# 110. Aldehyde Enol Esters as Novel Chain Terminators in Cationic Olefin Cyclizations

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Citronellal (**1**) has been transformed into enol acetates **2** which have been cyclized with various *Lewis* and *Brönsted* acids to dihydrocyclocitral (**4**). Application of this methodology to the synthesis of mono- and bicyclic ring systems has been examined.

**Introduction.** – Cationic olefin cyclizations have been widely utilized for the synthesis of terpenes and other naturally occurring ring systems. Cyclizations initiated by protonation of trisubstituted double bonds have been terminated by a variety of functional groups such as alkyl-, aryl-, carboxyl-, O-, F-, or (trialkylsilyl)-substituted double bonds or alkynes [1]. In this communication, we report the use of aldehyde enol acetates as cationic cyclization terminators for the preparation of monocyclic and bicyclic terpenoids and similar ring systems.

Aldehyde enol esters are attractive as cationic olefin cyclization terminators for several reasons. Aldehydes are easily, under mild conditions, transformed into enol esters, normally as (*E*/*Z*)-isomeric mixtures [2]. Ketones can also be transformed into enol esters, although under more stringent conditions, and be employed in cationic cyclization reactions [3]. However, regioselective ketone enol ester formation is often difficult to obtain. Cyclization of an aldehyde enol ester followed by aqueous workup again yields an aldehyde, which can be used in further synthetic manipulations. Thus, this scheme permits the formation of a C–C bond *via* cationic cyclization with retention of a heterofunctionality in a predictable manner.

**Results and Discussion.** – Treatment of citronellal (**1**) with a mixture of $Ac_2O$, $Et_3N$, and KOAc at 120° for 4 h followed by distillation furnished routinely enol acetates **2** ((*E*/*Z*) 2:1) in 80% yield *(cf. Scheme)*. A third product identified as the diacetate **3** was also formed in 3–6% yield. Enol acetates **2** underwent acid-induced cyclization to dihydrocyclocitral (**4**) with a variety of *Lewis* and *Brönsted* acids *(cf. Table)*.

The similar reactivity of *Lewis* and *Brönsted* acids was at first surprising until we observed that reactions with *Lewis* acids were much faster in the presence of a small amount of $H_2O$[2]). Under stringently dry conditions, the *Lewis*-acid-catalysed cyclizations were much slower and lower yielding. Catalytic amounts of *Lewis* acid as opposed to

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[2]) Solvents used without prior distillation in glassware which had not been oven-dried routinely provided enough $H_2O$.

*Scheme*

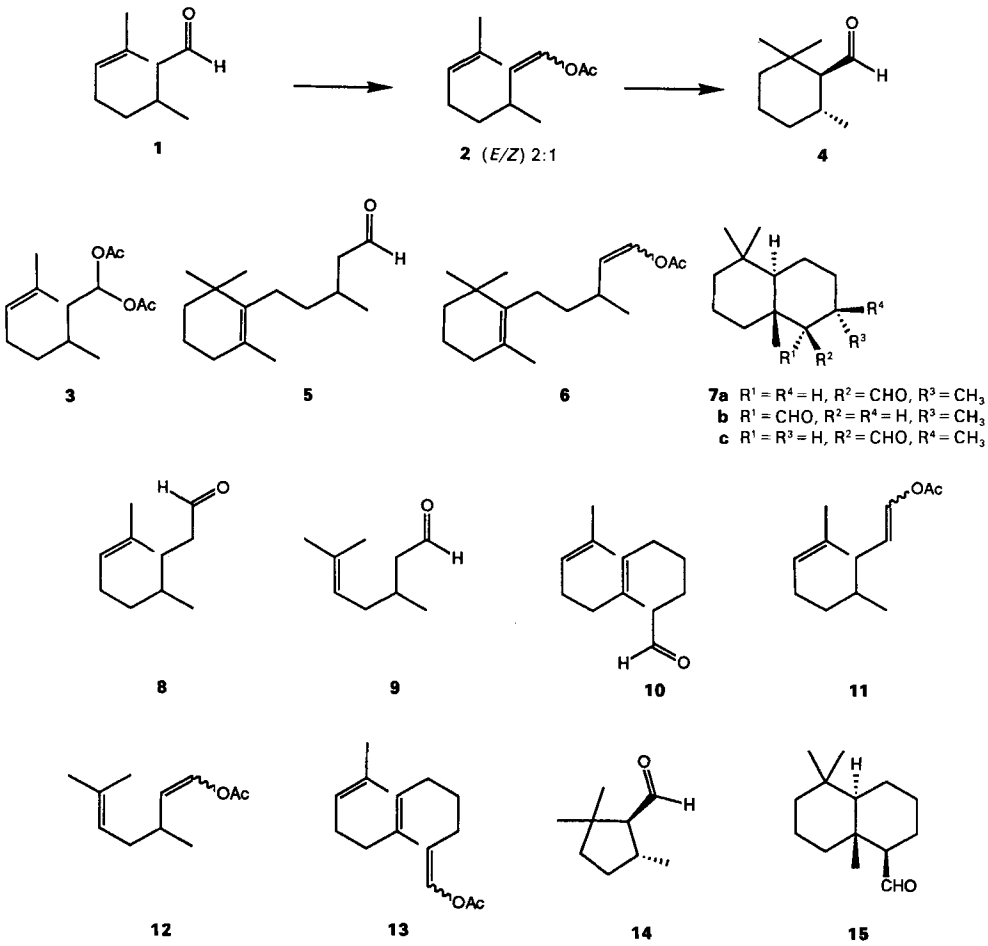


Table. *Cyclization of Enol Acetates* **2**

| *Entry* | Acid | mol-equiv. | Solvent | Temp. [°] | Time [h] | % Yield[a]) (*trans*/*cis*) |
|---|---|---|---|---|---|---|
| *1* | $SnCl_4$ | 1.2 | $CH_2Cl_2$ | 0 | 5.5 | 42 (18:1) |
| *2* | $SnCl_4$ | 0.2 | $CH_2Cl_2$ | 20 | 22 | 52 (15:1) |
| *3* | $SnCl_4$ | 0.2 | $CH_2Cl_2$ | 50 | 3 | 49 (14:1) |
| *4* | $BF_3 \cdot OEt_2$ | 0.2 | $CH_2Cl_2$ | 20 | 24 | 53 (14:1) |
| *5* | $TiCl_4$ | 0.2 | $CH_2Cl_2$ | 20 | 24 | 21 (13:1) |
| *6* | $CF_3CO_2H$ | 3.0 | toluene | 85 | 2 | 39 (14:1) |
| *7* | $MeSO_3H$ | 5.6 | toluene | 0 | 1 | 42 (16:1) |
| *8* | $H_2SO_4$ | 6.0 | toluene | 0 | 0.5 | 38 (17:1) |
| *9* | $H_3PO_4$ | 3.4 | toluene | 100 | 2 | 80[b]) (8:1) |

[a]) Yield determined by GC analysis after distillation from residues.
[b]) Yield determined after fractional distillation.

stoichiometric quantities resulted in a slower, but higher yielding reaction. Fortunately, the reaction time could be reduced by heating *(cf. Entries 1–3)*. Cyclization was most effectively achieved with 85% aq. $H_3PO_4$ solution *(cf. Entry 9)* yielding **4** as a 8:1 *trans/cis* mixture in 80% yield after distillation.

Cyclization of enol acetates **6**, obtained from aldehyde **5** in 79% yield, with 85% aqueous $H_3PO_4$ solution afforded the desired bicyclic drimane skeleton **7a** only after prolonged heating in a disappointing 14% yield. In contrast, $SnCl_4$-induced cyclization provided, after distillation, a mixture of bicyclic aldehydes in 53% yield. Equilibration with KOH/EtOH gave a mixture whose major component (80%) was **7a**. Five additional aldehyde resonances (all *d*), were observed by $^1$H-NMR. Two of these minor constituents, 7 and 3% of the mixture, showed mass spectra whose fragmentation patterns were similar to that of **7a**. The former of these two aldehydes, tentatively assigned structure **7c**, was not present in the mixture prior to equilibration and is believed to be the result of epimerization of **7b**, its supposed precursor. The latter aldehyde is tentatively assigned structure **7b**. The remaining aldehydes, 10% of the mixture, were not identified.

In order to examine further the scope of this reaction, aldehydes **8–10**[3]) were transformed into their corresponding enol acetates **11–13** as previously described. Enol acetates **11**, upon treatment with either 85% aqueous $H_3PO_4$ solution or $SnCl_4$, failed to yield any discernible cyclic aldehydes. Acid-induced cyclization of **12** with 85% aqueous $H_3PO_4$ solution gave the cyclopentanecarbaldehyde **14** in 42% yield (*trans/cis* > 30:1). Finally, triene **13**, upon exposure to $SnCl_4$ in $CH_2Cl_2$, underwent clean tandem cyclization to the bicyclic aldehyde **15** in 36% yield[4]). Attempted cyclization of **13** with 85% aqueous $H_3PO_4$ solution failed to provide **15** in reasonable yields (*i.e.* < 15%).

Our results indicate that aldehyde enol acetates are in certain cases viable chain terminators in cationic olefin cyclizations. Citronellal (**1**) has been transformed in a simple, high yielding, two-step process into the monocyclic terpernoid dihydrocyclocitral (**4**), which is of value in the perfume industry. Cyclization of enol acetates **6** to **7a** represents a rapid and novel construction of the drimane skeleton with a reactive functional group suitably positioned for the synthesis of naturally occurring sesquiterpenes. Applications of this methodology to the formation of a cyclopentane, **12**→**14**, and for a tandem polyene cyclization, **13**→**15**, have also been demonstrated.

## Experimental Part

*General. Varian Aerograph model 700* using He as carrier gas for prep. work, *Hewlett-Packard model 5890 A* using $H_2$ as a carrier gas for anal. work. IR spectra: *Perkin-Elmer-297* spectrometer. NMR spectra: in $CDCl_3$, *Bruker-WH-360* instrument; $\delta$ in ppm downfield from TMS ( = 0 ppm), coupling constants *J* in Hz. Mass spectra: *Finnigan* quadrupole instrument coupled with a GC; in *m/z* (% most important fragment).

*3,7-Dimethyl-1,6-octadienyl Acetate* (**2**; (*E*/*Z*) 2:1). Citronellal (**1**; 50 g, 0.32 mol) was added to a soln. of $Et_3N$ (68.9 g, 0.68 mol) and KOAc (5.0 g, 0.05 mol) in $Ac_2O$ (500 ml). The soln. was heated at 120° for 6 h, cooled to r.t., poured into $H_2O$ and extracted with petroleum ether (b.p. 30–50°). The org. phase was washed with sat. aq. $NaHCO_3$ and sat. aq. NaCl soln., dried ($Na_2SO_4$), and evaporated. Fractional distillation through a 10-cm *Vigreux* column yielded **2** (54.2 g, 85%). B.p. 103–106°/11 Torr. Separation by prep. GC afforded anal. samples of (*E*)-**2** and (*Z*)-**2**.

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[3]) Prepared by hydroformylation of (*E*)-6,10-dimethyl-1,5,9-undecatriene [5].

[4]) Aldehyde **15** was accompanied by a small amount (*ca.* 3–4% yield) of its C(1) epimer.

*Data of (E)-***2**: IR: 3070, 2950, 2905, 2840, 1755, 1668, 1445, 1363, 1288, 1210, 1080, 935. $^1$H-NMR: 1.02 (*d*, *J* = 7, 3 H); 1.32 (*m*, 2 H); 1.59 (*s*, 3 H); 1.68 (*s*, 3 H); 1.96 (*m*, 2 H); 2.12 (*s*, 3 H); 2.15 (*m*, 1 H); 5.07 (*t*, *J* = 7, 1 H); 5.29 (*dd*, *J* = 7.5, 12.5, 1 H); 7.07 (*d*, *J* = 12.5, 1 H). MS: 196 (0, $M^+$), 154 (7), 136 (22), 121 (33), 109 (18), 101 (13), 93 (18), 84 (48), 71 (59), 55 (35), 43 (100).

*Data of (Z)-***2**: IR: 3060, 2945, 2915, 2878, 1753, 1665, 1448, 1367, 1238, 1210, 1080, 1038, 884. $^1$H-NMR: 0.99 (*d*, *J* = 7, 3 H); 1.36 (*m*, 1 H); 1.58 (*s*, 3 H); 1.68 (*s*, 3 H); 1.93 (*m*, 1 H); 2.14 (*s*, 3 H); 2.68 (*m*, 1 H); 4.67 (*dd*, *J* = 7, 11, 1 H); 5.10 (*t*, *J* = 7, 1 H); 6.99 (*d*, *J* = 7, 1 H). MS: 196 (0, $M^+$), 154 (7), 136 (18), 121 (38), 109 (20), 101 (17), 93 (30), 84 (47), 71 (58), 55 (36), 43 (100).

*General Procedure for the Cyclization of Enol Acetates* (**2**) (*Table, Entries 1–8*). To a soln. of **2** (4 g, 0.02 mol) in the indicated solvent (80 ml) at 0° was added each acid in the designated amount. The mixtures were stirred at the indicated temp. until consumption of **2**, poured into $H_2O$, and then extracted with petroleum ether (b.p. 30–50°). The org. phase was washed with sat. aq. $NaHCO_3$ and sat. aq. NaCl soln., dried ($Na_2SO_4$), and evaporated. Bulb-to-bulb distillation (100°/0.5 Torr) afforded the products whose yields were determined by GC analysis.

*2,2,6-Trimethylcyclohexane-1-carbaldehyde* (**4**; *trans/cis* 8:1; *Table, Entry 9*). A soln. of **2** (30 g, 0.15 mol) in toluene (60 ml) was added to 85% aq. $H_3PO_4$ soln. (60 g) and heated at 100° for 2 h. After cooling to r.t., the mixture was poured into $H_2O$ and extracted with toluene. The org. phase was washed with sat. aq. $NaHCO_3$ and sat. aq. NaCl soln., dried ($Na_2SO_4$), and evaporated. Distillation through a 20-cm *Vigreux* column afforded **4** (20.8 g, 89% pure, 80% yield). B.p. 74–76°/14 Torr. Distillation through a 40-cm *Fischer* column gave pure **4** (> 98%; *trans/cis* 8:1). B.p. 67°/10 Torr. IR: 3000, 2710, 1715, 1675, 1450, 1365, 1200, 1018, 963. $^1$H-NMR: 0.83 (*d*, *J* = 7, 3 H); 0.95 (*m*, 1 H); 0.98 (*s*, 3 H); 1.03 (*s*, 3 H); 1.20 (*m*, 1 H); 1.37 (*m*, 1 H); 1.55 (*m*, 2 H); 1.63 (*dd*, *J* = 5, 12, 1 H); 1.78 (*m*, 1 H); 1.97 (*m*, 1 H); 9.64 (*d*, *J* = 6, 1 H). MS: 154 (14, $M^+$), 139 (9), 121 (15), 111 (12), 95 (14), 83 (28), 69 (65), 55 (56), 41 (100).

*3-Methyl-5-(2,6,6-trimethyl-1-cyclohexenyl)-1-pentenyl Acetate* (**6**; (*E*/*Z*) 2:1). At r.t., **5** (3 g, 13.5 mmol) was added to a soln. of $Et_3N$ (4.1 g, 0.04 mol) and KOAc (0.3 g, 3.2 mmol) in $Ac_2O$ (30 ml). The soln. was then heated at 120° for 4 h, cooled to r.t., poured into $H_2O$, and extracted with toluene. The org. phase was washed with sat. aq. $NaHCO_3$ and sat. aq. NaCl soln., dried ($Na_2SO_4$), and evaporated. Fractional distillation through a 10-cm *Vigreux* column yielded **6** (2.87 g, 92% pure, 74% yield). B.p. 90–96°/0.5 Torr. IR: 3115, 2775, 1753, 1670, 1440, 1365, 1215, 1040, 933. $^1$H-NMR ((*E*)-**6**): 0.98 (*s*, 6 H); 1.04 (*d*, *J* = 7, 3 H); 1.51 (*s*, 3 H); 2.11 (*s*, 3 H); 5.33 (*dd*, *J* = 4.5, 9, 1 H); 7.10 (*d*, *J* = 9, 1 H). $^1$H-NMR ((*Z*)-**6**): 0.98 (*s*, 6 H); 1.01 (*d*, *J* = 7, 3 H); 1.64 (*s*, 3 H); 2.14 (*s*, 3 H); 4.71 (*dd*, *J* = 7, 9, 1 H); 7.01 (*d*, *J* = 9, 1 H). MS ((*E*)-**6**): 264 (1, $M^+$), 204 (8), 189 (13), 148 (12), 126 (91), 107 (19), 95 (47), 85 (100), 67 (23), 55 (23), 43 (87). MS ((*Z*)-**6**): 264 (1, $M^+$), 204 (8), 189 (22), 148 (23), 123 (100), 107 (27), 95 (57), 84 (92), 67 (32), 55 (30), 43 (97).

*(1RS,2SR,4aRS,8aRS)-2,5,5,8a-Tetramethyldecahydronaphthalene-1-carbaldehyde* (**7a**). $SnCl_4$ (0.4 g, 1.6 mmol) was added to a soln. of **6** (2.0 g, 7.6 mmol) in $CH_2Cl_2$ (50 ml) at r.t. The soln. was heated at 50° for 8 h, cooled to r.t., poured into $H_2O$, and extracted with $Et_2O$. The org. phase was washed with sat. aq. $NaHCO_3$ and sat. aq. NaCl soln., dried ($Na_2SO_4$), and evaporated. Fractional distillation through a 10-cm *Vigreux* column afforded a mixture of aldehydes (900 mg), b.p. 70–72°/0.6 Torr. This mixture was then dissolved in a soln. of KOH (0.2 g) in EtOH (50 ml) and heated at reflux for 2 h. After cooling to r.t., the mixture was poured into $H_2O$, extracted with toluene, and dried ($Na_2SO_4$). Concentration and distillation *i.v.* gave **7a** (895 mg, 80% pure, 43% yield). B.p. (bulb-to-bulb dist.) 100–120°/0.9 Torr. IR: 2925, 1720, 1455, 1387, 1370, 1193, 1170, 1035, 987. $^1$H-NMR: 0.78 (*d*, *J* = 7, 3 H); 0.84 (*s*, 3 H); 0.86 (*s*, 3 H); 1.09 (*s*, 3 H); 1.90 (*dq*, *J* = 13, 3, 1 H); 2.08 (*m*, 1 H); 9.69 (*d*, *J* = 4, 1 H). $^{13}$C-NMR: 15.98 (*q*); 18.40 (*t*); 20.66 (*q*); 21.67 (*t*); 21.88 (*q*); 27.63 (*d*); 33.17 (*s*); 33.52 (*q*); 35.61 (*t*); 38.50 (*s*); 40.32 (*t*); 41.96 (*t*); 54.34 (*d*); 70.43 (*d*); 207.65 (*d*). MS: 222 (9, $M^+$), 207 (11), 189 (13), 138 (67), 123 (100), 109 (62), 95 (68), 84 (81), 69 (76), 55 (59), 43 (96).

*General Procedure for the Preparation of Enol Acetates* **11**–**13**. To a soln. of $Et_3N$ (3.6 g, 0.04 mol) and KOAc (0.5 g, 5.3 mmol) in $Ac_2O$ (50 ml) was added either **8** (5.0 g, 0.032 mol) or **9** (5.0 g, 0.036 mol). Similarly, **10** (1.0 g, 4.8 mmol) was treated with a soln. of $Et_3N$ (0.7 g, 6.9 mmol) in $Ac_2O$ (10 ml) containing a catalytic amount of KOAc. The solns. were heated at 120° for 5 h, cooled to r.t., poured into $H_2O$, and extracted with toluene. The org. phase was washed with sat. aq. $NaHCO_3$ and sat. aq. NaCl soln., dried ($Na_2SO_4$), and evaporated. Bulb-to-bulb distillation afforded **11**–**13**.

*4,8-Dimethyl-1,7-nonadienyl Acetate* (**11**; (*E*/*Z*) 1:1). Yield 88% from **8**. B.p. (bulb-to-bulb dist.) 100–120°/0.8 Torr. IR: 3060, 2875, 1750, 1685, 1430, 1365, 1210, 1145, 930. $^1$H-NMR ((*E*)-**11**): 0.88 (*d*, *J* = 7, 3 H); 1.61 (*s*, 3 H); 1.69 (*s*, 3 H); 2.18 (*s*, 3 H); 5.09 (br. *t*, *J* = 5, 1 H); 5.39 (*dt*, *J* = 7.5, 12, 1 H); 7.05 (*d*, *J* = 12, 1 H). $^1$H-NMR ((*Z*)-**11**): 0.90 (*d*, *J* = 7, 3 H); 2.15 (*s*, 3 H); 4.88 (*q*, *J* = 7, 1 H); 7.04 (*d*, *J* = 7, 1 H). MS ((*E*)-**11**): 210 (0, $M^+$), 168 (4), 150 (18), 135 (22), 107 (14), 69 (43), 55 (15), 43 (100). MS ((*Z*)-**11**): 210 (0, $M^+$), 168 (4), 150 (18), 135 (25), 107 (14), 69 (44), 55 (17), 43 (100).

*3,6-Dimethyl-1,5-heptadienyl Acetate* (**12**; (*E*/*Z*) 2:1). Yield 68% from **9**. B.p. 123–125°/25 Torr. IR: 2930, 1745, 1667, 1440, 1365, 1215, 1038, 935. $^1$H-NMR ((*E*)-**12**): 1.02 (*d*, *J* = 7, 3 H); 1.59 (*s*, 3 H); 1.70 (*s*, 3 H); 2.11 (*s*, 3 H); 5.10 (*m*, 1 H); 5.36 (*dd*, *J* = 7, 13, 1 H); 7.08 (*d*, *J* = 13, 1 H). $^1$H-NMR ((*Z*)-**12**): 0.99 (*d*, *J* = 7, 3 H); 1.60 (*s*, 3 H); 1.70 (*s*, 3 H); 2.13 (*s*, 3 H); 4.72 (*dd*, *J* = 7, 8, 1 H); 6.96 (*d*, *J* = 7, 1 H). MS ((*E*)-**12**): 182 (0, $M^+$), 122 (12), 113 (70), 71 (86), 43 (100). MS ((*Z*)-**12**): 182 (0, $M^+$), 122 (10), 113 (29), 71 (92), 43 (100).

*(6E)-7,11-Dimethyl-1,6,10-dodecatrienyl Acetate* (**13**; (*E*/*Z*) 1:1). Yield 70% from **10**. B.p. (bulb-to-bulb dist.) 120–130°/0.9 Torr. IR: 2920, 2855, 1738, 1670, 1437, 1365, 1225, 1040. $^1$H-NMR ((*E*)-**13**): 1.61 (*s*, 6 H); 1.68 (*s*, 3 H); 2.11 (*s*, 3 H); 5.10 (*m*, 2 H); 5.42 (*dt*, *J* = 7, 12, 1 H); 7.07 (*d*, *J* = 12, 1 H). $^1$H-NMR ((*Z*)-**13**): 2.14 (*s*, 3 H); 4.86 (*q*, *J* = 7, 1 H); 7.01 (br. *d*, *J* = 7, 1 H). MS ((*E*)-**13**): 250 (4, $M^+$), 175 (8), 147 (20), 121 (18), 109 (17), 93 (17), 81 (15), 69 (65), 43 (100). MS ((*Z*)-**13**): 250 (4, $M^+$), 175 (7), 147 (25), 121 (16), 109 (15), 95 (18), 81 (16), 69 (65), 43 (100).

*(1RS,5SR)-2,2,5-Trimethylcyclopentane-1-carbaldehyde* (**14**). A soln. of **12** (5.0 g, 0.027 mol) in toluene (11 g) was added to 85% aq. $H_3PO_4$ soln. (11 g) and heated at 100° for 90 min. After cooling to r.t., the mixture was poured into $H_2O$ and extracted with toluene. The org. phase was washed with sat. aq. $NaHCO_3$ and sat. aq. NaCl soln., dried ($Na_2SO_4$), and evaporated. Distillation afforded **14** (1.6 g, 42%). B.p. 50–51°/12 Torr. IR: 2870, 2720, 1715, 1460, 1385, 1218, 1177, 1079, 1025, 990. $^1$H-NMR: 1.00 (*s*, 6 H); 1.19 (*s*, 3 H); 1.30 (*m*, 1 H); 1.48 (*m*, 1 H); 1.60 (*m*, 1 H); 1.93 (*dd*, *J* = 2.5, 9, 1 H); 1.98 (*m*, 1 H); 2.51 (*m*, 1 H); 9.72 (*d*, *J* = 2.5, 1 H). MS: 140 (1, $M^+$), 84 (20), 71 (80), 55 (70), 53 (17), 43 (38), 41 (100), 39 (66).

*(1RS,4aRS,8aRS)-5,5,8a-Trimethyldecahydronaphthalene-1-carbaldehyde* (**15**). $SnCl_4$ (0.02 ml, 1.7 mmol) was added to a stirred soln. of **13** (690 mg, 2.7 mmol) in $CH_2Cl_2$ (10 ml) at r.t. After 24 h, the soln. was poured into $H_2O$ and extracted with $Et_2O$. The org. phase was washed with sat. aq. $NaHCO_3$ and sat. aq. NaCl soln., dried ($Na_2SO_4$), and evaporated. Distillation gave **15** (0.2 g, 36%)[5]). B.p. (bulb-to-bulb dist.) 140°/0.9 Torr. IR: 2920, 2870, 2710, 1715, 1440, 1383, 1360, 1167, 950. $^1$H-NMR: 0.83 (*s*, 3 H); 0.86 (*s*, 3 H); 1.01 (*s*, 3 H); 1.15–1.73 (*m*, 11 H); 1.80–2.02 (*m*, 3 H); 9.62 (*d*, *J* = 2, 1 H). $^{13}$C-NMR: 15.51 (*q*); 18.49 (*t*); 21.48 (*t*); 21.60 (*q*); 22.07 (*t*); 26.02 (*t*); 33.28 (*s*); 33.44 (*q*); 54.63 (*d*); 63.39 (*d*); 206.24 (*d*). MS: 208 (6, $M^+$), 138 (22), 123 (81), 109 (45), 95 (86), 81 (92), 69 (100), 55 (52), 41 (30).

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[5]) Contains C(1) epimer of **15** (*ca.* 3–4% yield).