Tetrahedron Vol. 49, No. 34, pp. 7487-7498, 1993
Printed in Great Britain

0040-4020/93 $6.00+.00

REACTIONS OF METHYLVINYL AND PHENYLVINYL KETONES WITH A TRICYCLIC KETONE DERIVED FROM 2-TETRALONE: CHARACTERISATION OF CRYSTALLINE PRODUCTS BY X-RAY DIFFRACTION.

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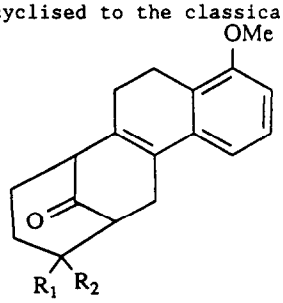
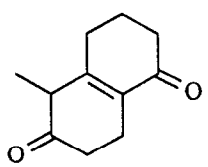
(*Received in UK* 24 *June* 1993)

Abstract Base catalysed reaction of the tricyclic ketone (6 ⇌ 7) with methylvinyl ketone gave the tetracyclic ketols, **11, 13, 15, 16,** and the pentacyclic ketols, **12, 17.** With phenylvinyl ketone, the tetracyclic ketol (**18**) was formed. The stereostructures of the ketols were identified by X-Ray diffraction.

The Robinson annelation reaction[1,2], for formation of six-membered ring α, β-unsaturated ketones by condensation of cyclohexanones with methylvinyl ketone or its equivalents, followed by intramolecular aldol condensation, has long been a paramount synthetic reaction in alicyclic chemistry. The reaction has been very widely applied to cyclohexanones[2], although unexpected products are sometimes formed, e.g. from the acid or alkaline cleavage of β-diketones (from cyclohexane diones)[3]. In 1960 an anomalous cyclisation was reported by W.S. Johnson[4], leading to the bridged ketols (**1a** and **1b**). Similarly, it was shown that the condensation of the octalindione (2) with methylvinyl ketone gives the two epimers (**3a** and **3b**). It appeared that these bridged intermediates underwent retro-aldol cleavage to the open-chain precursors which re-cyclised to the classical ketol precursors of the cyclohexenones before β-elimination.



1a R_1=α-Me, R_2=β-OH
b R_1=β-Me, R_2=α-OH



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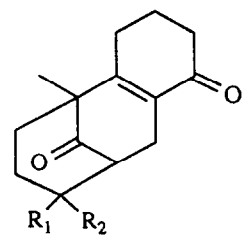
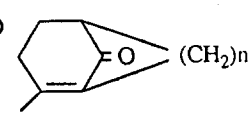


3a R_1=α-Me, R_2=β-OH
b R_1=β-Me, R_2=α-OH



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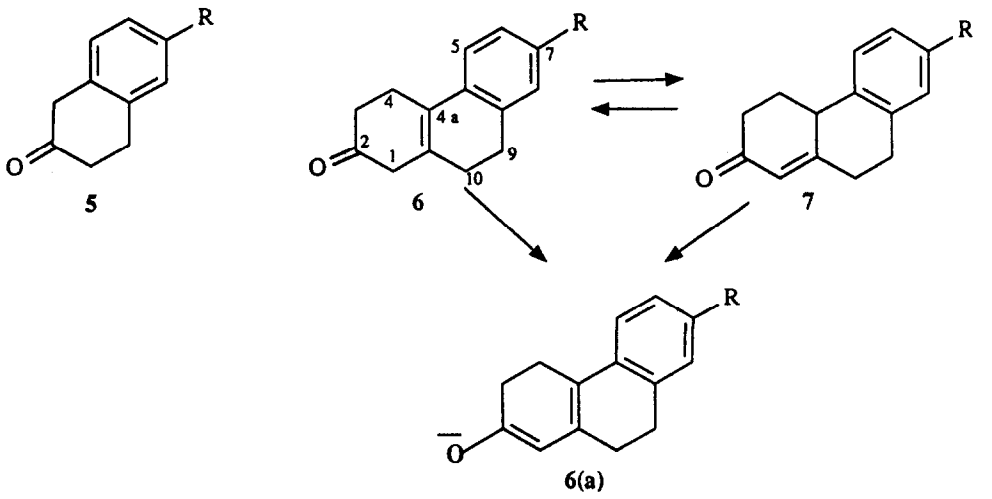
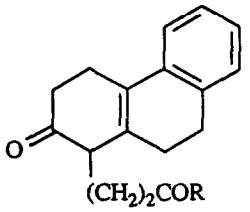
The bridged structures (1 and 3, a and b) are reminiscent of the bridged unsaturated ketones (4) obtained by Prelog[5] from the condensation of cyclic β-keto-carboxylic esters containing an 8 or higher membered ring. The corresponding precursor ketols may also have been involved in the smaller ring homologues, which of course, could not eliminate to the anti-Bredt's rule bridged cycloalkenones, and so would rearrange to the fused ketols. In the light of the existence of the reported anomalous ketols, we decided to examine in detail the products of condensation of the tricyclic ketone (6; R=H) with methylvinyl ketone. It seemed to us that this would be a good model on which to test the variety of bridged ketol structures actually formed, in view of the numerous theoretical possibilities. It seemed probable that, in fact, many such ketols could in general be involved in Robinson annelations but for various reasons their presence has been overlooked in previous work.



The tricyclic ketone 3,4,9,10-tetrahydrophenanthren-2(1H)-one 6; R=H is the principal product of the reaction of 3,4-dihydro-1H-naphthalen-2-one (2-tetralone) 5; R=H with methylvinyl ketone.[6] With base, 6; R=H equilibrates with its a, β-unsaturated isomer 7; R=H but the latter does not appear to have been obtained pure. The equilibrium mixture 6 ⇌ 7 can form four enolates, the active centres of which are at C1, C3, C4a and C10 and reaction with methylvinyl ketone can occur initially at any one of these to afford, for example, the diketone 8; R=Me. Base catalysed cyclisation of this can involve any one of the centres at C3, C4a, C10 to give, in each case, a pair of diastereoisomeric ketols[4,7], for example 9; R=H, or the unsaturated ketone 10; R=H which can undergo further reaction with methylvinyl ketone. We have isolated some of the many possible condensation products and identified their structures and configurations by X-ray diffraction.

Nagata et.al.[8] reacted 6-methoxy-2-tetralone 5; **R=OMe** with methylvinyl ketone and obtained **6**; **R=OMe** and the tetracyclic ketol **11**; **R=OMe**. Further condensation of **6**; **R=OMe** with methylvinyl ketone gave two compounds of structure **9**; **R=OMe** which were considered to be epimers at the alcohol centre, and a pentacyclic ketol **12**; **R=OMe**. The stereostructures of these compounds were, however, not assigned.



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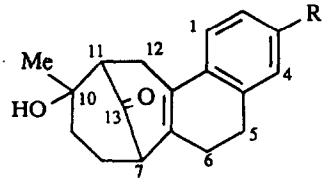

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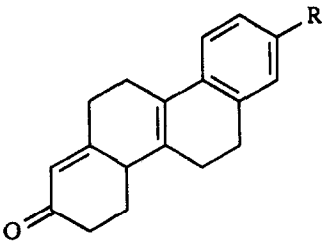

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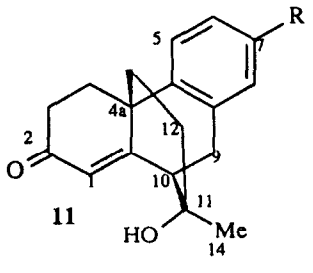
In our hands reaction of methylvinyl ketone with 2-tetralone 5; **R=H** in presence of methoxide gave a complex mixture (T.L.C.) which, after removal of 5; **R=H** and **6**; **R=H** by distillation, yielded a gum. In one experiment the principal component of this was (±)-4aS, 10R, 11R-4,4a,9,10-tetrahydro-11-hydroxy-11-methyl-4a,10-propanophenanthren - 2(3H)-one **11**; **R=H** and in another experiment, performed under slightly modified conditions, the principal component was (±)-9S,10S,12aS-5, 6, 10, 11,12,12a hexahydro-10-hydroxy-10-methyl-9,12a-methanocycloocta[a]naphthalen-8(9H)-one **13**. The formation of **11**; **R=H** and **13** involve initial reaction at 4a of methylvinyl ketone with the maximally conjugated enolate **6a** to give **14** followed by cyclisation to C10 and C3 respectively.



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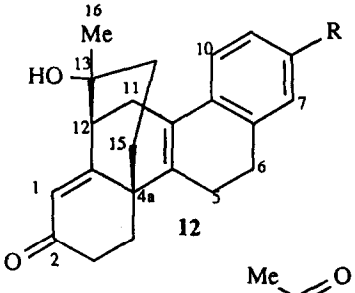

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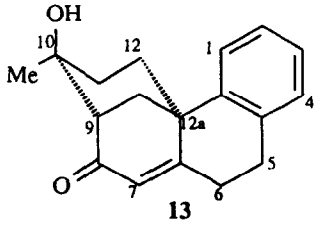

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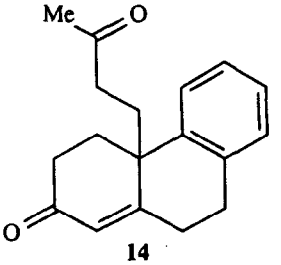

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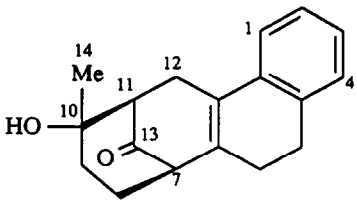
The structure of the ketol **11**; **R=H** ($C_{18}H_{20}O_2$ by elemental analysis) was inferred from classical spectroscopic techniques. In its E.I. mass-spectrum it showed a weak M^+ at m/z 268 and a relatively abundant ion at m/z 250. The base peak at m/z 197 was consistent with the loss of the C4a, C10 bridge with hydrogen transfer. The orientation of this bridge and the configuration at C11 followed from NMR spin-decoupling and NOE difference spectra. Thus, irradiation of the clean doublet, J7Hz, at δ2.64 (10H) collapsed the double doublet at δ3.25 (J16, 7Hz; 9αH) to a doublet, J16Hz. In an NOE experiment saturation of the 11 Me protons gave 2.5% and 7.5% enhancements of the 10H and 9βH signals at δ2.64 and 3.09 respectively. This structure was later confirmed by X-ray crystallography.

In our earlier studies,[7,9] the structures, configurations and, in many cases, conformations of condensation products were deduced from high resolution NMR. For the more extended systems of the present work, it proved difficult to derive unique structures by this technique; proton signals overlapped to such an extent that complete assignments could not be made. The crystalline products were examined by single-crystal X-ray diffraction and complete structures and conformations obtained more expeditiously.

Reaction of methylvinyl ketone with **6**; **R=H** gave a mixture from which six compounds were isolated by chromatography. Two of these were compounds **11**; **R=H** and **13** described above. The others were (±)-4aR,12S,13S-4,4a,5,6,11,12-hexahydro-13-hydroxy-13-methyl-4a,12-propanochrysen-2(3H)-one **12**; **R=H**, (±)-7R,10S,11R-5, 6, 7,8,9,10,11,12-octahydro-10-hydroxy-10-methyl-7,11- methanocycloocta[a]naphthalen-13-one **15**, (±)-7S,10S,11S-5,6,7,8,9,10,11,12-octahydro-10-hydroxy-10-methyl-7,11-methanocycloocta[a]naphthalen-13-one **16**and (±)-4aS,12R,13S-4,4a,5,6,11,12-hexahydro-13-hydroxy-13-methyl-4a,12-propanochrysen-2(3H)-one **17**.



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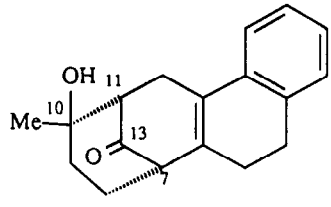

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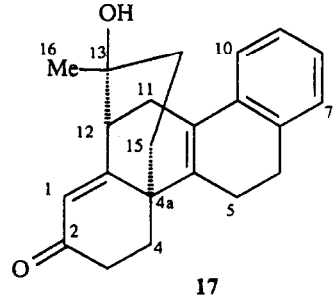
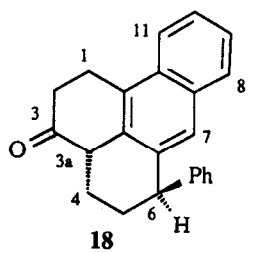


17

The compounds **12; R=H, 15, 16** and **17** can be formed by reaction of methylvinyl ketone at C1 of the enolate **6a** to give initially the diketone **8; R=Me**, which can cyclise at C3 to yield compounds **15** and **16** or it may give the chrysene derivative **10; R=H** which, by further reaction with methylvinyl ketone, can afford **12; R=H** and **17**. In principle, **12; R=H** and **17** are respectively derivable from **15** and **16** by reaction with another molecule of methylvinyl ketone, but models show that the required enolates would be very highly strained.

Initial attack on the **6** ⇌ **7** system apparently takes place on C1 or C4a, through the more conjugated and presumably more stable enolates. Modelling of these systems shows that they are conformationally quite mobile and further reaction to the tetra- and pentacyclic compounds is not difficult. The resultant ketols possess a new chiral centre at the tertiary alcohol carbon; in two cases, both epimers were obtained, **15/16** and **12/17**; in the other cases, only one epimer was isolated, that in which the hydroxy group is axial with respect to the six-membered ring. This would be the thermodynamically more stable epimer. However, the energy difference is probably small and the other epimer may also be present in lesser amount and was therefore not isolated.

We did not encounter in the above reactions any compound whose formation involved both active centres at C1 and C10 of **6; R=H** and **7; R=H**. Both of these centres, however, were employed when phenylvinyl ketone, derived from a Mannich base methciodide, was reacted with **6; R=H**. The product isolated was (±)-3aS,6R-1,2,3a,4,5,6, hexahydro-6-phenyl-benzo[de]anthracen-3(3H)-one **18**. Its precursor was probably the ketol **19** derived from the diketone **8; R=Ph**.



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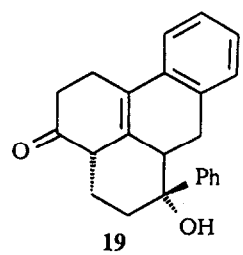

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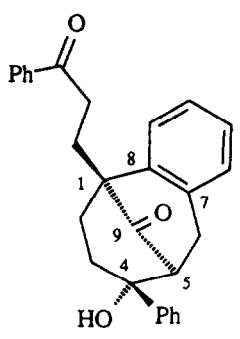

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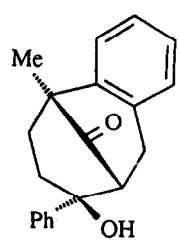

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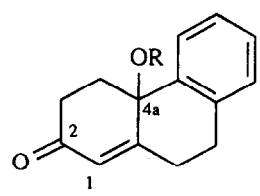


22

When 2-tetralone 5; R=H was reacted with an excess of phenylvinyl ketone, derived from Mannich base, we obtained the diketone **20**, namely (±)-1R,4R,5S-1-(2[1]-benzoylethyl)-4-hydroxy-4-phenyl-benzo(g)bicyclo[3,3,1] nonan-9-one. Its relative configuration is similar to that of the analogous compound **21** obtained[9] from 1-methyl-2-tetralone.

On standing in air, the tricyclic ketone **6** undergoes oxidation at C4a to give a product from which the ketol **22**; R=H was isolated in two crystalline forms, m.p. 181-182°C and 188-189°C. Presumably compound **7**; R=H and the hydroperoxide **22**; R=OH are intermediates in the formation of the ketol. The crystalline form m.p. 181-182°C, shows an OH band at 3420 cm^{-1} in the infrared (Nujol mull) whilst the other form, m.p. 188-189°C gives a band at 3350 cm^{-1}; otherwise the spectra are identical. The X-ray analyses of the two forms show that the only significant difference is in the crystal packing. The crystal data in Table 1 refer to the lower melting form, as does the plot of **22**; R=H. All the non-hydrogen atoms were located in both crystals, and the molecules have the identical conformations in the two crystal forms. We could however only locate the hydroxyl hydrogen (H20) in the lower melting form. One observable structural difference between the two forms is found to be that the shortest intermolecular hydroxyl O.....O distance in the higher melting form (5.743 Å) is larger than that of the lower melting form (4.091 Å). The melting point difference must arise from the different intermolecular interactions.

EXPERIMENTAL

Crystal structure determinations.

Table 1 summarises the crystal data, data collection parameters and refinements. All measurements were made on an Enraf Nonius CAD-4 diffractometer (Mo radiation, graphite monochromator, $\omega/2\theta$ scans) at 20°C. Accurate cell parameters were determined in all cases using the CELDIM routine. Decay and absorption were minimal and ignored in the data processing. The data were reduced to give the number of unique reflections and those with $|F| > 4\sigma|F|$ were then used in structure solution and refinement. Each structure was solved using the direct methods routine of SHELXS. The hydrogen atoms were all located from subsequent difference Fourier maps (except in **11** and **20** where the hydroxyl hydrogen only was located, the rest were placed geometrically). The structures were refined by full matrix least-squares analysis, the non-hydrogen atoms anisotropically, hydrogens in similar environments with common temperature factors.

Table 1

Compound	11	12	13	15	16	17	18	20	22
Mol. formula	$C_{18}H_{20}O_2$	$C_{22}H_{24}O_2$	$C_{18}H_{20}O_2$	$C_{18}H_{20}O_2$	$C_{18}H_{20}O_2$	$C_{22}H_{24}O_2$	$C_{23}H_{20}O$	$C_{28}H_{26}O_3$	$C_{14}H_{14}O_2$
M_r	268.35	320.43	268.35	268.35	268.35	320.43	312.41	410.52	214.26
Crystal system	monoclinic	ortho'mbic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	ortho'mbic	monoclinic
a (Å)	8.846(2)	6.896(4)	11.015(1)	7.597(1)	10.632(2)	13.11(2)	12.114(3)	10.035(3)	7.901(1)
b (Å)	20.142(2)	15.753(8)	10.327(4)	22.722(2)	7.742(1)	7.47(1)	8.623(1)	20.454(2)	11.802(3)
c (Å)	8.898(2)	31.113(3)	13.467(1)	8.233(2)	17.364(3)	17.08(2)	15.624(3)	21.383(2)	11.750(1)
α (°)	90.000	90.000	90.000	90.000	90.000	90.00	90.000	90.000	90.000
β (°)	116.229(9)	90.000	113.754(4)	97.832(9)	94.721(9)	94.94(6)	95.485(9)	90.000	100.182(6)
γ (°)	90.000	90.000	90.000	90.000	90.000	90.00	90.000	90.000	90.000
V (Å^3)	1422.2(5)	3380.2(4)	1402.2(3)	1418.3(4)	1424.5(4)	1666(3)	1624.6(5)	4389.1(7)	1078.4(2)
Space group	$P2_1/c$	P_{cab}	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	P_{cab}	$P2_1/n$
z	4	8	4	4	4	4	4	8	4
D_c (gcm^{-3})	1.25	1.26	1.27	1.26	1.25	1.27	1.28	1.24	1.32
μ (Mo-K_α) (cm^{-1})	0.46	0.43	0.45	0.44	0.44	0.39	0.40	0.44	0.49
F (000)	576.0	1376.0	576.0	576.0	576.0	684.0	664.0	1744.0	456.0
θ range	$1<\theta<22$	$1<\theta<22$	$1<\theta<25$	$1<\theta<22$	$1<\theta<22$	$1<\theta<22$	$1<\theta<22$	$1<\theta<22$	$1<\theta<22$
Total data measured	1947	2434	2727	1953	1984	2308	2247	3072	1486
Total data unique	1740	2067	2456	1733	1747	2023	1984	2686	1320
Reflections observed $\|F\|>4\sigma\|F\|$	1305	1237	1839	1458	1417	1330	1503	1091	941
R_{merg}	0.0150	0.0000 *	0.0205	0.0094	0.0079	0.0223	0.0136	0.0000 *	0.0132
R	0.0508	0.0453	0.0412	0.0452	0.0340	0.0408	0.0333	0.0824	0.0346
R_w	0.0508	0.0464	0.0520	0.0523	0.0405	0.0408	0.0379	0.0803	0.0365
No. of parameters	207	294	247	247	247	295	282	260	191
Max. final shift/esd	0.029	0.039	0.033	0.021	0.034	0.021	0.034	-0.034	0.018
Max. residual electron density (eÅ^{-3})	0.4825	0.1659	0.2624	0.2248	0.1662	0.1365	0.1067	0.2407	0.1214
Min. residual electron density (eÅ^{-3})	-0.1851	-0.1770	-0.0018	-0.1813	-0.1182	-0.1596	-0.1127	0.2494	-0.1849

* There were no equivalent reflections measured in these two data sets.

Figures were drawn using program SCHAKAL, courtesy of Professor E. Keller (University of Freiburg). The programs SHELXS and SHELX-76 are used by kind permission of Professor G.M. Sheldrick (University of Göttingen). The atomic co-ordinates, bond lengths and angles and thermal parameters for all the compounds given in the Table have been deposited at the Cambridge Crystallographic Data Centre.

Condensation of Methylvinyl Ketone with 2-Tetralone 5; **R=H**. (a) 2-Tetralone(12.2g) in dry methanol (90ml) was added to a stirred solution of sodium methoxide, from sodium (1.05g) and methanol (50ml), kept at 2 - 5°C under N_2. Methylvinyl ketone (6.14g) in methanol (35ml) was added over 45 min. to the stirred solution, retained at 2-5°C for 1h., at room temperature for 1h., then at 60-70°C for 0.5h. Usual work up gave 2-tetralone(2.9g), b.p. 80-90°C at 0.4 mm Hg, and the tricyclic ketone 6; **R=H**, b.p. 150-160°C at 0.4 mm Hg, m.p. 68°C (methanol)(lit[6] 67°C), ν_{max} (Nujol) cm^{-1} 3350, 1710, 1655, 1600, 1490, 770, 760, and 730, δH (360 MHz; $CDCl_3$) 2.24 (2H, m, 3H), 2.68 (2H, m, 9H), 2.87 (4H, m, 4H, 10H), 3.05 (2H, s, 1H), 7.16 (2H, m, ArH), and 7.22 (2H, m, ArH), δC (75.6 MHz; $CDCl_3$) 25.7, 28.0, 28.5, 38.8, and 44.4 (5x$\underline{C}H_2$), 121.9, 126.5, 126.6 and 127.4 (4x Ar$\underline{C}$H), 127.5, 130.9, 134.8, and 134.9 (4x quat.C), 209.9 (C=O), m/z (%) (EI) 199 (M + 1; 16), 198 (M; 100). The residual gum was set aside in ether at 0°C for 18h when (±)-4aS, 10R, 11R-4,4a,9,10-tetrahydro-11-hydroxy-11-methyl-4a,10-propanophenanthren-2(3H)-one 11; **R=H** (0.2g), m.p. 208-209°C (ethyl acetate) was deposited, ν_{max} (Nujol) cm^{-1} 3380 (str. and shp), 1650, 1630 (sh.), 1500 (sh.), 1490 (sh.), 770, 760 and 720, δH (360 MHz; $CDCl_3$) 1.34 (1H, m, partially obscured, 13H), 1.36 (3H, s, Me), 1.51 (1H, m, partially overlapping, 13H), 1.56 (1H, m, partially overlapping, 4H), 1.79 (1H, s, br., OH), 2.23 (1H, dt, J 13, 4Hz, 4H), 2.36, (2H, m, 12H), 2.54 (2H, m, CH_2), 2.64 (1H, d, J, 7Hz, 10H), 3.09 (1H, d, J 16 Hz, 9 βH), 3.25 (1H, dd, J 16, 7Hz, 9αH), 6.03 (1H, s, 1H), 7.10 (1H, d, J 7Hz, ArH), 7.19 (1H, dt, J 7, 2 Hz, ArH), 7.22 - 7.30 (2H, obscured m, 2 x ArH). Irradiation of the dd at δ 3.25 collapsed the doublets at δ 2.64 and δ 3.09 to singlets and irradiation of the doublet at δ 2.64 collapsed the double doublet at δ 3.25 to a doublet. N.O.E enhancements: 11 Me - 10H, 2.5%, 11 Me - 9βH, 7.5%. m/z% (E1) 268 (M; 2), 250 (M-H_2O; 50), 197 (100). [Found: C, 80.4; H, 7.6. $C_{18}H_{20}O_2$ requires C, 80.6; H, 7.5%].

Chromatography of the ethereal mother liquors using 60% ethyl acetate-hexane afforded the ketone 13; (140 mg), m.p. and mixed m.p. 165°C. (see below).

(b) The condensation was performed according to the published method[6] using 2-tetralone (15.6g) and methylvinyl ketone (5.5g). Usual work up gave 2-tetralone (5g), and the ketone 6; **R=H** (3g), m.p. 68-69°C (ethyl acetate). The remaining gum after removal of these volatile components was dissolved in boiling ethyl acetate and the solution was refrigerated. The deposited solid was (±)-9S, 10S, 12aS-

5,6,10,11,12,12a,-hexahydro-10-hydroxy-10-methyl-9,12a-methanocycloocta[a]naphthalen-8[9H]-one **13** (2.1g), m.p. 155-159°C raised to 165°C (ethyl acetate-hexane), λ_{max} (EtOH) 244 nm (log ε 4.98), ν_{max} (Nujol) cm^{-1} 3500, 1650, 770,δH (360 MHz; $CDCl_3$) 1.29 (3H, s, Me), 1.5 -1.8 (4H, series of m, 3 x CH; OH), 2.03 (1H, dt, J 13.5, 3Hz, 5H), 2.38 (1H, m, CH), 2.51 (1H, s, br., CH), 2.53-2.66 (2H, m, 2 x CH), 2.85 (1H, dd, J, 13.5, 3.5Hz, 5H), 2.8 - 3.06 (2H, m, 2 x CH), 6.07 (1H, s, 7H), 7.11 (1H, d, J 8Hz, ArH), 7.17 (1H, t, J 8Hz, ArH), 7.28 (1H, t, J 8Hz, ArH), 7.50 (1H, d, J 8Hz, ArH), δC(75.6MHz; $CDCl_3$) 29.2 (Me), 30.5, 30.6, 31.7, 33.6, 37.1 (5 x CH_2), 40.4 (quat.C) ,55.9 (CH), 67.4 (quat.C), 125.7, 126.1, 126.3, 126.8, 128.4; 135.4, 142.1, 166.3, (3 x quat. C),200.8 (C=O), m/z(%) (E.I) 268 (M; 5), 250 (M-H_2O;10), 196 (M- $[CH_2]_2$.C[OH]Me; 100) [Found: C, 80.75; H, 7.3 $C_{18}H_{20}O_2$ requires C, 80.6; H, 7.5%].

Condensation of Methylvinyl Ketone with the Tricyclic Ketone **6**; **R=H**. - A solution of the tricyclic ketone (3.3g) in a mixture of dry dioxan (15 ml) and dry methanol (15 ml) was added over 15 min. to a stirred, ice-cold solution of sodium methoxide in methanol (14 ml., 2%) under N_2. Then freshly distilled methylvinyl ketone (1.8g) in dry methanol (11 ml), cooled to 0°C, was added over 40 min. Stirring was continued for 2.5h at 0°C, then overnight at room temperature. Work up gave a gum which on rubbing with ether gave a solid (0.8g), m.p. 176-178°C. Crystallisation from ethyl acetate gave (±)-7R, 10S, 11R-5,6,7,8,9,10,11,12-octahydro-10-hydroxy-10-methyl-7,11-methanocycloocta[a]naphthalen-13-one **15**, m.p. 181°C, ν_{max} (Nujol) cm^{-1} 3380, 1705, 1650, 920, and 770, δC (75.6MHz; $CDCl_3$) 27.4 and 27.5 (CH_2), 28 (Me), 28.3, 30.6 and 32.2 (3 x CH_2), 50.8 and 57.2 (2 x CH), 78.4 (quat.C), 121.7, 126.3, 126.7; 126.8 (quat.C), 127.2; 133.9 , 134.5, 135.1 (3 x quat.C) and 214.6 (C=O) [Found: C, 80.6; H, 7.5. $C_{18}H_{20}O_2$ requires C, 80.6; H, 7.5%] Chromatography of the ether washings on silica using ethyl acetate-hexane (60/40) gave, in the early fractions, the ketone **6**; **R=H** (0.3g), m.p. 65-66°C, followed by (±)-7S, 10S, 11S-5,6,7,8,9,10,11,12-octahydro-10-hydroxy-10-methyl-7,11-methanocycloocta[a]naphthalen-13-one **16** (5mg), m.p. 139-140°C(ethylacetate), m/z (%) 268 (M^+; 58), 194 (100) [Found: C, 80.6; H, 7.6. $C_{18}H_{20}O_2$ requires C, 80.6; H, 7.5%].

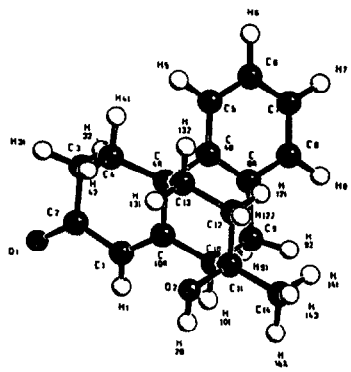
Later fractions gave (±)-4aR, 12S, 13S-4,4a,5,6,11,12-hexahydro-13-hydroxy-13-methyl-4a,12-propanochrysen-2(3H)-one **12**; **R=H** (20 mg), m.p. 208°C(ethyl acetate), depressed on mixing with compound **11**; R=H, ν_{max} (Nujol) cm^{-1} 3320, 1645, 930, 760 and 730, δC (75.6 MHz: $CDCl_3$) 22.8 (CH_2), 27.8 (Me), 28.9, 29.6, 32.3, 32.7, 33.3 and 34.4 (6 x CH_2), 41 (quat. C), 51.8(CH), 75.4 (quat. C), 122, 123, 126.6, 126.8, 127; 128, 135.2, 136 and 166.7 (4 x quat. C), 198.3 (C=O), [Found: C, 82.3, H, 7.5. $C_{22}H_{24}O_2$ requires C, 82.5; H, 7.5%].

The final compound to be eluted from the column was (±)4aS, 12R, 13S-4,4a,5,6,11,12-hexahydro-13-hydroxy-13-methyl-4a,12-propanochrysen-2(3H)-one **17** (10 mg), m.p. 225°C (ethyl acetate), ν_{max} (Nujol) cm^{-1} 3500, 1655, 770 and 730 [Found: C, 82.4; H, 7.6. $C_{22}H_{24}O_2$ requires C, 82.5; H, 7.5%].

Condensation of Phenylvinyl Ketone with the Tricyclic Ketone **6**; **R=H**. - Iodomethane (6g) in dry benzene (10 ml) was added over 90 min. to a stirred, ice-cold, solution of β-diethylaminopropiophenone (7.9g) in benzene (30 ml) and the mixture was stirred at 0°C for 2h, then left overnight at 0°C. The methoiodide was collected, suspended in a mixture of dry methanol (30 ml) and dioxan (150 ml) and added, under N_2, over 2.5h. to a stirred, ice-cold solution of the ketone **6**; **R=H**(7g) and sodium methoxide [from sodium (1.5g) in methanol (24ml)], prepared by adding the ketone under N_2 to the methoxide at 0°C. The temperature of the mixture was allowed to rise to ambient and stirring was continued overnight. Reaction was completed by warming the mixture to 60-70°C for 1 h. Work up gave a dark gum which, chromatographed on silica using 15-20% ethyl acetate in hexane gave (±)-3aS,6R-1,2,3a,4,5,6 hexahydro-6-phenyl-benz[de]anthracen-3(3H)-one **18** (184 mg), m.p. 132-133°C (ethyl acetate-hexane), ν_{max} (Nujol) cm^{-1} 1710, 1605, 1590, 1500, 780, 770 and 750, δH (360MHz; $CDCl_3$) 1.95-2.50 (5H, series of m), 2.90 (1H, m, CH), 3.22 (1H, m, CH), 3.75-3.95 (2H, series of m, 2 x CH), 4.22 (1H, m, 6H), 7.16-8.13 (IOH, series of m, 10 x ArH),δC (75.6 MHz; $CDCl_3$) 21.9, 22.5, 31.3 and 36.3 (4 x CH_2), 46.5 and 48.8 (2 x CH), 122.5, 125.4, 125.8, 126.3, 127.6, 128.5, 128.8 (ArCH), 129.5, 130.6, 132.2, 133, 138.2 and 146.1 (6 x quat.C), m/z (%) 312 (M^+; 100) (Found: C, 88.3; H, 6.45. $C_{23}H_{20}O$ requires C, 88.4; H, 6.45%).

Condensation of excess of Phenylvinyl Ketone with 2-tetralone. —— A stirred refluxing solution of N,N-dimethyl-N-(2-benzoylethyl) ammonium chloride (22g), 2-tetralone (6g) in ethanol (210 ml) was treated rapidly with a solution of sodium hydroxide (5.6g) in water (28 ml) and refluxing was continued for a further 30 minutes. The solution was cooled, diluted with water (100 ml) and extracted with chloroform (4 x 30 ml). The extract was washed with water, dried and solvent removed giving a yellow syrup. This was stirred with a little cold ether and the solid (5.0 g), m.p. 168-170°C, thus formed was crystallised from ethyl acetate-hexane. The product (±) -IR, 4R, 5S-1-(2'-benzoylethyl)-4-hydroxy-4-phenylbenzo[g]bicyclo [3,3,1]nonan-9-one **20**, m.p. 177-178°C. ν_{max}(Nujol)cm^{-1} 1705, 1685, 1600, 1585, 775, 740, 700, δC (75.6MHz; $CDCl_3$) 27.5, 30.0, 34.1, 34.6, 40.3, 52.6, 57.9, 81.9, 125.5, 127, 127.5, 127.6, 128, 128.2, 128.4, 128.6, 132.8, 134.9, 136.9, 139.5, 144.2, 200.3 and 213.3. [Found: C, 82.0; H, 6.5. $C_{28}H_{26}O_3$ requires C, 81.95; H, 6.3%.]

Autoxidation of 3,4,9,10-Tetrahydrophenanthren-2-(1H)-one **6; R=H.** — The sticky material remaining after a supply of **2: R=H** had been standing for several weeks was rubbed with methanol, and the solid, m.p. 171-172°C was collected. Crystallisation from ethyl acetate gave 3,4,9,10-tetrahydro-4a-hydroxyphenanthren-2-(4aH)-one **22, R=H,** m.p. 181-182°C, λ_{max} (EtOH) 230 nm (log e 4.1), ν_{max} (Nujol) cm-1 3420, 1665, 1635, 1490, 1235, 945, 775, 770, 750; δH (360 MHz; $CDCl_3$), 2.13 (1H, dt, J 13.5, 5Hz, 4αH), 2.28 (1H, s, br., exch. D_2O, OH), 2.46-3.10 (7H, series of m, 4βH and 3, 9, 10 CH_2), 5.97 (1H, s, 1H), 7.17 (1H, d, J 8 Hz, ArH), 7.26 (1H, dt, J 8, 2 Hz, ArH), 7.34 (1H, t, br, J 8 Hz, ArH), 7.61 (1H, d, br, J 8 Hz, ArH). δC (75.6 MHz; $CDCl_3$) 30.2, 30.4, 34.1, 36.7 (4 x CH_2), 67.4 (quat. C-O), 125.7, 126.4, 127.4, 128 (4 x ArCH), 128.6 (Cl), 135.8, 140.2 and 162.6 (3 x quat. C), 199.5 (C=O). [Found: C, 78.4; H, 6.5. $C_{14}H_{14}O_2$ requires C, 78.5; H, 6.6%]. The mother liquors from the above crystallization slowly deposited another crystalline form of **22, R=H** m.p. 188-189°C, ν_{max} (Nujol) cm^{-1} 3350, 1650, 1635, 940, 770. Its ^{13}C spectrum was identical with that given above. [Found: C, 78.6, H, 6.6. $C_{14}H_{14}O_2$ requires C, 78.5; H, 6.6%.]



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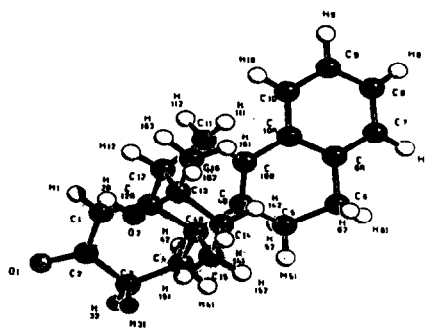

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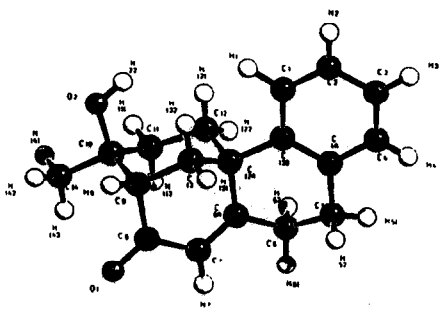

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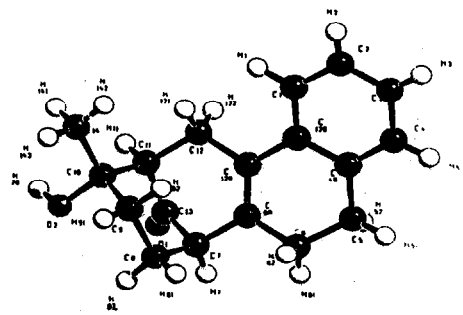

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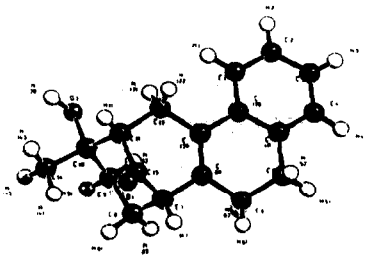

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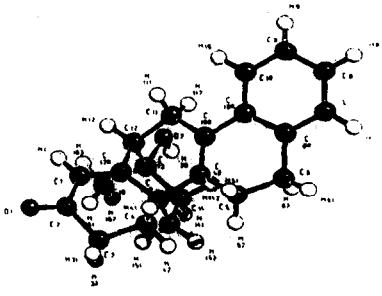

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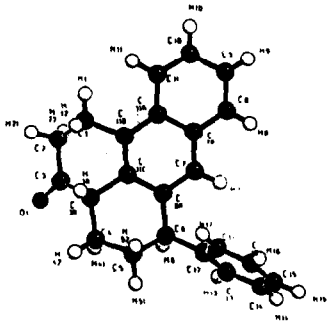

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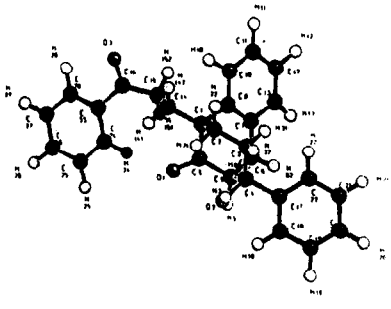

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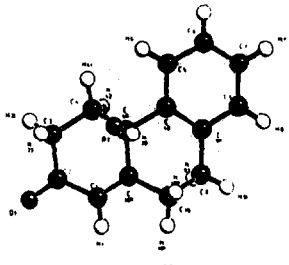

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Acknowledgements
We thank EOLAS for financial assistance (to DJW).

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