

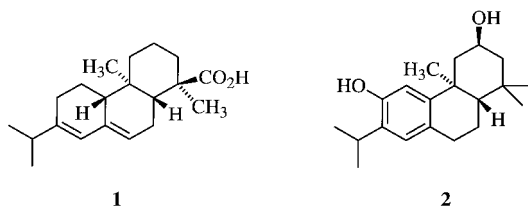
Synthesis of Functionalized 4a-Methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrenes

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The title compounds were constructed by a *Heck* reaction of functionalized aryl halides with homoallylic alcohols followed by *Michael* addition and subsequent cyclocondensation.

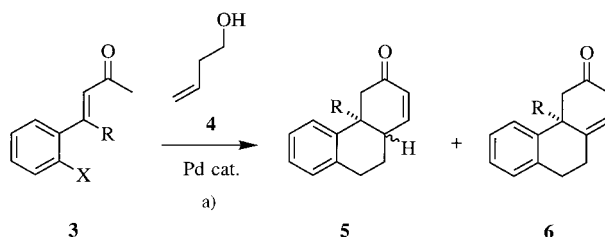
Introduction. – Abietic acid (**1**) and salviol (**2**) are two examples of a widespread family of diterpenes found in various plants such as juniper, pine tree and sage [1]. A partially hydrated phenanthrene moiety with a Me group at C(4) is a common structural unit of these natural products. Recently, we reported on a domino process [2] combining the *Heck* reaction [3] with classical carbonyl reactions giving convenient access to related structures [4]: the *Heck* reaction with allylic and homoallylic alcohols as olefinic coupling components leads to carbonyl compounds [5]; this is the basis for



reaction sequences that include the *Michael* addition, aldol condensation [6], or imine formation [7] depending on the presence of appropriate functional groups. For instance, bromoaryl ketone **3.1a** (R = H, X = Br) reacts with but-3-en-1-ol (**4**) under Pd catalysis and a subsequent *Robinson*-type annulation is completed under acidic conditions to give the functionalized hexahydrophenanthrene **5.1** in acceptable yield (R = H; *Scheme 1, Table 1, Entry 1*) [4]. In this paper, we report on our attempts to apply this reaction sequence for the synthesis of corresponding 4a-methylated phenanthrenes.

Results and Discussion. – In contrast to the reaction of bromoaryl ketone **3.1a**, the homologues compound (*E*)-**3.2a** (R = Me, X = Br) reacted sluggishly, presumably because of steric hindrance by the additional Me group: 59% of the starting material was recovered, though partially isomerized to the (*Z*)-isomer, and only 14% of the tricyclic annulation product **5.2** was obtained, exclusively in the *cis*-configuration. The corresponding iodoaryl ketone (*E*)-**3.2b** (R = Me, X = I) is significantly more reactive;

Scheme 1



a) 1. 1 mmol of **3**, 2.5 equiv. of **4**, 5 mol-% of Pd(OAc)₂, EtN(i-Pr)₂, LiCl, 10 ml of DMF, N₂, 80°, 3 d for *Entries 1 and 3*, and 5 d for *Entry 2*; 2. 1 equiv. of conc. HCl, CHCl₃, 40°, sonication, 4 h (for *Entries 1 and 3*) or 10 mol-% of TsOH, CHCl₃, reflux, 2 d (for *Entry 2*).

Table 1. Annelation Reactions of Halogenoaryl Ketones **3** with But-3-en-1-ol (**4**)

Entry	Substrate	R	X	Yield [%]	
				5 (<i>cis/trans</i>)	6
1	3.1a	H	Br	56 (1:4)	–
2	3.2a	Me	Br	14 (<i>cis</i>)	–
3	3.2b	Me	I	22 (4:1)	21

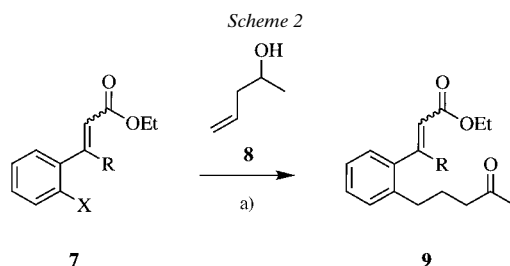
an overall yield of 43% for annelation products was attained: the α,β -unsaturated ketone **5.2** with the *cis/trans*-ratio of 4:1 (isomers clearly distinguished by NOESY experiments) as well as the β,γ -unsaturated ketone **6.2** (all products are, of course, racemic).

These results indicate that hydrated phenanthrene derivatives with a Me group at C(4a) can be constructed by our method, although the yields remain only moderate. Therefore, we studied α,β -unsaturated esters **7** as alternative coupling components.

With the pentenol **8** as olefinic coupling component, the bromoaryl ketone (*E*)-**7.1a** led to the open-chain product **9.1** in high yield (R=H; *Scheme 2*, *Table 2*, *Entry 1*). Obviously, the α,β -unsaturated ester moiety is not reactive enough to undergo an intramolecular *Michael* addition under the slightly basic conditions of the *Heck* reaction nor under the acidic conditions typically applied in the second reaction step (*cf. Scheme 1*). The Me-substituted analogue (*E*)-**7.2a** reacted in the same way (*Entries 2 and 3*), and the corresponding iodo derivative (*E*)-**7.2b** was somewhat more reactive (*Entries 5 and 6*).

Surprisingly the (*Z*)-isomers (*Z*)-**7.2a** and (*Z*)-**7.2b** turned out to be completely unreactive; the 10% yield of coupling product **9.2** of *Entry 10* might be due to an (*E/Z*)-isomerization prior to the *Heck* reaction. An interaction of the intermediary aryl palladium halide with the ester moiety, which is exclusively restricted to the (*Z*)-configuration, seemed to inhibit the coupling reaction.

To increase the reactivity for a cyclization reaction, we transformed the ester **9.2** to the aldehyde **13.2** in a two-step procedure (*Scheme 3*). Compound **9.2** was reduced with LiAlH₄, affecting both C=O groups and resulting in the formation of the diol **12.2**. A double *Swern* oxidation led to the desired aldehyde **13.2**, a sensitive oil with the tendency for auto-oxidation and polymerization. All attempts to cyclize **13.2** by *Michael* addition and subsequent aldol condensation failed: under basic conditions



a) 1 mmol of **7**, 2.5 equiv. of **8**, 5 mol-% of Pd(OAc)₂, EtN(i-Pn)₂, LiCl, 25 ml of DMF, N₂, 80°, 3–10 d.

Table 2. Heck Reaction of Halogenoaryl Esters **7** with Pent-4-en-2-ol **8**

Entry	Substrate	R	X	<i>t</i>	Yield [%]	
					9 (<i>E</i>)/(<i>Z</i>)	Recov. 7
1	(<i>E</i>)- 7.1a	H	Br	2 d	84 (100:0)	–
2	(<i>E</i>)- 7.2a	Me	Br	3 d	62 (87:13)	20
3	(<i>E</i>)- 7.2a	Me	Br	10 d	69 (84:16)	9
4	(<i>Z</i>)- 7.2a	Me	Br	3 d	trace	84
5	(<i>E</i>)- 7.2b	Me	I	3 d	62 (89:11)	19
6	(<i>E</i>)- 7.2b	Me	I	10 d	77 (82:18)	–
7	(<i>Z</i>)- 7.2b	Me	I	3 d	10 (80:20)	74 (16:84)

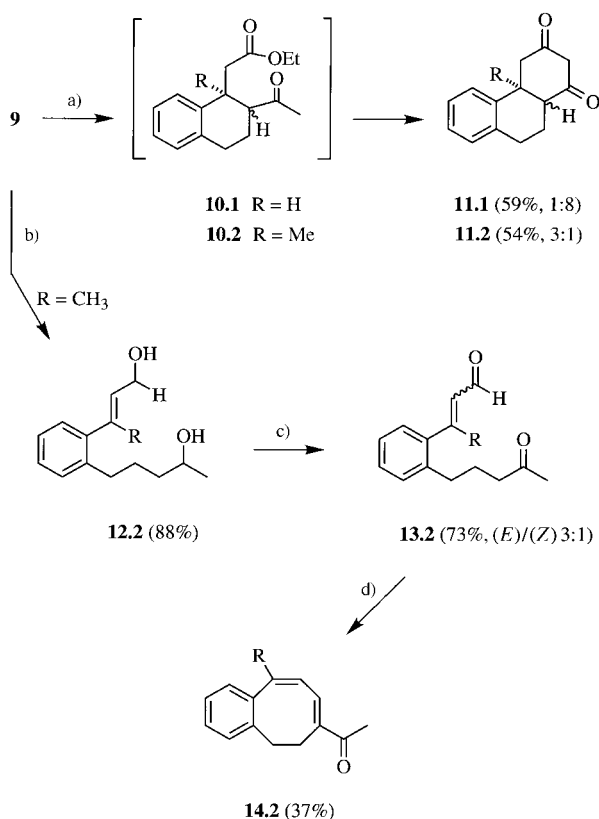
10% *t*-BuOK in THF at room temperature, complete polymerization was observed. The Lewis acid TiCl₄ caused some minor (*E/Z*)-isomerization. An excess of concentrated HCl in THF at reflux temperature led to the isolation of the benzocyclooctene **14.2**, obviously the aldol condensation product of the (*Z*)-isomer (*Z*)-**13.2**. However, under strongly basic conditions (excess NaH in THF/EtOH), the direct double cyclization of the functionalized esters **9** turned out to be successful: phenanthrenes 1,3-diones **11** were obtained in acceptable yields. The diastereoisomers were identified by NOESY spectra; for the *trans*-annulated products, the NOE's between H_{ax}–C(4) and H–C(10a), and between H_{ax}–C(10) and H–C(4a) (for *trans*-**11.1**), or the Me group at C(4a) (for *trans*-**11.2**) are characteristic. The *cis*-annulated products were identified by the NOE between H–C(10a) and H–C(4a) or Me–C(4a). For **11.1**, the *trans*-isomer clearly predominates; in contrast, for the Me-substituted derivative **11.2**, the *cis*-isomer is favored. This finding represents a significant drawback for plans to apply this method to natural product synthesis, since most target molecules of this type are *trans*-annulated. However, the acidity of H–C(10a) allows epimerization at this center and might help to solve this synthetic problem.

Experimental Part

1. *General*. Anal. TLC: precoated plastic sheets POLYGRAM SIL G/UV254 from Macherey-Nagel. M.p. (uncorr.): Reichert Thermovar. IR: Perkin-Elmer 983. UV/VIS: Perkin-Elmer 554; MeCN as solvent. NMR: Bruker DRX 500, Bruker WM 300. ¹H-NMR spectra (500 MHz or 300 MHz): in CDCl₃ (if not mentioned otherwise), TMS internal standard. ¹³C-NMR Spectra (125.8 MHz or 75.5 MHz): using CDCl₃ as solvent and internal standard. MS: MAT 311A (70 eV).

2. *Synthesis of the Coupling Components*. 2.1. *Ethyl* (*E*)-3-(2-Bromophenyl)prop-2-enoate ((*E*)-**7.1a**). A suspension of 3.70 g (20.0 mmol) of 2-bromobenzaldehyde, 4.92 g (21.0 mmol) of triethyl phosphonoacetate

Scheme 3



a) 5 Equiv. of NaH, trace amount of EtOH, THF, room temperature, 16 h; b) LiAlH₄, Et₂O, reflux, 2 h. c) Swern oxidation, –60°, 1 h.

and 526 mg (22.0 mmol) of LiOH in 25 ml of THF was stirred for 3 h at r.t. After filtration through silica gel, the solvent was evaporated and the product mixture fractionated by flash chromatography (FC). TLC (silica gel; petroleum ether/*t*-BuOMe 5:1): *R_f* 0.66 ((*E*)-**7.1a**), 0.11, 0.00. The fraction with *R_f* 0.66 gave 4.79 g (94%) of (*E*)-**7.1a**. Colorless oil. NMR Spectra are in accord with the reported data [8]. ¹H-NMR (300 MHz): 1.33 (*t*, *J* = 7.1, 3 H); 4.26 (*q*, *J* = 7.1, 2 H); 6.37 (*d*, *J* = 15.9, H–C(2)); 7.19 (*t*, *J* = 7.8, 1 H); 7.29 (*t*, *J* = 8.2, 1 H); 7.57 (*m*, 1 H); 7.60 (*m*, 1 H); 8.03 (*d*, *J* = 15.9, H–C(3)). ¹³C-NMR (75.5 MHz): 14.31 (*q*); 60.69 (*t*); 121.18 (*d*, C(2)); 125.29 (*s*, C–2'); 127.70, 127.77, 131.13, 133.43 (4*d*); 134.60 (*s*, C(1')); 142.91 (*d*, C(3)); 166.37 (*s*, C(1)).

2.2. Ethyl 3-Arylbut-2-enoates (**7.2**). General Procedure: A 1.6M soln. of BuLi (8.0 ml, 12 mmol) in hexane was added dropwise at 0° under N₂ to a soln. of 2.81 g (12.5 mmol) of triethyl phosphonoacetate in 20 ml of dry THF. After 30 min stirring at r. t., 10.0 mmol of the acetophenone in 5 ml of dry THF were added, and the reaction mixture was stirred for another 2 d. After hydrolysis with 15 ml of 1M HCl and extracting with AcOEt (3 × 10 ml), the combined org. layer was filtered through silica gel. The solvent was evaporated and the product mixture fractionated by FC.

2.2.1. Ethyl 3-(2-Bromophenyl)but-2-enoate (**7.2a**): 2-Bromoacetophenone (1.99 g, 10.0 mmol) was treated with triethyl phosphonoacetate according to the General Procedure. TLC (silica gel; petroleum ether/*t*-BuOMe 10:1): *R_f* 0.68, 0.57 ((*E*)-**7.2a**), 0.44 ((*Z*)-**7.2a**), 0.00. The first fraction with *R_f* 0.57 gave 1.62 g (60%) of (*E*)-**7.2a**. Colorless oil. UV/VIS: 224 (4.05), 243 (3.84, sh). IR (film): 3056w, 2979w, 1715s, 1641m, 1558w, 1466m, 1432w, 1366w, 1339w, 1287m, 1246m, 1176s, 1121w, 1091w, 1042w, 1026w, 878w, 760m, 656m. ¹H-NMR (500 MHz): 1.31 (*t*, *J* = 7.2, 3 H); 2.48 (*d*, *J* = 1.5, H–C(4)); 4.22 (*q*, *J* = 7.2, 2 H); 5.80 (*q*, *J* = 1.5, H–C(2)); 7.15 (*m*, 1 H);

7.16 (*m*, 1 H); 7.28 (*td*, $J = 7.5, 1.2$, 1 H); 7.55 (*m*, 1 H). NOE (500 MHz); spin saturation at 2.48: 2.48 (–100.0%, 3 H); 4.22 (+0.9%, 2 H); 5.80 (+1.0%, 1 H); 7.15 (+1.1 %, 1 H). ^{13}C -NMR (125 MHz): 14.25 (*q*); 20.32 (*q*, C(4)); 59.93 (*t*); 120.46 (*d*, C(2)); 120.62 (*s*, C(1')); 127.32, 128.81, 129.09, 132.96 (4*d*); 144.64, 156.94 (*s*); 166.26 (*s*, C(1)). EI-MS: 270/268 (4/4, M^+), 225/223 (20/21, $[M - \text{C}_2\text{H}_5\text{O}]^+$), 190 (12), 189 (77, $[M - \text{Br}]^+$), 162 (20), 161 (100, $[M - \text{Br} - \text{C}_2\text{H}_4]^+$), 144 (13, $[M - \text{Br} - \text{C}_2\text{H}_5\text{O}]^+$), 117 (18), 116 (58), 115 (78), 105 (12), 89 (13), 58 (14), 39 (11). Anal. calc. for $\text{C}_{12}\text{H}_{13}\text{BrO}_2$ (269.14): C 53.55, H 4.87; found C 53.76, H 4.87. Second fraction: 833 mg (31%) of (*Z*)-**7.2a**.

Data of (*Z*)-7.2a: Colorless oil. IR (film): 3053*w*, 2981*m*, 2908*w*, 1723*s*, 1646*w*, 1589*w*, 1563*w*, 1469*m*, 1428*m*, 1372*m*, 1352*w*, 1279*m*, 1233*s*, 1164*s*, 1121*w*, 1093*w*, 1046*m*, 1025*m*, 947*w*, 868*w*, 756*m*. UV/VIS: 217 (4.15). ^1H -NMR (500 MHz): 1.04 (*t*, $J = 7.1$, 3 H); 2.14 (*d*, $J = 1.5$, Me–C(4)); 3.96 (*q*, $J = 7.1$, 2 H); 5.99 (*q*, $J = 1.5$, H–C(2)); 7.06 (*dd*, $J = 7.5, 1.7$, 1 H); 7.14 (*m*, 1 H); 7.29 (*td*, $J = 7.5, 1.2$, 1 H); 7.55 (*dd*, $J = 7.9, 1.1$, 1 H). NOE (500 MHz); spin saturation at 2.14: 2.14 (–100.0%, 3 H); 5.99 (+5.0%, H–C(2)); 7.06 (+1.2%, 1 H). ^{13}C -NMR (75.5 MHz): 13.84 (*q*); 25.94 (*q*, C(4)); 59.68 (*t*); 119.72 (*d*, C(2)); 120.21 (*s*, C(2')); 127.08, 127.74, 128.49, 132.33 (4*d*); 142.46, 154.50 (2*s*); 164.93 (*s*, C(1)). EI-MS: 225/223 (16/17, $[M - \text{C}_2\text{H}_5\text{O}]\text{H}^+$), 190 (15), 189 (89, $[M - \text{Br}]^+$), 162 (21), 161 (100, $[M - \text{Br} - \text{C}_2\text{H}_4]^+$), 144 (11, $[M - \text{Br} - \text{C}_2\text{H}_5\text{O}]^+$), 117 (19), 116 (57), 115 (80), 105 (14), 91 (12), 89 (14), 58 (14), 39 (13). Anal. calc. for $\text{C}_{12}\text{H}_{13}\text{BrO}_2$ (269.14): C 53.55, H 4.87; found C 53.55, H 4.85.

2.2.2. Ethyl 3-(2-Iodophenyl)butenoate (7.2b): 2-Iodoacetophenone (2.46 g, 10.0 mmol) was treated with triethyl phosphonoacetate according to the *General Procedure*. TLC (silica gel; petroleum ether/*t*-BuOMe 10:1): R_f 0.77, 0.70 ((*E*)-**7.2b**), 0.66, 0.54 ((*Z*)-**7.2b**), 0.33, 0.00. The first fraction with R_f 0.70 gave 1.97 g (62%) of (*E*)-**7.2b**. Colorless oil. UV/VIS: 222 (4.25, sh). IR (film): 3055*w*, 2979*m*, 1712*s*, 1641*m*, 1582*w*, 1554*w*, 1461*m*, 1428*m*, 1366*m*, 1338*m*, 1284*m*, 1245*m*, 1177*s*, 1115*w*, 1088*w*, 1042*m*, 1014*m*, 945*w*, 877*m*, 760*m*, 742*w*, 647*m*. ^1H -NMR (300 MHz): 1.32 (*t*, $J = 7.1$, 3 H); 2.45 (*d*, $J = 1.4$, 3 H–C(4)); 4.22 (*q*, $J = 7.1$, 2 H); 5.75 (*q*, $J = 1.4$, H–C(2)); 6.99 (*m*, 1 H); 7.12 (*dd*, $J = 7.6, 1.7$, 1 H); 7.33 (*td*, $J = 7.5, 1.2$, 1 H); 7.84 (*dd*, $J = 7.9, 1.2$, 1 H). ^{13}C -NMR (75.5 MHz): 14.32 (*q*); 20.68 (*q*, C(4)); 59.99 (*t*); 95.25 (*s*, C–2'); 120.81 (*d*, C(2)); 127.85, 128.17, 129.07, 139.56 (*d*); 148.82, 159.13, 166.33 (*s*). EI-MS: 316 (0.26, M^+), 271 (12), 189 (65, $[M - \text{I}]^+$), 162 (14), 161 (100, $[M - \text{I} - \text{C}_2\text{H}_4]^+$), 144 (30, $[M - \text{I} - \text{C}_2\text{H}_5\text{O}]^+$), 117 (11), 116 (25), 115 (71), 105 (11). Anal. calc. for $\text{C}_{12}\text{H}_{13}\text{IO}_2$ (316.14): C 45.59, H 4.14; found C 45.60, H 4.11.

Second fraction: 840 mg (27%) of (*Z*)-**7.2b**. Colorless oil. UV/VIS: 221 (4.08). IR (film): 3051*w*, 2980*m*, 2906*w*, 1724*s*, 1645*m*, 1584*w*, 1465*m*, 1440*m*, 1426*m*, 1371*m*, 1351*w*, 1279*m*, 1231*s*, 1159*s*, 1116*w*, 1090*w*, 1046*m*, 1012*m*, 959*w*, 867*w*, 756*m*, 646*m*. ^1H -NMR (300 MHz): 1.04 (*t*, $J = 7.1$, 3 H); 2.13 (*d*, $J = 1.5$, Me–C(4)); 3.97 (*q*, $J = 7.1$, 2 H); 5.98 (*q*, $J = 1.5$, H–C(2)); 6.98 (*ddd*, $J = 7.8, 7.4, 1.7$, 1 H); 7.05 (*dd*, $J = 7.6, 1.7$, 1 H); 7.34 (*td*, $J = 7.5, 1.2$, 1 H); 7.83 (*dd*, $J = 7.9, 1.1$, 1 H). ^{13}C -NMR (75.5 MHz): 13.90 (*q*); 26.13 (*q*, C(4)); 59.74 (*t*); 95.15 (*s*, C(2')); 119.87 (*d*, C(2)); 126.78, 127.95, 128.44, 138.83 (4*d*); 146.70, 156.99 (2*s*); 164.85 (*s*, C(1)). EI-MS: 316 (0.07, M^+), 271 (6), 189 (59, $[M - \text{I}]^+$), 162 (11), 161 (100, $[M - \text{I} - \text{C}_2\text{H}_4]^+$), 144 (17, $[M - \text{I} - \text{C}_2\text{H}_5\text{O}]^+$), 117 (7), 116 (16), 115 (53), 105 (10), 91 (7), 89 (7), 63 (5), 39 (5). Anal. calc. for $\text{C}_{12}\text{H}_{13}\text{IO}_2$ (316.14): C 45.59, H 4.14; found C 45.51, H 4.11.

2.3. 4-Arylpent-3-en-2-ones (3.2). General Procedure. A soln. of 5 mmol of (*E*)-**7.2a** or (*E*)-**7.2b**, and 1.56 g (7.50 mmol) dimethyltitanocene [9] in 25 ml of dry THF was heated under N_2 at reflux temp. for 64 h. After hydrolysis with 10 ml of 1*M* HCl for 1 h at r. t. and extracting twice with 20 ml of methyl-*t*-BuOMe, the combined org. layer was filtered through silica. The solvent was evaporated, and the crude product mixture was purified by bulb-to-bulb distillation at 125°/0.5 mbar. The distillate was further purified by FC.

2.3.1. (*E*)-4-(2-Bromophenyl)pent-3-en-2-one ((E)-3.2a). The ester (*E*)-**7.2a** (1.35 g, 5.00 mmol) was treated with dimethyltitanocene according to the *General Procedure*. TLC (silica gel, petroleum ether/6:1): R_f 0.89, 0.85, 0.78 ((*E*)-**7.2a**), 0.56 ((*E*)-**3.2a**), 0.37, 0.00. The first fraction with R_f 0.78 gave 609 mg (45%) of recovered starting material (*E*)-**7.2a**. Second fraction with R_f 0.56: 542 mg (45%); 83% based on recovered starting material) of (*E*)-**3.2a**. Slightly yellow oil. UV/VIS: 223 (4.18), 251 (3.94, sh). IR (film): 3054*w*, 3003*w*, 2959*w*, 2916*w*, 1686*s*, 1616*s*, 1559*w*, 1467*m*, 1424*m*, 1371*m*, 1356*m*, 1284*w*, 1262*w*, 1244*w*, 1179*m*, 1121*w*, 1091*w*, 1027*m*, 963*w*, 857*w*, 755*m*, 724*w*, 671*w*, 639*w*. ^1H -NMR (300 MHz): 2.27 (*s*, 3 H–C(1)); 2.44 (*d*, $J = 1.4$, 3 H–C(5)); 6.18 (*q*, $J = 1.4$, H–C(3)); 7.13–7.20 (*m*, 2 H); 7.31 (*m*, 1 H); 7.60 (*m*, 1 H). ^{13}C -NMR (75.5 MHz): 20.73 (*q*, C(5)); 32.03 (*q*, C(1)); 120.75 (*s*, C(2)); 127.39, 127.50, 128.84, 129.14, 133.08 (5*d*); 144.87 (*s*, C(1')); 154.92 (*s*, C(4)); 198.80 (*s*, C(2)). EI-MS: 240/238 (7/7, M^+), 225/223 (5/6, $[M - \text{Me}]^+$), 160 (16), 159 (100, $[M - \text{Br}]^+$), 144 (16), 116 (54), 115 (37), 89 (8), 58 (8), 43 (32, $[\text{C}_2\text{H}_5\text{O}]^+$). Anal. calc. for $\text{C}_{11}\text{H}_{11}\text{BrO}$ (239.11): C 55.25, H 4.64; found C 55.40, H 4.64.

2.3.2. (*E*)-4-(2-Iodophenyl)pent-3-en-2-one ((E)-3.2b). The ester (*E*)-**7.2b** (1.90 g, 6.00 mmol) was treated with 1.42 g (6.82 mmol) of dimethyltitanocene according to the *General Procedure*. TLC (silica gel; petroleum

ether/*t*-BuOMe 5:1): R_f 0.70 ((*E*)-**7.2b**), 0.56 ((*E*)-**3.2b**), 0.00. The first fraction with R_f 0.70 gave 793 mg (42%) of recovered starting material (*E*)-**7.2b**. Second fraction with R_f 0.56: 864 mg (50%; 86% based on recovered starting material) of (*E*)-**3.2b**. Yellow oil. UV/VIS: 228 (4.11), 268 (3.56, sh). IR (film): 3051w, 3002w, 1688s, 1613s, 1554w, 1461m, 1428m, 1355m, 1282w, 1258w, 1244w, 1182m, 1039w, 1014m, 963w, 857w, 756m, 721w, 662m. $^1\text{H-NMR}$ (300 MHz): 2.28 (s, 3H-C(1)); 2.41 (d, $J = 1.4$, 3H-C(5)); 6.13 (q, $J = 1.3$, H-C(3)); 6.99 (td, $J = 7.4$, 1.7, 1 H); 7.13 (ddd, $J = 7.5$, 1.8, 0.2, 1 H); 7.34 (td, $J = 7.5$, 1.2, 1 H); 7.85 (ddd, $J = 7.9$, 1.2, 0.3, 1 H). $^{13}\text{C-NMR}$ (75.5 MHz): 20.95 (q, C(5)); 31.97 (q, C(1)); 95.35 (s, C(2')); 127.57, 127.72, 128.14, 129.05, 139.44 (5d); 148.66 (s, C(1')); 157.10 (s, C(4)); 198.79 (s, C(2)). EI-MS: 286 (0.5, M^+), 160 (17), 159 (100, $[M - I]^+$), 144 (31), 117 (5), 116 (23), 115 (39), 91 (9), 89 (8), 63 (6), 43 (39, $\text{C}_2\text{H}_3\text{O}^+$), 39 (6). Anal. calc. for $\text{C}_{11}\text{H}_{11}\text{IO}$ (286.11): C 46.18, H 3.88; found: C 46.45, H 3.84.

3. Palladium-Catalyzed Coupling Reactions and Subsequent Carbonyl Reactions.

3.1. *General Procedure for the Palladium-Catalyzed Coupling Reactions.* A mixture of 1.00 mmol of the ketone **3.2** or the esters **7**, 180 mg (2.50 mmol) of butenol **4** or pentenol **8**, 11.2 mg (50 μmol , 5 mol-%) $\text{Pd}(\text{OAc})_2$, 1.0 g (8.0 mmol) of $\text{EtN}(\text{i-Pr})_2$, and 42 mg (1.0 mmol) of LiCl in dry DMF (10 ml for **3.2** and 25 ml in the case of **7**) in a sealed tube was stirred under N_2 at 80° for 2–10 d. After addition of 50 ml of H_2O , the mixture was extracted three times with *t*-BuOMe (3×20 ml), the combined org. layer was washed with 50 ml of H_2O , and the H_2O layer re-extracted with 10 ml of AcOEt. After filtering the combined org. layer through silica gel, the soln. was concentrated at $50^\circ/0.5$ mbar by bulb-to-bulb distillation. For coupling reactions with ketones **3.2**, the crude product mixture was treated under acidic conditions in CHCl_3 before the reaction mixture was fractionated by FC.

3.2. *Coupling Reaction of 3.2a with But-3-en-1-ol (4; Entry 2 of Table I):* The ketone (*E*)-**3.2a** (239 mg, 1.00 mmol) and butenol **4** (180 mg, 2.50 mmol) were coupled under palladium catalysis according to the *General Procedure* (reaction time: 3 d). The crude product mixture was treated with 19 mg (10 mol-%) TsOH in 10 ml of CHCl_3 for 2 d at reflux temp. After neutralization with 100 mg of NaHCO_3 , the soln. was filtered through silica gel and concentrated. TLC (silica gel; petroleum ether/*t*-BuOMe 1:2): R_f 0.88, 0.81, 0.73 ((*E*)-**3.2a**, (*E*)-**3.2c** ($X = \text{H}$)), 0.62 ((*Z*)-**3.2a**), 0.50 (*cis*-**5.2**), 0.35, 0.27, 0.00. FC was performed with petroleum ether/*t*-BuOMe 15:1. First fraction: 97 mg of a mixture of starting material ((*E*)-**3.2a**) and (*E*)-4-phenylpent-3-en-2-one ((*E*)-**3.2c**; $X = \text{H}$) in the ratio 7.5:1.0. Second fraction: 52 mg (22%) of isomerized starting material ((*Z*)-**3.2a**) as a brown oil. UV/VIS: 220 (4.20), 249 (3.74, sh). IR (film): 2970w, 1688s, 1665s, 1618s, 1587w, 1467m, 1424m, 1370w, 1356m, 1260w, 1179m, 1094w, 1025s, 963w, 859w, 800w, 759s, 725w, 669m, 657m. $^1\text{H-NMR}$ (300 MHz): 1.83 (s, 3H-C(1)); 2.14 (d, $J = 1.5$, 3H-C(5)); 6.23 (q, $J = 1.4$, H-C(3)); 7.09 (dd, $J = 7.5$, 1.7, 1 H); 7.18 (t, $J = 7.7$, 1 H); 7.32 (dd, $J = 7.5$, 1.2, 1 H); 7.58 (d, $J = 8.5$, 1 H). $^{13}\text{C-NMR}$ (75.5 MHz): 26.30 (q, C(5)); 29.66 (q, C(1)); 120.30 (s, C(2')); 127.51, 128.19, 129.00, 129.16, 132.72 (5d); 142.09 (s, C(1')); 151.90 (s, C(4)); 197.81 (s, C(2)). EI-MS: 240/238 (2.5/2.5, M^+), 160 (14), 159 (100, $[M - \text{Br}]^+$), 144 (12), 116 (39), 115 (29), 89 (7), 58 (8), 43 (32). Anal. calc. for $\text{C}_{11}\text{H}_{11}\text{BrO}$ (239.11): C 55.25, H 4.64; found: C 55.05, H 4.60.

Third fraction: 30 mg (14%) of (*4aR**,*10aR**)-3,4,4a,9,10,10a-hexahydro-4a-methylphenanthren-3-one (*cis*-**5.2**). Colorless oil. UV/VIS: 212 (4.10), 228 (3.89, sh), 264 (2.84), 272 (2.77). IR (film): 3020w, 2933m, 2874m, 1676s, 1488m, 1445m, 1386m, 1331w, 1292w, 1250w, 1177w, 1141w, 1092w, 1076w, 1042w, 946w, 899w, 885w, 839w, 809w, 761m, 729m. $^1\text{H-NMR}$ (500 MHz): 1.42 (s, 3 H); 1.88 (m, $\text{H}_{\text{ax}}-\text{C}(10)$); 2.13 (m, $\text{H}_{\text{eq}}-\text{C}(10)$); 2.57 (d, $J = 16.2$, $\text{H}_\text{A}-\text{C}(4)$); 2.60 (m, H-C(10a)); 2.85 (m, 2 H-C(9)); 2.88 (d, $J = 16.2$, $\text{H}_\text{B}-\text{C}(4)$); 5.99 (dd, $J = 10.1$, 2.0, H-C(2)); 6.87 (dd, $J = 10.1$, 4.0, H-C(1)); 7.06 (dd, $J = 7.6$, 0.9, 1 H); 7.11 (t, $J = 7.3$, 1.3, 1 H); 7.18 (t, $J = 7.1$, 1 H); 7.28 (dd, $J = 7.9$, 1.1, 1 H). $^{13}\text{C-NMR}$ (125.8 MHz): 24.34 (t, C(10)); 28.81 (t, C(9)); 29.45 (q); 39.38 (s, C(4a)); 43.43 (d, C(10a)); 50.05 (t, C(4)); 126.13, 126.56, 126.68 (3d); 128.99 (d, C(2)); 129.17 (d); 134.76, 141.87 (2s); 152.36 (d, C(1)); 198.89 (s, C(3)). EI-MS: 213 (14, $[M + 1]^+$), 212 (86, M^+), 198 (16), 197 (100, $[M - \text{Me}]^+$), 179 (22), 169 (23), 155 (15), 153 (10), 142 (13), 141 (24), 129 (21), 128 (21), 115 (21), 91 (13), 81 (16). Anal. calc. for $\text{C}_{15}\text{H}_{16}\text{O}$ (212.29): C 84.87, H 7.60; found: C 84.80, H 7.59.

3.3. *Coupling Reaction of 3.2b with 4 (Entry 3 of Table I).* The ketone (*E*)-**3.2b** (286 mg, 1.00 mmol) and 180 mg (2.50 mmol) of **4** were coupled under palladium catalysis according to the *General Procedure* (reaction time: 3 d). The crude product mixture was treated with 0.1 g of conc. HCl in 10 ml of CHCl_3 in the ultrasonic bath for 4 h at 40° . After neutralization with 100 mg of NaHCO_3 , the soln. was filtered through silica gel and concentrated. TLC (silica gel; petroleum ether/*t*-BuOMe 1:2): R_f 0.81, 0.66 (**6**), 0.57 (*trans*-**5.2**), 0.48 (*cis*-**5.2**), 0.19, 0.00. FC was performed with petroleum ether/*t*-BuOMe 10:1. First fraction: 44 mg (21%) of 2,3,4,4a,9,10-hexahydro-4a-methylphenanthren-3-one (**6**). Slightly yellow oil. IR (film): 3055w, 3018m, 2960s, 2930s, 2843m, 1715s, 1600w, 1487w, 1444w, 1398m, 1377m, 1350m, 1307m, 1242m, 1179w, 1151w, 1076w, 1039m, 1005m, 969w, 937w, 867w, 837w, 766s, 737m, 704m, 669m. $^1\text{H-NMR}$ (500 MHz, CDCl_3): 1.36 (d, $J = 0.8$, 3 H); 2.50 (m, 2 H-C(10)); 2.59 (dd, $J = 13.8$, 0.8, $\text{H}_{\text{ax}}-\text{C}(4)$); 2.82–3.02 (m, 2 H-C(2), $\text{H}_{\text{eq}}-\text{C}(4)$, 2 H-C(9)); 5.55 (m,

H–C(1)); 7.10–7.15 (*m*, 2 H); 7.20–7.25 (*m*, 2 H). ¹H-NMR (500 MHz, C₆D₆): 1.17 (*d*, *J* = 0.8, 3 H); 2.07 (*ddd*, *J* = 13.1, 4.8, 2.8, H_{eq}–C(10)); 2.16 (*m*, H_{ax}–C(10)); 2.22 (*dd*, *J* = 13.5, 0.8, H_{ax}–C(4)); 2.52 (*ddd*, *J* = 21.9, 3.9, 2.2, H_A–(2)); 2.56–2.65 (*m*, H_B–C(2), 2 H–C(9)); 2.78 (*d*, *J* = 13.5); 5.04 (*m*, H–C(1)); 6.90–6.92 (*m*, H–C(5), H–C(8)); 6.98 (*t*, *J* = 7.3, 1 H); 7.02 (*t*, *J* = 7.5, 1 H). ¹³C-NMR (75.5 MHz, C₆D₆): 29.36 (*q*, Me); 30.04 (*t*, C(10)); 32.00 (*t*, C(9)); 39.63 (*t*, C(2)); 41.76 (*s*, C(4a)); 53.82 (*t*, C(4)); 116.80 (*d*, C(1)); 126.09, 126.66, 126.99, 129.03 (4*d*); 135.88, 143.66, 143.93 (3*s*); 207.07 (*s*, C(3)). EI-MS: 213 (9, [*M* + 1]⁺), 212 (55, *M*⁺), 198 (16), 197 (100, [*M*–Me]⁺), 170 (31), 169 (71), 155 (21), 154 (14), 153 (14), 152 (10), 141 (28), 128 (19), 115 (15), 91 (10). HR-MS: calc. for C₁₅H₁₆O (212.29): 212.12012; found 212.12018.

Second fraction: 10.1 mg (5%) of (4*a*R*,10*a*S*)-3,4,4*a*,9,10,10*a*-hexahydro-4*a*-methylphenanthren-3-one (*trans*-**5.2**). Slightly yellow oil. UV/VIS: 212 (4.11), 230 (3.93, sh), 272 (2.80), 334 (2.80). IR (film): 3023*w*, 2935*m*, 1675*s*, 1487*m*, 1446*w*, 1384*w*, 1324*w*, 1264*w*, 1240*w*, 1167*w*, 1065*w*, 1043*w*, 1027*w*, 882*w*, 801*w*, 759*m*, 721*w*. ¹H-NMR (500 MHz): 1.15 (*d*, *J* = 1.1, 3 H); 1.95 (*m*, 1 H, H_{ax}–C(10)); 2.04 (*m*, H_{eq}–C(10)); 2.53 (*dq*, *J* = 16.1, 1.1, H_{ax}–C(4)); 2.82 (*m*, H–C(10*a*)); 3.02 (*m*, 2 H–C(9)); 3.12 (*d*, *J* = 16.1, H_{eq}–C(4)); 6.12 (*ddd*, *J* = 9.9, 3.1, 1.1, H–C(2)); 6.78 (*dd*, *J* = 9.0, 2.0, H–C(1)); 7.11–7.21 (*m*, 4 H). ¹³C-NMR (75.5 MHz): 22.82 (*q*); 23.49 (*t*, C(10)); 28.94 (*t*, C(9)); 40.39 (*s*, C(4a)); 42.23 (*d*, C(10*a*)); 51.17 (*t*, C(4)); 123.97, 126.18, 126.38 (3*d*); 129.31 (*d*, C(2)); 129.69 (*d*); 134.44, 144.52 (*s*); 153.31 (*d*, C(1)); 199.41 (*s*, C(3)). EI-MS: 213 (11, [*M* + 1]⁺), 212 (63, *M*⁺), 198 (15), 197 (100, [*M*–Me]⁺), 179 (12), 169 (30), 157 (12), 155 (11), 142 (11), 141 (17), 129 (16), 115 (16), 91 (12), 81 (22). Anal. calc. for C₁₅H₁₆O (212.29): C 84.87, H 7.60; found: C 84.65, H 7.54.

Third fraction: 38 mg (18%) of *cis*-**5.2** as a colorless oil (for spectroscopic data, see 3.2).

3.4. *Coupling Reaction of (E)-7.1a with Pent-4-en-2-ol (8; Entry 1 of Table 2)*. The ester (*E*)-**7.1a** (255 mg, 1.00 mmol) and pentenol **8** (215 mg, 2.50 mmol) were coupled under Pd catalysis according to the *General Procedure* (reaction time: 2 d). TLC (silica gel; petroleum ether/*t*-BuOMe 1:1): *R*_f 0.50 ((*E*)-**9.1**), 0.20, 0.00. FC is performed with petroleum ether/*t*-BuOMe 3:1 to give 218 mg (84%) of *ethyl (E)-3-bromo-3-[2-(4-oxophenyl)phenyl]prop-2-enoate* ((*E*)-**9.1**). Colorless oil. UV/VIS: 221 (4.17), 228 (4.06, sh), 276 (4.28). IR (film): 3065*w*, 2961*m*, 1706*m*, 1628*m*, 1599*w*, 1481*w*, 1363*m*, 1261*s*, 1158*s*, 1097*s*, 1030*s*, 866*w*, 766*m*. ¹H-NMR (300 MHz): 1.35 (*t*, *J* = 7.1, 3 H); 1.85 (*m*, 2 H); 2.12 (*s*, 3 H); 2.47 (*t*, *J* = 7.1, 2 H); 2.76 (*t*, *J* = 7.7, 2 H); 4.29 (*t*, *J* = 7.1, 2 H); 6.37 (*d*, *J* = 15.7, 1 H); 7.17–7.33 (*m*, 3 H); 7.56 (*dd*, *J* = 7.7, 0.9, 1 H); 8.01 (*d*, *J* = 15.8, 1 H). ¹³C-NMR (75.5 MHz): 14.26 (*q*); 25.17 (*t*); 29.80 (*q*); 32.24, 42.69, 60.41 (3*t*); 119.70, 126.58, 126.61, 129.98, 130.01 (5*d*); 133.02, 141.22 (2*s*); 141.79 (*d*); 166.85, 208.08 (2*s*). EI-MS: 260 (16, *M*⁺), 214 (28, [*M*–C₂H₆O]⁺), 203 (23), 157 (27), 144 (26), 131 (20), 130 (22), 129 (100, C₉H₉O⁺), 128 (40), 116 (13), 115 (24), 43 (38, MeCO⁺). Anal. calc. for C₁₆H₂₀O₃ (260.33): C 73.82, H 7.74; found: C 73.58, H 7.80.

3.5. *Coupling Reaction of (E)-7.2b with Pent-4-en-2-ol (8; Entry 6 of Table 2)*. The ester (*E*)-**7.2b** (316 mg, 1.00 mmol) and **8** (215 mg, 2.50 mmol) were coupled under Pd catalysis according to the *General Procedure* (reaction time: 10 d). TLC (silica, petroleum ether/*t*-BuOMe 2:1): *R*_f 0.70, 0.35 ((*E*)-**9.2**), 0.28 ((*Z*)-**9.2**), 0.10, 0.00. FC was performed with petroleum ether/*t*-BuOMe 4:1; first fraction: 173 mg (63%) of (*E*)-**9.2**. Colorless oil. UV/VIS: 211 (4.39), 245 (3.92). IR (film): 3058*w*, 2980*w*, 2938*w*, 1711*s*, 1640*m*, 1599*m*, 1482*w*, 1443*m*, 1366*m*, 1337*m*, 1274*m*, 1174*s*, 1115*w*, 1095*w*, 1073*w*, 1042*m*, 946*w*, 878*w*, 765*m*, 704*w*. ¹H-NMR (300 MHz): 1.31 (*t*, *J* = 7.1, 3 H); 1.85 (*m*, 2 H); 2.12 (*s*, 3 H); 2.43 (*t*, *J* = 7.3, 2 H); 2.45 (*d*, *J* = 1.4, 3 H); 2.59 (*m*, 2 H); 4.21 (*q*, *J* = 7.1, 2 H); 5.76 (*q*, *J* = 1.4, 1 H); 7.05 (*d*, *J* = 8.0, 1 H); 7.10–7.27 (*m*, 3 H). ¹³C-NMR (125.8 MHz): 14.31, 21.49 (2*q*); 25.14 (*t*); 29.83 (*q*); 32.06, 43.17, 59.85 (3*t*); 119.69, 126.01, 127.34, 127.82, 129.28 (5*d*); 137.82, 143.79, 157.93, 166.48, 208.34 (5*s*). EI-MS: 274 (3, *M*⁺), 229 (19, [*M*–C₂H₅O]⁺), 228 (38, [*M*–C₂H₆O]⁺), 200 (11), 171 (35), 158 (35), 145 (12), 144 (19), 143 (100, C₁₀H₇O⁺), 142 (42), 141 (14), 129 (27), 128 (36), 115 (15), 43 (40, CH₃CO⁺). Anal. calc. for C₁₇H₂₂O₃ (274.36): C 74.42, H 8.08; found: C 74.40, H 8.02.

Second fraction: 39 mg (14%) of ((*Z*)-**9.2**). Slightly yellow oil. UV/VIS: 208 (4.34, sh). IR (film): 2981*m*, 1714*s*, 1642*m*, 1486*w*, 1442*m*, 1372*m*, 1278*m*, 1231*m*, 1158*s*, 1115*w*, 1046*m*, 947*w*, 870*w*, 756*w*. ¹H-NMR (300 MHz): 1.02 (*t*, *J* = 7.1, 3 H); 1.84 (*m*, 2 H); 2.10 (*s*, 3 H); 2.14 (*d*, *J* = 1.5, 3 H); 2.44–2.53 (*m*, 4 H); 3.95 (*q*, *J* = 7.1, 2 H); 5.97 (*q*, *J* = 1.5, 1 H); 6.96 (*dd*, *J* = 8.0, 1.1, 1 H); 7.17–7.26 (*m*, 3 H). ¹³C-NMR (125.8 MHz): 13.92 (*q*); 24.50 (*t*); 27.63, 29.81 (2*q*); 31.91, 43.18, 59.61 (*t*); 119.11, 125.83, 126.38, 127.30, 128.59 (5*d*); 136.90, 141.09, 156.14, 165.38, 208.63 (5*s*). EI-MS: 274 (5, *M*⁺), 229 (23, [*M*–C₂H₅O]⁺), 228 (38, [*M*–C₂H₆O]⁺), 217 (23), 171 (30), 161 (11), 158 (20), 145 (14), 144 (18), 143 (100, C₁₀H₇O⁺), 142 (31), 141 (11), 129 (23), 128 (28), 115 (13), 43 (32) [CH₃CO⁺]. Anal. calc. for C₁₇H₂₂O₃ (274.36): C 74.42, H 8.08; found: C 74.42, H 8.05.

3.6. *1,2,3,4,4*a*,9,10,10*a*-Octahydrophenanthrene-1,3-dione (11.1)*: A soln. of 195 mg (750 μmol) of (*E*)-**9.1** in 1 ml of dry THF/5 μl of dry EtOH was added to a suspension of 86 mg (3.75 mmol) of NaH (applied as a 60% mixture with mineral oil) in 10 ml of dry THF. After stirring for 16 h at r.t., the mixture was hydrolyzed dropwise with 10 ml 1*M* HCl and extracted with AcOEt (3 × 20 ml). The combined org. layer was filtered through silica gel and the solvent removed *in vacuo*. TLC (silica gel, petroleum ether/AcOEt 1:2): *R*_f 0.78, 0.34, 0.21 (**11.1**),

0.00. Purification by FC gave 94 mg (59%) of **11.1**. Colorless solid. M.p. 197°. According to ¹H-NMR ((D₆)DMSO) the *cis/trans*-ratio is 1:8. The minor *cis*-isomer was detected by the *s* of H–C(2) at 5.26 ppm (enol tautomer in (D₆)DMSO). IR (KBr): 3058w, 2923m, 2892m, 2541m, 1615s, 1524s, 1482s, 1367s, 1309s, 1224s, 1176m, 1131m, 1110w, 1074w, 1040w, 1006w, 972m, 953m, 923m, 826w, 761w, 748m, 433w. ¹H-NMR (500 MHz, CDCl₃; keto/enol ratio 6:1): signals of the keto form: 1.76 (*m*, H_{ax}–C(10)); 2.43 (*ddt*, *J* = 13.8, 5.2, 3.3, H_{eq}–C(10)); 2.60 (*dd*, *J* = 12.1, 3.0, H–C(10a)); 2.67 (*dd*, *J* = 15.9, 13.2, H_{ax}–C(4)); 2.93 (*m*, 2 H–C(9)); 3.07 (*td*, *J* = 12.9, 4.0, H–C(4a)); 3.44 (*ddd*, *J* = 16.1, 4.3, 1.5, H_{eq}–C(4)); 3.52 (*dd*, *J* = 17.5, 1.5, H_{eq}–C(2)); 3.58 (*d*, *J* = 17.5, H_{ax}–C(2)); 7.16–7.25 (*m*, 4 H); typical signal of the enol form are detected: 5.61 (*s*, H–C(2)). ¹H-NMR (500 MHz, (D₆)DMSO; exclusively signals of the enol form are detected): 1.37 (*m*, H_{ax}–C(10)); 2.19 (*t*, *J* = 11.3, H–C(10a)); 2.34–2.43 (*m*, H_{ax}–C(4), H_{eq}–C(10)); 2.82 (*m*, 2 H–C(9)); 3.00 (*td*, *J* = 12.0, 4.1, H–C(4a)); 3.07 (*dd*, *J* = 16.8, 4.5, H_{eq}–C(4)); 5.32 (*s*, H–C(2)); 7.09–7.17 (*m*, 3 H); 7.30 (*d*, *J* = 7.5, H–C(5)); 11.16 (*s*, OH). ¹³C-NMR (125.8 MHz, CDCl₃): 21.82 (*t*, C(10)); 28.87 (*t*, C(9)); 35.80 (*d*, C(4a)); 46.43 (*t*, C(4)); 51.74 (*d*, C(10a)); 57.59 (*t*, C(2)); 126.13, 126.52, 127.02, 129.48 (4*d*); 136.00, 136.82, 203.31, 203.59 (4*s*). EI-MS: 214 (14, M⁺), 186 (12), 185 (13), 157 (79), 144 (37), 143 (20), 141 (11), 130 (60), 129 (100), 128 (69), 116 (14), 115 (44), 91 (12), 77 (10), 71 (10), 64 (10), 63 (11), 51 (14), 40 (15). Anal. calc. for C₁₄H₁₄O₂ (214.26): C 78.48, H 6.59; found: C 78.48, H 6.61.

3.7. 1,2,3,4,4a,9,10,10a-Octahydro-4a-methylphenanthrene-1,3-dione (**11.2**). A soln. of 187 mg (682 μmol) of (*E*)-**9.2** in 1 ml of dry THF/5 μl of dry EtOH was added to a suspension of 86 mg (3.75 mmol) of NaH (applied as 60% mixture with mineral oil) in 10 ml of dry THF. After stirring for 16 h at r. t., the mixture was hydrolyzed dropwise with 10 ml, 1M HCl and extracted with AcOEt (3 × 20 ml). The combined org. layer was filtered through silica gel and the solvent removed *in vacuo*. TLC (silica gel; petroleum ether/AcOEt 1:2): *R*_f 0.92, 0.75, 0.30 (*trans*-**11.2**), 0.21 (*cis*-**11.2**), 0.00. Purification by FC gave 84 mg (54%) of **11.2** with the *cis/trans*-ratio 3:1. A pure sample of *trans*-**11.2** was obtained by crystallization from petroleum ether/AcOEt 4:1. Slightly yellow solid. M.p. 78°. IR (KBr): 3406m, 3060m, 3018m, 2964s, 1702w, 1605s, 1490m, 1445m, 1409m, 1374m, 1338m, 1255s, 1222s, 1175s, 1145w, 1126w, 1089w, 1067w, 1043w, 995w, 942w, 851w, 831w, 796w, 761s, 724w, 685w, 649w, 565w, 451w. ¹H-NMR (500 MHz, CDCl₃; keto/enol ratio 12:1) signals of the keto form: 1.05 (*s*, 3 H); 1.87 (*m*, H_{ax}–C(10)); 2.27 (*ddt*, *J* = 14.1, 6.2, 1.4, H_{eq}–C(10)); 2.83 (*d*, *J* = 15.1, H_{ax}–C(4)); 2.87–3.02 (*m*, 2 H–C(9), H–C(10a)); 3.32 (*dd*, *J* = 15.0, 2.1, H_{eq}–C(4)); 3.42 (*dd*, *J* = 17.6, 2.1, H_{eq}–C(2)); 3.54 (*d*, *J* = 17.6, H_{ax}–C(2)); 7.13–7.25 (*m*, 4 H); selected signals of the enol form: 1.20 (*s*, 3 H); 5.61 (*s*, H–C(2)). ¹³C-NMR (125.8 MHz, CDCl₃): signals of the keto form: 17.80 (*t*, C(10)); 25.02 (*q*); 28.84 (*t*, C(9)); 36.91 (*s*, C(4a)); 54.48 (*t*, C(4)); 55.09 (*d*, C(10a)); 57.62 (*t*, C(2)); 125.54, 126.60, 126.77, 129.72 (4*d*); 135.15, 142.01, 203.57, 203.84 (4*s*). EI-MS: 228 (64, M⁺), 213 (34, [M – Me]⁺), 171 (61), 158 (23), 144 (34), 143 (100), 142 (28), 141 (18), 130 (21), 129 (54), 128 (54), 115 (26). Anal. calc. for C₁₅H₁₆O₂ (228.29): C 78.92, H 7.06; found: C 78.92, H 7.06.

cis-**11.2**: ¹H-NMR (500 MHz, CDCl₃; keto/enol ratio 3:4): selected signals of the keto form: 1.38 (*s*, 3 H); 2.68 (*d*, *J* = 15.8, H_A–C(4)); 3.19 (*d*, *J* = 15.5, H_B–C(4)); selected signals of the enol form: 1.45 (*s*, 3 H); 2.48 (*d*, *J* = 17.6, H_A–C(4)); 2.73 (*d*, *J* = 17.6, H_B–C(4)); 5.54 (*s*, H–C(2)); 7.95 (*br. s*, OH). ¹³C-NMR (125.8 MHz, CDCl₃): signals of the keto form: 21.96, 27.64 (2*t*); 29.66 (*q*); 36.53 (*s*, C(4a)); 52.64, 55.96 (*t*); 56.07 (*d*, C(10a)); 126.02, 126.84, 126.92, 129.67 (4*d*); 134.75, 140.16, 202.61, 207.08 (4*s*); signals of the enol form: 23.69 (*t*); 27.77 (*q*, Me); 29.57 (*t*); 37.99 (*s*, C(4a)); 45.17 (*t*, C(4)); 49.51 (*d*, C(10a)); 102.80 (*d*, C(2)); 126.10, 126.24, 126.55, 129.32 (4*d*); 134.97, 142.40, 191.16, 192.49 (4*s*).

3.8. (*E*)-3-[2-(4-Hydroxy-1-pentyl)phenyl]but-2-en-1-ol ((*E*)-**12.2**). A soln. of 846 mg (3.08 mmol) of (*E*)-**9.2** was added dropwise at 0° to a suspension of 96 mg (2.5 mmol) of LiAlH₄ in 25 ml of dry Et₂O. After stirring for 2 h at reflux the mixture was cooled to r. t. and hydrolyzed with 300 μl of H₂O, 100 μl of 15 weight-% aq. NaOH soln., and again with 300 μl of H₂O. The precipitate was filtered off through silica gel and the solvent removed *in vacuo*. TLC (silica gel, petroleum ether/AcOEt 1:2): *R*_f 0.34 ((*E*)-**12.2**), 0.00. Purification by FC gave 633 mg (88%) of (*E*)-**12.2**. Colorless oil. IR (film): 3316 *s* (*br.*), 3059m, 3014m, 2931s, 2864s, 1658w, 1599w, 1483s, 1443s, 1374m, 1333w, 1212w, 1170w, 1129m, 1068m, 1008s, 942m, 860w, 808w, 759s, 704m. ¹H-NMR (300 MHz): 1.08 (*d*, *J* = 6.2, 3 H); 1.44 (*m*, 2 H); 1.65 (*m*, 2 H); 1.96 (*t*, *J* = 0.6, 3 H); 2.51 (*m*, 1 H); 2.67 (*m*, 1 H); 2.75–3.45 (*br.*, 2 OH); 3.79 (*q*, *J* = 6.2, 1 H); 4.26 (*m*, 2 H); 5.51 (*m*, 1 H); 7.03 (*d*, *J* = 7.1, 1 H); 7.07–7.25 (*m*, 3 H). ¹³C-NMR (75.5 MHz): 18.93, 23.68 (*q*); 27.71, 32.97, 38.93, 59.13 (3*t*); 67.27, 125.64, 126.86, 128.18, 128.24, 129.25 (6*d*); 138.90, 139.19, 144.43 (3*s*). EI-MS: 234 (0.33; M⁺), 183 (14), 159 (13), 158 (34), 157 (15), 156 (25), 155 (25), 147 (13), 146 (11), 145 (38), 144 (19), 143 (100), 142 (26), 141 (26), 131 (32), 130 (18), 129 (51), 128 (42), 117 (26), 115 (22), 91 (26), 45 (11), 43 (11). Anal. calc. for C₁₅H₂₂O₂ (234.34): C 76.88, H 9.46; found: C 76.79, H 9.47.

3.9. 3-[2-(4-Oxo-1-pentyl)phenyl]but-2-enal (**13.2**). A soln. of 881 mg (11.3 mmol) dry DMSO in 1 ml dry of CH_2Cl_2 was added at -60° under N_2 to a soln. of 713 mg (5.63 mmol) of oxalyl chloride in 20 ml of dry CH_2Cl_2 . After stirring for 30 min, a soln. of 601 mg (2.56 mmol) of diol **12.2** in 5 ml of dry CH_2Cl_2 was added, and stirring was continued for 1 h at -60° . The mixture was treated with 1.0 ml (8.0 mmol) of Et_3N , hydrolyzed at r. t. with 10 ml of H_2O . The org. layer was washed with 10 ml of 1M HCl and with 10 ml of sat. aq. NaHCO_3 soln., and filtered through silica. TLC (silica gel; petroleum ether/*t*-BuOMe 2:1): R_f 0.81, 0.72, 0.32, 0.29 (**13.2**), 0.11, 0.00. The solvent was removed *in vacuo* and purification by FC afforded 433 mg (73%) of **13.2** with a (*E*)/(*Z*)-ratio of 3:1 as a yellow oil. Because of its tendency to decompose at r. t. in the presence of air, **13.2** was immediately cyclized under appropriate conditions (see 3.10).

Selected spectroscopic data of **13.2**: $^1\text{H-NMR}$ (500 MHz): (*E*)-**13.2**: 1.85 (*m*, 2 H); 2.12 (*d*, $J=0.7$, 3 H); 2.45 (*t*, $J=7.1$, 2 H); 2.48 (*d*, $J=1.4$, 3 H); 2.59 (*m*, 2 H); 5.94 (*dd*, $J=8.0$, 1.4, 1 H); 7.07 (*d*, $J=7.5$, 1 H); 7.19–7.29 (*m*, 3 H); 10.16 (*d*, $J=8.0$, CHO); (*Z*)-**13.2**: selected signals: 2.26 (*d*, $J=1.4$, 3 H); 6.16 (*dq*, $J=8.4$, 1.4, 1 H); 9.23 (*d*, $J=8.4$, 1 H). $^{13}\text{C-NMR}$ (125.8 MHz): (*E*)-**13.2**: 20.00 (*q*); 25.11 (*t*); 29.96 (*q*); 32.08, 42.93 (2*t*); 126.16, 126.86, 128.36, 129.52, 130.20 (5*d*); 137.36, 142.53, 160.98 (3*s*); 193.31 (*d*); 208.25 (*s*); (*Z*)-**13.2**: 24.77 (*t*); 27.39, 29.94 (*q*); 32.01, 42.98 (2*t*); 126.13, 128.02, 128.47, 129.23, 129.93 (5*d*); 138.07, 138.16, 163.25 (3*s*); 190.97 (*d*); 208.14 (*s*). EI-MS: 229 (1.7, M^+), 211 (13), 203 (12), 158 (12), 157 (11), 156 (25), 146 (41), 145 (16), 144 (100), 142 (10), 141 (20), 130 (28), 129 (11), 128 (40), 127 (31), 126 (10), 118 (11), 116 (18), 114 (28), 90 (23), 76 (12), 70 (11), 42 (72).

3.10. 1-(5,6-Dihydro-10-methylbenzocycloocten-7-yl)ethanone (**14.2**). A soln. of 117 mg (500 μmol) of **13.2** and 1.0 ml (12 mmol) of conc. HCl in 25 ml of THF was heated for 5 d at 80° . TLC (silica gel; petroleum ether/*t*-BuOMe 2:1): R_f 0.93, 0.85, 0.67, 0.52 (**14.2**), 0.19, 0.11, 0.00. The fraction with R_f 0.52 yielded 39 mg (37%) of **14.2**. Colorless solid. M.p. 48° . IR (film): 2965*m*, 2934*m*, 1662*s*, 1628*m*, 1569*w*, 1491*w*, 1430*m*, 1375*m*, 1355*m*, 1246*s*, 1218*w*, 1195*w*, 1143*w*, 1125*w*, 1030*w*, 947*w*, 876*w*, 841*w*, 797*w*, 765*m*, 754*m*. UV/VIS: 206 (4.13, sh), 229 (3.86), 288 (3.70). $^1\text{H-NMR}$ (500 MHz): 2.18 (*t*, $J=1.6$, 3 H); 2.20 (*s*, 3 H); 2.73 (*tt*, $J=6.5$, 1.6, 2 H–C(6)); 3.00 (br., *s*, 2 H–C(5)); 6.07 (*m*, H–C(9)); 6.78 (*m*, H–C(8)); 7.18–7.25 (*m*, 4 H). $^{13}\text{C-NMR}$ (125.8 MHz): 25.93, 26.11 (2*q*); 30.14 (*t*, C(5)); 31.39 (*t*, C(6)); 122.98 (*d*, C(9)); 125.77, 126.68, 127.92, 128.94 (4*d*); 136.76 (*d*, C(8)); 139.23, 140.05, 140.09, 201.13 (4*s*). EI-MS: 212 (31, M^+), 197 (19), 184 (14), 170 (15), 169 (100, [$M - \text{MeCO}$] $^+$), 155 (26), 155 (26), 154 (42), 153 (27), 152 (18), 145 (19), 141 (30), 129 (19), 128 (25), 115 (21), 43 (42, MeCO^+). HR-MS: calc. for $\text{C}_{15}\text{H}_{16}\text{O}$ (212.29): 212.1201; found: 212.1202.

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