(7)); 41.1 (*t*, C(8)); 41.4 (*m*, C(2)); 84.3 (*t*, CH_2=C(4)); 201.6 (*d*, C(1)); 119.3 (*s*, 2 CH_3–*C*=C(6)); 142.8 (*s*, C(6)); 157.9 (*s*, C(4)); 208.1 (*s*, C(9)). MS: 224 (2, M^+, $C_{13}H_{20}O_3$), 124 (14), 109 (29), 99 (20), 71 (11), 55 (12), *43* (100), 41 (13).

1.3. *(E)-4-(1',2'-Epoxy-2',6',6'-trimethyl-3'-cyclohexenyl)-3-buten-2-one* (**3**). 1.3.1. *At 325°*. Thermolysis of compound **3** (451 mg, 2.19 mmol) at 325° (conversion 30%) produced a mixture containing **18** [14] (73%, ^{1}H-NMR, GC). Chromatography (20 g SiO_2, AcOEt/hexane 1:9) gave pure **18** (38 mg, 28%).

1.3.2. *At 560°*. Thermolysis of **3** (513 mg, 2.49 mmol) at 560° (conversion 100%) gave a mixture (360 mg) which contained **19** (*ca.* 85%; NMR, GC). The mixture was chromatographed (20 g SiO_2, AcOEt/hexane 1:6) yielding pure **19** [33] (185 mg, 36%).

1.4. *(E)-4-(1',2'-Epoxy-2',6',6'-trimethyl-3'-methylidenecyclohexyl)-3-buten-2-one* (**4**). Thermolysis of **4** (*ca.* 10 mg) at 455° (63% conversion) gave a mixture which contained **20** (52%; GC).

4-(7',7'-Dimethyl-3',4'-dimethylidene-2'-oxa-1'-cycloheptylidene)-2-butanone (**20**). ^{1}H-NMR: 1.15 (*s*, 2 CH_3–C(7')); 1.20–1.70 (*m*, 2H–C(6')); 2.13 (*s*, 3H–C(1)); 2.15–2.40 (*m*, 2H–C(5')); 3.20 (*d*, J = 6, 2H–C(3)); 4.45 (*s*, CH_2=C(3')); 4.93, 5.22 (2*m*, $w_{1/2}$ = 3, CH_2=C(4')); 5.24 (*t*, J = 6, H–C(4)).

1.5. *(E)-4-(1',2'-Epoxy-2',6',6'-trimethyl-3'-oxocyclohexyl)-3-buten-2-one* ((±)-**5**). 1.5.1. (±)-**5**. Thermolysis of (±)-**5** (506 mg, 2.28 mmol) at 520° (conversion 94%) gave a mixture which was filtered through a plug of SiO_2 (Et_2O). The mixture (470 mg) was chromatographed (75 g SiO_2; AcOEt/hexane 3:7) to produce fractions which were estimated to contain (^{1}H-NMR, GC) **21** (7%), **22A** (6%), **22B** (15%), and **23** (10%). The isomers **22A** and **22B** were separated by HPLC (Et_2O/hexane 1:4).

4-(3'-Oxobutylidene)-5,5-dimethyl-2-methylidene-3-oxacycloheptanone (**21**). IR: 3080*w* (sh), 2962*m*, 2925*m*, 2865*w*, 1735*m*, 1717*s* (br.), 1678*w* (sh), 1610*m*, 1470*w*, 1459*w*, 1448*w*, 1405*w*, 1385*w*, 1356*m*, 1295*m*, 1275*s*, 1235*m*, 1157*m*, 1107*m*, 1087*w*, 1048*m*, 1022*w*, 980*w*, 956*w*, 938*w*, 908*m*, 887*w*. ^{1}H-NMR: 1.22 (*s*, 2 CH_3–C(5)); 2.14 (*s*, 3H–C(4')); 1.00–2.60 (*m*, 2H–C(6), 2H–C(7)); 3.21 (*d*, J = 7, 2H–C(2')); 4.87, 5.23 (2*m*, $w_{½}$ = 2, CH_2=C(2)); 5.40 (*t*, J = 7, H–C(1')). MS: 222 (2, M^+, $C_{13}H_{18}O_3$), 179 (14), 137 (10), 123 (33), 109 (15), 95 (12), 86 (19), 84 (29), 67 (11), 55 (18), 44 (16), *43* (100), 41 (18).

8-Acetyl-1,5,5-trimethyl-9-oxabicyclo[4.2.1]non-6-en-2-one, Isomer A (**22A**; 90% pure). UV (0.614 mg in 10 ml pentane): 218 (3690). IR: 2965*m*, 2930*w*, 2870*w*, 1720*s*, 1710*s*, 1625*w*, 1468*w*, 1450*w*, 1420*w*, 1388*w*, 1375*w*, 1368*w*, 1353*m*, 1318*w*, 1278*w*, 1245*w*, 1220*w*, 1192*w*, 1164*w*, 1136*w*, 1083*m*, 1060*w*, 930*w*, 896*w*, 888*w*. ^{1}H-NMR: 1.19, 1.26 (2*s*, 2 CH_3–C(5)); 1.66 (*s*, CH_3–C(1)); 2.26 (*s*, CH_3–CO); 1.0–2.3 (*m*, H–C(3), 2H–C(4)); 2.82–3.60 (*m*, H–C(3)); 4.00 (*m*, $w_{½}$ = 3, H–C(8)); 5.38 (*m*, $w_{½}$ = 3, H–C(7)). MS: 179 (17, $M^+ - CH_3CO$), 123 (34), 97 (19), 68 (24), 55 (18), *43* (100), 41 (25).

Isomer B (**22B**). UV (0.970 mg in 10 ml pentane): 229 (2990). IR: 2982*m*, 2930*m*, 2870*w*, 2820*w*, 1720*s* (br.), 1620*w*, 1467*w*, 1448*w*, 1440*w*, 1420*w*, 1388*w*, 1376*w*, 1368*m*, 1353*m*, 1336*w*, 1318*w*, 1295*w*, 1255*w*, 1218*m*, 1205*w*, 1197*w*, 1181*w*, 1152*w*, 1131*w*, 1111*w*, 1088*m*, 1058*w*, 1012*w*, 977*w*, 930*w*, 909*w*, 890*w*. ^{1}H-NMR: 1.22 (3H), 1.35 (6H) (2*s*, 2 CH_3–C(5), CH_3–C(1)); 2.23 (*s*, CH_3–CO); 1.1–2.2 (*m*, H–C(3), 2H–C(4)); 3.20 (*d*, J = 4, H–C(8)); 3.05–3.45 (*m*, H–C(3)); 5.21 (*d*, J = 4, H–C(7)). ^{13}C-NMR: 16.1, 21.4, 24.3, 29.5 (4*q*, CH_3–C(1), 2 CH_3–C(5), CH_3–CO); 39.0 (*t*, C(4)); 50.1 (*t*, C(3)); 60.5 (*d*, C(8)); 103.1 (*d*, C(7)); 39.6 (*s*, C(5)); 95.8 (*s*, C(1)); 174.7 (*s*, C(6)); 207.7 (*s*, CH_3–CO); 219.1 (*s*, C(2)). MS: 179 (34, $M^+ - CH_3CO$), 125 (24), 123 (65), 109 (22), *43* (100), 41 (19).

1.5.2. *(–)*-**5**. 1.5.2.1. *At 455°*. Thermolysis of (–)-**5** [17] (54 mg, 0.24 mmol; $[\alpha]_D = -131°$ ($CHCl_3$, c = 1.0); conversion 37%) gave a mixture which was chromatographed (12 g SiO_2; AcOEt/hexane 1:4) to yield fractions which were estimated to contain (^{1}H-NMR, GC) **21** (51%), **22A** (16%), and **22B** (27%). The purified products and the starting material were all *racemic*.

1.5.2.2. *At 390°*. Compound (–)-**5** (28 mg, 0.13 mmol; $[\alpha]_D = -131°$ ($CHCl_3$, c = 1.0)) was thermolyzed to produce a mixture (30 mg) which contained according to GC **5** (95%), **21** (4%), and **22A** + **B** (1%). The mixture had $[\alpha]_D = -34°$.

1.5.2.3. *At 324°*. Thermolysis of (–)-**5** (37 mg, 0.17 mmol; $[\alpha]_D = -131°$ ($CHCl_3$, c = 1.0)) was thermolyzed to produce pure unconverted (–)-**5** (GC; $[\alpha]_D = -130°$ ($CHCl_3$, c = 1.0)).

1.6. *4-{[(2',3'-Epoxy-2',4',4'-trimethylcyclohexane)-2"-oxiran]-3'-yl}-3-buten-2-one* (**6**). Compound **6** (114 mg, 0.48 mmol) was thermolyzed at 520° (conversion 94%). The mixture (102 mg) was chromatographed (20 g SiO_2; AcOEt/hexane 1:4) to produce fractions which were estimated to contain (^{1}H-NMR, GC) **14** (16%) [25] and **24** (10%) [28].

1.7. *(E,1'RS,2'SR,3'SR,4'SR)-4-(1',2';3',4'-Diepoxy-2',6',6'-trimethylcyclohexyl)-3-buten-2-one* (**7**). 1.7.1. *In a Silylated Tube*. Compound **7** [20] (94 mg, 0.42 mmol) was thermolyzed at 450° (conversion 89%) to yield a mixture whose GC analysis indicated **25** (52%), **26** (14%), **28A** (7%), and **28B** (18%).

1.7.2. *In an Untreated Quartz Tube*. Thermolysis of **7** (1.125 g, 5.07 mmol) at 450° (conversion 67%). The mixture was chromatographed (Et_2O/pentane 2:1) to given fractions which contained (^{1}H-NMR, GC) **25** (37%), **26** (5%), **27** (3%), **28A** (7%), and **28B** (18%).

4-(5',5'-Dimethyl-2'-methylidene-3',8'-dioxabicyclo[5.1.0]oct-4-ylidene)-2-butanone (**25**; contaminated with *ca.* 20% of **26**). B.p. 95°/0.04 Torr. IR: 3120*w*, 3080*w*, 2970*s*, 2930*m*, 2875*m*, 1721*s*, 1678*m*, 1641*s*, 1630*s*, 1471*m*, 1461*m*, 1450*m*, 1424*m*, 1395*m*, 1386*m*, 1365*s*, 1342*s*, 1312*m*, 1290*m*, 1275*m*, 1265*m*, 1240*s*, 1220*m*, 1189*w*, 1159*s*, 1128*m*, 1115*s*, 1085*m*, 1058*m*, 1025*m*, 992*w*, 982*w*, 955*w*, 912*m*, 842*m*. ^{1}H-NMR: 1.20 (*s*, 2 CH_3–C(5')); 1.65–1.98 (*m*, 2H–C(6')); 2.16 (*s*, 3H–C(1)); 3.15–3.48 (*m*, H–C(1'), H–C(7')); 3.22 (*d*, J = 7, 2H–C(3)); 4.65 and 4.85 (2*d*, J = 1.5, CH_2=C(2')); 5.08 (*t*, J = 7, H–C(4)). ^{13}C-NMR: 27.5, 29.2, 29.5 (3*q*, 3 CH_3); 39.7, 40.0 (2*t*, C(3), C(6')); 98.5 (*t*, CH_2=C(2')); 53.7, 54.7 (2*d*, C(1'), C(7')); 104.3 (*d*, C(4)); 38.8 (*s*, C(5')); 155.6, 159.5 (2*s*, C(3'), C(4')); 206.3 (*s*, C(2)). MS: 222 (1, M^+, $C_{13}H_{18}O_3$), 151 (10), 109 (12), 95 (10), 91 (10), 81 (18), 79 (10), 69 (29), 67 (10), 55 (39), 53 (11), *43* (100), 41 (31), 39 (17).

(E,1'RS,2'SR,3'RS,4'RS)-4-(1',2';3',4'-Diepoxy-2',6',6'-trimethylcyclohexyl)-3-buten-2-one (**26**). B.p. 100°/0.03 Torr. UV (0.128 mg in 10 ml): 226 (10000). UV (2.3 mg in 2 ml). 280 sh (120), end absorption to 400. IR: 3000*m*, 2990*m*, 2965*s*, 2930*m*, 2915*m* (sh), 2870*w*, 1700*s*, 1678*s*, 1636*m*, 1626*s*, 1460*m*, 1450*m*, 1425*w*, 1395*w*, 1379*m*, 1363*s*, 1354*s*, 1300*m*, 1274*s*, 1254*m*, 1242*s*, 1167*w*, 1160*m*, 1075*w*, 1056*w*, 1028*w*, 1025*w*, 1000*w*, 982*s*, 968*w*, 920*w*, 909*w*, 868*w*, 840*m*. ^{1}H-NMR (100 MHz, CCl_4): 0.88, 1.28, 1.36 (3*s*, 2 CH_3–C(6'), CH_3–C(2')); 1.68–1.80 (*m*, 2H–C(5')); 2.16 (*s*, 3H–C(1)); 2.98–3.13 (*m*, H–C(3'), H–C(4')); 6.46 (*AB* system, J = 15, δ_A = 6.13, δ_B = 6.80, H–C(3), H–C(4)). ^{13}C-NMR: 18.1, 27.5, 27.7, 28.2 (4*q*, 4 CH_3); 35.3 (*t*, C(5')); 52.9, 53.9 (2*d*, C(3'), C(4')); 133.2, 140.3 (2*d*, C(3), C(4)); 33.4 (*s*, C(6')); 64.7, 70.8 (2*s*, C(1'), C(2')); 197.3 (*s*, C(2)). MS: 222 (1, M^+, $C_{13}H_{18}O_3$), 125 (48), 123 (21), 107 (11), 98 (33), 96 (11), 83 (18), 55 (14), *43* (100).

5-Acetyl-3,8,8-trimethyl-4-oxabicyclo[4.3.0]non-2-en-7-one, Isomer A (**28A**). B.p. 70°/0.04 Torr. UV (0.626 mg in 25 ml MeCN): 240 sh (1240). UV (1.090 mg in 2 ml MeCN): 294 (220), end absorption to 390. IR: 3060*w*, 3022*w*, 2963*m*, 2930*m*, 2905*m*, 2870*m*, 1740*s*, 1720*s*, 1675*s*, 1468*w*, 1445*m*, 1432*w*, 1420*w*, 1382*s*, 1358*s*, 1338*w*, 1325*m*, 1289*s*, 1275*m*, 1250*w*, 1229*s*, 1210*m*, 1197*m*, 1180*m*, 1150*s*, 1110*m*, 1060*s*, 1035*w*, 911*w*, 881*m*, 855*w*. ^{1}H-NMR (300 MHz): 1.09 (*s*, 2 CH_3–C(8)); 1.77 (*dd*, J_1 = 2.04, J_2 = 0.98, CH_3–C(3)); 1.89 (*AB* system, J = 13.3, δ_A = 1.76, split into *d*, J = 1.3, partly overlapping with signal at 1.77, δ_B = 2.02, split into *d*, J = 7.3, 2H–C(9)); 2.24 (*s*, CH_3–CO); 2.74–2.75 (*m*, H–C(1)); 3.13 (*ddd*, J_1 = 8.2, J_2 = 2.2, J_3 = 1.3, H–C(6)); 4.49–4.51 (*m*, H–C(2)); 4.77 (*d*, J = 2.2, H–C(5)). ^{13}C-NMR: 20.1, 26.0, 27.1, 27.4 (4*q*, 4 CH_3); 42.7 (*t*, C(9)); 27.4 (*d*, overlapping with *q*, C(1)); 47.2 (*d*, C(6)); 78.3 (*d*, C(5)); 102.0 (*d*, C(2)); 43.5 (*s*, C(8)); 150.3 (*s*, C(3)); 209.5, 220.8 (2*s*, C(7), CH_3CO). MS: 222 (7, M^+, $C_{13}H_{18}O_3$), 180 (4), 179 (43), *95* (100). 43 (26), 41 (15).

Isomer B (**28B**). M.p. 84–86° (Et_2O/pentane). UV (0.413 mg in 20 ml MeCN): 233 (2500). UV (1.717 mg in 2 ml MeCN): 300 (270), 305 sh (206), end absorption to 370. IR: 3060*w*, 2961*s*, 2925*s*, 2900*m*, 2870*m*, 1740*s*, 1720*s*, 1675*m*, 1467*m*, 1456*m*, 1445*m*, 1431*m*, 1415*m*, 1381*s*, 1358*s*, 1330*m*, 1305*m*, 1285*w*, 1269*s*, 1240*m*, 1211*w*, 1194*m*, 1172*s*, 1132*m*, 1117*s*, 1090*s*, 1070*m*, 1041*m*, 1030*w* (sh), 1001*w*, 952*w*, 940*w*, 911*m*, 866*w*. ^{1}H-NMR (300 MHz): 1.04, 1.09 (2*s*, 2 CH_3–C(9)); 1.69 (*AB* system, J = 12.3, δ_A = 1.64, split into *d*, J = 7.1, broadened, δ_B = 1.75, broadened, 2H–C(10)); 1.82 (*dd*, J_1 = 2.1, J_2 = 1.0, CH_3–C(3)); 2.31 (*s*, CH_3–CO); 2.90–3.00 (*m*, H–C(1)); 3.02–3.07 (*m*, H–C(6)); 4.29 (*d*, J = 2.5, H–C(5)); 4.40–4.41 (*m*, H–C(2)). MS: 222 (6, M^+, $C_{13}H_{18}O_3$), 180 (11), 179 (11), *95* (100), 43 (26), 41 (13). Anal. calc. for $C_{13}H_{18}O_3$ (222.27): C 70.24, H 8.16; found: C 70.17, H 8.15.

1.8. *(E,1′RS,2′SR,3′RS,6′RS)-4-(2′,3′-Epoxy-4′,4′-dimethylbicyclo[4.1.0]hept-3′-yl)-3-buten-2-one* (**8**).

1.8.1. *In a Silylated Tube.* Compound **8** [22] (107 mg, 0.49 mmol) was thermolyzed at 520° (conversion 85%) to give a mixture from which, after distillation (100°/0.03 Torr) the following yields were determined (^{1}H-NMR, GC): **9** [22] (5%), **29** [22] (45%), and **30** (7%).

1.8.2. *In an Untreated Quartz Tube.* Thermolysis of **8** (75 mg, 0.34 mmol) at 520° (conversion 100%) and chromatography (Et_2O/hexane 1:3) gave **30** (40 mg, 53%).

(1′RS,2′SR,6′RS)-4-(3′-Oxo-2′,4′,4′-trimethylbicyclo[4.1.0]hept-2′-yl)-3-buten-2-one (**30**). B.p. 90°/0.04 Torr. UV (1.182 mg in 50 ml): 237 (11800). UV (1.219 mg in 2 ml): 345 (70), end absorption to 450. IR: 3090*w*, 3018*m*, 2980*m*, 2960*m*, 2925*m* (sh), 2920*m*, 2870*m*, 2860*m*, 1700*m*, 1674*s*, 1610*w*, 1460*m*, 1455*m*, 1442*m*, 1420*w*, 1390*m*, 1370*m*, 1357*s*, 1300*m* (sh), 1283*s*, 1265*m*, 1239*m*, 1210*w*, 1185*w*, 1168*m*, 1152*w*, 1138*w*, 1085*w*, 1040*m*, 1025*m*, 995*w*, 975*m*. ^{1}H-NMR: 0.35–1.55 (*m*, H–C(1′), H–C(6′), 2H–C(7′)); 0.83, 1.10, 1.27 (3*s*, CH_3–C(2′), 2 CH_3–C(4′)); 1.81 (*AB* system, J = 13, δ_A = 1.60, δ_B = 2.02, split into *d*, J = 4, 2H–C(5′)); 2.40 (*s*, 3H–C(1)); 7.25 (*AB* system, J = 15, δ_A = 6.90, δ_B = 7.60, H–C(3), H–C(4)). ^{13}C-NMR (contaminated with 25% of **31**): 24.1, 28.3, 28.5, 30.0 (4*q*, 4 CH_3); 11.8 (*t*, C(7′)); 43.3 (*t*, C(5′)); 16.6, 27.9 (2*d*, C(1′), C(6′)); 135.6, 136.1 (2*d*, C(3), C(4)); 42.7 (*s*, C(4′)); 59.1 (*s*, C(2′)); 197.8, 204.8 (2*s*, C(2), C(3′)). MS: 220 (1, M^+, $C_{14}H_{20}O_2$), *123* (100), 81 (44), 67 (12), 57 (32), 43 (23), 41 (21). Anal. calc. for $C_{14}H_{20}O_2$ (220.31): C 76.33, H 9.15; found: C 76.36, H 9.21.

1.9. *(E,1′RS,2′SR,3′RS,6′SR)-4-(2′,3′-Epoxy-4′,4′-dimethylbicyclo[4.1.0]hept-3′-yl)-3-buten-2-one* (**9**).

1.9.1. *In a Silylated Tube.* Compound **9** (148 mg, 0.67 mmol) was thermolyzed at 520° (conversion 88%) to give a mixture from which, after distillation (110°/0.04 Torr), the following yields were determined (^{1}H-NMR, GC): **8** (13%) [22], **29** [22] (37%), and **30** (7%).

1.9.2. *In an Untreated Quartz Tube.* Thermolysis of **9** (353 mg, 1.60 mmol) at 520° (conversion 50%) gave a mixture, whose fractions after chromatography (Et_2O/hexane 3:1 to 1:1) contained (^{1}H-NMR, GC) **30** (20%) and **31** (40%).

(1′RS,2′RS,6′RS)-4-(3′-Oxo-2′,4′,4′-trimethylbicyclo[4.1.0]hept-2′-yl)-3-buten-2-one (**31**). UV (0.284 mg in 25 ml): 209 (12700). UV (2.370 mg in 5 ml): 310 (200), end to absorption 390. IR: 3070*w*, 3060*w*, 3005*m*, 2965*s*, 2930*s*, 2905*m*, 2860*m*, 1695*s*, 1673*s*, 1622*m*, 1610*s*, 1465*m*, 1455*s*, 1422*m*, 1379*m*, 1365*m*, 1355*s*, 1337*w*, 1312*w*, 1288*m*, 1275*m*, 1251*s*, 1220*m*, 1190*m*, 1175*m*, 1163*m* (sh), 1140*w*, 1095*w*, 1046*w* (sh), 1025*s*, 1002*m*, 975*m*, 950*w*, 942*w*, 905*s*. ^{1}H-NMR: 0.12–0.37 (*m*, 1H) and 0.61–1.35 (*m*, 3H), H–C(1′), H–C(6′), 2H–C(7′)); 1.10, 1.20, 1.45 (3*s*, CH_3–C(2′), 2 CH_3–C(4′)); 2.07 (*AB* system, J = 14, δ_A = 1.80, split into *d*, J = 4, δ_B = 2.34, split into *d*, J = 4, 2H–C(5′)); 2.30 (*s*, 3H–C(1)); 6.56 (*AB* system, J = 17, δ_A = 6.06, δ_B = 7.06, H–C(2), H–C(3)). ^{13}C-NMR: 25.7, 26.8, 28.7, 29.8 (4*q*, 4 CH_3), 9.5 (*t*, C(7′)); 35.6 (*t*, C(5′)); 9.5, 19.9 (2*d*, C(1′), C(6′)); 128.9, 151.5 (2*d*, C(3), C(4)); 42.4, 50.7 (2*s*, C(2′), C(4′)); 198.5, 217.5 (2*s*, C(2), C(3)). MS: 220 (2, M^+, $C_{14}H_{20}O_2$), 177 (22), 149 (12), 136 (24), 123 (12), 122 (27), 121 (34), *109* (100), 107 (20), 105 (14), 96 (18), 95 (14), 94 (11), 93 (81), 91 (26), 81 (23), 80 (12), 79 (20), 77 (23), 70 (42), 69 (33), 67 (14), 65 (10), 55 (17), 53 (16), 43 (97), 42 (12), 41 (53), 39 (23). Anal. calc. for $C_{14}H_{20}O_2$ (220.30): C 76.33, H 9.15; found: C 76.11, H 9.38.

1.10. *(E,1′RS,2′SR,3′SR,4′SR)-1-(1′,2′;3′,4′-Diepoxy-2′,6′,6′-trimethylcyclohexyl)-3-methyl-1,3-butadiene* (**10**). 1.10.1. *In a Silylated Tube.* Compound **10** (461 mg, 2.09 mmol) was thermolyzed at 440° (80% conversion).

From the fractions after chromatography (Et_2O/pentane 1:3 to 1:1), the following product yields were determined (^{1}H-NMR, GC): **32** (5%), **33** [21] (5%), **34** [21] (3%), **35** [21] (3%), **36** (11%), and **37** (29%).

1.10.2. *In an Untreated Quartz Tube.* Compound **10** (1.25 g, 5.68 mmol) was thermolyzed at 400° (47% conversion) and chromatographed (Et_2O/pentane 1:2) to give fractions from which the following product yields were determined (^{1}H-NMR, GC): **33** (7%), **34** (5%), **36** (18%), and **37** (19%).

(E,1′RS,2′SR,3′RS,4′RS)-1-(1′2′,3′,4′-Diepoxy-2′,6′,6′-trimethylcyclohexyl)-3-methyl-1,3-butadiene (**32**). ^{1}H-NMR (80 MHz) signals of a 3:2 mixture **32**/**35**, which may be assigned to **32**: 0.93, 1.25, 1.40 (3*s*, CH_3–C(2′), 2 CH_3–C(6′)); 1.83 (*m*, $w_{1/2} \approx 3$, CH_3–C(3′)); 3.1–3.4 (*m*, H–C(3′), H–C(4′)); 5.0 (*m*, $w_{1/2} = 4$, 2H–C(4)); 6.02 (*AB* system, $J = 16$, $\delta_A = 5.77$, $\delta_B = 6.27$, H–C(1), H–C(2)).

(2-Hydroxy-4,4-dimethyl-7-(1′-methylvinyl)-1,5-cycloheptadien-1-yl) Methyl Ketone (**36**). UV (0.350 mg in 25 ml MeCN): 293 (6800). UV (1.818 mg in 2 ml MeCN): End absorption to 390. IR: 3080*w*, 3010*m*, 2960*s*, 2935*m*, 2925*m*, 2910*m* (sh), 2868*m*, from 1950 to 1100 broad absorption, 1700*m*, 1638*s*, 1600*s* (br.), 1465*s*, 1458*s*, 1448*s*, 1438*s*, 1379*m*, 1362*m*, 1355*m* (sh), 1330*m*, 1305*m*, 1285*m*, 1245*m*, 1225*w*, 1205*w*, 1180*w*, 1145*w* (br.), 1111*w*, 1015*w* (br.), 980*w* (br.), 950*m*, 937*w* (sh), 930*m*, 902*m*, 872*w*. ^{1}H-NMR (300 MHz): 1.00, 1.06 (2*s*, 2 CH_3–C(4)); 1.76–1.78 (*m*, CH_3–C(1′)); 1.97 (*dd*, $J_1 = 12.3$, $J_2 = 2.05$, H–C(3)); 2.15 (*s*, CH_3–CO); 3.27 (*d*, $J = 12.3$, H–C(3)); 3.64 (*d*, $J = 8.3$, broadened, H–C(7)); 4.84–4.86 and 4.89–4.91 (2*m*, 2H–C(2′)); 5.55 (*AB* system, $J = 11.8$, $\delta_A = 5.45$, split into *dd*, $J_1 = 2.05$, $J_2 = 0.55$, H–C(5), $\delta_B = 5.66$, split into *d*, $J = 8.3$, H–C(6)); 16.89 (*s*, OH). ^{13}C-NMR: 22.0, 22.4, 27.1, 32.0 (4*q*, 4 CH_3); 48.8 (*t*, C(3)); 117.7 (*t*, C(2′)); 43.2 (*d*, C(7)); 125.3, 140.2 (2*d*, C(5), C(6)); 34.6 (*s*, C(4)); 112.3 (*s*, C(1)); 145.8 (*s*, C(1′)); 187.8 (*s*, C(2)); 195.4 (*s*, CO). MS: 220 (8, M^+, $C_{14}H_{22}O_2$), 177 (15), 163 (10), 159 (12), 137 (14), 135 (18), 121 (14), 119 (11), 107 (14), 105 (12), 93 (17), 91 (22), 79 (14), 77 (17), 55 (12), 43 (100), 41 (47), 39 (21).

2-Acetyl-4,8,8-trimethylbicyclo[4.3.0]non-4-en-7-one (**37**). B.p. 100°/0.03 Torr. UV (0.360 mg in 10 ml): 212 sh (4300). UV (2.544 mg in 2 ml): end absorption to 390. IR: 3030, 3000*w* (sh), 2960*s*, 2928*s*, 2910*s*, 2862*m*, 1735*s*, 1710*s*, 1655*w*, 1463*m*, 1450*m*, 1445*m*, 1435*m*, 1420*w*, 1375*m*, 1359*m*, 1351*m*, 1330*w*, 1302*w*, 1298*w*, 1275*w*, 1260*w*, 1239*w*, 1205*m*, 1200*w*, 1182*m*, 1160*m*, 1130*m*, 1115*m*, 1093*m*, 1070*m*, 1050*w*, 962*w*, 870*m*. ^{1}H-NMR (300 MHz): 1.04, 1.06 (2*s*, 2 CH_3–C(8)); 1.57 (*AB* system, $J = 10.9$, $\delta_A = 1.55$, broadened, $\delta_B = 1.60$, split into *dd*, $J_1 = 6.5$, $J_2 = 1.1$, 2H–C(9)); 1.71 (*m*, $w_{1/2} = 5$, CH_3–C(4)); 2.14 (*AB* system, $J = 20$, $\delta_A = 1.96$, broadened, $w_{1/2} = 10$, $\delta_B = 2.32$, broadened, $w_{1/2} = 10$, 2H–C(3)); 2.23 (*s*, CH_3CO); 2.86–2.93 (2H) and 3.05–3.10 (1H) (2*m*, H–C(1), H–C(2), H–C(6)); 5.17–5.18 (*m*, H–C(5)). ^{13}C-NMR: 23.7, 24.7, 24.9, 28.4, (4*q*, 4 CH_3); 26.1, 36.4 (2*t*, C(3), C(9)); 31.6 (*d*, C(1)); 47.1, 50.4 (2*d*, C(2), C(6)); 115.8 (*d*, C(5)); 45.1 (*s*, C(8)); 134.7 (*s*, C(4)); 209.2, 220.3 (2*s*, C(7), CO–CH_3). MS: 220 (10, M^+, $C_{14}H_{20}O_2$), 105 (27), *93* (100), 92 (27), 91 (20), 77 (17), 43 (30), 41 (11).

1.11. *(E,1′SR,2′SR,3′RS,6′RS)-4-(2′,3′-Epoxy-4′,4′-dimethylbicyclo[4.1.0]hept-3′-yl)-3-methyl-1,3-butadiene* (**11**). 1.11.1. *In a Silylated Tube.* Thermolysis of **11** [24] (76 mg, 0.349 mmol) at 520° (conversion 76%) gave a mixture which, after distillation, contained (^{1}H-NMR and GC) **12** [24] (12%), **38** (15%), **39** (12%), **40** (1%), and **41** [24] (6%).

1.11.2. *In an Untreated Quartz Tube.* Compound **11** (43 mg, 0.197 mmol) was thermolyzed at 390° (conversion 88%) and chromatographed (Et_2O/hexane 1:10) to yield **39** (11 mg, 29%).

1-(5′,5′-Dimethyl-2′-methylidene-3′-oxabicyclo[5.1.0]oct-4′-ylidene)-2-methyl-1-butene (**38**). B.p. 70°/0.03 Torr. UV (0.392 mg in 25 ml): 245 sh (1700). UV (0.392 mg in 5 ml): end absorption to 390. IR: 3115*w*, 3070*m*, 3000*m*, 2960*s*, 2920*s*, 2860*s*, 1660*m*, 1630*s*, 1465*m* (sh), 1455*m* (sh), 1445*m*, 1435*m*, 1382*m*, 1370*m*, 1360*m*, 1338*m*, 1315*m*, 1305*s*, 1275*w*, 1220*s* (sh), 1209*s*, 1180*m*, 1165*s* (sh), 1110*s*, 1088*s*, 1050*s*, 1031*m*, 1015*m*, 981*m*, 960*w*, 940*w*, 918*w*, 885*s*. ^{1}H-NMR: 1.08, 1.20 (2*s*, 2 CH_3–C(5′)); 0.25–0.75 (1H) and 0.75–2.00 (5H) (*m*, H–C(1′), 2H–C(6′), H–C(7′), 2H–C(8′)); 1.75 (*m*, $w_{1/2} = 3.5$, CH_3–C(2)); 2.79 (*d*, $J = 7$, 2H–C(3)); 4.08, 4.50 (2*d*, $J = 2$, CH_2=C(2′)); 4.70 (*m*, $w_{1/2} = 4$, 2H–C(1)); 5.02 (*t*, $J = 7$, H–C(4)). MS: 218 (5, M^+, $C_{15}H_{22}O$), 204 (16), *203* (100), 147 (16), 145 (15), 137 (14), 135 (17), 133 (18), 123 (21), 122 (15), 121 (41), 120 (12), 119 (28), 109 (14), 107 (48), 105 (40), 97 (15), 95 (25), 93 (38), 91 (39), 83 (14), 81 (38), 80 (13), 79 (62), 77 (34), 70 (12), 69 (35), 67 (28), 66 (15), 65 (14), 55 (42), 53 (29), 43 (39), 41 (69), 39 (34).

(E)-1-(2′,3′,3′-Trimethylbicyclo[3.1.0]hex-2′-yl)-4-methyl-2,4-pentadien-1-one (**39**). B.p. 70°/0.03 Torr. UV (0.289 mg in 20 ml): 266 (15000). IR: 3081*m*, 3010*m*, 2975*s*, 2955*s*, 2920*s*, 2915*s*, 2870*m*, 2855*m*, 1812*w*, 1699*m*, 1680*m* (sh), 1670*s*, 1609*s*, 1585*s*, 1460*m*, 1449*m*, 1432*m*, 1417*w* (sh), 1388*m*, 1367*s*, 1350*w*, 1317*m*, 1303*m*, 1268*s*, 1241*w*, 1200*w*, 1180*w*, 1155*w*, 1135*w*, 1093*w*, 1082*m*, 1061*w*, 1045*s*, 1021*m*, 979*m*, 901*s*, 889*w*, 872*w*, 857*w*. ^{1}H-NMR (90% pure): 0.85, 1.10, 1.25 (3*s*, CH_3–C(2′), 2 CH_3–C(3′)); 0.35–2.12 (*m*, H–C(1′), 2H–C(4′), H–C(5′), 2H–C(6′)); 1.92 (*m*, $w_{1/2} = 3$, CH_3–C(4)); 5.40 (*m*, $w_{1/2} = 5$, 2H–C(5)); 7.04 (*AB* system, $J = 15$, $\delta_A = 6.80$, $\delta_B = 7.28$, H–C(2), H–C(3)). MS: 218 (5, M^+, $C_{15}H_{22}O$), 203 (13), 185 (21), 175 (32), 135 (13), 133 (19), 129 (11), 124 (11), *123* (100), 121 (23), 119 (33), 109 (18), 107 (34), 105 (32), 95 (40), 93 (26), 91 (41), 82 (13), 81 (77), 79 (27), 77 (27), 69 (29), 67 (40), 65 (13), 57 (51), 55 (33), 53 (14), 45 (12), 44 (14), 43 (79), 41 (61), 39 (20).

(E,1RS,2RS,6RS)-2-(3'Methyl-1',3'-butadien-1'-yl)-2,4,4-trimethylbicyclo[4.1.0]heptan-3-one (**40**). B.p. 90°/0.04 Torr. UV (0.320 mg in 25 ml): 229 (20000). UV (2.430 mg in 5 ml): 300 (15), end absorption to 390. IR: 3080*w*, 3005*m*, 2965*s*, 2940*m*, 2923*m*, 2905*m*, 2881*m*, 1696*s*, 1603*w*, 1468*m*, 1456*m* (sh), 1451*m*, 1435*w*, 1379*m*, 1368*w*, 1358*w*, 1338*w*, 1312*w*, 1275*w*, 1227*w*, 1190*w*, 1165*w*, 1140*w*, 1071*w*, 1049*w*, 1028*s*, 1000*w*, 991*w*, 971*m*, 901*w*, 888*m*, 842*w*. ^{1}H-NMR: 0.35 (*dd*, $J_1 = 9$, $J_2 = 4$, 1H) and 0.60–1.32 (*m*, 3H) (H–C(1), H–C(6), 2H–C(7)); 1.06, 1.20, 1.40 (3*s*, CH_3–C(2), 2 CH_3–C(4)); 1.87 (*m*, $w_{1/2} = 3$, CH_3–C(3')); 1.96 (*AB* system, $J = 15$, $\delta_A = 1.67$, split into *d*, $J = 5$, $\delta_B = 2.25$, split into *d*, $J = 4$, 2H–C(5)); 4.92 (*m*, $w_{1/2} = 3$, 2H–C(4')); 5.98 (*AB* system, $J = 17$, $\delta_A = 5.82$, $\delta_B = 6.13$, H–C(1'), H–C(2')). ^{13}C-NMR (75 MHz): 18.6, 26.7, 28.4, 29.1 (4*q*, 4 CH_3); 10.2 (*t*, C(7)); 36.1 (*t*, C(5)); 115.6 (*t*, C(4')); 9.3, 20.2 (2*d*, C(1), C(6)); 130.6, 134.4 (2*d*, C(1'), C(2')); 42.0, 49.4 (2*s*, C(2), C(4)); 141.5 (*s*, C(3')); 217.6 (*s*, C(3)). MS: 218 (25, M^+, $C_{15}H_{22}O$), 162 (12), 147 (32), 135 (19), 134 (23), 133 (20), 121 (20), 120 (21), 119 (71), 108 (21), *107* (100), 106 (22), 105 (55), 95 (23), 94 (16), 93 (69), 92 (20), 91 (64), 82 (14), 81 (12), 80 (19), 79 (32), 78 (10), 77 (33), 69 (16), 67 (15), 65 (13), 55 (34), 53 (20), 43 (17), 41 (65), 39 (29). Anal. calc. for $C_{15}H_{22}O$ (218.33): C 82.52, H 10.16; found: C 82.62, H 10.09.

1.12. *(E,1'RS,2'SR,3'RS,6'SR)-4-(2',3'-Epoxy-4',4'-dimethylbicyclo[4.1.0]hept-3'-yl)-3-methyl-1,3-butadiene* (**12**). 1.12.1. *In a Silylated Tube.* Compound **12** [24] (49 mg, 0.225 mmol) was thermolyzed at 520° (77% conversion) to give a mixture which contained (^{1}H-NMR, GC) after distillation **11** (24%), **38** (12%), **39** (9%), **40** (9%), and **41** [24] (5%).

1.12.1. *In an Untreated Quartz Tube.* Compound **12** (87 mg, 0.40 mmol) was thermolyzed at 390° (93% conversion) to give a mixture which contained after distillation **40** (55%) and intractable material (^{1}H-NMR, GC).

2. Additional Thermolyses. – 2.1. *Divinyl Ether* **13**. Compound **13** (35 mg, 0.17 mmol; contaminated with the *endo*-isomer **14** (10%)) was thermolyzed at 560° (conversion 39%) to produce a mixture of **1** (38%) and **14** (36%) according to GC and ^{1}H-NMR. This mixture was chromatographed (10 g SiO_2; AcOEt/hexane 1:9) to give two fractions: one containing **13/14**, and the other consisting of pure **1** (NMR).

2.2. *(E)-4-(3',7',7'-Trimethyl-2'-oxabicyclo[3.2.0]hept-3'-enyl)-3-buten-2-one* (**18**). 2.2.1. *At 325°.* Compound **18** (27 mg, 0.13 mmol; 90% pure by GC) was thermolyzed at 325° (conversion 30%) to yield a mixture (22 mg) of **3** (30%) and **19** (20%) according to ^{1}H-NMR and GC.

2.2.2. *At 390°.* The mixture obtained from the thermolysis experiment at 325° (22 mg) was thermolyzed at 390° to produce a mixture (20 mg) of **18** (13%) and **19** (64%).

2.3. *Dihydrofuran* **22B**. Thermolysis of **22B** (27 mg, 0.12 mmol) at 520° (conversion 90%) and chromatography (12 g SiO_2, AcOEt/hexane 1:4) gave fractions from which following product yields were determined (^{1}H-NMR and GC): **22A** (*ca.* 1%) and **5** (21%). ^{1}H-NMR and GC of the mixture showed the presence of **23** (*ca.* 6%) which was not isolated from the column.

2.4. *(3E,8Z)-6,6-Dimethyl-3,8-undecadiene-2,5,10-trione* (**27**). Compound **27** [20] (259 mg, 1.17 mmol) was thermolyzed on untreated quartz at 400° (conversion 98%) and chromatographed (Et_2O/pentane 2:1) yielding several fractions, which, according to ^{1}H-NMR and GC, contained **28A** (15%), **28B** (15%), and **53** (22%).

2.5. *Methyl 1,6,6-Trimethyl-10-oxatricyclo[5.2.1.0^{2,4}]dec-7-enyl Ketone* (**54**). 2.5.1. *At 520°.* Compound **54** [22] (54 mg, 0.24 mmol) was thermolyzed through a silylated *Pyrex* tube at 520° (79% conversion) to give a mixture which contained after distillation (110°/0.04 Torr; ^{1}H-NMR, GC): **8** (5%), **9** (1%), **29** (5%), and **55** (32%).

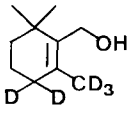
2.5.2. *At 390°.* Compound **54** (27 mg, 0.12 mmol) was thermolyzed at 390° (15% conversion) to give a mixture which contained (^{1}H-NMR and GC) **8** (11%), **9** (1%), and **55** (58%).

3. Additional Experiments. – 3.1. *Synthesis of (D$_5$)-***1**. Cyclocitral (mixture of α and β; 3.0 g, 19.7 mmol) was deuterated (3 ×) according to the method of *Dawson et al.* [12], and the crude material was reduced with $NaBH_4$ (1.5 g, 39.7 mmol) in CH_3OD (25 ml) under Ar at 0° for 1 h followed by workup with Et_2O/hexane/HCl (aq.) to yield **65**/**66** (2.1 g, 67%). Integration of the signals in the ^{1}H-NMR (80 MHz, $CDCl_3$) at 3.70 (**66**) and 4.14 (**65**) ppm showed that **65** was present in *ca.* 10:1 excess.

This mixture (2.1 g, 13.2 mmol) was treated with $VO(acac)_2$ (20 mg) and (*t*-butyl)hydroperoxide in di(*t*-butyl)peroxide (80%, 3 ml) in benzene (30 ml) at 0° for 15 min and then at r.t. for 3 h. The reaction was then worked up with Et_2O, Na_2SO_3 (5% aq.), $Fe(II)SO_4$ (aq.), and H_2O, and the residue, after the org. layer was dried ($MgSO_4$) and evaporated, was chromatographed (SiO_2, 75 g, AcOEt/hexane 1:4) to produce **67** (1.37 g, 59%).

[2'-methyl-$^2H_3$,3',3'-$^2H_2$]-4-(1',2'-Epoxy-2',6',6'-trimethylcyclohexyl)methanol (**67**). ^{1}H-NMR: 1.05 (*s*, 2 CH_3–C(6')); 0.8–2.0 (*m*, 2H–C(5'), 2H–C(4'), OH); 3.77 (*m* (*t*-like), 2H–C(1)).

The alcohol **67** (1.37 g) was allowed to react at 0° for 30 min with *Collins* reagent, prepared from CrO_3 (4.7 g) and pyridine (7.43 g) in CH_2Cl_2 (250 ml), before working up by filtering through a bed of SiO_2 with CH_2Cl_2, extracting with 1M HCl, H_2O, and drying to yield **43** (1.053 g, 76%; pure by TLC). This material was treated with 5% NaOH (aq., 3 ml) in acetone (40 ml) at 45° for 2 h, then extracted between hexane and $NaHCO_3$ (½ satd.),



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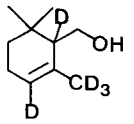

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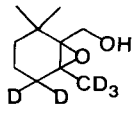

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dried, and the material from the org. phase chromatographed (75 g SiO_2, AcOEt/hexane 1:4) to yield (D_5)-**1** (486 mg, 39%).

*(D_5)-***1**. ^{1}H-NMR: 0.95, 1.14 (2*s*, 2 CH_3–C(2)); 0.8–1.6 (*m*, 2H–C(4'), 2H–C(5')); 2.29 (*s*, 3H–C(1)); 6.69 (*AB* system, J = 16, δ_A = 6.30, δ_B = 7.08, H–C(3), H–C(4)). MS shows 13% D_4 and 87% D_5.

3.2. *Hydrolysis of* **17**. The divinyl ether **17** (28 mg, *ca.* 80% pure) was hydrolyzed in THF (1.5 ml), H_2O (1.5 ml), and AcOH (0.5 ml) for 1 h, Et_2O was added, washed with $NaHCO_3$ (½ sat.), dried ($MgSO_4$), and evaporated to yield **62** [6] (13 mg).

3.3. *Alkaline Cleavage of* **36**. A soln. of **36** (72 mg, 0.33 mmol) and KOH (180 mg, 3.21 mmol) in MeOH (6 ml) and H_2O (4 ml) was refluxed overnight and worked up with Et_2O. Distillation of the crude product (70°/0.05 Torr) yielded 25 mg **63** (44%).

3,3-Dimethyl-6-(1'-methylvinyl)-4-cycloheptenone (**63**). B.p. 70°/0.05 Torr. IR: 3080*w*, 3010*w*, 2962*s*, 2935*m*, 2925*m*, 2910*m*, 2870*m*, 1702*s*, 1648*m*, 1465*m*, 1460*m*, 1449*m*, 1407*w*, 1380*w*, 1375*w*, 1363*m*, 1350*w*, 1328*w*, 1301*w*, 1275*w* (br.), 1230*w*, 1210*w*, 1190*w*, 1100*w*, 895*m*. ^{1}H-NMR (300 MHz): 1.06, 1.11 (2*s*, 2 CH_3–C(3)); 1.75 (*m*, CH_3–C(1')); 2.61 (*AB* system, J = 17.1, δ_A = 2.56, split into *d*, J = 3.5, broadened, δ_B = 2.67, split into *d*, J = 10.2, 2H–C(7)); 2.67 (*AB* system, J = 12.4, δ_A = 2.43, broadened, δ_B = 2.92, broadened, 2H–C(2)); 3.30–3.35 (*m*, H–C(6)); 4.80–4.81 (*m*, 2H–C(2')); 5.48 (*AB* system, J = 11.9, δ_A = 5.44, split into *dd*, J_1=J_2 = 1.4, H–C(4), δ_B = 5.52, split into *dd*, J_1 = 3.8, J_2 = 0.1, H–C(5)). MS: 178 (15, M^+, $C_{12}H_{18}O$); 163 (14), 136 (17), 135 (24), 123 (14), 122 (55), 121 (54), 119 (16), 109 (16), 108 (13), 107 (39), 105 (26), 94 (32), *93* (100), 87 (15), 79 (99), 77 (40), 69 (28), 68 (12), 67 (33), 65 (15), 55 (25), 53 (27), 51 (15), 43 (18), 41 (66), 39 (49). Anal. calc. for $C_{12}H_{18}O$ (178.26): C 80.85, H 10.18; found: C 80.79, H 10.22.

3.4. *Aromatization of* **37**. A soln. of **37** (62 mg, 0.28 mmol) and NBS (113 mg, 0.63 mmol) in CCl_4 (5 ml) was heated with stirring at 60° for 1 h, before cooling, filtering, and washing the residue with pentane. The crude product was treated with LiF (30 mg, 1 mmol) and Li_2CO_3 (90 mg, 1.2 mmol) in DMF (5 ml) for 2 h at 120°. Workup yielded 38 mg **64** (62%).

4-Acetyl-2,2,6-trimethyl-1-indanone (**64**). B.p. 120°/0.05 Torr. UV (0.133 mg in 20 ml): 224 (34000). UV (0.266 mg in 20 ml): 237 sh (11000), 244 sh (9300), 251 sh (6800), 305 (3000), 316 (3100). IR: 3040*w*, 3000*w*, 2960*m*, 2925*m*, 2900*w* (sh), 2865*w*, 1718*s*, 1683*s*, 1609*w*, 1574*m*, 1470*m*, 1462*m*, 1455*m* (sh), 1445*w*, 1430*m*, 1380*m*, 1355*m*, 1321*m*, 1305*m*, 1290*w*, 1250*s*, 1195*m*, 1131*w*, 1160*w*, 1117*m*, 1039*w*, 996*w*, 970*w*, 956*w*, 905*w*, 879*m*. ^{1}H-NMR: 1.20 (*s*, 2 CH_3–C(2)); 2.45 (*m*, $w_{1/2}$ = 3, CH_3–C(6)); 2.62 (*s*, CH_3CO); 3.30 (*m*, $w_{1/2}$ = 3, 2H–C(3)); 7.75 and 7.92 (2*m*, $w_{1/2}$ = 3.5, H–C(5), H–C(7)). MS: 217 (11), 216 (65, M^+, $C_{14}H_{16}O_2$), 201 (50), 188 (11), 174 (14), *173* (100), 159 (18), 158 (12), 146 (22), 145 (28), 129 (16), 128 (20), 115 (17), 77 (12), 43 (16). Anal. calc. for $C_{14}H_{16}O_2$ (216.27): C 77.75, H 7.46; found: C 77.59, H 7.58.

3.5. Wittig *Reaction of* **29**. A soln. of methylidenetriphenylphosphorane in THF was added dropwise to a soln. of **29** (49 mg, 0.223 mmol) in dry Et_2O (5 ml) until TLC indicated a complete conversion of **29** to **38**. The reaction mixture was worked up with pentane, filtered through SiO_2. Kugelrohr distillation (70°, 0.03 Torr), yielded 42 mg **38** (86%).

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