22. Synthesis of (±)-4-Demethoxydaunomycinone by Double *Diels-Alder* Additions to 2,3,5,6-Tetramethylidene-7-oxanorbornane[1])

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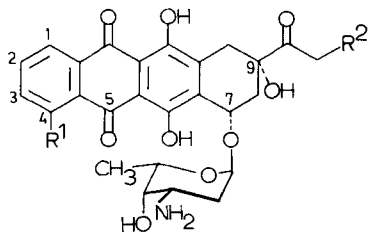
Summary

Sequential *Diels-Alder* additions of methylvinyl ketone and dehydrobenzene to 2,3,5,6-tetramethylidene-7-oxanorbornane (**4**) yielded the (5,12-epoxy-1,2,3,4,5,6,11,12-octahydro-2-naphtacenyl)methyl ketone (**10**) which, in few steps was oxidized to a precursor of (±)-4-demethoxydaunomycinone. The preparations of two precursors of anthracyclinones, the (5-acetoxy-) and (12-acetoxy-1,2,3,4-tetrahydro-2-naphtacenyl)methyl ketones (**14**, **15**) are presented. The synthesis of 6,13-epoxy-6,13-dihydropentacene (**8**) is also reported.

The anthracycline antibiotics daunorubicin **1** [2], carcinomycin **2** [3] and especially adriamycin **3** [4] have proved to be useful for the treatment of human cancers [5]. Unfortunately, these cytotoxic drugs display side-effects such as cardiotoxicity [6]. It has been shown recently that structural modification of the aglycone portion (anthracyclinone) can improve the activity of these compounds [7]; for instance, 4-demethoxydaunomycin has been reported to be more potent against cancers than the natural daunorubicin [5a] [8].



1 $R^1 = CH_3O$, $R^2 = H$
2 $R^1 = OH$, $R^2 = H$
3 $R^1 = CH_3O$, $R^2 = OH$

[1]) Anthracyclinones, Part II; Part I: [1].
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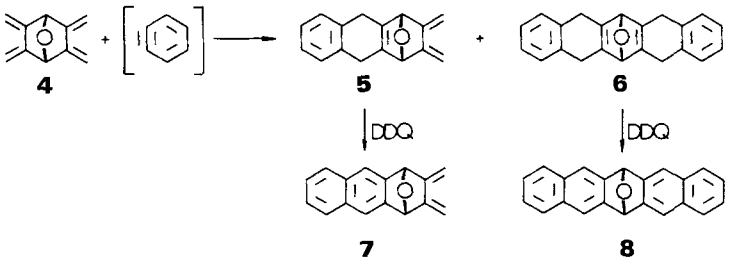
2,3,5,6-Tetramethylidene-7-oxanorbornane (**4**) [9] can add sequentially two different dienophiles [1] and generate in a simple way a wide variety of modified anthracyclinone precursors. We show now how the tetraene **4** can be engaged in the synthesis of a known precursor of the very important (±)-4-demethoxydaunomycinone.



With strong dienophiles such as tetracyanoethylene [10], dimethylacetylenedicarboxylate [11] or benzoquinone [1], the formation of the monoadducts was at least 100 times faster than the cycloadditions of the latter to yield the corresponding 'symmetrical' bis-adducts. The reaction of **4** with dehydrobenzene (1 to 1.5 mol-equiv.) generated *in situ* [12] (anthranilic acid, pentyl nitrite, dimethoxyethane, 85°) yielded mixtures containing the expected monoadduct **5** (20–22% after purification) together with the bis-adduct **6** (3–6%). The structures of these compounds were deduced from their spectra and were confirmed by their oxidation with dichlorodicyanoquinone (DDQ) into the corresponding naphto derivatives **7** and **8**.

The relatively low selectivity of the cycloaddition of dehydrobenzene to **4** and **5** was anticipated from the relatively high exothermicity of these reactions and the known high reactivity of this dienophile [13]. In order to overcome this problem and also the bad yields observed in the reaction of **4** with dehydrobenzene[3]), we first added methylvinyl ketone to **4**: In the presence of anhydrous $ZnCl_2$ and under N_2, this reaction ($CHCl_3$, hydroquinone, 20 h, 20°) yielded a 95:5 mixture of the two *exo/endo* adducts **9** (whose configuration has not yet been assigned unambigously [16]) (86%). The tricyclic diene **9** added dehydrobenzene giving the pentacyclic adduct **10** (48–60%) contaminated by *ca.* 15% of the aromatized derivative **11**. Oxidation of **10** with DDQ in benzene or toluene yielded **11** (86–95%).

Acid promoted ($CF_3COOH/CHCl_3$, 20°) isomerization of the oxanorbornadiene derivative **11** did not give the expected [17] phenols **12/13**, which are too sensitive to aerial oxidation, but a polymeric material (phenol coupling, *etc.*) and the quinone **16**. When the reaction mixture was neutralized ($NaHCO_3$) and stirred with silica gel and CH_2Cl_2/ether in an open flask, the quinone **16** was formed as major product. In analogy to one of *Kende*'s routes to the synthesis of anthracyclinones [18a], treatment with Zn dust and acetic anhydride (110–120°, 40 min) reduced **16** to the diacetate **17** (88–97%).

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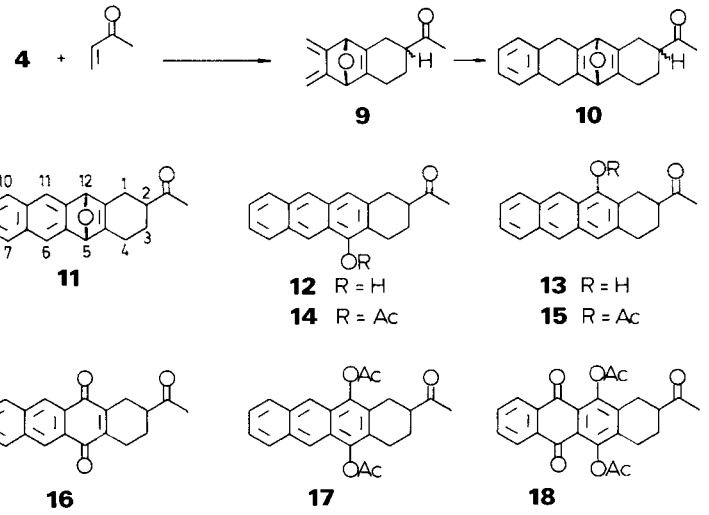
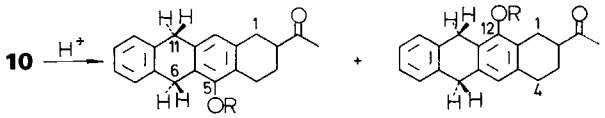
[3]) Substituted dehydrobenzenes [14] generated under strongly basic conditions [15] lead only to polymerization of the tetraene **4**.



Oxidation of **17** with CrO_3 in aqueous AcOH (N_2, 20°, 1.5 h) yielded the diacetate of (±)-4-demethoxy-7,9-bis(desoxy)daunomycinone[4]), a precursor of (±)-4-demethoxydaunomycinone[5]) [19].

All the new compounds described here gave satisfactory elemental analysis. Their structures were easily deduced from their spectral data (*cf.* exper. part) and were consistent with their modes of formation and transformation.

When the oxanorbornadiene → phenol rearrangement of **11** was carried out in Ac_2O containing 10% of CF_3COOH, a mixture of the acetates **14/15** (50±5:50±5) was isolated. This mixture was more stable than the phenols **12/13** to aerial oxidation. Unfortunately we failed to find conditions for the preparative separation of the two isomers. However, the isomerization of **10** in $CHCl_3/CF_3COOH$ 97:3



4) As found by *Wiseman et al.* [18b] for the CrO_3/AcOH oxidation of (5,12-diacetoxy-2-hydroxy-1,2,3,4-tetrahydro-2-naphtacenyl) methyl ketone (**17**) into (±)-4-demethoxy-7-deoxydaunomycinone (**18**), we observed the presence of 10–30% (as a function of concentration of the reagents and temperature) of a mixture of by-products that showed spectral characteristics consistent with 6-acetoxy- and 11-acetoxy-2-acetyl-1,2,3,4-tetrahydro-6,11-naphtacenequinone.

5) By using 2-alkoxy-1-buten-3-one [20] instead of methylvinyl ketone as dienophile, we can obtain, in principle, the 9-oxy-substituted anthracyclinones in a more direct way. The 2-methoxy, 2-ethoxy and 2-trimethylsilyoxy-1-buten-3-ones gave adducts with yields not higher than 60% when added to 4, 7 and related derivatives. The 2-arylcarbonyloxy-1-buten-3-ones, however, reacted faster and furnished adducts with excellent yields [21]. The synthesis of these new dienophiles and their applications to the anthracyclinone synthesis will be reported elsewhere [21].

(N_2, 20°, 20 h) yielded the two phenols **19** and **20** with a regioselectivity somewhat better (product ratio **19**/**20** = 30 ± 5 : 70 ± 5) than in the case of the isomerization **11** → **14** + **15**. The phenols **19** and **20** were easily separated by chromatography and were readily acetylated to **21** and **22**, respectively. DDQ oxidation of **21** yielded the (5-acetoxy-1,2,3,4-tetrahydro-2-naphtacenyl) methyl ketone (**14**), an anthracyclinone precursor. Similarly, **22** furnished the (12-acetoxy-1,2,3,4-tetrahydro-2-naphtacenyl) methyl ketone (**15**).

The structure **20** was assigned to the major compound more polar than the minor isomer, in accordance with the fact that **20** has its two polar substituents (OH and carbonyl) in a somewhat 'parallel' alignment, whereas a more 'antiparallel' alignment prevails in **19**. This assignment was confirmed by 360-MHz-^{1}H-NMR. and ^{13}C-NMR. spectroscopy and with the help of lanthanide induced shift reagents [22].

Coordination of the lanthanide ion was expected at both carbonyl and phenol O-atoms. It was in fact stronger with the carbonyl than with the hydroxyl group, probably because of steric hindrance in the latter case. The ratio of the induced δ_C for C(5) and carbonyl C-atom in **19** was expected to be larger than the induced shift ratio for C(12) and the carbonyl C-atom in **20** because of less steric hindrance to the OH coordination in **19** than in **20**. With Yb(dpm)$_3$ (0.1 to 0.25 mol-equiv.) in $CDCl_3$, the ratio $\Delta\delta$(C(5))/$\Delta\delta$(C=O) = 0.59–0.70 was measured for **19** and $\Delta\delta$(C(12))/$\Delta\delta$(C=O) = 0.35–0.44 for **20**. Two other structural probes were the lanthanide induced shift (δ_C) ratio $\Delta\delta$(C(1))/$\Delta\delta$(C(2)) (expected to be smaller for

Table. *^{13}C-NMR. data (δ_C) of the naphtacenyl derivatives* **14**, **15**, **17**, **19**, **20**, **21**, **22** (0.2–0.5M in $CDCl_3$, FT mode)

Compound	C(1)	C(2)	C(3)	C(4)	C(4a)	C(5)	C(5a)
14	31.8	47.6	24.9	23.6	124.9[a])	143.6	125.5[a])
90 MHz	br. *t*	br. *d*	br. *t*	br. *t*	br. *s*	*s*	*s*
15	25.3	47.2	25.3	29.3	134.3[a])	124.8[b])	131.6[a])
23.63 MHz	br. *t*	br. *d*	br. *t*	br. *t*	br. *s*	*d*	br. *s*
17	23.8[a])	46.6	25.6	24.4[a])	124.7[c])	141.8[b])	124.9[c])
15.08 MHz	br. *t*	br. *d*	br. *t*	br. *t*	*s*	br. *s*	*s*
$^1J_{CH}$[± 2 Hz]	130	126	129	130	–	–	–
19	30.9	47.3	24.8	22.3	119.2	150.2	119.8
15.08 MHz	br. *t*	br. *d*	br. *t*	*t* × *m*	*s*	br. *s*	*s*
$^1J_{CH}$	131	125	131	129	–	–	–
LIS[h])	0.33	0.44	0.31	0.42	0.39	0.59	0.22
20	24.4	47.8	25.1	28.8	134.3	119.8	134.8
15.08 MHz	br. *t*	br. *d*	br. *t*	*t*	*s*	*d*	*s*
$^1J_{CH}$	~ 129	~ 126	~ 129	128	–	157	–
LIS[h])	0.37	0.40	0.25	0.14	0.16	0.10	0.11
21	30.7	47.3	24.7	22.9	125.9	146.2	125.9
15.08 MHz	br. *t*	br. *d*	br. *t*	br. *t*	br. *s*	br. *s*	br. *s*
$^1J_{CH}$	~ 128	~ 126	~ 128	~ 130	–	–	–
22	24.6	47.2	24.9	28.4	134.7[a])	125.2	134.9[a])
15.08 MHz	br. *t*	br. *d*	br. *t*	br. *t*	br. *s*	br. *d*	br. *s*
$^1J_{CH}$	~ 128	~ 126	~ 128	~ 130	–	157	–

Table (cont.)

Compound	C(6)	C(6a)	C(7)	C(8)	C(9)	C(10)	C(10a)
14	119.3	131.8[b])	128.0[c])	125.5[d])	125.6[d])	128.4[c])	131.7[b])
90 MHz	*d*	br. *s*	*d*×*m*	*d*×*m*	*d*×*m*	*d*×*m*	br. *s*
15	125.5[b])	131.6[a])	127.9[c])	125.5[d])	125.5[d])	128.4[c])	131.0[a])
23.63 MHz	*d*	br. *s*	*d*	*d*×*m*	*d*×*m*	*d*×*m*	br. *s*
17	119.8	131.7	128.2	125.8	125.8	128.2	131.7
15.08 MHz	br. *d*	br. *s*	*d*×*t*	*d*×*d*	*d*×*d*	*d*×*t*	br. *s*
$^1J_{CH}$[±2 Hz]	155	–	163[e])	161[f])	161[f])	163[e])	–
19	28.4	135.5	125.8	127.3	127.7	125.8	136.0
15.08 MHz	*t*	*s*	*d*×*m*	br. *d*	br. *d*	*d*×*m*	*s*
$^1J_{CH}$	129	–	159	157	157	159	–
LIS[h])	0.27	0.06	~0	~0	~0	~0	~0
20	35.3	136.2	125.9	127.8	127.3	125.9	135.6
15.08 MHz	*t*	*s*	*d*×*m*	*d*×*d*	*d*×*d*	*d*×*m*	*s*
$^1J_{CH}$	127	–	159	157	157	159	–
LIS[h])	0.04	0.02	~0	~0	~0	~0	0.04
21	29.2	134.2[a])	126.1	127.4[b])	127.6[b])	126.1	135.0[a])
15.08 MHz	*t*	br. *s*	br. *d*	br. *d*	br. *d*	br. *d*	br. *d*
$^1J_{CH}$	<130	–	156	~155	~155	156	–
22	35.1	135.1[a])	126.0[b])	127.2[c])	127.5[c])	126.0[b])	135.8[a])
15.08 MHz	*t*	br. *s*	*d*×*m*	br. *d*	br. *d*	*d*×*m*	br. *s*
$^1J_{CH}$	~130	–	157	156	156	157	–

Table (cont.)

Compound	C(11)	C(11a)	C(12)	C(12a)	CH_3	C=O	CH_3	COO
14	125.4[d])	131.2[b])	124.9[d])	134.0[b])	28.1	210.0	20.6	168.7
90 MHz	*d*	*s*×*(d)*	*d*	*s*	*qa*	br. *s*	*qa*	*qa*
15	119.1	125.3[d])	143.7	124.4[d])	28.1	210.4	20.7	169.0
23.63 MHz	*d*	br. *s*	*s*	*s*	*qa*	br. *s*	*qa*	*qa*
17	119.8	124.7[c])	141.5[b])	124.7[c])	28.0	209.9	20.5	168.7; 168.6
15.08 MHz	br. *d*	*s*	br. *s*	*s*	*qa*	br. *s*	*qa*	*qa*
$^1J_{CH}$[±2 Hz]	155	–	–	–	127	–	130	–[g])
19	35.1	134.9	119.9	133.5	27.8	211.5	–	–
15.08 MHz	*t*	*s*	*d*	*s*	*qa*	br. *s*		
$^1J_{CH}$	131	–	157	–	127	–		
LIS[h])	0.05	0.09	0.17	0.19	0.42	(1.00)		
20	28.6	118.8	150.5	119.8	27.7	210.8	–	–
15.08 MHz	*t*	*s*	*s*	*s*	*qa*	br. *s*		
$^1J_{CH}$	128	–	–	–	127	–		
LIS[h])	0.13	0.18	0.44	0.22	0.42	(1.00)		
21	35.3	135.2[a])	125.7	135.9[a])	28.0	210.5	20.4	168.8
15.08 MHz	*t*	br. *s*	*d*	br. *s*	*qa*	br. *s*	*qa*	*qa*
$^1J_{CH}$	<130	–	~155	–	127	–	130	–[g])
22	29.2	124.9	146.2	125.2	27.8	210.3	20.3	168.7
15.08 MHz	*t*	br. *s*	br. *s*	br. *s*	*qa*	br. *s*	*qa*	*qa*
$^1J_{CH}$	130	–	–	–	127	–	130	–[g])

[a])[b])[c])[d]) Groups of carbon atoms whose δ_C assignments can be internally interchanged; [e]) $^3J_{CH}$=5–6; [f]) $^3J_{CH}$=8; [g]) $^2J_{CH}$=6–7; [h]) relative induced shifts for the addition of *ca.* 0.25 mol-equiv. of Yb (dpm)$_3$.

19 than for **20**) and $\Delta\delta$(C(4))/$\Delta\delta$(C(2)) (expected to be larger for **19** than for **20**). We measured $\Delta\delta$(C(1))/$\Delta\delta$(C(2))=0.66–0.75 for **19** and 0.86–0.92 for **20** and $\Delta\delta$(C(4))/$\Delta\delta$(C(2))=0.82–0.95 for **19** and 0.27–0.35 for **20**. The signal attributions to the C-atoms mentioned above (see *Table*) could be made unambigously by virtue of the signal multiplicities [23] and by considering the hydroxyl substituent effect on the δ_C of *ortho* and *para* (shielding effect) *vs. meta* aromatic C-atoms [24] and on the *ortho vs. meta* alkyl substituents (γ-effect [25]). The hyperfine structure of the signals observed for C(6,11) of **19** and **20** (fine triplets) together with that of the signals observed for C(1,3,4) (broad triplets due to long-range ^2J(CH) and ^3J(CH) couplings [26]) allowed a distinction to be made between these groups of C-atoms.

The results reported here demonstrate once more [1] that 2,3,5,6-tetramethylidene-7-oxanorbornane (**4**) is not only a molecule of theoretical interest [27] but also a useful synthon for the preparation of polycyclic polyfunctionalized systems. This is possible because the addition of the first equivalent of a dienophile to **4** is a faster reaction than the formation of the corresponding 'symmetrical' bis-adduct, thus allowing isolation of the *Diels-Alder* monoadduct in good yield.

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Experimental Part

General Remarks. Melting points (m.p.) and boiling points (b.p.) (not corrected), *Tottoli* apparatus; IR. spectra ($\tilde{\nu}$[cm^{-1}]), *Beckman* IR-20A and *Beckman* IR-4230 spectrometers; UV. spectra, *Pye Unicam* SP 1800 instrument (λ_{max}[nm](ε)); Mass spectra (MS.) in electron ionization mode, CEC 21-490 *Bell-Howell* spectrometer (*m/z*[amu](% base peak)); ^{1}H-NMR. spectra, *Bruker* WP 80 CW or *Bruker* WH-360 (only for **19** and **20**) spectrometers (δ ppm, apparent coupling constant *J* Hz, number of protons, tentative attribution); *s*=singlet, *d*=doublet, *t*=triplet, *qa*=quadruplet, *m*=multiplet, δ_{TMS}=0.0 ppm, br.=broad, *w*=weak, *s*=strong, *vs*=very strong. Sometimes the ^{1}H-NMR. spectrum was strongly dependent upon the concentration of the sample measured. ^{13}C-NMR. spectra, *Bruker* WP 60 spectrometer (15.08 MHz, spectrum width: 3750 Hz, 4096 points, FT Mode): δ ppm, apparent coupling constants ^nJ(CH) Hz, tentative attribution. Distinction between *ortho* and *meta*-carbons in 1,2-disubstituted benzenes was based on the fact that the hyperfine structure of the *ortho*-C-atoms shows a larger multiplicity (more complex lines) than the *meta*-ones [24a–c] [28] due to long range ^nJ(CH) couplings [29]. Elementary analysis were performed by the microanalytical laboratory of the University of Geneva (Dr. *K. Eder*). Abbreviations: i.V.=*in vacuo*, RT.=room temperature, TLC.=thin layer chromatography, sh.=shoulder, DME=dimethoxyethane. The procedures reported have not been optimized.

1,4-Epoxy-2,3-dimethylidene-1,2,3,4,9,10-hexahydroanthracene (**5**). A solution of anthranilic acid (2.86 g, 0.0208 mol) in 20 ml of DME and a solution of pentyl nitrite (2.64 g, 0.0225 mol) in 20 ml of DME were added simultaneously and dropwise (25–40 min) to a solution of 2,3,5,6-tetramethylidene-7-oxanorbornane (**4**) [9] (2.5 g, 0.017 mol) in 20 ml DME at 85°. After the addition was completed, the reaction mixture was maintained at 85° for *ca.* 30 min until cessation of gaz evolution. After cooling to 20°, 100 ml of CH_2Cl_2 were added. The mixture was then washed with 10% aqueous solution of KOH (40 ml). The aqueous layer was extracted with CH_2Cl_2 (3×, 30–40 ml). The combined organic layers were mixed and washed with H_2O (5×, 30–40 ml). After removal of the solvent

i.V., the brown residue was purified on TLC. (Al_2O_3 F. 254 *Merck* or *Camag* DSF 5), 3 successive elutions with pentane/CH_2Cl_2 4:1). The first fraction contained **5**; it was extracted with ether and crystallized from MeOH. Yield: 0.83 g (22%) of **5**, colourless crystals, m.p. 122–123° (MeOH). – UV. (EtOH 96%): 212 (14200), 225 (sh., 11040), 233 (sh., 9800), 243 (sh., 7200), 273 (800). – IR. (KBr): 3060, 3020, 3000, 2870, 2820, 1650, 1580, 1500, 1455–1430*s*, 970–960*s*, 890*vs*, 845*vs*, 770, 740*vs*. – ^{1}H-NMR. (80 MHz, 19.5 mg in 0.4 ml $CDCl_3$): 7.22 (*s*, 4 H, ar.); 5.25 (*s*, 2 H, olefinic); 5.11 (*s*, 4 H, 2 olefinic, 2 H–C(1,4)); 3.56 (*m*, 4 H, benzylic). – ^{13}C-NMR.: 143.8 (*d*, $^3J_{CH}$ = 8, C(2,3)); 138.9 (*t*, $^3J_{CH}$ = 5.4, C(4a,10a)) (*cf.* ^{13}C-NMR. spectra of 5,6-dimethylidene-7-oxanorborn-2-ene and derivatives [30]); 132.7 (br. *s*, C(5a,9a)); 128.9 (br. *d*, $^1J_{CH}$ = 156, C(7,8)); 125.9 (*d*×*m*, $^1J_{CH}$ = 159, $^3J_{CH}$ ≃ 2, C(6,9)); 100.7 (*t*, $^1J_{CH}$ = 159, H_2C=(C)); 84.4 (*d*×*qi*, $^1J_{CH}$ = 166, $^3J_{CH}$ ≃ 6, C(1,4)); 26.4 (*t*, $^1J_{CH}$ = 129, C(5,10)). – MS. (70 eV): 222 (40), 194 (26), 193 (100), 179 (19), 178 (26), 170 (18), 169 (13), 165 (13), 142 (15), 141 (26).

$C_{16}H_{14}O$ (222.3) Calc. C 86.45 H 6.35% Found C 86.34 H 6.51%

1,4-Epoxy-2,3-dimethylidene-1,2,3,4-tetrahydroanthracene (**7**). A solution of DDQ (1.42 g, 0.0066 mol) in benzene (30 ml) was added portionwise to a solution of **5** (1.385 g, 0.0062 mol) in benzene (20 ml) maintained at 20°. After 2 h at 20° (the solution must be green), the precipitate of dichlorodicyanodihydroxybenzene was filtered off and washed with benzene. The benzene solution was washed with aqueous saturated solution of $NaHSO_3$ then H_2O (5×10 ml). After drying (Na_2SO_4) and removal of the solvent i.V., a white solid was obtained. Yield: 1.12 g (82%) of **7**, m.p. 136–138° (MeOH or EtOH). – UV. (EtOH 96%): 242 (31500), 272 (4450), 281 (4050), 295 (sh., 2250), 309 (1350), 315 (sh., 800), 323 (1700). – IR. (KBr): 3080, 3060, 3025, 3000, 1650, 1640, 1612, 1508, 1425, 1270*s*, 955*vs*, 905*vs*, 900, 890–880*vs*, 845*vs*, 795*s*, 755*vs*, 735*s*, 710*s*. – ^{1}H-NMR. (80 MHz, $CDCl_3$): 7.7 (*d*×*d*, *J* = 6 and 3, 2 H); 7.6 (*s*, 2 H); 7.34 (*d*×*d*, *J* = 6 and 3); 5.64 (*s*, 2 H); 5.26 (*s*, 2 H); 5.17 (*s*, 2 H). – ^{13}C-NMR. ($CDCl_3$): 144.7 (br. *s*, C(2,3)); 141.8 (br. *s*, C(4a,10a)); 133.1 (br. *s*, C(5a,9a)); 128.1 (*d*×*m*, $^1J_{CH}$ = 155, C(6,9)); 125.9 (*d*×*d*×*d*, $^1J_{CH}$ = 161, $^3J_{CH}$ = 2 and 8, C(7,8) (*cf.* ^{13}C-NMR. spectrum of naphtalene [24a]); 118.0 (*d*×*d*, $^1J_{CH}$ = 156, $^3J_{CH}$ = 6, C(5,10)); 103.3 (*t*, $^1J_{CH}$ = 160, H_2C=(C)); 83.5 (*d*×*m*, $^1J_{CH}$ = 166, $^nJ_{CH}$ ≃ 3 and 6, C(1,4)). – MS. (70 eV): 221 (17), 220 (100), 203 (6), 202 (4), 192 (31), 191 (93), 190 (14), 189 (26), 168 (12), 165 (12), 163 (4), 152 (4), 140 (4), 139 (8).

$C_{16}H_{12}O$ (220.27) Calc. C 87.24 H 5.49% Found C 87.30 H 5.54%

6,13-Epoxy-5,6,7,12,13,14-hexahydropentacene (**6**). During Al_2O_3 TLC. isolation of **5** (see above), **6** remained in the starting line. After extraction with CH_2Cl_2/ether ≃ 1:1, the crude **6** was purified on TLC. SiO_2 plates (2 successive elutions with CH_2Cl_2). After recrystallization from benzene, 0.2 g of **6** (4%) was isolated as colourless crystals, m.p. 187–190° (benzene). – UV. (EtOH 96%): 210 (17700), 230 (sh., 7600), 261 (2400), 267 (sh., 2350), 274 (2200). – IR. (KBr): 3060, 3005, 3000, 2880, 2830, 1580, 1495*s*, 1455, 1440, 1425, 1285, 1175, 1030*s*, 960*s*, 840*vs*, 770*s*, 740*vs*, 625, 610. – ^{1}H-NMR. (80 MHz, $CDCl_3$): 7.0 (br. *s*, 8 H, arom.); 5.16 (*s*, 2 H, H–C(6,13)); 3.58 (*m*, 8 H, benzylic). – ^{13}C-NMR. ($CDCl_3$): 146.6 (br. *t*, $^3J_{CH}$ ≃ 10, C(5a,6a,12a,13a)); 133.3 (br. *s*, C(4a,7a,11a,14a)); 129.1 (*d*×*d*×*d*, $^1J_{CH}$ = 156, $^2J_{CH}$ = 2, $^3J_{CH}$ = 6, C(2,3,9,10)); 126.1 (*d*×*m*, $^1J_{CH}$ = 160, C(1,4,8,11)); 85.8 (*d*×*m*, $^1J_{CH}$ = 163, $^3J_{CH}$ = 8, C(6,13)); 28.9 (*t*×*m*, $^1J_{CH}$ = 129, $^3J_{CH}$ ≃ 2, C(5,7,12,14)). – MS. (70 eV): 299 (25), 298 (100), 269 (52), 142 (23), 141 (60).

$C_{22}H_{18}O$ (298.4) Calc. C 88.56 H 6.08% Found C 88.68 H 6.19%

6,13-Epoxy-6,13-dihydropentacene (**8**). A solution of DDQ (0.35 g, 0.004 mol) in toluene (15 ml) was added to a solution of **6** (0.57 g, 0.0019 mol) in toluene (15 ml). After 3 h at 20°, the precipitate of dichlorodicyanodihydroxybenzene was filtered off and washed with toluene. The combined toluene solutions were washed with aqueous saturated solution of $NaHSO_3$ and H_2O (5× 10 ml). After drying (Na_2SO_4) and removal of the solvent i.V., a white solid was obtained. Yield: 0.35 g (62%), m.p. 275° (dec.). Compound **8** has very low solubility in most organic solvents. – IR. (KBr): 3070, 3020, 1615, 1510, 1450, 1340, 1135–1125*vs*, 1180*vs*, 940*s*, 895*s*, 825*vs*, 760*vs*, 645*s*, 610. – ^{1}H-NMR. (80 MHz, $CDCl_3$): 7.8 (br. *s*, 4 H); 7.8 (*m*, 4 H); 7.4 (*m*, 4 H); 6.35 (*s*, 2 H). – MS. (70 eV): 295 (22), 294 (87), 293 (24), 266 (37), 265 (100), 263 (33), 143 (16), 142 (15).

Exo- *and* endo-*(5,8-epoxy-6,7-dimethylidene-1,2,3,4,5,6,7,8-octahydro-2-naphtyl) methyl ketone* (**9**). A mixture of 2,3,5,6-tetramethylidene-7-oxanorbornane [9] (11.4 g, 0.078 mol), freshly distilled methyl vinyl ketone (30 g, 0.43 mol), hydroquinone (0.010 g) and freshly fused $ZnCl_2$ (2 g) in $CHCl_3$ (75 ml)

was stirred under N_2 at RT. for 20 h. The solvent and methyl vinyl ketone were evacuated i.V. (15 Torr, RT.), the residue was dissolved in a minimum of CH_2Cl_2 and quickly filtered through a SiO_2 column (70–230 mesh, 200 g, elution with CH_2Cl_2/AcOEt 2:1). After addition of ~5 mg of hydroquinone, the solvent was evacuated i.V. (1 Torr, RT.). Yield: 14.5 g (86%) of a 95:5 or 5:95 mixture of the *exo/endo* **5** that was used directly in the next cycloaddition. The crude **5** could be purified by distillation i.V., b.p.: 120°/0.1 Torr; yield: 71% [16].

5,12-Epoxy-1,2,3,4,5,6,11,12-octahydro-2-naphtacenyl methyl ketone (**10**). The reaction was carried out as described for the synthesis of **5**, using **9** (11.4 g, 0.0527 mol) in DME (60 ml), anthranilic acid (14.5 g, 0.106 mol) in DME (90 ml) and pentyl nitrite (14.1 ml, 12.4 g, 0.105 mol) in 90 ml DME. The crude, brownish adduct was treated with 25 ml of MeOH/diisopropyl ether 1:3 and left overnight at RT. The precipitate was filtered off and washed with MeOH/diisopropyl ether 1:3; yield: 7.72 g (50%) of **10** contamined by 10–15% of the aromatized derivative **11**. M.p. 122–132° (MeOH), **11** being not removed after several recrystallizations (TLC., NMR.). – IR. (KBr): 3070, 3010–2990, 1920–2890, 2860, 2840, 2820, 1715*vs*, 1575*w*, 1495, 1440–1420*s*, 1370*s*, 1350*s*, 1280, 1205, 1165*s*, 840*vs*, 765*s*, 755*s*, 620. – ^{1}H-NMR. (80 MHz, $CDCl_3$): 7.15 (*s*, 4 H); 5.07 (*s*, 2 H); 3.61 (*m*, 4 H, 2 H–C(6,11)); 1.4–2.8 (*m*, 7 H); 2.15 (*s*, 3 H, $COCH_3$). – ^{13}C-NMR. ($CDCl_3$): 210.5 (*s*, C=O); 149.0, 147.4, 146.7 and 146.3 (br. *s*, C(4a,5a,11a,12a)); 133.4 (br. *s*, C(6a,10a)); 129.2 (br. *d*, $^1J_{CH}$ = 156, C(8,9)); 126.2 (*d*×*m*, $^1J_{CH}$ = 159, C(7,10)) [*cf.* ^{13}C-NMR. spectra of **5**,**7**]; 86.1 and 85.6 (*d*×*d*, $^1J_{CH}$ = 163, $^3J_{CH}$ = 7, C(5,12)); 48.0 (*d*×*m*, $^1J_{CH}$ = 125, C(2)); 28.8 (br. *t*, $^1J_{CH}$ = 130, C(6,11)) [*cf.* **5** and **6**]; 27.8 (*qa*, $^1J_{CH}$ = 127, CH_3CO); 24.8 (br. *t*, $^1J_{CH}$ = 131, C(1,4)); 23.7 (*t*, $^1J_{CH}$ = 127, C(3)). This spectrum demonstrates the absence of isomerization of the acetyl group in **10** during its formation. Work is underway to determine whether this substituent is *exo* or *endo* [16]. – MS. (70 eV): 293 (20), 292 (20), 249 (53), 247 (30), 231 (32), 229 (16), 221 (27), 219 (19), 193 (40), 191 (17), 179 (31), 178 (24), 164 (19), 155 (27), 149 (27), 141 (32), 121 (23), 91 (25), 71 (28), 69 (35), 45 (73), 43 (100).

5,12-Epoxy-1,2,3,4,5,12-hexahydro-2-naphtacenyl methyl ketone (**11**). A solution of DDQ (1.5 g, 6.6 mmol) in toluene (25 ml) was added to a solution of **10** (1.85 g, 6.3 mmol) in toluene (50 ml). After stirring at 20° for 2 h, the precipitate was filtered off and washed with toluene. The toluene solutions were mixed and washed with aqueous saturated solution of $NaHSO_3$ and H_2O (5×, 10 ml). After drying (Na_2SO_4) and solvent removal i.V., a white solid was obtained. Yield: 1.74 g (95%) of **11** pure enough for the following transformations. M.p. 160–162° (EtOH). – UV. (EtOH 96%): 235 (34000), 260 (sh., 10700), 269 (9200), 278 (sh., 4500), 297 (400), 304 (350), 310 (600), 324 (650). – IR. (KBr): 3065, 3010, 2930, 2860, 2840, 1715*vs*, 1510, 1455, 1440*s*, 1420, 1370*s*, 1355*s*, 1210*s*, 1165*s*, 885*s*, 840*vs*, 800, 765*s*. – ^{1}H-NMR. (80 MHz, $CDCl_3$): 7.65 (*d*×*d*, *J* = 6 and 3, 2 H); 7.47 (*s*, 2 H); 7.36 (*d*×*d*, *J* = 6 and 3, 2 H); 5.45 (*s*, 2 H); 2.02 (*s*, 3 H); 2.75–1.5 (*m*, 7 H). – ^{13}C-NMR. ($CDCl_3$): 209.8 (*s*, C=O); 147.0, 145.1, 144.7 and 144.3 (br. *s*, C(4a,5a,11a,12a)); 131.7 (br. *s*, C(6a,10a)); 127.7 (*d*×*m*, $^1J_{CH}$ = 159, C(7,10)); 125.6 (*d*×*d*, $^1J_{CH}$ = 160, $^3J_{CH}$ = 7, C(8,9)); 117.0 (*d*×*d*, $^1J_{CH}$ = 160, $^3J_{CH}$ = 4.5, C(6,11)); 83.4 and 83.2 (br. *s*, $^1J_{CH}$ = 168, C(5,12)); 47.2 (br. *d*, $^1J_{CH}$ = 129, C(2)); 27.6 (*qa*, $^1J_{CH}$ = 127, CH_3CO); 24.3, 23.3 and 22.4 (*t*, $^1J_{CH} \simeq 130$, C(1,3,4)). This spectrum shows that the configuration of the acetyl substituent has not been affected during the formation of **11** (no doubling of the peaks due to epimerization). – MS. (70 eV, *Hewlett-Packard* HP 5980 A): 290 (3), 272 (5), 247 (11), 229 (40), 219 (16), 217 (16), 215 (28), 203 (15), 202 (30), 192 (34), 191 (40), 189 (29), 178 (29), 165 (27), 152 (16), 141 (16), 139 (16), 115 (14), 91 (15), 71 (41), 43 (100).

$C_{20}H_{18}O_2$ (290.3) Calc. C 82.73 H 6.25% Found C 82.75 H 6.33%

2-Acetyl-1,2,3,4-tetrahydro-5,12-naphtacenequinone (**16**). Trifluoroacetic acid (0.9 ml) was added to a solution of **11** (0.68 g, 2.34 mmol) in $CHCl_3$ (15 ml). After 20 h at 20°, the solution was washed with aqueous $NaHCO_3$-solution and water. After drying (Na_2SO_4) and removal of the solvent i.V., the residue was stirred in CH_2Cl_2 and silica gel (*Merck* H_{254}) in an open beaker. After filtration and solvent removal, the brownish residue was purified by TLC. (SiO_2, CH_2Cl_2/ether 98:2, 2 elutions). Yield: 0.475 g (66%); m.p. 189–192° (EtOH or AcOEt). – UV. (EtOH 96%): 210 (18200), 231 (49150), 275 (sh., 23100), 284 (25900), 296 (23100), 404 (4900). – IR. ($CHCl_3$): 3040, 2930, 2860, 1715*vs*, 1670*vs*, 1625*s*, 1595, 1465, 1290*vs*. – IR. (KBr): 3055–3010, 2940, 2860, 1705*vs*, 1655*vs*, 1615*vs*, 1590*s*, 1455, 1295*vs*, 1250*s*, 1200*s*, 1165*s*, 1145*s*, 930*s*, 760*vs*, 710*s*. – ^{1}H-NMR. (80 MHz, 19 mg in 0.3 ml $CDCl_3$): 8.47 (*s*, 2 H); 7.96 (*d*×*d*, *J* = 6 and 3, 2 H); 7.59 (*d*×*d*, *J* = 6 and 3, 2 H); 2.29 (*s*, 3 H); 3.2–1.5 (*m*, 7 H). – ^{13}C-NMR. ($CDCl_3$): 209.4 (*m*, $^2J_{CH} \simeq 3$, $COCH_3$); 183.7 (*d*, $^3J_{CH}$ = 3.7, C(5,12)); 145.2 and 144.5 (br. *s*, C(4a,12a)); 134.6 (br. *s*, C(6a,10a)); 128.6 and 128.2 (*s*, C(5a,11a)); 129.9 (br. *d*, $^1J_{CH}$ = 164,

2 C); 129.1 ($d \times d$, $^1J_{CH} = 164$, $^3J_{CH} = 9.2$, 2 C) and 128.3 ($d \times d$, $^1J_{CH} = 164$, $^3J_{CH} = 4.6$, 2 C, C(6,7,8,9,10,11); 45.6 (br. d, $^1J_{CH} = 130$, C(2)); 27.9 (qa, $^1J_{CH} = 127$, CH_3CO); 24.8, 23.1 and 22.8 (br. t, $^1J_{CH} = 132$–133, C(1,3,4)). – MS. (70 eV): 305 (23), 304 (100), 286 (7), 285 (5), 262 (76), 261 (94), 260 (22), 250 (23), 247 (6), 244 (10), 215 (9), 202 (9), 155 (8), 133 (13), 127 (8), 126 (5).

$C_{20}H_{16}O_3$ (304.3) Calc. C 78.93 H 5.30% Found C 79.05 H 5.25%

5,12-Diacetoxy-1,2,3,4-tetrahydro-2-naphtacenyl methyl ketone (**17**). A mixture of **16** (0.178 g, 0.58 mmol) and zinc powder (0.7 g) in Ac_2O (10 ml) was stirred for 40 min at 110–120°. After cooling to RT., the precipitate was filtered off and washed with $CHCl_3$ (25 ml). Neutralization with aqueous $NaHCO_3$-solution and solid $NaHCO_3$ (this during 3 h at 20°) yielded an aqueous layer which was extracted with $CHCl_3$ (3×, 10 ml) and the organic extracts were dried (Na_2SO_4) and concentrated i.V. Yield: 0.223 g (97%) of **17** pure enough for the next transformation. The crude **17** washed with cold ether yielded 0.2 g (88%) of pure **17**. M.p. 226–229° ($CHCl_3$/EtOH). – UV. (EtOH 96%): 226 (10600), 253 (sh., 90400), 260 (130150), 320 (sh., 1500), 334 (2900), 350 (5200), 369 (5850). – IR. (KBr): 3060, 3020*w*, 2945, 2900–2880–2850*w*, 1755*vs*, 1710*s*, 1640–1630, 1535, 1450–1440, 1430, 1375*s*, 1220–1200*vs*, 1150*s*, 1040*s*, 885*s*, 855, 760–750. – ^{1}H-NMR. (80 MHz, 16 mg in 0.3 ml $CDCl_3$): 8.30 (*s*, 2 H); 8.01 and 7.47 ($d \times d$, $J = 6$ and 3, 4 H); 3.3–1.5 (*m*, 7 H); 2.56 (*s*, 6 H); 2.27 (*s*, 3 H). – ^{13}C-NMR. ($CDCl_3$): see *Table*. – MS. (70 eV): 390 (22), 366 (4), 350 (5), 349 (8), 348 (35), 306 (100), 298 (7), 290 (5), 263 (5), 262 (12), 261 (9), 257 (6), 256 (3), 84 (17), 43 (32).

$C_{24}H_{22}O_5$ (390.4) Calc. C 73.83 H 5.68% Found C 73.77 H 5.61%

5,12-Diacetoxy-2-acetyl-1,2,3,4-tetrahydro-6,11-naphtacenequinone (**18**). The diacetate **17** (0.221 g, 0.57 mmol) was added to a stirred solution of CrO_3 (0.2 g, 2.22 mmol) in 80% AcOH (10 ml) for 2 h under N_2 and at RT. After addition of $CHCl_3$ (25 ml), the solution was neutralized with a saturated solution of $NaHCO_3$ and washed with water. After drying (Na_2SO_4), solvent removal i.V., the crude anthracyclinone **18** is obtained (0.21 g). Purification by preparative TLC. (SiO_2 *Merck;* CH_2Cl_2/ether 97:3) yielded 0.134 g (56%) of **18**, yellow crystals, m.p. 195–198° (MeOH). – UV. (EtOH 96%): 211 (30650), 236 (sh., 18400), 261 (45100), 280 (sh., 14700), 296 (sh., 4100), 344 (4500), 410 (sh., 800). – IR. (KBr): 3080*w*, 2960–2940, 2860*w*, 1770*vs*, 1715–1705*s*, 1675*vs*, 1585*s*, 1435, 1370*s*, 1345*vs*, 1270*s*, 1250*s*, 1190*vs*, 1015*s*, 970, 795, 730, 705, 635. – ^{1}H-NMR. (80 MHz, 10.8 mg in 0.3 ml $CDCl_3$): 8.22 ($d \times d$, $J = 6$ and 3, 2 H); 7.77 ($d \times d$, $J = 6$ and 3, 2 H); 3.4–1.4 (*m*, 7 H); 2.55 (*s*, 6 H); 2.3 (*s*, 3 H). – MS. (70 eV): 420 (10), 378 (24), 336 (100), 321 (11), 320 (33), 316 (15), 294 (8), 293 (28), 292 (8), 291 (21), 290 (8), 278 (26), 277 (19), 275 (15).

5-Hydroxy-1,2,3,4,6,11-hexahydro-2-naphtacenyl methyl ketone (**19**). Trifluoroacetic acid (1.2 ml) was added to a solution of the oxanorbornadiene **10** (4 g, 0.0137 mol) in $CHCl_3$ (40 ml). After 20 h at RT. and under N_2, the mixture was neutralized with a saturated solution of aqueous $NaHCO_3$. The organic layer was dried (Na_2SO_4) and concentrated i.V. to dryness. The residue was chromatographed on Kieselgel H Typ 60 (200 g) column (⌀ = 4 cm, h = 50 cm, CH_2Cl_2/ether 98:2, 3 to 3.5 atm (*Jobin-Yvon*)). The first fraction contained 0.538 g of pure **19**; the second fraction 0.85 g of a mixture of **19**+**20**; the third fraction, 0.582 g of **20** contaminated by 15% of the quinone **16** (arising from the acidic isomerization of **11** contained in the starting material and aerial oxidation) and finally a fourth fraction yielded 1.106 g of **20** (see below). After rechromatographying the two intermediate fractions in the same conditions, 0.90 g of **19** (22%); 1.75 g of **20** (44%) and 0.083 g of a mixture of **19**+**20** were obtained in total. The phenols **19** and **20** were washed with ether/MeOH and then recristallized from benzene (**19** was more difficult to recrystallized than **20**).

Caracteristics of **19**: m.p. 132–134° (benzene). – UV. (EtOH 96%): 212 (27950), 234 (sh., 9650), 266 (1600), 272 (1850), 283 (1500), 296 (sh., 500), 405 (90). – IR. (KBr): 3400 br., 3080, 3020, 2950, 2860, 1695*vs*, 1620, 1595, 1575*s*, 1490*s*, 1435*vs*, 1355, 1270*s*, 1240*s*, 1230*s*, 1200*s*, 1175*s*, 1110, 1040, 740*vs*. – ^{1}H-NMR. (360 MHz, 10 mg in 0.5 ml $CDCl_3$, *cf. Fig.*): 7.29 and 7.26 ($d \times d$, $J = 6$ and 4, 2 H); 7.18 ($d \times d$, $J = 6$ and 4, 2 H); 6.69 (*s*, 1 H); 4.78 (*s*, 1 H, OH); 3.89 (*s*, 4 H, 2 H–C(6,11)); 2.9 (*m*, $J_{gem} \simeq 15$, 2 H–C(1)); 2.82 ($d \times d \times d$, $J_{gem} = 17$, $J_{4e,3a} = 11$, $J_{4e,3e} = 6$, H_e–C(4)); 2.70 (*m*, $J_{2a,3a} = 11$, $J_{2a,1a} \simeq 11$, $J_{2a,1e} \simeq 6$, $J_{2a,3e} \simeq 3$, H_a–C(2)); 2.59 (*m*, $J_{gem} = 17$, $J_{4a,3a} = 11$, $J_{4a,3e} = 6$, H_a–C(4)); 2.22 ($m \times d$, $J_{gem} = 13$, $J_{3e,4a} = 6$, $J_{3e,4e} = 3$, $J_{3e,2a} \simeq 3$, H_e–C(3)); 1.75 (*m*, $J_{gem} = 13$, $J_{3a,2a} = 11$, $J_{3a,4a} = 11$, $J_{3a,4e} = 6$, H_a–C(3)); 2.23 (*s*, 3 H, CH_3CO). – ^{13}C-NMR. ($CDCl_3$): see *Table*. – MS. (70 eV): 293 (23), 292 (100, M^+), 277 (11), 249 (39), 248 (9), 247 (26), 245 (7), 234 (9), 231 (11), 222 (8), 221 (9), 43 (8).

$C_{20}H_{20}O_2$ (292.36) Calc. C 82.16 H 6.90% Found C 82.07 H 7.04%

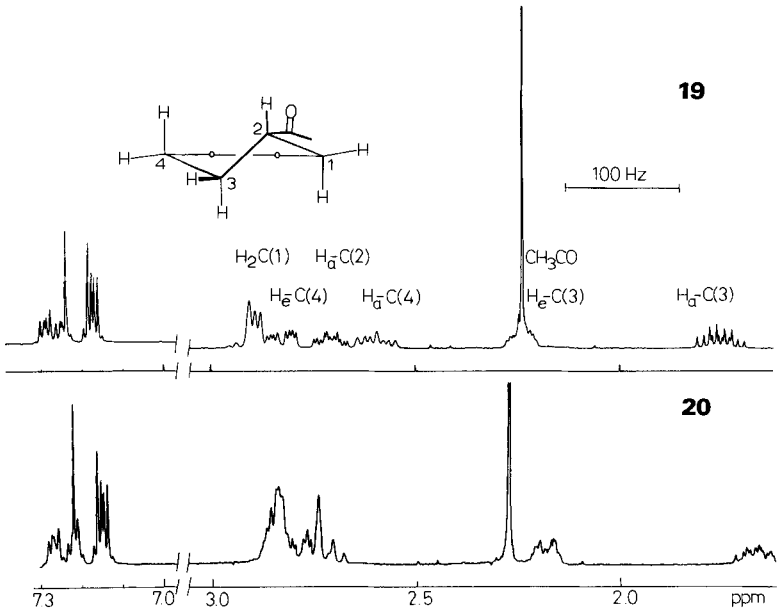

Fig. *Partial ^{1}H-NMR. spectra* (360 MHz, $CDCl_3$) *of* **19** *and* **20**. Signal attribution was confirmed by double irradiation experiments (the other signals are singlets)

12-Hydroxy-1,2,3,4,6,11-hexahydro-2-naphtacenyl methyl ketone (**20**). The major fraction (the more polar product) of the above chromatographic separation is composed of **20**. M.p.: 136–139° (benzene). – UV. (EtOH 96%): 212.5 (24550), 234 (sh., 8600), 265 (1300), 271 (1450), 282 (1100), 310 (sh., ~125), 360 (sh., 30). – IR. (KBr): 3400 br., 3060, 3020, 2940, 2930, 2860, 2840, 2820, 1695*vs*, 1620, 1595, 1575*s*, 1490*s*, 1435*vs*, 1350*s*, 1295, 1280*s*, 1250*s*, 1230*s*, 1210*s*, 1195*s*, 1175*s*, 1110, 1085, 1045, 1005, 920, 740*vs*, 720. – ^{1}H-NMR. (360 MHz, 9.5 mg in 0.5 ml $CDCl_3$, *cf. Fig.*): 7.29 and 7.24 ($d \times d$, J=6 and 4, 2 H); 7.18 ($d \times d$, J=6 and 4, 2 H); 6.67 (*s*, 1 H); 4.9 (*s*, 1 H, OH); 3.89 (br. *s*, 4 H, 2 H–C(6,11)); 2.89–2.67 (*m*, 5 H); 2.17 (*m*, 1 H, H_e–C(3)); 1.67 (*m*, 1 H, H_a–C(3)); 2.27 (*s*, 3 H, CH_3CO). – ^{13}C-NMR. ($CDCl_3$): *cf. Table*. – MS. (70 eV): 293 (23), 292 (100), 277 (19), 249 (20), 248 (9), 247 (20), 245 (6), 234 (6), 231 (8), 221 (7), 69 (11), 43 (9).

$C_{20}H_{20}O_2$ (292.36) Calc. C 82.16 H 6.90% Found C 82.28 H 6.87%

5-Acetoxy-1,2,3,4,6,11-hexahydro-2-naphtacenyl methyl ketone (**21**). The phenol **19** (221 mg, 0.75 mmol) was heated in acetic anhydride (1 ml) and pyridine (0.9 ml) to 110° for 40 min. After cooling to RT., the mixture was dissolved in $CHCl_3$ (20 ml) and washed successively with diluted hydrochloric acid, saturated aqueous $NaHCO_3$-solution and water. After drying (Na_2SO_4), the solvent was evacuated i.V. and the residue recrystallized from MeOH. Yield: 195 mg (78%), m.p. 96–98°. – IR. (KBr): 3020, 2940, 2850, 1760*vs*, 1705*vs*, 1625*w*, 1590*w*, 1570*w*, 1485, 1435*s*, 1370*s*, 1215*vs*, 1200–1190*vs*, 1105, 1035*s*, 755*s*, 740*s*. – ^{1}H-NMR. (80 MHz, $CDCl_3$): 7.22 (*m*, 4 H); 6.92 (*s*, 1 H); 3.85 (*s*, 2 H); 3.72 (*s*, 2 H); 3.0–1.1 (*m*, 7 H); 2.35 (*s*, 3 H); 2.12 (*s*, 3 H). – ^{13}C-NMR. ($CDCl_3$): see *Table*. – MS. (70 eV): 334 (46), 293 (20), 292 (100), 291 (27), 275 (81), 274 (85), 249 (34), 247 (28), 234 (9), 231 (17), 229 (8).

12-Acetoxy-1,2,3,4,6,11-hexahydro-2-naphtacenyl methyl ketone (**22**). The phenol **20** was acylated according to the same procedure as described for **21**. Yield: 80%, m.p. 153–155° (MeOH). – IR. (KBr): 3020, 2940, 2860, 2840, 2820, 1760*vs*, 1710*vs*, 1625, 1595, 1570, 1500, 1490*s*, 1440*s*, 1370*s*, 1200*vs*, 885*s*, 735*s*, 725*s*. – ^{1}H-NMR. (80 MHz, $CDCl_3$): 7.24 (m, 4 H); 6.94 (*s*, 1 H); 3.87 (*s*, 2 H); 3.74 (*s*, 2 H); 3.0–1.4 (*m*, 7 H); 2.39 (*s*, 3 H); 2.16 (*s*, 3 H). – MS. (70 eV): 334 (42), 293 (20), 292 (100), 291 (47), 275 (42), 274 (46), 249 (16), 247 (20), 231 (14).

5-Acetoxy-1,2,3,4-tetrahydro-2-naphtacenyl methyl ketone (**14**). A solution of DDQ (0.19 g, 0.84 mmol) in toluene (3 ml) was added to a solution of **21** (0.185 g, 0.55 mmol) in toluene (2 ml). After 2 h at RT., the solution was filtered and the precipitate washed with toluene. The organic solution was washed with saturated aqueous $NaHSO_3$-solution and then with water (5×). After drying (Na_2SO_4) and solvent removal i.V., the crude **14** was purified by TLC. (SiO_2, *Merck;* CH_2Cl_2/ether 97:3). The first fraction yielded 0.055 g (30%) of yellowish crystals; m.p. 136–139° (MeOH). – UV. (EtOH 96%): 224 (10500), 252 (sh., 64700), 260 (125000), 288 (sh., 4350), 302 (sh., 5350), 316 (6050), 350 (3950), 368 (4900), 388 (4000). – IR. ($CHCl_3$): 3060*w*, 3000*w*, 2940, 2860*w*, 1770*vs*, 1715*vs*, 1660*w*, 1630*w*, 1610*w*, 1370*s*, 1300, 1185, 1040, 900, 870. – ^{1}H-NMR. (80 MHz, 15 mg in 0.3 ml $CDCl_3$): 8.34 (*s*, 1H); 8.26 (*s*, 1H); 7.99 (*m*, 2H); 7.70 (*s*, 1H); 7.44 (*m*, $J=7$ and 3 (and 1?), 2H); 3.4–1.5 (*m*, 7H); 2.55 (*s*, 3H); 2.25 (*s*, 3H). – ^{13}C-NMR. ($CDCl_3$): see *Table*. – MS. (70 eV): 332 (31), 291 (26), 290 (100), 247 (27), 245 (23), 215 (35), 202 (24), 43 (42).

12-Acetoxy-1,2,3,4-tetrahydro-2-naphtacenyl methyl ketone (**15**). The acetate **22** was oxidized to **15** following the procedure described for the oxidation of **21** to **14**. Yield: 34% (after TLC. and recrystallisation from MeOH); m.p. 156–160°. – UV. (EtOH 96%): 226 (13350), 252 (92900), 260 (176000), 288 (sh., 6600), 292 (6750), 318 (sh., 2900), 332 (3400), 349 (4500), 367 (5800), 388 (4950), 410 (sh., 400), 465 (200), 496 (180). – IR. (KBr): 3060 sh., 2940, 2840 sh., 1760*vs*, 1715*vs*, 1620*w*, 1570*w*, 1530*w*, 1430, 1370, 1355, 1310, 1210–1195*vs*, 1050*s*, 870*s*, 745*s*.– ^{1}H-NMR. (80 MHz, 32.5 mg in 0.55 ml $CDCl_3$): 8.35 (*s*, 1H); 8.29 (*s*, 1H); 7.97 (*m*, 2H, H–C(7,10)); 7.69 (*s*, 1H); 7.46 (*m*, $J=7$ and 3 (and 1?), 2H); 3.2–1.5 (*m*, 7H); 2.57 (*s*, 3H); 2.26 (*s*, 3H). – ^{13}C-NMR. ($CDCl_3$): see *Table*. – MS. (70 eV): 332 (36), 291 (7), 290 (100), 275 (6), 247 (6), 246 (5), 245 (4), 232 (7), 231 (4), 215 (2), 43 (2).

$C_{22}H_{20}O_3$ (332.4) Calc. C 79.49 H 6.06% Found C 79.55 H 6.15%

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