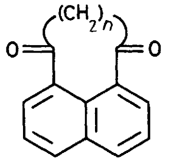
peri-Diketones with the Ring System of Cyclo-octa[*de*]naphthalene

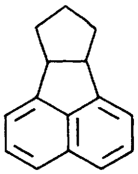
David A. Jackson, Philip H. Lacy, and Donald C. C. Smith *
Department of Chemistry, The University, Manchester M13 9PL

peri-Diketones of naphthalene having an eight-membered ring are obtained by oxidative cleavage of cyclopent[*a*]acenaphthylenes prepared from acenaphthylene-1,2-dione. Cyclo-octa[*de*]naphthalenes with two *peri* β-keto ester ketone carbonyl groups exist as mono-enols. The parent 9,10-dihydrocyclo-octa[*de*]naphthalene-7,11(8*H*)-dione is a stable though reactive diketone, reduced to a pinacol with exceptional ease and forming stable adducts with water or methanol.

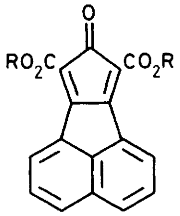
Enhanced reactivity shown by *peri*-diketones (**1**), (**3**), and (**4**),[1] made it of interest to synthesize and examine cyclo-octa[*de*]-naphthalenes having *peri* carbonyl groups, *e.g.* the diketone (**2**). Ring cleavage of suitable cyclopent[*a*]acenaphthylenes offers a route to such diketones, and known compounds having this structure include the hydrocarbon (**5**) made by trapping 1,8-naphthalyne with cyclopentene,[2] 8*H*-cyclopent[*a*]acenaphthylene,[3] and the purple antiaromatic 8-oxocyclopent[a]acenaphthylene-7,9-dicarboxylic esters (**6**)[4] and (**7**).[5]



(**1**) n = 2
(**2**) n = 3
(**3**) n = 4
(**4**) n = 5



(**5**)



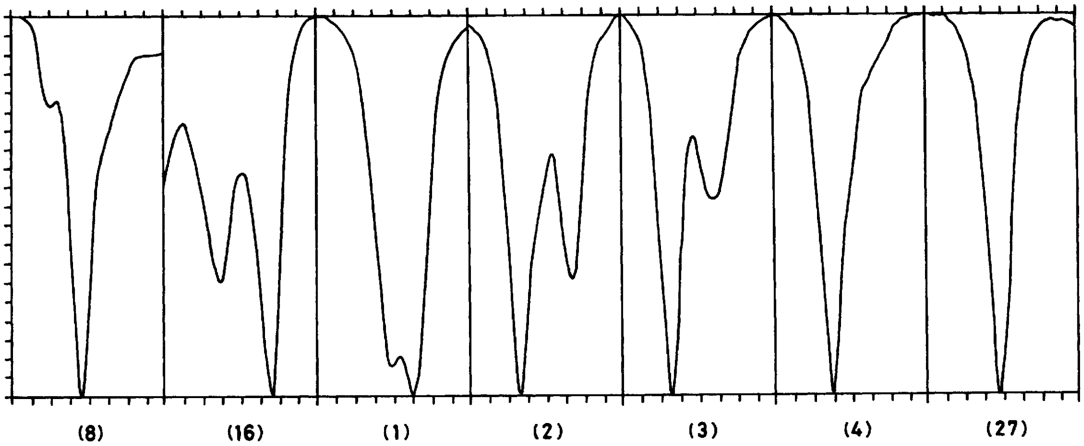
(**6**) R = Me
(**7**) R = Et

Results and Discussion

The epimeric diesters (**9**) and (**10**) were synthesized by condensing acenaphthylene-1,2-dione (**8**) with dimethyl pentenedioate (dimethyl glutaconate) as in Scheme 1. The diester (**9**) was oxidised by lead(IV) acetate to dimethyl 11-hydroxy-7-oxocyclo-octa[*de*]naphthalene-8,10-dicarboxylate (**11**). To reduce the conjugated 8,9-double bond of this substance while preserving the keto ester groups, magnesium and methanol were employed (*cf.* refs. 6 and 7). This afforded three diesters, all having lost the conjugated double bond, but all having been reduced further: the diol (**12**) resulting from a transannular pinacol reduction; and the regioisomers (**13**) and (**14**) resulting from a partial reduction of one aromatic ring. Surprisingly this same mixture was obtained by a reduction with magnesium and methanol of the diester (**9**); here reduction failed if attempted under nitrogen or in the presence of methyl borate to scavenge magnesium methoxide, suggesting that the mesomeric anion derived from esters (**9**) or (**10**) is first oxidised by air to the diester (**11**) before reduction may occur. This oxidation was observed when the diester (**9**) was exposed to air in methanol containing magnesium methoxide.

With the ultimate aim of synthesizing the *peri*-diketone (**2**), the diol (**12**) was cleaved with lead(IV) acetate to the diester (**15**);

Figure. The effect of increasing ring size upon the i.r. bands due to ketone (C=O) stretching in the cycloalka[*de*]naphthalenes (**8**), (**16**), and (**1**)—(**4**). For comparison 1,8-diacetylnaphthalene (**27**) is included



	(**8**)	(**16**)	(**1**)	(**2**)	(**3**)	(**4**)	(**27**)
Size of the diketone rings:	5	6	7	8	9	10	—
$\nu_{max.}(CS_2)/cm^{-1}$	1 749	1 700	1 691	1 704	1 704	1 700	1 692
	1 734	1 674	1 679	1 676	1 681	—	—

Table. Dynamic ^{1}H n.m.r. data that reflect rates of conformational inversion and reaction half-lives determined from u.v. absorption measurements that reflect the approximate rates of addition reactions by *peri*-diketones **(1)**—**(4)**

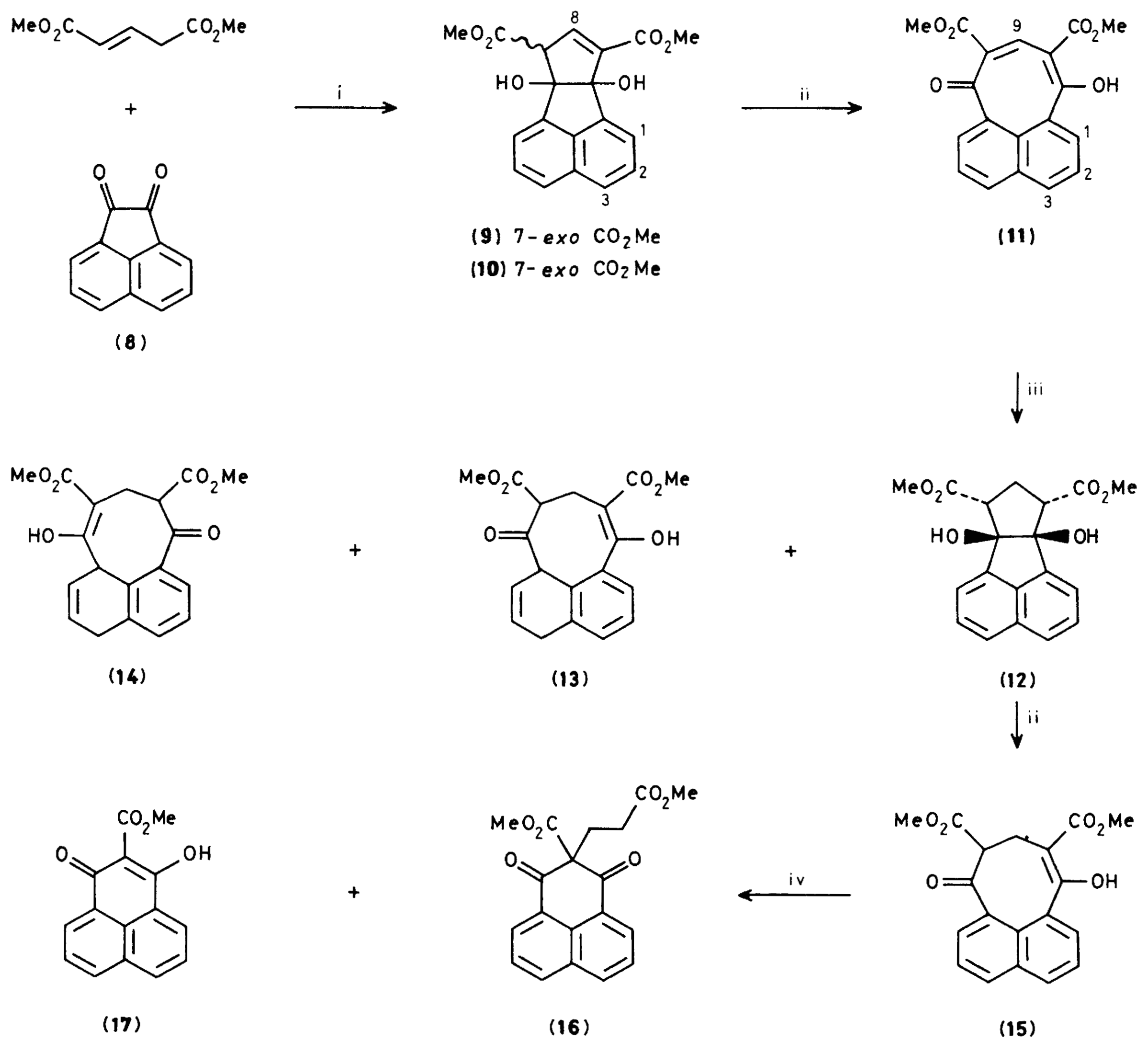
Compound		**(1)**	**(2)**	**(3)**	**(4)**
Coalescence temperatures	α*	—†	—†	−39	+51
of methylene signals in	β*		—†	−45	+46
300 MHz spectra (°C)	γ*				+58
Additions in water.					
Approximate $t_{0.5}$ (min)‡		1.5	150	270	0.04
Final loss of diketone (%)		30	100	90	20
Crystalline products recoverable		Diketone	Hydrate	—§	—§
Additions in methanol.					
Approximate $t_{0.5}$ (min).‡		35	1 200	360	2.2
Final loss of diketone (%)		60	100	90	90
Crystalline products recoverable		Diketone	Methyl hemiacetal	Methyl hemiacetal	Dimethyl acetal

* Positions of methylene groups relative to carbonyl.

† Not observed down to −65 °C despite the magnetic nonequivalence predicted by force field calculations.

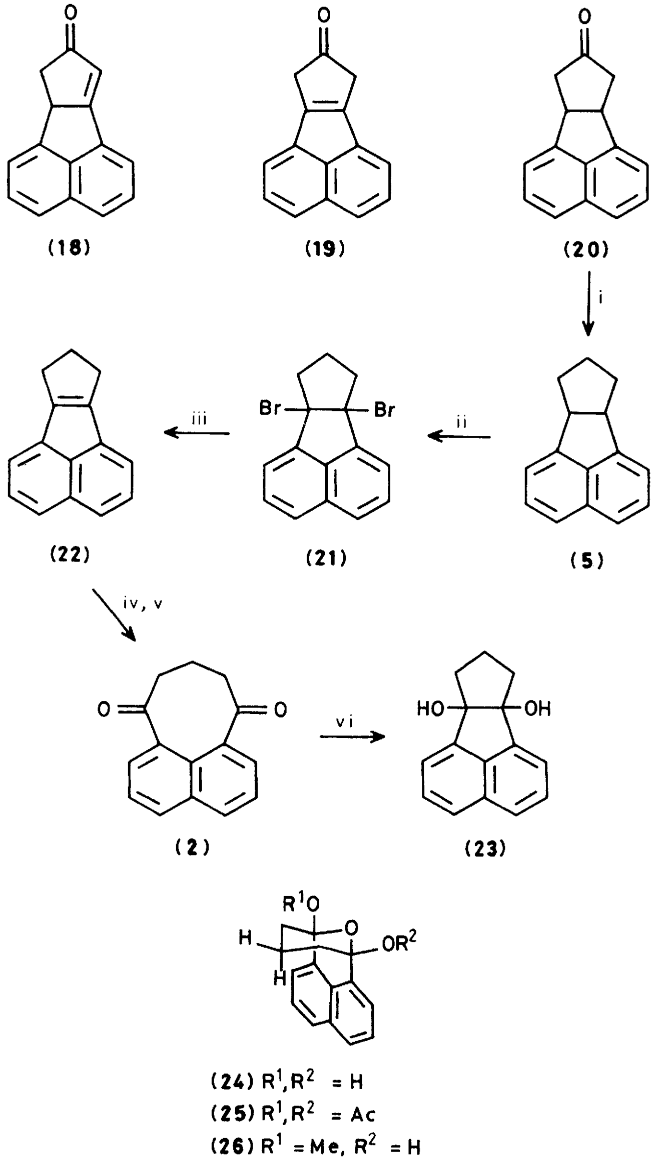
‡ Times of half-completion ($t_{0.5}$) with roughly the same amount of catalyst (acetic acid in water or methanol), calculated as $t_{0.5}$ (observed at room temperature) × number of drops of catalyst added to 3 ml of diketone solution × % concentration of acetic acid in the catalyst ÷ 100.

§ Not attempted due to the ease of transannular aldol reactions.



Scheme 1. *Reagents:* i, sodium methoxide–methanol; ii, Pb(OAc)$_4$–acetic acid; iii, magnesium–methanol; iv, spontaneous reaction

as with diesters (**11**), (**13**), and (**14**) this exists entirely as a mono-enol, but before it could be deprived of its ester groups by hydrolysis and decarboxylation it suffered a spontaneous transannular aldol reaction followed by ring opening, to give the phenalenones (**16**) and (**17**). This rearrangement seemed to preclude synthesis of the diketone (**2**) from the diester (**15**), so a fresh approach was tried based upon the cyclopent[*a*]acenaphthylene (**5**); first, however, a more convenient synthesis of the latter was devised. The purple diester (**6**) was reduced by zinc and acetic acid, a reaction perhaps assisted by anti-aromaticity, and the products were hydrolysed and decarboxylated before characterisation, to afford the ketones (**18**), (**19**), and (**20**). The ketone (**20**) was reduced to the known hydrocarbon (**5**), and this in three steps gave the desired *peri*-diketone (**2**) as outlined in Scheme 2.



Scheme 2. *Reagents:* i, hydrazine–potassium hydroxide; ii, *N*-bromosuccinimide; iii, zinc–ethanol; iv, ozone–acetic acid; v, dimethyl sulphide–acetic acid; vi, zinc–acetic acid

In the diketone (**2**) no enol tautomer was detectable, and its spectroscopic parameters fall into line with those of its ring homologues (**1**), (**3**), and (**4**), except for its u.v. absorption which is at shorter wavelength [$\lambda_{max.}$(MeOH) (**1**) 230 and 315 nm; (**2**) 221, 285, and 290 nm; (**3**) 226 and 304 nm; and (**4**) 225 and 301 nm]. It has been remarked that acenaphthylene-1,2-dione (**8**) differs from other *o*-quinones in showing two i.r. carbonyl-stretching bands.[8] The spectra in the Figure show that this distinction is shared with its non-quinonoid ring homologues (**16**), (**1**), (**2**), and (**3**), and only when the *peri*-ring is ten-membered, in diketone (**4**), or absent, in 1,8-diacetylnaphthalene, is a single carbonyl-stretching band observed. The diketone (**2**), unlike its ring homologues (**3**) and (**4**), shows no n.m.r. evidence for slowing of conformational inversion when cooled (Table). It also differs from its ring homologues (**3**) and (**4**) in failing to undergo a transannular aldol reaction; but enhanced carbonyl reactivity is observed, thus zinc and acetic acid, which does not reduce typical ketones, reduces the diketone (**2**) to the pinacol (**23**). After the manner of diketone (**1**) (*cf.* ref. 9), the diketone (**2**) dissolves in aqueous alkali as the salt of an acidic hydrate (**24**); but whereas the analogous salt from (**1**) gives back the diketone on acidification, the hydrate (**24**) is stable, and with acetic anhydride under acidic conditions gives a di-*O*-acetyl derivative (**25**). As with the diketones (**1**), (**3**), and (**4**), the diketone (**2**) adds methanol or water with catalysis by acetic acid (Table); these additions are relatively slow but go to completion, and in this way methanol affords the bridged hemiacetal (**26**). Chair conformations as shown in structures (**24**)—(**26**) are suggested by the n.m.r. spectra, there being a frequency separation of the signals of the 9-*endo* and the 9-*exo* protons attributable to shielding by the aromatic rings.

Experimental

*Epimeric Dimethyl 6b,9a-dihydro-6b,9a-dihydroxy-7*H*-cyclopent*[a]*acenaphthylene-7,9-dicarboxylates* (**9**) *and* (**10**).—A stirred suspension of acenaphthylene-1,2-dione (**8**) (2.6 g) in dimethyl pentenedioate (2.8 g),[10] and methanol (30 ml) was treated with 1M sodium methoxide in methanol (1 ml); after 10 min all solid had dissolved, and after 3 h the solution was diluted with aqueous acetic acid and extracted with ethyl acetate. The extract was washed with aqueous sodium hydrogen carbonate, dried (Na_2SO_4), and concentrated to a glass (4.3 g) that crystallised from ether giving the 7-*exo* ester (**9**) as colourless *prisms* (1.8 g), m.p. 158—160 °C (Found: C, 67.3; H, 4.8. $C_{19}H_{16}O_6$ requires C, 67.3; H, 4.7%); $\lambda_{max.}$(EtOH) 221, 278, 288, 298, and 315 nm (log ε 4.72, 3.77, 3.86, 3.74, and 2.95); $\nu_{max.}$($CHCl_3$) 3 500 (br, OH), 1 740, 1 720 (C=O), and 1 640 cm^{-1} (C=C); δ_H(60 MHz; $CDCl_3$) 3.82 (3 H, s), 3.85 (3 H, s), 3.95 (1 H, d, *J* 3 Hz), 4.1 (1 H, s, exch.), 4.2 (1 H, s, exch.), 6.8 (1 H, d, *J* 3 Hz), and 7.3—7.9 (6 H, m); *m*/*z* 340 (M^+, 10%) and 255 (100). The mother liquor with ether yielded first more crystals (1.0 g) m.p. 128—150 °C then gave from chloroform and tetrachloromethane the 7-*endo* ester (**10**) as colourless *prisms* (57 mg), m.p. 149—150 °C (Found: C, 67.3; H, 4.7. $C_{19}H_{16}O_6$ requires C, 67.3; H, 4.7%); $\lambda_{max.}$(MeOH) 221, 278, 288, 298, and 316 nm (log ε 4.75, 3.77, 3.86, 3.74, and 2.97); $\nu_{max.}$($CHCl_3$) 3 540 (OH), 1 740, 1 720 (C=O), and 1 640 cm^{-1} (C=C); δ_H(60 MHz; $CDCl_3$) 3.3 (3 H, s), 3.8 (3 H, s), 4.0 (1 H, d, *J* 3 Hz), 4.2 (2 H, s, exch.), 6.6 (1 H, d, *J* 3 Hz), and 7.4—7.9 (6 H, m); *m*/*z* 340 (M^+, 8%) and 255 (100).

Reduction of the Diester (**9**) *with Magnesium and Methanol.*—Methanol (50 ml) and magnesium turnings (5 g), having started to react, were added to the diester (**9**) (220 mg), then allowed to boil with some external cooling until all the metal had reacted. The resulting solution was treated with dilute hydrochloric acid and extracted with ethyl acetate. The extract was washed with aqueous sodium hydrogen carbonate, dried (Na_2SO_4), and concentrated to a glass (171 mg). An aliquot (108 mg) was separated on a t.l.c. plate (20 × 20 × 0.2 cm of silica) developed with ethyl acetate and 1,1,1-trichloroethane (1:1). Elution of a faster moving zone gave both the regioisomers (**13**) and (**14**) (37 mg) which from acetone gave large colourless prisms, m.p. 176—186 °C; further recrystallisations failed to change this melting point and it is suspected that *mixed crystals* are formed by these isomers (Found: C, 66.7; H, 5.3. $C_{19}H_{18}O_6$ requires C, 66.7; H, 5.3%); $\lambda_{max.}$(MeOH) 215sh and 272 nm (log ε 4.29 and 4.27); $\nu_{max.}$($CHCl_3$) 2 950br (OH), 1 747, 1 712, 1 655 (C=O), and 1 620 cm^{-1} (C=C); n.m.r. integration showed a 78:22 ratio for the regioisomers, and without specifying whether diester (**13**) or diester (**14**) is the major constituent, the following signals are segregated according to their integrated intensities: δ_H(300 MHz; $CDCl_3$) major regioisomer, 2.28 (1 H, dd, *J* 15 and 12 Hz), 2.96 (1 H, dd, *J* 15 and 2 Hz), 3.22 (1 H, dd, *J* 20 and 6 Hz), 3.62—3.66 (2 H, m), 3.68 (3 H, s), 3.88 (3 H, s), 4.94 (6a-H, dd, *J* 6 and 2 Hz), 5.87 (1 H, symmetrical m), 6.40 (1 H, m), 7.26—7.40 (3 H, m), and 12.87 (1 H, s, exch.); *minor regioisomer*, 2.35 (1 H, dd, *J* 15 and 12 Hz), 2.47 (1 H, symmetrical m), 2.63 (1 H, dd, *J* 17 and 6 Hz), 2.83 (1 H, dd, *J* 15 and 2 Hz), 3.48 (1 H, dd, *J* 12 and 2 Hz), 3.67 (3 H, s), 3.87 (3 H, s), 4.14 (6a-H, d, *J* 6 Hz), 6.12 (1 H, symmetrical m), 6.40 (1 H, m), 7.12 (1 H, dd, *J* 7 and 2 Hz), 7.26—7.40 (2 H, m), and 12.77 (1 H, s, exch.); *m/z* 342 (M^+, 9%), 128 (100), and 127 (100).

Elution of a slower moving zone gave dimethyl 6b,8,9,9a-tetrahydro-6b,9a-dihydroxy-7*H*-cyclopent[*a*]acenaphthylene-7-*exo*,9-*exo*-dicarboxylate (**12**) (28 mg) giving from 1,1,1-trichloroethane, colourless *plates* (11 mg), m.p. 155—157 °C (Found: C, 66.4; H, 5.3. $C_{19}H_{18}O_6$ requires C, 66.7; H, 5.3%); $\lambda_{max.}$(MeOH) 224, 275, 285, 296, and 315 nm (log ε 4.83, 3.83, 3.91, 3.74, and 2.71); $\nu_{max.}$($CHCl_3$) 3 450br (OH) and 1 735 cm^{-1} (C=O); δ_H(60 MHz; $CDCl_3$) 2.0—3.7 (4 H, m), 3.8 (6 H, s), 4.4 (2 H, s, exch.) and 7.2—7.8 (6 H, m); *m/z* 342 (M^+, 55%), 293 (25), 292 (65), 265 (30), 264 (35), 238 (80), and 197 (100).

Dimethyl 11-*Hydroxy*-7-*oxocyclo-octa*[de]*naphthalen*-8,10-*dicarboxylate* (**11**).—The diester (**9**) (5.53 g) in acetic acid (500 ml) was mixed with 0.072M lead(IV) acetate in acetic acid (225 ml) and the mixture kept overnight; it was then concentrated under reduced pressure to provide a gum. An ethyl acetate extract of the latter was washed with water, dried (Na_2SO_4), and concentrated to give a glass which was dissolved in acetone. This solution was decolourised with charcoal, filtered, and concentrated to afford, from acetone, colourless *prisms* (5.24 g), m.p. 178—180 °C (Found: C, 67.8; H, 4.4. $C_{19}H_{14}O_6$ requires C, 67.5; H, 4.2%); $\lambda_{max.}$(Et_2O) 227 and 302 nm (log ε 4.72 and 4.14); $\lambda_{max.}$(MeOH) 221 and 306 nm (log ε 4.78 and 4.21); solutions in ether are colourless, but those in methanol are yellow, caused by end-absorption extending beyond 500 nm; $\nu_{max.}$($CHCl_3$) 3 000br (OH), 1 720, 1 690, 1 660 (C=O), 1 620 and 1 600 cm^{-1} (C=C); δ_H(60 MHz; $CDCl_3$) 3.5 (3 H, s), 3.8 (3 H, s), 7.3 (1 H, s), 7.4—8.0 (6 H, m), and 13.2 (1 H, s, exch.); *m/z* 338 (M^+, 20%), 337 (14), 321 (18), 307 (24), 305 (13), 279 (58), 278 (22), 275 (24), and 247 (100).

The Action of Air and Magnesium Methoxide upon the Diester (**9**).—Magnesium (1.0 g) was allowed to react with methanol (50 ml) after which the diester (**9**) (496 mg) in methanol (40 ml) was added. This mixture after being kept in darkness and exposed to the air for 1 week, was poured into dilute hydrochloric acid and promptly extracted with ethyl acetate to yield, on work-up, an oil (383 mg). Chromatography of this on silica and elution with ethyl acetate (10%) in 1,1,1-trichloroethane afforded first impure naphthalene-1,8-dicarboxylic anhydride (198 mg) which recrystallised from 1,1,1-trichloroethane as red needles and sublimed melting <275 °C; *m/z* 198 (M^+, 78%), 154 (100), and 126 (83). Further elution afforded the diester (**11**) (37 mg), m.p. 170—178 °C which was raised to 178—180 °C on recrystallisation from 1,1,1-trichloroethane–light petroleum (b.p. 60—80 °C).

Reduction of the Diester (**11**) *with Magnesium and Methanol*.—The diester (**11**) (2.10 g) was reduced according to the procedure already employed for the diester (**9**), using magnesium (16 g) and methanol (500 ml), to yield a glass (2.06 g). Trituration of this with acetone gave crystals which were washed with ether to leave the diesters (**13**) and (**14**) as prisms (0.77 g), m.p. 163—172 °C. The mother liquor and washings were concentrated and chromatographed on silica: ether (5%) in chloroform eluted the diesters (**13**) and (**14**) which crystallised from acetone as prisms which were washed with ether (0.12 g), m.p. 147—172 °C. Next, ether (25%) in chloroform eluted the diol (**12**), to give thick plates from 1,1,1-trichloroethane (0.26 g), m.p. 153—155 °C.

Oxidation of the Diol (**12**) *with Lead*(IV) *Acetate*.—The diol (**12**) (120 mg) in acetic acid (3 ml) was mixed with 0.064M lead(IV) acetate in acetic acid (5.5 ml) and the mixture kept overnight; it was then worked up as for the diester (**11**) to give a straw coloured glass (85 mg); δ_H(60 MHz; $CDCl_3$) 2.5—4.2 (3 H, m), 3.5 (3 H, s), 3.8 (3 H, s), 7.1—8.0 (6 H, m), and 12.9 (1 H, s), consistent with the structure (**15**). On removal of solvent and storage this sample developed a different spectrum and became a mixture. It was resolved on a t.l.c. plate (20 × 20 × 0.2 cm of silica) developed with ethyl acetate and 1,1,1-trichloroethane (1:4). Elution of a faster-moving zone gave 2-methoxycarbonyl-2-methoxycarbonylethylphenalene-1,3-dione (**16**) (30 mg) as a colourless *gum* which was purified by precipitation from ether with pentane (Found: C, 67.0; H, 4.7. $C_{19}H_{16}O_6$ requires C, 67.1; H, 4.7%); $\lambda_{max.}$(MeOH) 234, 330, and 340 nm (log ε 4.68, 4.08, and 4.08); $\nu_{max.}$(CS_2) 1 760, 1 743, 1 700, and 1 674 cm^{-1} (C=O); δ_H(60 MHz; $CDCl_3$) 2.2—2.9 (4 H, m), 3.5 (3 H, s), 3.6 (3 H, s), 7.7 (2 H, dd, *J* 8, 7 Hz), 8.2 (2 H, dd, *J* 8, 1 Hz), and 8.4 (2 H, dd, *J* 7, 1 Hz); *m/z* 341 (56%), 340 (51), and 309 (100); after storage this compound solidified and with ether gave prisms, m.p. 70—71 °C. Elution of a slower-moving zone afforded 3-hydroxy-2-methoxycarbonylphenalen-1-one (**17**) (17 mg) which gave yellow *needles* from methanol, m.p. 268—270 °C (decomp.) (Found: C, 70.9; H, 4.2. $C_{15}H_{10}O_4$ requires C, 70.9; H, 4.0%); $\lambda_{max.}$(MeOH) 218, 233, 240, 284, 330, 339, 352, 385, and 410sh nm (log ε 4.29, 4.36 4.37, 3.40, 3.84, 3.86, 3.87, 3.75, and 3.50); $\nu_{max.}$($CHCl_3$) 3 590 (OH), 1 650, and 1 590 cm^{-1} (C=O); δ_H (60 MHz; $CDCl_3$) 4.0 (3 H, s), 7.4—8.6 (6 H, m), and 14.8 (1 H, s, exch.); *m/z* 254 (M^+, 30%) and 222 (100).

Reduction of the Diester (**6**).—The diester (**6**) (20.3 g) was stirred with boiling acetic acid (250 ml) and treated gradually with zinc powder (50 g); before half the amount had been added the purple colour faded to yellow. The mixture was stirred at boiling point under reflux for 1 h and then cooled, filtered, and the filtrate concentrated under reduced pressure; the residue was then taken up in ethyl acetate (400 ml) and 2M HCl (100 ml). Concentration of the organic phase yielded a gum which was boiled under reflux with water (200 ml)–sulphuric acid (5 ml) for 2 h. The mixture was cooled and the products were extracted with ethyl acetate. The extract was washed with aqueous sodium hydrogen carbonate, dried (Na_2SO_4), and concentrated and the residue distilled at 220 °C (bath temperature) and 0.05 mmHg. The distillate was extracted with ether, an insoluble brown solid (0.6 g) being rejected, and the extract concentrated. Recrystallisation of the residue from methanol gave 6*b*,7,9,9*a*-*tetrahydrocyclopent*[a]*acenaphthylen*-8(8H)-*one* (**20**) as cream prisms (3.1 g, 26%), m.p. 97—98 °C (Found: C, 86.5; H, 5.7. $C_{15}H_{12}O$ requires C, 86.5; H, 5.8%); $\lambda_{max.}$(MeOH) 226, 278, 288, 300, 306, 316, and 320 nm (log ε 4.81, 3.78, 3.85, 3.64, 3.43, 2.97, and 3.08); $\nu_{max.}$(CS_2) 1 745 cm^{-1} (C=O); δ_H(60 MHz; $CDCl_3$) 2.1—3.3 (4 H, m), 4.1—4.7 (2 H, m), and 6.9—7.6 (6 H, m); *m/z* 208 (M^+, 26%), 168 (48), 166 (51), and 165 (100). The mother liquors from recrystallisation of ketone (**20**) were concentrated, sublimed at 150—190 °C/0.01 mmHg, and chromatographed on t.l.c. grade silica using a dry column technique assisted by suction. 1,1,1-Trichloroethane containing ethyl acetate (10% initially but rising with each fraction) eluted first 7,9-*dihydrocyclopent*[a]*acenaphthylen*-8-*one* [**19**) (30 mg), orange needles from methanol, m.p. 167—170 °C (Found: C, 87.4; H, 4.7. $C_{15}H_{10}O$ requires C, 87.3; H, 4.9%); $\lambda_{max.}$(EtOH) 229, 268, 279, 312, 323, 334, 339, 353sh, 424sh, 452sh, and 482sh nm (log ε 4.57, 3.67, 3.61, 3.90, 3.99, 3.74, 3.74, 3.49, 2.29, 2.00, and 1.37); $\nu_{max.}(CS_2)$ 1 755 cm^{-1} (C=O); δ_H(60 MHz; $CDCl_3$) 3.35 (4 H, s) and 7.4—7.9 (6 H, m); *m/z* 206 (M^+, 36%) and 178 (100). Next eluted was further ketone (**20**) (351 mg), then 6*b*,7-*dihydrocyclopent*[a]*acenaphthlen*-8-*one* (**18**) (49 mg), as cream prisms from ether, m.p. 114—116 °C (Found: C, 87.2; H, 4.8. $C_{15}H_{10}O$ requires C, 87.3; H, 4.9%); $\lambda_{max.}$(EtOH) 228, 256, 328sh, and 347 nm (log ε 4.55, 4.39, 4.00, and 4.17); $\nu_{max.}(CS_2)$ 1 709 (C=O) and 1 625 cm^{-1} (C=C); δ_H(60 MHz; $CDCl_3$) 7.4 (1 H, dd, *J* 16 and 6 Hz), 6.9 (1 H, dd, *J* 16 and 7 Hz), 4.6 (1 H, m), 6.2 (1 H, d, *J* 2 Hz), and 7.2—7.9 (6 H, m); *m/z* 206 (M^+, 76%), 205 (100), 178 (69), 176 (62), and 165 (85).

6*b*,8,9,9*a*-*Tetrahydro*-7H-*cyclopent*[a]*acenaphthylene* (**5**).—The ketone (**20**) (2.57 g), hydrazine hydrate (99—100%, 5.11 g), and ethanediol (20 ml) were treated with potassium hydroxide (2.91 g) and warmed until homogeneous; the mixture was heated under nitrogen first at 125—130 °C for 1 h causing solid to form, and then at 200—210 °C for 1 h causing the solid to dissolve with foaming. After cooling, the solution was diluted with water and light petroleum (b.p. 60—80 °C). The organic layer yielded hydrocarbon (**5**) (2.28 g), m.p. 66—67 °C, which crystallised as needles from methanol, m.p. 67—68 °C (lit.,[2] 68—69 °C) (Found: C, 92.6; H, 7.3. Calc. for $C_{15}H_{14}$: C, 92.7; H, 7.3%); $\lambda_{max.}$(cyclohexane) 228, 244, 278, 289, 300, 305, 315, and 320 nm (log ε 4.79, 3.19, 3.82, 3.86, 3.69, 3.52, 2.98, and 3.10); δ_H(60 MHz; $CDCl_3$) 0.9—2.2 (6 H, m), 3.9 (2 H, m), and 7.0—7.6 (6 H, m); *m/z* 194 (M^+, 92%), 166 (47), and 165 (100).

6*b*,9*a*-*Dibromo*-6*b*,8,9,9*a*-*tetrahydro*-7H-*cyclopent*[a]*acenaphthylene* (**21**).—The hydrocarbon (**5**) (1.1 g) in nearly boiling tetrachloromethane (25 ml) was treated with *N*-bromosuccinimide (2.0 g) and benzoyl peroxide (0.06 g). Heating caused vigorous foaming and separation of succinimide and, after 20 min, the mixture was cooled and filtered. Concentration of the filtrate afforded a light brown solid (1.63 g), m.p. 100—116 °C, which crystallised from light petroleum (b.p. 60—80 °C) as light brown *prisms* (1.03 g), m.p. 120—121 °C (Found: C, 50.8; H, 3.3; Br, 45.2. $C_{15}H_{12}Br_2$ requires C, 51.2; H, 3.4; Br, 45.4%); $\lambda_{max.}$(cyclohexane) 229, 287, 298, and 306sh nm (log ε 4.87, 3.87, 3.96, and 3.83); δ_H(60 MHz; $CDCl_3$) 0.9 (1 H, m), 1.6 (1 H, m), 2.7 (4 H, m), and 7.4—7.7 (6 H, m); *m/z* 354, 352, and 350 (M^+, 4, 8, and 4%), 274 (39), 273 (39), and 192 (100).

8,9-*Dihydro*-7H-*cyclopent*[a]*acenaphthylene* (**22**).—A mixture of the dibromo compound (**21**) (1.06 g), zinc powder (10 g), and ethanol (50 ml) was boiled under reflux for 0.5 h and then diluted with water and light petroleum (b.p. 60—80 °C) and filtered. The organic layer in the filtrate yielded on concentration a yellow solid which was sublimed at 90—110 °C/0.05 mmHg and then recrystallised from methanol to give yellow *plates* (0.52 g), m.p. 73—74 °C (Found: C, 93.7; H, 6.3. $C_{15}H_{12}$ requires C, 93.7; H, 6.3); $\lambda_{max.}$(cyclohexane) 230, 274, 284, 309, 324, 332, 337, 365sh, 414, 431, 441, 460sh, and 494 nm (log ε 4.71, 3.64, 3.69, 3.94, 4.01, 3.67, 3.57, 2.50, 2.61, 2.54, 2.52, 2.28, and 1.74); δ_H(60 MHz; $CDCl_3$) 2.2—3.0 (6 H, m) and 7.2—7.7 (6 H, m); *m/z* 192 (M^+, 76%), 191 (100), 190 (27), 189 (38), and 165 (33).

9,10-*Dihydrocyclo-octa*[de]*naphthalene*-7,11(8H)-*dione* (**2**).—A solution of the hydrocarbon (**22**) (79 mg; freshly chromatographed on silica to remove autoxidation products) in ethyl acetate (25 ml) and acetic acid (5 ml) was cooled to −40 °C and treated with ozonised oxygen until the yellow colour had vanished. After being swept with oxygen to remove unused ozone, the solution was treated with methyl sulphide (0.2 ml) and finally allowed to attain room temperature. It was then washed with water, dried (Na_2SO_4), and concentrated to give colourless crystals (84 mg) which on recrystallisation from tetrachloromethane afforded colourless *prisms* (61 mg), m.p. 140—141 °C (Found: C, 80.3; H, 5.1. $C_{15}H_{12}O_2$ requires C, 80.3; H, 5.4%); $\lambda_{max.}$(MeOH) 221, 285, and 290sh nm (log ε 4.72, 3.78, and 3.78); methanolic solutions (3 ml) with acetic acid (5 drops) gave a spectrum changing ($t_{0.5}$ = 4 h) with isosbestic points at 265, 288, and 297 nm, into the spectrum of the adduct (**26**); similarly changing spectra were obtained using water as the solvent. In either solvent 1M sodium hydroxide (1 drop), in place of acetic acid, gave the spectrum of the adducts immediately; $\nu_{max.}(CS_2)$ 1 704 and 1 676 cm^{-1} (C=O); δ_H(300 MHz; CD_2Cl_2) 2.15 (2 H, m), 2.83 (4 H, m), 7.41 (2 H, dd, *J* 7 and 1 Hz), 7.57 (2 H, dd, *J* 8 and 7 Hz), and 7.99 (2 H, dd, *J* 8 and 1 Hz); the signals at 2.15 and 2.83 showed no temperature dependence down to −65 °C; *m/z* 224 (M^+, 26%) and 196 (100).

6*b*,8,9,9*a*-*Tetrahydro*-7H-*cyclopent*[a]*acenaphthylene*-6*b*,9*a*-*diol* (**23**).—A solution of the diketone (**2**) (32 mg) in warm acetic acid (20 ml) and zinc powder (3.3 g) was boiled under reflux for 0.5 h after which it was cooled and mixed with water and ethyl acetate. The organic layer was separated, washed, dried (Na_2SO_4), and concentrated to give a crystalline residue (28 mg) which provided colourless *prisms* from ethyl acetate, m.p. 208—209 °C (Found: C, 80.0; H, 6.3. $C_{15}H_{14}O_2$ requires C, 79.6; H, 6.2%); $\lambda_{max.}$(MeOH) 222, 275, 285, 296, and 314 nm (log ε 4.67, 3.77, 3.84, 3.66, and 2.79); $\nu_{max.}$(KBr) 3 362 cm^{-1} (OH); δ_H(300 MHz; $CDCl_3$) 0.89 (1 H, m), 1.69 (1 H, m), 2.09 (2 H, m), 2.35 (2 H, m), 2.88 (2 H, s, br, exch.), 7.57 (2 H, d, *J* 7 Hz), 7.62 (2 H, dd, *J* 8 and 7 Hz), and 7.80 (2 H, d, *J* 8 Hz); *m/z* 226 (M^+, 99%), 208 (40), 197 (34), 184 (41), 183 (70), 181 (73), and 180 (100).

7,11-*Epoxy*-8,9,10,11-*tetrahydro*-7H-*cyclo-octa*[de]*naphthalene*-7,11-*diol* (**24**).—The diketone (**2**) (38 mg) dissolved in aqueous 1M sodium hydroxide (10 ml) with warming was extracted with ether to yield the diol (**24**) (17 mg); a second ether extraction made after acidification of the solution with aqueous 1M hydrochloric acid (12 ml) yielded further diol (**24**) (16 mg). The diol (**24**) was obtained as colourless *needles* from ether–pentane, m.p. 180—181 °C (Found: 74.6; H, 5.8. $C_{15}H_{14}O_3$ requires C, 74.4; H, 5.8%); $\lambda_{max.}(Et_2O)$ 225, 274, 285, 296, and 314 nm (log ε 4.89, 3.82, 3.91, 3.74, and 2.71); $\nu_{max.}$(KBr) 3 430 and 3 340 cm^{-1} (OH); δ_H(300 MHz; $CDCl_3$) 0.9 (m, 9-*endo* H), 1.61 (m, 9-*exo* H), 1.78—1.96 (4 H, m), 3.80 (2 H, s, exch.), 7.42 (2 H, t, *J* 8 Hz), 7.47 (2 H, d, *J* 7 Hz), and 7.68 (2 H, d, *J* 8 Hz); *m/z* 242 (M^+, 13%), 225 (19), 224 (55), 199 (23), 197 (27), and 196 (100).

Di-O-*acetyl derivative* (**25**). The diol (**24**) (22 mg) suspended in acetic acid (1 ml) containing perchloric acid (60%; 1 drop) dissolved immediately on addition of acetic anhydride (1 ml). After 0.5 h, the mixture was diluted with aqueous sodium acetate and extracted with ether; work-up of the latter yielded a solid which, from ether, afforded cream *prisms* (16 mg), m.p. 149—150 °C (Found: C, 69.7; H, 5.6. $C_{19}H_{18}O_5$ requires C, 69.9; H, 5.6%); $\lambda_{max.}$(MeOH) 225, 276, 286, 297, and 315 nm (log ε 4.85, 3.80, 3.89, 3.73, and 2.66); $\nu_{max.}(CS_2)$ 1 786m and 1 763s cm^{-1} (C=O); δ_H(300 MHz; $CDCl_3$) 1.05 (m, 9-*endo* H), 1.75 (m, 9-*exo* H), 1.91 (2 H, m), 2.12 (6 H, s), 2.34 (2 H, m), 7.40 (2 H, d, *J* 7 Hz), 7.52 (2 H, t, *J* 7 Hz), and 7.83 (2 H, d, *J* 8 Hz); *m/z* 326 (M^+, 37%), 267 (15), 225 (58), 224 (85), 199 (40), 197 (52), and 196 (100).

7,11-*Epoxy*-8,9,10,11-*tetrahydro*-7-*methoxy*-7H-*cyclo-octa*-[de]*naphthen*-11-*ol* (**26**).—The diketone (**2**) (28 mg) suspended in methanol (10 ml) and acetic acid (0.5 ml) was left until the crystals had dissolved (1 h) and then kept for a futher 18 h. Concentration under reduced pressure left a crystalline residue yielding, from ether–pentane, colourless *prisms* (28 mg), m.p. 167—168 °C (Found: C, 74.8; H, 6.4. $C_{16}H_{16}O_3$ requires C, 75.0; H, 6.3%); $\lambda_{max.}$(MeOH) 224, 275, 285, 296, and 314 nm (log ε 4.91, 3.84, 3.90, 3.77, and 2.70); $\nu_{max.}$(KBr) 3 376 cm^{-1} (OH); δ_H(300 MHz; $CDCl_3$) 1.00 (m, 9-*endo* H), 1.68 (m, 9-*exo* H), 1.78—2.05 (4 H, m), 3.33 (3 H, s), 3.50 (1 H, s, exch.), 7.45 (1 H, d, *J* 7 Hz), 7.52 (1 H, t, *J* 7 Hz), 7.54 (1 H, t, *J* 7 Hz), 7.63 (1 H, d, *J* 7 Hz), and 7.83 (2 H, d, *J* 8 Hz); *m/z* 256 (M^+, 30%), 224 (63), 213 (88), and 196 (100).

Acknowledgements

The authors thank David Hutchinson for the 300 MHz spectra, and the S.E.R.C. for studentships (to D. A. J. and P. H. L.).

References

1 D. A. Jackson, D. C. C. Smith, and C. I. F. Watt, *J. Chem. Soc., Perkin Trans. 1*, 1987, 2437.
2 J. Meinwald and G. W. Gruber, *J. Am. Chem. Soc.*, 1971, **93**, 3802.
3 K. Yamamoto, M. Morioka, and I. Murata, *Tetrahedron Lett.*, 1975, 3009.
4 J. T. Craig and M. D. W. Robins, *Aust. J. Chem.*, 1968, **21**, 2237.
5 C. F. H. Allen and J. A. Van Allan, *J. Org. Chem.*, 1952, **17**, 845.
6 J. A. Profitt and H. H. Ong, *J. Org. Chem.*, 1979, **44**, 3972.
7 R. Brettle and S. M. Shibib, *J. Chem. Soc., Perkin Trans. 1*, 1981, 2912.
8 L. J. Bellamy, 'Advances in Infrared Group Frequencies,' Methuen, London, 1968, pp. 128—132.
9 G. Ashworth, D. Berry, and D. C. C. Smith, *J. Chem. Soc., Perkin Trans. 1*, 1979, 2995.
10 E. P. Kohler and G. H. Reid, *J. Am. Chem. Soc.*, 1925, **47**, 2803.

Received 28*th September* 1987; *Paper* 7/00023E