

A Novel Synthesis of γ,δ -Unsaturated Aldehydes from α -Formyl- γ -lactones

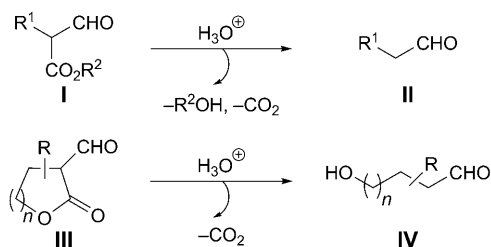
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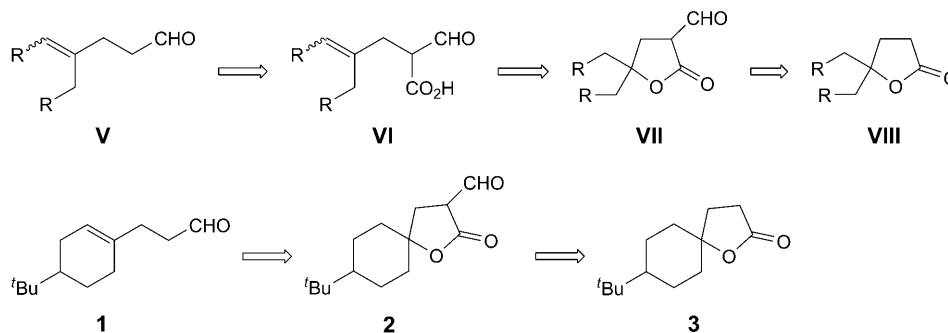
A preparatively useful one-step transformation of γ,γ -disubstituted α -formyl- γ -lactones into trisubstituted γ,δ -unsaturated aldehydes is described, by means of catalytic amounts of either AcOH or AcOEt in the vapor phase over a glass support. A mechanistic rationale is proposed.

Introduction. – The dealkoxycarbonylation of α -formyl ester **I** to afford aldehyde **II** is typically effected by means of an aqueous acid [1]. Thus, if the substrate is α -formyllactone **III**, the product would be expected to be ω -hydroxyaldehyde **IV** (*Scheme 1*). Surprisingly, the only reported example of this transformation is the conversion of 2-oxotetrahydrofuran-3-carboxaldehyde to 4-hydroxybutanal (**IV**; $n = 1$, $R = H$) [2]. In this context, we wondered whether an extension of this methodology, by using catalytic nonaqueous conditions, might lead to the synthesis of trisubstituted γ,δ -unsaturated aldehydes **V** from α -formyllactone **VII**, readily prepared from γ,γ -disubstituted γ -lactone **VIII**. It was hoped that such conditions would result in opening of the lactone ring, *via* heterolytic cleavage of the tertiary alkyl–O bond, to afford unsaturated α -formylcarboxylic acid **VI**, which would then undergo rapid decarboxylation to **V** (*Scheme 2*). The primary motivation of this work was to find a novel access to fragrance aldehyde ($\pm$)-3-[4-(*tert*-butyl)cyclohex-1-en-1-yl]propanal (**1**) [3] from the known lactone **3** [4] *via* the corresponding α -formyllactone **2**¹⁾.

Scheme 1. *Hydrolytic Dealkoxycarbonylation of α -Formyl Esters or α -Formyllactones*



¹⁾ For an elegant one-step transformation of **2** (*cis/trans* 64:36) to **1**, published after we started our studies, by using a *Piria–Limpricht*-type reduction (HCO_2H (excess), $[Zn^{II}/Mn^{II}/pumice]$, 370° ; 60% yield), see [5].

Scheme 2. retro-Synthesis of **V** (from **VIII**) and **1** (from **3**)

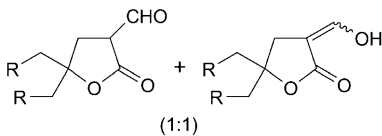
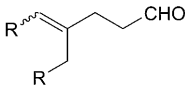
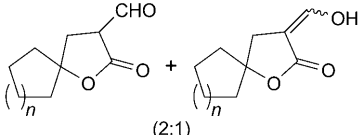
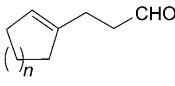
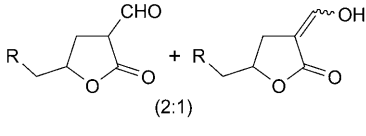
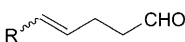
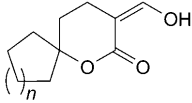
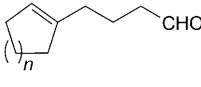
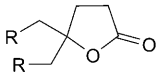
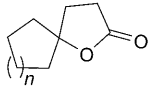
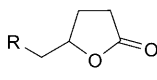
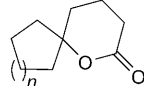
Results and Discussion. – To test the aforementioned idea prior to investigating the synthesis of **1**, we decided to carry out a short model study using structurally related substrates. Accordingly, we prepared, in 51–89% yields, α -formyl- γ -lactones **15–23** and α -formyl- δ -lactones **24** and **25**²⁾ from γ -lactones **4–12** and δ -lactones **13** and **14**, respectively (*Table 1*), by treatment with HCOOEt and MeOK as base. Disubstituted γ -lactones **4** and **5** were accessible from the double addition of either EtMgBr or PrMgBr to succinic anhydride, and an analogous method was used to prepare δ -(spiro)lactones **13** and **14** [6]; γ -(spiro)lactones **6–10** were synthesised by the radical addition of the corresponding cycloalkanol to acrylic acid in the presence of di(*tert*-butyl) peroxide as the radical initiator [7]. Monosubstituted γ -lactones **11** and **12** were commercially available.

We then submitted **15–25** to pyrolysis conditions in which a THF or a THF/EtOH solution³⁾ of each compound was passed through a quartz column packed with small quartz tubes heated at temperatures between 430° and 500°, in the presence or absence of catalytic amounts of AcOH or AcOEt. Subsequent isolation and purification of the product mixtures by column chromatography on silica gel afforded unsaturated aldehydes **26–36** in unoptimized yields ranging from 10 to 53% (*Table 1*). Thus, although the desired reaction takes place for all these substrates, it is only preparatively useful when the substrate is a γ,γ -disubstituted γ -lactone such as **15–21** (*Table 1*, *Entries 1–8*). The reaction also appears to be favored by acid catalysis (*Entries 1* and *2*). In contrast, when the substrate is monosubstituted in the γ -position, as for **22** and **23**, the yield drops dramatically to *ca.* 10%, and the major isolated products, the consequence of a hydrolytic *retro*-Claisen condensation reaction, are the corresponding γ -lactones **11** and **12**, respectively, in *ca.* 30% yield (*Entries 9* and *10*). δ,δ -Disubstituted δ -lactones **24** and **25** show intermediate behavior; pyrolysis of these compounds in the presence of AcOH gives low yields (15 and 17%, *resp.*) of δ,ε -unsaturated aldehydes **35**

²⁾ In the crystalline and gaseous states, the tautomeric compositions of **15–25** were not determined. However, as shown by inspection of the ¹H- and ¹³C-NMR spectra, in CDCl₃ solution, **15–23** are aldehyde/enol mixtures; **24** and **25** are totally in the enol form (*cf. Exper. Part*).

³⁾ EtOH was employed to solubilize those α -formyllactones which were sparingly soluble in THF.

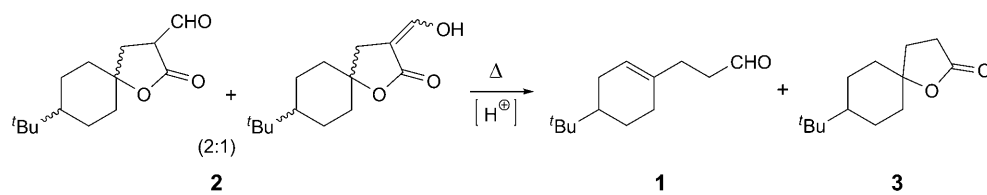
Table 1. Pyrolysis of α -Formyl- γ - and α -Formyl- δ -lactones **15**–**25**^{a)}

Entry	Substrate ^{b)}	Additive [%] ^{c)}	Temp.	Product	Yield [%]
	 (1:1)				
1	15 R = Me	–	470°, 3 h	26 ((<i>E</i>)/(<i>Z</i>) 1:1)	30
2	15 R = Me	AcOH (4)	470°, 3 h	26 ((<i>E</i>)/(<i>Z</i>) 1:1)	42
3	16 R = Et	–	470°, 3 h	27 ((<i>E</i>)/(<i>Z</i>) 1.5:1)	45
	 (2:1)				
4	17 <i>n</i> = 1	AcOH (14)	450°, 4 h	28	23
5	18 <i>n</i> = 2	AcOH (6)	450°, 3 h	29	53
6	19 <i>n</i> = 3	AcOH (11)	450°, 3 h	30	39
7	20 <i>n</i> = 4	AcOEt (34)	430°, 10 h	31	26
8	21 <i>n</i> = 8	AcOEt (27)	460°, 8 h	32 ((<i>E</i>)/(<i>Z</i>) 1:1)	41
	 (2:1)				
9	22 R = C ₆ H ₁₃	AcOEt (52)	490°, 2.5 h	33 ((<i>E</i>)/(<i>Z</i>) 3:1)	10 ^{d)}
10	23 R = C ₇ H ₁₅	AcOEt (23)	470°, 2 h	34 ((<i>E</i>)/(<i>Z</i>) 2.3:1)	10 ^{e)}
	 (2:1)				
11	24 <i>n</i> = 1	AcOH (32)	500°, 6 h	35	15
12	25 <i>n</i> = 2	AcOH (7)	460°, 13 h	36	17 ^{f)}
^{a)} Solvent: THF (<i>Entries</i> 1–8, 10, and 12), THF/EtOH 12:1 (<i>Entry</i> 9), and THF/EtOH 14:1 (<i>Entry</i> 11). ^{b)} Prepared from the corresponding lactones 4 – 14 (51–89% yield, cf. <i>Exper. Part</i>). ^{c)} Molar percentage. ^{d)} By-product: 11 (ca. 30% yield). ^{e)} By-product: 12 (ca. 30% yield). ^{f)} By-product: 14 (ca. 20% yield).					
	 4 R = Me 5 R = Et	 6 <i>n</i> = 1 9 <i>n</i> = 4 7 <i>n</i> = 2 10 <i>n</i> = 8 8 <i>n</i> = 3	 11 R = Me(CH ₂) ₅ 12 R = Me(CH ₂) ₆	 13 <i>n</i> = 1 14 <i>n</i> = 2	

and **36**; in the latter case, a major by-product is **14** (ca. 20% yield), the result again of a *retro-Claisen* condensation reaction.

These results are consistent with our aforementioned mechanistic hypothesis which proposed that the desired reaction pathway proceeds by initial opening of the lactone ring *via* cleavage of the alkyl–O bond. It is thus logical that this process is favored when the alkyl–O is attached to a quaternary center as opposed to a tertiary center, and when the substrate is a γ -lactone, which is more strained than the corresponding δ -lactone. In addition, whereas it is clear why the presence of AcOH might favor the desired reaction by general acid catalysis, it is unclear why AcOEt has a similar effect. Maybe, under the high reaction temperatures, AcOH is generated *in situ* by a β -elimination reaction. The *retro-Claisen* condensation reaction, found to be a major side reaction in three experiments and observed to some extent in the majority of cases, may be rationalized by supposing that this hydrolysis reaction is catalytic in nature, and that the reaction conditions result in decarboxylation of the putative hydrolysis products, formic acid or acetic formic anhydride.

We were now ready to apply our findings to the synthesis of **1**. Thus, formylation of **3** (*trans/cis* 70 : 30) under the aforementioned conditions afforded **2** in 88% yield as a diastereoisomer mixture of aldehyde and enol tautomers. We then screened various pyrolysis conditions in which 15% (by weight) solutions of **2** (0.5 g) in THF, toluene, or BuOH, containing cat. amounts of AcOH, were passed through a Pyrex® column packed with small glass beads. The product mixture was then analyzed by gas chromatography (Table 2). It had been serendipitously discovered that the use of glass beads accelerated the desired transformation and thus allowed the use of lower reaction temperatures in comparison to the previous experiments performed with quartz tubes (*vide supra*). In a first series of experiments conducted at 425° (Entries 1 –

Table 2. Pyrolysis of **2** to **1**: Screening Experiments^{a)}


Entry	Solvent	AcOH [%] (by weight)	Temp.	Conversion [%]	Yield [%] of products		
					1	3	by-products
1	THF	5	425°	> 99	47	4	49
2	THF	2	425°	94	50	2	42
3	THF	1	425°	78	53	2	23
4	THF	2	320°	40	26	3	11
5	THF	2	350°	93	70	3	20
6	toluene	2	350°	63	46	2	15
7	BuOH	2	350°	66	38	7	21

^{a)} A 15% (by weight) solution of **2** (0.5 g, 2.1 mmol) containing AcOH was introduced during 30 min by an automatic syringe pump under a slight flow of N₂ (two bubbles per second) at the top of a 15-cm Pyrex® column (diameter 1.7 cm) packed with glass beads (diameter 0.5 cm). The pyrolyzate was collected by means of a dry ice/acetone cold trap at –78° and analyzed by gas chromatography.

3), the amount of AcOH was optimized to 2% (by weight), resulting in a 94% conversion of **2** and a 50% yield of **1** (Entry 2). Lowering the temperature to 320° considerably slowed down the reaction (40% conversion, see Entry 4) but at 350°, the reaction proceeded well with 93% conversion and a 70% yield of **1** (Entry 5). The use of toluene or BuOH as solvent gave inferior conversions and lower yields of **1** (Entries 6 and 7). In all these experiments, it should be noted that small amounts (*ca.* 2–7% yield) of **3**, formed by hydrolysis of **2**, were identified. Finally, the reaction conditions described in Entry 5 were scaled-up by using 7.5 g of **2**, and **1** was isolated in 51% yield (see *Exper. Part*).

Conclusion. – Although the acid-catalyzed pyrolytic decarboxylation of γ,γ -disubstituted α -formyl- γ -lactones affords moderate yields of trisubstituted γ,δ -unsaturated aldehydes, this reaction is much less efficient when the γ -position of the substrate is monosubstituted. Under the same conditions, α -formyl- δ -(spiro)lactones only give low yields of the corresponding cyclic δ,ϵ -saturated aldehydes.

The authors thank René Challand and Mauro Schindler for careful experimental work.

Experimental Part

1. *General.* See [8].

2. *Preparation of 4–10, 13, and 14.* 2.1. 5,5-Diethyldihydrofuran-2(3H)-one (**4**) [9]. A soln. of EtBr (66 g, 0.6 mol) in THF (120 ml) was added dropwise under N₂ and at r.t. during 20 min to a mechanically stirred slurry of Mg turnings (12 g, 0.49 mol) in THF (20 ml) containing a trace of I₂. After further 10 min refluxing, the clear soln. was cooled to r.t. and diluted with more THF (320 ml). To this stirred soln. maintained at –30° was now added dropwise during 1 h a soln. of succinic anhydride (20 g, 0.2 mol) in THF (400 ml). After a further hour at –30° and 3 h at –15°, the milky mixture was allowed to attain r.t. and stirred during 16 h. Then the clear yellow-green soln. was added dropwise under N₂ to cold 5% aq. HCl soln. (500 ml). Neutralization with NaHCO₃ was followed by saturation with NaCl. Extraction (Et₂O), workup, and fractional distillation *in vacuo* (10-cm Vigreux® column) afforded **4** (15.3 g, 54%). Pale-yellow oil. B.p. 48°/0.07 mbar. ¹H-NMR: 0.94 (*t*, *J* = 7.6, 6 H); 1.63–1.78 (*m*, 4 H); 1.98–2.06 (*m*, 2 H); 2.55–2.63 (*m*, 2 H). ¹³C-NMR: 7.8 (2*q*); 29.2 (*t*); 29.8 (*t*); 30.9 (2*t*); 89.6 (*s*); 177.1 (*s*). MS: 142 (0, *M*⁺), 113 (100), 95 (11), 87 (13), 69 (8).

2.2. Dihydro-5,5-dipropylfuran-2(3H)-one (**5**) [10]. As described for **4**, with PrBr (24.6 g, 0.2 mol) in THF (40 ml) and Mg turnings (4 g, 0.17 mol) in THF (15 ml). Dilution with THF (80 ml), reaction with succinic anhydride (6.7 g, 0.07 mol) in THF (120 ml), treatment with 5% aq. HCl soln. (200 ml), and workup as described for **4** afforded **5** (3.8 g, 32%). Colorless oil. B.p. (bulb-to-bulb dist.) 90–100°/0.3 mbar. ¹H-NMR: 0.94 (*t*, *J* = 7.2, 6 H); 1.29–1.44 (*m*, 4 H); 1.56–1.69 (*m*, 4 H); 1.99–2.05 (*m*, 2 H); 2.54–2.60 (*m*, 2 H). ¹³C-NMR: 14.4 (2*q*); 16.8 (2*t*); 29.2 (*t*); 30.9 (*t*); 41.0 (2*t*); 89.1 (*s*); 177.1 (*s*). MS: 170 (0, *M*⁺), 127 (100), 115 (8), 85 (8), 71 (15).

2.3. 1-Oxaspiro[4.4]nonan-2-one (**6**) [6]. According to [7], cyclopentanol was converted to **6** in 15% yield. ¹H-NMR: 1.63–1.90 (*m*, 6 H); 1.96–2.05 (*m*, 2 H); 2.17–2.24 (*m*, 2 H); 2.55–2.62 (*m*, 2 H). ¹³C-NMR: 23.8 (2*t*); 29.9 (*t*); 32.5 (*t*); 38.5 (2*t*); 95.1 (*s*); 176.9 (*s*). MS: 140 (7, *M*⁺), 111 (100), 98 (57), 83 (16), 67 (29).

2.4. 1-Oxaspiro[4.5]decan-2-one (**7**) [6]. According to [7], cyclohexanol was converted to **7** in 24% yield. ¹H-NMR: 1.33–1.63 (*m*, 6 H); 1.65–1.84 (*m*, 4 H); 1.99–2.05 (*m*, 2 H); 2.55–2.61 (*m*, 2 H). ¹³C-NMR: 22.6 (2*t*); 25.0 (*t*); 28.6 (*t*); 32.9 (*t*); 36.9 (2*t*); 86.4 (*s*); 176.8 (*s*). MS: 154 (22, *M*⁺), 125 (10), 111 (100), 98 (23), 55 (15).

2.5. 1-Oxaspiro[4.6]undecan-2-one (**8**) [11]. According to [7], cycloheptanol was converted to **8** in 30% yield. ¹H-NMR: 1.39–1.83 (*m*, 10 H); 1.90–1.99 (*m*, 2 H); 2.00–2.07 (*m*, 2 H); 2.53–2.60 (*m*, 2 H).

^{13}C -NMR: 22.2 (2*t*); 28.7 (1*t*); 29.1 (2*t*); 34.2 (1*t*); 40.0 (2*t*); 90.3 (s); 176.9 (s). MS: 168 (5, M^+), 150 (5), 139 (7), 125 (18), 111 (100).

2.6. *1-Oxaspiro[4.7]dodecan-2-one* (**9**) [11]. According to [7], cyclooctanol was converted to **9** in 34% yield. ^1H -NMR: 1.41–1.78 (*m*, 12 H); 1.96–2.08 (*m*, 4 H); 2.54–2.61 (*m*, 2 H). ^{13}C -NMR: 22.0 (2*t*); 24.5 (1*t*); 27.9 (2*t*); 28.9 (1*t*); 32.9 (1*t*); 35.5 (2*t*); 90.2 (s); 176.8 (s). MS: 182 (2, M^+), 153 (5), 139 (12), 122 (25), 111 (100).

2.7. *1-Oxaspiro[4.11]hexadecan-2-one* (**10**) [9]. According to [7], cyclododecanol was converted to **10** in 22% yield. ^1H -NMR: 1.22–1.64 (*m*, 20 H); 1.77–1.88 (*m*, 2 H); 2.00 (*t*, $J = 8.3$, 2 H); 2.56 (*t*, $J = 8.3$, 2 H). ^{13}C -NMR: 19.4 (2*t*); 22.2 (2*t*); 22.6 (2*t*); 25.9 (1*t*); 26.2 (2*t*); 28.7 (1*t*); 32.5 (1*t*); 33.5 (2*t*); 89.5 (s); 176.5 (s). MS: 238 (16, M^+), 183 (29), 111 (100), 98 (43), 55 (29).

2.8. *6-Oxaspiro[4.5]decan-7-one* (**13**) [6]. According to [6]. ^1H -NMR: 1.60–1.74 (*m*, 4 H); 1.81–2.02 (*m*, 8 H); 2.51 (*t*, $J = 7.0$, 2 H). ^{13}C -NMR: 17.8 (1*t*); 23.8 (2*t*); 29.4 (1*t*); 32.3 (1*t*); 39.5 (2*t*); 93.2 (s); 171.4 (s). MS: 154 (18, M^+), 125 (44), 112 (80), 97 (76), 67 (100).

2.9. *6-Oxaspiro[5.5]undecan-2-one* (**14**) [6]. According to [6]. ^1H -NMR: 1.27–1.63 (*m*, 6 H); 1.67–1.92 (*m*, 8 H); 2.49 (*t*, $J = 6.9$, 2 H). ^{13}C -NMR: 16.1 (1*t*); 21.7 (2*t*); 25.4 (1*t*); 29.6 (1*t*); 32.6 (1*t*); 37.4 (2*t*); 83.0 (s); 171.2 (s). MS: 168 (47, M^+), 140 (14), 125 (81), 112 (74), 97 (100).

3. *Preparation of 15–25*. 3.1. *General Procedure*. MeOK (7 g, 0.1 mol) was added portionwise during 1 h to a mechanically stirred soln. of **4–14** (0.1 mol), resp., and HCOOEt (11.1 g, 0.15 mol) in Et₂O (130 ml) under N₂, maintained at 15°. After a further 2 h at r.t., a soln. of AcOH (13 g, 0.22 mol) in H₂O (100 ml) was added dropwise during 30 min. Extraction (Et₂O) and washing of the combined org. phase with H₂O and then sat. aq. NaCl soln. afforded, after workup, bulb-to-bulb distillation *in vacuo*, and recrystallization from cyclohexane, **15–25**, resp. (*vide infra*).

3.2. *5,5-Diethyltetrahydro-2-oxofuran-3-carboxaldehyde* (aldehyde-**15**) and *5,5-Diethyldihydro-3-(hydroxymethylene)furan-2(3H)-one* (enol-**15**). In CDCl₃ soln., aldehyde/enol *ca.* 1:1 and (*E*)/(*Z*)-enol *ca.* 9:1. Yield 88%. White crystals. M.p. 68–70°. ^1H -NMR: 0.88–0.98 (*m*, 18 H); 1.64–1.76 (*m*, 12 H); 2.11 (*dd*, $J = 10.6$, 13.7, 1 H, aldehyde); 2.51 (*dd*, $J = 8.3$, 13.7, 1 H, aldehyde); 2.63 (*d*, $J = 1.9$, 2 H, (*Z*)-enol); 2.66 (*d*, $J = 2.4$, 2 H, (*E*)-enol); 3.78 (*dd*, $J = 8.3$, 10.6, 1 H, aldehyde); 7.02 (br. s, 1 H, (*Z*)-enol); 7.67 (br. s, 1 H, (*E*)-enol); 9.46 (br. *d*, $J = 7.0$, 1 H, (*E*)-enol); 9.85 (s, 1 H, aldehyde); 10.21 (br. s, 1 H, (*Z*)-enol). MS: 170 (18, M^+), 152 (20), 141 (100), 124 (29), 95 (32).

Data of Aldehyde-15. ^{13}C -NMR: 7.6 (*q*); 7.8 (*q*); 29.0 (1*t*); 31.2 (1*t*); 31.4 (1*t*); 54.5 (*d*); 89.9 (s); 171.8 (s); 194.6 (*d*).

Data of (E)-Enol-15. ^{13}C -NMR: 7.6 (2*q*); 31.8 (2*t*); 32.3 (1*t*); 88.2 (s); 103.4 (s); 153.5 (*d*); 175.2 (s).

3.3. *Tetrahydro-2-oxo-5,5-dipropylfuran-3-carboxaldehyde* (aldehyde-**16**) and *(Z)-Dihydro-3-(hydroxymethylene)-5,5-dipropylfuran-2(3H)-one* (enol-**16**). In CDCl₃ soln., aldehyde/enol *ca.* 1:1. Yield 89%. Viscous oil. ^1H -NMR: 0.88–1.00 (*m*, 12 H); 1.24–1.45 (*m*, 8 H); 1.50–1.76 (*m*, 8 H); 2.10 (*dd*, $J = 10.5$, 13.7, 1 H, aldehyde); 2.51 (*dd*, $J = 8.3$, 13.7, 1 H, aldehyde); 2.62 (*d*, $J = 2.0$, 2 H, enol); 3.74 (*dd*, $J = 8.3$, 10.5, 1 H, aldehyde); 6.99 (br. s, 1 H, enol); 9.85 (s, 1 H, aldehyde); 10.28 (br. s, 1 H, enol). MS: 170 (18, M^+), 152 (20), 141 (100), 124 (29), 95 (32).

Data of Aldehyde-16. ^{13}C -NMR: 30.0 (1*t*); 54.5 (*d*); 89.0 (s); 171.4 (s); 194.7 (*d*).

Data of Enol-16. ^{13}C -NMR: 33.2 (1*t*); 89.4 (s); 101.4 (s); 156.0 (*d*); 175.2 (s).

3.4. *2-Oxo-1-oxaspiro[4.4]nonane-3-carboxaldehyde* (aldehyde-**17**) and *3-(Hydroxymethylene)-1-oxaspiro[4.4]nonan-2-one* (enol-**17**). In CDCl₃ soln., aldehyde/enol *ca.* 2:1 and (*Z*)/(*E*)-enol *ca.* 5:1. Yield 51%. White crystals. M.p. 94–97°. ^1H -NMR: 1.59–2.13 (*m*, 24 H); 2.30 (*dd*, $J = 9.7$, 13.3, 1 H, aldehyde); 2.67 (*dd*, $J = 8.2$, 13.3, 1 H, aldehyde); 2.83 (*d*, $J = 2.0$, 2 H, (*Z*)-enol); 2.85 (*d*, $J = 2.6$, 2 H, (*E*)-enol); 3.75–3.82 (*m*, 1 H, aldehyde); 6.99 (br. s, 1 H, (*Z*)-enol); 7.60 (br. s, 1 H, (*E*)-enol); 7.86 (br. s, 1 H, (*E*)-enol); 9.86 (s, 1 H, aldehyde); 10.19 (br. s, 1 H, (*Z*)-enol). MS: 168 (13, M^+), 150 (31), 139 (100), 122 (47), 111 (43).

Data of Aldehyde-17. ^{13}C -NMR: 31.5 (1*t*); 54.8 (*d*); 94.8 (s); 171.3 (s); 194.7 (*d*).

Data of (Z)-Enol-17. ^{13}C -NMR: 33.9 (1*t*); 95.4 (s); 101.5 (s); 155.7 (*d*); 174.9 (s).

3.5. *2-Oxo-1-oxaspiro[4.5]decane-3-carboxaldehyde* (aldehyde-**18**) and *3-(Hydroxymethylene)-1-oxaspiro[4.5]decane-2-one* (enol-**18**). In CDCl₃ soln., aldehyde/enol *ca.* 2:1 and (*Z*)/(*E*)-enol *ca.* 5:1. Yield 55%. White crystals. M.p. 110–112°. ^1H -NMR: 1.32–1.92 (*m*, 30 H); 2.15 (*dd*, $J = 10.0$, 13.7, 1 H, aldehyde); 2.44 (*dd*, $J = 8.2$, 13.7, 1 H, aldehyde); 2.61 (br. s, 2 H, (*Z*)-enol); 2.64 (br. s, 2 H, (*E*)-enol);

3.74–3.82 (*m*, 1 H, aldehyde); 7.01 (br. *s*, 1 H, (*Z*)-enol); 7.63 (br. *s*, 1 H, (*E*)-enol); 8.22 (br. *s*, 1 H, (*E*)-enol); 9.86 (*s*, 1 H, aldehyde); 10.24 (br. *s*, 1 H, (*Z*)-enol). MS: 182 (29, *M*⁺), 164 (55), 154 (100), 139 (93), 111 (75).

Data of Aldehyde-18: ¹³C-NMR: 32.1 (*t*); 54.0 (*d*); 86.5 (*s*); 171.3 (*s*); 194.8 (*d*).

Data of (Z)-Enol-18: ¹³C-NMR: 35.2 (*t*); 87.1 (*s*); 101.0 (*s*); 156.4 (*d*); 175.0 (*s*).

3.6. 2-Oxo-1-oxaspiro[4.6]undecane-3-carboxaldehyde (aldehyde-19) and 3-(Hydroxymethylene)-1-oxaspiro[4.6]undecan-2-one (enol-19). In CDCl₃ soln., aldehyde/enol *ca.* 2:1 and (*Z*)/(*E*)-enol *ca.* 5:1. Yield 64%. White crystals. M.p. 141–144°. ¹H-NMR: 1.36–2.04 (*m*, 36 H); 2.19 (*dd*, *J* = 10.0, 13.5, 1 H, aldehyde); 2.44 (*dd*, *J* = 8.7, 13.5, 1 H, aldehyde); 2.63 (br. *s*, 2 H, (*Z*)-enol); 2.66 (br. *s*, 2 H, (*E*)-enol); 3.72–3.79 (*m*, 1 H, aldehyde); 7.00 (br. *s*, 1 H, (*Z*)-enol); 7.64 (br. *s*, 1 H, (*E*)-enol); 8.15 (br. *s*, 1 H, (*E*)-enol); 9.86 (*s*, 1 H, aldehyde); 10.22 (br. *s*, 1 H, (*Z*)-enol). MS: 196 (14, *M*⁺), 178 (31), 168 (42), 139 (57), 55 (100).

Data of Aldehyde-19: ¹³C-NMR: 33.6 (*t*); 54.0 (*d*); 90.2 (*s*); 171.4 (*s*); 195.0 (*d*).

Data of (Z)-Enol-19: ¹³C-NMR: 36.8 (*t*); 90.9 (*s*); 101.1 (*s*); 156.1 (*d*); 175.0 (*s*).

3.7. 2-Oxo-1-oxaspiro[4.7]dodecane-3-carboxaldehyde (aldehyde-20) and 3-(Hydroxymethylene)-1-oxaspiro[4.7]undecan-2-one (enol-20). In CDCl₃ soln., aldehyde/enol *ca.* 2:1 and (*Z*)/(*E*)-enol *ca.* 9:1. Yield 67%. White crystals. M.p. 131–132°. ¹H-NMR: 1.40–1.80 (*m*, 36 H); 1.92–2.10 (*m*, 6 H); 2.16 (*dd*, *J* = 10.2, 13.5, 1 H, aldehyde); 2.44 (*dd*, *J* = 8.4, 13.5, 1 H, aldehyde); 2.60 (*d*, *J* = 1.8, 2 H, (*Z*)-enol); 2.63 (*d*, *J* = 2.3, 2 H, (*E*)-enol); 3.75 (*dd*, *J* = 8.4, 10.2, 1 H, aldehyde); 6.99 (br. *s*, 1 H, (*Z*)-enol); 7.62 (br. *s*, 1 H, (*E*)-enol); 9.86 (*s*, 1 H, aldehyde); 10.27 (br. *s*, 1 H, (*Z*)-enol). MS: 210 (10, *M*⁺), 192 (22), 182 (22), 139 (49), 55 (100).

Data of Aldehyde-20: ¹³C-NMR: 32.2 (*t*); 54.2 (*d*); 90.2 (*s*); 171.3 (*s*); 194.8 (*d*).

Data of (Z)-Enol-20: ¹³C-NMR: 35.6 (*t*); 90.9 (*s*); 101.2 (*s*); 156.3 (*d*); 174.9 (*s*).

3.8. 2-Oxo-1-oxaspiro[4.11]hexadecane-3-carboxaldehyde (aldehyde-21) and 3-(Hydroxymethylene)-1-oxaspiro[4.11]hexadecan-2-one (enol-21). In CDCl₃ soln., aldehyde/enol *ca.* 2:1 and (*Z*)/(*E*)-enol *ca.* 5:1. Yield 72%. White crystals. M.p. 134–136°. ¹H-NMR: 1.16–1.68 (*m*, 60 H); 1.70–1.90 (*m*, 6 H); 2.11 (*dd*, *J* = 10.0, 13.5, 1 H, aldehyde); 2.45 (*dd*, *J* = 8.2, 13.5, 1 H, aldehyde); 2.58 (*d*, *J* = 2.0, 2 H, (*Z*)-enol); 2.61 (*d*, *J* = 2.5, 2 H, (*E*)-enol); 3.73 (*dd*, *J* = 8.3, 10.0, 1 H, aldehyde); 6.98 (br. *s*, 1 H, (*Z*)-enol); 7.59 (br. *s*, 1 H, (*E*)-enol); 9.87 (*s*, 1 H, aldehyde); 10.25 (br. *s*, 1 H, (*Z*)-enol). MS: 266 (15, *M*⁺), 248 (24), 238 (16), 183 (59), 55 (100).

Data of Aldehyde-21: ¹³C-NMR: 31.9 (*t*); 54.0 (*d*); 89.8 (*s*); 194.9 (*d*).

Data of (Z)-Enol-21: ¹³C-NMR: 35.0 (*t*); 156.2 (*d*).

3.9. 5-Heptyltetrahydro-2-oxofuran-3-carboxaldehyde (aldehyde-22; *ca.* 2:1 diastereoisomer mixture) and 5-Heptyldihydro-3-(hydroxymethylene)furan-2(3H)-one (enol-22; diastereoisomer mixture). In CDCl₃ soln., aldehyde/enol *ca.* 2:1 and (*Z*)/(*E*)-enol *ca.* 2:1. Yield 64%. White crystals. M.p. 69–70°. ¹H-NMR: 0.88 (*t*, *J* = 6.7, 12 H); 1.19–1.53 (*m*, 40 H); 1.54–1.83 (*m*, 8 H); 1.93–2.02 (*m*, 1 H); 2.21–2.31 (*m*, 1 H); 2.38–2.54 (*m*, 3 H); 2.79–2.88 (*m*, 1 H); 2.91–3.04 (*m*, 2 H); 3.67–3.77 (*m*, 2 H, aldehyde); 4.48–4.67 (*m*, 4 H); 7.03 (br. *s*, 1 H, (*Z*)-enol); 7.64 (br. *s*, 1 H, (*E*)-enol); 8.42 (br. *s*, 1 H, (*E*)-enol); 9.80 (*s*, 1 H, aldehyde); 9.86 (*s*, 1 H, aldehyde); 10.16 (br. *s*, 1 H, (*Z*)-enol). MS: 212 (9, *M*⁺), 166 (6), 124 (37), 85 (100).

Data of cis/trans-Aldehyde-22: ¹³C-NMR: 27.0, 27.5 (2*t*); 53.6, 54.1 (2*d*); 80.1, 80.5 (2*s*); 171.6, 172.0 (2*s*); 193.8, 194.9 (2*d*).

Data of (Z)/(E)-Enol-22: ¹³C-NMR: 78.6, 80.8 (2*s*); 100.3, 102.9 (2*s*); 152.3, 156.2 (2*d*); 174.2, 175.7 (2*s*).

3.10. Tetrahydro-5-octyl-2-oxofuran-3-carboxaldehyde (aldehyde-23; *ca.* 1.2:1 diastereoisomer mixture) and Dihydro-3-(hydroxymethylene)-5-octylfuran-2(3H)-one (enol-23; diastereoisomer mixture). In CDCl₃ soln., aldehyde/enol and (*Z*)/(*E*)-enol *ca.* 2:1. Yield 74%. M.p. 70–71°. ¹H-NMR: 0.88 (*t*, *J* = 6.7, 12 H); 1.19–1.52 (*m*, 48 H); 1.55–1.82 (*m*, 8 H); 1.92–2.02 (*m*, 1 H); 2.21–2.31 (*m*, 1 H); 2.38–2.52 (*m*, 3 H); 2.79–2.88 (*m*, 1 H); 2.91–3.04 (*m*, 2 H); 3.66–3.76 (*m*, 2 H, aldehyde); 4.47–4.66 (*m*, 4 H); 7.01 (br. *s*, 1 H, (*Z*)-enol); 7.61 (br. *s*, 1 H, (*E*)-enol); 7.72 (br. *s*, 1 H, (*E*)-enol); 9.80 (*s*, 1 H, aldehyde); 9.86 (*s*, 1 H, aldehyde); 10.18 (br. *s*, 1 H, (*Z*)-enol). MS: 226 (6, *M*⁺), 180 (6), 163 (12), 138 (29), 55 (100).

Data of *cis/trans-Aldehyde-23*: $^{13}\text{C-NMR}$: 27.0, 27.5 (2*t*); 53.6, 54.1 (2*d*); 80.0, 80.4 (2*s*); 171.5, 171.9 (2*s*); 193.8, 194.9 (2*d*).

Data of (Z)/(E)-*Enol-23*: $^{13}\text{C-NMR}$: 78.2, 80.8 (2*s*); 100.4, 103.4 (2*s*); 151.5 (*d*), 156.1 (2*d*); 175.6 (*s*).

3.11. (8*Z*)-8-(Hydroxymethylene)-6-oxaspiro[4.5]decan-7-one (**24**). Yield 73%. White crystals. M.p. 126–127°. $^1\text{H-NMR}$: 1.57–1.75 (*m*, 4 H); 1.84–2.02 (*m*, 6 H); 2.40–2.47 (*m*, 2 H); 7.19 (*d*, *J* = 12.3, 1 H); 12.53 (*d*, *J* = 12.3, 1 H). $^{13}\text{C-NMR}$: 20.3 (*t*); 23.7 (2*t*); 31.6 (*t*); 38.7 (2*t*); 92.1 (*s*); 97.2 (*s*); 163.4 (*d*); 171.9 (*s*). MS: 182 (13, *M*⁺), 164 (28), 136 (21), 119 (50), 67 (100).

3.12. (3*Z*)-3-(Hydroxymethylene)-1-oxaspiro[5.5]undecan-2-one (**25**). Yield 85%. White crystals. M.p. 122–123°. $^1\text{H-NMR}$: 1.28–1.42 (*m*, 1 H); 1.43–1.65 (*m*, 5 H); 1.66–1.88 (*m*, 6 H); 2.36–2.44 (*m*, 2 H); 7.18 (*br. d*, *J* = 12.3, 1 H); 12.59 (*d*, *J* = 12.3, 1 H). $^{13}\text{C-NMR}$: 18.4 (*t*); 21.6 (2*t*); 25.4 (*t*); 31.7 (*t*); 36.2 (2*t*); 81.8 (*s*); 97.0 (*s*); 163.6 (*d*); 172.0 (*s*). MS: 196 (26, *M*⁺), 178 (70), 133 (68), 95 (100), 81 (96).

4. Pyrolysis of **15–25**. 4.1. General Procedure. A 15% (by weight) soln. of **15–25** (10 mmol) in THF or THF/EtOH, in the presence or absence of AcOH or AcOEt (see Table I), was introduced by an automatic syringe pump (Bioblock Scientific-Razel Scientific Instruments, Inc.) under a slight flow of N₂ (two bubbles per second) at the top of a packed pre-heated (430°–500°) quartz column (length 15 cm, diameter 1.7 cm) packed with quartz tubes (length 5 mm, diameter 3 mm). The pyrolyzate was collected by means of a dry ice/acetone cold trap at –78° and analyzed by GC. Isolation of the products **26–36** was effected by concentration at 760 mbar (15-cm Vigreux® column), CC (silica gel, cyclohexane/AcOEt mixtures), and bulb-to-bulb distillation *in vacuo*.

4.2. 4-Ethylhex-4-enal (**26**; (E)/(Z) 1:1). Yield 42%. Mixture not separated. Colorless oil. $^1\text{H-NMR}$: 0.94–1.02 (*m*, 6 H); 1.55–1.63 (*m*, 6 H); 1.95–2.10 (*m*, 4 H); 2.30–2.40 (*m*, 4 H); 2.46–2.55 (*m*, 4 H); 5.15–5.30 (*m*, 2 H); 9.76 (*t*, *J* = 1.8, 1 H); 9.78 (*t*, *J* = 1.8, 1 H).

Data of (E)-**26**: $^{13}\text{C-NMR}$: 12.7 (*q*); 13.0 (*q*); 23.0 (*t*); 28.7 (*t*); 42.3 (*t*); 118.8 (*d*); 139.5 (*s*); 202.8 (*d*). MS: 126 (4, *M*⁺), 108 (46), 97 (46), 69 (60), 55 (100).

Data of (Z)-**26**: $^{13}\text{C-NMR}$: 12.7 (*q*); 13.2 (*q*); 22.4 (*t*); 29.3 (*t*); 42.5 (*t*); 118.9 (*d*); 139.7 (*s*); 202.4 (*d*). MS: 126 (2, *M*⁺), 108 (46), 97 (45), 69 (60), 55 (100).

4.3. 4-Propylhept-4-enal (**27**; (E)/(Z) 1.5:1). Mixture not separated. Yield 45%. Colorless oil. $^1\text{H-NMR}$: 0.85–0.99 (*m*, 12 H); 1.34–1.46 (*m*, 4 H); 1.90–2.06 (*m*, 8 H); 2.28–2.36 (*m*, 4 H); 2.44–2.56 (*m*, 4 H); 5.10–5.20 (*m*, 2 H); 9.76 (*t*, *J* = 1.8, 1 H); 9.78 (*t*, *J* = 1.8, 1 H).

Data of (E)-**27**: $^{13}\text{C-NMR}$: 14.0 (*q*); 14.5 (*q*); 21.0 (*t*); 21.6 (*t*); 29.0 (*t*); 32.3 (*t*); 42.4 (*t*); 127.9 (*d*); 136.6 (*s*); 202.7 (*d*). MS: 154 (2, *M*⁺), 136 (26), 110 (18), 95 (56), 82 (100), 69 (45), 55 (92), 41 (50).

Data of (Z)-**27**: $^{13}\text{C-NMR}$: 13.8 (*q*); 14.6 (*q*); 21.0 (*t*); 21.2 (*t*); 22.5 (*t*); 38.7 (*t*); 42.8 (*t*); 128.3 (*d*); 136.2 (*s*); 202.4 (*d*). MS: 154 (2, *M*⁺), 136 (24), 110 (18), 95 (54), 82 (100), 69 (39), 55 (84), 41 (47).

4.4. 3-(Cyclopent-1-en-1-yl)propanal (= Cyclopent-1-ene-1-propanal; **28**)⁴. Yield 23%. Colorless oil. $^1\text{H-NMR}$: 2.58 (*dt*, *J* = 7, 2, 2 H); 5.34 (*m*, 1 H); 9.77 (*t*, *J* = 2, 1 H). $^{13}\text{C-NMR}$: 23.4 (*t*); 23.7 (*t*); 32.5 (*t*); 35.3 (*t*); 42.0 (*d*); 124.4 (*d*); 142.6 (*s*); 202.6 (*d*). MS: 124 (26, *M*⁺), 106 (10), 95 (52), 79 (59), 67 (100).

4.5. 3-(Cyclohex-1-en-1-yl)propanal (= Cyclohex-1-ene-1-propanal; **29**) [5]. Yield 53%. Colorless oil. Spectrally identical with an authentic sample.

4.6. 3-(Cyclohept-1-en-1-yl)propanal (= Cyclohept-1-ene-1-propanal; **30**). Yield 39%. Colorless oil. $^1\text{H-NMR}$: 1.40–1.52 (*m*, 4 H); 1.68–1.77 (*m*, 2 H); 2.03–2.13 (*m*, 4 H); 2.32 (*br. t*, *J* = 7.4, 2 H); 2.49 (*dt*, *J* = 2.0, 7.4, 2 H); 5.57 (*br. t*, *J* = 6.4, 1 H); 9.75 (*t*, *J* = 2.0, 1 H). $^{13}\text{C-NMR}$: 26.7 (*t*); 27.2 (*t*); 28.2 (*t*); 32.4 (*t*); 32.5 (*t*); 32.8 (*t*); 42.2 (*t*); 127.0 (*d*); 142.5 (*s*); 202.8 (*d*). MS: 152 (14, *M*⁺), 134 (52), 108 (60), 93 (100), 67 (91).

4.7. 3-(Cyclooct-1-en-1-yl)propanal (= Cyclooct-1-ene-1-propanal; **31**). Yield 26%. Colorless oil. $^1\text{H-NMR}$: 1.38–1.58 (*m*, 8 H); 2.03–2.19 (*m*, 4 H); 2.33 (*br. t*, *J* = 7.4, 2 H); 2.54 (*dt*, *J* = 7.4, 2.0, 2 H); 5.34 (*br. t*, *J* = 8.2, 1 H); 9.77 (*t*, *J* = 2.0, 1 H). $^{13}\text{C-NMR}$: 26.2 (*t*); 26.3 (*t*); 26.5 (*t*); 28.7 (*t*); 29.1 (*t*); 29.5 (*t*); 29.9 (*t*); 42.1 (*t*); 124.7 (*d*); 138.7 (*s*); 202.9 (*d*). MS: 166 (26, *M*⁺), 148 (24), 109 (66), 81 (100), 67 (99).

4.8. 3-(Cyclododec-1-en-1-yl)propanal (= Cyclododec-1-ene-1-propanal; **32**; (E)/(Z) 1:1) [13]. Yield 41%. Colorless oil.

⁴) Although **28** has been reported as a starting material, see [12], neither its preparation nor its spectral characterization has been described.

Data of (E)-**32**: $^1\text{H-NMR}$: 1.18–1.54 (*m*, 16 H); 2.00–2.15 (*m*, 4 H); 2.33 (*br. t*, $J = 7.6$, 2 H); 2.52 (*dt*, $J = 7.6$, 1.8, 2 H); 5.13 (*br. t*, $J = 7.7$, 1 H); 9.76 (*t*, $J = 1.8$, 1 H). $^{13}\text{C-NMR}$: 22.3 (*t*); 22.5 (*t*); 24.0 (*t*); 24.3 (*t*); 24.6 (*t*); 24.7 (*t*); 25.0 (*2t*); 25.9 (*t*); 27.2 (*t*); 28.4 (*t*); 42.3 (*t*); 126.9 (*d*); 137.1 (*s*); 202.9 (*d*). MS: 222 (14, M^+), 204 (8), 135 (22), 109 (34), 83 (100).

Data of (Z)-**32**: $^1\text{H-NMR}$: 1.18–1.53 (*m*, 16 H); 2.02–2.10 (*m*, 4 H); 2.34–2.40 (*m*, 2 H); 2.45–2.51 (*m*, 2 H); 5.36 (*br. t*, $J = 7.6$, 1 H); 9.78 (*t*, $J = 1.8$, 1 H). $^{13}\text{C-NMR}$: 21.2 (*t*); 23.8 (*t*); 24.3 (*t*); 24.4 (*t*); 24.8 (*t*); 25.4 (*t*); 25.9 (*t*); 26.5 (*t*); 26.8 (*t*); 27.4 (*t*); 35.2 (*t*); 42.7 (*t*); 129.6 (*d*); 135.5 (*s*); 202.5 (*d*). MS: 222 (20, M^+), 204 (14), 135 (40), 83 (92), 67 (100).

4.9. Undec-4-enal (**33**; (E)/(Z) 3:1) [14]. Yield 10%. Mixture not separated. Colorless oil.

Data of (E)-**33**: $^1\text{H-NMR}$: 0.88 (*t*, $J = 6.9$, 3 H); 1.18–1.40 (*m*, 8 H); 1.92–2.03 (*m*, 2 H); 2.28–2.38 (*m*, 2 H); 2.46–2.52 (*m*, 2 H); 5.34–5.52 (*m*, 2 H); 9.76 (*t*, $J = 1.8$, 1 H). $^{13}\text{C-NMR}$: 14.1 (*q*); 22.6 (*t*); 25.2 (*t*); 28.8 (*t*); 29.4 (*t*); 31.7 (*t*); 32.5 (*t*); 43.6 (*t*); 127.7 (*d*); 132.2 (*d*); 202.3 (*d*). MS: 168 (0.5, M^+), 150 (11), 124 (25), 97 (30), 84 (100).

Data of (Z)-**33**: $^1\text{H-NMR}$: 0.88 (*t*, $J = 6.9$, 3 H); 1.18–1.40 (*m*, 8 H); 2.01–2.08 (*m*, 2 H); 2.33–2.41 (*m*, 2 H); 2.46–2.52 (*m*, 2 H); 5.28–5.46 (*m*, 2 H); 9.77 (*t*, $J = 1.8$, 1 H). $^{13}\text{C-NMR}$: 14.1 (*q*); 20.1 (*t*); 22.6 (*t*); 27.2 (*t*); 29.0 (*t*); 29.5 (*t*); 31.8 (*t*); 43.9 (*t*); 127.0 (*d*); 131.8 (*d*); 202.2 (*d*). MS: 168 (0.2, M^+), 150 (3), 124 (22), 97 (23), 84 (100).

4.10. Dodec-4-enal (**34**; (E)/(Z) 2.3:1) [15]. Yield 10%. Mixture not separated. Colorless oil.

Data of (E)-**34**: $^1\text{H-NMR}$: 0.88 (*t*, $J = 6.9$, 3 H); 1.18–1.40 (*m*, 10 H); 1.92–2.02 (*m*, 2 H); 2.28–2.38 (*m*, 2 H); 2.45–2.54 (*m*, 2 H); 5.33–5.53 (*m*, 2 H); 9.76 (*t*, $J = 1.8$, 1 H). $^{13}\text{C-NMR}$: 14.1 (*q*); 22.7 (*t*); 25.3 (*t*); 29.1 (*t*); 29.2 (*t*); 29.5 (*t*); 31.9 (*t*); 32.5 (*t*); 43.6 (*t*); 127.7 (*d*); 132.2 (*d*); 202.3 (*d*). MS: 182 (0, M^+), 138 (10), 110 (10), 97 (20), 84 (100).

Data of (Z)-**34**: $^1\text{H-NMR}$: 0.88 (*t*, $J = 6.9$, 3 H); 1.18–1.41 (*m*, 10 H); 1.99–2.09 (*m*, 2 H); 2.32–2.42 (*m*, 2 H); 2.44–2.53 (*m*, 2 H); 5.27–5.37 (*m*, 1 H); 5.38–5.48 (*m*, 1 H); 9.77 (*t*, $J = 1.8$, 1 H). $^{13}\text{C-NMR}$: 14.1 (*q*); 20.1 (*t*); 22.7 (*t*); 27.3 (*t*); 29.2 (*t*); 29.3 (*t*); 29.6 (*t*); 31.9 (*t*); 43.9 (*t*); 127.1 (*d*); 131.8 (*d*); 202.2 (*d*). MS: 182 (0, M^+), 138 (24), 110 (14), 97 (31), 84 (100).

4.11. 4-(Cyclopent-1-en-1-yl)butanal (=Cyclopent-1-ene-1-butanal; **35**). Yield 15%. Colorless oil. $^1\text{H-NMR}$: 1.75–1.90 (*m*, 4 H); 2.08–2.15 (*m*, 2 H); 2.18–2.25 (*m*, 2 H); 2.26–2.33 (*m*, 2 H); 2.43 (*dt*, $J = 7.2$, 1.8, 2 H); 5.34–5.38 (*m*, 1 H); 9.77 (*t*, $J = 1.8$, 1 H). $^{13}\text{C-NMR}$: 20.2 (*t*); 23.4 (*t*); 30.4 (*t*); 32.4 (*t*); 34.9 (*t*); 43.5 (*t*); 124.4 (*d*); 143.5 (*s*); 202.7 (*s*). MS: 138 (1.6, M^+), 120 (33), 94 (100), 79 (100), 67 (55).

4.12. 4-(Cyclohex-1-en-1-yl)butanal (=Cyclohex-1-ene-1-butanal; **36**). Yield 17%. Colorless oil. $^1\text{H-NMR}$: 1.49–1.66 (*m*, 4 H); 1.70–1.80 (*m*, 2 H); 1.86–1.94 (*m*, 2 H); 1.94–2.02 (*m*, 4 H); 2.42 (*dt*, $J = 7.3$, 1.8, 2 H); 5.39–5.43 (*m*, 1 H); 9.78 (*t*, $J = 1.8$, 1 H). $^{13}\text{C-NMR}$: 20.1 (*t*); 22.5 (*t*); 22.9 (*t*); 25.2 (*t*); 28.1 (*t*); 37.3 (*t*); 43.4 (*t*); 122.1 (*d*); 136.5 (*s*); 202.8 (*d*). MS: 152 (2.9, M^+), 134 (64), 108 (63), 93 (75), 79 (100), 67 (48).

5. 8-(tert-Butyl)-2-oxo-1-oxaspiro[4.5]decan-3-carboxaldehyde (aldehyde-**2**; (5 α ,8 β)/(5 α ,8 α) 2.3:1) and 8-(tert-butyl)-3-(hydroxymethylene)-1-oxaspiro[4.5]decan-2-one (enol-**2**; (E)/(Z) ca. 2:1; (5 α ,8 β)/(5 α ,8 α) 1:1) (aldehyde/enol ca. 2:1). A mixture of 8-(tert-butyl)-1-oxaspiro[4.5]decan-2-one (**3**) [4] (*trans/cis* 2.3:1; 9.8 g, 47 mmol), HCOOEt (7 g, 94 mmol), and MeOK (5 g, 71 mmol) in $t\text{BuOMe}$ (300 ml) was mechanically stirred at 40° during 2 h under N_2 . The mixture was then cooled to r.t. and poured into cold 10% aq. HCl soln. (200 ml). Extraction (Et_2O), workup, and crystallization from pentane afforded **2** (diastereoisomer mixtures of aldehyde and enol tautomers; 9.8 g, 88%). White crystals. M.p. 123–125°. B.p. 135°/0.1 mbar. $^1\text{H-NMR}$: 0.84–0.90 (3s, 54 H); 0.97–1.23 (*m*, 14 H); 1.32–2.03 (*m*, 40 H); 2.08 (*dd*, $J = 10.1$, 13.4, 1 H, aldehyde); 2.23 (*dd*, $J = 10.2$, 13.4, 1 H, aldehyde); 2.40–2.51 (*m*, 2 H, aldehyde); 2.58 (*br. d*, $J = 1.9$, 2 H, (Z)-enol); 2.60 (*br. d*, $J = 2.5$, 2 H, (E)-enol); 2.66 (*br. d*, $J = 1.9$, 2 H, (Z)-enol); 2.68 (*br. d*, $J = 2.4$, 2 H, (E)-enol); 3.74–3.82 (*m*, 2 H, aldehyde); 7.02 (*br. s*, 1 H, (Z)-enol); 7.67 (*br. s*, 1 H, (E)-enol); 8.53 (*br. s*, 1 H, (E)-enol); 8.68 (*br. s*, 1 H, (E)-enol); 9.87 (*s*, 2 H, aldehyde); 10.23 (*br. s*, 1 H, (Z)-enol). MS (major peak: 70%): 238 (7, M^+), 220 (20), 119 (31), 94 (36), 57 (100). MS (minor peak: 30%): 238 (11, M^+), 220 (32), 182 (77), 119 (81), 94 (100).

Data of (5 α ,8 β)-Aldehyde-**2**: $^{13}\text{C-NMR}$: 29.6 (*t*); 54.2 (*d*); 87.3 (*s*); 171.2 (*s*); 194.7 (*d*).

Data of (5 α ,8 α)-Aldehyde-**2**: $^{13}\text{C-NMR}$: 33.3 (*t*); 53.9 (*d*); 85.7 (*s*); 171.5 (*s*); 194.8 (*d*).

Data of (Z)-Enol-**2**: $^{13}\text{C-NMR}$: 86.3, 88.0 (2s); 100.9 (*s*), 101.0 (2s); 156.3, 156.4 (2d); 174.9, 175.1 (2s).

Data of (E)-Enol-**2**: ^{13}C -NMR: 83.6, 85.4 (2s); 103.5, 103.9 (2s); 152.6 (2d); 173.8, 173.9 (2s).

6. Pyrolysis of **2**. 6.1. Screening Experiments. See Table 2.

6.2. 3-[4-(tert-Butyl)cyclohex-1-en-1-yl]propanal (= 4-(1,1-Dimethylethyl)cyclohex-1-ene-1-propanal; **1**). A soln. of **2** (7.5 g, 31.5 mmol) in THF (45 ml) containing AcOH (150 mg, 2.5 mmol) was added with an automatic syringe pump during 12 h onto the top of a pre-heated (350°) 15 cm quartz column (diameter 1.7 cm) packed with glass beads (diameter 0.5 cm) under a slight flow of N₂ (one bubble per 1.5 s). The product was collected in a dry ice/acetone cold trap at –78°. The cooled column was rinsed with THF (15 ml), and the combined orange soln. was concentrated at 15 mbar to afford a brown oil (5.8 g). Bulb-to-bulb distillation (110–150°/0.6 mbar) then afforded a pale-yellow oil (3.55 g) which was purified by CC (silica gel, cyclohexane/AcOEt 19:1): **1** (3.1 g, 51%). Colorless oil. Identical in all respects to an authentic sample [5].

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