# Synthesis of *cis-Hedione*® and Methyl Jasmonate *via* Cascade *Baylis–Hillman* Reaction and *Claisen* Ortho Ester Rearrangement

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Dedicated to Dr. *Ferdinand Näf* on the occasion of his 65th birthday

The exocyclically unsaturated conjugated keto esters **10**, obtained *via* a *Claisen* ortho ester rearrangement of the allylic hydroxy ketones **9**, were either directly hydrogenated or partially isomerized into the endocyclically unsaturated tetrasubstituted didehydrojasmonoid intermediates **14**, prior to a more selective hydrogenation with Pd/C in cyclohexane to the disubstituted oxocyclopentaneacetates **15** (*Scheme 2*). The key intermediates **9** were obtained either by a four-step sequence, including acetal protection/deprotection from enone **1**, in the specific case of hydroxy ketone **9a** (*Scheme 1*), or more directly and generally by a *Baylis–Hillman* reaction from cyclopent-2-en-1-one (**16**) and the appropriate aldehydes **17** (*Scheme 2*). The judicious choice of these aldehydes opens versatile modifications for the stereoselective introduction of the partially *cis*- or epimerized *trans*-C(2) jasmonoid side chain, while the *Baylis–Hillman* reaction, catalyzed by chiral [1,1′-binaphthalene]-2,2′-diols (BINOLs) **19** (*Scheme 3*), may be efficiently conducted in a one-pot cascade fashion including the ortho ester *Claisen* rearrangement.

**Introduction.** – The thermodynamically more stable methyl (−)-(1*R*,2*R*,*Z*)-jasmonate[3]) was isolated and characterized in 1962 from *Jasmanirus grandiflorum* L. by *Demole et al*. [2] and later from *Rosmarinus officinalis* L. by *Crabalona* [3]. The precious, elegant, and radiant jasmine scent associated to this molecule and its analogues[4]), largely appreciated and used by the fragrance industry, as well as the biological activity of its corresponding acid[5]), motivated numerous racemic, diastereo- and enantioselective syntheses, summarized in several reviews [6]. More recently, the minor methyl (+)-(1*R*,2*S*,*Z*)-epijasmonate[6]), also known as a pheromone [8][7]), was shown to be essentially responsible for the floral odor, although all stereoisomers may impart synergic effects or improve a perfume composition as fixatives or enhancers. For more than

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[1]) Deceased on 28th August, 1998.
[2]) Retired since 31st July, 1994, work performed in 1992–1993.
[3]) For a recent enantioselective synthesis, see [1].
[4]) For analogues and a structure-odor relationship study, see [4].
[5]) For plant growth inhibitory activities of the acid or Me ester, see [5a–c], and for their anti-cancer and bloodparasites cytotoxic properties, see [5d–e].
[6]) For the corresponding biologically active unstable (+)-(*Z*)-*cis*-acid, see [7]. Some of the biological activities reported for the *trans* isomer are artefacts due to epimerization.
[7]) This compound additionally shows several other biological activities such as plant defence [7], plant-growth regulation [9], induction of tubers in potato stolons [10], promotion of coiling in tendrils of climbing plants [11], as well as signal transmission in interplant communication [12].

30 years, *Firmenich SA* has commercialized under the trade name of *Hedione*®[8]) the racemate of a 9:1 equilibrated mixture of the structurally closely related methyl *trans*-dihydrojasmonates[9]). More recent industrial development has allowed the commercial availability of the even olfactively more active '*rac*-high-*cis*-*Hedione*'(>70% *cis*) [16] as well as optically active methyl (+)-(1*R*,2*S*)-dihydroepijasmonate [17]. We now wish to report on our efforts directed towards an alternative process, based on a cascade *Baylis–Hillman* reaction/orthoester *Claisen* rearrangement, to construct this jasmonoid skeleton with versatile stereocontrol as well as modifications of the C(2) side chain.

**Results and Discussion.** – Our procedure to introduce the methyl acetate substituent at C(1) as well as the *cis*-configuration at the C(2)=C(3) bond of the side chain of the targeted *cis*-*Hedione* or methyl epijasmonate backbones was initially based on an orthoester *Claisen* rearrangement[10]) followed by hydrogenation. Unfortunately, direct photo-oxidation (MeOH, AcONa, $O_2$, Rose Bengal, *hv*, then $Me_2S$ [20]) of the exocyclic-enone **1** (*Scheme 1*) afforded the desired hydroxy enone in only 6% isolated yield, along with 5,6-dioxodecanoic acid (5% yield)[11]). Alternatively, *Payne* epoxidation ($H_2O_2$, NaOH, [21]) of enone **1** also failed to produce the corresponding $\alpha,\beta$-epoxy ketone **2** as a potential precursor in more than 3% yield[12]). Under alternative 3-chloroperbenzoic acid (*m*CPBA) oxidation conditions, enone **1** afforded the new unsaturated lactone **3** in 11% yield[13]). We then decided to reduce enone **1** (DIBAL-H (diisobutylaluminium hydride), $CH_2Cl_2$, 10° [23]; 94%) to the corresponding allylic alcohol **4** [24] prior to a stereoselective epoxidation (*m*CPBA, $CH_2Cl_2$ [25]; 96%) in favor of the unreported epoxy alcohol **5**[14]). Oxidation of this alcohol turned out to be difficult due to side reactions, and the best conditions (pyridinium chlorochromate (PCC), $CH_2Cl_2$,

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[8]) Methyl *trans*-3-oxo-2-pentylcyclopentaneacetate also possesses some biological activities [13].

[9]) Very recently, *Kao Corp.* seems to have re-invented [14] a more than 40 years old industrial process [15].

[10]) An analogous orthoester *Claisen* rearrangement of 2-(1-hydroxyethyl)cyclohex-2-en-1-one and $MeC(OEt)_3$ was earlier reported [18]. For a photo-*Claisen* rearrangement starting from **9** (R=H, Me; *Scheme* 2) leading to aldehydes or ketones contrasting with our thermal orthoester *Claisen* procedure, see [19].

[11]) Replacement of the sensitizer Rose Bengal by methylene blue, *meso*-tetraphenylporphyrine, eosine, or 9*H*-fluoren-9-one proved to be even less efficient in terms of chemical yield or regioselectivity.

[12]) Oxidation of **1** failed also with the following reagents: trichloroisocyanuric acid/KOH under non-aqueous conditions [22a] as well as NaOCl/pyridine [22b] or $H_2O_2$/NaOCl [22c]; $H_2O_2/K_2CO_3$ in MeOH [22d]; $H_2O_2$ in AcOH [22e]; $H_2O_2/Bu_4NF$ in DMSO [22f]; $H_2O_2/Et_3N$ in toluene [22g]; $H_2O_2\cdot$urea/NaOH in MeOH [22h]; $H_2O_2\cdot$urea/DBU in THF [22i]; $^t$BuOOH/DBU [22j]; $NaBO_3\cdot 4H_2O$ in dioxane [22k]; dimethyldioxane/acetone/$CH_2Cl_2$ [22l].

[13]) Further oxidation with an excess of *m*CPBA afforded the corresponding epoxy lactone in 22% yield after column chromatography ($SiO_2$, hexane/AcOEt 95:5): IR: 3000, 2950, 2930, 2860, 1745, 1460, 1325, 1105, 1045. $^1$H-NMR (200 MHz; *J* in Hz): $\delta$ 0.93 (*t*, *J*=7, 3 H); 1.4 (*m*, 3 H); 1.55 (*m*, 3 H); 1.87 (*m*, 1 H); 1.97 (*m*, 1 H); 2.12 (*m*, 1 H); 2.2 (*m*, 1 H); 2.6 (*td*, *J*=7, 10, 1 H); 2.74 (*td*, *J*=7, 10, 1 H); 3.3 (*t*, *J*=7, 1 H).

[14]) When this epoxy alcohol was treated for 15 min in refluxing THF with 2.8 mol-equiv of lithium diisopropylamide (LDA), the corresponding bis-allylic diol was obtained in 76% yield: IR: 3600, 3400, 3000, 2950, 2925, 2850, 1445, 1375, 1035. $^1$H-NMR (200 MHz; *J* in Hz): $\delta$ 0.92 (*t*, *J*=7, 3 H); 1.39 (*m*, 4 H); 1.48 (*m*, 1 H); 1.65 (*m*, 1 H); 1.76 (*m*, 2 H); 2.3 (*m*, 2 H); 2.5 (*m*, 2 OH); 4.36 (*t*, *J*=5, 1 H); 4.85 (*m*, 1 H); 5.8 (br. *s*, 1 H).

[26]) led to the isolation of the desired epoxy ketone **2** in only 12% yield[15])[16]). Alternatively, in view of this drawback, we also protected enone **1** as its corresponding acetal **6** (ethylene glycol, cyclohexane, fumaric acid [36a]; 55%) before epoxidation (*m*CPBA, $CH_2Cl_2$; 93%). Treatment of epoxide **7** with an excess of base (2.0 mol-equiv. of LDA, THF, $-20°$; 66%) afforded the allylic alcohol **8**. Deprotection (HCl, $H_2O$/THF, (43% yield); or acetone/$H_2O$, pyridine·TsOH, 20° [36b] (94% yield)) finally gave access to the desired allylic alcohol **9a**. Subsequent orthoester *Claisen* rearrangement ($MeC(OMe)_3$, pivalic acid, 110°), gave the unsaturated keto ester **10a** as a 1:6:3 $\beta,\gamma$-deconjugated/(*Z*)/(*E*) mixture in 88% yield. The (*E*)/(*Z*) ratio is not totally under kinetic control, being also influenced by a deconjugation/conjugation process under the acidic reaction conditions. Alternatively, this sequence was reversed, and the *Claisen* rearrangement was conducted with allylic hydroxy acetal **8** ($MeC(OMe)_3$, propanonic acid, 110°) to give methyl ester **11** in 86% yield as a *ca.* 7:3 (*Z*)/(*E*) mixture of stereoisomers. Further deprotection of **11** (acetone/$H_2O$, pyridine·TsOH, 20° [36b]) gave quantitatively a 7:3 (*Z*)/(*E*) mixture of conjugated enone **10a**.

*Ikan* and *Ravid* already reported in 1974 that either methyl acetate enolate addition or *Reformatzky* reaction to the endocyclic-enone **12**, allowed the isolation of the tertiary allylic hydroxy ester **13a** in 84% yield [37]. After *Jones* oxidation, the tetrasubstituted enone **14a** [38] (87% yield) was hydrogenated under basic conditions (MeOH, NaOH, 5% Pd/C, 20°) to afford methyl *trans*-dihydrojasmonate **15a** in 43% yield. We repeated this sequence and performed the hydrogenation under neutral conditions (cyclohexane, 10% Pd/C, 20°) to obtain *Hedione*® (**15a**) as a 38:62 trans/cis mixture. Similarly, hydrogenation of **10a** ((*Z*)/(*E*) 7:3, MeOH, 5% Pd/C, 20°) gave a 1:1 *trans*/*cis* mixture in 98% yield. An almost identical result was obtained when a 1:3:6 $\beta,\gamma$-deconjugated/(*Z*)/(*E*) mixture **10a** (*vide supra*) was hydrogenated (cyclohexane, 5% Pd/C, *ca.* 0°; 98%). We also repeated the sequence with the ethyl esters **13b** (75%) and **14b** [39] (93%). It is noteworthy that treatment of any mixture **10a** with either 0.04 mol-equiv. of $^t$BuOK/hexane at 60° or KF/$Al_2O_3$ at 120° [40] afforded pure (*E*)-**10a** in 78–90% yield. Pure (*E*)-**10a** delivered quantitatively a 57:43 *trans*/*cis* mixture **15a** after hydrogenation at 1 atm. in the presence of 5% Pd/C in cyclohexane at 20°. The exocyclic enone **10a** as the mentioned 1:3:6 mixture could also be partially isomerized in 74% yield to a 9:53:28:10 mixture of $\beta,\gamma$-deconjugated-**10a**/**14a**/(*Z*)-**10a**/(*E*)-**10a** when heated at 120° for 6 h with 0.028 mol-equiv. of $[RuH(\eta^5\text{-}C_8H_{11})_2]BF_4$ [41][17]). Hydrogenation of such a mixture gave quantitatively *Hedione*®

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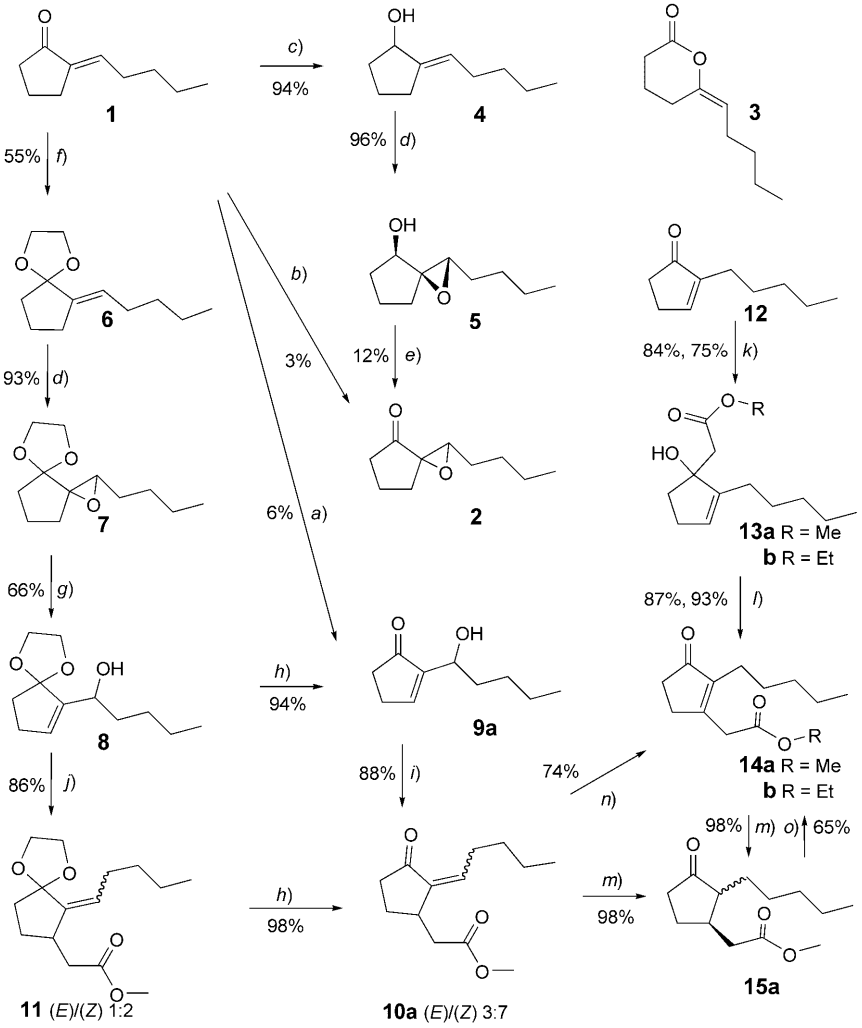
[15]) In contrast, the following oxidation conditions were inefficient: *Jones* reagent, $Et_2O$; $MnO_2$, hexane; poly(4-vinylpyridinium dichromate), cyclohexane [27]; pyridinium dichromate (PDC), DMF [28]; PDC, $CH_2Cl_2$; *Oxone*®, acetone [29]; 2,2,6,6-tetramethylpiperidin-1-yloxy (TEMPO), iodobenzene diacetate or *m*CPBA [30] and *Dess–Martin* periodinane, $CH_2Cl_2$ [31]. The *Oxone*®/$CF_3C(O)Me$ conditions [32] afforded cleanly and quantitatively the isomerized (2*RS*)-2-[(1*SR*)-1-hydroxypentyl]cyclopentanone [33] *via* 1,2-H-shift with concomitant epoxide-ring opening.

[16]) Keto epoxide **2** was also obtained in 5% yield by addition of pentanal (NaOH, EtOH, [34]) to 2-chlorocyclopentan-1-one [35], while deprotection of **7** failed.

[17]) The isomerization to **14a** was inefficient under the following conditions: 10% (*w*/*w*) of conc. HCl soln., MeOH, 65°; 10% of $RhCl_3 \cdot nH_2O$, MeOH, 65°; 10% (*w*/*w*) of MeONa, MeOH, 65°; $I_2$, 65°. In contrast, 5% (*w*/*w*) of 10% Pd/C and decahydronaphthalene at 180° or 5% (*w*/*w*) of $Ru_3(CO)_{12}$ or $[RuCl_2(p\text{Cym})]_2$ neat at 180° gave maximally 23–25% of **14a** after 6 h.

*Scheme 1*




*a*) $O_2$, *hv*, Rose Bengal, then $Me_2S$. *b*) $H_2O_2$, NaOH. *c*) DIBAL-H, 10°, $CH_2Cl_2$. *d*) *m*CPBA, 0°, $CH_2Cl_2$. *e*) PCC, $CH_2Cl_2$. *f*) Ethylene glycol, cyclohexane, fumaric acid. *g*) LDA 2 equiv., THF, −20°. *h*) pyridine·TsOH, acetone/$H_2O$. *i*) $MeC(OMe)_3$, pivalic acid, 110°. *j*) $MeC(OMe)_3$, propanoic acid, 110°. *k*) $MeCO_2R$, $(Me_3Si)_2NLi$, THF; or $BrCH_2COOR$, Zn, benzene. *l*) *Jones* oxidation. *m*) 5–10% Pd/C, $H_2$, cyclohexane. *n*) $[RuH(\eta^5\text{-}C_8H_{11})_2]BF_4$, 120°. *o*) $HIO_3$, DMSO, 65°.

(**15a**) as a 47:53 *trans/cis* mixture (cyclohexane, 5% Pd/C, 20°), prior to epimerization (MeOH, MeONa, 98%) to a 92:8 *trans*/*cis* mixture.

At this point, we realized that allylic hydroxy ketones of type **9a** would be accessible *via* a *Baylis–Hillman* reaction[18]), starting from commercially available cyclopent-2-en-1-one (**16**)[19]). Although numerous conditions have been reported for the catalyzed *Morita–Baylis–Hillman* reaction[20]), we were attracted by the procedure of *Yamada* and *Ikegami* [45] (1.0 mol-equiv. of **16**, 1.5 mol-equiv. of **17**; 0.1 mol-equiv. of *rac*-[1,1′-binaphthalene]-2,2′-diol (BINOL), 0.2 mol-equiv. of $Bu_3P$, THF, 20°) and, using pentanal (**17a**), could thus isolate hydroxy enone **9a** in 92% yield after 3 h at 20° and filtration through a short $SiO_2$ column (*Scheme 2*).

The BINOL may be replaced by either the less expensive [biarene]-2,2′-diol or catechol (= benzen-1,2-diol), albeit with a lower 50–60% chemical yield, due to the presence of by-products necessitating a careful chromatographic purification. By analogy, starting from heptanal (**17b**), hydroxy enone **9b** was obtained in 33% yield after bulb-to-bulb distillation. When this freshly distilled pure alcohol was submitted to orthoester *Claisen* conditions, we isolated in 98% yield an unsaturated ester **10b** as 16 : 52 : 32 $\beta,\gamma$-deconjugated/(*Z*)/(*E*) mixture. We noticed that both **9a**,**b** are unstable when neat and readily polymerize even at 20°. For this reason, we performed both the *Baylis–Hillman* reaction and the orthoester *Claisen* rearrangement in a one-pot cascade procedure. This allowed us to isolate **10a** in 89% overall yield as a 10 : 30 : 60 $\beta,\gamma$-deconjugated/(*Z*)/(*E*) mixture, while **10b** was similarly obtained in 91% overall yield as a 15 : 29 : 56 mixture of the analogous isomers. This latter mixture was either directly hydrogenated (10% Pd/C, cyclohexane, 20°; 92%) to afford **15b** (53 : 47 *trans/cis* mixture) or treated with 5% $Pd/Al_2O_3$ at 135° with 92 : 8 $N_2/H_2$[21]) to produce a 55 : 45 mixture of **14c**/**15b**. Subsequent hydrogenation (MeOH, 5% Pd/C, 20°) afforded quantitatively **15b** (68 : 32 *trans/cis* mixture).

To access the jasmonate family, we started with a '*Diels–Alder*-protected' 6 : 1 *endo/exo* mixture of the *cis*-aldehyde **17c**, easily obtained in 45% yield by thermal [4 + 2]-cycloaddition of the corresponding commercially available (2*Z*)-pent-2-enenitrile to cyclopentadiene[22]), followed by DIBAL-H reduction at 20° in 80% yield. The crude *cis*-aldehyde **17c** was used since purification by either column chromatography ($SiO_2$) or distillation resulted in extensive epimerization. Subsequent *Baylis–Hillman* reaction afforded **9c** (34% yield) as a complex 2 : 13 : 2 : 10 : 1 : 10 : 14 : 1 stereoisomer

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[18]) Amazingly, both hydroxy enones **9a** and **9b** were, at this time, unreported in the literature and thus could be patented as intermediates [42]. For known analogues of **9** with R = H or alkyl substituents (*Scheme 2*), see [43] (R = H); [44] (R = Me); [45] (R = Et, $Me(CH_2)_6$); [46] (R = Pr); [47] (R = $^i$Pr, $Me(CH_2)_4$); [48] (R = $Me_2CHCH_2$); [48b] (R = $Me(CH_2)_5$); [49] (R = $Me(CH_2)_7$); [50] (R = $Ph(CH_2)_2$).

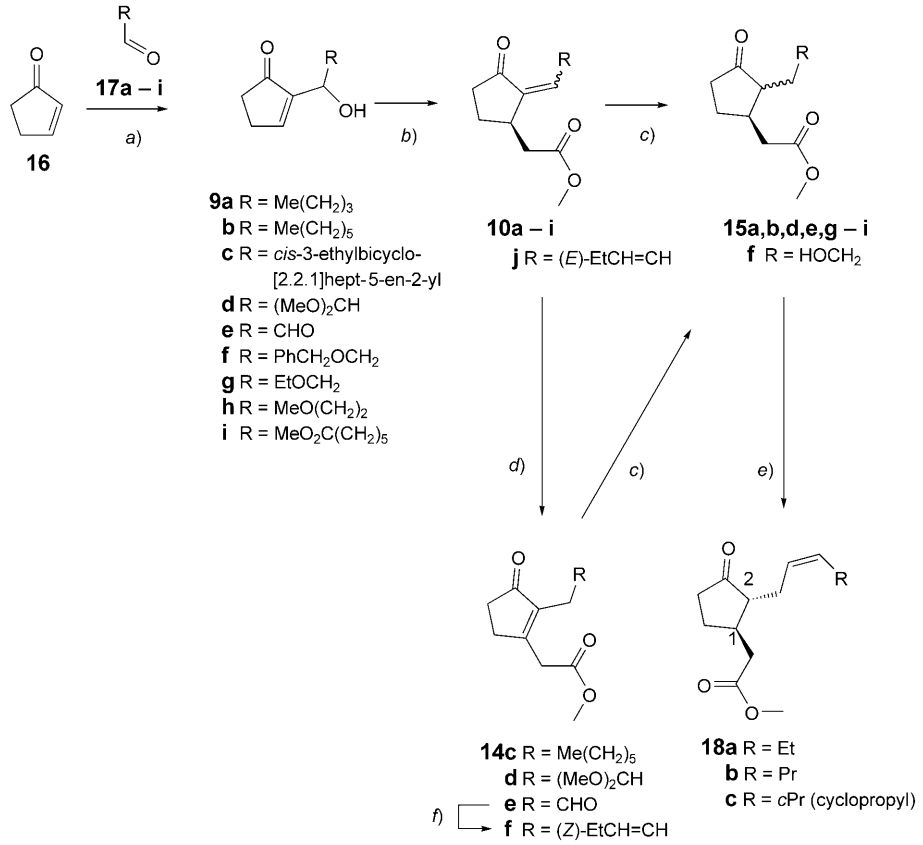
[19]) For an easy access to **16** from cyclopentanone or cyclopentadiene, see [51a–d] and [51e], respectively. Alternatively, the conditions of *Nicolaou et al.* [51a] were also applied to *trans*-**15a**, thus affording **14a** in 65% yield (*Scheme 1*).

[20]) Nonexhaustive examples of *Morita–Baylis–Hillman* conditions involve $Et_2AlI$ [44], MeONa/MeOH [48b], 1*H*-imidazole in $H_2O$ [52]; 1*H*-1,2,3-triazole in $H_2O$ [53]; 1,4-diazabicyclo[2.2.2]octane (DABCO) in $H_2O$ [54], DABCO in ionic liquids [55], *N*,*N*,*N*′,*N*′-tetramethylpropane-1,3-diamine [56]; proazaphosphatrane sulfide [57] and air-stable trialkylphosphonium salts [58]. For reviews, see [59]; for a new interpretation of the mechanism following studies in protic and aprotic solvents, see [60].

[21]) According to a procedure initially developed at *Firmenich SA* by Dr. *R. Weinstein* with an analogous skeleton and extended by Dr. *F. Näf* and *R. Decorzant* to **10a**, obtained *via* an independent approach.

[22]) This cycloaddition was initially performed at *Firmenich SA* by *C. Vial*. Dr. *R. L. Snowden* and *S. Linder* are acknowledged for the details of the DIBAL-H reduction.

*Scheme 2*




*a*) Aldehyde **17** (1.5 mol-equiv.), $Bu_3P$ (0.2 mol-equiv.), BINOL (0.1 mol-equiv.), THF, 20°. *b*) $MeC(OMe)_3$, pivalic acid, 110°. *c*) 10% Pd/C, cyclohexane. *d*) 5% $Pd/Al_2O_3$, $N_2/H_2$ 92:8, 135°. *e*) $[Ph_3PCH_2R]$ Br, BuLi, toluene, −20° to 20°. *f*) $[Ph_3PPr]Br$, $NaN(SiMe_3)_2$, THF, 20°.

mixture indicating that epimerization already occurs under the reaction conditions. Further orthoester *Claisen* rearrangement led in 55% isolated yield to a 15:15:70 stereoisomer mixture **10c**. During distillation, we observed a *retro-Diels–Alder* reaction generating the conjugated (*E,E*)-dienone derivative **10j**, thus explaining the moderate yield.

The fact that the configurational integrity of the *cis*-aldehyde **17c** is already eroded during the first step, and that a supplementary 1,4-hydride reduction is necessary to distinguish both unsaturations present in **10c**, prompted us to abandon this approach and to generate the desired (*Z*)-configuration of the jasmonate side chain *via* the conventional *Wittig* procedure. Consequently, we started from glyoxal dimethyl acetal (**17d**) to prepare hydroxy enone **9d** in 96% yield. The subsequent rearrangement permitted the isolation of a 2:3 (*Z*)/(*E*) mixture of the dimethyl acetal drivative **10d** in 96%

yield, which was readily isomerized (HCl, MeOH, 60°; 87%)[23]) to the pure tetrasubstituted dimethyl acetal derivative **14d**. Hydrogenation (MeOH, 5% Pd/C, 20°; 60–80%) of either **14d** or the (*E*)/(*Z*) mixture **10d** afforded in both cases an equilibrated 9:1 mixture **15d** of the *trans/cis* dimethyl acetal derivatives. Deprotection (AcOH, $H_2O$, 40°) of (*E*)/(*Z*)-**10d** furnished in 36% yield a 1:1:2 mixture of (*Z*)-**10e**/(*E*)-**10e**/**14e**, while under the same conditions, the saturated acetal derivative **15d** gave in 83% yield a 9:1 mixture of the known *trans*/*cis* aldehyde derivative **15e** [61]. Pure aldehyde derivative **14e** was preferably selectively isolated in 55% yield by an identical deprotection of pure acetal derivative **14d**. A *Wittig* reaction ([$Ph_3$PPr]Br, NaN($SiMe_3$)$_2$, THF/DMF, 20° [62]; 44%) furnished the known didehydrojasmonate (*Z*)-**14f** [63][24]), to 93% stereoisomerically pure. The saturated aldehyde derivative **15e** afforded, with either ($Ph_3$PPr)Br and BuLi in THF or toluene at −30° or −20° to 20° [61][65] (yield 57–62%), or with ($Ph_3$PPr)Br and $NaNH_2$/$^t$BuOK in THF at −70° to 20° [66] (yield 31%) the methyl jasmonate **18a** as a 9:1 *trans/cis* mixture of (*Z*)/(*E*) isomers 95:5. Similar *Wittig* conditions (($Ph_3$PBu)Br, BuLi, toluene, −30° to 20° (yield 34%) or [$Ph_3$P($CH_2$-cyclopropyl)] Br, BuLi, toluene, −30° to 20°, (yield 35%)) furnished the analogous methyl esters **18b** (*trans/cis* 9:1, *Z/E* 95:5) and **18c** (*trans/cis* 95:5, *Z/E* 7:3)[25]).

Rather than an acetal derivative, we also used the commercially available aldehyde **17f** with a benzyl ether protection, to obtain hydroxy enone **9f** in 65% yield. Subsequent orthoester *Claisen* rearrangement furnished a 14:29:57 mixture **10f** of $\beta,\gamma$-deconjugated/(*Z*)/(*E*) isomers in 68% yield. Hydrogenation with concomitant deprotection quantitatively afforded the (hydroxyethyl)oxo ester **15f** as a 9:1 *trans*/*cis* mixture. Its oxidation (PCC, $CH_2Cl_2$, 60%) gave the corresponding aldehyde derivative **15e**. As oxa analogue of methyl jasmonate, we also prepared, from the known aldehydes **17g**,**h** [63][69] the *Baylis–Hillman* products **9g**,**h** in 27 and 53% yield, respectively. Subsequent rearrangements gave the unsaturated keto esters **10g**,**h** in 53 and 93% yield, respectively, as 22:39:39 and 5:75:20 $\beta,\gamma$-deconjugated/(*Z*)/(*E*) mixtures. Hydrogenation of **10g** in cyclohexane at 20° over 10% Pd/C furnished in 78% yield ester **15g** as 4:6 *trans*/*cis* mixture, while hydrogenation of **10h** in MeOH gave in 79% yield **15h** as a 9:1 equilibrated *trans*/*cis* mixture, thus underlining again the influence of the solvent for minimizing epimerization.

Finally, methyl 6-formylhexanoate **17i** [70] was chosen to allow access to hydroxy enone **9i** (53%), which was rearranged to unsaturated keto diester **10i** as a 5:85:10 $\beta,\gamma$-deconjugated/(*Z*)/(*E*) mixture. Hydrogenation in cyclohexane quantitatively afforded a 34:66 mixture **15i** of *trans*/*cis* dimethyl diesters. It is noteworthy that substrate **9i**, *via* an appropriate *Carroll* rearrangement, is a potential precursor of a known intermediate of a prostaglandin $PGF_{10}$ synthesis [71].

The next step was to study the asymmetric version of this process, as this was the key point of interest which had originally attracted our attention to the *Baylis–Hillman*

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[23]) These standard conditions were initially used at *Firmenich SA* by Dr. *G. Lem* on an analogous skeleton.

[24]) Compound (*Z*)-**14f** is a direct precursor in the synthesis of the corresponding natural acid, isolated from *Vicia faba* L. [64].

[25]) For a potential highly (*Z*)-stereoselective addition of a modified allyltriarylphosphonium bromide, leading to methyl 3,7-didehydrojasmonate [67], see [68].

reaction[26]) [45]. When the reaction between cyclopent-2-en-1-one (**16**) and pentanal (**17a**) was catalyzed by 0.1/0.2 mol-equiv. of (+)-(*R*)-[1,1′-binaphthalene]-2,2′-diol (**19a**)/$Bu_3P$, we obtained hydroxy enone **9a** (*Scheme 3*), which showed, by GC analysis on a chiral phase, a 52:48 enantiomer ratio. With respect to the instability of **9a** (*vide supra*), we decided to perform directly a cascade reaction and to determine the global yield and optical purity by GC analysis on a chiral phase of the hydrogenated and equilibrated *trans-Hedione®* (**15a**) as earlier reported [17b]. In the case of catalysts (+)-(*R*)-**19a**,**b** almost no final induction was observed (see *Table*). Using commercially available or known 3,3′-disubstituted [1,1′-binaphthalene]-2,2′-diols (+)-(*R*)-**19c**–**g** [73][27]), as suggested by *McDougal* and *Schaus* [78], we observed insignificant final asymmetric inductions as indicated in the *Table*. The situation was unchanged when either $Ca(O^iPr)_2$ or the bimetallic low-temperature conditions of *Sasai et al.* [72x] were used with (+)-(*R*)-**19a**[28]). The measured final e.e.s result from both the asymmetric *Baylis–Hillman* reaction and the *Claisen* chirality transfer. A rapid racemization of the transient allylic alcohol under acidic conditions may be excluded[29]). Although erosion may result from Pd/C [79], total racemization by isomerization/hydrogenation *via* **14a** may also be excluded in view of the stringent conditions required[17]). This was demonstrated by isolating after column chromatography $SiO_2$ + 5% $AgNO_3$, cyclohexane/AcOEt 93:7 the pure stereoisomers (−)-(*S*,*Z*)-**10a** ($[\alpha]_D^{20} = -1.4$, $c = 1.0$ $CHCl_3$; 22% e.e.) and (+)-(*R*,*E*)-**10a** ($[\alpha]_D^{20} = +21.3$, $c = 1.0$ $CHCl_3$; 22% e.e.) from a 8:2 (*Z*)/(*E*) *Claisen*-reaction mixture, issued from (−)-(*S*)-**9a** ($[\alpha]_D^{20} = -8.4$, $c = 2.3$, $CHCl_3$; 22% e.e.). Their independent hydrogenation with *Raney*-Ni in either EtOH or AcOEt [79] afforded (+)-(1*S*,2*S*)-**15a** and (−)-(1*R*,2*R*)-**15a** in 22 and 15% e.e., respectively, thus confirming both the nonexclusive thermodynamic origin of isomer (*E*)-**10a** (depending on the reaction time, temperature, and acidic conditions) and the moderate diastereoselectivity of the *Claisen*-reaction kinetic mixture. When hydrogenation was performed with 10% Pd/C in cyclohexane, the optical purity was 21 and 13% e.e., respectively, suggesting with both catalysts a more rapid isomerization of the stereoisomer (*E*)-**10a** towards **14a** as compared to its hydrogenation.

In view of the poor inductions in the *Baylis–Hillman* reaction, the thermally less exigent *Claisen* rearrangement under either *Ireland* [80] or the less basic *Fehr* conditions [17c] was not attempted. In the *Baylis–Hillman* reaction of **16** and **17a** catalyzed with (+)-(*R*)-**19d**, we increased the enantioselectivity to 31% e.e. (albeit with 15%

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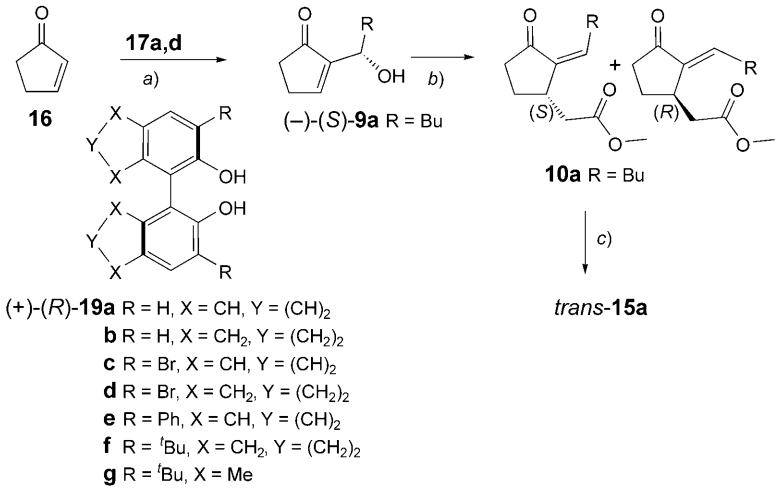
[26]) For enantioselective *Baylis–Hillman* reactions, see [72].

[27]) We initially prepared {5,6:5′,6′-bis(ethane-1,2-diyldioxy)[1,1′-biphenyl]-2,2′-diyl}bis[diphenylphosphine] for the enantioselective isomerization of geranyldiethylamine to citronellal (see [74], p. 105). This new diphosphine was later independently developed [75] and exploited [76] by *Genêt et al*. Rather than 5,6,5′,6′-hetero-analogues of (+)-(*R*)-**19a**,**b** [77], dimerization of either sesamol (=1,3-benzodioxol-5-ol) or 2,3-dihydro-1,4-benzodioxin-6-ol, afforded the corresponding 4,5,4′,5′-hetero-substituted 2,2′-diols [77c]. The efficiency of diols (+)-(*R*)-**19c**,**d** as analogues of (+)-(*R*)-**19a**,**b** [77] as well as others possessing induced atropisomerism derived from [1,1′-biphenyl]-2,2′,6,6′-tetrol shall be reported in due course. (+)-(*R*)-**19f** has an $[\alpha]_D^{20} = +49$ ($c = 0.7$, $CHCl_3$).

[28]) Contrasting with the structure of the catalyst reported in their publication, Japanese authors used, in their *Exper. Part*, a 2:3 ratio of $Ca(O^iPr)_2$ and (+)-(*R*)-BINOL (**19a**) [45]. Even traces of exceeding free BINOL may catalyze the reaction (see *Table*, *Footnote d*)).

[29]) Indeed, when (−)-(*S*)-**9a** was heated at 80–110° with 0.1 mol-equiv. of pivalic acid in EtOH/toluene, no racemization was observed after 8 h.

*Scheme 3*




*a*) **17** (1.5 mol-equiv.), (+)-(*R*)-**19** (0.1 mol-equiv.), $Bu_3P$ (0.2 mol-equiv.), THF, 20°. *b*) $MeC(OMe)_3$, pivalic acid, 110°. *c*) 10% Pd/C, cyclohexane, then MeONa, MeOH.

Table. *Global Inductions and Yields of* (+)-trans-*Hedione* **15a** *in the Presence of* (+)-(R)-*BINOL Analogues* **19a**–**g** *for the Asymmetric* Baylis–Hillman *Reaction of* **16** *and* **17a** *Followed by Acidic Orthoester* Claisen *Rearrangement, Hydrogenation, and Epimerization*

| | Reaction time [h] for *B.-H.* reaction at 20° | (–)-(*S*)-**9a** | (+)-(1*S*,2*S*)-**15a** | |
|---|---|---|---|---|
| | | e.e. [%] | e.e. [%] | global yield [%] |
| (+)-(*R*)-**19a** | 3, 15[a]), 144[b]) | 4, 5[a]), 18[b]) | 2, 2[a]), 8[b]) | 82, 20[a]), 8[b]) |
| (+)-(*R*)-**19b** | 3 | 6 | 1 | 54 |
| (+)-(*R*)-**19c** | 48 | 5 | 2 | 81 |
| (+)-(*R*)-**19d** | 15, 96[c]) | 22, 10[c]) | 12, 4[c]) | 68, 22[c]) |
| (+)-(*R*)-**19e**[d]) | 15 | | 2.5 | 93 |
| (+)-(*R*)-**19f** | 15 | 2 | 1 | 68 |
| (+)-(*R*)-**19g** | 15 | 1.5 | 1 | 71 |

[a]) With 0.1 mol-equiv. of $Ca(OiPr)_2$/**19a** 2:3. [b]) With 0.16 mol-equiv. of L-*Selectride*/**19a** 1:1 at –22°. [c]) With 0.16 mol-equiv. of L-*Selectride*/**19d** 1:1. [d]) With 0.01 mol-equiv of **19e**.

yield) when $Bu_3P$ was replaced by (–)-1,1′-(ethane-1,2-diyl)bis[(2*S*,5*S*)-2,5-dimethylphospholane], while the antipode (+)-(*R*)-**9a** was obtained after 18 h at 20° with 8% e.e., when the mismatching (+)-1,1′-(ethane-1,2-diyl)bis[(2*R*,5*R*)-2,5-dimethylphospholane] was used[30]).

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[30]) The following sterically more crowded or less basic bis[phosphines] were inactive: (+)-1,1′-(ethane-1,2-diyl)bis[(2*R*,5*R*)-2,5-diethylphospholane]; (–)-1,1′-(1,2-phenylene)bis[(2*R*,5*R*)-2,5-dimethylphospholane]; (+)-(*S*)-{1-[(1*R*)-2-(dicyclohexylphosphino)ferrocen-1-yl]ethyl}dicyclohexylphosphine, and (–)-(*R*)-{1-[(1*S*)-2-(diphenylphosphino)ferrocen-1-yl]ethyl}dicyclohexylphosphine.

**Conclusions.** – Our one-pot, two-step cascade sequence is formally a short cut corresponding to a *Michael* addition of dimethyl malonate to cyclopent-2-en-1-one with concomitant trapping of the resulting enolate with an appropriate aldehyde followed by mesylation/elimination of the aldol product and final de(methoxycarbonyl)ation. The resulting exocyclic unsaturation allows by hydrogenation over Pd/C in cyclohexane to partially control the *trans*/*cis* configuration at C(2) ($\geq$50%). A better stereoselectivity is obtained by isomerization of the exocyclic C=C bond into the tetrasubstituted endocyclic position prior to hydrogenation ($\geq$62% for pure **14a**). By versatile modification of the aldehyde, this procedure allows to modify the substitution at C(2). The asymmetric version gave almost no global inductions, due to poor enantioselectivity during the *Baylis–Hillman* reaction associated with the only partial diastereoselectivity during the ortho ester *Claisen* acidic rearrangement as well as partial isomerization of the exocyclic to the endocyclic position of the resulting C=C bond during hydrogenation. None of the presented jasmonoid analogues **10**, **14**, **15**, and **18**, exhibits better olfactory properties than the natural products.

We thank Mrs *C. Cantatore,* Mr. *H. Pamingle*, and *K. Saidi* for their valuable experimental skill. Dr. *J. McKew* is acknowledged for the preparation of (+)-(*R*)-**19e**.

## Experimental Part

*General*. See [81]. Chiral GC separations. *Chirasil-Dex-CB* column (25 m, 0.25 mm); He flow 2.5 ml/min, at 150° for 20 min; $t_R$ [min] (−)-(*S*)-**9a**, 6.93; (+)-(*R*)-**9a**, 7.44; (+)-(*R*,*Z*)-**10a**, 11.31; (−)-(*S*,*Z*)-**10a**, 11.54; (+)-(*R*,*E*)-**10a**, 12.93; (−)-(*S*,*E*)-**10a**, 14.11; (−)-(1*R*,2*R*)-**15a**, 9.92; (+)-(1*S*,2*S*)-**15a**, 10.58; (+)-(1*R*,2*S*)-**15a**, 11.46; (−)-(1*S*,2*R*)-**15a**, 12.00.

*General Procedure A:* Baylis–Hillman *Reaction*. A soln. of cyclopent-2-en-1-one (**16**; 1.0 mol-equiv.), the appropriate aldehyde **17** (1.5 mol-equiv.), [1,1′-binaphthalene]-2,2′-diol (0.1 mol-equiv.), and $Bu_3P$ (0.2 mol-equiv.) in THF (800 ml/mol) was stirred at 20° under Ar for 3–15 h. The crude mixture was evaporated and the residue passed through a short column of $SiO_2$ (cyclohexane/$Et_2O$ 7:3) to separate the desired product from the apolar aldehyde, $Bu_3P$, and the polar [1,1′-binaphthalene]-2,2′-diol.

*General Procedure B:* Claisen *Reaction*. A mixture of hydroxy ketone **9** (1.0 mol-equiv.), trimethyl orthoacetate (1770 ml/mol), and pivalic acid (0.17 mol-equiv.) was heated at 110° for 3 h with distillation of MeOH. The mixture was evaporated and the residue bulb-to-bulb distilled to afford **10** as a (*E*)/(*Z*) mixture contaminated by traces of $\beta,\gamma$-deconjugated (*E*)-isomers.

*(2*RS*,3*RS*)-2-Butyl-1-oxaspiro[2.4]heptan-4-one* (**2**). A soln. of hydroxy epoxide **5** (0.85 g, 5 mmol) in $CH_2Cl_2$ (5 ml) was added to a suspension of PCC (1.6 g, 7.5 mmol) and anh. AcONa (123 mg, 1.5 mmol) in $CH_2Cl_2$ (5 ml). After 2 h at 20°, $Et_2O$ was added, and the mixture was filtered. The filtrate was washed with $H_2O$, dried ($Na_2SO_4$), and evaporated and the residue purified by CC (15 g $SiO_2$, hexane/AcOEt 95:5 → 9:1): **2** (12%).

Alternatively, 2N NaOH (2.5 ml, 5 mmol) was added at 10° over 20 min to a soln. of enone **1** (1.64 g, 10 mmol) and 30% $H_2O_2$ soln. (3 ml, 30 mmol) in MeOH (15 ml). After 4 h at 20°, the mixture was poured into $H_2O$, extracted with $Et_2O$, washed with $H_2O$, dried ($Na_2SO_4$), and evaporated and the residue purified by CC (40 g $SiO_2$, hexane/AcOEt 95:5 → 8:2): **2** (3%). IR: 3000, 2950, 2930, 2860, 1740, 1460, 1400, 1100, 995, 910. $^1$H-NMR (200 MHz): 0.92 (*t*, *J*=7, 3 H); 1.4 (*m*, 4 H); 1.54 (*m*, 3 H); 1.97 (*m*, 1 H); 2.11 (*m*, 2 H); 2.2 (*m*, 1 H); 2.42 (*dd*, *J*=7, 9, 1 H); 3.18 (*t*, *J*=5, 1 H).

*(5*E*)-Dec-5-eno-5-lactone* (**3**). A soln. of 70% *m*CPBA (7.4 g, 30 mmol) in $CH_2Cl_2$ (25 ml) was added at 20° to a soln. of enone **1** (10 g, 26 mmol) and $NaHCO_3$ (2.7 g, 32 mmol) in $CH_2Cl_2$ (75 ml) and $H_2O$ (10 ml). After 5 h and 20% of conversion, the mixture was poured into brine, washed with $H_2O$ to neutral, dried ($Na_2SO_4$), and evaporated, and the residue purified by CC ($SiO_2$, cyclohexane/$Et_2O$ 85:15): pure **3** (11%). IR: 3000, 2930, 2859, 1760, 1694, 1345, 1238, 1198, 1140, 1049, 968. $^1$H-NMR: 0.9 (*t*, *J*=7, 3 H); 1.32 (*m*, 4 H); 1.86 (*quint.*,

$J=7$, 2 H); 1.98 ($q$, $J=7$, 2 H); 2.5 ($t$, $J=5$, 2 H); 2.6 ($t$, $J=5$, 2 H); 5.18 ($t$, $J=7$, 1 H). $^{13}$C-NMR: 13.9 ($q$); 18.4 ($t$); 22.2 ($t$); 22.4 ($t$); 25.3 ($t$); 30.7 ($t$); 31.8 ($t$); 110.0 ($d$); 148.2 ($s$); 169.0 ($s$). MS: 168 (23, $M^{+\cdot}$), 125 (42), 112 (22), 97 (97), 83 (45), 55 (100), 42 (18).

*(2*E*)-2-Pentylidenecyclopentan-1-ol* (**4**). At 0°, 1M DIBAL-H in $CH_2Cl_2$ (100 ml, 100 mmol) was added dropwise to a soln. of enone **1** (14.4 g, 95 mmol) in $CH_2Cl_2$ (50 ml). After 4 h at 20°, MeOH (25 ml) was added at 0° followed by 2N $H_2SO_4$ and $H_2O$. The org. layer was washed with $H_2O$ and 5% $NaHCO_3$ soln., dried ($Na_2SO_4$), and evaporated, and the residue distilled: **4** (86%). B.p. 68°/0.8 Torr. IR: 3580, 3000, 2950, 2910, 2850, 1450, 1375, 1035, 920. $^1$H-NMR: 0.89 ($t$, $J=7$, 3 H); 1.3 ($m$, 4 H); 1.6 ($m$, 2 H); 1.81 ($m$, 2 H); 1.99 ($q$, $J=7$, 2 H); 2.17 ($m$, 1 H); 2.34 ($m$, 1 H); 2.6 (br. $s$, OH); 4.38 (br. $s$, 1 H); 5.52 ($t$, $J=5$, 1 H). $^{13}$C-NMR: 14.0 ($q$); 22.1 ($t$); 22.5 ($t$); 27.0 ($t$); 29.1 ($t$); 31.6 ($t$); 35.6 ($t$); 75.5 ($d$); 124.3 ($d$); 145.6 ($s$). MS: 154 (10, $M^{+\cdot}$), 111 (32), 97 (100), 93 (10), 83 (14), 79 (19), 55 (25), 41 (19). Unpleasant, dirty, dusty, floral.

*(2*RS*,3*RS*)-2-Butyl-1-oxaspiro[2.4]heptan-4-ol* (**5**). At 0°, 80% *m*CPBA (17.6 g, 82 mmol) was added portionwise to a soln. of **4** (12.6 g, 81.8 mmol) in $CH_2Cl_2$ (200 ml). After 2 h at 0°, the mixture was diluted with hexane, washed with 10% $Na_2CO_3$ soln. and brine, dried ($Na_2CO_3$), and evaporated, and the residue distilled: **5** (96%). B.p. 58°/0.05 Torr. IR: 3459, 2957, 2930, 2872, 1466, 1457, 1400, 1379, 1316, 1295, 1240, 1153, 1099, 1032, 988, 950, 932, 909, 857. $^1$H-NMR: 0.95 ($t$, $J=7$, 3 H); 1.4 ($m$, 4 H); 1.55 ($m$, 3 H); 1.64 ($m$, 2 H); 1.75 ($m$, 1 H); 1.92 ($m$, 2 H); 2.0 ($m$, 1 H); 3.02 ($t$, $J=5$, 1 H); 3.92 ($t$, $J=7$, 1 H). $^{13}$C-NMR: 14.0 ($q$); 19.6 ($t$); 22.5 ($t$); 26.4 ($t$); 28.5 ($t$); 29.5 ($t$); 33.9 ($t$); 60.9 ($d$); 69.3 ($s$); 71.9 ($d$). MS: 170 (0, $M^{+\cdot}$), 84 (100), 71 (20), 55 (36), 41 (20).

*(6*E*)-6-Pentylidene-1,4-dioxaspiro[4.4]nonane* (**6**). A mixture of enone **1** (30.4 g, 0.2 mol), ethylene glycol (80 ml, 1.84 mol), and fumaric acid (2.0 g, 17.2 mmol) in cyclohexane (200 ml) was heated under reflux for 4 days with $H_2O$ separation. The cold mixture was washed with sat. $NaHCO_3$ soln. and brine to neutral, dried ($Na_2SO_4$), and evaporated, and the residue distilled through a *Vigreux* column: pure **6** (55%). B.p. 120°/10 Torr. IR: 2956, 2926, 2873, 1650, 1465, 1437, 1309, 1202, 1145, 1114, 1043, 1002, 944, 924, 852, 825. $^1$H-NMR: 0.9 ($t$, $J=7$, 3 H); 1.35 ($m$, 4 H); 1.75 ($q$, $J=7$, 2 H); 1.81 ($m$, 2 H); 2.02 ($q$, $J=7$, 2 H); 2.34 ($m$, 2 H); 3.95 ($m$, 2 H); 4.05 ($m$, 2 H); 5.61 ($m$, 1 H). $^{13}$C-NMR: 14.0 ($q$); 20.8 ($t$); 22.5 ($t$); 26.3 ($t$); 28.9 ($t$); 31.3 ($t$); 36.5 ($t$); 64.5 (2$t$); 114.2 ($s$); 125.0 ($d$); 140.6 ($s$). MS: 196 (18, $M^{+\cdot}$), 167 (38), 139 (100), 99 (40), 67 (20), 55 (18), 41 (18).

*2-Butyl-1,5,8-trioxadispiro[2.0.4.3]undecane* (**7**). To a soln. of **6** (10.9 g, 56 mmol) in $CH_2Cl_2$ (100 ml) at 0° was added 80% *m*CPBA (12 g, 56 mmol), and the mixture was stirred for 1 h. The cold mixture was diluted with hexane, washed with cold 5% $Na_2CO_3$ soln. and $H_2O$, dried ($Na_2SO_4$), and evaporated, and the residue distilled: **7** (93%). B.p.: 75°/0.8 Torr. IR: 2957, 2931, 2873, 1649, 1467, 1435, 1325, 1191, 1096, 1070, 1036, 948, 868. $^1$H-NMR: 0.91 ($t$, $J=7$, 3 H); 1.49 ($m$, 2 H); 1.51 ($m$, 2 H); 1.7–1.95 ($m$, 8 H); 3.09 ($t$, $J=5$, 1 H); 3.91 ($m$, 2 H); 4.05 ($m$, 2 H). $^{13}$C-NMR: 14.0 ($q$); 18.7 ($t$); 22.5 ($t$); 24.9 ($t$); 28.5 ($t$); 29.1 ($t$); 34.3 ($t$); 60.0 ($d$); 65.4 (2$t$); 68.7 ($s$); 113.1 ($s$). MS: 212 (0, $M^{+\cdot}$), 169 (8), 99 (100), 86 (11), 55 (18), 42 (8).

*1-(1,4-Dioxaspiro[4.4]non-6-en-6-yl)pentan-1-ol* (**8**). At −20°, 2.5M BuLi in hexane (6 ml, 15 mmol) was added to a soln. of diisopropylamine (2.7 ml, 20 mmol) in hexane (20 ml). Then a soln. of **7** (1.06 g, 5 mmol) in THF (5 ml) was added dropwise at −20°, and after 2 h at −20°, the mixture was poured into $NH_4Cl$ soln. and extracted with $Et_2O$, the extract washed with $H_2O$, dried ($Na_2SO_4$), and evaporated, and the residue distilled: **8** (66%). B.p. 90°/0.8 Torr. IR: 3434, 2955, 2930, 2872, 2859, 1648, 1465, 1453, 1377, 1338, 1316, 1209, 1135, 1042, 1016, 948, 918, 857. $^1$H-NMR: 0.92 ($t$, $J=7$, 3 H); 1.1–1.55 ($m$, 6 H); 1.7 ($q$, $J=5$, 2 H); 2.07 ($t$, $J=7$, 1 H); 2.38 ($m$, 1 H); 3.7 ($s$, OH); 3.96 ($m$, 2 H); 4.06 ($m$, 2 H); 4.24 ($t$, $J=7$, 1 H); 6.02 (br. $s$, 1 H). $^{13}$C-NMR: 14.1 ($q$); 22.7 ($t$); 27.8 ($t$); 28.1 ($t$); 35.1 ($t$); 35.9 ($t$); 64.7 ($t$); 64.9 ($t$); 67.6 ($d$); 120.6 ($s$); 133.4 ($d$); 143.5 ($s$). MS: 212 (0, $M^{+\cdot}$), 183 (20), 170 (19), 155 (100), 111 (64), 87 (17), 83 (18).

*2-(1-Hydroxypentyl)cyclopent-2-en-1-one* (**9a**). In a *Pyrex* vessel, a soln. of enone **1** (7.2 g, 47.4 mmol), Rose Bengal (0.1 g, 0.1 mmol), and AcONa (0.1 g, 1.2 mmol) in MeOH (95 ml) and $H_2O$ (5 ml) was irradiated with a *Philips-HPK125W* Hg lamp while $O_2$ was bubbled through the soln. After 3 h, 1.5–2 l of $O_2$ was absorbed, and $Me_2S$ (15 ml) was added. After 1 h at 20°, the mixture was evaporated, the residue diluted with $Et_2O$ (50 ml), the soln. washed with brine (3×20 ml), dried ($Na_2SO_4$), and evaporated and the residue purified by CC ($SiO_2$, cyclohexane/AcOEt 35:65): **9a** (6%) and 5,6-dioxodecanoic acid (5%).

Alternatively, a mixture of **8** (1.5 g, 7 mmol) and 10% HCl soln. (1 ml) in THF (15 ml) was stirred at 20° for 2 h. Then the mixture was washed with sat. $NaHCO_3$ soln. and brine, dried ($Na_2SO_4$), and evaporated, and the residue bulb-to-bulb distilled: **9a** (43%).

Hydroxy ketone **9a** was also obtained in 94% yield according to the procedure used for the deprotection of (*Z*)-**10a** or in 92% yield according to *Procedure A*.

*Data of* **9a**: B.p. 120°/0.3 Torr. IR: 3412, 2925, 2858, 1682, 1630, 1439, 1335, 1251, 1193, 1041, 1000, 923, 885. $^1$H-NMR: 0.88 (*t*, *J* = 7, 3 H); 1.32 (*m*, 4 H); 1.68 (*m*, 2 H); 2.47 (*dd*, *J* = 5, 7, 2 H); 2.6 (br. *s*, 2 H); 3.3 (br. *s*, OH); 4.44 (*t*, *J* = 5, 1 H); 7.49 (*s*, 1 H). $^{13}$C-NMR: 14.0 (*q*); 22.6 (*t*); 26.6 (*t*); 27.6 (*t*); 35.3 (*t*); 35.6 (*t*); 67.7 (*d*); 148.0 (*s*); 158.1 (*d*); 210.1 (*s*). MS : 168 (0, $M^{+\cdot}$), 150 (18), 135 (6), 121 (9), 111 (100), 83 (15), 55 (11).

*2-(1-Hydroxyheptyl)cyclopent-2-en-1-one* (**9b**). According to *Procedure A*: **9b** (33%). IR: 3410, 2940, 1690, 1040. $^1$H-NMR: 0.87 (*t*, *J* = 7, 3 H); 1.2–1.4 (*m*, 8 H); 1.64 (*m*, 2 H); 2.43 (*m*, 2 H); 2.6 (*m*, 2 H); 3.23 (*s*, OH); 4.45 (*t*, *J* = 7, 1 H); 7.5 (*s*, 1 H). $^{13}$C-NMR: 14.1 (*q*); 22.6 (*t*); 25.4 (*t*); 26.6 (*t*); 29.2 (*t*); 31.8 (*t*); 35.3 (*t*); 36.0 (*t*); 67.4 (*d*); 148.4 (*s*); 158.2 (*d*); 209.9 (*s*). MS: 196 (0.5, $M^{+\cdot}$), 178 (10), 135 (7), 121 (8), 111 (100), 83 (13), 55 (11).

*2-[(3-Ethylbicyclo[2.2.1]hept-5-en-2-yl)hydroxymethyl]cyclopent-2-en-1-one* (**9c**). According to *Procedure A*: **9c** (34%) as a 2 : 13 : 2 : 10 : 1 : 10 : 14 : 1 stereoisomer mixture. IR: 3400, 2960, 1695, 1000. $^1$H-NMR (characteristic signals from the mixture): 0.79 (*t*, *J* = 7, 3 H); 3.1 (br. *s*, 1 OH); 4.19 (*d*, *J* = 7, 1 H); 5.92 (*m*, 1 H); 6.12 (*m*, 1 H); 7.45 (*d*, *J* = 7, 1 H). MS: 232 (0.5, $M^{+\cdot}$), 167 (8), 149 (100), 137 (12), 111 (18), 66 (44).

*2-(1-Hydroxy-2,2-dimethoxyethyl)cyclopent-2-en-1-one* (**9d**). According to *Procedure A*: **9d** (96%). IR: 3430, 2922, 2830, 1690, 1632, 1440, 1344, 1248, 1189, 1125, 1040, 972. $^1$H-NMR: 2.47 (*m*, 2 H); 2.67 (*m*, 2 H); 3.3 (br. *s*, OH); 3.42 (*s*, 3 H); 3.45 (*s*, 3 H); 4.53 (*s*, 2 H); 7.68 (br. *s*, 1 H). $^{13}$C-NMR: 27.0 (*t*); 35.1 (*t*); 55.3 (*q*); 55.5 (*q*); 67.6 (*d*); 104.9 (*d*); 143.7 (*s*); 161.2 (*d*); 209.2 (*s*). MS: 186 (0, $M^{+\cdot}$), 123 (11), 75 (100), 47 (12).

*2-[2-(Benzyloxy)-1-hydroxyethyl]cyclopent-2-en-1-one* (**9f**). According to *Procedure A*: **9f** (65%). IR: 3442, 2855, 1690, 1632, 1452, 1327, 1249, 1193, 1098, 1027, 999. $^1$H-NMR: 2.42 (*m*, 2 H); 2.6 (*m*, 2 H); 3.15 (br. *s*, OH); 3.48 (*dd*, *J* = 7, 9, 1 H); 3.71 (*dd*, *J* = 4, 7, 1 H); 4.59 (*q*, *J* = 7, 2 H); 4.69 (*m*, 1 H); 7.3 (*m*, 5 H); 7.6 (br. *s*, 1 H). $^{13}$C-NMR: 26.8 (*t*); 35.2 (*t*); 66.9 (*d*); 72.7 (*t*); 73.3 (*t*); 127.8 (3*d*); 128.5 (2*d*); 137.8 (*s*); 144.9 (*s*); 160.0 (*d*); 208.8 (*s*). MS: 232 (0, $M^{+\cdot}$), 111 (66), 108 (21), 91 (100), 65 (15).

*2-(2-Ethoxy-1-hydroxyethyl)cyclopent-2-en-1-one* (**9g**). According to *Procedure A*: **9g** (27%). IR: 3429, 2972, 2865, 1739, 1690, 1632, 1439, 1347, 1248, 1111, 1063, 1030, 1000, 885. $^1$H-NMR: 1.2 (*t*, *J* = 7, 3 H); 2.44 (*m*, 2 H); 2.62 (*m*, 2 H); 3.4 (*dd*, *J* = 7, 8, 1 H); 3.54 (*m*, OH); 3.55 (*m*, 1 H); 3.66 (*dd*, *J* = 4, 7, 1 H); 3.74 (*m*, 1 H); 4.65 (*m*, 1 H); 7.68 (br. *s*, 1 H). $^{13}$C-NMR: 15.1 (*q*); 26.8 (*t*); 35.2 (*t*); 66.7 (*t*); 66.8 (*d*); 72.9 (*t*); 145.1 (*s*); 159.9 (*d*); 208.9 (*s*). MS: 170 (0.5, $M^{+\cdot}$), 152 (21), 123(11), 111 (100), 95 (19), 79 (18), 59 (17).

*2-(1-Hydroxy-3-methoxypropyl)cyclopent-2-en-1-one* (**9h**). According to *Procedure A*: **9h** (53%). IR: 3418, 2920, 2871, 1690, 1630, 1440, 1333, 1250, 1191, 1111, 1000, 923, 788. $^1$H-NMR: 1.84 (*m*, 1 H); 2.04 (*m*, 1 H); 2.46 (*m*, 2 H); 2.62 (*m*, 2 H); 3.37 (*s*, 3 H); 3.6 (*t*, *J* = 7, 2 H); 3.75 (*d*, *J* = 5, OH); 4.64 (*m*, 1 H); 7.59 (br. *s*, 1 H). $^{13}$C-NMR: 26.6 (*t*); 35.0 (*t*); 35.4 (*t*); 58.9 (*q*); 67.4 (*d*); 71.2 (*t*); 148.0 (*s*); 158.4 (*d*); 209.1 (*s*). MS: 170 (0.5, $M^{+\cdot}$), 152 (28), 138 (32), 111 (100), 109 (30), 82 (31), 45 (27).

*Methyl 7-hydroxy-7-(5-oxocyclopent-1-en-1-yl)heptanoate* (**9i**). According to *Procedure A*: **9i** (53%). IR: 3437, 2928, 2857, 1732, 1691, 1630, 1436, 1334, 1250, 1194, 1171, 1087, 1038, 1000, 788. $^1$H-NMR: 1.38 (*m*, 3 H); 1.48 (*m*, 1 H); 1.67 (*m*, 4 H); 2.31 (*t*, *J* = 7, 2 H); 2.46 (*m*, 2 H); 2.61 (*m*, 2 H); 2.88 (br. *s*, OH); 3.68 (*s*, 3 H); 4.43 (br. *t*, *J* = 7, 1 H); 7.46 (br. *s*, 1 H). $^{13}$C-NMR: 24.8 (*t*); 25.1 (*t*); 26.6 (*t*); 28.9 (*t*); 34.0 (*t*); 35.3 (*t*); 35.6 (*t*); 51.5 (*q*); 67.7 (*d*); 147.8 (*s*); 157.9 (*d*); 174.2 (*s*); 210.0 (*s*). MS: 240 (0.5, $M^{+\cdot}$), 222 (3), 190 (21), 130 (8), 111 (100), 87 (21), 55 (13).

*Methyl (2Z)-3-Oxo-2-pentylidenecyclopentaneacetate* ((*Z*)-**10a**). A mixture of **11** (250 mg, 0.93 mmol) and pyridine · TsOH (50 mg) in acetone/$H_2O$ 9 : 1 (10 ml) was stirred at 20° for 1 h and then evaporated. The residue was dissolved in hexane and the soln. washed with 5% $NaHCO_3$ soln. and $H_2O$, dried ($Na_2SO_4$), and evaporated: **10a** (98%) as 3 : 7 (*E*)/(*Z*) mixture.

Alternatively, according to *Procedure B*: $\beta,\gamma$-deconjugated-**10a**/(*Z*)-**10a**/(*E*)-**10a** 11 : 61 : 28 (88%).

Alternatively, by a one-pot cascade procedure from cyclopentenone **16**: $\beta,\gamma$-deconjugated-**10a**/(*Z*)-**10a**/(*E*)-**10a** 10 : 30 : 60 (89% overall).

*Data of (Z)-***10a**: IR: 3000, 2950, 2925, 2850, 1710, 1630, 1430, 1360, 1260, 1165, 1110. $^1$H-NMR: 0.9 (*t*, *J* = 7, 3 H); 1.38 (*m*, 4 H); 1.58 (*m*, 1 H); 2.2 (*m*, 1 H); 2.3 (*m*, 2 H); 2.38 (*dd*, *J* = 9, 14, 1 H); 2.6 (*dd*, *J* = 7, 15, 1 H); 2.7 (*m*, 2 H); 3.15 (*m*, 1 H); 3.7 (*s*, 3 H); 5.9 (*dt*, *J* = 2, 7, 1 H). $^{13}$C-NMR: 13.9 (*q*); 22.4 (*t*); 26.7 (*t*); 27.5 (*t*); 31.5 (*t*); 38.2 (*t*); 38.7 (*d*); 39.4 (*t*); 51.7 (*q*); 137.8 (*s*); 141.7 (*d*); 172.6 (*s*); 207.7 (*s*). MS: 224 (58, $M^{+\cdot}$), 195 (10), 167 (20), 151 (100), 135 (28), 121 (41), 109 (68), 93 (52), 79 (59), 67 (30).

*Methyl (2E)-3-Oxo-2-pentylidenecyclopentaneacetate* ((*E*)-**10a**). CC purification ($SiO_2$, cyclohexane/AcOEt 7 : 3) of the above mixture for anal. purposes gave (*E*)-**10a** (54%). IR: 3000, 2950, 2925, 2850, 1710, 1630, 1430, 1360, 1260, 1160, 1110. $^1$H-NMR: 0.92 (*t*, *J* = 7, 3 H); 1.37 (*m*, 2 H); 1.46 (*m*, 2 H); 1.88 (*m*, 1 H); 2.05 (*m*, 1 H); 2.19 (*q*, *J* = 7, 2 H); 2.3–2.5 (*m*, 4 H); 3.42 (*m*, 1 H); 3.7 (*s*, 3 H); 6.6 (*dt*, *J* = 2, 7, 1 H). $^{13}$C-NMR: 13.9 (*q*); 22.5 (*t*); 25.2 (*t*); 29.0 (*t*); 30.8 (*t*); 35.0 (*d*); 35.8 (*t*); 38.6 (*t*); 51.8 (*q*); 138.4 (*d*); 139.8 (*s*); 172.4 (*s*); 206.3 (*s*). MS: 224 (57), 195 (9), 167 (15), 151 (100), 121 (32), 109 (62), 93 (48), 79 (60), 67 (31), 55 (30), 41 (41).

*Methyl (2Z)-2-Heptylidene-3-oxocyclopentaneacetate* ((*Z*)-**10b**). According to *Procedure B*: β,γ-deconjugated-**10b**/(*Z*)-**10b**/(*E*)-**10b** 16:58:32 (98%).

Alternatively, by a one-pot cascade procedure from cyclopentenone **16**: β,γ-deconjugated-**10b**/(*Z*)-**10b**/(*E*)-**10b** 15:29:56 (91% overall).

*Data of* (*Z*)-**10b**: IR: 3000, 2950, 2925, 2850, 1705, 1630, 1430, 1360, 1260, 1160, 1111. $^1$H-NMR: 0.89 (*t*, *J* = 7, 3 H); 1.29 (*m*, 6 H); 1.58 (*m*, 2 H); 1.89 (*m*, 1 H); 2.05 (*m*, 1 H); 2.2 (*m*, 1 H); 2.3 (*m*, 2 H); 2.65 (*m*, 3 H); 3.15 (*m*, 1 H); 3.71 (*s*, 3 H); 5.91 (*dt*, *J* = 2, 7, 1 H). MS: 252 (52, $M^{+\cdot}$), 195 (13), 179 (100), 167 (16), 161 (20), 135 (28), 121 (35), 109 (36), 79 (37). Floral, green, soapy, jasmine, very weak.

*Methyl (2*E*)-2-Heptylidene-3-oxocyclopentaneacetate* ((*E*)-**10b**). CC ($SiO_2$, cyclohexane/AcOEt 7:3) for anal. purposes gave (*E*)-**10b** (50%). IR: 3000, 2950, 2925, 2850, 1705, 1630, 1430, 1362, 1260, 1160, 1110. $^1$H-NMR: 0.9 (*t*, *J* = 7, 3 H); 1.3 (*m*, 6 H); 1.48 (*quint.*, *J* = 7, 2 H); 1.89 (*m*, 1 H); 2.06 (*m*, 1 H); 2.2 (*q*, *J* = 7, 1 H); 2.3–2.5 (*m*, 5 H); 3.45 (*m*, 1 H); 3.71 (*s*, 3 H); 6.59 (*t*, *J* = 7, 1 H). $^{13}$C-NMR: 14.1 (*q*); 22.6 (*t*); 25.2 (*t*); 28.6 (*t*); 29.1 (*t*); 29.2 (*t*); 31.6 (*t*); 35.0 (*d*); 35.8 (*t*); 38.6 (*t*); 51.8 (*q*); 138.4 (*d*); 139.8 (*s*); 172.4 (*s*); 206.3 (*s*). MS: 252 (47, $M^{+\cdot}$), 195 (11), 179 (100), 135 (22), 121 (31), 109 (39), 79 (4).

*Methyl 2-[(3-Ethylbicyclo[2.2.1]hept-5-en-2-yl)methylene]-3-oxocyclopentaneacetate* (**10c**). According to *Procedure B*: **10c** (55%) as a 15:15:70 stereoisomer mixture. Main stereoisomer: IR: 3391, 2955, 2930, 2870, 1736, 1702, 1629, 1460, 1435, 1407, 1377, 1306, 1260, 1230, 1170, 1093, 1051, 1002, 892. $^1$H-NMR: 0.92 (*t*, *J* = 7, 3 H); 1.42 (*sext.*, *J* = 7, 2 H); 1.57 (*m*, 2 H); 1.68 (*m*, 2 H); 1.89 (*m*, 1 H); 2.0–2.57 (*m*, 6 H); 2.61 (*m*, 1 H); 3.28 (*m*, 1 H); 3.7 (*s*, 3 H); 6.09 (*m*, 1 H); 6.25 (*m*, 2 H). MS: 288 (0, $M^{+\cdot}$), 222 (8), 193 (100), 149 (15), 133 (10), 119 (12), 107 (10), 105 (12), 91 (23), 79 (14).

*Methyl [2-(2,2-Dimethoxyethylidene)-3-oxocyclopentaneacetate* (**10d**). According to *Procedure B*: **10d** (96%) as a 2:3 (*Z*)/(*E*) mixture. IR: 3418, 2920, 2871, 1690, 1630, 1440, 1333, 1250, 1191, 1111, 1000, 923. $^1$H-NMR (main (*E*)-isomer in the mixture): 2.05 (*m*, 1 H); 2.4 (*m*, 4 H); 2.64 (*m*, 2 H); 3.32 (*s*, 3 H); 3.34 (*s*, 3 H); 3.7 (*s*, 3 H); 5.12 (*d*, *J* = 6, 1 H); 6.47 (*d*, *J* = 6, 1 H). MS: (*Z*)-**10d**: 242 (7, $M^{+\cdot}$), 210 (65), 195 (27), 178 (40), 169 (100), 151 (72), 137 (52), 119 (71), 109 (47), 91 (66), 79 (33); (*E*)-**10d**: 242 (21, $M^{+\cdot}$), 211 (72), 169 (92), 151 (100), 137 (30), 123 (32), 109 (59), 91 (34), 75 (68).

*Methyl 3-Oxo-2-(2-oxoethylidene)cyclopentaneacetate* (**10e**). A soln. of acetal **10d** (2.0 g, 8.26 mmol) in AcOH (10 ml) and $H_2O$ (10 ml) was heated at 40° for 3 h. The aq. phase was saturated with NaCl, and the mixture was extracted with $Et_2O$. The org. phase was washed with brine, dried ($Na_2SO_4$), and evaporated, and the residue bulb-to-bulb distilled: (*Z*)-**10e**/(*E*)-**10e**/**14e** 1:1:2 (36%). GC/IR: 3420, 2952, 1720, 1697, 1435, 1406, 1353, 1257, 1169, 1118, 1065, 1000. MS: (*Z*)-**10e**: 196 (3, $M^{+\cdot}$), 168 (100), 165 (20), 137 (11), 109 (100), 79 (39), 77 (19). (*E*)-**10e**: 196 (3, $M^{+\cdot}$), 168 (100), 165 (21), 122 (27), 109 (99), 95 (35), 79 (45), 57 (25).

*Methyl 2-[2-(Benzyloxy)ethylidene]-3-oxocyclopentaneacetate* (**10f**). According to *Procedure B*: β,γ-deconjugated-**10f**/(*Z*)-**10f**/(*E*)-**10f** 14:29:57 (68%). IR ((*E*)-**10f** in mixture): 3647, 2949, 1730, 1649, 1454, 1435, 1362, 1158, 1079, 1000. $^1$H-NMR (*E*-**10f** in mixture): 1.5–2.5 (*m*, 5 H); 2.6 (*m*, 2 H); 3.68 (*s*, 3 H); 4.2–2.8 (*m*, 4 H); 6.64 (*t*, *J* = 5, 1 H); 7.3 (*m*, 5 H). MS: (*E*)-**10f**: 288 (0.5, $M^{+\cdot}$), 197 (25), 165 (8), 91(100), 65 (8).

*Methyl 2-(2-Ethoxyethylidene)-3-oxocyclopentaneacetate* (**10g**). According to *Procedure B*: β,γ-deconjugated-**10g**/(*Z*)-**10g**/(*E*)-**10g** 22:39:39 (53%). ((*Z*)-**10g** in the mixture): IR: 2972, 1730, 1649, 1436, 1352, 1261, 1166, 1103, 1002, 932, 753. $^1$H-NMR: 1.22 (*t*, *J* = 7, 3 H); 1.5–2.5 (*m*, 4 H); 2.68 (*m*, 2 H); 3.19 (*m,* 1 H); 3.51 (*q*, *J* = 7, 2 H); 3.71 (*s*, 3 H); 4.2 (*m*, 1 H); 4.58 (*m*, 1 H); 6.01 (*t*, *J* = 5, 1 H). MS: 226 (58, $M^{+\cdot}$), 197 (40), 180 (22), 170 (27), 165 (42), 153 (99), 137 (27), 125 (100), 121 (39), 111 (59), 79 (54).

*Methyl (2Z)-2-(3-Methoxypropylidene)-3-oxocyclopentaneacetate* (**10h**). According to *Procedure B*: β,γ-deconjugated-**10h**/(*Z*)-**10h**/(*E*)-**10h**. 5:75:20 (93%). IR ((*Z*)-**10h** in mixture): 2949, 2876, 1733, 1712, 1637, 1435, 1366, 1261, 1166, 1111, 1037, 999, 877. $^1$H-NMR ((*Z*)-**10h** in mixture): 1.6–2.5 (*m*, 4 H); 2.65 (*m*, 2 H); 2.97 (*m*, 2 H); 3.18 (*m*, 1 H); 3.33 (*s*, 3 H); 3.48 (*t*, *J* = 7, 2 H); 3.71 (*s*, 3 H); 5.99 (*t*, *J* = 5, 1 H). $^{13}$C-NMR ((*Z*)-**10h** in mixture): 26.6 (*t*); 28.2 (*t*); 38.2 (*t*); 38.7 (*d*); 39.2 (*t*); 51.7 (*q*); 58.5 (*q*); 71.7 (*t*); 137.3 (*d*); 139.1 (*s*); 172.5 (*s*); 207.6 (*s*). MS: (*Z*)-**10h**: 226 (2, $M^{+\cdot}$), 194 (82), 163 (10), 153 (17), 135 (30), 121 (100), 107 (12), 91 (29), 79 (57), 45 (90); (*E*)-**10h**: 226 (2, $M^{+\cdot}$), 194 (78), 153 (14), 135 (27), 121 (88), 91 (25), 79 (48), 45 (100). Without character.

*Methyl (7*E*)-7-[2-(2-Methoxy-2-oxoethyl)-5-oxocyclopentylidene]heptanoate* ((*E*)-**10i**). According to *Procedure B*: β,γ-deconjugated-**10i**/(*Z*)-**10i**/(*E*)-**10i** 5:10:85 (96%). ((*E*)-**10i** in the mixture): IR: 2947, 2857, 1730, 1644, 1435, 1362, 1309, 1260, 1165, 1191, 1002, 978. $^1$H-NMR: 1.38 (*m*, 3 H); 1.5 (*m*, 2 H); 1.65 (*m*, 3 H); 1.88 (*m*, 1 H); 2.06 (*m*, 1 H); 2.2 (*q*, *J* = 7, 2 H); 2.32 (*t*, *J* = 7, 2 H); 2.42 (*m*, 2 H); 3.42 (*m*, 1 H); 3.68 (*s*, 3 H); 3.70 (*s*, 3 H); 6.58 (*t*, *J* = 5, 1 H). $^{13}$C-NMR: 24.7 (*t*); 25.2 (*t*); 28.3 (*t*); 28.9 (*t*); 29.0 (*t*); 33.9 (*t*); 35.0 (*d*); 35.8 (*d*); 38.6 (*t*); 51.5 (*q*); 51.8 (*q*); 137.8 (*d*); 140.0 (*s*); 172.3 (*s*); 174.0 (*s*); 206.3 (*s*). MS: 296 (13, $M^{+\cdot}$), 264 (19), 246 (12), 191 (100), 163 (40), 121 (20), 79 (35).

*Methyl (2*E*)-3-Oxo-2-[(2*E*)-pent-2-enylidene]cyclopentaneacetate* ((*E*)-**10j**). During the distillation of **10c**, (*E*)-**10j** (33%) was obtained. IR: 2958, 2873, 1730, 1630, 1436, 1261, 1165, 1000, 893. $^1$H-NMR: 1.07 (*t*, *J* = 7, 3 H); 1.89 (*m*, 1 H); 2.09 (*m*, 1 H); 2.27 (*m*, 2 H); 2.4 (*m*, 2 H); 2.51 (*m*, 2 H); 3.57 (*m*, 1 H); 3.7 (*s*, 3 H); 6.28 (*m*, 2 H); 6.94 (*d*, *J* = 9, 1 H). $^{13}$C-NMR: 13.0 (*q*); 25.4 (*t*); 26.6 (*t*); 35.4 (*d*); 35.8 (*t*); 39.0 (*t*); 51.8 (*q*); 124.9 (*d*); 133.5 (*d*); 137.1 (*s*); 149.2 (*d*); 172.4 (*s*); 206.8 (*s*). MS: 222 (6, $M^{+\cdot}$), 193 (100), 149 (12), 133 (9), 119 (12), 105 (13), 91 (22). Hedione, green, mastic.

*Methyl (6Z)-6-Pentylidene-1,4-dioxaspiro[4.4]nonane-7-acetate* (**11**). A mixture of **8** (246 mg, 1.16 mmol), propanoic acid (10 µl) and trimethyl orthoacetate (2 ml) was heated under reflux for 75 min and then evaporated. The residue was distilled: **11** (86%) as a 7:3 (*Z*)/(*E*) mixture. IR: 2954, 2929, 2872, 1735, 1650, 1457, 1435, 1377, 1303, 1266, 1245, 1063, 999, 945, 891. $^1$H-NMR: 0.9 (*t*, *J* = 7, 3 H); 1.2–1.47 (*m*, 6 H); 1.7 (*m*, 1 H); 1.91 (*m*, 1 H); 2.2 (*m*, 1 H); 2.3 (*dd*, *J* = 9, 14, 1 H); 2.59 (*dd*, *J* = 5, 15, 1 H); 2.9 (*m*, 1 H); 3.29 (*d*, *J* = 14, 2 H); 3.66 (*s*, 3 H); 3.93 (*m*, 2 H); 4.07 (*m*, 2 H); 5.50 (*dt*, *J* = 4, 8, 1 H). $^{13}$C-NMR: 14.0 (*q*); 22.5 (*t*); 27.1 (*t*); 28.4 (*t*); 31.9 (*t*); 36.2 (*t*); 39.2 (*d*); 39.7 (*t*); 51.5 (*q*); 64.1 (*t*); 64.2 (*t*); 114.7 (*s*); 130.5 (*d*); 141.0 (*s*); 173.2 (*s*). MS: 268 (18), 237 (17), 211 (100), 195 (55), 137 (33), 99 (24), 79 (15).

*Methyl 1-Hydroxy-2-pentylcyclopent-2-eneacetate* (**13a**). According to [37]: **13a** (80%) $^{13}$C-NMR: 14.1 (*q*); 22.6 (*t*); 26.0 (*t*); 27.6 (*t*); 28.8 (*t*); 32.0 (*t*); 38.8 (*t*); 42.4 (*t*); 51.8 (*q*); 83.7 (*s*); 126.4 (*d*); 147.1 (*s*); 173.5 (*s*). For other analyses, see [37]. Jasmine, buttery, floral, rancid, dirty, vomit.

*Ethyl 1-Hydroxy-2-pentylcyclopent-2-ene-1-acetate* (**13b**). A mixture of enone **12** (2.28 g, 15 mmol), ethyl bromoacetate (2.2 ml, 20 mmol), and granular activated Zn (washed with diluted HCl, $H_2O$, and MeOH, dried at 100°/0.1 Torr) in benzene (40 ml) was heated under reflux. The reaction started after *ca.* 30 min; heating under reflux was continued for 45 min. The cold mixture was diluted with $Et_2O$, washed with sat. $NH_4Cl$ soln., dried, and evaporated. The remaining oil (4.8 g) was purified by CC ($SiO_2$ (60 g), hexane/AcOEt 95:5 → 9:1): **13b** (84%). IR: 3000, 2950, 2920, 2850, 1720, 1690, 1625, 1460, 1365, 1020. $^1$H-NMR: 0.9 (*t*, *J* = 7, 3 H); 1.3 (*t*, *J* = 7, 3 H); 1.34 (*m*, 3 H); 1.51 (*m*, 1 H); 1.95 (*m*, 2 H); 2.15 (*m*, 3 H); 2.39 (*m*, 2 H); 2.42 (*d*, *J* = 16, 1 H); 2.72 (*d*, *J* = 16, 1 H); 3.6 (br. *s*, 1 OH); 4.19 (*q*, *J* = 7, 2 H); 5.5 (br. *s*, 1 H). $^{13}$C-NMR: 14.1 (*q*); 14.2 (*q*); 22.6 (*t*); 26.0 (*t*); 27.6 (*t*); 28.8 (*t*); 32.0 (*t*); 38.8 (*t*); 42.6 (*t*); 60.7 (*t*); 83.8 (*s*); 126.3 (*d*); 147.1 (*s*); 173.1 (*s*). MS: 240 (0, $M^{+\cdot}$), 222 (52), 193 (18), 166 (50), 134 (64), 119 (38), 105 (53), 93 (72), 92 (68), 91 (100), 79 (51).

*Methyl 3-Oxo-2-pentylcyclopent-1-ene-1-acetate* (**14a**). Under Ar, β,γ-deconjugated-**10a**/(*Z*)-**10a**/(*E*)-**10a** 10:30:60 (650 mg, 2.9 mmol) was heated at 120° for 6 h in the presence of $[RuH(\eta^5\text{-}C_8H_{11})_2]BF_4$ (32.5 mg, 0.08 mmol). Bulb-to-bulb distillation afforded β,γ-deconjugated-**10a**/**14a**/(*Z*)-**10a**/(*E*)-**10a** 9:53:28:10 (74%). For analyses, see [37].

Alternatively, pure **14a** (84%) was obtained according to [37].

Alternatively, a soln. of $HIO_3$ (2.64 g, 15 mmol) in DMSO (15 ml) protected from light was heated at 80° for 1 hour. Then a soln. of *Hedione®* *trans*/*cis* (9:1; **15a**; 2.26 g, 10 mmol) in DMSO (10 ml) was added at 65°. After 18 h at 65°, the cold soln. was extracted with $Et_2O$ and $H_2O$. The org. phase was dried ($Na_2SO_4$) and evaporated and the residues purified by CC ($SiO_2$, cyclohexane/AcOEt 9:1): **14a** (65%). Floral, jasmine, very weak, vague.

*Ethyl 3-Oxo-2-pentylcyclopent-1-ene-1-acetate* (**14b**). To a soln. of **13b** (0.96 g, 4 mmol) in $Et_2O$ (40 ml) was added 2.5M *Jones* reagent (2 ml, 5 mmol) at 0°. The cooling bath was removed, and stirring was continued for 10 min. The org. layer was washed with $H_2O$, 5% $NaHCO_3$ soln., dried ($Na_2SO_4$), and evaporated. The residue was distilled: **14b** (93%). B.p. 120°/0.9 Torr. IR: 2955, 2930, 2850, 1725, 1690, 1640, 1460, 1440, 1365, 1300, 1180, 1110, 1022. $^1$H-NMR: 0.87 (*t*, *J* = 7, 3 H); 1.28 (*m*, 4 H); 1.28 (*t*, *J* = 7, 3 H); 1.37 (*m*, 2 H); 2.19 (*t*, *J* = 7, 2 H); 2.4 (*m*, 2 H); 2.61 (*m*, 2 H); 3.46 (*s*, 2 H); 4.19 (*q*, *J* = 7, 2 H). $^{13}$C-NMR: 14.0 (*q*); 14.2 (*q*); 22.5 (*t*); 23.2 (*t*); 28.0 (*t*); 29.7 (*t*); 31.8 (*t*); 34.3 (*t*); 37.0 (*t*); 61.3 (*t*); 143.2 (*s*); 163.8 (*s*); 169.2 (*s*); 209.2 (*s*). MS: 238 (2, $M^{+\cdot}$), 220 (6), 182 (10), 165 (5), 151 (100), 135 (10), 121 (10), 109 (33), 79 (12).

*Methyl 2-Heptyl-3-oxocyclopent-1-ene-1-acetate* (**14c**). *Formier* gas ($N_2/H_2$ 92:8) was bubbled (10 bubbles/min) through a stirred suspension of **10b** (2.52 g, 10 mmol) in the presence of 5% $Pd/Al_2O_3$ (20 mg) at 135° for 8 h. After filtration and purification by CC (5% $AgNO_3/SiO_2$, cyclohexane/AcOEt 97:3), **14c** was isolated in 45% yield from the totally saturated material. IR: 2960, 2930, 2850, 1725, 1690, 1640, 1460, 1440, 1365, 1300, 1180, 1110, 1020. $^1$H-NMR: 0.89 (*t*, *J* = 7, 3 H); 1.26 (*m*, 8 H); 1.36 (*m*, 2 H); 2.18 (*t*, *J* = 7, 2 H); 2.4 (*m*, 2 H); 2.6 (*m*, 2 H); 3.46 (*s*, 2 H); 3.73 (*s*, 3 H). $^{13}$C-NMR: 14.1 (*q*); 22.6 (*t*); 23.3 (*t*); 28.4 (*t*); 29.1 (*t*); 29.7 (*t*); 29.6 (*t*); 31.8 (*t*); 34.4 (*t*); 36.6 (*t*); 52.3 (*q*); 143.3 (*s*); 163.5 (*s*); 169.6 (*s*); 209.2 (*s*). MS: 252 (2, $M^{+\cdot}$), 179 (100), 168 (19), 135 (12), 109 (35), 79 (22), 41 (18). Cocoa butter, fatty-lard, milky, buttery.

*Methyl 2-(2,2-Dimethoxyethyl)-3-oxocyclopent-1-ene-1-acetate* (**14d**). A soln. of acetal **10d** (800 mg, 3.3 mmol) in MeOH (5 ml) and a trace amount of conc. HCl was heated for 3 h at 60°. A trace of $NaHCO_3$ was added to the cold mixture. The filtrate was evaporated and the residue bulb-to-bulb distilled: **14d** (87%). B.p. 150°/0.1 mbar. IR: 2930, 2832, 1736, 1696, 1649, 1434, 1352, 1255, 1192, 1170, 1117, 1080, 1049, 1010, 971.

$^1$H-NMR: 2.43 (*m*, 2 H); 2.53 (*d*, *J* = 7, 2 H); 2.67 (*m*, 2 H); 3.33 (*s*, 6 H); 3.54 (*s*, 2 H); 3.73 (*s*, 3 H); 4.39 (*t*, *J* = 7, 1 H). $^{13}$C-NMR: 27.7 (*t*); 30.1 (*t*); 34.2 (*t*); 36.8 (*t*); 52.2 (*q*); 54.2 (2*q*); 103.4 (*d*); 138.2 (*s*); 167.1 (*s*); 169.6 (*s*); 208.9 (*s*). MS: 242 (0.5, $M^{+\bullet}$), 210 (47), 195 (8), 151 (36), 123 (17), 109 (16), 91 (17), 75 (100).

*Methyl 3-Oxo-2-(2-oxoethyl)cyclopent-1-ene-1-acetate* (**14e**). A soln. of acetal **14d** (330 mg, 1.36 mmol) in $H_2O$ (8 ml) and AcOH (8 ml) was stirred at 60° for 2 h. The cold mixture was evaporated, the residue diluted with $Et_2O$, the soln. extracted with brine, washed with sat. aq. $NaHCO_3$ soln. and brine to neutral, dried ($Na_2SO_4$), and evaporated, and the residue bulb-to-bulb distilled: **14e** (55%). B.p. 170°/0.1 mbar. IR: 2952, 2839, 1722, 1694, 1648, 1435, 1352, 1255, 1192, 1171, 1118, 1062, 1010. $^1$H-NMR: 2.5 (*m*, 2 H); 2.76 (*m*, 2 H); 3.39 (*s*, 2 H); 3.45 (*s*, 2 H); 3.7 (*s*, 3 H); 9.65 (*s*, 1 H). $^{13}$C-NMR: 30.7 (*t*); 34.1 (*t*); 37.0 (*t*); 38.2 (*t*); 52.5 (*q*); 134.9 (*s*); 168.0 (*s*); 168.9 (*s*); 197.0 (*d*); 207.8 (*s*). MS: 196 (3, $M^{+\bullet}$), 168 (85), 137 (12), 109 (100), 79 (43), 53 (17).

*Methyl (2Z)-3-Oxo-2-(pent-2-enyl)cyclopent-1-ene-1-acetate* (**14f**). At 20°, 1M sodium bis(trimethylsilyl)-amide in THF (0.74 ml, 0.74 mmol) was added dropwise to a soln. of triphenylpropylphosphonium bromide (0.29 g, 0.74 mmol) in THF (1 ml). After 1 h, DMF (0.25 ml) and a soln. of keto aldehyde **14e** (40 mg, 0.2 mmol) in THF (0.3 ml) were added. After 2 h at 20°, the mixture was poured onto ice, and extracted with $Et_2O$. The org. phase was washed with brine to neutrality, dried ($Na_2SO_4$), and evaporated and the residue purified by CC ($SiO_2$, $Et_2O$/cyclohexane 2 : 3): (*Z*)-**14f** (44%) contaminated by 7% of (*E*)-isomer. IR: 2969, 2926, 1739, 1698, 1644, 1437, 1354, 1259, 1172, 1119, 1087, 1048, 879. $^1$H-NMR: 0.99 (*t*, *J* = 7, 3 H); 2.15 (*q*, *J* = 7, 2 H); 2.42 (*m*, 2 H); 2.61 (*m*, 2 H); 2.97 (*d*, *J* = 7, 2 H); 3.48 (*s*, 2 H); 3.72 (*s*, 3 H); 5.2 (*m*, 1 H); 5.41 (*m*, 2 H). $^{13}$C-NMR: 14.1 (*q*); 20.6 (*t*); 21.3 (*t*); 29.9 (*t*); 34.2 (*t*); 36.6 (*t*); 52.3 (*q*); 124.4 (*d*); 133.0 (*d*); 141.8 (*s*); 164.0 (*s*); 169.5 (*s*); 208.6 (*s*). MS: 222 (21, $M^{+\bullet}$), 193 (100), 149 (72), 133 (51), 105 (48), 91 (69), 79 (57), 77 (44), 55 (39). Jasmine, floral.

*Methyl* trans-*3-Oxo-2-pentylcyclopentaneacetate* (*trans*-**15a**). A soln. of **10a** (3.01 g, 13.1 mmol: *β*,*γ*-deconjugated/(*Z*)/(*E*)-**10a** 10 : 30 : 60) in cyclohexane (30 ml) was hydrogenated at 0° under 1 atm of $H_2$ over 5% Pd/C (300 mg). After 18 h, the mixture was filtered and evaporated, and the residue bulb-to-bulb distilled: **15a** (98%) as a 52 : 48 *trans/cis* mixture.

A soln. of enone **14a** (1.0 g, 4.1 mmol) in cyclohexane (10 ml) was hydrogenated at 20° under 1 atm. of $H_2$ over 10% Pd/C (50 mg). After 1.5 h, the mixture was evaporated and the residue bulb-to-bulb distilled: **15a**, (98%) as a 38 : 62 *trans/cis* mixture. Epimerization with a trace of MeONa/MeOH afforded quantitatively **15a** as a 92 : 8 *trans/cis* mixture. For analyses, see [17]. Jasmine, floral, somewhat rancid, weak.

*Methyl* trans-*3-Oxo-2-heptylcyclopentaneacetate* (*trans*-**15b**). A soln. of **10b** (3.0 g, 11.9 mmol; *β*,*γ*-deconjugated/(*Z*)(*E*)-**10b** 15 : 29 : 56) in cyclohexane (30 ml) was hydrogenated at 1 atm $H_2$ over 10% Pd/C (100 mg). After 18 h, the mixture was evaporated and the residue bulb-to-bulb distilled: **15b** (92%) as a 53 : 47 *trans/cis* mixture. Epimerization with a trace of MeONa/MeOH afforded quantitatively **15b** as a 9 : 1 *trans*/*cis* mixture for analyses. B.p. 160°/0.1 mbar. IR: 2923, 2853, 1733, 1435, 1167, 1014, 721. $^1$H-NMR: 0.87 (*t*, *J* = 7, 3 H); 1.24 (*m*, 10 H); 1.38 (*m*, 1 H); 1.54 (*m*, 2 H); 1.8 (*m*, 1 H); 2.12 (*m*, 1 H); 2.24 (*m*, 1 H); 2.35 (*m*, 3 H); 2.64 (*m*, 1 H); 3.72 (*s*, 3 H). $^{13}$C-NMR: 14.1 (*q*); 23.7 (*t*); 27.2 (*t*); 27.5 (*t*); 27.9 (*t*); 29.1 (*t*); 29.9 (*t*); 31.8 (*t*); 37.7 (*t*); 38.1 (*t*); 39.0 (*d*); 51.7 (*d*); 54.2 (*q*); 172.7 (*s*); 219.7 (*s*). MS: 254 (3, $M^{+\bullet}$), 181 (22), 156 (39), 83 (100), 55 (17). MS: *cis*-**15b**: 254 (5, $M^{+\bullet}$), 181 (28), 156 (32), 83 (100), 55 (21). Fruity, floral, velvety, veloutone, peach, very weak.

*Methyl* trans-*2-(2,2-Dimethoxyethyl)-3-oxocyclopentaneacetate* (*trans*-**15d**). A soln. of **10d** (1.0 g, 4.13 mmol; (*Z*)-/(*E*)-**10d** 2 : 3) in MeOH (10 ml) was hydrogenated at 1 atm $H_2$ over 10% Pd/C (100 mg). After 2 h, the mixture was evaporated and the residue bulb-to-bulb distilled: **15d** (60%) as a 9 : 1 *trans*/*cis* mixture. IR: 3000, 1730, 1715, 1170, 720. $^1$H-NMR: 1.51 (*m*, 1 H); 1.78 (*m*, 1 H); 1.89 (*m*, 2 H); 2.18 (*m*, 1 H); 2.35 (*m*, 4 H); 2.72 (*m*, 1 H); 3.32 (*s*, 3 H); 3.34 (*s*, 3 H); 3.71 (*s*, 3 H); 4.62 (*dd*, *J* = 7, 9, 1 H). $^{13}$C-NMR: 27.4 (*t*); 31.2 (*t*); 37.3 (*t*); 38.5 (*t*); 38.9 (*d*); 50.3 (*d*); 51.6 (*q*); 53.1 (*q*); 53.4 (*q*); 102.7 (*d*); 172.7 (*s*); 218.9 (*s*). MS: 244 (0, $M^{+\bullet}$), 212 (8), 181 (23), 139 (27), 89 (37), 75 (100). MS: *cis*-**15d**: 244 (0, $M^{+\bullet}$), 213 (12), 181 (13), 139 (21), 89 (35), 75 (100). Without character.

*Methyl* trans-*3-Oxo-2-(2-oxoethyl)cyclopentaneacetate* (*trans*-**15e**). A mixture of **15d** (0.43 g, 1.76 mmol), $H_2O$ (8 ml), and AcOH (8 ml) was stirred for 3 h at 40°. The cold mixture was evaporated, the residue diluted with $Et_2O$, the soln. washed with brine, sat. aq. $NaHCO_3$ soln., and brine to neutral, dried ($Na_2SO_4$), and evaporated, and the residue bulb-to-bulb distilled: **15e** (83%) as a 9 : 1 *trans/cis* mixture.

Alternatively, a suspension of **15f** (85 mg, 0.425 mmol), PCC (140 mg, 0.65 mmol), and $SiO_2$ (100 mg) in $CH_2Cl_2$ (2 ml) was stirred for 15 min at 20°. $Et_2O$ (2 ml) and *Celite* (100 mg) were added, and the mixture was passed through a short column of $SiO_2$ ($Et_2O$). The filtrate was evaporated and the residue bulb-to-bulb distilled: **15e** (60%, 9 : 1 *trans*/*cis*). IR: 2955, 2930, 2869, 1737, 1701, 1464, 1408, 1378, 1229, 1170, 1087, 1003, 968, 901, 800. $^1$H-NMR: 1.59 (*m*, 1 H); 2.25–2.4 (*m*, 5 H); 2.43 (*m*, 1 H); 2.57 (*m*, 1 H); 2.71 (*dd*, *J* = 7, 16, 1

H); 2.9 (*dd*, *J* = 7, 16, 1 H); 3.69 (*s*, 3 H); 9.77 (*s*, 1 H). $^{13}$C-NMR: 27.6 (*t*); 37.0 (*t*); 38.4 (*d*); 38.6 (*t*); 42.4 (*t*); 49.2 (*d*); 51.7 (*q*); 172.5 (*s*); 199.8 (*d*); 217.7 (*s*). MS: 198 (3, $M^{+\cdot}$), 167 (20), 156 (35), 125 (17), 97 (100), 83 (46), 55 (29). MS: *cis*-**15e**: 193 (3, $M^{+\cdot}$), 167 (19), 156 (34), 125 (15), 97 (100), 83 (49), 55 (33). Without character.

*Methyl* trans-*2-(2-Hydroxyethyl)-3-oxocyclopentaneacetate* (*trans*-**15f**). A soln. of **10f** (1.15 g, 4.0 mmol; *β*,*γ*-deconjugated/(*Z*)/(*E*)-**10f** 14 : 29 : 57) in MeOH (10 ml) was hydrogenated at 1 atm $H_2$ over 10% Pd/C (100 mg). After 18 h, the mixture was filtered and evaporated and the residue bulb-to-bulb distilled: **15f** (98%) as a 9 : 1 *trans*/*cis* mixture. IR: 2949, 1730, 1436, 1163, 1041. $^1$H-NMR: 1.57 (*m*, 1 H); 1.78 (*m*, 2 H); 1.98 (*m*, 1 H); 2.2 (*m*, 1 H); 2.25–2.45 (*m*, 4 H); 2.66 (*m*, 1 H); 2.89 (br. *s*, OH); 3.71 (*s*, 3 H); 3.76 (*m*, 2 H). $^{13}$C-NMR: 27.5 (*t*); 30.7 (*t*); 37.4 (*t*); 38.4 (*t*); 38.6 (*d*); 51.8 (*q*); 53.0 (*d*); 61.0 (*t*); 172.7 (*s*); 221.2 (*s*). MS: 200 (0, $M^{+\cdot}$), 182 (18), 168 (19), 156 (27), 140 (18), 125 (20), 109 (78), 83 (100), 55 (53).

*Methyl* trans-*2-(2-Ethoxyethyl)-3-oxocyclopentaneacetate* (*trans*-**15g**). As described for **15b**: **15g** (78%) as 40 : 60 *trans*/*cis* mixture, which spontaneously epimerized in $CDCl_3$ to a 95 : 5 *trans*/*cis* mixture. IR: 2950, 2862, 1730, 1435, 1377, 1256, 1194, 1160, 1105, 997. $^1$H-NMR: 1.16 (*t*, *J* = 7, 3 H); 1.49 (*m*, 1 H); 1.84 (*sext.*, *J* = 7, 2 H); 1.9 (*m*, 1 H); 2.2 (*m*, 2 H); 2.25–2.4 (*m*, 3 H); 2.72 (*m*, 1 H); 3.44 (*m*, 2 H); 3.51 (*t*, *J* = 7, 2 H); 3.71 (*s*, 3 H). $^{13}$C-NMR: 15.2 (*q*); 27.4 (*t*); 27.8 (*t*); 37.5 (*t*); 38.2 (*d*); 38.7 (*t*); 51.6 (*d*); 51.6 (*q*); 66.0 (*t*); 67.6 (*t*); 172.7 (*s*); 219.2 (*s*). MS: 228 (0, $M^{+\cdot}$), 156 (40), 109 (17), 83 (100), 73 (40). MS: *cis*-**15g**: 228 (0, $M^{+\cdot}$), 156 (40), 109 (12), 83 (100), 73 (40). Cheese, curdled milk.

*Methyl* trans-*2-(3-Methoxypropyl)-3-oxocyclopentaneacetate* (*trans*-**15h**). As described for **15d**: **15h** (79%) as a 9 : 1 *trans*/*cis* mixture. B.p. 180°/0.1 mbar. IR: 2928, 2867, 1730, 1436, 1408, 1380, 1334, 1256, 1193, 1159, 1112, 1016. $^1$H-NMR: 1.45–1.77 (*m*, 4 H); 1.83 (*m*, 1 H); 2.11 (*m*, 2 H); 2.24 (*m*, 2 H); 2.34 (*m*, 2 H); 2.64 (*m*, 1 H); 3.31 (*s*, 3 H); 3.37 (*t*, *J* = 7, 2 H); 3.7 (*s*, 3 H). $^{13}$C-NMR: 24.4 (*t*); 26.6 (*t*); 27.2 (*t*); 37.6 (*t*); 38.1 (*d*); 38.8 (*t*); 51.6 (*q*); 53.8 (*d*); 58.5 (*q*); 72.7 (*t*); 172.6 (*s*); 219.4 (*s*). MS: 228 (0.5, $M^{+\cdot}$), 196 (9), 155 (37), 123 (100), 45 (15). MS: *cis*-**15h**: 228 (0.5, $M^{+\cdot}$), 196 (9), 155 (37), 123 (100), 45 (15). Vaguely mushroom, hedione, weak.

*Methyl* trans-*2-(2-Methoxy-2-oxoethyl)-5-oxocyclopentaneheptanoate* (*trans*-**15i**). As described for **15b**: **15i** (96%) as a 66 : 34 *trans*/*cis* mixture. IR: 2929, 2855, 1735, 1435, 1193, 1166, 1013. $^1$H-NMR: 1.32 (*m*, 5 H); 1.43 (*m*, 1 H); 1.54 (*m*, 2 H); 1.62 (*m*, 2 H); 1.8 (*m*, 2 H); 2.2 (*m*, 2 H); 2.25–2.4 (*m*, 5 H); 2.63 (*m*, 1 H); 3.66 (*s*, 3 H); 3.71 (*s*, 3 H). $^{13}$C-NMR: 24.9 (*t*); 26.5 (*t*); 27.2 (*t*); 27.8 (*t*); 28.9 (*t*); 29.5 (*t*); 34.0 (*t*); 37.7 (*t*); 38.1 (*d*); 38.9 (*t*); 51.5 (*q*); 51.7 (*q*); 54.2 (*d*); 172.6 (*s*); 174.2 (*s*); 219.6 (*s*). MS: 298 (2, $M^{+\cdot}$), 235 (12), 193 (20), 156 (75), 83 (100), 55 (16). MS: *cis*-**15i**: 298 (2, $M^{+\cdot}$), 235 (12), 193 (18), 156 (80), 83 (100), 55 (18).

*3*-endo-*Ethylbicyclo[2.2.1]hept-5-ene-2*-endo-*carbaldehyde* (*cis-endo*-**17c**). Cyclopentadiene dimer (54.36 g, 0.412 mol) and 70% (2*Z*)-pent-2-enenitrile (95.16 g, 0.82 mol; *Fluka*) were heated at 180° for 23 h in a 500-ml *Berghof* autoclave. After cooling, the mixture was distilled through a *Vigreux* column, and the fraction 33–51°/0.06 mbar (69.9 g, 83% pure) was redistilled over a *Widmer* column: 3-*exo/endo*-ethylbicyclo[2.2.1]-hept-5-ene-2-*exo/endo*-carbonitrile 1 : 2 (45%), separated by prep. GC for analyses. 3-*endo*-Ethylbicyclo[2.2.1]-hept-5-ene-2-*endo*-carbonitrile: IR: 2960, 2945, 2890, 2250, 1460, 1385, 1345, 1255, 1160. $^1$H-NMR: 0.98 (*t*, *J* = 7, 3 H); 1.2 (*m*, 1 H); 1.29 (*d*, *J* = 7, 1 H); 1.46 (*m*, 1 H); 1.57 (*d*, *J* = 7, 1 H); 2.2 (*m*, 1 H); 2.98 (br. *s*, 1 H); 3.02 (*dd*, *J* = 3.5, 9, 1 H); 3.19 (br. *s*, 1 H); 6.22 (*m*, 1 H); 6.28 (*m*, 1 H). $^{13}$C-NMR: 12.8 (*q*); 24.6 (*t*); 33.2 (*d*); 44.4 (*d*); 45.3 (*d*); 46.8 (*d*); 48.4 (*t*); 120.9 (*s*); 134.6 (*d*); 136.1 (*d*). MS: 147 (1, $M^{+\cdot}$); 105 (5); 66 (100); 39 (8). Pinanol, camphoraceous, pinene.

At 20°, 1.0M DIBAL-H in hexane (66 ml, 0.066 mol) was added dropwise to a soln. of a distilled enriched fraction of *cis-endo*/*cis-exo* carbonitrile 6 : 1 (4.86 g, 0.33 mol) in THF (60 ml). After 2 h, the mixture was poured onto 10% $H_2SO_4$ soln. at 0°. After extraction with $Et_2O$, the org. phase was washed with brine to neutral, dried ($Na_2SO_4$) and evaporated and the crude residue (> 80%) used as such for the next reaction. A sample was purified by CC ($SiO_2$, cyclohexane/AcOEt 97 : 3) for anal. purpose: *cis-endo*-**17c**. IR: 3070, 2976, 2944, 2884, 2823, 2727, 1730, 1461. $^1$H-NMR: 0.98 (*t*, *J* = 7, 3 H); 1.01 (*m*, 1 H); 1.38 (*d*, *J* = 7, 1 H); 1.43 (*sept.*, *J* = 5, 1 H); 1.56 (*d*, *J* = 7, 1 H); 2.43 (*m*, 1 H); 2.88 (*m*, 1 H); 3.0 (*s*, 1 H); 3.07 (*s*, 1 H); 6.23 (*m*, 1 H); 6.33 (*m*, 1 H); 9.36 (*d*, *J* = 4, 1 H). $^{13}$C-NMR: 13.4 (*q*); 23.4(*t*); 45.4 (*d*); 46.0 (*d*); 47.5 (*d*); 49.4 (*t*); 55.7 (*d*); 135.0 (*d*); 135.7 (*d*); 207.6 (*d*). MS: 150 (2, $M^{+\cdot}$), 85(9), 66 (100), 39 (10).

*3*-exo-*Ethylbicyclo[2.2.1]hept-5-ene-2*-exo-*carbaldehyde* (*cis-exo*-**17c**). During the purification of the main *cis-endo* stereoisomer; the intermediate 3-*exo*-ethylbicyclo[2.2.1]hept-5-ene-2-*exo*-carbonitrile was isolated. IR: 2960, 2940, 2880, 2350, 1460, 1380, 1335. $^1$H-NMR: 1.06 (*t*, *J* = 7, 3 H); 1.5 (*m*, 2 H); 1.51 (*d*, *J* = 7, 1 H); 1.68 (*d*, *J* = 7, 1 H); 1.8 (*sext.*, *J* = 7, 1 H); 2.42 (*d*, *J* = 8, 1 H); 2.72 (br. *s*, 1 H); 3.18 (br. *s*, 1 H); 6.04 (*m*, 1 H); 6.23 (*m*, 1 H). $^{13}$C-NMR: 13.4 (*q*); 26.3 (*t*); 33.7 (*d*); 43.5 (*d*); 44.3 (*t*); 45.7 (*d*); 48.0 (*d*); 121.7 (*s*); 134.3 (*d*); 139.6 (*d*). MS: 147 (0.5, $M^{+\cdot}$), 118 (4), 105 (5), 91 (5), 66 (100), 39 (10).

During the purification of the main *cis-endo* stereoisomer, the *cis-exo*-**17c** was isolated. IR: 3071, 2977, 2888, 2818, 2717, 1731, 1460. $^1$H-NMR: 0.98 (*t*, *J* = 7, 3 H); 1.21 (*m*, 1 H); 1.45 (*d*, *J* = 7, 1 H); 1.61 (*m*, 1 H);

1.69 (*d*, *J* = 7, 1 H); 1.75 (*m*, 1 H); 2.24 (*m*, 1 H); 2.72 (br. *s*, 1 H); 2.98 (br. *s*, 1 H); 6.09 (*m*, 1 H); 6.22 (*m*, 1 H); 9.77 (*d*, *J* = 4, 1 H). $^{13}$C-NMR: 13.9 (*q*); 24.6 (*t*); 43.5 (*t*); 44.0 (*d*); 45.0 (*d*); 45.8 (*d*); 53.2 (*d*); 135.7 (*d*); 139.1 (*d*); 206.9 (*d*). MS: 150 (1, $M^{+\cdot}$), 85 (12), 66 (100), 39 (6).

*Methyl* trans-*3-Oxo-2[(2Z)-pent-2-enyl]cyclopentaneacetate* (**18a**). Triphenylpropylphosphonium bromide (1430 mg, 3.7 mmol) was added to a suspension of $NaNH_2$ (272 mg, 3.4 mmol) in THF (7 ml). After 5 min at 20°, *t*BuOK (34 mg, 0.3 mmol) was added and after 1 h at 20°, the temp. was cooled down to −70°. A soln. of **15e** (730 mg, 3.68 mmol) in THF (3 ml) was added dropwise, then the temp. was raised gradually to 20°. The mixture was poured onto ice and diluted with $Et_2O$, the org. phase washed with brine to neutrality, dried ($Na_2SO_4$), and evaporated, and the residue bulb-to-bulb distilled: methyl jasmonate (*Z*)-**18a** (31%) as a 9 : 1 *trans/cis* mixture.

Alternatively, 1.6M BuLi in hexane (0.85 ml, 1.35 mmol) was added dropwise at 0° to a suspension of triphenylpropylphosphonium bromide (540 mg, 1.4 mmol) in toluene (3 ml). After 1 h at 20°, the mixture was cooled down to −20°, and a soln. of **15e** (250 mg, 1.26 mmol) in toluene (4 ml) was added dropwise in 1 h. After 2 h at −20° and 1 h at 20°, $H_2O$ and then hexane were added. The mixture was filtered and evaporated and the residue bulb-to-bulb distilled: (*Z*)-**18a** (62%) as a 9 : 1 *trans*/*cis* mixture of (*Z*)/(*E*)-isomers 95 : 5. B.p. 175°/0.1 mbar. IR: 2961, 1725, 1436, 1408, 1375, 1335, 1258, 1229, 1194, 1162, 1069, 985. $^1$H-NMR: 0.95 (*t*, *J* = 7, 3 H); 1.5 (*quint.*, *J* = 7, 1 H); 1.9 (*m*, 1 H); 2.07 (*quint.*, *J* = 7, 2 H); 2.1–2.4 (*m*, 7 H); 2.7 (*m*, 1 H); 3.7 (*s*, 3 H); 5.25 (*m*, 1 H); 5.45 (*m*, 1 H). $^{13}$C-NMR: 14.2 (*q*); 20.6 (*t*); 25.5 (*t*); 27.3 (*t*); 37.6 (*t*); 38.1 (*d*); 38.7 (*t*); 51.3 (*q*); 53.9 (*d*); 125.6 (*d*); 133.7 (*d*); 172.3 (*s*); 217.9 (*s*). MS: 224 (30, $M^{+\cdot}$), 193 (12), 156 (22), 151 (39), 109 (27), 95 (32), 83 (100), 79 (29), 67 (28), 55 (27), 41 (40). Jasmine, mushroom, humus, delphone.

*Methyl* trans-*2-[(2Z)Hex-2-enyl]-3-oxocyclopentaneacetate* (**18b**). As described for **18a** (BuLi at −30°): **18b** (34%) as a 9 : 1 *trans/cis* mixture of (*Z*)/(*E*)-isomers 95 : 5. IR: 2956, 2872, 1730, 1436, 1408, 1377, 1335, 1259, 1229, 1193, 1162, 983. $^1$H-NMR: 0.91 (*t*, *J* = 7, 3 H); 1.38 (*sext.*, *J* = 7, 2 H); 1.5 (*m*, 1 H); 1.89 (*m*, 1 H); 2.02 (*sext.*, *J* = 7, 2 H); 2.11 (*m*, 1 H); 2.2–2.4 (*m*, 6 H); 2.71 (*m*, 1 H); 3.70 (*s*, 3 H); 5.3 (*m*, 1 H); 5.48 (*m*, 1 H). $^{13}$C-NMR: 13.8 (*q*); 22.7 (*t*); 25.7 (*t*); 27.2 (*t*); 29.4 (*t*); 37.7 (*t*); 38.1 (*d*); 38.8 (*t*); 51.6 (*q*); 54.0 (*d*); 125.8 (*d*); 132.3 (*d*); 172.5 (*s*); 218.9 (*s*). MS: 238 (25, $M^{+\cdot}$), 207 (8), 165 (35), 156 (28), 147 (15), 135 (18), 109 (21), 95 (29), 83 (100), 79 (29), 67 (27), 55 (33), 41 (29). Methyl jasmonate, vitamins.

*Methyl* trans-*2-(3-Cyclopropylprop-2-enyl)-3-oxocyclopentaneacetate* (**18c**). As described for **18a** (BuLi at −30°): **18c** (35%) as a 95 : 5 *trans*/*cis* mixture of 7 : 3 (*Z*)/(*E*)-isomers. IR: 2990, 1730, 1720, 1040. $^1$H-NMR: 0.31 (*m*, 3 H); 0.72 (*m*, 2 H); 1.52 (*m*, 2 H); 1.94 (*m*, 1 H); 2.12 (*m*, 1 H); 2.2–2.4 (*m*, 3 H); 2.5 (*m*, 2 H); 2.78 (*m*, 1 H); 3.70 (*s*, 3 H); 4.82 (*t*, *J* = 7, 1 H); 5.23 (*m*, 1 H). $^{13}$C-NMR: 6.9 (*t*); 7.0 (*t*); 9.7 (*d*); 25.9 (*t*); 27.3 (*t*); 37.8 (*t*); 38.0 (*d*); 38.8 (*t*); 51.6 (*q*); 54.2 (*d*); 123.9 (*d*); 136.4 (*d*); 172.6 (*s*); 219.0 (*s*). MS: 236 (6, $M^{+\cdot}$), 218 (5), 193 (10), 163 (69), 121 (28), 91 (45), 83 (100), 81 (62), 79 (87), 77 (33), 67 (35), 55 (35), 41 (39).

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