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132. Photochemical Reactions

137th Communication[1])

Preparation and Photolysis of (*E*/*Z*)-7-Methyl-β-ionone

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(8.V.84)

Summary

The title compounds (*E*/*Z*)-**7** were prepared in 66% overall yield by reaction of β-ionone ((*E*)-**1**) with lithium dimethylcuprate, trapping of the intermediate enolate with benzeneselenenyl bromide and oxidation with H_2O_2. Analogously, (*E*/*Z*)-7-methyl-α-ionone ((*E*/*Z*)-**12**) was obtained in 65% yield from α-ionone ((*E*)-**11**). $^1n,\pi^*$-Excitation ($\lambda > 347$ nm, pentane) of (*E*)-**7** causes rapid (*E*/*Z*)-isomerization and subsequent reaction of (*Z*)-**7** to **15** (66%). The formation of **15** is explained by twisting of the dienone chromophore due to repulsive interaction of the 7-CH_3-group with the CH_3-groups of the cyclohexene ring. On the other hand, irradiation ($\lambda > 347$ nm, Et_2O) of (*E*)-**7** in the presence of acid leads to (*Z*)-**7** (5%) and to the novel compound **16** (88%).

1. Introduction. – Since 1955, the photochemistry of β-ionone ((*E*)-**1**) has been subject of various studies [2] which have shown that irradiation of (*E*)-**1** gives the 2*H*-pyran **2** as main product, *via* (*Z*)-**1** as intermediate. In addition, *retro*-γ-ionone **3** was obtained by a 1,5-sigmatropic H-shift (see *Scheme 1*). In 1974, it had been reported from this laboratory that an α-methyl substituent in dienone (*E*)-**4** had no effect on its photochemical behavior since only the corresponding products **5** and **6** were isolated [3].

The investigation of the photochemistry of (*E*)-**7** (see *Scheme 2*) was of particular interest, since from the NMR data it was evident that, in contrast to (*E*)-**1** and (*E*)-**4**, the rotation of the side chain in (*E*)-**7** is hindered due to steric interaction of the

[1]) 136th Communication, see [1].

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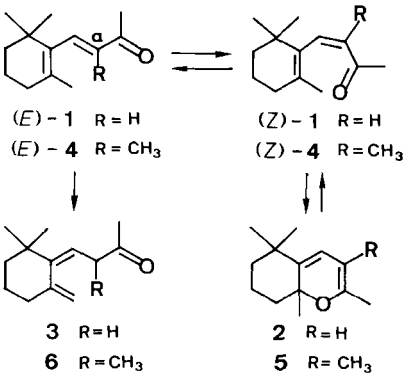
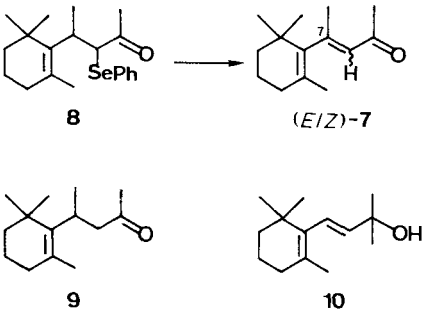
7-CH_3-group with the CH_3-groups of the cyclohexene ring[5])[6]). Therefore, on photolysis of (*E*)-**7**, a dependence of product formation upon the ground-state conformation was expected to be found.

Scheme 1



Scheme 2



2. Preparation of 7-Methyl-β-ionone ((*E*/*Z*)-7). – Reaction of β-ionone ((*E*)-**1**) with lithium dimethylcuprate [6], trapping of the enolate with benzeneselenenyl bromide [7], and subsequent oxidation of **8** with H_2O_2 [7] afforded (*E*)-**7** (21%), (*Z*)-**7** (45%), **9** [8] [9] (3%), and **10** [8] (4%)[7]). Treatment of (*Z*)-**7** with a *ca.* 0.5M solution of NaOMe in MeOH led to a *ca.* 9:2 mixture of (*E*/*Z*)-**7** (92%).

3. Photolyses. – *Irradiation (λ > 347 nm) of* (E)-**7** caused rapid (*E*/*Z*)-isomerization and subsequent formation of the tricyclic enol ether **15** (see *Figure*). In a typical experiment on photolysis of (*E*)-**7** in pentane (quantitative conversion), (*Z*)-**7** and **15** were isolated in 26 and 66% yield, respectively. If acid was not strictly excluded, compound **16** was obtained in addition to (*Z*)-**7** and **15**. To determine the effect of acid, (*E*)-**7** was irradiated in Et_2O saturated with HCl affording **16** as main product (88%) besides (*Z*)-**7** (5%), but compound **15** was not detected.

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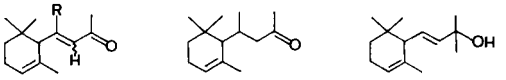
[5]) In ionone derivatives numbering according to the carotinoid nomenclature [4] is used. In the *Exper. Part* the systematic name according to the IUPAC nomenclature is given.

[6]) For a detailed investigation of the stereodynamic behavior of (*E*)-**7** and related compounds by ^{13}C-NMR spectroscopy, see a forthcoming paper by *Müllen et al.* [5].

[7]) Reaction of α-ionone ((*E*)-**11**) under the same conditions led to (*E*)-**12** (13%), (*Z*)-**12** (52%), **13** [9] [10] (3%), and **14** [11] (2%). Treatment of (*Z*)-**12** with *ca.* 0.5M NaOMe in MeOH gave a *ca.* 6:1 mixture of (*E*/*Z*)-**12**.



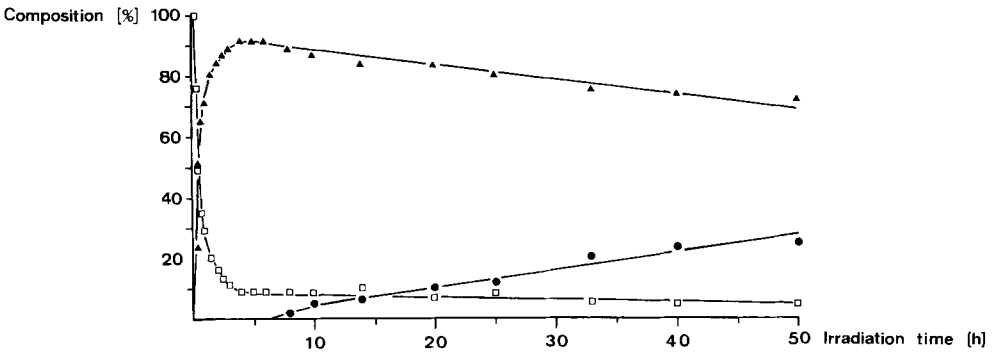


Figure. *Photolysis ($\lambda > 347$ nm, C_6D_{12}) of* (E)-7. *Composition of the mixture as function of the irradiation time:*(*E*)-7 = □, (*Z*)-7 = ▲, **15** = ●.

In conjunction with this differing behavior of (*E*)-**7** on photolysis in neutral or acidic medium, the photochemical reactivity of (*E*)-**1** and (*E*)-**4** in the presence of HCl was also examined. Thus, irradiation ($\lambda > 347$ nm, Et_2O, HCl) of (*E*)-**1** and (*E*)-**4** afforded the same products as previously obtained in neutral solution [2] [3], namely from (*E*)-**1** 90% of **2** and from (*E*)-**4** 17% of (*Z*)-**4**, 61% of **5**, and 6% of **6** (see *Scheme 1*)[8]).

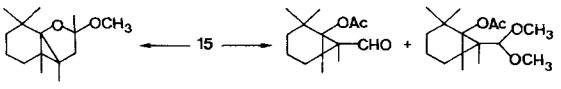
4. Structure of the Compounds. – Only the most relevant spectral data are discussed herein; full data and assignment of the NMR signals are presented in the *Exper. Part.*

7-Methyl-ionones (E/Z)-**7** *and* (E/Z)-**12**. The assignment of the enone double bond configuration is based on the chemical shift of the ^{1}H-NMR signal of the 7-CH_3-group. Due to the anisotropy effect of the carbonyl group in (*E*)-**7** and (*E*)-**12**, the *d* of the 7-CH_3-group is shifted downfield to 2.12 and 2.09 ppm, respectively, whereas the corresponding signals of (*Z*)-**7** and (*Z*)-**12** appear at 1.89 and 1.69 ppm, respectively. Additionally, due to the same effect, the signal of the doubly allylic H-atom of (*Z*)-**12** at 4.10 ppm is shifted *ca.* 2 ppm downfield in comparison with that of (*E*)-**12**.

Further evidence for the above assignment was obtained by oxydation of (*E*)- and (*Z*)-**7** to γ,δ-epoxyenones which showed different reactivity. On thermolysis (160°), the γ,δ-epoxyenone derived from (*Z*)-**7** underwent the characteristic (*Z*)-epoxyenone/furan rearrangement, whereas the γ,δ-epoxyenone derived from (*E*)-**7** proved to the stable [12] [13]. Furthermore, on treatment with 80% H_2SO_4, (*Z*)-7-methyl-α-ionone ((*Z*)-**12**) was transformed to a *ca.* 1:1 mixture of the corresponding β-ionone compound (*Z*)-**7** and the aforementioned bicyclic dienol ether **16**.

Tricyclic Enol Ether **15**. The structure was derived from the spectral data (see *Exper. Part*). The presence of the enol ether moiety which is evidenced by an IR band at 1667 cm^{-1} was proven by methanolysis of **15** leading to the acetal **17** (73%, see *Scheme 3*). Furthermore, ozonolysis of **15** in MeOH afforded the formyl acetate **18** (38%) and its dimethyl acetal **19** (34%).

Scheme 3



17 18 19

[8]) Chromatography fractions containing (*Z*)-**4** and **5** in various ratios gradually changed to a *ca.* 1:3 equilibrium mixture of (*Z*)-**4** and **5**.

Bicyclic Dienol Ether **16**. In particular, the UV maximum at 259 nm and the IR band at 1651 and 1608 cm^{-1} are characteristic for the dienol ether moiety. Spectroscopic proof for the dihydropyran moiety was obtained by measurement of $J(^1H,^{13}C(4))$. The values of 158 and 160 Hz for **16** and **20** [12], respectively, are in good agreement with the value determined for the coupling constant of 3,4-dihydro-2*H*-pyran (J = 163 Hz), but significantly smaller than that of 2,3-dihydrofuran (J = 175 Hz) [12]. Although the position of the *t* (108.6 ppm) of CH_2=C(5) in the ^{13}C-NMR spectrum makes the structure **16** more favorable than the alternative structure **21**, we proved the assignment of **16**. Photolysis ($\lambda > 347$ nm, Et_2O, HCl) of (*E*/*Z*)-(5-^{12}C,5-D_3)-**7** (D_3 = 85%, D_2 = 15%)[9][10] (see *Scheme 4*) afforded, with considerable loss of deuterium, (^{12}C,D_2)-**16** (D_3 = 1%, D_2 = 10%, D_1 = 40%), in the ^{13}C-NMR of which the *t* at 108.6 ppm was missing.

Scheme 4

5. Discussion. – Photolysis of (*E*)-**7** causes rapid (*E*/*Z*)-isomerization and subsequent formation of **15**. In contrast to (*Z*)-β-ionone ((*Z*)-**1**), which could be detected only below −50° [2f] due to thermal as well as photochemical reaction to the pyran **2**, the β-methyl analog (*Z*)-**7** is stable at r.t. This finding may be explained by a strong steric interaction of the β-CH_3-group and the CH_3-groups of the cyclohexene ring, preventing the dienone moiety to assume a planar conformation. The twisting of the dienone chromophore is well demonstrated by the unusual position of the UV maxima of (*E*)- and (*Z*)-**7** at 233 and 231 nm, respectively, in comparison with those of (*E*)- and (*Z*)-**1** (291 and 285 nm, resp., [2f]). The dependence of the dienone conformation on the CH_3-substitution at C(β) is also evidenced in the ^{13}C-NMR spectra of (*E*)- and (*Z*)-**7**. The repulsive interaction of the β-CH_3-group and the CH_3-groups of the cyclohexene ring slows down the rotation around the C(β),C(γ)-bond. Thus, the coalescence temperature for the *q* of the geminal CH_3-groups of (*E*)-**7** is > 60°; the (*Z*)-isomer of **7** exhibits two signals for these C-atoms up to 100°, where coalescence is not yet reached.

From inspection of *Dreiding* models of (*E*)- and (*Z*)-**7** it is possible to assume that the steric interaction is minimal in an orthogonal arrangement of the enone side chain and the cyclohexene moiety. Therefore, instead of formation of a 2*H*-pyran of type **2**, (*Z*)-**7** photoisomerizes to the tricyclic compound **15** with bond formation between the carbonyl O-atom and C(γ), and between C(β) and C(δ). This transformation formally represents a [π2a + π4s] cycloaddition[11].

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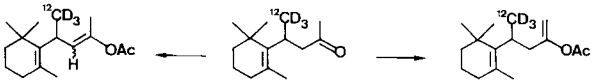
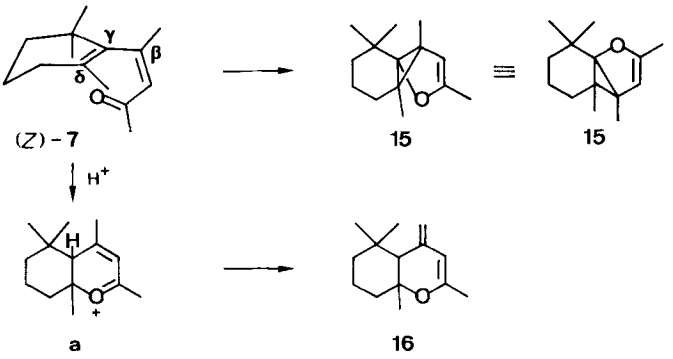
[9]) Compound (*E*/*Z*)-(5-^{12}C,5-D_3)-**7** was obtained in 13% overall yield by reaction of β-ionone ((*E*)-**1**) with $^{12}CD_3MgI$ in the presence of Cu_2I_2 leading to (5-^{12}C,5-D_3)-**9**, transformation of the latter to the enol acetates (*E*/*Z*)-**22** and **23**, and reaction of (*E*/*Z*)-**22** with MeLi/PhSeBr and subsequent oxidation with H_2O_2 (see *Exper. Part*).



[10]) $^{12}CH_3I$ was not commercially available, therefore $^{12}CD_3I$ was used.

[11]) Transformations similar to (*Z*)-**7**→**15** were reported by *Le Roux et al.* [14a] and *Bos et al.* [14b] where a 2-oxabicyclo[3.1.0]hexene derivative analogous to **15** was postulated, however, only as an intermediate. The reaction (*Z*)-**7**→**15** reflects a general photochemical behavior of conformationally constrained trienes [15].

Scheme 5



On photolysis of (*E*)-**7** in the presence of acid, the transformation (*Z*)-**7**→**15** is suppressed, instead the bicyclic dienol ether **16** is isolated in 88% yield[12]). The formation of **16** may involve protonation at C(γ) which releases the repulsive interaction between the β-CH_3-group and the geminal CH_3-groups and makes bond formation between the carbonyl O-atom and C(δ) possible. Subsequent proton elimination from the β-CH_3-group in **a** leads to **16**[13])[14]).

6. Conclusion. – The introduction of the CH_3-group at C(7) of the dienone chromophore of β-ionone gives rise to a dramatic change of the photochemical behavior of (*E*)-**7** in comparison with that of β-ionone ((*E*)-**1**) and 8-methyl-β-ionone ((*E*)-**4**), respectively. This differing behavior discloses a marked dependence of the course of the photoisomerization on the ground state conformation of the dienone.

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Experimental Part

General. See [16], except as noted below. Anal. 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) according to [17] ('flash chromatography'). Anal. 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 CCl_4 solutions on a *Varian-HA-100* instrument (100 MHz) or, exceptionally (as indicated below), on a *Bruker-WP-80-CW* (80 MHz) or *WM-300* (300 MHz) instrument in $CDCl_3$ solutions. *Filter solution A* ($Pb(NO_3)_2$/KBr), see [18].

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[12]) The transformation of (*Z*)-**7**→**16** occurred also in a dark process, but much more slowly. An acid-catalyzed transformation of **15**→**16** was not observed.

[13]) On photolysis of (*E*)-**1** and (*E*)-**4** in the presence of acid, products arising from protonation at C(γ) were, however, not detected.

[14]) On photolysis at $\lambda > 280$ and $\lambda = 254$ nm, respectively, (*E*)-**7** shows differing behavior; the results will be reported in a forthcoming paper.

1. Preparations. – 1.1. (E/Z)-*7-Methyl-β-ionone* ((E/Z)-**7**). To a suspension of Cu_2I_2 (15.6 g, 81.9 mmol) in Et_2O (600 ml), a 1.6M solution of MeLi in Et_2O (100 ml, 160 mmol) was added at −40°, and the mixture was stirred for 20 min. β-Ionone ((*E*)-**1**; 12.8 g, 66.6 mmol) in Et_2O (100 ml) was then added slowly at −40°, and the mixture was allowed to warm up to −10° over 20 min. Again at −40°, a solution of PhSeBr in THF (120 ml) [prepared by reaction of diphenyl diselenide (25.7 g, 82.3 mmol) and Br_2 (2.92 ml, 57.0 mmol) in THF at 0°] was added rapidly. The cooling bath was removed, and the mixture was allowed to warm up to r.t., poured into Et_2O/pentane 1:1 (1000 ml) and aq. NH_4Cl (satd.; 500 ml) and worked up. The crude product was dissolved in pyridine (20 ml) and CH_2Cl_2 (500 ml), and H_2O_2 (15%; 200 ml, 882 mmol) was added dropwise at r.t. (highly exothermic reaction). After 1 h at r.t., aq. $NaHCO_3$ (10%; 125 ml) was added, the org. phase was washed with 1M aq. HCl and worked up. Column chromatography (SiO_2, acetone/CH_2Cl_2/hexane) 1:100:100) of the residue yielded (*E*)-**7** (2.94 g, 21%), (*Z*)-7 (6.24 g, 45%), **9** [8] [9] (0.39 g, 3%), and **10** [8] (0.55 g, 4%). (E)-*4-(2',6',6'-Trimethyl-1'-cyclohexen-1'-yl)-3-penten-2-one* ((E)-**7**): B.p. 60°/0.01 Torr. UV (0.0591 mg in 5 ml): 233 (13800). UV (4.8 mg in 5 ml): 331 (43), end absorption to 400. IR: 2960*s*, 2925*s*, 2905*s* (sh), 2860*m*, 2850*m* (sh), 2830*m*, 1682*s*, 1645*w*, 1596*s*, 1470*w* (sh), 1456*m*, 1440*m*, 1429*m*, 1418*m* (sh), 1380*m*, 1373*m* (sh), 1367*m*, 1358*m*, 1350*m*, 1340*w* (sh), 1285*w*, 1270*w*, 1218*m*, 1201*m*, 1190*w* (sh), 1163*m*, 1057*w*, 1040*w*, 1015*w*, 968*w* (sh), 958*m*, 875*w*, 859*w* (sh), 850*w*. ^{1}H-NMR: 0.98 (*s*, $2CH_3$–C(6')); 1.34–2.10 (*m*, 6H); 1.48 (*s*, CH_3–C(2')); 2.09 (*s*, 3H–C(1)); 2.12 (*d*, *J* = 1.5, 3H–C(5)); 5.78 (*m*, $w_{½}$ = 3, H–C(3)). ^{13}C-NMR (62°): 20.8, 29.0, 31.8 (4*q*, 2*q* at 29.0, $4CH_3$); 22.5 (*q*, C(5)); 19.3 (*t*, C(4')); 31.6 (*t*, C(3')); 39.7 (*t*, C(5')); 126.7 (*d*, C(3)); 34.3 (*s*, C(6')); 126.3, 143.4 (2*s*, C(1'), C(2')); 157.5 (*s*, C(4)); 198.2 (*s*, C(2)). MS: 206 (14, M^+, $C_{14}H_{22}O$), 192 (15), *191* (100), 176 (5), 173 (6), 163 (9), 149 (19), 137 (15), 136 (15), 135 (12), 123 (25), 107 (14), 95 (14), 91 (12), 43 (39), 41 (12). Anal. calc. for $C_{14}H_{22}O$ (206.32): C 81.50, H 10.75; found: C 81.31, H 10.91.

(*Z*)-*4-(2',6',6'-Trimethyl-1'-cyclohexen-1'-yl)-3-penten-2-one* ((Z)-**7**). B.p. 60°/0.01 Torr. UV (0.157 mg in 10 ml): 231 (10700). UV (4.7 mg in 5 ml): 332 (66), end absorption to 430. IR: 3010*w* (sh), 2965*s*, 2935*s*, 2915*s*, 2870*m*, 2855*m* (sh), 2835*m*, 1695*s*, 1666*m*, 1654*m* (sh), 1602*s*, 1472*w*, 1460*m*, 1441*m*, 1430*m*, 1382*w*, 1370*w*, 1359*m*, 1353*m*, 1281*w*, 1265*w*, 1254*w*, 1207*w* (sh), 1194*m*, 1170*w* (sh), 1161*m*, 1128*w*, 1059*w*, 1031*w*, 1012*w*, 973*w*, 941*w*, 887*w*, 870*w*, 835*w*. ^{1}H-NMR: 0.86, 1.04 (2*s*, $2CH_3$–C(6')); 1.44 (*s*, CH_3–C(2')); 1.22–2.10 (*m*, 6H); 1.89 (*d*, *J* = 1.5, 3H–C(5)); 2.00 (*s*, 3H–C(1)); 5.99 (*m*, $w_{½}$ = 3, H–C(3)). ^{13}C-NMR: 20.9, 27.9, 29.7, 30.6 (4*q*, $4CH_3$); 27.9 (*q*, C(5)); 18.9 (*t*, C(4')); 31.3 (*t*, C(3')); 39.6 (*t*, C(5')); 128.9 (*d*, C(3)); 34.3 (*s*, C(6')); 127.0, 138.2 (2*s*, C(1'), C(2')); 154.1 (*s*, C(4)); 198.7 (*s*, C(2)). MS: 206 (4, M^+, $C_{14}H_{22}O$), 192 (16), *191* (100), 176 (8), 163 (5), 161 (5), 149 (18), 136 (12), 123 (17), 43 (17). Anal. calc. for $C_{14}H_{22}O$ (206.32): C 81.50, H 10.75; found: C 81.26, H 10.63.

1.2. (E/Z)-*7-Methyl-α-ionone* ((E/Z)-**12**). Treatment of α-ionone[15] ((*E*)-**11**; 12.8 g, 66.6 mmol) under the same conditions as described above for β-ionone ((*E*)-**1**) afforded (*E*)-**12** (1.85 g, 13%), (*Z*)-**12** (7.15 g, 52%), **13** [9] [10] (0.41 g, 3%), and **14** [11] (0.26 g, 2%). (E)-*4-(2',6',6'-Trimethyl-2'-cyclohexen-1'-yl)-3-penten-2-one* ((E)-**12**): B.p. 60°/0.01 Torr. UV (0.258 mg in 20 ml): 238 (13200). UV (5.5 mg in 5 ml): 332 (52), end absorption to 400. IR: 3025*w*, 2960*s*, 2920*s*, 2865*m*, 2840*m*, 1686*s*, 1604*s*, 1473*w* (sh), 1468*m*, 1459*m* (sh), 1447*m*, 1433*m*, 1385*m*, 1379*m* (sh), 1363*m*, 1351*m*, 1303*w*, 1279*w*, 1203*s*, 1196*m* (sh), 1161*m*, 1148*m*, 1139*w*, 1128*w*, 1079*w*, 1014*w*, 963*m*, 931*w*, 872*w*. ^{1}H-NMR ($CDCl_3$): 0.81, 0.93 (2*s*, $2CH_3$–C(6')); 1.50 (*m*, $w_{½}$ = 5, CH_3–C(2')); 2.09 (*d*, *J* = 1, 3H–C(5)); 2.15 (*s*, 3H–C(1)); 0.8–2.2 (*m*, 4H); 2.23 (*m*, $w_{½}$ = 4, H–C(1')); 5.53 (*m*, $w_{½}$ = 9, H–C(3')); 6.09 (*m*, $w_{½}$ = 3, H–C(3)). ^{13}C-NMR: 23.1, 28.4, 28.6, 32.0 (5*q*, 2*q* at 28.4, $5CH_3$); 22.7, 30.9 (2*t*, C(4'), C(5')); 61.2 (*d*, C(1')); 122.7, 126.4 (2*d*, C(3'), C(3)); 32.9 (*s*, C(6')); 132.8 (*s*, C(2')); 159.8 (*s*, C(4)); 198.4 (*s*, C(2)). MS: 206 (11, M^+, $C_{14}H_{22}O$), 191 (11), 163 (15), 150 (18), 136 (15), *135* (100), 123 (55), 109 (20), 108 (14), 107 (83), 105 (10), 91 (30), 79 (11), 77 (10), 69 (11), 43 (43), 41 (19).

(*Z*)-*4-(2',6',6'-Trimethyl-2'-cyclohexen-1'-yl)-3-penten-2-one* ((Z)-**12**). B.p. 60°/0.01 Torr. UV (0.228 mg in 10 ml): 242 (12100). UV (6.0 mg in 5 ml): 338 (67), end absorption to 410. IR: 3030*w*, 3005*w*, 2960*s*, 2940*m*, 2875*m*, 2855*m* (sh), 2845*m*, 1688*s*, 1607*s*, 1472*w*, 1462*m*, 1450*m*, 1440*m*, 1387*m*, 1380*m*, 1375*m*, 1365*m*, 1353*m*, 1325*w*, 1293*w*, 1228*w*, 1197*m*, 1176*s*, 1139*w*, 1127*w*, 1081*w*, 1017*w* (br.), 969*m*, 923*w*, 863*w*, 840*w*. ^{1}H-NMR: 0.79, 0.97 (2*s*, $2CH_3$–C(6')); 1.47 (*m*, $w_{½}$ = 4, CH_3–C(2')); 1.69 (*d*, *J* = 1, 3H–C(5)); 2.08 (*s*, 3H–C(1)); 1.0–2.2 (*m*, 4H); 4.10 (*m*, $w_{½}$ = 5, H–C(1')); 5.47 (*m*, $w_{½}$ = 9, H–C(3')); 6.14 (*m*, $w_{½}$ = 3, H–C(3)). ^{13}C-NMR: 22.9, 23.1, 27.6, 28.4, 32.2 (5*q*, $5CH_3$); 22.7, 32.7 (2*t*, C(4'), C(5')); 49.4 (*d*, C(1')); 122.3, 128.0 (2*d*, C(3), C(3')); 32.4 (*s*, C(6')); 133.0 (*s*, C(2')); 159.6 (*s*, C(4)); 198.3 (*s*, C(2)). MS: 206 (16, M^+, $C_{14}H_{22}O$), 192 (14), *191* (100), 173 (6), 163 (8), 149 (14), 136 (15), 135 (32), 123 (21), 109 (10), 107 (21), 95 (12), 91 (17), 43 (29), 41 (15). Anal. calc. for $C_{14}H_{22}O$ (206.32): C 81.50, H 10.75; found: C 81.34, H 10.87.

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[15]) Crude α-ionone (*Fluka; pract., ca.* 85%) was purified *via* its hydrogensulfite adduct [19].

1.3. *Equilibration of* (Z)-**7**. NaOMe (7.50 g, 139 mmol) was added to a solution of (*Z*)-**7** (7.50 g, 36.3 mmol) in MeOH (300 ml), and the mixture was refluxed for 4 h. MeOH was evaporated under vacuum, the residue was dissolved in Et_2O/pentane 1:1 (500 ml) and worked up. Column chromatography (SiO_2, acetone/CH_2Cl_2/hexane 1:100:100) of the crude product yielded (*E*)-**7** (5.59 g, 75%) and (*Z*)-**7** (1.31 g, 17%).

1.4. *Equilibration of* (Z)-**12**. Treatment of (*Z*)-**12** (300 mg, 1.45 mmol) with NaOMe (300 mg, 5.56 mmol) in MeOH (12 ml) as described in *1.3* afforded, after column chromatography (SiO_2, Et_2O/pentane 1:4), (*E*)-**12** (227 mg, 76%) and (*Z*)-**12** (40 mg, 13%).

1.5. (E/Z)-7-*((*^{12}C,$^{2}H_3$*)Methyl)-β-ionone* ((E/Z)-*(5-*^{12}C,5-D_3*)*-**7**). $^{12}CD_3I$ (1.20 g, 8.3 mmol) was added under Ar to a mixture of Mg turnings (190 mg, 7.8 mmol) and Et_2O (6.5 ml). The resulting clear solution was cooled to −15°, and Cu_2I_2 (26 mg, 0.14 mmol) was added in 1 portion. Under vigorous stirring, a solution of (*E*)-**1** (1.00 g, 5.2 mmol) in Et_2O (1.3 ml) was added dropwise. After 1 h, the mixture was allowed to warm up to r.t. over 3 h. Satd. aq. $(NH_4)_2SO_4$ was added, the mixture extracted with Et_2O, the org. phases were washed with satd. aq. $Na_2S_2O_3$ and worked up. Column chromatography (SiO_2, hexane/Et_2O 9:1) of the crude product yielded (5-^{12}C,5-D_3)-**9** (285 mg, 26%).

A mixture of (5-^{12}C,5-D_3)-**9** (459 mg, 2.18 mmol), isopropenyl acetate (2.1 g, 21 mmol), and conc. H_2SO_4 (5 drops) was refluxed for 7 h. The mixture was washed 3 times with H_2O and worked up in Et_2O. Unreacted isopropenyl acetate was removed under vacuum. Column chromatography (SiO_2, hexane/Et_2O 9:1) of the crude product afforded a mixture of (*E*/*Z*)-**22** and **23** (484 mg, 88%; ratio 14:3:3, determined by capillary GC).

To a 1.6M solution of MeLi in Et_2O (2.27 ml, 3.63 mmol) and THF (4.7 ml), a solution of the aforementioned mixture (*E*/*Z*)-**22**/**23** (391 mg, 1.54 mmol) in THF (2.4 ml) was added dropwise at −20°. The mixture was warmed to 0°, stirred for 10 min and again cooled to −78°. A solution of PhSeBr (1.18 g, 5.0 mmol) in THF (7.1 ml) was added rapidly, the mixture stirred for 10 min and then poured into 0.5N aq. HCl (40 ml) and Et_2O/pentane 1:1 (40 ml). Workup in Et_2O afforded 1.18 g of crude product, which was dissolved in pyridine (0.5 ml) and CH_2Cl_2 (12 ml). Aq. H_2O_2 (15%, 4.8 ml) was added dropwise at 0° and the mixture stirred for 0.5 h at r.t. and diluted with CH_2Cl_2 (3 ml). Then, aq. $NaHCO_3$ (10%) was added, the org. phase separated, washed twice with aq. HCl (2N), and worked up in CH_2Cl_2. Column chromatography (SiO_2, CH_2Cl_2/hexane 4:1) yielded (*E*)-(5-^{12}C,5-D_3)-**7** (115 mg, 36%) and (*Z*)-(5-^{12}C,5-D_3)-**7** (59 mg, 19%). (E)-*4-(2',6',6'-Trimethyl-1'-cyclohexen-1'-yl) (5-*$^{12}C,5,5,5$-$^{2}H_3$*)-3-penten-2-one* ((E)-*(5-*^{12}C,5-D_3*)*-**7**). In comparison to that of (*E*)-**7**, the IR shows an additional band at 2107*w*; bands below 1100 cm^{-1}: 1083*w*, 1041*w*, 1018*w*, 979*w*, 957*w*, 868*w*, 849*w*. ^{1}H-NMR in comparison with that of (*E*)-**7**: *d* at 2.12 is missing; signal at 5.78 changed to *s*. ^{13}C-NMR: *q* at 22.5 (C(5)) is missing. MS: 209 (9, M^+, $C_{14}H_{19}D_3O$), 195 (14), *194* (100), 119 (15), 152 (16), 139 (14), 138 (11), 126 (17), 43 (36), 41 (9); *ca.* 85% D_3, 15% D_2.

(Z)-*4-(2',6',6'-Trimethyl-1'-cyclohexen-1'-yl) (5-*$^{12}C,5,5,5$-$^{2}H_3$*)-3-penten-2-one* ((Z)-*(5-*^{12}C,5-D_3*)*-**7**). In comparison to that of (*Z*)-**7**, the IR shows additional bands at 2235*w* and 2210*w* (sh); bands below 1100 cm^{-1}: 1084*w*, 1040*w*, 986*w*, 976*w*, 950*w*, 899*w*, 869*w*. ^{1}H-NMR in comparison with that of (*Z*)-**7**: *d* at 1.89 is missing; signal at 5.99 changed to *s*. ^{13}C-NMR: *q* at 22.5 (C(5)) is missing. MS: 209 (8, M^+, $C_{14}H_{19}D_3O$), 195 (23), *194* (100), 193 (10), 152 (22), 139 (17), 138 (12), 126 (27), 43 (22), 41 (9); *ca.* 85% D_3, 15% D_2.

2. Photolysis Experiments. – 2.1. *Photolyses of* (E)-**7** *in Neutral Medium at* $\lambda > 347$ *nm*. 2.1.1. *In Pentane*. A solution of (*E*)-**7** (318 mg, 1.54 mmol) in pentane (25 ml, degased in 3 freezing/melting cycles at 0.01 Torr) was irradiated (lamp *B*, filter *A*; conversion *ca.* 100%). Column chromatography (SiO_2, Et_2O/pentane 1:4 to 1:1) afforded **15** (208 mg, 66%) and (*Z*)-**7** (82 mg, 26%). *(1R*,5S*,6S*)-3,5,6,10,10-Pentamethyl-2-oxatricyclo[4.4.0.0*^{1,5}*]dec-3-ene* (**15**): B.p. 50°/0.02 Torr. UV (0.463 mg in 10 ml): 224 (4100). IR: 3075*w*, 2985*m*, 2940*s*, 2920*s*, 2865*s*, 2715*w*, 1667*s*, 1475*m*, 1459*m* (sh), 1455*m*, 1447*m*, 1435*w* (sh), 1379*s*, 1360*m*, 1313*w*, 1288*w*, 1257*s*, 1187*m*, 1153*w*, 1137*w*, 1117*w*, 1080*s*, 1041*m*, 991*w*, 980*w*, 961*m*, 923*w*, 904*w*, 872*w*, 842*w*. ^{1}H-NMR (C_6D_6): 0.96, 1.09, 1.22, 1.28 (4*s*, CH_3–C(5), CH_3–C(6), $2CH_3$–C(10)); 0.8–1.8 (*m*, 6H); 1.62 (*d*, $J = 1$, CH_3–C(3)); 4.48 (*m*, $w_{½} = 3$, H–C(4)). ^{13}C-NMR (CD_2Cl_2): 12.8, 13.5, 16.1, 26.0, 26.7 (5*q*, $5CH_3$); 19.5, 28.1, 38.1 (3*t*, C(7), C(8), C(9)); 104.8 (*d*, C(4)); 16.6, 32.3, 38.0 (3*s*, C(5), C(6), C(10)); 81.1 (*s*, C(1)); 152.6 (*s*, C(3)). MS: 206 (7, M^+, $C_{14}H_{22}O$), 192 (14), *191* (100), 176 (7), 149 (13), 136 (10), 123 (12), 43 (13). Anal. calc. for $C_{14}H_{22}O$ (206.32): C 81.50, H 10.75; found: C 81.47, H 10.65.

2.1.2. *In* C_6D_{12}. A solution of (*E*)-**7** (52.3 mg, 0.25 mmol) in C_6D_{12} (0.6 ml) was irradiated (lamp *B*, filter *A*). The photolysis was followed by ^{1}H-NMR (60 MHz; see *Fig.*).

2.2. *Photolyse in Acidic Medium at* $\lambda > 347$ *nm*. 2.2.1. *Photolysis of* (E)-**7**. A solution of (*E*)-**7** (598 mg, 2.90 mmol) in Et_2O (200 ml) was acidified by bubbling HCl gas for 20 s. Irradiation (lamp *B*, filter *A*; conversion 100%) and column chromatography (SiO_2, hexane/Et_2O 9:1) yielded **16** (529 mg, 88%) and (*Z*)-**7** (29 mg, 5%). *1,3,7,7-Tetramethyl-5-methyliden-2-oxabicyclo[4.4.0]dec-3-ene* (**16**): B.p. 45°/0.07 Torr. UV (0.195 mg in 10 ml):

259 (13000). IR: 3085*w*, 3055*w*, 2990*m*, 2975*m*, 2950*s*, 2935*s*, 2905*m* (sh), 2885*m*, 2875*m*, 2850*m*, 1656*s* (sh), 1651*s*, 1608*m*, 1474*m*, 1460*m*, 1448*m*, 1430*m*, 1387*m* (sh), 1382*s*, 1375*m*, 1365*m*, 1360*m*, 1343*s*, 1320*w*, 1310*w*, 1291*m*, 1285*m*, 1257*m*, 1215*w*, 1202*w*, 1184*m*, 1177*w* (sh), 1152*s*, 1109*m*, 1040*m*, 991*m*, 972*w*, 960*m*, 943*w*, 931*w*, 897*m*, 869*s*, 855*w*, 835*w*. ^{1}H-NMR: 0.75, 0.87, 1.04 (3*s*, CH_3–C(1), $2CH_3$–C(7)); 0.7–2.1 (*m*, 6H); 1.61 (*s*, H–C(6)); 1.68 (*s*, CH_3–C(3)); 4.32, 4.70 (2*m*, $w_{1/2} = 4$, CH_2=C(5)); 5.11 (*m*, $w_{1/2} = 3$, H–C(4)). ^{13}C-NMR(CD_2Cl_2): 20.3, 21.6, 26.7, 32.6 (4*q*, $4CH_3$); 18.3 (*t*, C(9)); 39.1, 41.4 (2*t*, C(8), C(10)); 108.6 (*t*, CH_2=C(5)); 53.8 (*d*, C(6)); 102.4 (*d*, C(4)); 33.6 (*s*, C(7)); 76.8 (*s*, C(1)); 139.6 (*s*, C(5)); 151.7 (*s*, C(3)). MS: 206 (18, M^+, $C_{14}H_{22}O$), 191 (8), 163 (7), 137 (6), 136 (8), 135 (11), 124 (10), *123* (100), 43 (19). Anal. calc. for $C_{14}H_{22}O$ (206.32): C 81.50, H 10.75; found: C 81.52, H 10.79.

2.2.2. *Photolysis of* (E/Z)-*(5-^{12}C,5-D_3)*-**7**. A solution of (*E*/*Z*)-(5-^{12}C,5-D_3)-**7** (105 mg, 0.51 mmol) in Et_2O (10 ml) was acidified and irradiated as described above. At a conversion of 77%, (^{12}C,D_2)-**16** (75 mg, 92%; D_3 1%, D_2 10%, D_1 40%) was isolated; *t* at 108.6 is missing.

2.2.3. *Photolysis of* (E)-*β-Ionone* ((E)-**1**). A solution of (*E*)-**1** (541 mg, 2.82 mmol) in Et_2O (200 ml) was acidified and irradiated as described above. At a conversion of 76%, **2** (368 mg, 90%) was isolated.

2.2.4. *Photolysis of* (E)-*8-Methyl-β-ionone* ((E)-**4**). A solution of (*E*)-**4** (119 mg, 0.58 mmol) in Et_2O (120 ml) was acidified and irradiated as described above. At a conversion of 82%, (*Z*)-**4** (17%), **5** (61%), and **6** (6%) were obtained. (Z)-*3-Methyl-4-(2',6',6'-trimethyl-1'-cyclohexen-1'-yl)-3-buten-2-one* ((Z)-**4**): ^{1}H-NMR (characteristic signals of a *ca.* 1:6 mixture (*Z*)-**4**/**5**, which were assigned to (*Z*)-**4**; 80 MHz; $CDCl_3$): 1.95 (*d*, *J* = 1.5, CH_3–C(3)); 2.23 (*s*, 3H–C(1)); 6.35–6.50 (*m*, H–C(4)).

4-(2',2'-Dimethyl-6'-methyliden-1'-cyclohexyliden)-3-methyl-2-butanone (**6**). B.p. 75°/0.01 Torr. UV (0.587 mg in 25 ml): 221 (6000). UV (4.366 mg in 25 ml): 289 (300), 296 (300), 306 (sh, 220), 317 (sh, 105). IR: 3078*m*, 2970*s*, 2925*s*, 2865*s*, 2843*s*, 1720*s* (sh), 1710*s*, 1675*m*, 1630*m*, 1455*s* (sh), 1425*s*, 1440*s*, 1420*m* (sh), 1382*m*, 1375*s* (sh), 1352*s*, 1320*m* (sh), 1282*w*, 1263*w*, 1242*m*, 1215*m*, 1205*m*, 1170*s*, 1133*m*, 1083*w*, 1055*m*, 973*m*, 943*m*, 965*m* (sh), 900*s*, 892*s*, 883*m*, 865*m*, 850*w*. ^{1}H-NMR ($CDCl_3$): 1.01 (*s*, $2CH_3$–C(2')); 1.09 (*d*, *J* = 7, CH_3–C(3)); 1.1–1.9 (*m*, 2H–C(3'), 2H–C(4')); 2.06 (*s*, 3H–C(1)); 2.0–2.3 (*m*, 2H–C(5')); 3.48–3.82 (*dq*, *J* = 10, 7, H–C(3)); 4.57, 4.98 (2*d*, *J* = 2.5, CH_2=C(6)); 5.05 (*d*, *J* = 10, H–C(4)). ^{13}C-NMR: 17.3, 27.0, 27.5, 28.1 (4*q*, $4CH_3$); 23.5, 37.5, 41.5 (3*t*, C(3'), C(4'), C(5')); 111.4 (*t*, CH_2=C(6')); 46.9 (*d*, C(3)); 119.6 (*d*, C(4)); 38.2 (*s*, C(2')); 146.2, 151.1 (2*s*, C(1'), C(6')); 209.7 (*s*, C(2)). MS: 206 (8, M^+, $C_{14}H_{22}O$), 191 (45), 164 (14), *163* (100), 135 (13), 133 (13), 121 (30), 119 (11), 107 (69), 105 (25), 95 (26), 93 (38), 91 (36), 81 (21), 79 (27), 77 (26), 69 (42), 67 (12), 65 (11), 55 (28), 53 (18), 43 (76), 41 (40). Anal. calc. for $C_{14}H_{22}O$ (206.32): C 81.50, H 10.75; found: C 81.70, H 10.72.

3. Additional Experiments. – 3.1. *Methanolysis of* **15**. To a solution of **15** (203 mg, 0.99 mmol) in MeOH (10 ml), TsOH (*ca.* 10 mg) was added and the mixture stirred for 7 h at r.t. The mixture was washed with satd. aq. $NaHCO_3$ and worked up in Et_2O. Column chromatography (Al_2O_3, hexane/Et_2O 9:1) yielded *3-Methoxy-3,5,6,10,10-pentamethyl-2-oxatricyclo[4.4.0.0^{1,5}]decane* (**17**) (171 mg, 73%). B.p. 60°/0.05 Torr. IR: 2990*m*, 2925*s* (sh), 2875*m* (sh), 2870*m*, 2825*m*, 1475*m*, 1459*m* (sh), 1450*m*, 1378*s*, 1361*m*, 1323*m*, 1292*w*, 1271*w*, 1228*m*, 1205*m*, 1181*m*, 1161*m*, 1144*m*, 1130*m*, 1103*m*, 1083*s*, 1068*m* (sh), 1057*s*, 1041*s*, 1028*m*, 990*w*, 979*w*, 955*m*, 943*m*, 919*w*, 913*w*, 866*s*, 847*w*. ^{1}H-NMR: 0.98 (3H), 1.01 (6H), 1.23 (3H), 1.26 (3H) (4*s*, CH_3–C(3), CH_3–C(5), CH_3–C(6), $2CH_3$–C(10)); 1.1–1.7 (*m*, 6H); 1.93 (*AB*, $\delta_A = 1.85$, $\delta_B = 2.01$, *J* = 13, 2H–C(4)); 3.15 (*s*, CH_3O–C(3)). ^{13}C-NMR (CD_2Cl_2): 16.4, 17.5, 19.7, 27.2, 27.5 (5*q*, $5CH_3$); 49.1 (*q*, overlapping with *t*, CH_3O–C(3)); 19.3, 29.2, 39.2, 49.1 (4*t*, C(4), C(7), C(8), C(9)); 28.5, 31.8, 32.2 (3*s*, C(5), C(6), C(10)); 78.4 (*s*, C(1)); 111.6 (*s*, C(3)). MS: 206 (7, $M^+ - 32$), 192 (14), *191* (100), 176 (12), 149 (18), 136 (10), 123 (14), 43 (14). Anal. calc. for $C_{15}H_{26}O_2$ (238.36): C 75.58, H 11.00; found: C 75.48, H 11.04.

3.2. *Ozonolysis of* **15**. Ozone was bubbled through a solution of **15** (365 mg, 1.77 mmol) in MeOH (10 ml) at −78° until conversion was quantitative. After bubbling N_2 through the solution, Me_2S (1 ml) was added at −78°, the mixture was stirred for 0.5 h at r.t. and worked up in Et_2O. Column chromatography of the crude product afforded **18** (160 mg, 38%) and **19** (170 mg, 34%). *(1R*,6S*,7S*)-7-Formyl-2,2,6,7-tetramethylbicyclo[4.1.0]hept-1-yl acetate* (**18**; *ca.* 90% pure). UV (2.3 mg in 2 ml): 275 (sh, 30); end absorption to 400. IR: 3035*w*, 2995*w* (sh), 2975*m*, 2945*s*, 2880*m*, 2760*w*, 2730*w*, 2715*w*, 1753*s*, 1703*s*, 1478*m*, 1463*m*, 1451*m*, 1435*w*, 1392*m*, 1380*m*, 1368*s*, 1252*m*, 1225*s*, 1173*m*, 1070*m*, 1062*m*, 1050*m*, 1025*w*, 998*w*, 978*m*, 948*m*, 933*m*, 912*w*, 895*w*. ^{1}H-NMR (90 MHz): 1.10, 1.38, 1.40 (3*s*, $2CH_3$–C(2), CH_3–C(6), CH_3–C(7)); 0.7–1.9 (*m*, 6H); 2.05 (*s*, CH_3COO); 9.04 (*s*, CHO). ^{13}C-NMR (C_6D_6, coalescence spectrum at +80°): 11.4, 17.6, 20.4, 28.0, 29.1 (5*q*, $5CH_3$); 18.7, 30.3, 40.4 (3*t*, C(3), C(4), C(5)); 199.0 (*d*, CHO); 32.2, 36.5, 40.4 (3*s*, *s* at 40.4 is overlapping with *t*, C(2), C(6), C(7)); 74.0 (*s*, C(1)); 170.9 (*s*, COO). MS: 238 (0.3, M^+, $C_{14}H_{22}O_3$), 194 (3), 178 (39), 163 (27), 150 (22), 136 (13), *135* (100), 121 (15), 107 (34), 105 (10), 93 (28), 91 (17), 79 (18), 77 (13), 69 (10), 60 (15), 55 (11), 45 (16), 43 (30), 41 (16). Anal. calc. for $C_{14}H_{22}O_3$ (238.32): C 70.55, H 9.31; found: C 70.50, H 9.23.

(1R,6S*,7S*)-7-(Dimethoxymethyl)-2,2,6,7-tetramethylbicyclo[4.1.0]hept-1-yl Acetate* (**19**). B.p. 95°/0.04 Torr. IR: 3030*w* (sh), 2990*m*, 2935*s*, 2880*m*, 2830*m*, 1754*s*, 1481*m*, 1464*m*, 1448*m*, 1385*m*, 1376*m* (sh), 1364*m*, 1348*w*, 1328*w*, 1282*w*, 1224*s*, 1202*m*, 1191*m*, 1166*m*, 1106*s*, 1075*s*, 1062*s* (sh), 1049*m*, 1045*m* (sh), 1029*m*, 969*m*, 954*m*, 927*m*. ^{1}H-NMR: 0.98, 1.00, 1.06, 1.12 (4*s*, 2 CH_3–C(2), CH_3–C(6), CH_3–C(7)); 1.20–1.78 (*m*, 6H); 1.95 (*s*, CH_3COO); 3.23, 3.36 (2*s*, $(CH_3O)_2CH$–C(7)); 3.94 (*s*, $(CH_3O)_2CH$–C(7)). ^{13}C-NMR (CD_2Cl_2): 10.5, 21.3, 21.6, 27.4, 30.2 (5*q*, 5 CH_3); 56.1, 56.8 (2*q*, $(CH_3O)_2CH$–C(7)); 19.3, 30.0, 39.0 (3*t*, C(3), C(4), C(5)); 108.1 (*d*, $(CH_3O)_2CH$–C(7)); 29.0, 32.0, 35.7 (3*s*, C(2), C(6), C(7)); 72.8 (*s*, C(1)); 170.4 (*s*, COO). MS: 241 (5, $M^+ - 43$), 210 (33), 195 (9), 182 (46), 167 (35), 135 (28), 125 (79), 113 (14), 112 (71), 111 (49), 109 (33), 107 (23), *99* (100), 97 (30), 95 (39), 94 (15), 93 (24), 86 (23), 82 (26), 81 (17), 79 (16), 75 (36), 69 (26), 67 (17), 55 (25), 43 (28), 42 (18), 41 (53). Anal. calc. for $C_{16}H_{28}O_4$ (284.38): C 67.57, H 9.93; found: C 67.45, H 9.91.

3.3. *Treatment of* (Z)-*(5-^{12}C,5-D_3)*-**7** *with HCl.* HCl gas was bubbled for 10 s through a solution of (*Z*)-(5-^{12}C,5-D_3)-**7** (42 mg, 0.20 mmol) in Et_2O (4 ml) and the solution stirred for 20 h at r.t. (conversion 58%). The mixture was washed with satd. aq. $NaHCO_3$ and worked up in Et_2O. Column chromatography (Al_2O_3, *Woelm B*, Act. III, hexane/Et_2O 9:1) afforded (^{12}C,D_2)-**16** (19 mg, 79%).

3.4. *Treatment of* (E)-**7** *with HCl.* HCl gas was bubbled for 10 s through a solution of (*E*)-**7** (78 mg, 0.38 mmol) in Et_2O (8 ml) and the solution stirred for 28 h at r.t. After workup, (*E*)-**7** was recovered quantitatively.

3.5. *Treatment of* **15** *with HCl.* HCl gas was bubbled for 10 s through a solution of **15** (45 mg, 0.22 mmol) in Et_2O (4 ml) and the solution stirred for 28 h at r.t. After workup, a complex mixture was obtained. Compound **16** could not be detected by ^{1}H-NMR analysis of the crude product.

3.6. *Transformation of* (Z)-**12** *to* (Z)-**7** *and* **16**. To (*Z*)-**12** (50 mg, 0.26 mmol) was added H_2SO_4 (80%, 1 ml), dropwise at –20°. After stirring for 10 min at 0°, ice was added, and the mixture was extracted with Et_2O. The org. phase was washed with aq. Na_2CO_3 and worked up giving a *ca.* 1:1 mixture of (*Z*)-**7** and **16** (35 mg, 70%).

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