15. Photochemical Reactions

133rd Communication[1])

Photochemistry of Epoxydienes of the Ionone Series: Influence of a Methyl Group at the Diene Side Chain on the Oxirane Cleavage

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Summary

On triplet excitation ($\lambda > 280$ nm, acetone), the epoxydiene (*E*)-**2** undergoes (*E*)/(*Z*)-isomerization exclusively, leading to the conformers (*Z*)-**2A** and (*Z*)-**2B.** On singlet excitation ($\lambda = 254$ nm), apart from (*Z*)-**2A** + **B,** the cyclobutenes **3A** + **B** are formed. However, the epoxydiene (*E*)-**2** does not undergo reactions leading to carbene and C,O-bond cleavage products, which are normally observed on singlet and triplet excitation, respectively, of the epoxydienes of the ionone series.

1. Introduction. – As reported in [1], on $^1n,\pi^*$-excitation, the epoxyenone (*E*)-**1** (*Scheme 1*) undergoes (*E*)/(*Z*)-isomerization of the enone side chain exclusively, and on $^1\pi,\pi^*$-excitation, products arising from a carbene intermediate are formed. However, the expected isomerization *via* C(6),O-bond cleavage[3]) of the oxirane was not observed on either mode of excitation.

Since the triplet sensitization of epoxydienes is known to induce efficiently C(6),O-bond cleavage [3], the behavior of the epoxydiene (*E*)-**2** was investigated to gain some additional information on the possible reasons for the lack of C,O-bond cleavage products in the corresponding epoxyenone (*E*)-**1**.

Compound (*E*)-**2** was obtained by reaction of (*E*)-**1** with methylenetriphenylphosphorane in 99% yield.

2. Photolyses. – 2.1. *Singlet Excitation of* (E)-**2.** The photolysis ($\lambda = 254$ nm) of a *ca.* 0.02M solution of (*E*)-**2** in CH_3CN (73% conversion) gave[4]) (*Z*)-**2A** (8%), (*Z*)-**2B** (2%), **3A** (5%) and **3B** (5%).

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[1]) 132nd Communication, see [1].

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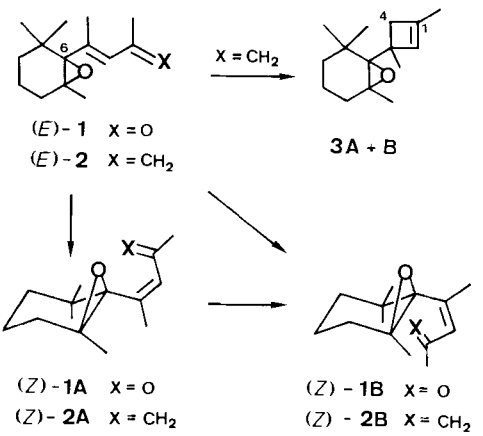
[3]) In ionone derivatives numbering according to the carotinoid nomenclature is used [2].

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

Scheme 1



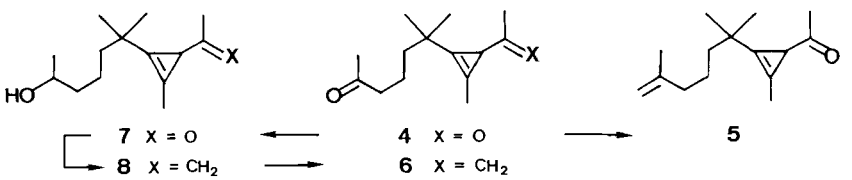
2.2. *Triplet Excitation of* (E)-**2**. *a*) Photolysis of a *ca.* 0.02M solution of (*E*)-**2** in acetone ($\lambda > 280$ nm, 46% conversion) gave[4]) (*Z*)-**2A** (76%) and (*Z*)-**2B** (12%). *b*) Irradiation of (*E*)-**2** under the same conditions up to 85% conversion gave, apart from (*Z*)-**2A** (13%) and (*Z*)-**2B** (*ca.* 1%), only intractable material.

3. Structure of the Compounds. – *Epoxydienes* (E)-**2**, (Z)-**2A** *and* (Z)-**2B**. *Wittig* reaction of the epoxyenones (*E*)-**1** and (*Z*)-**1A** + **B** *(Scheme 1)* with methylenetriphenylphosphorane gave (*E*)-**2** and (*Z*)-**2A** + **B** in 99% and 81% yield, respectively. The assignment of their structure follows conclusively from comparison of the spectral data with those of the corresponding epoxyenones (*E*)-**1**, (*Z*)-**1A** and (*Z*)-**1B** (see *Exper. Part*). The epoxydiene (*Z*)-**2A** was smoothly transformed into (*Z*)-**2B** when warmed to *ca.* 120° in C_6D_{12}.

Following the thermolysis (*Z*)-**2A**→(*Z*)-**2B** by ^{1}H-NMR measurements, an activation energy $E_a = 23.9 \pm 2.0$ kcal/mol was determined [4].

Cyclobutenes ***3A*** + ***B***. The structures were assigned by the spectral data. In particular the ^{13}C-NMR spectrum of **3A** indicates that the epoxy-cyclohexyl moiety is still intact. For the cyclobutene moiety a *t* (46.5 ppm), a *d* (137.2 ppm) and 2 *s* (47.5, 141.8 ppm) are evident in the ^{13}C-NMR spectrum, and characteristic signals in the ^{1}H-NMR spectrum are an *AB*-system (J = 13 Hz) at 2.56 ppm (2H-C(4)), a *m* ($w_{½}$ = 4 Hz) at 5.88 ppm (H–C(2)) and a *m* ($w_{½}$ = 4 Hz) at 1.68 ppm (CH_3–C(1)). The ^{1}H-NMR spectrum of **3B** obtained in *ca.* 70% purity is very similar to that of **3A** (see *Exper. Part*). For the proof of the structures, **3A** and **3B** were thermolyzed separately at 120° in toluene. Compound (*E*)-**2** was obtained quantitatively from **3A** and as the main product from **3B**.

Scheme 2



4. Transformation of the Cyclopropene Diketone 4 into the Methylidene Derivatives 5 and 6 *(Scheme 2)*. – Since on singlet excitation (λ = 254 nm) of (*E*)-**2**, the cyclopropene ketone **6** could not be detected, it was prepared from the corresponding cyclo-

propene diketone **4** [1] and photolyzed to determine, if it was a labile intermediate in the photolysis of (*E*)-**2**.

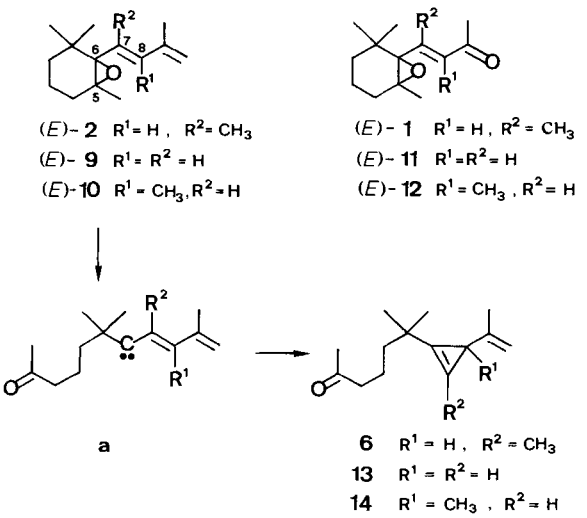
The reaction of **4** with methylenetriphenylphosphorane gave exclusively the cyclopropenyl methyl ketone **5** in 81% yield. However, the synthesis of **6** could be achieved by selective reduction of **4** with $NaBH_4$ (**4**→**7**), subsequent reaction of the alcohol **7** with methylenetriphenylphosphorane (**7**→**8**), and *Collins* oxidation of **8** to give the cyclopropene ketone **6** in 44% overall yield.

The cyclopropene derivatives **5** and **6** can easily be distinguished by their IR and ^{1}H-NMR spectra. Thus, **5** shows an IR band at 1680 cm^{-1}, which is characteristic for a conjugated carbonyl group, whereas the IR band of **6** at 1720 cm^{-1} indicates a saturated aliphatic ketone. Furthermore, the ^{1}H-NMR spectrum of **5** shows a *s* for the cyclopropene-H-atom at 2.28 ppm, while the corresponding *s* in the ^{1}H-NMR spectrum of **6** appears at 2.07 ppm. For the complete spectral data of **5** and **6** see *Exper. Part.*

5. Discussion. – On photolysis of the epoxydiene (*E*)-**2** product formation arising from oxirane cleavage was not observed. On triplet excitation, (*E*)-**2** undergoes (*E*)/(*Z*)-isomerization exclusively, leading to the conformers (*Z*)-**2A** and (*Z*)-**2B**, whereas on singlet excitation of (*E*)-**2**, apart from (*Z*)-**2A** + **B**, the cyclobutenes **3A** + **B** are formed by an electrocyclic reaction of the diene side chain. Thus, on triplet excitation the epoxydiene (*E*)-**2** shows behaviour analogous to that of the corresponding epoxyenone (*E*)-**1** on ^{1}n,π*-excitation. For the lack of C,O-bond cleavage, the steric factors or a rapid radiationless decay by twisting of the C(7),C(8) double bond, which were both discussed in [1], may be also here responsible.

In contrast to the ^{1}π,π*-excitation of the epoxyenone (*E*)-**1**, which efficiently produces carbene products, that of the epoxydiene (*E*)-**2** does not give rise to the transformation of (*E*)-**2**→**a**→**6** (*Scheme 3*). To prove that the cyclopropene **6** is not a labile intermediate on photolysis of (*E*)-**2**, it was prepared (see *above*), photolyzed separately, and found to be comparatively stable upon irradiation (λ = 254 nm). Furthermore,

Scheme 3



comparison of the $^1\pi,\pi^*$-excitationf the epoxydienes (*E*)-**2**, (*E*)-**9** and (*E*)-**10** with that of the corresponding epoxyenones (*E*)-**1**, (*E*)-**11** and (*E*)-**12** shows an important effect. While the yields of carbene products are similar on photolysis ($\lambda = 254$ nm) of (*E*)-**1**, (*E*)-**11** and (*E*)-**12** (*ca.* 20–30%) [1] [5], there is a dramatic difference in the diene series. On $^1\pi,\pi^*$-excitation of (*E*)-**9**, the cyclopropene **13** is isolated in 49% yield [6], whereas (*E*)-**10**, substituted by a CH_3-group at C(8) produces only 6% of the methyl-homologous cyclopropene **14** [3], and as shown here, there is no cyclopropene **6** formed on photolysis of (*E*)-**2**, which is substituted by a CH_3-group at C(7) on the diene side chain.

These findings demonstrate that different photo-processes are affected differently by the presence of CH_3-groups on the diene moiety. The carbene formation is hampered by CH_3-groups on both the C(7)- and C(8)-positions, whereas C,O-cleavage is only prevented in the case of (*E*)-**2** with a CH_3-group at C(7). On photolysis of (*E*)-**10**, bearing a CH_3-group at C(8), C,O-cleavage occurs.

It has been reported [4] that the CH_3-group at C(7) in (*E*)-**1** and (*E*)-**2** show a sterically repulsive interaction with the CH_3-groups on the cyclohexane ring. As observed in the NMR spectra of (*E*/*Z*)-**1** and (*E*/*Z*)-**2** this interaction hinders rotation around the C(6), C(7)-bond. A CH_3-group at C(8), however, does not cause this effect in the NMR. The C,O-cleavage on triplet excitation of (*E*)-**2**, (*E*)-**9** and (*E*)-**10** follows the same trend as the NMR measurements of steric hinderance, indicating the possibility that the C,O-cleavage of (*E*)-**1** and (*E*)-**2** is prevented by steric reasons as discussed in [1]. However, carbene formation is already diminished in the case of (*E*)-**10**, a compound which shows no particular steric effects in the NMR, so it may be concluded that in the case of carbene formation the CH_3-groups in the side chain of (*E*)-**2** and (*E*)-**10** are exerting primarily an electronic effect, or increase the rate of (*E*)/(*Z*)-isomerization.

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Experimental Part

General. See [1]. Chromatographic separations were performed according to [7].

1. Preparation of (*E*)-2. – To a solution of (*E*)-**1** (3.52 g, 15.9 mmol) in abs. Et_2O (150 ml) was added in portions $(C_6H_5)_3PCH_2$ (*ca.* 0.2 M solution in THF). After complete conversion of the starting material (TLC), the mixture was poured into pentane/H_2O and worked up. The resulting mixture was suspended in pentane, filtered through *Celite* and chromatographed (160 g SiO_2, Et_2O/hexane 1:20) to give (*E*)-**2** (3.48 g, 99%).

(E)-*4-(1',2'-Epoxy-2',6',6'-trimethyl-1'-cyclohexyl)-2-methyl-1,3-pentadiene* ((*E*)-**2**) (*ca.* 1:1 mixture of two conformers). B.p. 75°/0.07 Torr. UV (0.226 mg in 10 ml pentane): 237 (11000). IR: 3080*w*, 2960*s* sh, 2940*s*, 2920*s* sh, 2870*m*, 1640*w*, 1625*w*, 1595*w*, 1460*m*, 1450*m*, 1380*s*, 1360*m*, 1250*w*, 1235*w*, 1185*w*, 1170*w*, 1145*w*, 1050*m*, 970*w*, 935*w*, 895*s*, 890*m* sh, 865*w*. ^{1}H-NMR (100 MHz, $CDCl_3$): 0.98, 1.01, 1.02, 1.04, 1.12, 1.18 (6*s*, CH_3-C(2'), 2 CH_3–C(6')); 1.1–1.9 (*m*, 2 H–C(3'), 2 H–C(4'), 2 H–C(5')); 1.80 (*d*, $J = 1$, 3 H–C(5) of one conformer), 1.85 (*m*, $w_{1/2} = 3$, 3 H–C(5), CH_3–C(2)); 4.81, 4.97 (2*m*, $w_{1/2} = 5$, 2 H–C(1)); 5.57, 5.90 (2*m*, $w_{1/2} = 4$, H–C(3)). ^{13}C-NMR (75 MHz, $CDCl_3$): 16.7, 19.4, 21.7, 23.6, 23.8, 24.0, 25.4, 26.4, 27.0 (10*q*, 2*q* overlapped at 27.0, C(5), CH_3–C(2), CH_3–C(2'), 2 CH_3–C(6')); 17.2, 17.3, 30.0, 30.4, 35.9, 37.0 (6*t*, C(3'), C(4'), C(5')); 114.8, 115.0 (2*t*, C(1)); 131.2, 131.4 (2*d*, C(3)); 34.2, 34.5 (2*s*, C(6')); 64.2, 65.6, 74.6, 74.7 (4*s*, C(1'), C(2')); 133.1, 134.5, 141.3, 141.5 (4*s*, C(2), C(4)). MS: 220 (4, M^+, $C_{15}H_{24}O$), 205 (5), 147 (16), 138 (12),

137 (100), 136 (15), 135 (74), 121 (16), 120 (10), 119 (29), 109 (16), 107 (14), 105 (14), 93 (11), 91 (16), 81 (12), 79 (13), 77 (12), 69 (18), 55 (16), 53 (15), 43 (44), 41 (37).

$C_{15}H_{24}O$ (220.36) Calc. C 81.76 H 10.98% Found C 81.65 H 10.83%

2. Photolysis Experiments. – 2.1. *Singlet Excitation of* (*E*)-**2** *($\lambda = 254$ nm).* A solution of (*E*)-**2** (0.81 g, 3.68 mmol) in CH_3CN (200 ml) was irradiated under Ar (quartz, lamp *A*; 73% conversion). Chromatography (160 g SiO_2, Et_2O/hexane 1:3) of the reaction mixture gave[4]: (*E*)-**2** (215 mg), (*Z*)-**2A** + **B** (*ca.* 4:1 mixture, 60 mg, 10%), **3A** (28 mg, 5%) and **3B** (70% pure, 40 mg, 5%).

(*Z*)-**2A**: b.p. 80°/0.07 Torr. UV (0.637 mg in 25 ml pentane): 234 (8400). IR: 3085*w*, 2930*s*, 2875*m*, 2850*m* sh, 1655*w*, 1640*w*, 1590*w*, 1475*m*, 1460*m* sh, 1450*s*, 1435*m* sh, 1380*s*, 1360*m*, 1290*w*, 1270*w*, 1235*w*, 1190*w*, 1170*w* br., 1145*w*, 1050*m* br., 985*w*, 970*m*, 955*w*, 940*w*, 910*w*, 910*s*, 895*s*. ^{1}H-NMR (100 MHz, $CDCl_3$): 1.04, 1.10, 1.22 (3*s*, CH_3-C(2'), 2 CH_3-C(6')); 1.2–1.9 (*m*, 2 H–C(3'), 2 H–C(4'), 2 H–C(5')); 1.79, 1.82 (2*m*, $w_{1/2} = 4$, CH_3–C(2), 3 H–C(5)); 4.89, 4.96 (2*m*, $w_{1/2} = 5$, 2 H–C(1)); 5.84 (*m*, $w_{1/2} = 4$, H–C(3)). ^{13}C-NMR (75 MHz, $CDCl_3$): 22.1, 23.5, 24.8, 27.2, 27.4 (5*q*, CH_3–C(2), C(5), CH_3–C(2'), 2 CH_3–C(6')); 17.1, 29.8, 36.9 (3*t*, C(3'), C(4'), C(5')); 114.3 (*t*, C(1)); 133.4 (*d*, C(3)); 34.5 (*s*, C(6')); 61.9, 72.8 (2*s*, C(1'), C(2')); 133.1, 142.3 (2*s*, C(2), C(4)). MS: 220 (5, M^+, $C_{15}H_{24}O$), 205 (5), 147 (21), 138 (14), *137* (100), 136 (18), 135 (97), 121 (24), 120 (16), 119 (37), 109 (21), 107 (20), 105 (20), 93 (14), 91 (21), 81 (11), 79 (14), 77 (13), 69 (22), 55 (16), 53 (13), 43 (79), 41 (36).

$C_{15}H_{24}O$ (220.36) Calc. C 81.76 H 10.98% Found C 81.84 H 10.85%

(*Z*)-**2B** (contamined with *ca.* 15% of (*Z*)-**2A**): UV (0.080 mg in 5 ml pentane): 241 (10200). IR: 3085*w*, 2970*s*, 2930*s*, 2875*s*, 2850*m* sh, 1630*m* br., 1595*w*, 1460*s* sh, 1450*s*, 1435*m* sh, 1380*s*, 1365*m*, 1180*m*, 1170*w*, 1145*w*, 1070*m*, 1050*m*, 1025*m*, 985*m*, 975*m*, 960*w*, 935*w*, 900*s*, 890*s*, 845*w*. ^{1}H-NMR (100 MHz, $CDCl_3$): 1.04, 1.10, 1.20 (3*s*, CH_3–C(2'), 2 CH_3–C(6')); 1.84 (*m*, $w_{1/2} = 3$, CH_3–C(2), 3 H–C(5)); 1.2–1.9 (*m*, 2 H–C(3'), 2 H–C(4'), 2 H–C(5')); 4.87, 5.04 (2*m*, $w_{1/2} = 4$, 2 H–C(1)); 5.78 (*m*, $w_{1/2} = 4$, H–C(3)). ^{13}C-NMR (75 MHz, $CDCl_3$): 21.9, 23.7, 24.3, 26.8, 27.4 (5*q*, CH_3–C(2), C(5), CH_3–C(2'), 2 CH_3–C(6')); 17.4, 31.7, 38.1 (3*t*, C(3'), C(4'), C(5')); 114.5 (*t*, C(1)); 128.9 (*d*, C(3)); 34.4 (*s*, C(6')); 66.5, 70.7 (2*s*, C(1'), C(2')); 134.9, 141.0 (2*s*, C(2), C(4)). MS: 220 (3, M^+, $C_{15}H_{24}O$), 205 (5), 147 (17), 138 (13), *137* (100), 136 (17), 135 (88), 121 (21), 120 (13), 119 (33), 109 (18), 107 (18), 105 (18), 93 (14), 91 (22), 81 (12), 79 (16), 77 (16), 69 (21), 55 (18), 53 (14), 43 (52), 41 (39).

3-(1',2'-Epoxy-2',6',6'-trimethyl-1'-cyclohexyl)-1,3-dimethylcyclobutene (*isomer A*, **3A**). B.p. 60°/0.05 Torr. IR: 3040*w*, 2960*s*, 2930*s*, 2910*s*, 2870*s*, 2850*m*, 1650*w* br., 1470*w*, 1460*m* sh, 1450*m*, 1440*m*, 1380*s*, 1370*m*, 1360*m*, 1345*w*, 1280*w*, 1185*w*, 1145*w*, 1070*w*, 1040*m*, 1030*m*, 985*w*, 975*w*, 950*w*, 935*w*, 905*m*, 890*w*, 865*w*, 840*w*, 670*w*. ^{1}H-NMR (80 MHz, $CDCl_3$): 1.13, 1.18, 1.31, 1.37 (4*s*, CH_3–C(3), CH_3–C(2'), 2 CH_3–C(6')); 1.68 (*m*, $w_{1/2} = 4$, CH_3–C(1)); 0.95–2.00 (*m*, 2 H–C(3), 2 H–C(4'), 2 H–C(5')); 2.56 (*AB*-system, $J = 13$, $\delta_A = 2.15$, broadened, $\delta_B = 2.96$, broadened, 2 H–C(4)); 5.88 (*m*, $w_{1/2} = 4$, H–C(2)). ^{13}C-NMR (25 MHz, $CDCl_3$): 16.4, 21.7, 25.7, 26.0, 26.2 (5*q*, CH_3–C(1), CH_3–C(3), CH_3–C(2'), 2 CH_3–C(6')); 16.8, 33.4, 41.0 (3*t*, C(3'), C(4'), C(5')); 46.5 (*t*, C(4)); 137.2 (*d*, C(2)); 35.5 (*s*, C(6')); 47.5 (*s*, C(3)); 63.5, 72.0 (2*s*, C(1'), C(2')); 141.8 (*s*, C(1)). MS: 220 (4, M^+, $C_{15}H_{24}O$), 147 (17), 138 (13), *137* (100), 136 (15), 135 (74), 121 (20), 120 (12), 119 (36), 109 (22), 107 (18), 105 (16), 93 (14), 91 (18), 85 (10), 81 (16), 79 (15), 77 (12), 69 (26), 67 (10), 55 (21), 53 (12), 43 (54), 41 (37).

$C_{15}H_{24}O$ (220.36) Calc. C 81.76 H 10.98% Found C 81.70 H 10.91%

Isomer B (**3B**). ^{1}H-NMR (80 MHz, $CDCl_3$; signals of a *ca.* 70% pure sample which can be assigned to **3B**): 1.07, 1.14, 1.25, 1.42 (4*s*, CH_3–C(3), CH_3–C(2'), 2 CH_3–C(6')); 1.67 (*m*, $w_{1/2} = 5$, CH_3–C(1)); 2.95 (*B*-part of an *AB*-system, $J = 13$, broadened, H–C(4)); 6.01 (*m*, $w_{1/2} = 4$, H–C(2)).

2.2. *Triplet Excitation of* (E)-**2** *($\lambda > 280$ nm, acetone). a)* A solution of (*E*)-**2** (1.00 g, 4.55 mmol) in acetone (200 ml) was irradiated under Ar (*Pyrex*, lamp *B*; 46% conversion). Chromatography of the reaction mixture (75 g SiO_2, benzene/hexane 1:4) afforded[4]: (*E*)-**2** (536 mg), (*Z*)-**2A** (295 mg, 64%) and (*Z*)-**2A** + **B** (1:1 mixture, 118 mg, 24%). *b)* Irradiation of a solution of (*E*)-**2** (430 mg, 1.94 mmol) in acetone (120 ml) under the same conditions up to 85% conversion gave (*E*)-**2** (65 mg), (*Z*)-**2A** + **B** (*ca.* 10:1 mixture, 51 mg, 14%) and intractable material.

2.3. *Irradiation of* **6** *($\lambda = 254$ nm).* A solution of **6** (10 mg, 0.045 mmol) in CD_3CN (0.6 ml) was irradiated (lamp *A*) in a quartz NMR tube. After 19 h, ^{1}H-NMR analysis of the reaction mixture showed *ca.* 50% of **6** apart from intractable material.

3. Additional Experiments. – 3.1. *Transformation of* (Z)-**1A** + **B** *into* (Z)-**2A** + **B.** To a solution of (*Z*)-**1A** + **B** (85:15 mixture, 227 mg, 1.02 mmol) in abs. Et_2O (5 ml) was added with stirring a *ca.* 0.3 M solution of $(C_6H_5)_3PCH_2$ in abs. Et_2O (5 ml) at 0° under Ar. The mixture was stirred for 16 h at ambient temp., worked up as described for (*E*)-**2** and chromatographed (SiO_2, benzene/hexane/Et_2O 1:8:1) to give (*Z*)-**2A** (134 mg, 60%) and (*Z*)-**2A** + **B** (1:1-mixture, 46 mg, 21%).

3.2. *Thermolysis of* (Z)-**2A.** A solution of 60 mg (0.27 mmol) of a 7:1 mixture of (*Z*)-**2A** and (*Z*)-**2B** in 0.5 ml of C_6D_{12} was sealed at 0.01 Torr in a NMR tube[5]) and heated at 120° for 2 h affording a 1:7 mixture of (*Z*)-**2A** and (*Z*)-**2B** as estimated by ^{1}H-NMR analysis.

3.3. *Thermolysis of* **3A** + **3B.** *a)* A solution of **3A** (13 mg, 0.06 mmol) in (D_8)toluene (0.5 ml) in a NMR tube was heated at 120° for 15 h. ^{1}H-NMR analysis of the reaction mixture showed **3A** (10%) and (*E*)-**2** (90%). *b)* A solution of **3B** (*ca.* 70% pure, 15 mg) in (D_8)toluene (0.6 ml) was heated to 120° for 52 h. From the ^{1}H-NMR analysis the following product distribution was estimated: (*E*)-**2** (60%), (*Z*)-**2B** (10%).

3.4. *Transformation of* **4** *into* **5** *and* **6.** – 3.4.1. *Preparation of* **5.** To a solution of **4** (230 mg, 1.04 mmol) in abs. THF (20 ml) was added in portions $(C_6H_5)_3PCH_2$ (*ca.* 0.2 M solution in THF) at 0° under Ar. After complete conversion of the starting material (TLC) the reaction mixture was worked up as described for (*E*)-**2** and chromatographed (20 g SiO_2, Et_2O/hexane 1:1) to give **5** (183 mg, 81%).

3-Methyl-2-(1',1',5'-trimethyl-5'-hexenyl)-2-cyclopropenyl methyl ketone (**5**). B.p. 50°/0.01 Torr. UV (3.775 mg in 25 ml CH_3CN): 279 (145). IR: 3070*w*, 2960*s*, 2940*s*, 2920*s* sh, 2860*m*, 2840*m*, 1680*s*, 1645*m*, 1470*m*, 1440*m* br., 1385*w*, 1370*w*, 1360*m*, 1350*s*, 1235*m*, 1180*s*, 1110*w*, 1075*m*, 1020*w*, 975*w*, 955*w*, 890*s*. ^{1}H-NMR (80 MHz, $CDCl_3$): 1.10, 1.16 (2*s*, 2 CH_3–C(1'); 1.2–2.1 (*m*, 2 H–C(4'), 2 H–C(3'), 2 H–C(2')); 1.72 (*m*, $w_{1/2}$ = 3, CH_3–C(5')); 1.92 (*s*, CH_3–C(3)); 2.09 (*s*, CH_3–CO); 2.28 (*s*, H–C(1)); 4.71 (*m*, $w_{1/2}$ = 6, 2 H–C(6')). ^{13}C-NMR (25 MHz, $CDCl_3$): 10.0, 22.3, 25.7, 26.1, 26.3 (5*q*, CH_3–CO, CH_3–C(3), CH_3–C(5'), 2 CH_3–C(1')); 22.9, 38.3, 40.8 (3*t*, C(4'), C(3'), C(2')); 110.2 (*t*, C(6')); 34.0 (*d*, C(1)); 35.0 (*s*, C(1')); 102.7, 115.8, 145.3 (3*s*, C(2), C(3), C(5')); 213.4 (*s*, CO). MS: 220 (3, M^+, $C_{15}H_{24}O$), 178 (14), 177 (94), 149 (10), 138 (12), 137 (76), 135 (18), 122 (14), 121 (98), 119 (11), 109 (39), 107 (84), 105 (25), 95 (66), 94 (18), 93 (66), 91 (31), 83 (28), 81 (30), 79 (43), 77 (27), *69* (100), 67 (34), 65 (12), 57 (10), 55 (64), 53 (30), 43 (68), 41 (71).

$C_{15}H_{24}O$ (220.36) Calc. C 81.76 H 10.98% Found C 81.74 H 11.14%

3.4.2. *Reduction of* **4** *with* $NaBH_4$. To a solution of **4** (175 mg, 0.79 mmol) in i-PrOH (10 ml) was added dropwise a solution of $NaBH_4$ (100 mg, 2.6 mmol) in i-PrOH (40 ml) at 0°. After complete conversion of **4,** the reaction mixture was poured into H_2O and worked up in Et_2O. Chromatography (15 g SiO_2, Et_2O/hexane 1:4) afforded **4** (15 mg) and **7** (137 mg, 78%).

2-(5'-Hydroxy-1',1',5'-trimethylhexyl)-3-methylcyclopropenyl methyl ketone (**7**). IR: 3620*w*, 3460*w* br., 2960*s*, 2920*s*, 2870*m*, 2850*m*, 1680*s*, 1470*m*, 1460*m*, 1440*m* br., 1385*m*, 1360*m*, 1350*m*, 1235*m*, 1180*s*, 1115*m* br., 1080*m* br., 1025*w*, 975*w*. ^{1}H-NMR (80 MHz, $CDCl_3$): 1.08, 1.15 (2*s*, 2 CH_3–C(1')); 1.19 (*d*, *J* = 6, 3 H–C(6')); 1.3–1.8 (*m*, 2 H–C(2'), 2 H–C(3'), 2 H–C(4'), OH); 1.94 (*s*, CH_3–C(3)); 2.08 (*s*, CH_3–CO); 2.29 (*s*, H–C(1)); 3.60 4.10 (*m*, H–C(5')). MS: 224 (1, M^+, $C_{14}H_{24}O_2$), 182 (18), *181* (100), 137 (33), 123 (12), 121 (14), 107 (18), 105 (10), 95 (18), 93 (26), 91 (22), 83 (10), 81 (24), 79 (19), 77 (13), 69 (33), 67 (14), 55 (26), 53 (13), 45 (20), 43 (78), 41 (28).

3.4.3. *Transformation of* **7** *into* **8.** A solution of **7** (98 mg, 0.44 mmol) in abs. Et_2O was treated with $(C_6H_5)_3PCH_2$ at ambient temp. as described for **4.** Chromatography (15 g SiO_2, Et_2O/hexane 1:4) of the crude product gave **8** (79 mg, 81%).

6-Methyl-6-(3'-isopropenyl-2'-methyl-cycloprop-1'-en-1'-yl)-2-heptanol (**8**). IR: 3620*m*, 3490*w* br, 3070*w*, 2960*s*, 2940*s*, 2910*s*, 2870*m*, 2840*m*, 1870*w*, 1630*m*, 1465*m*, 1445*m* br, 1380*m*, 1370*m*, 1360*m*, 1315*w*, 1290*w*, 1240*w* br., 1150*w* br., 1090*m* br., 1035*w*, 870*s*. ^{1}H-NMR (80 MHz, $CDCl_3$): 1.10, 1.12 (2*s*, CH_3–C(6), 3 H–C(7)); 1.18 (*d*, *J* = 6, CH_3–C(1)); 1.40 (*m*, $w_{1/2}$ = 4, CH_3–C(1")); 1.2–1.8 (*m*, 2 H–C(3), 2 H–C(4), 2 H–C(5), OH); 2.04 (*s*, CH_3–C(2')); 2.07 (*s*, H–C(3')); 3.60–4.00 (*m*, H–C(2)); 4.67, 4.75 (2*m*, $w_{1/2}$ = 4, 2 H–C(2")). MS: 222 (1, M^+, $C_{15}H_{26}O$), 147 (5), *135* (100), 133 (28), 119 (30), 107 (14), 105 (15), 91 (18), 79 (11), 77 (11), 69 (32), 55 (17), 45 (13), 43 (11), 41 (24).

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[5]) The tube was previously washed with 40% aq. KOH, H_2O and EtOH, and dried under vacuum at ambient temp.

3.4.4. *Oxidation of* **8**. To a mixture of CrO_3 (210 mg, 2.12 mmol), dry CH_2Cl_2 (6 ml) and pyridine (0.35 ml, 4.8 mmol) was added a solution of **8** (79 mg, 0.34 mmol) in dry CH_2Cl_2 (*ca.* 1 ml) with stirring at ambient temp. After 30 min, the mixture was filtered over *Celite*, worked up in Et_2O and chromatographed (15 g SiO_2, Et_2O/hexane 2:1) to give **6** (54 mg, 69%).

6-Methyl-6-(3'-isopropenyl-2'-methylcycloprop-1'-en-1'-yl)-2-heptanone (**6**). B.p. 50°/0.01 Torr. UV (2.106 mg in 10 ml CH_3CN): 272 (60), 278 (60). IR: 3070*w*, 2960*s*, 2940*s*, 2910*s*, 2900*s* sh, 2850*m*, 1870*w*, 1720*s*, 1630*w*, 1465*w*, 1445*m* br., 1410*w*, 1380*w*, 1370*m*, 1360*m*, 1315*w*, 1290*w*, 1180*w* br., 1155*w*, 1085*w*, 870*m*. ^{1}H-NMR (80 MHz, $CDCl_3$): 1.10, 1.13 (2*s*, CH_3–C(6), 3 H–C(7)); 1.48 (*m*, $w_{1/2}$ = 3, CH_3–C(1")); 1.2–2.0 (*m*, 2 H–C(4), 2 H–C(5)); 2.05 (*s*, CH_3–C(2')); 2.07 (*s*, H–C(3')); 2.13 (*s*, 3 H–C(1)); 2.41 (*m*, *t*-like, *J* = 6.5, 2 H–C(3)); 4.64, 4.74 (2*m*, $w_{1/2}$ = 5, 2 H–C(2")). ^{13}C-NMR (25 MHz, $CDCl_3$): 10.3, 19.5, 26.3, 26.6, 29.8 (5*q*, C(1), C(7), CH_3–C(6), CH_3–C(2'), CH_3–C(1")); 19.5, 41.1, 44.3 (3*t*, C(3), C(4), C(5)); 106.2 (*t*, C(2")); 28.4 (*d*, C(3')); 35.0 (*s*, C(6)); 107.9, 121.3 (2*s*, C(1'), C(2')); 151.4 (*s*, C(1")); 208.7 (*s*, C(2)). MS: 220 (1, M^+, $C_{15}H_{24}O$), 147 (17), 137 (22), 136 (14), *135* (100), 121 (16), 120 (18), 119 (48), 109 (17), 107 (17), 105 (22), 93 (17), 91 (23), 85 (14), 79 (15), 77 (15), 69 (32), 55 (13), 43 (77), 41 (30).

$C_{15}H_{24}O$ (220.36) Calc. C 81.76 H 10.98% Found C 81.80 H 10.82%

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