14. Photochemical Reactions

132nd Communication[1])

Photochemistry of 5,6-Epoxy-5,6-dihydro-7-methyl-β-ionone: Influence of a Methyl Group at the Enone Side Chain on the Oxirane Cleavage[2])

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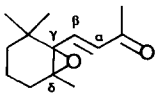
(23.XI.83)

Summary

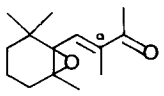
$^1n,\pi^*$-Excitation of the γ,δ-epoxy-enone (*E*)-**3** leads exclusively to the conformers (*Z*)-**3A** + **B**. On $^1\pi,\pi^*$-excitation of (*E*)-**3**, in addition to (*Z*)-**3A** + **B**, products **6**–**9** arising from a carbene intermediate **e** are formed. However, products of an isomerization *via* C(γ),O-bond cleavage of the oxirane were not formed on either mode of excitation. On thermolysis, at 80° the conformer (*Z*)-**3A** is transformed into (*Z*)-**3B**, which on photolysis returns to (*Z*)-**3A** and (*E*)-**3**. At 160°, however, (*Z*)-**3B** rearranges to the isomers **6**, **10** and **11**.

1. Introduction. – Previous reports from this laboratory have disclosed that, in general, $^1n,\pi^*$-excitation of α,β-unsaturated γ,δ-epoxyketones of type **1** with an acyclic enone chromophore leads to (*E*/*Z*)-isomerization and C(γ),O-bond cleavage of the oxirane moiety [2]. However, selective $^1\pi,\pi$-excitation causes to a substantial extent reactions which include cleavage of the C(γ),C(δ)-bond of the oxirane ring.

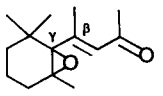
Photoisomerization *via* these primary processes is also observed on irradiation of the substrate (*E*)-**2** which incorporates a CH_3-substituent in the *α-position* of the enone chromophore [2] [3].



(*E*)-**1**



(*E*)-**2**



(*E*)-**3**

[1]) 131st Communication, see [1].

[2]) Presented in Part by *B.F.* at the IX[th] IUPAC Symposium on Photochemistry, July 25–30 1982, Pau (France).

[3]) On leave January to June 1981 – from Akademia Rolnicza, Instytut Podstaw Chemii, Wrocław, Poland.

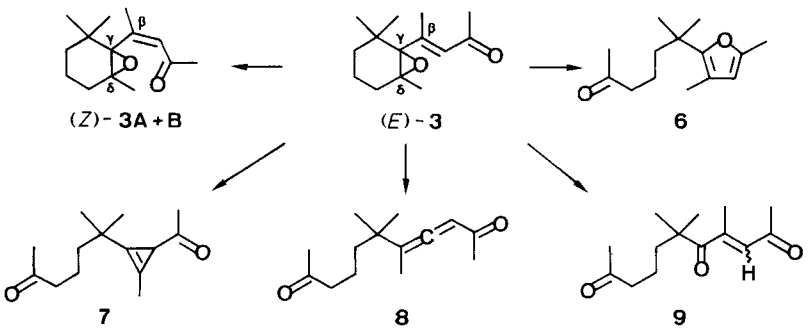
[4]) *F. Hoffmann-La Roche & Co. Ltd.*, Basle, Switzerland.

Continuing these investigations, the study of the photochemistry of (*E*)-**3**[5]) seemed to be of particular interest, since from the NMR data it is evident that, in contrast to (*E*)-**1** and (*E*)-**2**, in (*E*)-**3** the rotation of the side chain around the C(*β*),C(γ)-bond is hindered, due to steric interaction of the *β*-CH_3-group with the geminal CH_3-groups at C(1)[6]).

2. Photolyses. – 2.1. *Irradiation of* (E)-**3**. 2.1.1. *At* $\lambda > 347$ *nm.* The photolysis of a *ca.* 0.05M solution of (*E*)-**3** in CH_3CN (*ca.* 85% conversion) gave[7]) (*Z*)-**3A** (57%) and (*Z*)-**3B** (10%)[8]). The same product distribution was obtained on irradiation of a 0.35M solution of (*E*)-**3** in CD_3CN in a NMR tube.

2.1.2. *At* $\lambda = 254$ *nm.* The photolysis of a *ca.* 0.05M solution of (*E*)-**3** in CH_3CN (*ca.* 80% conversion) afforded[7]) (*Z*)-**3A** (48%), (*Z*)-**3B** (5%), **6** (10%), **7** (20%) [2], **8** (*ca.* 2%) and **9** (*ca.* 2%).

Scheme 2



From the irradiation of a *ca.* 0.3M solution of (*E*)-**3** in CD_3CN in a NMR tube (*ca.* 95% conversion) the following product distribution was estimated on the basis of ^{1}H-NMR and capillary GC analysis: (*Z*)-**3A** (40%), **6** (25%) and **7** (30%) [2].

2.2. *Irradiation of* (Z)-**3A** *at* $\lambda = 254$ *nm.* The photolysis of a CD_3CN-solution containing (*Z*)-**3A** (80%), (Z)-**3B** (5%) and (*E*)-**3** (15%) was followed by ^{1}H-NMR analysis. After 4 h the following product distribution was estimated: (*Z*)-**3A** (35%), (*E*)-**3** (10%), **6** (20%) and **7** (30%) [2].

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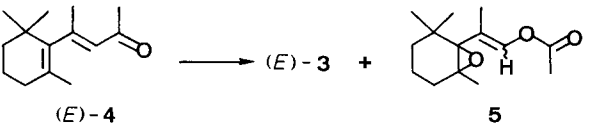
[5]) Epoxidation of (*E*)-**4** [4] with *m*-chloroperbenzoic acid afforded (*E*)-**3** (88%) and **5** (3%).

Scheme 1



[6]) In ionone derivatives numbering according to the carotinoid nomenclature [5] is used.

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

[8]) Compound (*Z*)-**3B** is sensitive to acid and undergoes transformation to **6** and **10**.

2.3. *Irradiation of* (Z)-**3B** *at* $\lambda > 347$ *nm.* Photolysis of a *ca.* 0.1M solution of (*Z*)-**3B** in CH_3CN afforded after complete conversion apart from (*E*)-**3** (15%) and (*Z*)-**3A** (50%) only intractable material.

3. Structure of the Compounds. – *Epoxyenone* (E)-**3**. The NMR spectra of (*E*)-**3** at 25° show signals of two conformers arising from hindered rotation around the C(*β*),C(*γ*)-bond (ratio *ca.* 2:1).

In the ^{1}H-NMR spectrum of (*E*)-**3** the signals of the olefinic H-atom and the olefinic CH_3-group, of the major conformer are at 6.14 ppm (*m*, $w_{1/2}$ = 3 Hz) and 2.07 ppm (*d*, *J* = 1.5 Hz), respectively. Corresponding signals of the minor conformer appear at 5.83 ppm (*m*, $w_{1/2}$ = 3 Hz) and 2.02 ppm (*d*, *J* = 1.5 Hz), respectively. The major conformer exhibits ^{13}C-NMR signals of the enone moiety at 126.6 (*d*), 154.7 (*s*) and 197.8 ppm (*s*), whereas the corresponding signals of the minor conformer are at 126.8 (*d*), 152.7 (*s*) and 197.6 ppm (*s*). A rapid exchange spectrum is obtained above 150° in (D_7)DMF. The UV spectrum of (*E*)-**3** includes a π,π^*-band at λ = 241 nm (ε = 12100) and the IR spectrum shows characteristic strong bands of the enone at 1690 and 1613 cm^{-1}.

Epoxyenones (Z)-**3A** + **B** *(Scheme 3).* The structural proof of these compounds is based on comparison of their NMR spectra with those of (*E*)-**3**, indicating that the constitution of the epoxyenone remained intact. In contrast to the conformers of (*E*)-**3** (see *above*), (*Z*)-**3A** and (*Z*)-**3B** may be separated by chromatography. Both conformers are stable at room temperature, however, at *ca.* 80°, (*Z*)-**3A** is transformed quantitatively into (*Z*)-**3B**[9]).

In the ^{1}H-NMR spectrum of (*Z*)-**3A** a *m* at 5.78 ppm and a *d* (*J* = 1.5 Hz) at 1.80 ppm are observed for the olefinic H-atom and the olefinic CH_3-group, respectively. The ^{13}C-NMR spectrum of (*Z*)-**3A** includes signals of the enone side chain at 131.6 (*d*) 142.2 (*s*) and 200.6 ppm (*s*). These data, as well as the UV maximum at 224 nm (ε = 4600) and the IR bands at 1705 and 1645 cm^{-1} indicate a non planar (*Z*)-enone chromophore. The ^{1}H-NMR spectrum of the conformer (*Z*)-**3B** shows the corresponding signals for the olefinic H-atom and the olefinic CH_3-group at 6.11 and 1.85 ppm, respectively, and its ^{13}C-NMR spectrum exhibits signals of the enone moiety at 125.9 (*d*), 153.8 (*s*) and 195.9 ppm (*s*). The UV spectrum of (*Z*)-**3B** shows a π,π^*-band at 237 nm (ε = 7500), and in the IR significant bands arising from the enone chromophore appear at 1690 and 1607 cm^{-1}.

The stereochemical assignment of (*Z*)-**3A** and (*Z*)-**3B** is based on their different reactivity and on the fact that only (*Z*)-**3B** is obtained on epoxidation of (*Z*)-7-methyl-*β*-ionone ((*Z*)-**4**). Since the enone side chain in (*Z*)-**4** is twisted about 90° around the C(*β*),C(*γ*)-bond, as known from NMR data [4], it seems reasonable that the C(*γ*),C(*δ*)-double bond is attacked from the less hindered side leading to (*Z*)-**3B.**

On treatment with HCl in CH_2Cl_2 in the temperature range of −20° to −10° only (*Z*)-**3B** is converted to the furan **6** and the dienol ether **10**, whereas (*Z*)-**3A** could be quantitatively recovered. This different behavior of the conformers shows that only (*Z*)-**3B** fulfils the stereoelectronic requirements for facile oxirane ring opening, *i.e.* the *trans*-diaxial-arrangement of the two O-atoms involved.

A further significant difference is observed between the thermolyses of (*Z*)-**3A** and the corresponding (*Z*)-epoxyenones without a CH_3-substituent in *β*-position. While the latter produce furans of type **6** exclusively, thermolysis (160°, cyclohexane) of (*Z*)-**3A** affords – *via* (*Z*)-**3B** –, in addition to the furan **6** formed *via* **a** in 45% yield[10]), the enol ethers **10** and **11** in 20% and 16% yield, respectively. The formation of **10** and **11**

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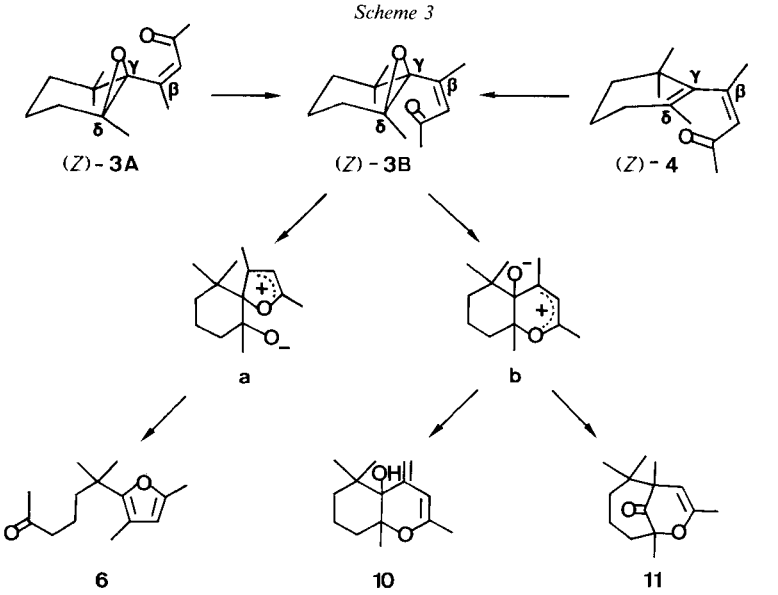
[9]) Following the thermolysis (*Z*)-**3A**→(*Z*)-**3B** by time dependent ^{1}H–NMR measurements an activation energy E_a = 25.4 ± 1.7 kcal/mol was determined [6].

[10]) For a discussion of the isomerization of (*Z*)-epoxyenones to furans, see [6] [7].

Scheme 3



presumably proceeds by a nucleophilic attack at C(δ) leading to intermediate **b**. Subsequent H-transfer or a 1,2-alkyl shift furnishes **10** and **11**, respectively (see *Scheme 3*[11]).

Furan **6**. The structure of **6** was assigned by comparison of its spectra with those of the analogous furans obtained from the photolyses of (*E*)-**1** [2] and (*E*)-**2** [3].

Cyclopropene **7**. This compound was identical with the cyclopropene produced on irradiation (λ = 254 nm) of (*E*)-**2** [2].

Allene Diketone **8**. The structure was derived by comparison of the spectra of **8** with those of the analogous products obtained from photolyses of (*E*)-**1** and (*E*)-**2** [2]. Significant signals in the ^{1}H-NMR spectrum are a *d* (J = 2.5 Hz) at 1.78 ppm for the CH_3-group and a *q* (J = 2.5 Hz) at 5.65 ppm for the H-atom of the allene moiety, which is also evidenced by the IR band at 1942 cm^{-1}. The IR bands at 1720 and 1680 cm^{-1} indicate a saturated and an unsaturated carbonyl group, respectively, and the ^{1}H-NMR spectrum shows 2 *s* at 2.10 and 2.17 ppm from the CH_3-groups of the methyl ketone moieties.

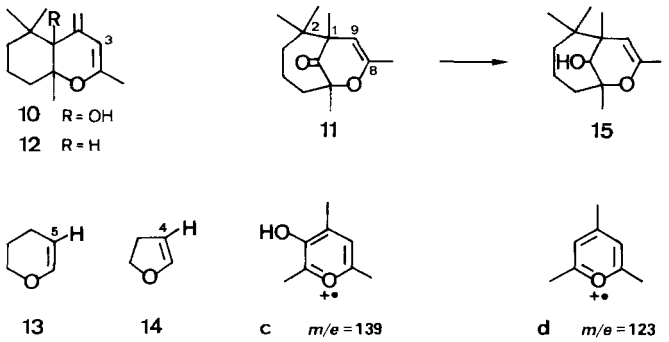
Triketone **9**. The structure of this oxidation product is evidenced by spectral data (see assignment of the NMR data in the *Exper. Part*); the configuration of the double bond has not been assigned.

Dienolether **10**. The structure was derived by comparison of the spectral data with those of **12** [4] (see *Scheme 4*). The dienol-ether moiety is evidenced by the IR bands at 1655 and 1605 cm^{-1} and the UV maximum at 258 nm (ε = 10800). In the ^{13}C-NMR spectrum the signals of the olefinic C-atoms appear at 151.2 (*s*), 144.1 (*s*), 105.9 (*t*) and 103.5 ppm (*d*), and the *s* of the quaternary C-atoms, which are substituted by a hydroxy or ether function, at 79.6 and 75.2 ppm. The ^{1}H-NMR spectrum shows two *m* at 4.73 ppm (2 H) and 5.18 ppm (1 H) for the olefinic H-atoms. Spectroscopic proof for the dihydropyran moiety was obtained by measurement of the (^{1}H, ^{13}C(3))-coupling constant. The values of 160 and 158 Hz for **10** and **12**, respectively, are in good agreement with the value determined for the (^{1}H, ^{13}C(5))-coupling constant of 3,4-dihydro-2*H*-pyran (**13**), J = 163 Hz, but significantly smaller than that for the (^{1}H, ^{13}C(4))-coupling constant of 2,3-dihydrofuran (**14**), J = 175 Hz.

Keto-Enol Ether **11**. The structure was elucidated from the spectral data. Thus, the enol-ether moiety is evidenced by an IR band at 1680 cm^{-1}, by a *d* (J = 1 Hz) at 1.75 and a *q* (J = 1 Hz) at 4.49 ppm of CH_3–C(8) and H–C(9), respectively, in the ^{1}H-NMR spectrum, and a *d* (103.1 ppm) and a *s* (148.0 ppm) of C(9) and C(8), respectively, in the ^{13}C-NMR spectrum. The IR band at 1710 cm^{-1} is characteristic for the cyclohexanone/

[11]) Compound **11** is only formed on thermolysis of (*Z*)-**3A** in the presence of Na_2CO_3 in *Pyrex* tubes, which were previously treated with KOH. In the presence of catalytic amounts of acid, only compounds **6** and **10** are formed.

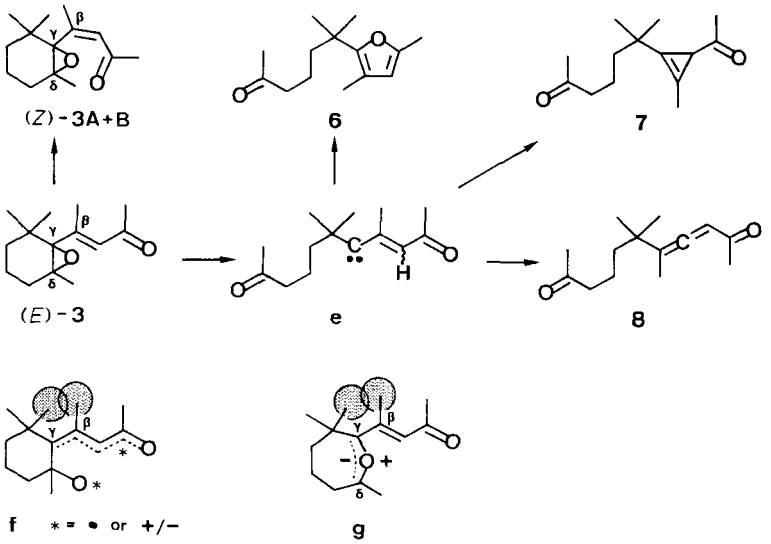
Scheme 4



cycloheptanone system. The *s* at 37.8 ppm in the ^{13}C-NMR spectrum, which was assigned to C(2) indicates that C(2) is not in the α-position to a carbonyl group, whereas the *s* of C(1) appears at 50.0 ppm and is shifted *ca.* 10 ppm upfield in the reduction product **15** (see *Scheme 4;* for the NMR data of **15** s. *Exper. Part*). Evidence for the structures **11** and **15** is also obtained from their base peaks in the MS, which are assigned to the fragments **c** (*m/e* = 139) and **d** (*m/e* = 123).

4. Discussion. – On ^{1}n,π*-excitation ($\lambda > 347$ nm), the epoxy-enone (*E*)-**3** undergoes (*E*/*Z*)-isomerization leading to the conformers (*Z*)-**3A** and (*Z*)-**3B**. On $^1\pi,\pi^*$-excitation of (*E*)-**3**, (*E*/*Z*)-isomerization of the enone side chain is also observed, however, the main process is the formation of the carbene intermediate **e** (s. *Scheme 5*) which produces the furan **6**[12])[13]), the cyclopropene **7**, and the allene diketone **8**. In addition,

Scheme 5



[12]) The furan **6** is also formed together with the enol ether **10** in a thermal or acid-catalyzed reaction from (*Z*)-**3B**. However, since compound **10** has not been detected on $^1\pi,\pi^*$-excitation of (*E*)-**3** and (*Z*)-**3A**, it is likely, that under these conditions **6** is formed *via* the carbene intermediate **e**.

[13]) Since the cyclopropene **7** is stable to the irradiation conditions, under which **6** is obtained from either (*E*)-**3** or (*Z*)-**3A**, the furan **6** is not a product of **7**.

the triketone **9** is formed presumably by oxidation of **e**. It is worth noting that the low yield of **8** in comparison to that of the allenes obtained from (*E*)-**1** and (*E*)-**2** [2] is consistent with the fact that in carbenes H-atoms migrate faster than CH_3-groups [8].

In contrast to the epoxy-enones (*E*)-**1** and (*E*)-**2**, (*E*)-**3** does not undergo isomerization *via* C(*γ*),O-bond cleavage of the oxirane ((*E*)-**3**→**f**) on either $^1n,\pi^*$-or $^1\pi,\pi^*$-excitation. Also products of an ylide intermediate **g** were not detected on $^1\pi,\pi^*$-excitation of (*E*)-**3**[14]).

These findings may be explained by a strong steric interaction between the *β*-CH_3-group and the geminal CH_3-groups. In contrast to the case of (*E*)-**1** and (*E*)-**2**, this repulsion may prevent (*E*)- and (*Z*)-**3** from assuming a conformation with an orbital overlap between the enone and the epoxide suitable for the oxirane cleavage. In the same manner this steric interaction would certainly destabilize the intermediates **f** and **g** by hindering the conjugation with the enone side chain (see *Scheme 5*)[15]). Further to this hypothesis based on stereoelectronic factors, it cannot be excluded that the absence of products arising from C(*γ*),O-bond cleavage of the oxirane, which is known to arise from a triplet excited state [10], may also be due to a rapid radiationless decay by twisting of the olefinic bond leading to (*E*/*Z*)-isomerization only[16]).

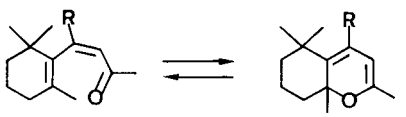
Conclusion. – Comparison of the results of the present investigation with that of the photolyses of (*E*)-**1** and (*E*)-**2** shows that the CH_3-group in *β*-position of the enone has a marked effect on the behavior of (*E*)-**3**. First of all, the steric interaction of the *β*-CH_3-group and the geminal CH_3-groups in (*E*)-**3** and (*Z*)-**3** slows down the rotation around the C(*β*),C(*γ*)-bond giving rise to the formation of two conformers (*Z*)-**3A** and (*Z*)-**3B**, which are separable at room temperature. To the best of our knowledge, such an effect was hitherto not observed in the epoxy-ionone series. There is no influence of the *β*-CH_3-group on the (*E*/*Z*)-isomerization of the enone side chain and on the formation of the carbene intermediate **e**. In contrast to the case of (*E*)-**1** and (*E*)-**2**, however, there are no products formed *via* the ylide intermediate **g** and the intermediate **f**, arising from C(*γ*),C(*δ*)- and C(*γ*),O-bond cleavage of the oxirane, respectively.

This work was supported by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung* 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).

[14]) On laser flash photolysis (*λ* = 265 nm) of (*E*)-**3** a transient ylide could not be detected either (experiments by *N. Bischofberger*).

[15]) The same steric interaction hinders the isomerization of (*Z*)-**4** to the pyran **16** [4], whereas (*Z*)-*β*-ionone ((*Z*)-**17**) spontaneously undergoes cyclization to the pyran **18** [9].

Scheme 6



(*Z*) - **4** R = CH_3 **16** R = CH_3

(*Z*) - **17** R = H **18** R = H

[16]) For examples see [11].

Experimental Part

General. See [10]. Analytical gas chromatography (GC) was performed using a 25 m × 0.36 mm *Ucon 50 HB 5100* capillary column. *Filter solution A* see [12].

1. Preparation of the Epoxy-enone (*E*)-3. – A mixture of 1.9 g (9.22 mmol) of (*E*)-**4** [4] in 70 ml of CH_2Cl_2 and 30 ml of 0.5 M aq. $NaHCO_3$ was cooled to 0°, and with stirring a solution of 2.2 g (11.5 mmol) of *m*-chloroperbenzoic acid (90%) in 30 ml of CH_2Cl_2 was added dropwise. The mixture was stirred for 1 h at 0° then for 1 h at 25°, the org. phase was separated, washed twice with 2 M NaOH and worked up. The residue was chromatographed[17]) (SiO_2, hexane/pentane/Et_2O 4:4:3) affording 1.8 g (88%) of (*E*)-**3** and 0.06 g (3%) of **5**.

(E)-4-(2',6',6'-Trimethyl-1',2'-epoxycyclohexyl)-3-penten-2-one ((*E*)-**3**) (*ca.* 2:1 mixture of two conformers). B.p. 80°/0.01 Torr. UV (0.221 mg in 10 ml): 241 (12100); (5.8 mg in 10 ml); 335 (43), end absorption to 400. IR: 2995*m* sh, 2965*s*, 2950*s*, 2935*s* sh, 2875*m*, 2855*w*, 1690*s*, 1613*s*, 1476*w*, 1463*m*, 1452*m*, 1434*m*, 1387*m*, 1378*s*, 1365*s*, 1356*s*, 1288*w*, 1268*w*, 1237*m*, 1232*m*, 1212*s*, 1190*w*, 1168*m*, 1147*w*, 1082*w*, 1075*w*, 1067*w*, 1052*w*, 1041*w*, 1023*w*, 1012*w* sh, 970*w* sh, 963*w*, 944*w*, 938*w*, 922*w*, 910*w*, 892*w*, 882*w*, 860*w*, 851*w* sh, 838*w*. ^{1}H-NMR (signals of the major conformer): 0.94, 1.02 and 1.11 (3*s*, CH_3–C(2') and 2 CH_3–C(6')); 1.20–1.95 (*m*, 2 H–C(3'), 2 H–C(4') and 2 H–C(5')); 2.07 (*d*, J = 1.5, 3 H–C(5)); 2.12 (*s*, 3 H–C(1)); 6.14 (*m*, $w_{1/2}$ = 3, H–C(3)). Characteristic signals of the minor conformer: 0.98, 1.07 (2*s*, 2 CH_3); 2.02 (*d*, J = 1.5, 3H–C(5)); 5.83 (*m*, $w_{1/2}$ = 3, H–C(3)). ^{13}C-NMR (major conformer): 21.0, 21.8, 25.1, 26.7 and 31.9 (5*q*, CH_3–C(2'), 2 CH_3–C(6'), C(1) and C(5)); 17.1 (*t*, C(4')); 30.1 and 36.8 (2*t*, C(3') and C(5')); 126.6 (*d*, C(3)); 33.6 (*s*, C(6')), 64.1 and 74.4 (2*s*, C(1') and C(2')); 154.7 (*s*, C(4)); 197.8 (*s*, C(2)). Signals of the minor conformer: 19.1, 24.0 and 26.0 (3*q*); 21.8 and 26.7 (presumably 2*q* overlapping with signals of major isomer); 17.0, 29.5 and 35.6 (3*t*); 126.8 (*d*); 34.1, 65.3, 74.2, 152.7 and 197.6 (5*s*). MS: 222 (0.2, M^+, $C_{14}H_{22}O_2$), 207 (2), 149 (9), 138 (10), *137* (100), 123 (2), 121 (4), 111 (3), 109 (3), 107 (2), 105 (2), 95 (3), 93 (3), 91 (3), 79 (3), 77 (3), 69 (3), 67 (2), 55 (4), 53 (3), 43 (22), 41 (6). Anal. calc. for $C_{14}H_{22}O_2$ (222.32): C 75.63, H 9.97; found: C 75.88, H 10.23.

[2-(2',6',6'-Trimethyl-1',2'-epoxycyclohexyl-1-propen-1-yl] acetate (**5**) (*ca.* 90% pure). B.p. 105°/0.06 Torr. UV (0.148 mg in 5 ml): 207 (10700), 215 sh, (9300). IR: 3095*w*, 2940*s* sh, 2930*s*, 2870*m*, 1758*s*, 1672*m*, 1472*m* sh, 1460*m*, 1452*m* sh, 1448*m* sh, 1435*m* sh, 1375*s*, 1368*s*, 1290*w*, 1280*w*, 1210*s*, 1170*w*, 1145*w*, 1110*s*, 1080*w* sh, 1070*w* sh, 1050*m* sh, 1040*m*, 1010*w*, 1000*w*, 973*w*, 940*m*, 920*m*, 905*m*, 895*w*, 872*w*, 840*w*. ^{1}H-NMR: 0.96, 1.00 and 1.11 (3*s*, CH_3–C(2') and 2 CH_3–C(6')); 1.66 (*m*, $w_{1/2}$ = 5, 3H–C(3)); 0.8–1.9 (*m*, 2H–C(3'), 2H–C(4') and 2H–C(5')); 2.07 (*s*, CH_3CO_2); 6.7–7.0 (*m*, H–C(1)). MS: 238 (4, M^+, $C_{14}H_{22}O_3$), 196 (19), 138 (14), 137 (14), 135 (21), 127 (10), 125 (22), 123 (59), 122 (17), 121 (14), 120 (13), 112 (16), 111 (80), 110 (11), 109 (43), 108 (23), 107 (11), 95 (19), 93 (11), 85 (20), 81 (13), 71 (12), 69 (14), 55 (18), *43* (100), 41 (22). Anal. calc. for $C_{14}H_{22}O_3$ (238.32): C 70.55, H 9.31; found: C 70.60, H 9.25.

2. Photolysis Experiments. – 2.1. *Irradiation of (E)-3.* 2.1.1. *At λ>347 nm.* A solution of 600 mg (2.70 mmol) of (*E*)-**3** was irradiated in 60 ml of MeCN (filter *A*, lamp *B*, *ca.* 85% conversion). Chromatography (SiO_2, hexane/pentane/Et_2O 4:4:3) gave 293 mg (57%) of (*Z*)-**3A** and 51 mg (10%) of (*Z*)-**3B.**

(*Z*)-**3** (conformer **A**): UV (0.578 mg in 25 ml): 224 (4600); UV (1.865 mg in 2 ml): 306 (62). IR: 2990*m* sh, 2950*s*, 2930*s*, 2875*m*, 2850*m*, 1705*s*, 1685*m* sh, 1645*m* br., 1475*m*, 1460*m*, 1450*m*, 1435*m* sh, 1375*s*, 1365*m*, 1349*m*, 1255*w*, 1230*w*, 1197*m*, 1185*m* sh, 1170*w*, 1160*w*, 1146*w*, 1070*w* sh, 1055*m*, 1040*m*, 1000*w*, 985*w*, 970*w*, 955*w*, 938*w*, 910*m*, 890*w*, 880*w*, 875*m*. ^{1}H–NMR: 1.03, 1.09 and 1.18 (3*s*, CH_3–C(2') and 2 CH_3–C(6')); 0.80–2.00 (*m*, 2H–C(3'), 2H–C(4') and 2H–C(5')); 1.80 (*d*, J = 1.5, 3H–C(5)); 2.06 (*s*, 3H–C(1)); 5.78 (*m*, H–C(3)). ^{13}C–NMR: 20.9, 23.4, 26.5, 27.7 and 30.3 (5*q*, C(1), C(5), CH_3–C(2') and 2 CH_3–C(6')); 16.7 (*t*, C(4')); 29.7 and 37.0 (2*t*, C(3') and C(5')); 131.6 (*d*, C(3)); 33.7 (*s*, C(6')); 63.5 and 72.8 (2*s*, C(1') and C(2')); 142.2 (*s*, C(4)); 200.6 (*s*, C(2)). MS: 222 (10, M^+, $C_{14}H_{22}O_2$), 207 (3), 149 (7), 139 (17), 138 (11), *137* (100), 43 (27). Anal. calc. for $C_{14}H_{22}O_2$ (222.32): C 75.63, H 9.97; found: C 75.62, H 10.06.

(*Z*)-**3** (conformer **B**): UV (0.215 mg in 10 ml): 237 (7500); UV (2.356 mg in 2 ml): 335 (40). IR: 2995*m*, 2960*s*, 2930*s*, 2875*m*, 2860*m* sh, 1690*s*, 1607*s*, 1470*m* sh, 1460*m* sh, 1450*m*, 1430*m* sh, 1395*m*, 1385*m*, 1377*m*, 1370*m* sh, 1361*m*, 1355*m*, 1290*w*, 1260*w*, 1230*w*, 1215*m*, 1205*w*, 1187*m*, 1163*m*, 1147*w*, 1075*w*, 1050*w*, 1020*w*, 985*w*, 937*w*, 910*m*, 892*w*, 885*w*, 870*w*. ^{1}H–NMR: 0.84, 0.94 and 1.00 (3*s*, CH_3–C(2') and 2 CH_3–C(6')); 1.04–2.20 (*m*, 2H–C(3'), 2H–C(4') and 2H–C(5')); 1.85 (*d*, J = 1.5, 3H–C(5)); 2.04 (*s*, 3H–C(1)); 6.11 (*m*, $w_{1/2}$ = 4, H–C(3)). ^{13}C–NMR: 21.9, 22.9, 26.4, 27.0 and 31.2 (5*q*, C(1), C(5), CH_3–C(2') and 2 CH_3–C(6')); 17.4 (*t*, C(4')); 31.5 and 37.8 (2*t*, C(3') and C(5')); 125.9 (*d*, C(3)); 33.8 (*s*, C(6')); 66.0 and 71.5 (2*s*, C(1') and C(2')); 153.8 (*s*, C(4)); 195.9 (*s*, C(2)). MS: 222 (10, M^+, $C_{14}H_{22}O_2$), 207 (3), 149 (9), 139 (9), 138 (13), *137* (100), 43 (26).

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[17]) *'Flash'* chromatography [13].

2.1.2. *At λ = 254 nm. a)* A solution of 1.0 g (4.50 mmol) of (*E*)-**3** in 100 ml of CH_3CN was irradiated (quartz, lamp *A*, *ca.* 80% conversion). Chromatography[17]) (SiO_2, hexane/pentane/Et_2O/ 2:2:3) gave mixed fractions and from their ^1H–NMR analysis the product yields were estimated to be as follows: (*Z*)-**3A** (48%), (*Z*)-**3B** (5%), **6** (10%), 7 (20%) [2], **8** (*ca.* 2%) and **9** (*ca.* 2%). *b)* A solution of 35 mg (0.16 mmol) of (*E*)-**3** in 0.5 ml CD_3CN was irradiated in a quartz NMR tube[18]) (lamp *A*). At *ca.* 95% conversion of (*E*)-**3** the following product distribution was estimated (^1H–NMR and capillary GC): (*Z*)-**3A** (40%), **6** (25%) and 7 (30%) [2].

6-Methyl-6-(3',5'-dimethyl-2'-furyl)heptan-2-one (**6**). B.p. 70°/0.01 Torr. UV (0.234 mg in 10 ml): 223 (8570); (4.2 mg in 5 ml): 284 (37). IR: 3100*w*, 2970*s* sh, 2955*s*, 2925*s*, 2910*m* sh, 2885*m*, 1721*s*, 1626*w*, 1572*w* sh, 1568*w*, 1561*w* sh, 1475*w* sh, 1460*m*, 1454*m*, 1437*m*, 1411*m*, 1390*m*, 1383*m*, 1363*m*, 1357*m* sh, 1263*m*, 1228*w*, 1284*w*, 1169*m* sh, 1159*m*, 1155*m* sh, 1140*w*, 1121*m*, 1093*w*, 999*w*, 978*w*, 958*w*. ^1H–NMR: 1,25 (*s*, 3H–C(7), CH_3–C(6)); 1.30–1.62 (*m*, 2H–C(4) and 2H–C(5)); 1.96 (*s*, 3H–C(1), CH_3–C(3')); 2.14 (*d*, J = 1, CH_3–C(5')); 2.21 (*t*, J = 6, overlapping with *d* at 2.14, 2H–C(3)); 5.53 (*m*, $w_{½}$ = 3, H–C(4')). ^{13}C–NMR: 11.6 and 13.3 (2*q*, CH_3–C(3') and CH_3–C(5')); 27.4 and 29.6 (3*q*, 2*q* overlapping at 29.6, C(1), C(7) and CH_3–C(6)); 19.5, 42.2 and 44.1 (3*t*, C(3), C(4) and C(5)); 110.5 (*d*, C(4')); 36.9 (*s*, C(6)); 113.6 (*s*, C(3')); 147.6, 153.3 (2*s*, C(2'), C(5')); 209.0 (*s*, C(2)). MS: 222 (9, M^+, $C_{14}H_{22}O_2$), 207 (2), 149 (7), 138 (10), *137* (100), 43 (13). Anal. calc. for $C_{14}H_{22}O_2$ (222.32): C 75.63, H 9.97; found: C 75.64, H 10.36.

5,6,6-Trimethyl-3,4-undecadien-2,10-dione (**8**) (*ca.* 90% pure). B.p. 80°/0.01Torr. UV (0.130 mg in 5 ml): 220 (9900); UV (1.26 mg in 2 ml): end absorption to 380. IR: 3000*w* sh, 2960*s*, 2930*m*, 2870*m*, 1942*m*, 1720*s*, 1680*s*, 1605*m* br., 1460*m*, 1445*m*, 1420*m* sh, 1408*m*, 1355*s*, 1230*s*, 1177*m*, 1166*m*, 1108*w*, 1030*w*, 1015*w* sh, 992*w*, 955*w*. ^1H–NMR: 1.07 (*s*, 2 CH_3–C(6)); 0.8–1.8 (*m*, 2H–C(7) and 2H–C(8)); 1.78 (*d*, J = 2.5, CH_3–(5)); 2.10 and 2.17 (2*s*, 3H–C(1) and 3H–C(11)); 2.3–2.5 (*m*, 2H–C(9)); 5.65 (*q*, J = 2.5, H–C(3)). MS: 222 (3, M^+, $C_{14}H_{22}O_2$), 207 (7), 137 (21), 123 (18), 121 (13), 109 (18), 96 (10), 95 (12), 69 (19), *43* (100).

4,6,6-Trimethyl-3-undecen-2,5,10-trione (**9**). B.p. 110°/0.04 Torr. UV (0.187 mg in 10 ml): 231 (6900); UV (7.6 mg in 7 ml): end absorption to 390. IR: 2970*m*, 2935*m*, 2860*w* sh, 1723*s*, 1693*s*, 1615*s*, 1465*m*, 1445*m*, 1410*m* sh, 1389*m* sh, 1363*s*, 1198*m*, 1152*m*, 1042*m*, 1018*w* sh, 992*m*, 949*w*. ^1H–NMR: 1.10 (*s*, 2 CH_3–C(6)); 1.42–1.56 (*m*, 2H–C(7) and 2H–C(8)); 1.95 (*d*, J = 1.5, CH_3–C(4)); 2.02 and 2.08 (2*s*, 3H–C(1) and 3H–C(11)); 2.25–2.42 (*m*, 2H–C(9)); 5.93 (*q*, J = 1.5, H–C(3)). ^{13}C–NMR: 22.2, 23.9, 29.7 and 29.9 (5*q*, 2*q* overlapping at 23.9, C(1), C(11), CH_3–C(4) and 2 CH_3–C(6)); 18.3, (*t*, C(8)); 38.9 (*t*, C(7)); 44.0 (*t*, C(9)); 125.0 (*d*, C(3)); 46.4 (*s*, C(6)); 156.3 (*s*, C(4)); 196.4, 208.8 and 216.3 (3*s*, C(2), C(5) and C(10)). MS: 238 (< 1, M^+, $C_{14}H_{22}O_3$), 153 (8), 127 (25), 113 (8), *112*, (100), 111 (16), 110 (8), 109 (78), 71 (16), 69 (94), 55 (8), 43 (93), 41 (23). Anal. calc. for $C_{14}H_{22}O_3$ (238.32): C 70.55, H 9.31; found: C 70.36, H 9.44.

2.2. *Irradiation of* (*Z*)-**3A.** A solution of 30 mg (0.14 mmol) of (*E*)-**3** in 0.4 ml CD_3CN was irradiated in a quartz NMR tube[18]) (lamp *B*, filter *A*). After 4 h the following product distribution was determined (^1H–NMR) (*E*)-**3** (15%), (*Z*)-**3A** (80%), (*Z*)-**3B** (5%). Irradiation was continued with lamp *A* and the reaction was followed by ^1H–NMR. After 4 h the following product distribution was estimated (^1H–NMR and capillary GC): (*Z*)-**3A** (35%), (*E*)-**3** (10%), **6** (20%) and **7** (30%) [2].

2.3. *Irradiation of* (*Z*)-**3B.** A solution of 210 mg (0.95 mmol) of crude (*Z*)-**3B** (prepared as described in *Sect. 3.1*) in 10 ml of CH_3CN was irradiated (filter *A*, lamp *B*, *ca.* 100% conversion). Chromatography[17]) (SiO_2, hexane/pentane/Et_2O 2:2:1) afforded 31 mg (15%) of (*E*)-**3** and 106 mg (50%) of (*Z*)-**3A.**

3. Additional Experiments. – 3.1. *Epoxidation of* (*Z*)-**4.** To a solution of 102 mg (0.50 mmol) of (*Z*)-**4** [4] in 5 ml of Et_2O were added 3 ml of 0.5M aq. $NaHCO_3$ and a solution of 160 mg (0.83 mmol) of *m*-chloroperbenzoic acid (90%) in 3 ml of Et_2O. The mixture was stirred for 4 h at 0° and worked up in Et_2O as described for (*E*)-**3**. Chromatography[17]) of the residue (SiO_2, pentane/hexane/Et_2O 2:2:1) afforded 70 mg (64%) of (*Z*)-**3B**.

3.2. *Acid-Catalyzed Rearrangements of* (*Z*)-**3A** *and* (*Z*)-**3B.** *a)* To a solution of (*Z*)-**3A** (85 mg, 0.38 mmol) in CH_2Cl_2 (5 ml) was added two drops of 2N HCl at –20°. After stirring for 1 h, the mixture was slowly warmed to –10°, treated with 1N $NaHCO_3$ solution and worked up giving 83 mg of starting material ((*Z*)-**3A**). *b)* Analogous treatment of (*Z*)-**3B** (23 mg, 0.10 mol) in CH_2Cl_2 (2 ml) with one drop of 2N HCl gave after workup a 4:1 mixture (21 mg) of **6** and **10** (^1H–NMR analysis). *c)* To a solution of 340 mg (1.5 mmol) of crude (*Z*)-**3B** (prepared as described in *Sect. 3.1*) in 100 ml CH_2Cl_2 was added with stirring 5 drops of *conc.* HCl at 25°. After 30 min, the mixture was worked up and the residue chromatographed[17]) (SiO_2, hexane/pentane/Et_2O 2:2:1) giving 48 mg (14%) of **10** and 160 mg (48%) of **6**.

1,3,7,7-Tetramethyl-5-methylidene-2-oxabicyclo[4.4.0]dec-3-en-6-ol (**10**). B.p. 80°/0.01 Torr. UV (0.130 mg in 5 ml): 258 (10800). IR: 3610*m*, 3510*w* br., 3090*w*, 3050*w*, 2980*s*, 2970*s*, 2950*s* sh, 2935*s*, 2920*s*, 2870*s*,

[18]) The tube was previously washed with 40% aq. NaOH, H_2O and EtOH and dried under vacuum.

2855*m* sh, 1655*s*, 1605*m*, 1479*m*, 1458*m*, 1450*m* sh, 1428*m*, 1380*s*, 1370*s*, 1360*m*, 1336*s*, 1315*m*, 1300*m*, 1277*m*, 1263*m* sh, 1228*m*, 1185*s*, 1160*s*, 1120*m*, 1074*s*, 1043*m*, 1025*m*, 990*m* sh, 986*s*, 955*m*, 937*m*, 897*w*, 877*s*, 860*m*. ^{1}H–NMR: 0.88, 0.90 and 1.09 (3*s*, CH_3–C(1) and 2 CH_3–C(7)); 1.16 (*s*, OH); 0.80–1.90 (*m*, 2H–C(8), 2H–C(9) and 2H–C(10)); 1.71 (*m*, $w_{1/2}$ = 2.5, CH_3–C(3)); 4.73 (*m*, $w_{1/2}$ = 3, CH_2=C(5)); 5.18 (*m*, $w_{1/2}$ = 3, H–C(4)). ^{13}C–NMR: 20.0, 20.3, 23.7 and 26.1 (4*q*, CH_3–C(1), CH_3–C(3) and 2 CH_3–C(7)); 17.7, 34.4 and 36.2 (3*t*, C(8), C(9) and C(10)); 105.9 (*t*, CH_2 = C(5)); 103.5 (*d*, C(4)); 37.5 (*s*, C(7)); 75.2 and 79.6 (2*s*, C(1) and C(6)); 144.1 and 151.2 (2*s*, C(3) and C(5)). MS: 222 (22, M^+, $C_{14}H_{22}O_2$), 207 (5), 153 (11), 151 (10), 140 (12), 139 (50), 138 (21), *137* (100), 125 (13), 123 (14), 111 (18), 109 (25), 96 (15), 95 (12), 69 (26), 55 (17), 43 (88), 41 (28).

3.3. *Thermolysis of* (*Z*)-**3A** *and* (*Z*)-**3B.** *a)* A solution of (*Z*)-**3A** (70 mg, 0.32 mmol) in C_6D_{12} (0.7 ml) was sealed in an NMR tube[18]) at 0.01 Torr. After heating to 80° for 90 min, ^{1}H–NMR analysis indicated (*Z*)-**3B** exclusively. *b)* Two solutions of (*Z*)-**3A** (300 mg, 1.35 mmol) in C_6H_{12} (*ca.* 3 ml, filtered through Al_2O_3 bas., *Super I*) and anh. Na_2CO_3 (10 mg, 0.1 mmol) were sealed in *Pyrex* tubes[18]) and heated to 170° for 2 h. Chromatography[17]) (SiO_2, Et_2O/hexane 1:7) gave **6** (272 mg, 45%), **10** (120 mg, 20%) and **11** (98 mg, 16%).

1,2,2,6,8-Pentamethyl-7-oxabicyclo[4.3.1]dec-8-en-10-one (**11**). IR: 3060*w*, 2975*s*, 2940*s* sh, 2920*s*, 2870*m*, 1710*s*, 1680*s*, 1465*m*, 1447*s*, 1430*m*, 1391*m*, 1380*s*, 1375*s*, 1369*s*, 1330*s*, 1252*w*, 1190*w*, 1175*m*, 1155*m*, 1145*s*, 1113*s*, 1075*m*, 1065*m*, 1035*m*, 1010*w*, 980*m*, 910*w*, 875*w*. ^{1}H–NMR: 0.83, 0.91, 0.99 (3*s*, CH_3–C(1), 2 CH_3–C(2)); 1,32 (*s*, CH_3–C(6)); 1.75 (*d*, *J* = 1, CH_3–C(8)); 0.8–2.2 (*m*, 2 H–C(3), 2 H–C(4), 2 H–C(5)); 4.49 (*d*, *J* = 1, H–C(9)). ^{13}C–NMR: 20.2, 20.4, 23.1, 25.0, 25.2 (5*q*, CH_3–C(1), 2 CH_3–C(2), CH_3–C(6), CH_3–C(8)); 19.7, 40.1, 42.4 (3*t*, C(3), C(4), C(5)); 103.1 (*d*, C(9)); 37.8 (*s*, C(2)); 50.0 (*s*, C(1)); 83.3 (*s*, C(6)); 148.0 (*s*, C(8)); 211.1 (*s*, C(10)). MS: 222 (10, M^+, $C_{14}H_{22}O_2$), 207 (6), *139* (100), 111 (15), 55 (10), 43 (38), 41 (21).

3.4. *Reduction of* **11** *with* $LiAlH_4$. To a solution of **11** (50 mg, 0.23 mmol) in abs. Et_2O (15 ml) was added $LiAlH_4$ (60 mg, 1.6 mmol) and the mixture was stirred at ambient temp. for 40 min. Workup with sat. $(NH_4)_2SO_4$ gave **15** (46 mg, 91%).

1,2,2,6,8-Pentamethyl-7-oxabicyclo[4.3.1]dec-8-en-10-ol (**15**). IR: 3630*m*, 3055*w*, 2960*s*, 2940*s*, 2915*s*, 2870*s*, 1680*m*, 1445*m*, 1425*w*, 1390*m*, 1375*m*, 1360*m*, 1333*s*, 1305*w*, 1240*w*, 1222*w*, 1175*s*, 1150*m*, 1130*m*, 1118*m*, 1085*m*, 1058*s*, 1045*m*, 1030*m*, 980*m*, 950*w*, 925*w*, 895*w*, 845*w*. ^{1}H–NMR (80 MHz): 0.90, 1.05, 1.08 (3*s*, CH_3–C(1), 2 CH_3–C(2)); 1.35 (*s*, CH_3–C(6)); 1.70 (*m*, $w_{1/2}$ = 2.5, CH_3–C(8)); 0.7–2.2 (*m*, 2 H–C(3), 2 H–C(4), 2 H–C(5), OH); 3.68 (*d*, *J* = 6, after D_2O exchange: *s*, H–C(10)); 4.10 (*m*, $w_{1/2}$ = 2.5, H–C(9)). ^{13}C–NMR (75 MHz): 20.2, 26.8, 28.3, 29.4, 30.0 (5*q*, CH_3–C(1), 2 CH_3–C(2), CH_3–C(6), CH_3–C(8)); 19.4, 40.0, 44.5 (3*t*, C(3), C(4), C(5)); 84.8 (*d*, C(10)), 103.5 (*d*, C(9)); 38.2, 39.8 (2*s*, C(1), C(2)); 78.6 (*s*, C(6)); 146.4 (*s*, C(8)). MS: 224 (8, M^+, $C_{14}H_{24}O_2$); 209 (3), 142 (17), 139 (10), *123* (100); 115 (17), 99 (11), 85 (15), 69 (17), 55 (18), 43 (63), 41 (32).

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