

132. Photochemical Reactions

137th Communication¹⁾

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

by Keitaro Ishii²⁾, Peter Mathies, Takehiko Nishio³⁾, Hans Richard Wolf⁴⁾, Bruno Frei and Oskar Jeger*

Laboratorium für Organische Chemie der Eidgenössischen Technischen Hochschule, Universitätsstrasse 16,
CH-8092 Zürich

(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 H₂O₂. Analogously, (*E/Z*)-7-methyl- α -ionone ((*E/Z*)-**12**) was obtained in 65% yield from α -ionone ((*E*)-**11**). ¹n, π^* -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-CH₃-group with the CH₃-groups of the cyclohexene ring. On the other hand, irradiation ($\lambda > 347$ nm, Et₂O) 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].

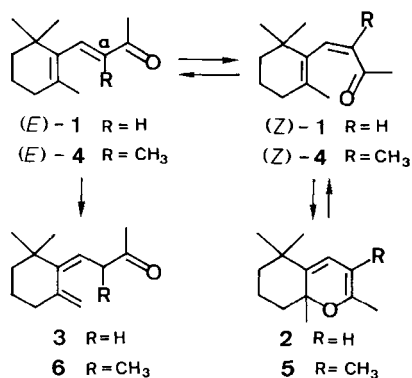
²⁾ Taken in part from the Ph.D. thesis of K. I., Diss. ETHZ No. 6858 (1981). Present address: Meiji College of Pharmacy 1-35-23, Nozawa Setagaya-ku, Tokyo 154, Japan.

³⁾ Present address: Department of Chemistry, University of Tsukuba, Sakura-mura, Niihari-gun, Ibaraki 305, Japan.

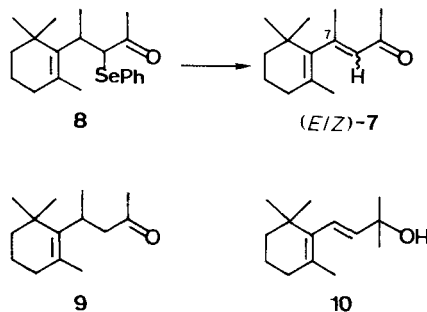
⁴⁾ F. Hoffmann-La Roche & Co. Ltd., Basle, Switzerland.

7-CH₃-group with the CH₃-groups of the cyclohexene ring⁵⁾). Therefore, on photolysis of (*E*)-7, a dependence of product formation upon the ground-state conformation was expected to be found.

Scheme 1

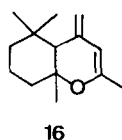
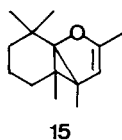


Scheme 2



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 H₂O₂ [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%).

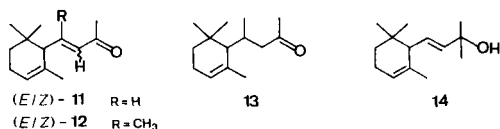
3. Photolyses. – Irradiation ($\lambda > 347$ nm) of (*E*)-7 caused rapid (*E/Z*)-isomerization and subsequent formation of the tricyclic enol ether 15 (see Figure). In a typical experiment on photolysis of (*E*)-7 in pentane (quantitative conversion), (*Z*)-7 and 15 were isolated in 26 and 66% yield, 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 Et₂O saturated with HCl affording 16 as main product (88%) besides (*Z*)-7 (5%), but compound 15 was not detected.



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 ¹³C-NMR spectroscopy, see a forthcoming paper by Mullen *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.



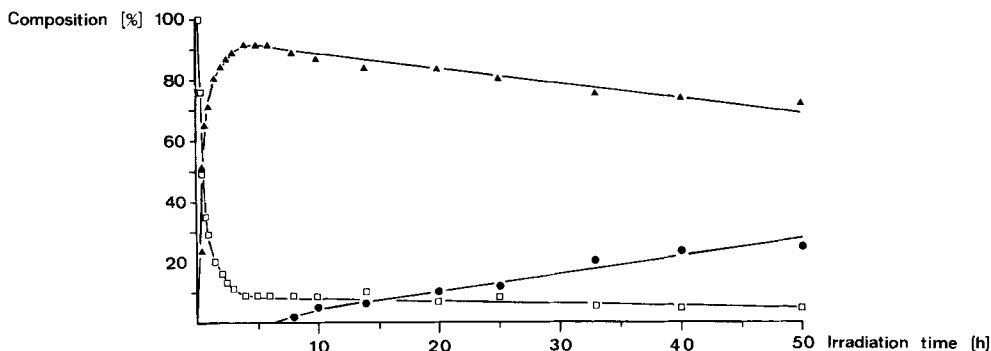


Figure. Photolysis ($\lambda > 347$ nm, C_6D_{12}) of (E)-7. Composition of the mixture as function of the irradiation time: (E)-7 = □, (Z)-7 = ▲, 15 = ●.

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.

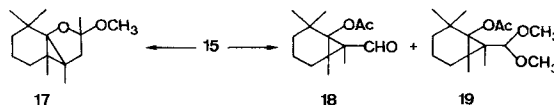
4. Structure of the Compounds. – Only the most relevant spectral data are discussed herein; full data and assignment of the NMR signals are presented in the *Exper. Part*.

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 1H -NMR signal of the 7- CH_3 -group. Due to the anisotropy effect of the carbonyl group in (E)-7 and (E)-12, the δ 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 be 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



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 $J(^1\text{H}, ^{13}\text{C}(4))$. 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 $\text{CH}_2=\text{C}(5)$ 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** ($\text{D}_3 = 85\%$, $\text{D}_2 = 15\%$)⁹⁾ (see Scheme 4) afforded, with considerable loss of deuterium, ($^{12}\text{C}, \text{D}_2$)-**16** ($\text{D}_3 = 1\%$, $\text{D}_2 = 10\%$, $\text{D}_1 = 40\%$), in the ^{13}C -NMR of which the t at 108.6 ppm was missing.

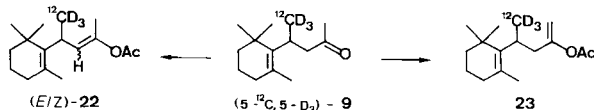
Scheme 4



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 $\text{C}(\beta)$ 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 $\text{C}(\beta), \text{C}(\gamma)$ -bond. Thus, the coalescence temperature for the q of the geminal CH_3 -groups of (*E*)-**7** is $> 60^\circ$; 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 $\text{C}(\gamma)$, and between $\text{C}(\beta)$ and $\text{C}(\delta)$. This transformation formally represents a $[\pi 2a + \pi 4s]$ cycloaddition¹¹⁾.

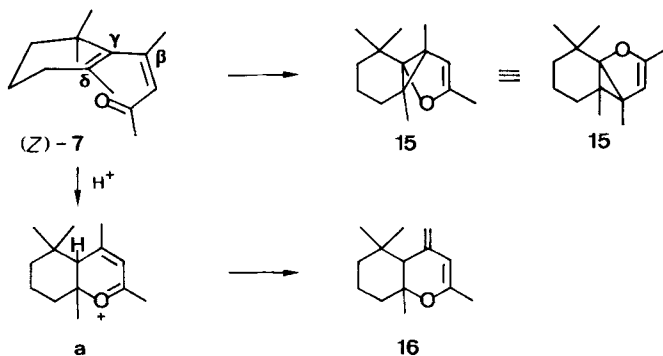
⁹⁾ Compound (*E/Z*)-(5- ^{12}C , 5- D_3)-**7** was obtained in 13% overall yield by reaction of β -ionone ((*E*)-**1**) with $^{12}\text{CD}_3\text{MgI}$ in the presence of Cu_2I_2 leading to (5- ^{12}C , 5- D_3)-**9**, transformation of the latter to the enol acetates (*E/Z*)-**22** and **23**, and reaction of (*E/Z*)-**22** with MeLi/PhSeBr and subsequent oxidation with H_2O_2 (see *Exper. Part*).



¹⁰⁾ $^{12}\text{CH}_3\text{I}$ was not commercially available, therefore $^{12}\text{CD}_3\text{I}$ was used.

¹¹⁾ Transformations similar to (*Z*)-**7** $\rightarrow$ **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** $\rightarrow$ **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% yield¹²). The formation of **16** may involve protonation at C(γ) which releases the repulsive interaction between the β -CH₃-group and the geminal CH₃-groups and makes bond formation between the carbonyl O-atom and C(δ) possible. Subsequent proton elimination from the β -CH₃-group in **a** leads to **16**¹³¹⁴).

6. Conclusion. – The introduction of the CH₃-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.

This work was supported by the *Swiss National Science Foundation* 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). We are also grateful to Mr. *K. Job* for the preparation of starting material.

Experimental Part

General. See [16], except as noted below. Anal. GC was performed using a 25 m $\times$ 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; SiO₂) according to [17] ('flash chromatography'). Anal. pure samples were obtained, in general, after repeated column chromatography on SiO₂; in some cases, further purification was necessary with an HPLC (*Du Pont Instruments*, Model 830, UV detector), using a 25 cm $\times$ 23.6 mm SiO₂ column. In general, ¹H-NMR spectra were taken in CCl₄ 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 CDCl₃ solutions. *Filter solution A* (Pb(NO₃)₂/KBr), see [18].

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. $60^\circ/0.01$ Torr. UV (0.0591 mg in 5 ml): 233 (13800). UV (4.8 mg in 5 ml): 331 (43), end absorption to 400. IR: 2960s, 2925s, 2905s (sh), 2860m, 2850m (sh), 2830m, 1682s, 1645w, 1596s, 1470w (sh), 1456m, 1440m, 1429m, 1418m (sh), 1380m, 1373m (sh), 1367m, 1358m, 1350m, 1340w (sh), 1285w, 1270w, 1218m, 1201m, 1190w (sh), 1163m, 1057w, 1040w, 1015w, 968w (sh), 958m, 875w, 859w (sh), 850w. $^1\text{H-NMR}$: 0.98 (s, 2 CH_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, $w_{1/2} = 3$, H-C(3)). $^{13}\text{C-NMR}$ (62°): 20.8, 29.0, 31.8 (4q, 2q at 29.0, 4 CH_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 (2s, C(1'), C(2')); 157.5 (s, C(4)); 198.2 (s, C(2)). MS: 206 (14, M^+ , $\text{C}_{14}\text{H}_{22}\text{O}$), 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 $\text{C}_{14}\text{H}_{22}\text{O}$ (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. $60^\circ/0.01$ Torr. UV (0.157 mg in 10 ml): 231 (10700). UV (4.7 mg in 5 ml): 332 (66), end absorption to 430. IR: 3010w (sh), 2965s, 2935s, 2915s, 2870m, 2855m (sh), 2835m, 1695s, 1666m, 1654m (sh), 1602s, 1472w, 1460m, 1441m, 1430m, 1382w, 1370w, 1359m, 1353m, 1281w, 1265w, 1254w, 1207w (sh), 1194m, 1170w (sh), 1161m, 1128w, 1059w, 1031w, 1012w, 973w, 941w, 887w, 870w, 835w. $^1\text{H-NMR}$: 0.86, 1.04 (2s, 2 CH_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, $w_{1/2} = 3$, H-C(3)). $^{13}\text{C-NMR}$: 20.9, 27.9, 29.7, 30.6 (4q, 4 CH_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 (2s, C(1'), C(2')); 154.1 (s, C(4)); 198.7 (s, C(2)). MS: 206 (4, M^+ , $\text{C}_{14}\text{H}_{22}\text{O}$), 192 (16), 191 (100), 176 (8), 163 (5), 161 (5), 149 (18), 136 (12), 123 (17), 43 (17). Anal. calc. for $\text{C}_{14}\text{H}_{22}\text{O}$ (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 -ionone¹⁵ ((*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. $60^\circ/0.01$ Torr. UV (0.258 mg in 20 ml): 238 (13200). UV (5.5 mg in 5 ml): 332 (52), end absorption to 400. IR: 3025w, 2960s, 2920s, 2865m, 2840m, 1686s, 1604s, 1473w (sh), 1468m, 1459m (sh), 1447m, 1433m, 1385m, 1379m (sh), 1363m, 1351m, 1303w, 1279w, 1203s, 1196m (sh), 1161m, 1148m, 1139w, 1128w, 1079w, 1014w, 963m, 931w, 872w. $^1\text{H-NMR}$ (CDCl_3): 0.81, 0.93 (2s, 2 CH_3 -C(6')); 1.50 (m, $w_{1/2} = 5$, 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, $w_{1/2} = 4$, H-C(1')); 5.53 (m, $w_{1/2} = 9$, H-C(3')); 6.09 (m, $w_{1/2} = 3$, H-C(3)). $^{13}\text{C-NMR}$: 23.1, 28.4, 28.6, 32.0 (5q, 2q at 28.4, 5 CH_3); 22.7, 30.9 (2t, C(4'), C(5')); 61.2 (d, C(1')); 122.7, 126.4 (2d, 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^+ , $\text{C}_{14}\text{H}_{22}\text{O}$), 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. $60^\circ/0.01$ Torr. UV (0.228 mg in 10 ml): 242 (12100). UV (6.0 mg in 5 ml): 338 (67), end absorption to 410. IR: 3030w, 3005w, 2960s, 2940m, 2875m, 2855m (sh), 2845m, 1688s, 1607s, 1472w, 1462m, 1450m, 1440m, 1387m, 1380m, 1375m, 1365m, 1353m, 1325w, 1293w, 1228w, 1197m, 1176s, 1139w, 1127w, 1081w, 1017w (br.), 969m, 923w, 863w, 840w. $^1\text{H-NMR}$: 0.79, 0.97 (2s, 2 CH_3 -C(6')); 1.47 (m, $w_{1/2} = 4$, 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, $w_{1/2} = 5$, H-C(1')); 5.47 (m, $w_{1/2} = 9$, H-C(3')); 6.14 (m, $w_{1/2} = 3$, H-C(3)). $^{13}\text{C-NMR}$: 22.9, 23.1, 27.6, 28.4, 32.2 (5q, 5 CH_3); 22.7, 32.7 (2t, C(4'), C(5')); 49.4 (d, C(1')); 122.3, 128.0 (2d, 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^+ , $\text{C}_{14}\text{H}_{22}\text{O}$), 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 $\text{C}_{14}\text{H}_{22}\text{O}$ (206.32): C 81.50, H 10.75; found: C 81.34, H 10.87.

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 Et₂O/pentane 1:1 (500 ml) and worked up. Column chromatography (SiO₂, acetone/CH₂Cl₂/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 (SiO₂, Et₂O/pentane 1:4), (*E*)-**12** (227 mg, 76%) and (*Z*)-**12** (40 mg, 13%).

1.5. (*E/Z*)-**7**-((¹²C,²H₃)Methyl)-β-ionone ((*E/Z*)-(5-¹²C,⁵-D₃)-**7**). ¹²CD₃I (1.20 g, 8.3 mmol) was added under Ar to a mixture of Mg turnings (190 mg, 7.8 mmol) and Et₂O (6.5 ml). The resulting clear solution was cooled to -15°, and Cu₂I₂ (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 Et₂O (1.3 ml) was added dropwise. After 1 h, the mixture was allowed to warm up to r.t. over 3 h. Satd. aq. (NH₄)₂SO₄ was added, the mixture extracted with Et₂O, the org. phases were washed with satd. aq. Na₂S₂O₃ and worked up. Column chromatography (SiO₂, hexane/Et₂O 9:1) of the crude product yielded (5-¹²C,⁵-D₃)-**9** (285 mg, 26%).

A mixture of (5-¹²C,⁵-D₃)-**9** (459 mg, 2.18 mmol), isopropenyl acetate (2.1 g, 21 mmol), and conc. H₂SO₄ (5 drops) was refluxed for 7 h. The mixture was washed 3 times with H₂O and worked up in Et₂O. Unreacted isopropenyl acetate was removed under vacuum. Column chromatography (SiO₂, hexane/Et₂O 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 Et₂O (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 Et₂O/pentane 1:1 (40 ml). Workup in Et₂O afforded 1.18 g of crude product, which was dissolved in pyridine (0.5 ml) and CH₂Cl₂ (12 ml). Aq. H₂O₂ (15%, 4.8 ml) was added dropwise at 0° and the mixture stirred for 0.5 h at r.t. and diluted with CH₂Cl₂ (3 ml). Then, aq. NaHCO₃ (10%) was added, the org. phase separated, washed twice with aq. HCl (2N), and worked up in CH₂Cl₂. Column chromatography (SiO₂, CH₂Cl₂/hexane 4:1) yielded (*E*)-(5-¹²C,⁵-D₃)-**7** (115 mg, 36%) and (*Z*)-(5-¹²C,⁵-D₃)-**7** (59 mg, 19%). (*E*)-4-(2',6',6'-Trimethyl-1'-cyclohexen-1'-yl) (5-¹²C,⁵,5,5-²H₃)-3-penten-2-one ((*E*)-(5-¹²C,⁵-D₃)-**7**). In comparison to that of (*E*)-**7**, the IR shows an additional band at 2107w; bands below 1100 cm⁻¹: 1083w, 1041w, 1018w, 979w, 957w, 868w, 849w. ¹H-NMR in comparison with that of (*E*)-**7**: *d* at 2.12 is missing; signal at 5.78 changed to *s*. ¹³C-NMR: *q* at 22.5 (C(5)) is missing. MS: 209 (9, *M*⁺, C₁₄H₁₉D₃O), 195 (14), 194 (100), 119 (15), 152 (16), 139 (14), 138 (11), 126 (17), 43 (36), 41 (9); *ca.* 85% D₃, 15% D₂.

(*Z*)-4-(2',6',6'-Trimethyl-1'-cyclohexen-1'-yl) (5-¹²C,⁵,5,5-²H₃)-3-penten-2-one ((*Z*)-(5-¹²C,⁵-D₃)-**7**). In comparison to that of (*Z*)-**7**, the IR shows additional bands at 2235w and 2210w (sh); bands below 1100 cm⁻¹: 1084w, 1040w, 986w, 976w, 950w, 899w, 869w. ¹H-NMR in comparison with that of (*Z*)-**7**: *d* at 1.89 is missing; signal at 5.99 changed to *s*. ¹³C-NMR: *q* at 22.5 (C(5)) is missing. MS: 209 (8, *M*⁺, C₁₄H₁₉D₃O), 195 (23), 194 (100), 193 (10), 152 (22), 139 (17), 138 (12), 126 (27), 43 (22), 41 (9); *ca.* 85% D₃, 15% D₂.

2. Photolysis Experiments. – 2.1. *Photolyses of (E)-7 in Neutral Medium at λ > 347 nm*. 2.1.1. *In Pentane*. A solution of (*E*)-**7** (318 mg, 1.54 mmol) in pentane (25 ml, degassed in 3 freezing/melting cycles at 0.01 Torr) was irradiated (lamp B, filter A; conversion *ca.* 100%). Column chromatography (SiO₂, Et₂O/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: 3075w, 2985m, 2940s, 2920s, 2865s, 2715w, 1667s, 1475m, 1459m (sh), 1455m, 1447m, 1435w (sh), 1379s, 1360m, 1313w, 1288w, 1257s, 1187m, 1153w, 1137w, 1117w, 1080s, 1041m, 991w, 980w, 961m, 923w, 904w, 872w, 842w. ¹H-NMR (C₆D₆): 0.96, 1.09, 1.22, 1.28 (4s, CH₃-C(5), CH₃-C(6), 2CH₃-C(10)); 0.8–1.8 (*m*, 6H); 1.62 (*d*, *J* = 1, CH₃-C(3)); 4.48 (*m*, *v*_{1/2} = 3, H-C(4)). ¹³C-NMR (CD₂Cl₂): 12.8, 13.5, 16.1, 26.0, 26.7 (5*q*, 5CH₃); 19.5, 28.1, 38.1 (3*r*, 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*⁺, C₁₄H₂₂O), 192 (14), 191 (100), 176 (7), 149 (13), 136 (10), 123 (12), 43 (13). Anal. calc. for C₁₄H₂₂O (206.32): C 81.50, H 10.75; found: C 81.47, H 10.65.

2.1.2. *In C₆D₁₂*. A solution of (*E*)-**7** (52.3 mg, 0.25 mmol) in C₆D₁₂ (0.6 ml) was irradiated (lamp B, filter A). The photolysis was followed by ¹H-NMR (60 MHz; see Fig.).

2.2. *Photolysis in Acidic Medium at λ > 347 nm*. 2.2.1. *Photolysis of (E)-7*. A solution of (*E*)-**7** (598 mg, 2.90 mmol) in Et₂O (200 ml) was acidified by bubbling HCl gas for 20 s. Irradiation (lamp B, filter A; conversion 100%) and column chromatography (SiO₂, hexane/Et₂O 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: 3085w, 3055w, 2990m, 2975m, 2950s, 2935s, 2905m (sh), 2885m, 2875m, 2850m, 1656s (sh), 1651s, 1608m, 1474m, 1460m, 1448m, 1430m, 1387m (sh), 1382s, 1375m, 1365m, 1360m, 1343s, 1320w, 1310w, 1291m, 1285m, 1257m, 1215w, 1202w, 1184m, 1177w (sh), 1152s, 1109m, 1040m, 991m, 972w, 960m, 943w, 931w, 897m, 869s, 855w, 835w. ¹H-NMR: 0.75, 0.87, 1.04 (3s, CH₃–C(1), 2CH₃–C(7)); 0.7–2.1 (m, 6H); 1.61 (s, H–C(6)); 1.68 (s, CH₃–C(3)); 4.32, 4.70 (2m, w_{1/2} = 4, CH₂=C(5)); 5.11 (m, w_{1/2} = 3, H–C(4)). ¹³C-NMR(CD₂Cl₂): 20.3, 21.6, 26.7, 32.6 (4q, 4CH₃); 18.3 (t, C(9)); 39.1, 41.4 (2t, C(8), C(10)); 108.6 (t, CH₂=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⁺, C₁₄H₂₂O), 191 (8), 163 (7), 137 (6), 136 (8), 135 (11), 124 (10), 123 (100), 43 (19). Anal. calc. for C₁₄H₂₂O (206.32): C 81.50, H 10.75; found: C 81.52, H 10.79.

2.2.2. *Photolysis of (E/Z)-(5-¹²C,5-^D₃)-7*. A solution of (E/Z)-(5-¹²C,5-^D₃)-7 (105 mg, 0.51 mmol) in Et₂O (10 ml) was acidified and irradiated as described above. At a conversion of 77%, (¹²C,^D₃)-16 (75 mg, 92%; ^D₃ 1%, ^D₂ 10%, ^D₁ 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 Et₂O (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 Et₂O (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): ¹H-NMR (characteristic signals of a ca. 1:6 mixture (Z)-4/5, which were assigned to (Z)-4; 80 MHz; CDCl₃): 1.95 (d, J = 1.5, CH₃–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: 3078m, 2970s, 2925s, 2865s, 2843s, 1720s (sh), 1710s, 1675m, 1630m, 1455s (sh), 1425s, 1440s, 1420m (sh), 1382m, 1375s (sh), 1352s, 1320m (sh), 1282w, 1263w, 1242m, 1215m, 1205m, 1170s, 1133m, 1083w, 1055m, 973m, 943m, 965m (sh), 900s, 892s, 883m, 865m, 850w. ¹H-NMR (CDCl₃): 1.01 (s, 2CH₃–C(2')); 1.09 (d, J = 7, CH₃–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 (2d, J = 2.5, CH₂=C(6)); 5.05 (d, J = 10, H–C(4)). ¹³C-NMR: 17.3, 27.0, 27.5, 28.1 (4q, 4CH₃); 23.5, 37.5, 41.5 (3t, C(3'), C(4'), C(5')); 111.4 (t, CCH₂=C(6')); 46.9 (d, C(3)); 119.6 (d, C(4)); 38.2 (s, C(2')); 146.2, 151.1 (2s, C(1'), C(6')); 209.7 (s, C(2)). MS: 206 (8, M⁺, C₁₄H₂₂O), 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 C₁₄H₂₂O (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. NaHCO₃ and worked up in Et₂O. Column chromatography (Al₂O₃, hexane/Et₂O 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: 2990m, 2925s (sh), 2875m (sh), 2870m, 2825m, 1475m, 1459m (sh), 1450m, 1378s, 1361m, 1323m, 1292w, 1271w, 1228m, 1205m, 1181m, 1161m, 1144m, 1130m, 1103m, 1083s, 1068m (sh), 1057s, 1041s, 1028m, 990w, 979w, 955m, 943m, 919w, 913w, 866s, 847w. ¹H-NMR: 0.98 (3H), 1.01 (6H), 1.23 (3H), 1.26 (3H) (4s, CH₃–C(3), CH₃–C(5), CH₃–C(6), 2CH₃–C(10)); 1.1–1.7 (m, 6H); 1.93 (AB, δ_A = 1.85, δ_B = 2.01, J = 13, 2H–C(4)); 3.15 (s, CH₃O–C(3)). ¹³C-NMR (CD₂Cl₂): 16.4, 17.5, 19.7, 27.2, 27.5 (5q, 5CH₃); 49.1 (q, overlapping with t, CH₃O–C(3)); 19.3, 29.2, 39.2, 49.1 (4t, C(4), C(7), C(8), C(9)); 28.5, 31.8, 32.2 (3s, 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 C₁₅H₂₆O₂ (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 N₂ through the solution, Me₂S (1 ml) was added at –78°, the mixture was stirred for 0.5 h at r.t. and worked up in Et₂O. 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: 3035w, 2995w (sh), 2975m, 2945s, 2880m, 2760w, 2730w, 2715w, 1753s, 1703s, 1478m, 1463m, 1451m, 1435w, 1392m, 1380m, 1368s, 1252m, 1225s, 1173m, 1070m, 1062m, 1050m, 1025w, 998w, 978m, 948m, 933m, 912w, 895w. ¹H-NMR (90 MHz): 1.10, 1.38, 1.40 (3s, 2CH₃–C(2), CH₃–C(6), CH₃–C(7)); 0.7–1.9 (m, 6H); 2.05 (s, CH₃COO); 9.04 (s, CHO). ¹³C-NMR (C₆D₆, coalescence spectrum at +80°): 11.4, 17.6, 20.4, 28.0, 29.1 (5q, 5CH₃); 18.7, 30.3, 40.4 (3t, C(3), C(4), C(5)); 199.0 (d, CHO); 32.2, 36.5, 40.4 (3s, 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⁺, C₁₄H₂₂O₃), 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 C₁₄H₂₂O₃ (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: 3030w (sh), 2990m, 2935s, 2880m, 2830m, 1754s, 1481m, 1464m, 1448m, 1385m, 1376m (sh), 1364m, 1348w, 1328w, 1282w, 1224s, 1202m, 1191m, 1166m, 1106s, 1075s, 1062s (sh), 1049m, 1045m (sh), 1029m, 969m, 954m, 927m. ¹H-NMR: 0.98, 1.00, 1.06, 1.12 (4s, 2 CH₃–C(2), CH₃–C(6), CH₃–C(7)); 1.20–1.78 (m, 6H); 1.95 (s, CH₃COO); 3.23, 3.36 (2s, (CH₃O)₂CH–C(7)); 3.94 (s, (CH₃O)₂CH–C(7)). ¹³C-NMR (CD₂Cl₂): 10.5, 21.3, 21.6, 27.4, 30.2 (5q, 5CH₃); 56.1, 56.8 (2q, (CH₃O)₂CH–C(7)); 19.3, 30.0, 39.0 (3t, C(3), C(4), C(5)); 108.1 (d, (CH₃O)₂CH–C(7)); 29.0, 32.0, 35.7 (3s, 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 C₁₆H₂₈O₄ (284.38): C 67.57, H 9.93; found: C 67.45, H 9.91.

3.3. *Treatment of (Z)-(5-¹²C,5-D₃)-7 with HCl.* HCl gas was bubbled for 10 s through a solution of (Z)-(5-¹²C,5-D₃)-7 (42 mg, 0.20 mmol) in Et₂O (4 ml) and the solution stirred for 20 h at r.t. (conversion 58%). The mixture was washed with satd. aq. NaHCO₃ and worked up in Et₂O. Column chromatography (Al₂O₃, Woelm B, Act. III, hexane/Et₂O 9:1) afforded (¹²C,D₂)-**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 Et₂O (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 Et₂O (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 ¹H-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 H₂SO₄ (80%, 1 ml), dropwise at –20°. After stirring for 10 min at 0°, ice was added, and the mixture was extracted with Et₂O. The org. phase was washed with aq. Na₂CO₃ and worked up giving a ca. 1:1 mixture of (Z)-7 and **16** (35 mg, 70%).

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