24. Photochemical Reactions

142nd Communication[1])

Photochemistry of a 6,7-Epoxy-1,3-diene of the Ionone Series

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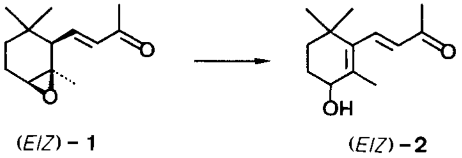
On singlet excitation (λ = 254 nm), the epoxydiene (*E*)-**3** underwent (*E*)/(*Z*)-isomerization, electrocyclic ring closure of the diene side chain leading to the cyclobutenes **4A** + **B**, and rearrangement to the cyclohexanones **5A** + **B**. Compounds **5A** + **B** were presumably formed in a series of processes including a 1,3-acyl shift of the homoconjugated ketone **8**, arising from (*Z*)-**3** by a 1,5-H-shift accompanied by cleavage of the C,O-bond of the oxirane.

1. Introduction. – In [1], it has been shown that the α,β-unsaturated δ,ε-epoxyketone (*E*)-**1** undergoes (*E*)/(*Z*)-isomerization and subsequent γ-H-abstraction leading to the 4-hydroxy-β-ionones (*E*/*Z*)-**2** [2] (*Scheme 1*). Based on these findings, the photochemistry of the corresponding epoxydiene (*E*)-**3**[4]) (*Scheme 2*) was investigated, since it was of interest to check, whether cleavage of the epoxide could be induced *via* an initial 1,5-sigmatropic shift of the H–C(6)[5]).

Scheme 1



2. Results and Discussion. – On triplet excitation (λ > 280 nm, acetone), the epoxydiene (*E*)-**3** underwent (*E*)/(*Z*)-isomerization exclusively. On the other hand, photolysis of (*E*)-**3** (λ = 254 nm, MeCN, 82% conversion) afforded, in addition to (*Z*)-**3** (11%), the

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[1]) 141st Communication: [1].

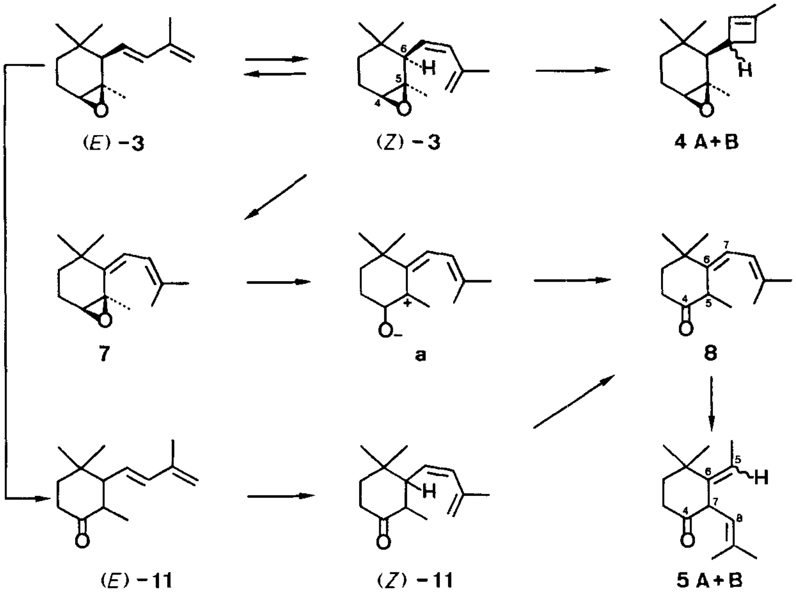
[2]) Taken in part of the Ph. D. thesis of *P. M.*, ETHZ No. 7679 (1984).

[3]) Presented in part by *P. M.* at the 'Herbstversammlung der Schweizerischen Chemischen Gesellschaft', October 14, 1983, Bern.

[4]) Compound (*E*)-**3** was obtained by reaction of (*E*)-**1** with methylene triphenylphosphorane in 81% yield.

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

Scheme 2



cyclobutenes **4A** (20%) and **4B** (15%), and the cyclohexanones **5A** (4%) and **5B** (6%)[6]) (*Scheme 2*).

The cyclobutenes **4A** + **B** are produced by an electrocyclic ring closure of the diene side chain, a well-known reaction of 1,3-dienes [4]. On the other hand, the formation of compounds **5A** + **B** involves a series of processes. Thus, it may be assumed that, in contrast to the photolysis (n,π*- as well as π,π*-excitation) of the epoxyenone (*E*)-**1** furnishing the 4-hydroxy-β-ionones (*E*/*Z*)-**2** *via* γ-H-abstraction and cleavage of the oxirane, the epoxydiene (*Z*)-**3** reacts by an initial 1,5-shift of H–C(6)[5]), leading, if concerted, to the conjugated epoxydiene **7**. The latter, which was not detected, undergoes a subsequent photochemical transformation leading to the homoconjugated cyclohexanone **8**. The photoisomerization of conjugated epoxydienes to carbonyl compounds *via* C,O-bond cleavage of the oxirane (**7**→**a**) is a well-known process [5]; however, it was observed normally on triplet excitation, whereas the rearrangement described in this paper – (*E*/*Z*)-**3**→**7**→**8**→**5A** + **B** – occurred on singlet excitation of the epoxydiene (*E*)-**3** (λ = 254 nm)[7]). Presumably, under the irradiation conditions, the homoconjugated

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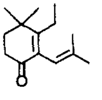
[6]) The structures of the photoproducts were deduced from their spectral data (see *Exper. Part*). As structure proof, the cyclobutenes **4A** and **4B** were thermolyzed (110°, toluene) leading to the epoxydiene (*E*)-**3**. Furthermore, compounds **5A** and **5B** were transformed to the cyclohexenone **6** by treatment with acid.



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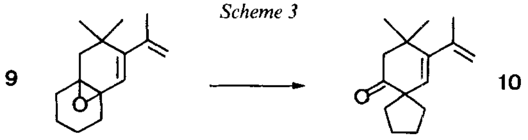
[7]) An example of photoisomerization *via* C,O-bond cleavage on singlet excitation of an epoxydiene was found recently. Thus, irradiation (λ = 254 nm, MeCN) of **9** led to the ketodiene **10** [6].

Scheme 3



ketone **8**, which was not detected either, underwent a rapid 1,3-acyl shift [7] leading finally to the products **5A + B**. To prove this hypothesis, the cyclohexanone (*E*)-**11** was prepared by reaction of (*E*)-**3** with BF_3OEt_2, and subsequently photolyzed. Irradiation (λ = 254 nm, MeCN) of (*E*)-**11** gave, indeed, **5A** (13%) and **5B** (20%), besides intractable material. Analogously to (*Z*)-**3**, the intermediate (*Z*)-diene (*Z*)-**11** presumably underwent a 1,5-sigmatropic H-shift leading to the aforementioned compound **8**.

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Experimental Part

General. See [1].

1. Preparations. – 1.1. *Preparation of (*E*)-***3**. A soln. of BuLi in hexane (1.6M, 42 ml, 67 mmol) was added at 0° and under Ar to a suspension of methyltriphenylphosphonium bromide (30.8 g, 86.2 mmol) in abs. THF (150 ml) and stirred for 1 h at r.t. The soln. of methylenetriphenylphosphorane (*ca.* 0.4M) was then slowly added *via* a canula to a soln. of (*E*)-**1** [8] (9.50 g, 45.6 mmol) in abs. THF (150 ml) at 0° and the mixture was stirred for 15 h at r.t. Workup and chromatography (Et_2O/pentane 1:4) and distillation (60°, 0.02 Torr) afforded (*E*)-**3** (7.58 g, 81%).

*(*E*,1′*RS*,2′*RS*,3′*SR*)-1-(2′,3′-Epoxy-2′,6′,6′-trimethylcyclohexyl)-3-methyl-1,3-butadiene* ((*E*)-**3**). B.p. 60°/0.02 Torr. UV (0.207 mg in 10 ml pentane): 226 (sh, 26300), 231 (28200), 238 (sh, 18700). IR: 3080*w*, 3030*w*, 2960*s*, 2920*s*, 2880*m*, 2860*m*, 1773*w*, 1605*m*, 1465*m* (sh), 1450*m*, 1435*m*, 1385*m*, 1375*m*, 1360*m*, 1350*w*, 1310*w* (sh), 1300*m*, 1250*w*, 1230*w*, 1180*w*, 1145*w*, 1090*w*, 1055*w*, 1045*w*, 970*s*, 905*m*, 885*s*, 860*w*. ^{1}H-NMR (100 MHz, CCl_4): 0.72, 0.86 (2*s*, 2 CH_3–C(6′)); 1.16 (*s*, CH_3–C(2′)); 1.86 (*m*, $w_{1/2}$ = 3, CH_3–C(3)); 0.6–2.0 (*m*, H–C(1′), 2H–C(4′), 2H–C(5′)); 2.88 (*dd*, $J_1 = J_2 = 2$, H–C(3′)); 4.82 (*m*, $w_{1/2}$ = 3, 2H–C(1)); 5.80 (*AB*, *J* = 15.5, δ_A = 5.54, *A* part split to *d*, *J* = 10, H–C(1)), δ_B = 6.08, H–C(2)). ^{13}C-NMR: 18.8, 24.0, 27.2, 28.3 (4*q*, 4 CH_3); 22.0, 29.4 (2*t*, C(4′), C(5′)); 31.3 (*s*, C(6′)); 52.7, 59.4 (2*d*, C(3′), C(1′)); 59.2 (*s*, C(2′)); 114.8 (*t*, C(4)); 128.2, 135.5 (2*d*, C(1), C(2)); 142.0 (*s*, C(3)). MS: 206 (14, M^+, $C_{14}H_{22}O$), 191 (18), 177 (8), 173 (10), 163 (16), 137 (22), 135 (26), 123 (79), 121 (37), 119 (17), 110 (51), 109 (88), 107 (98), 105 (32), *95* (100), 93 (75), 91 (75), 81 (60), 79 (41), 77 (26), 69 (43), 67 (42), 65 (21), 55 (51), 53 (23), 43 (96), 41 (75). Anal. calc. for $C_{14}H_{22}O$ (206.32): C 81.50, H 10.75; found: C 81.29, H 10.69.

1.2. *Preparation of (*E*)-***11**. To a soln. of (*E*)-**3** (3.00 g, 14.5 mmol) in pentane (200 ml) $BF_3 \cdot Et_2O$ (0.15 ml, 1.2 mmol) was added slowly at 0°. After stirring for 10 min at r.t., the reaction was quenched by the addition of H_2O (5 ml). Workup, chromatography (Et_2O/pentane 1:5) and distillation (70°, 0.01 Torr) afforded (*E*)-**11** (1.60 g, 53%).

*(*E*)-3-(3′-Methyl-1′,3′-butadienyl)-2,4,4-trimethylcyclohexanone* ((*E*)-**11**). B.p. 70°/0.01 Torr. UV (0.317 mg in 25 ml pentane) 226 (22750), 231 (24700), 238 (sh, 16750). UV (2.706 mg in 2 ml pentane): 287 (sh, 20), end absorption to 330. IR: 3080*w*, 3010*w* (sh), 2960*s*, 2925*s*, 2900*m* (sh), 2865*s*, 1775*w*, 1720*s* (sh), 1710*s*, 1605*m*, 1465*m* (sh), 1455*m* (sh), 1450*m*, 1445*m*, 1435*m* (sh), 1425*m* (sh), 1385*m*, 1375*m*, 1365*m*, 1330*w*, 1310*w*, 1185*w*, 1160*m*, 1060*w*, 1005*w*, 965*m*, 940*w*, 885*s*, 865*w*. ^{1}H-NMR (100 MHz, $CDCl_3$): 0.85 (*d*, *J* = 6, CH_3–C(2)); 0.87 (*s*, CH_3–C(4)); 1.31 (*s*, CH_3–C(4)); 1.77 (*m*, $w_{1/2}$ = 3, CH_3–C(3′)); 1.4–2.7 (*m*, 2H–C(5), 2H–C(6), H–C(3)); 1.88 (*dq*, $J_1 = J_2 = 6$, H–C(2)); 4.86 (*m*, $w_{1/2}$ = 3, 2H–C(4′)); 5.59 (*AB*, *J* = 16, δ_A = 5.12, *A* part split do *d*, *J* = 11, H–C(1′); δ_B = 6.06, H–C(2′)). ^{13}C-NMR: 13.0, 18.7, 26.7, 29.7 (4*q*, 4 CH_3); 34.0 (*s*, C(4)); 35.9, 38.2 (2*t*, C(5), C(6)); 43.7, 59.3 (2*d*, C(2), C(3)); 125.5 (*t*, C(4′)); 127.0, 137.0 (2*d*, C(1′), C(2′)); 141.5 (*s*, C(3′)); 212.8 (*s*, C(1)). MS: 206 (70, M^+, $C_{14}H_{22}O$), 191 (18), 150 (12), 138 (22), 137 (25), 135 (16), 126 (9), 121 (11), 111 (25), 110 (12), *109* (100), 108 (23), 107 (27), 97 (12), 96 (17), 95 (23), 94 (11), 93 (72), 91 (28), 81 (29), 79 (17), 77 (24), 70 (10), 69 (24), 67 (26), 56 (20), 55 (27), 53 (14), 43 (17), 41 (43). Anal. calc. for $C_{14}H_{22}O$ (206.33): C 81.50, H 10.75; found: C 81.23, H 10.76.

2. Photolysis Experiments. – 2.1. *Photolysis of (*E*)-***3** *in MeCN at λ = 254 nm.* A soln. of (*E*)-**3** (2.00 g, 9.69 mmol) in MeCN (200 ml) was irradiated (quartz, lamp *A*, 82% conversion). After chromatography (Et_2O/pentane 1:5) and HPLC (SiO_2, p = 55 atm, Et_2O/pentane 1:10, λ_{DET} = 210 nm); product distribution (^{1}H-NMR): (*Z*)-**3** (11%), **4A** (20%), **4B** (15%), **5A** (4%), **5B** (6%), and intractable material (presumably polymers).

*(Z,1′*RS*,2′*RS*,3′*SR*)-1-(2′,3′-Epoxy-2′,6′,6′-trimethylcyclohexyl)-3-methyl-1,3-butadiene* ((*Z*)-**3**). B.p. 60°/0.01 Torr. UV (0.286 mg in 25 ml pentane): 227 (11 500), 232 (sh, 11 100), 241 (sh, 7000). IR: 3080*w*, 3010*m*, 2960*s*, 2930*s*, 2865*m*, 1630*w*, 1475*w* (sh), 1465*m* (sh), 1460*m* (sh), 1450*s*, 1435*m* (sh), 1420*w* (sh), 1385*m*, 1375*m*, 1365*m*, 1305*w*, 1250*w*, 1230*w*, 1180*w*, 1145*w*, 1095*w*, 1040*w*, 965*w*, 890*s*, 860*w*. ^{1}H-NMR (100 MHz, $CDCl_3$): 0.77, 0.87 (2*s*, 2CH_3–C(6′)); 1.22 (*s*, CH_3–C(2′)); 0.7–2.0 (*m*, 2H–C(4′), 2H–C(5′)); 1.89 (*m*, $w_{1/2}$ = 3, CH_3–C(3)); 2.71 (*d*, *J* = 11, H–C(1′)); 3.02 (*dd*, $J_1 = J_2 = 2$, H–C(3′)); 4.90 (*m*, $w_{1/2}$ = 5, 2H–C(4)); 5.73 (*AB*, *J* = 12.0, δ_A = 5.41, *A* part split to *d*, *J* = 12.0, H–C(1); δ_B = 6.06, H–C(2)). ^{13}C-NMR: 23.7, 24.2, 27.1, 28.4 (4*q*, 4 CH_3); 22.1, 29.2 (2*t*, C(4′), C(5′)); 31.1 (*s*, C(6′)); 45.2 (*d*, C(1′)); 59.3 (*s*, C(2′)); 59.7 (*d*, C(3′)); 115.1 (*t*, C(4)); 128.7, 132.9 (2*d*, C(1), C(2)); 141.7 (*s*, C(3)). MS: 206 (8, M^+, $C_{14}H_{22}O$), 191 (10), 173 (6), 163 (8), 149 (9), 135 (14), 132 (12), 123 (22), 121 (24), 110 (25), 109 (46), 107 (50), 105 (24), 95 (74), 93 (56), 91 (59), 81 (40), 79 (38), 77 (37), 69 (41), 67 (43), 65 (20), 55 (57), 44 (78), 43 (59), *41* (100). Anal. calc. for $C_{14}H_{22}O$ (206.33): C 81.50, H 10.75; found C: 81.33, H 10.66.

*(1′*RS*,2′*RS*,3′*SR*)-3-(2′,3′-Epoxy-2′,6′,6′-trimethylcyclohexyl)-1-methyl-1-cyclobutene, Isomer A* (**4A**). B.p. 60°/0.01 Torr. IR: 3040*w*, 2960*s*, 2930*s*, 2910*s* (sh), 2860*s*, 2850*m* (sh), 2830*w*, 1635*w*, 1460*m* (sh), 1450*m* (sh), 1440*m*, 1435*m* (sh), 1385*w*, 1375*m*, 1360*m*, 1315*w*, 1305*w*, 1275*m*, 1265*w* (sh), 1230*w*, 1200*w*, 1180*w*, 1160*w*, 1140*w*, 1120*w*, 1090*w*, 1040*w*, 990*w*, 970*w*, 950*w*, 910*w*, 895*s*, 880*w* (sh), 860*w*. ^{1}H-NMR (100 MHz, CCl_4): 0.76, 0.84 (2*s*, 2 CH_3–C(6′)); 1.22 (*s*, CH_3–C(2′)); 1.67 (*m*, $w_{1/2}$ = 4, CH_3–C(1)); 1.0–2.2 (*m*, 2H–C(4′), 2H–C(5′), H–C(1′), H–C(3)); 2.4–2.8 (*m*, H–C(3′), 2H–C(4)); 5.84 (*m*, $w_{1/2}$ = 4, H–C(2)). ^{13}C-NMR: 16.6, 26.9, 27.0, 27.2 (4*q*, overlapping with *t* at *ca.* 27, 4 CH_3); 22.3, *ca.* 27, 42.4 (3*t*, C(4′), C(5′), C(4)); 32.0 (*s*, C(6′)); 38.7, 51.6, 58.6 (3*d*, C(3), C(1′), C(3′)); 59.2 (*s*, C(2′)); 132.4 (*d*, C(2)); 143.2 (*s*, C(1)). MS: 206 (33, M^+, $C_{14}H_{22}O$), 191 (18), 188 (15), 177 (9), 173 (32), 163 (23), 150 (13), 145 (30), 137 (25), 135 (27), 133 (14), 132 (15), 131 (24), 123 (49), 121 (41), 119 (27), 110 (43), 109 (95), 107 (94), 105 (44), 95 (89), 93 (84), 91 (86), 81 (63), 79 (53), 77 (48), 69 (48), 67 (49), 55 (61), 53 (32), 43 (73), *41* (100). Anal. calc. for $C_{14}H_{22}O$ (206.33): C 81.50, H 10.75; found: C 81.24, H 10.75.

Isomer B (**4B**). B.p. 60°/0.01 Torr. IR: 3040*w*, 2960*s*, 2920*s*, 2860*m*, 2850*m* (sh), 1635*w*, 1470*w* (sh), 1460*m* (sh), 1440*m*, 1380*m*, 1375*m*, 1360*m*, 1305*w*, 1275*w*, 1265*w*, 1230*w*, 1200*w*, 1180*w*, 1160*w*, 1145*w*, 1090*w*, 1060*w*, 1045*w*, 985*w*, 915*w*, 890*m*, 885*w*, 860*w*. ^{1}H-NMR (100 MHz, CCl_4): 0.84, 0.86 (2*s*, 2 CH_3–C(6′)); 1.92 (*s*, CH_3–C(2′)); 1.67 (*m*, $w_{1/2}$ = 4, CH_3–C(1)); 1.1–2.0 (*m*, 2H–C(4′), 2H–C(5′), H–C(1′)); 2.3–2.8 (*m*, H–C(3′), H–C(3), 2H–C(4)); 5.86 (*m*, $w_{1/2}$ = 4, H–C(2)). ^{13}C-NMR: 16.6, 28.2, 27.5, 27.7 (4*q*, overlapping with *t* at 27.5 or 27.7, 4 CH_3); 22.1, 27.5 or 27.7, 37.6 (3*t*, C(4′), C(5′), C(4)); 32.5 (*s*, C(6′)); 39.0, 50.5, 58.9 (3*d*, C(3), C(1′), C(3′)); 59.3, (*s*, C(2′)); 133.6 (*d*, C(2)); 144.3 (*s*, C(1)); $J_{C(2)-H}$ = 168 Hz. MS: 206 (29, M^+, $C_{14}H_{22}O$), 191 (19), 188 (12), 177 (9), 173 (28), 163 (19), 150 (12), 145 (26), 137 (22), 135 (27), 133 (12), 132 (12), 131 (23), 123 (44), 121 (40), 119 (25), 110 (41), 109 (90), 107 (90), 105 (38), 95 (92), 93 (88), 91 (84), 81 (59), 79 (46), 77 (44), 69 (48), 67 (47), 55 (59), 53 (30), 43 (70), *41* (100). Anal. calc. for $C_{14}H_{22}O$ (206.33): C 81.50, H 10.75; found: C 81.38, H 10.89.

4,4-Dimethyl-3-ethylidene-2-(2′-methyl-1′-propenyl)cyclohexanone, Isomer A (**5A**). B.p. 60°/0.01 Torr. IR: 3050*w* (sh), 3030*w*, 2970*w*, 2930*s*, 2870*s*, 1720*s* (sh), 1710*s*, 1650*w*, 1475*w* (sh), 1465*m* (sh), 1460*m*, 1450*m*, 1420*w* (sh), 1410*w*, 1385*m*, 1375*m*, 1365*w*, 1330*w*, 1320*w*, 1225*w*, 1160*w* (sh), 1145*m*, 1090*w*, 895*w*, 850*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.06, 1.22 (2*s*, 2 CH_3–C(4)); 1.51 (*d*, *J* = 7.0, 3H–C(2″)); 1.72 (*m*, $w_{1/2}$ = 3.0) and 1.78 (*d*, *J* = 1.5) (3H–C(3′) and CH_3–C(2′)); 1.60 (*ddd*, J_1 = 14.0, J_2 = 6.5, J_3 = 5.5, H–C(5)); 2.01 (*ddd*, J_1 = 14.0, J_2 = 9.0, J_3 = 7.0, H–C(5)); 2.34 (*dddd*, J_1 = 17.5, J_2 = 9.0, J_3 = 6.5, J_4 = 1.5, H–C(6)); 2.57 (*ddd*, J_1 = 17.5, J_2 = 7.0, J_3 = 5.5, H–C(6)); 4.11 (*dm*, *J* = 8.5, $w_{1/2}$ = 4.0, H–C(2)); 5.07 (*dm*, *J* = 8.5, $w_{1/2}$ = 3.7, H–C(1′)); 5.49 (*qd*, J_1 = 6.8, J_2 = 1.2, H–C(1″)). ^{13}C-NMR: 12.7, 18.2, 26.0, 29.4, 30.1 (5*q*, 5 CH_3); 35.2, 35.5 (2*t*, C(5), C(6)); 35.3 (*s*, C(4)); 52.8 (*d*, C(2)); 119.1, 120.7, (2*d*, C(1′), C(1″)); 136.1, 145.6 (2*s*, C(3), C(2′)); 211.1 (*s*, C(1)). MS: 207 (16, M^+ + 1), *206* (100, M^+, $C_{14}H_{22}O$), 192 (11), 191 (76), 189 (3), 177 (12), 173 (17), 163 (40), 151 (10), 150 (25), 147 (14), 137 (18), 136 (12), 135 (71), 134 (14), 133 (17), 123 (21), 121 (35), 119 (22), 109 (32), 108 (20), 107 (71), 105 (23), 95 (29), 93 (40), 91 (48), 83 (13), 81 (24), 79 (29), 77 (30), 69 (31), 67 (34), 65 (15), 55 (38), 53 (22), 43 (30), 41 (61).

Isomer B (**5B**). B.p. 60°/0.01 Torr. IR: 3040*w* (sh), 2960*s*, 2930*s*, 2870*m*, 1715*s*, 1675*w*, 1465*m* (sh), 1460*m*, 1455*m*, 1405*m*, 1385*w* (sh), 1380*m* (sh), 1375*m*, 1360*m*, 1320*w*, 1280*w*, 1205*w*, 1155*w*, 1125*w* (sh), 1090*w*, 1030*w*, 950*w*, 875*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.31, 1.32 (2*s*, 2 CH_3–C(4)); 1.56, 1.81 (2*m*, $w_{1/2}$ = 3.0, CH_3–C(2′), 3H–C(3′)); 1.77 (*dd*, J_1 = 7.0, J_2 = 2.0, 3H–C(2″)); 1.70 (*ddd*, J_1 = 14.0, $J_2 = J_3$ = 5.2, H–C(5)); 2.02 (*ddd*, J_1 = 14.0, J_2 = 9.3, J_3 = 6.5, H–C(5)); 2.3–2.5 (*m*, 2H–C(6)); 3.95 (*dm*, *J* = 8.0, $w_{1/2}$ = 6.0, H–C(2)); 5.26 (*qd*, J_1 = 7.4, J_2 = 2.2, H–C(1″)); 5.37 (*dm*, *J* = 8.0, $w_{1/2}$ = 4.0, H–C(1′)). ^{13}C-NMR (20 MHz): 15.5, 18.1, 25.9, 27.2, 28.4 (5*q*, 5 CH_3); 35.6 (*s*, C(4)); 35.7, 37.3 (2*t*, C(5), C(6)); 55.7 (*d*, C(2)); 119.7, 122.3 (2*d*, C(1′), C(1″)); 135.3, 141.4 (2*s*, C(3), C(2′)); 210.9 (*s*, C(1)). MS: 207 (17, M^+ + 1), *206* (100, M^+, $C_{14}H_{22}O$), 205 (14), 192 (15), 191 (96), 189 (12), 179 (21), 177 (33), 173 (25), 163 (40), 150 (41), 147 (20), 137 (19), 135 (68), 133 (19), 123 (20), 121 (39), 119 (22), 109 (28), 107 (62), 105 (28), 95 (25), 93 (41), 91 (50), 83 (13), 81 (22), 79 (31), 77 (39), 69 (35), 67 (25), 65 (20), 58 (19), 55 (45), 53 (26), 43 (99), 41 (75).

2.2. *Irradiation of (E)-***3** *in Acetone at* $\lambda > 280$ *nm.* A soln. of (*E*)-**3** (680 mg, 3.30 mmol) in acetone (60 ml) was irradiated (*Pyrex*, lamp *B*, 2 h). HPLC (SiO_2, p = 50 atm, Et_2O/pentane 1:400, λ_{DET} = 240 nm) afforded (*Z*)-**3** (224 mg, 33%) and (*E*)-**3** (401 mg, 59%).

2.3. *Irradiation of (E)-***11** *in MeCN at* $\lambda = 254$ *nm.* A soln. of (*E*)-**11** (1.00 g, 4.85 mmol) in MeCN (100 ml) was irradiated (quartz, lamp *A*, 95% conversion). Chromatography (Et_2O/pentane 1:5) afforded **5A** (13%), **5B** (20%), and intractable material (presumably polymers).

3. Additional Experiments. – 3.1. *Thermolysis of the Cyclobutenes* **4A** *and* **4B**. Two separate solns. of the cyclobutenes **4A** and **4B** (20 mg, 0.097 mmol) in toluene (5 ml) were heated under reflux for 5 h affording 1:2 mixtures of (*E*)-**3** and **4A** and of (*E*)-**3** and **4B**, respectively (^{1}H-NMR).

3.2. *Acid-Catalyzed Rearrangement of* **5A** *and* **5B**. *a*) To a soln. of **5A** (50 mg, 0.24 mmol) in EtOH (0.5 ml), conc. H_2SO_4 (1 ml) H_2O (1.5 ml) and EtOH (5 ml) was added and the mixture stirred at ambient temp. for 3 h. Workup with H_2O yielded **6** (43 mg, 86%). *b*) Analogous transformation of **5B** (62 mg, 0.30 mmol) afforded **6** (52 mg, 84%).

4,4-Dimethyl-3-ethyl-2-(2'-methyl-1'-propenyl)-2-cyclohexenone (**6**). B.p. 75°/0.01 Torr. UV (0.633 mg in 25 ml pentane): 231 (10250), 262 (sh, 3500). UV (18.536 mg in 25 ml pentane): 328 (sh, 50), endabsorption to 380. IR: 3040*w* (sh), 2970*s*, 2935*s*, 2880*m*, 2860*m* (sh), 1675*s* (sh), 1670*s* (sh), 1665*s*, 1590*m*, 1470*m*, 1450*m*, 1440*m* (sh), 1420*w*, 1375*m*, 1365*m*, 1350*m*, 1335*m*, 1300*m*, 1280*m*, 1260*w*, 1230*w*, 1200*m*, 1145*w*, 1105*w*, 1050*w*, 1040*w*, 1020*w*, 1010*w* (sh), 980*w*, 955*w*, 940*w*, 920*w*, 895*w*. ^{1}H-NMR (100 MHz, $CDCl_3$): 1.00 (*t*, *J* = 7.5, 3H–C(2")); 1.17 (*s*, 2 CH_3–C(4)); 1.42, 1.82 (2*m*, $w_{1/2}$ = 3, CH_3–C(2'), 3H–C(3')); 1.72–1.90 (*m*, 2H–C(5)); 2.16 (*q*, *J* = 7.5, 2H–C(1")); 2.38–2.55 (*m*, 2H–C(6)); 5.60 (*m*, $w_{1/2}$ = 5, H–C(1')). ^{13}C-NMR: 12.6, 19.0, 24.7, 26.4, 26.4 (5*q*, 5 *C*H_3); 23.2, 34.1, 37.2 (3*t*, C(1"), C(5), C(6)); 35.7 (*s*, C(4)); 118.8 (*d*, C(1')); 132.9, 135.1 (2*s*, C(2), C(2')); 166.5 (*s*, C(3)); 195.1 (*s*, C(1)). MS: 206 (92, M^+, $C_{14}H_{22}O$), 192 (15), *191* (100), 178 (11), 177 (67), 173 (49), 163 (11), 162 (11), 159 (32), 150 (15), 149 (15), 147 (10), 145 (16), 135 (4), 133 (17), 121 (22), 119 (16), 109 (13), 107 (34), 105 (109), 95 (10), 93 (25), 91 (34), 79 (19), 77 (26), 69 (15), 67 (11), 65 (12), 55 (26), 53 (15), 43 (19), 41 (41). Anal. calc. for $C_{14}H_{22}O$ (206.33): C 81.50, H 10.75; found: C 81.59, H 10.88.

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