Fresh Routes to Derivatives of Cyclohepta[*de*]naphthalene

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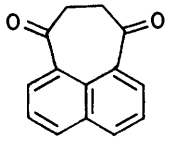
2,3-Dihydrocyclohepta[*de*]naphthalene-1,4-dione (1) is formed by cyclising methyl 3-(1-naphthoyl)propionate. It forms only monoacetals, gives a hemiacetal salt with alkali, and can be dehydrogenated to a quinone (14) that undergoes ring-contraction to a phenalenone (15) on acetalisation.

Acenaphthylene traps dichloroketen inefficiently, allowing formation of the dimer (19) of tetrachloroallene, but dechlorination of the acenaphthylene adduct (16) followed by opening of its cyclobutanone ring with acid gives cyclohepta[*de*]naphthalen-2(1*H*)-one (21). This and the isomeric cyclohepta[*de*]naphthalen-1(2*H*)-one (23) obtainable from the dione (1), were reduced to alcohols with the object of preparing cyclohepta[*de*]naphthalene (26) by ester pyrolysis.

WITH aluminium chloride methyl 3-(1-naphthoyl)-propionate, which gave by rearrangement 3-(2-naphthoyl)propionic acid but was reported not to cyclise to a diketone with a seven-membered ring (as had been described for the analogous ester derived from acenaphthene [1]) is now found to give 2,3-dihydrocyclohepta[*de*]naphthalene-1,4-dione (1) and 2,3-dihydroanthracene-1,4-dione (2). The dione (2), also made by reducing 1,4-anthraquinone, is oxidised and self-condenses readily,[2,3] this possibly accounting for some of the tar formation with aluminium chloride. The dione (1) is of special interest because its carbonyl groups are in a *peri*-relationship. It can be reduced to epimeric diols that dehydrate in acid giving the ether (3), and with sodium tetrahydroborate or methylmagnesium iodide it yields the hemiacetals (4) and (5) respectively.



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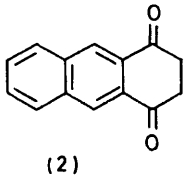

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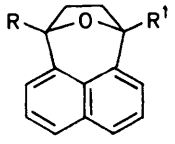
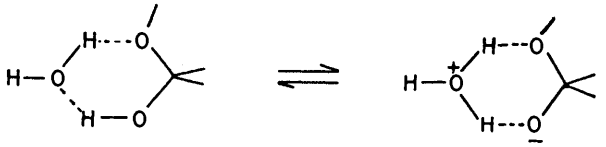


(3) R = R^1 = H
(4) R = OH, R^1 = H
(5) R = OH, R^1 = Me
(6) R = R^1 = OH
(7) R = OH, R^1 = ONa
(8) R = OH, R^1 = OMe
(9) R = R^1 = OMe

RESULTS AND DISCUSSION

The dione (1) is an acid, being soluble in aqueous sodium hydroxide but only sparingly soluble in water; its absorption band at 318 nm decreases with acetic acid catalysis to an equilibrium value indicating 24% of the hydrate (6). At high pH the band at 318 nm decreases further owing to formation of the hemiacetal salt (7), and this leads to a value of 11.8 for its pK_a. This is considerably lower than the pK_a values reported for related hydroxylic acids such as the hydrates of aldehydes,[4] and so the acid strength of the hemiacetal (4) was also measured. Here the u.v. spectrum shows virtually no change with ionisation, but the solubility rises sharply and measuring this in order to determine pK_a [5] leads to a value of 12.0. The acidity of hemiacetals may be attributed to an inductive effect, and to



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solvation before ionisation analogous to that of carboxylic acids, as in the partial formula (10), making the entropy of ionisation less negative.

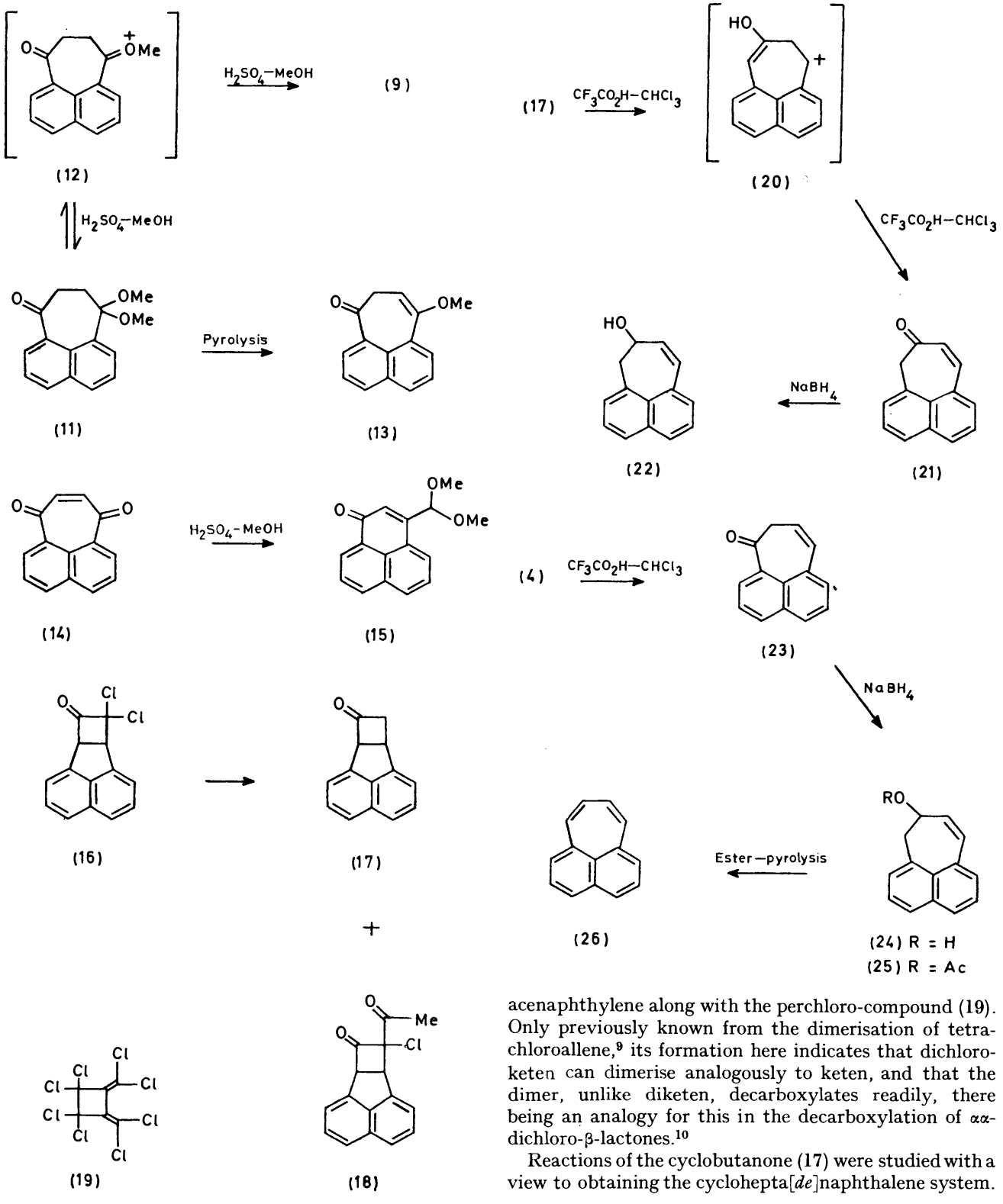
Acetalisation of the dione (1) in ethane-1,2-diol gives only a monoacetal. In methanol, the absorption band of the dione at 318 nm decreases with acetic acid catalysis to an equilibrium value indicating 60% of the hemiacetal (8). Incidentally 1,8-diacetylnaphthalene shows parallel behaviour, giving 100% of the hemiacetal. In methanolic sulphuric acid at room temperature, the dione (1) gives the monoacetal (11), presumably because the intermediate cation (12) adds methanol faster on the charged side, but in boiling methanolic sulphuric acid the more stable bridged acetal (9) is obtained. The monoacetal (11) eliminates methanol on sublimation, giving 4-methoxycyclohepta[*de*]naphthalen-1(2*H*)-one (13).

The quinone (14) formed by dehydrogenating the dione (1) with selenium dioxide, gives with methanolic sulphuric acid, by ring-contraction, the acetal (15). The only previous example of this type of quinone, its 2-hydroxy-3-methoxycarbonyl derivative, also underwent ring-contraction in acid.[6]

As a complimentary approach to preparing cyclohepta[*de*]naphthalenes, cycloaddition of acenaphthylene

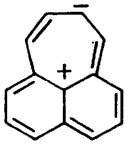
with dichloroketen was examined. Generation of the keten using zinc and trichloroacetyl bromide,[7] gives directly a low yield of the desired chlorine-free ketone (17) together with the dione (18) resulting from acylation of an intermediate zinc enolate formed in dechlorination of the initial adduct. Dichloroketen prepared from triethylamine and dichloroacetyl chloride gives the expected adduct (16),[8] but that acenaphthylene traps this keten inefficiently is indicated by recovery of unreacted acenaphthylene along with the perchloro-compound (19). Only previously known from the dimerisation of tetrachloroallene,[9] its formation here indicates that dichloroketen can dimerise analogously to keten, and that the dimer, unlike diketen, decarboxylates readily, there being an analogy for this in the decarboxylation of αα-dichloro-β-lactones.[10]

Reactions of the cyclobutanone (17) were studied with a view to obtaining the cyclohepta[*de*]naphthalene system.



Sodium tetrahydroborate gives *endo*-1,2,2a,8b-tetrahydrocyclobuta[*a*]acenaphthylen-1-ol. With sodium methoxide in CH_3OD the cyclobutanone (17) exchanges only one proton, identified by n.m.r. spectroscopy as the *exo* proton of the methylene group. With a solution of trifluoroacetic acid the cyclobutanone (17) isomerises to cyclohepta[*de*]naphthalen-2(1*H*)-one (21). Cyclobutanones undergo such cleavage of the 2,3-bond in acids if there is an aryl or vinyl substituent to delocalise positive charge on the 3-position,[11] and the intermediate cation (20) has this feature. The cycloheptenone (21) could not be isolated but gives with sodium tetrahydroborate the crystalline alcohol (22). This is a possible intermediate for preparing cyclohepta[*de*]naphthalene (26) itself, but its isomer (24) was found to be more accessible: the hemiacetal (4) is dehydrated quantitatively in chloroform containing trifluoroacetic acid to the cycloheptenone (23), and this was reduced to the alcohol (24). Pyrolysis of the acetate (25) gave only a poor yield of cyclohepta[*de*]naphthalene (26).

The n.m.r. chemical shifts of analogous vinylic protons on the seven-membered ring in alcohol (24) and hydrocarbon (26) differ considerably: completion of peripheral conjugation causes upfield shifts of τ 3.4 to 4.1 and of τ 4.2 to 4.7, respectively. This could be due to a ring-current effect, or to an accumulation of π-electron density on the periphery of the ring system as in resonance contributors such as (27) that have a Hückel



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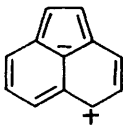

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complement of fourteen peripheral π electrons. Resonance contributors of acenaphthylene having $(4n + 2)$ peripheral π electrons are of the opposite type [*e.g.* (28)], and though their effect might be lessened by electron repulsion they would cause a downfield shift of the proton signals. Mean τ values for all the protons (3.8 in cyclohepta[*de*]naphthalene, and 2.7 in acenaphthylene) do not oppose this concept.

EXPERIMENTAL

3-(2-Naphthoyl)propionic Acid.—Methyl 3-(1-naphthoyl)-propionate (3.2 g), m.p. 24—25 °C, prepared by esterifying 3-(1-naphthoyl)propionic acid, m.p. 127—129 °C, was added dropwise to a stirred melt of aluminium chloride (25 g) and sodium chloride (5 g) at 140 °C. After 0.5 h at 140 °C, the melt was poured onto ice, extracted with benzene, filtered, and concentrated to give a semi-solid residue which was washed with boiling tetrachloromethane leaving behind 3-(2-naphthoyl)propionic acid (0.45 g), giving prisms from chloroform (0.24 g), m.p. 156—162 °C (Found: C, 73.8; H, 5.4. Calc. for $C_{14}H_{12}O_3$: C, 73.7; H, 5.3%).

2,3-Dihydrocyclohepta[de]*naphthalene-1,4-dione* (1) *and 2,3-dihydroanthracene-1,4-dione* (2).—Methyl 3-(1-naphthoyl)propionate (17.3 g) was added dropwise to a stirred melt of aluminium chloride (250 g) and sodium chloride (50 g) at 140 °C. After 1 h at 140 °C the melt was poured onto ice (2 kg) then stirred with a filter-aid (Celite 545, 20 g), ethyl acetate (500 ml), and concentrated hydrochloric acid (100 ml). After filtration the organic layer was washed (aqueous $NaHCO_3$), dried (Na_2SO_4), and concentrated to a viscous oil (11.4 g) which was distilled from glass wool at 0.05 mmHg. A yellow oil that partly crystallised (5.6 g) came over at 220—270 °C (bath temperature), giving the dione (1) (2.8 g) as *cream prisms*, m.p. 88—90 °C (from tetrachloromethane) (Found: C, 79.8; H, 5.0. $C_{14}H_{10}O_2$ requires C, 80.0; H, 4.8%); $\nu_{max.}$(CS_2) 1 690 and 1 680 cm^{-1}; $\lambda_{max.}$(MeOH) 318 nm (log ε 3.90); $\lambda_{max.}$(1N-NaOH) 264 (sh), 275 (sh), 286, 295, 302, 312, and 317 nm (log ε 3.57, 3.77, 3.85, 3.72, 3.47, 3.11, and 3.03; τ(CCl_4) 1.8—2.1 (4 H, m), 2.4—2.7 (2 H, m), and 7.0 (4 H, s); *m/e* 210 (M^+, 100%), 209 (96), 181 (25), 154 (64), and 126 (82). Further crops of crystals from tetrachloromethane were found to be mixtures of the diones (1) and (2): the latter was isolated by crystallisation from ether, as cream plates (66 mg), m.p. 161—170 °C (Found: C, 79.7; H, 4.8), identical with an authentic sample prepared from naphthazarin,[2] which showed two modifications: plates, m.p. 169—172 °C, sometimes resolidifying to needles, m.p. 181—183 °C.

1,2,3,4-Tetrahydro-1,4-epoxycyclohepta[de]*naphthalene* (3).—The dione (1) (500 mg) in benzene (50 ml) was stirred with a suspension of lithium tetrahydroaluminate (245 mg) in ether (80 ml) and boiled for 6 h. After hydrolysis of excess of reagent with moist ether the product was isolated as an oil (534 mg) which gave crystals from benzene (337 mg), m.p. 45—85 °C; τ($CDCl_3$) 2.2—2.7 (6 H, m), 4.6 (1.7 H, m), 5.0 (0.3 H, m), 7.1 (2 H, br, exchangeable), and 7.8—8.1 (4 H, m); *m/e* (15 eV) 214 (M^+, 100%). This mixture of *cis* and *trans* diols (202 mg) in 95% ethanol (12 ml) and concentrated hydrochloric acid (3 ml) was set aside for 17 h, then diluted with water. The product was isolated with benzene, filtered through silica, and purified by vacuum sublimation to give the *ether* (3) (111 mg), m.p. 84—87 °C (Found: C, 85.4; H, 5.9. $C_{14}H_{12}O$ requires C, 85.7; H, 6.1%); τ($CDCl_3$) 2.35 (2 H, dd), 2.65 (2 H, t), 2.9 (2 H, dd), 4.6 (2 H, m), 7.6 (2 H, m), and 8.1 (2 H, m); *m/e* 196 (M^+, 22%) and 168 (100).

1,2,3,4-Tetrahydro-1,4-epoxycyclohepta[de]*naphthalen-1-ol* (4).—The dione (1) (1.0 g) in ethanol (100 ml) was mixed with a freshly prepared solution of sodium tetrahydroborate (0.41 g) in water (100 ml). After 0.5 h, the solution was acidified (HCl) and extracted with ether giving the *hemiacetal* (4) (0.90 g), m.p. 169—170 °C (from methanol) (Found: C, 78.9; H, 5.8. $C_{14}H_{12}O_2$ requires C, 79.2; H, 5.7%); τ($CDCl_3$) 2.2—2.9 (6 H, m), 4.5 (1 H, dd, *J* 7 and 1 Hz), 5.7 (1 H, br, exchangeable), and 7.4—8.4 (4 H, m); *m/e* 212 (M^+, 46%), 184 (90), and 167 (100).

1,2,3,4-Tetrahydro-4-methyl-1,4-epoxycyclohepta[de]*naphthalen-1-ol* (5).—The dione (1) (520 mg) in benzene (50 ml) was added to methylmagnesium iodide, prepared in ether from iodomethane (1.6 g), and boiled for 12 h. Hydrolysis (aqueous NH_4Cl) and extraction with ether gave the *hemiacetal* (5) (400 mg), m.p. 191—192 °C (from benzene) (Found: C, 79.7; H, 6.3. $C_{15}H_{14}O_2$ requires C, 79.6; H, 6.2%); τ($CDCl_3$) 2.3—2.9 (6 H, m), 5.6 (1 H, s, exchangeable), 7.6—8.0 (4 H, m), and 8.1 (3 H, s); *m/e* 226 (M^+, 47%), 198 (80), and 181 (100).

Determination of pK_a *of the Dione* (1).—Boiled-out distilled water at 25 °C was saturated with the dione (1),

then diluted fivefold for spectroscopy ($\lambda_{max.}$ 318 nm); acetic acid (1 drop) added to the solution (5 ml) caused the spectrum to change during 0.5 h with isosbestic points at 257 and 288 nm, into a composite spectrum of the dione (1) and its hydrate (6), having additional maxima at 270, 282, and 294 nm, and E_{330} decreased by 24%. Standard buffer solutions,[12] incorporating an equal volume of standard aqueous solution of the dione (1) in place of 30% of the water, gave a family of absorption curves with approximate isosbestic points at 258 and 293 nm; the extinction values are in Table 1.

TABLE 1

pH	E_{330}	pK *
9.6	0.70	
10.5	0.65	11.6
11.0	0.60	11.7
11.5	0.49	11.8
12.0	0.30	11.8
12.5	0.14	11.8
0.7M-NaOH	0.04	

* $pK = pH + \log\left[\frac{E - 0.04}{0.70 - E}\right]$, assuming that the percentage hydration of un-ionised dione is unaffected by pH.

Determination of pK_a *of the Hemiacetal* (4).—The solubility method [4] requires measurements of concentration for saturated solutions of the hemiacetal of various pH. The hemiacetal (4) has for its strongest absorption band $\lambda_{max.}$(H_2O) 283 nm (log ε 3.87) and $\lambda_{max.}$(1N-NaOH) 285 nm (log ε 3.87), and so values of $E_{max.}$ for this band can be employed as a measure of concentration at any intermediate pH. An excess of crystalline hemiacetal (4) was equilibrated overnight at 25 °C with a range of standard buffer solutions,[12] then filtered and quantitatively diluted with the appropriate buffer solution for u.v. spectroscopy leading to the extinction values ($E_{max.}$) shown in Table 2.

TABLE 2

pH	$E_{max.}$(283—285 nm)	pK *
9.6	3.05	
10.5	3.15	12.0
11.0	3.30	12.1
11.5	3.90	12.1
12.0	7.10	12.1
12.5	16.0	11.9
13.0	50	11.8
0.7M-NaOH	160	

* $pK = pH - \log\left[\frac{E_{max.}}{3.05} - 1\right]$ assuming that the solubility of un-ionised hemiacetal is unaffected by pH.[4]

Acid-catalysed Reactions of the Dione (1) *with Methanol.*—(*a*) Acetic acid (1 drop) added to the dione (1) in methanol (5 ml) caused the u.v. spectrum to change during 4 h with isosbestic points at 252 and 290 nm into a composite spectrum of the dione (1) and hemiacetal (8), and E_{330} decreased by 60%.

(*b*) The dione (1) in methanol containing sulphuric acid (0.08%) gave immediately the composite spectrum produced in (*a*), which during 1 h changed with isosbestic points at 259 and 288 nm into a simpler spectrum having $\lambda_{max.}$ 302 nm (log ε 3.85). Accordingly, the dione (1) (110 mg) in methanol (100 ml) and 4% methanolic sulphuric acid (2 ml) was set aside for 1 h then neutralised with aqueous sodium carbonate. An ether extract, washed (aqueous NaOH), dried ($MgSO_4$), and concentrated gave a colourless gum (118 mg), homogeneous and distinct on t.l.c. from the dione (1); $\nu_{max.}$ (film) 1 690 cm^{-1}; τ($CDCl_3$) 1.9—2.2 (4 H, m), 2.3—2.6 (2 H, m), 7.0 (6 H, s), and 7.3—7.5 (4 H, m); *m/e* 256 (M^+, 80%), 255 (75), 225 (75), 224 (80), 209 (100), and 165 (100). Vacuum sublimation at 0.05 mmHg through glass wool at 110 °C gave *4-methoxycyclohepta*[de]*naphthalen-1(2H)-one* (13) as an oil (95 mg) (Found: C, 80.0; H, 5.4. $C_{15}H_{12}O_2$ requires C, 80.3; H, 5.4%); $\nu_{max.}$ (film) 1 685 (s) and 1 645 (m) cm^{-1}; $\lambda_{max.}$(MeOH) 310, 330 (sh), and 353 (sh) nm (log ε 3.74, 3.62, and 2.94); τ($CDCl_3$) 1.7—2.1 (4 H, m), 2.3—2.7 (2 H, m), 4.85 (1 H, t), 6.3 (3 H, s), and 6.8 (2 H, d); *m/e* 224 (M^+, 48%), 223 (39), 210 (64), and 209 (100).

(*c*) The dione (1) (226 mg) and methanol (50 ml) containing sulphuric acid (1 ml) were boiled under reflux for 1 h, then neutralised with aqueous sodium carbonate. Extraction with ether gave a green solid, which was recrystallised from methanol and then sublimed at 150 °C and 0.05 mmHg, giving *1,2,3,4-tetrahydro-1,4-dimethoxy-1,4-epoxycyclohepta*[de]*naphthalene* (9), m.p. 124—127 °C (from methanol-1,1,1-trichloroethane) (Found: C, 75.3; H, 6.2. $C_{16}H_{16}O_3$ requires C, 75.0; H, 6.3%); $\lambda_{max.}$(MeOH) 263 (sh), 274, 284, 290 (sh), and 295 nm (log ε 3.58, 3.79, 3.88, 3.75, and 3.72); τ(CCl_4) 2.2—2.7 (6 H, m), 6.5 (6 H, s), 7.5—7.8 (2 H, m), and 7.9—8.2 (2 H, m); *m/e* 256 (M^+, 13%), 255 (8), 213 (54), and 197 (100).

The Effect of Acid on the U.v. Spectrum of 1,8-*Diacetylnaphthalene.*—The spectrum in methanol, having $\lambda_{max.}$ 295 nm (log ε 3.81), altered immediately with acetic acid (1 drop) to have $\lambda_{max.}$ 265, 275, 285, and 297 nm (log ε 3.53, 3.68, 3.84, and 3.69).

The Ethylenemonoacetal from the Dione (1).—The dione (1) (195 mg) in ethane-1,2-diol (20 ml) containing sulphuric acid (3.7 mg) was set aside for 20 h, then neutralised with aqueous sodium hydrogencarbonate. Extraction with ether gave *prisms* (168 mg), m.p. 99—100 °C [from ether–light petroleum (b.p. 40—60 °C)] (Found: C, 75.6; H, 5.6. $C_{16}H_{14}O_3$ requires C, 75.6; H, 5.6%); $\nu_{max.}$(CS_2) 1 698 cm^{-1}; $\lambda_{max.}$(EtOH) 306 nm (log ε 3.88); τ($CDCl_3$) 2.0—2.7 (6 H, m), 6.1 and 6.4 (4 H, A_2B_2 spectrum), and 7.1—7.6 (4 H, m).

Cyclohepta[de]*naphthalene-1,4-dione* (14).—The dione (1) (752 mg) in warm benzene (30 ml) was mixed with a solution of selenium dioxide (755 mg) in warm 2-methylpropan-2-ol (40 ml) and boiled for 2 h. After washing (aqueous NaCl) and concentration, the product was stirred overnight with chloroform, ethyl acetate, and mercury, then chromatographed on silica; ethyl acetate eluted orange flakes (676 mg), m.p. 166—173 °C. Sublimation at 100—110 °C and 0.01 mmHg, followed by recrystallisation, gave *yellow needles*, m.p. 175—176 °C (from acetone) (Found: C, 80.4; H, 3.6. $C_{14}H_8O_2$ requires C, 80.8; H, 3.9%); $\nu_{max.}$($CHCl_3$) 1 660m, 1 642s, 1 623m, and 1 565s cm^{-1}; $\lambda_{max.}$(MeOH) 241 and 350 nm (log ε 4.11 and 3.89); τ($CDCl_3$) 1.54 (2 H, dd, *J* 8 and 1.5 Hz), 1.80 (2 H, dd, *J* 8 and 1.5 Hz), 2.35 (2 H, t, *J* 8 Hz), and 3.01 (2 H, s); *m/e* 208 (M^+, 48%), 180 (40), and 152 (100).

3-(Dimethoxymethyl)phenalenone (15).—The quinone (14) (54 mg) in chloroform (5 ml) was mixed with a 1% solution of sulphuric acid in methanol (5 ml), set aside overnight, and then neutralised with aqueous sodium hydrogencarbonate. The product was isolated with ether, sublimed at 140 °C and 0.05 mmHg and recrystallised giving *yellow needles* (53 mg), m.p. 82—84 °C (from ether–cyclohexane) (Found: C, 75.6; H, 5.6. $C_{16}H_{14}O_3$ requires C, 75.6; H, 5.6%); $\nu_{max.}$(CS_2) 1 700 cm^{-1}; $\lambda_{max.}$(MeOH) 225 (sh), 248, 255, 306 (sh), 319, 364, and 382 (sh) nm (log ε 4.02, 4.26, 4.22, 3.53, 3.60, 3.94, and 3.91) (resembling closely the u.v.

spectrum of phenalenone); τ($CDCl_3$) 1.4—2.7 (6 H, m), 3.1 (1 H, s), 4.4 (1 H, s), and 6.6 (6 H, s); *m/e* 254 (M^+, 20%), 224 (19), 223 (15), 195 (20), and 130 (100).

Addition of Dichloroketen to Acenaphthylene.—(*a*) Zinc powder (60 g), acenaphthylene (15 g), and ether (100 ml) were stirred under nitrogen, trichloroacetyl bromide (16 ml) was introduced gradually during 0.5 h so as to maintain an exothermic reaction, and the mixture was kept until boiling ceased (1 h). Acetic acid was introduced gradually, followed by water and additional ether, and after filtration the ether layer was washed (aqueous Na_2CO_3) and concentrated to a glass (7.9 g). Distillation without fractionation at 0.05 mmHg yielded an oil (2.1 g) which was redistilled through a fractionating column giving, after a forerun of acenaphthylene, 2a,8b-*dihydrocyclobuta*[a]*acenaphthylen*-1-(2H)-*one* (17) (1.12 g), b.p. 120—128 °C at 0.005 mmHg, giving plates, m.p. 73—78 °C (from hexane) and an analytical sample, m.p. 79—80 °C (from methanol) (Found: C, 86.7; H, 5.1. $C_{14}H_{10}O$ requires C, 86.6; H, 5.2%); $\nu_{max.}$(CS_2) 1 785 cm^{-1}; $\lambda_{max.}$(EtOH) 281, 291, 303 (sh), and 323 nm (log ε 3.76, 3.83, 3.65, and 3.15); *m/e* 194 (M^+, 9%), 165 (30), and 152 (100); τ($CDCl_3$) 2.0—2.6 (6 H, m), 4.87 (1 H, m), 5.82 (1 H, m), 6.42 (1 H, m), and 7.22 (1 H, m). Irradiation at τ 4.87 simplified the signals at τ 5.82 (1 H, dd, *J* 10 and 4.5 Hz), 6.42 (1 H, dd, *J* 18.5 and 10 Hz), and 7.22 (1 H, dd, *J* 18.5 and 4.5 Hz). Irradiation at τ 5.82 simplified the signals at τ 4.87 (1 H, br d, *J* 3 Hz), 6.42 (1 H, dd, *J* 18.5 and 3 Hz), and 7.22 (1 H, dd, *J* 18.5 and 3 Hz). Hence the coupling constants are similar to those of cyclobutanone.[13] In CD_3OD the non-aromatic protons resonate at τ 4.7, 5.6, 6.8, and 7.4, and after treatment with NaOD, only the signal at τ 6.8 gradually disappears. A chloroform extract of the residue from the second distillation (0.7 g) was chromatographed on silica; 1,1,1-trichloroethane eluted 2-*acetyl*-2-*chloro*-2a,8b-*dihydrocyclobuta*[a]-*acenaphthylene*-1(2H)-*one* (18) (170 mg) as colourless needles, m.p. 100—101 °C (from ether–pentane) (Found: C, 70.6; H, 4.1; Cl, 13.5. $C_{16}H_{11}ClO_2$ requires C, 71.0; H, 4.1; Cl, 13.1%); $\nu_{max.}$($CHCl_3$) 1 770 and 1 690 cm^{-1}; $\lambda_{max.}$(EtOH) 226, 279, 290, 300, 315, and 319 nm (log ε 4.78, 3.80, 3.89, 3.73, 2.94, and 2.54); τ($CDCl_3$) 2.2—2.7 (6 H, m), 4.8 (1 H, d, *J* 3 Hz), 5.4 (1 H, d, *J* 3 Hz), and 7.8 (3 H, s); *m/e* 272 and 270 (M^+, 5 and 12%), and 228 (100).

(*b*) Acenaphthylene (5 g) and triethylamine (22 ml) in hexane (100 ml) were boiled under nitrogen with stirring while a solution of dichloroacetyl chloride (13 ml) in hexane (20 ml) was added gradually, then the mixture was boiled for 1 h and allowed to cool. After stirring with ether and water the mixture was filtered, and concentration of the organic layer and distillation of the residue at 0.05 mmHg without fractionation gave an oil (8.6 g), b.p. 90—170 °C. Redistillation through a fractionating column gave acenaphthylene (4.2 g), b.p. 71—92 °C, and a residue from which boiling hexane extracted an oil (1.4 g). This was taken up in 1,1,1-trichloroethane and washed repeatedly with concentrated hydrochloric acid to remove *NN*-diethyldichloroacetamide (*cf.* ref. 14), then washed with aqueous sodium acetate, and concentrated (1.12 g). An aliquot (0.86 g) was chromatographed on silica, and 1,1,1-trichloroethane eluted first perchloro-1,2-dimethylenecyclobutane (19) (0.31 g) as colourless prisms, m.p. 90—91 °C [from light petroleum (b.p. 40—60 °C)] (Found: C, 20.4; Cl, 79.6. Calc. for C_6Cl_8: C, 20.0; Cl, 80.5%); $\nu_{max.}$ (hexane) exactly as reported [9] plus 780s cm^{-1}; $\lambda_{max.}$ (cyclohexane) 298 (sh), 310, and 323 (sh) nm (log ε 4.13, 4.24, and 4.12); *m/e* 360, 358, 356, 354, and 352 (M^+, 6, 15, 21, 18, and 6%), and 284 (100). Further elution with 1,1,1-trichloroethane gave 2,2-dichloro-2a,8b-dihydrobuta[*a*]acenaphthylen-1(2*H*)-one (16) (0.27 g), m.p. 114—115 °C (from ether) (*cf.* lit.,[8] m.p. 115—116 °C) (Found: C, 63.6; H, 3.1; Cl, 26.6. Calc. for $C_{14}H_8Cl_2O$: C, 63.8; H, 3.1; Cl, 26.8%); $\nu_{max.}$(CS_2) 1 812 cm^{-1}; $\lambda_{max.}$(EtOH) 280, 290, and 301 (sh) nm (log ε 3.83, 3.89, and 3.75); τ($CDCl_3$) 2.2—2.7 (6 H, m), 4.6 (1 H, d, *J* 7 Hz), and 5.2 (1 H, d, *J* 7 Hz); *m/e* 266, 264, and 262 (M^+, 1, 5, and 8%), and 199 (100).

endo-1,2,2a,8b-*Tetrahydrocyclobuta*[a]*acenaphthylen*-1-*ol*.—The ketone (17) (209 mg) in ethanol (50 ml) was mixed with a suspension of sodium tetrahydroborate (202 mg) in water (10 ml) and set aside overnight. The product was isolated with ether and recrystallised from 1,1,1-trichloroethane giving *prisms* (142 mg), m.p. 108—110 °C (Found: C, 85.5; H, 6.3. $C_{14}H_{12}O$ requires C, 85.7; H, 6.2%); $\nu_{max.}$($CHCl_3$) 3 530 cm^{-1}; τ($CDCl_3$) 2.5—3.0 (6 H, m), 5.6 (2 H, m), 6.4 (1 H, m), 7.1 (1 H, m), 8.2 (1 H, br, exchangeable), and 8.5 (1 H, m).

1,2-*Dihydrocyclohepta*[de]*naphthalen*-2-*ol* (22).—The ketone (17) (148 mg), $CDCl_3$ (0.4 ml), and trifluoroacetic acid (0.1 ml) were heated in a jacket of boiling chloroform. N.m.r. signals at τ 3.6 (1 H, d, *J* 13 Hz) and 5.9 (2 H, s) attributable to the ketone (21) were monitored and indicated maximum conversion (*ca.* 50%) after 90 min. The solution was then augmented with chloroform, washed (aqueous NaCl), dried (Na_2SO_4), and concentrated to a yellow gum. Previous attempts to isolate the ketone (21) chromatographically had led to its decomposition, so the whole product was taken up in ethanol (40 ml), mixed with a suspension of sodium tetrahydroborate (150 mg) in water (10 ml), and set aside overnight. The product was extracted with ether, washed (aqueous NaCl), dried (Na_2SO_4), and concentrated to a gum. This was chromatographed on a preparative t.l.c. plate (20 × 20 × 0.2 cm of silica) and developed with ethyl acetate (10%) in 1,1,1-trichloroethane (3 passes). A faster-moving zone on elution gave *endo*-1,2,2a,8b-tetrahydrocyclobuta[*a*]acenaphthylen-1-ol (31 mg), and a slower-moving zone on elution gave a gum (42 mg) which crystallised from 1,1,1-trichloroethane as *colourless prisms*, m.p. 112—115 °C (Found: C, 85.2; H, 6.1. $C_{14}H_{12}O$ requires C, 85.7; H, 6.2%); $\lambda_{max.}$(EtOH) 231, 243 (sh), 253, 296 (sh), 309, and 324 (log ε 4.28, 3.84, 3.66, 3.64, 3.78, and 3.63); τ($CDCl_3$) 2.2—2.8 (6 H, m), 3.4 (1 H, dd, *J* 12 and 1 Hz), 3.95 (1 H, dd, *J* 12 and 3 Hz), 5.4 (1 H, m), 6.7 (2 H, m), and 7.8 (1 H, br, exchangeable); *m/e* 196 (M^+, 60%), 181 (20), 167 (25), 166 (19), 165 (100), and 152 (40).

Cyclohepta[de]*naphthalen*-1(2H)-*one* (23).—The hemiacetal (4) (592 mg) in $CDCl_3$ (2.5 ml) and trifluoroacetic acid (1 ml) was set aside for 2 d at *ca.* 40 °C, at which point n.m.r. spectra showed 95% conversion into the ketone (23). The solution was augmented with chloroform, washed (aqueous NaCl), dried (Na_2SO_4), and concentrated to an almost colourless oil (580 mg), almost homogeneous on t.l.c.; $\nu_{max.}$ (film) 1 690 cm^{-1}; $\lambda_{max.}$(EtOH) 246, 308, 333, and 349 nm (log ε 4.15, 3.72, 3.67, and 3.63); τ($CDCl_3$) 2.0—2.8 (6 H, m), 3.25 (1 H, dd, *J* 11 and 1 Hz), 4.1 (1 H, dt, *J* 11 and 7 Hz), and 6.6 (2 H, dd, *J* 7 and 1 Hz); *m/e* 194 (M^+, 29%), 166 (16), and 165 (100).

1,2-*Dihydrocyclohepta*[de]*naphthalen*-1-*ol* (24).—The ketone (23) (580 mg) in ethanol (40 ml) was mixed with a suspension of sodium tetrahydroborate (580 mg) in water (10 ml), set aside for 2 d, then diluted with water. An

ether extract was washed (aqueous NaCl), dried (Na_2SO_4), and concentrated to a *gum* (535 mg), almost homogeneous on t.l.c.; $\nu_{max.}$($CHCl_3$) 3 590 and 3 540 cm^{-1}; $\lambda_{max.}$(EtOH) 231, 243 (sh), 253, 296 (sh), 309, and 323 nm (log ε 4.26, 3.86, 3.68, 3.63, 3.76, and 3.63); τ($CDCl_3$) 2.3—2.9 (6 H, m), 3.4 (1 H, d, *J* 12 Hz), 4.2 (1 H, dt, *J* 12 and 5 Hz), 5.0 (1 H, X quartet), 7.0 (1 H, br, exchangeable), and 7.3 (2 H, m); *m/e* 196 (M^+, 60%), 181 (36), 179 (20), 178 (35), 168 (67), 167 (100), 166 (23), 165 (74), 153 (26), and 152 (39). An aliquot in ether was purified for analysis by precipitation with pentane (Found: C, 86.2; H, 6.3. $C_{14}H_{12}O$ requires C, 85.7; H, 6.2%).

The Acetate Ester (25) *and its Pyrolysis.*—The alcohol (24) (532 mg) in pyridine (10 ml) and acetic anhydride (2 ml) was set aside overnight, then diluted with ether, washed [aqueous 2N-HCl (3 ×) and then aqueous $NaHCO_3$], dried (Na_2SO_4), and concentrated to an oil that was chromatographed on silica. Ethyl acetate in 1,1,1-trichloroethane eluted the ester (25) as an oil (495 mg), homogeneous on t.l.c.; $\nu_{max.}$ 1 735 cm^{-1}; τ($CDCl_3$) 2.2—2.8 (6 H, m), 3.3 (1 H, dd, *J* 12 and 1 Hz), 3.7 (1 H, X quartet), 4.2 (1 H, dt, *J* 12 and 5 Hz), 7.1 (2 H, m), and 8.0 (3 H, s); *m/e* 238 (M^+, 4%), 196 (1), 195 (3), 179 (37), 178 (100), 165 (19), and 152 (23). Vacuum sublimation of an aliquot at 130 °C and 0.05 mmHg gave in good yield a sublimate consisting of the ester (25) with only traces of the hydrocarbon (26). Sublimation of the ester (25) (152 mg) under an atmosphere of nitrogen (20 cmHg) at 220 °C along a tube packed with glass-wool gave an orange oil (36 mg) containing very little unchanged ester (25), and depositing red crystals. These were difficult to purify by recrystallisation, so the product was chromatographed on a preparative t.l.c. plate (20 × 20 × 0.2 cm of silica) and developed with cyclohexane (2 passes); the front and rear of the orange zone were eluted separately, and the latter yielded cyclohepta[*de*]-naphthalene (*cf.* ref. 15) (26) (11 mg) giving thick red prisms from methanol, m.p. 73—79 °C; $\lambda_{max.}$ (ether) 229, 238, 246, 272 (sh), 284, 297, 310 (sh), 328, 340, 352, 360, 367, 420, 447, 477, 511, and 553 nm (log ε 4.50, 4.45, 4.45, 3.44, 3.56, 3.61, 3.60, 3.75, 3.84, 3.72, 3.59, 3.10, 2.48, 2.53, 2.49, 2.31, and 1.91); τ($CDCl_3$) 2.8—3.3 (4 H, m), 3.5 (2 H, dd, *J* 7 and 1 Hz), 4.1 (2 H, m), and 4.7 (2 H, m); *m/e* 178 (M^+, 100%), 177 (8), 176 (17), 165 (27), 152 (39), 89 (10), and 76 (10).

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