1368. *Ring-*c *Expansion and Fine Structure of* 7,12-*Dihydro*-1-*hydroxypleiadene*-7,12-*dione and Related Compounds. Transannular Reactions of* 7-, 8-, *and* 9-*Membered Rings Fused to Planar Systems*

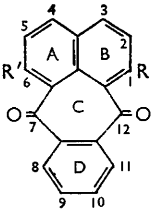
By M. E. C. Biffin, L. Crombie, and J. A. Elvidge

The reaction between 7,12-dihydro-1-hydroxypleiadene-7,12-dione and diazomethane, which gives "Fieser's compound," involves insertion of a methylene between the 12-carbonyl and the 1-hydroxynaphthalene residue. The product (VI), and its relatives, undergo acid- or base-catalysed transannular condensation to give black crystalline ketones of the type (X), whilst treatment with hydriodic acid gives directly the reduced compound (XI; R = OH, R′ = H). "Fieser's compound" yields the oxo-lactone (XIV) on oxidation, and zinc–acetic acid reduction gives a hemi-ketal (XVIII). Methanol–acid treatment of the eight-membered-ring diol (XX) readily gives a bridged ether (XXI) but in the seven-membered-ring series solvolysis to a dimethyl ether (XXII; R = OMe) occurs, the bridged ether being more strained. Reduction of 7,12-dihydro-1-methoxypleiadene-7,12-dione with lithium aluminium hydride–aluminium chloride gives 7,12-dihydro-1-methoxypleiadene (XXIV), and p.m.r. results giving information on the flexing of the molecule about the 7,12-axis are under study.

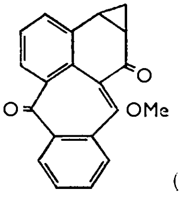
Attempts to insert two methylenes into 7,12-dihydro-1,6-dihydroxypleiadene-7,12-dione lead only to the insertion of one, and this result is ascribed to cross-ring steric repulsion which would be set up when the trigonal hydridisation at C-7 became tetrahedral during formation of the intermediate for the second expansion, cf. (XII) and (XXVIII).

A suggestion that a tautomeric structure (XXXIV) may be needed to accommodate the chemistry of 7,12-dihydro-1-hydroxypleiadene-7,12-dione could involve tropone-like character (XXXV) in ring c. However, spectral evidence, interpreted by information from model compounds, confirms the classical structure (XXXIII).

Although 7,12-dihydro-1-hydroxypleiadene-7,12-dione (I; R = OH, R′ = H) is not appreciably affected by prolonged contact with excess of ethereal diazomethane, a fairly rapid reaction occurs in the presence of tetrachloroethane as co-solvent to give a yellow compound m. p. 209·5—211·5° ("Fieser's compound"). Fieser[1] showed that the compound, $C_{20}H_{14}O_3$, contained one methoxyl and he formulated it either as (II), derived from a tautomer of (I; R = OH, R′ = H), or as (III). The tautomerism and fine-structure [cf. (XXXIII), (XXXIV), and (XXXV)] of 7,12-dihydro-1-hydroxypleiadene-7,12-dione is discussed later. First, the structure of Fieser's compound is elucidated as (VI), and then the chemistry and transannular reactions of systems of type (I), where ring c is 7-, 8-, or 9-membered, are considered.



(I)



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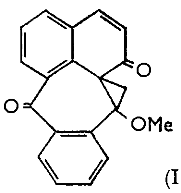

(III)

In the infrared, Fieser's compound had rather broad carbonyl absorption at 1677 cm.$^{-1}$ whilst the proton magnetic resonance (p.m.r.) spectrum showed resonances at τ 5·97 (OMe) and 2·75—1·65 p.p.m. (9 aromatic protons), with an AB quartet at 5·68 and 5·40 p.p.m.

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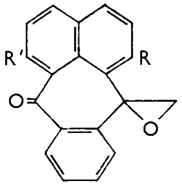
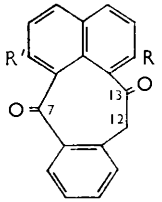
[1] L. F. Fieser, *J. Amer. Chem. Soc.*, **1933**, **55**, 4963.

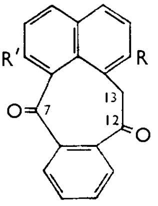
(J = 14 c./sec.). Two types of structure, epoxide (IV) or (V), or ring-expanded (VI)—(IX), give possible interpretation of the p.m.r. results. Epoxide structures were disfavoured because Fieser's compound was unattacked by alcoholic hydrochloric acid saturated with magnesium chloride, and because it formed a 2,4-dinitrophenylhydrazone still retaining a carbonyl absorption at 1678 cm.$^{-1}$. Under higher resolution, the infrared carbonyl peak from the parent compound could be resolved into two bands at $\nu_{max.}$ 1679 and 1684 cm.$^{-1}$ Of the four remaining structures (VI)—(IX), further work shows (VI) to represent Fieser's compound.



(IV: R = OMe, R' = H)
(V: R = H, R' = OMe)

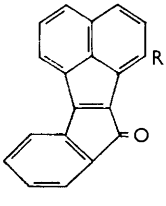


(VII: R = OMe, R'= H)
(VIII: R = H, R' = OMe)

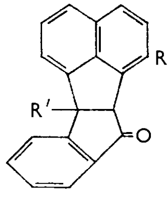


(VI: R = OMe, R'= H)
(IX: R = H, R' = OMe)

In order to locate the inserted methylene group it was decided to demethylate Fieser's compound and to study the hydrogen-bonding proclivities of the phenolic hydroxyl. Various methods were tried. Aluminium chloride gave tars whilst hydriodic acid gave a new cream-coloured compound, m. p. 169°. On re-methylation however, the latter did not give back Fieser's compound, something more than demethylation having occurred. Pyridine hydrochloride and Fieser's compound gave a new product which formed silky black needles, $C_{20}H_{12}O_2$. In the p.m.r. spectrum of the latter there was only a methoxyl (τ 5·97) and 9 aromatic protons (2·82—1·83). In the infrared spectrum carbonyl absorption was present, $\nu_{max.}$ 1705 cm.$^{-1}$. The black compound is therefore formulated as the substituted indenone (X; R = OMe). It can also be made by refluxing Fieser's compound with 2N-aqueous potassium hydroxide, and by acid-catalysed reactions. As a by-product in the pyridine hydrochloride reaction, and from a treatment with boron tribromide at —80°, the corresponding phenol (X; R = OH) has been obtained as purple-red needles. Both the phenol and its methyl ether were obtained by treatment with boron trichloride at —80°.



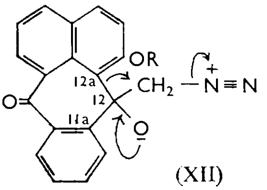
(X)



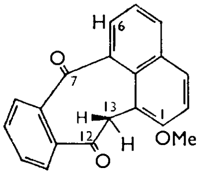
(XI)

The compound, $C_{19}H_{12}O_2$, obtained by treating Fieser's compound with hydrogen iodide, showed ultraviolet shifts similar to those of 1-naphthol when alkali was added: it gave an acetate. The p.m.r. spectrum of the phenol $C_{19}H_{12}O_2$, showed an AB quartet at τ 5·27, 4·48, but the splitting (6·5 c./sec.) was very different from that in Fieser's compound: it also had complex resonances at τ 2·875—2·115 (9 aromatic H and 1 OH). Structure (XI; R = OH, R' = H) seemed probable and was confirmed by showing that the methyl ether was identical with the hydrogenation product of (X; R = OMe). Compound (XI; R = OH, R' = H) presumably arises by reduction of the initial aldol product (XI; R = R' = OH) by hydriodic acid, and its hydrogen bonding shows that structure (VI) is correct for Fieser's compound. The infrared spectrum of a dilute solution of the compound (XI; R = OH, R′ = H) reveals intramolecular hydrogen-bonding (3390 cm.$^{-1}$; c <0·0005M, CCl_4), so the phenol and the carbonyl group must be on the same side of the molecule. Structure (VII) is not acceptable, as the phenolic hydroxyl in this would be chelated and form a very broad band at a still lower wavelength: also the carbonyl vibration in the phenol (1690 cm.$^{-1}$) is too high for a chelated carbonyl in such a structure. On the other hand, structure (VI) accommodates the infrared data for the derived phenol and explains the transannular condensation reaction.

We have confirmed an earlier observation[1] that 7,12-dihydro-1-methoxypleiadene-7,12-dione, (I; R = OMe, R′ = H) does not react with diazomethane, even with various forms of catalysis. It seems therefore, that the chelation of the 12-carbonyl of 7,12-dihydro-1-hydroxypleiadene-7,12-dione (XXXIII) aids reaction, enhancing the electrophilicity of C-12, reaction being completed as in (XII): here the more nucleophilic 12,12a-*o*-hydroxynaphthalene bond moves in preference to the 11a,12-bond.



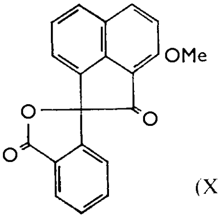
(XII)



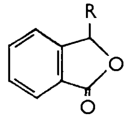
(XIII)

A model of Fieser's compound [cf. (XIII)] shows it to be rigid so that the two hydrogens on C-13 form an AB system. Also the 7-carbonyl is twisted permanently out of the plane of the naphthalene residue: this has significance, as indicated later.

Oxidation of Fieser's compound with sodium dichromate in glacial acetic acid gave the black methoxy-compound (X; R = OMe), and a colourless compound, m. p. 236—238°, $C_{20}H_{12}O_4$, $\nu_{max.}$ 1774 and 1745 cm.$^{-1}$. The two infrared bands are assigned to an α-unsaturated γ-lactone and to a 5-membered-ring carbonyl, respectively. In the p.m.r. spectrum there is only a singlet at τ 5·68 (OMe) and a complex of 9 aromatic protons between 1·43 and 2·74. The compound is therefore given constitution (XIV) resulting from further oxidation of the first-formed transannular aldol (XI; R′ = OH, R = OMe). The frequency, 1774 cm.$^{-1}$, seems at first rather high for an α-unsaturated γ-lactone (usually 1740—1760 cm.$^{-1}$),[2] but the electron-attracting group attached to the phthalide residue would account for the raised value. Thus, phthalide (XV) absorbs at 1750 cm.$^{-1}$ but compound (XVI) absorbs[3] at 1775 cm.$^{-1}$.



(XIV)



(XV: R = H)

(XVI: R = CO_2H)

Treatment of Fieser's compound with zinc and acetic acid gives a compound, $C_{20}H_{16}O_3$, formulated originally as a dihydro-derivative of (II) or (III).[1] However, the infrared spectrum shows that this compound lacks a carbonyl group but has a hydroxyl, which from its absorption frequency appears to be tertiary[4] (3595 cm.$^{-1}$, CCl_4). In agreement, active manganese dioxide in acetone, or (bispyridine)chromium(VI) oxide in pyridine left it unaffected. In the p.m.r. spectrum the compound displayed a sharp singlet at τ 6·14

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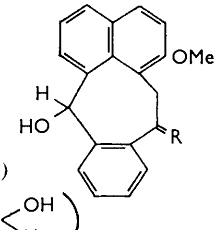
[2] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1958.

[3] J. F. Grove and H. A. Willis, *J.*, 1951, 877.

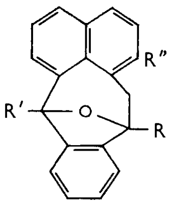
[4] A. R. M. Cole and P. R. Jeffries, *J.*, 1956, 4391.

(OMe), an AB quartet at 6·63 and 5·98 ($J = 18$ c./sec.) (CH_2), and a singlet at 3·63 due to a proton Ar•CH(O)•Ar. The zinc–acetic acid product is thus the transannular hemi-ketal (XVIII) derived from the initial reduction product (XVII). The alternative structure (XIX) is not acceptable as this would give an AMX pattern from the system Ar•CH_2CH(O)•Ar. In agreement with structure (XVIII) acetylation causes a downfield shift of the methylene quartet to τ 6·16 and 5·59 ($J = 17$ c./sec.).



(XVII: R = O)

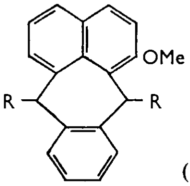
(XX: R = $<^{OH}_{H}$)



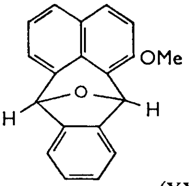
(XVIII: R = OH, R′ = H, R″ = OMe)
(XIX: R = H, R′ = OH, R″ = OMe)
(XXI: R = R′ = H, R″ = OMe)

Reduction of Fieser's compound with lithium aluminium hydride gives the expected diol (XX), oxidised back to Fieser's compound with active manganese dioxide. Working up the reduction with mineral acid, or boiling the diol with methanol containing acid gives the transannular ether (XXI). The latter is formed directly by refluxing Fieser's compound with lithium aluminium hydride–aluminium chloride in tetrahydrofuran.

Reduction of the 7-membered ring C of the pleiadenediones (I) provides some contrasts with Fieser's compound (VI) with its 8-membered ring C. The diol (XXII; R = OH), formed by reducing 7,12-dihydro-1-methoxypleiadene-7,12-dione (I; R = OMe, R′ = H) with lithium aluminium hydride, is converted by boiling, acidified methanol, not into the transannular ether (XXIII) but into the solvolysis product, the bis-methyl ether (XXII; R = OMe). Dreiding stereomodels suggest that the ether (XXIII) has more angle-strain than the ether (XXI), making understandable the contrast between these 7- and 8-membered ring C systems which contain planar elements.*



(XXII)
(XXIV: R = H)



(XXIII)

When 7,12-dihydro-1-methoxypleiadene-7,12-dione (I; R = OMe, R′ = H) is refluxed with lithium aluminium hydride–aluminium chloride, an internal ether is not formed as happens with Fieser's compound, but 7,12-dihydro-1-methoxypleiadene (XXIV) is obtained. The p.m.r. spectrum is interesting. There is a sharp band at τ 6·10 (OMe) and nine aromatic protons with resonances 2·34—2·99 p.p.m.: one of the methylene groups is represented by a sharp two-proton singlet at 5·40 and the other by a broad two-proton band at 5·56. The molecule must be flexible † for only then can the protons of the methylene come to resonance as singlets. The reasons for the difference in the two methylene bands will be discussed elsewhere when results using a variable-temperature probe are reported.

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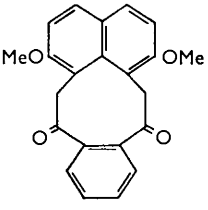
* The corresponding thioether and sulphone have been reported,[5] but the longer C–S bond length results in less strain.

† Estimates of the inversion barriers of *symmetrical* 7,12-dihydropleiadenes are available.[6]

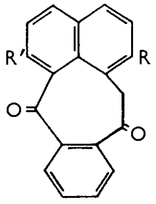
[5] M. P. Cava and R. H. Schlessinger, *J. Amer. Chem. Soc.*, 1963, **85**, 835.

[6] P. T. Lansbury and J. F. Bieron, *J. Amer. Chem. Soc.*, 1964, **86**, 2524; P. T. Lansbury, *ibid.*, 1959, **81**, 4325.

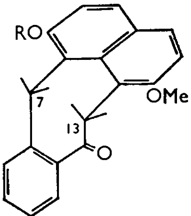
Extension of the ring expansion to give compounds with 9- or higher-membered C rings by insertion of more than one methylene would be a valuable development and, to this end, 7,12-dihydro-1,6-dihydroxypleiadene-7,12-dione (I; R = R′ = OH) was treated with diazomethane in tetrachloroethane–ether. The product was not (XXV) but (XXVI). Expansion, as in the formation of Fieser's compound, occurs on one side of the molecule but then the second hydrogen-bonded system does not undergo the same reaction and the hydroxyl merely slowly methylates. The cause of this is considered to be steric: in the system (XXVII) expansion would be initiated by conversion of C-7 from trigonal to tetrahedral hybridisation on attack by diazomethane, with formation of an intermediate resembling (XII). However, this is evidently precluded by the severe compression, which cannot be relieved by rotation in this rigid system [cf. (XXVIII) where



(XXV)



(XXVI: R = R′ = OMe)
(XXVII: R = OMe, R′ = OH)

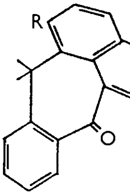


(XXVIII)

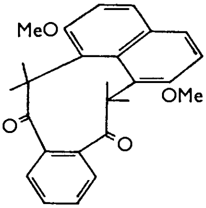
the distance between the centres of the inward-pointing 7,13-hydrogens is ~0·9 Å.] Unfavourable mesomeric influence originating with the C-1 methoxyl in (XXVII) and decreasing the electrophilicity at C-7 is probably of minor importance.

Neither 7,12-dihydro-1-hydroxypleiaden-7-one (XXIX; R = OH, R′ = H) nor 7,12-dihydro-1,6-dihydroxypleiaden-7-one (XXIX; R = R′ = OH) underwent ring expansion. In the first case, the 1-methoxy-compound was formed. In the second, 7,12-dihydro-6-hydroxy-1-methoxypleiaden-7-one (XXIX; R = OMe, R′ = OH) was formed and was slowly converted into 7,12-dihydro-1,6-dimethoxypleiaden-7-one. Catalysis (lithium chloride–methanol) did not effect ring expansion. Again the cause of failure is probably steric.

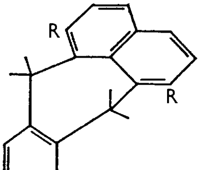
In the case of 7,12-dihydro-1-hydroxy- (I; R = OH, R′ = H) and -1,6-dihydroxypleiadene-7,12-dione (I; R = R′ = OH) conversion of one carbonyl carbon to tetrahedral hybridisation is sterically reasonable because the remaining carbonyl points outward,



(XXIX)



(XXXI) boat



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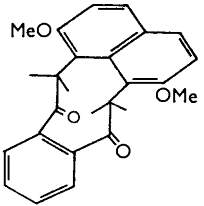
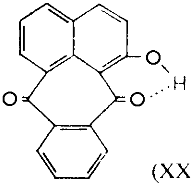


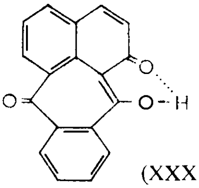
(XXXII) (chair)

away from the new axial group (cf. XXIX). But when the 12-position is already a tetrahedral centre, the conversion of the remaining trigonal centre into a tetrahedral one would cause compression, as in (XXX): relief would not be possible as the structure could only flex to give an identical structure. Compression thus disfavours the formation of a species of type (XII) necessary for the expansion. Even if the double ring expansion of 7,12-dihydro-1,6-dihydroxypleiadene-7,12-dione (I; R = R′ = OH) proceeded, it would lead to a 9-membered ring C showing major steric compression of the inward pointing hydrogens in either boat (XXXI) or chair (XXXII) conformation.

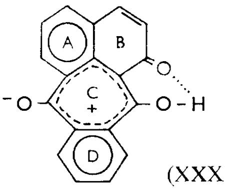
During earlier work on 7,12-dihydro-1-hydroxypleiadene-7,12-dione (XXXIII), Fieser [1] encountered a number of apparent anomalies and attempted accommodation in terms of the tautomeric formula (XXXIV). Resonance contributions from a tropone-like system (XXXV) might be envisaged though it has been noted in other investigations [7] that the fusion of first one, and then a second, benzenoid ring to a tropone system greatly diminishes the polar resonance contributors, which would not therefore add much to stabilisation of the system.



(XXXIII)



(XXXIV)



(XXXV)

At a first examination, certain spectral evidence might be construed in favour of the tautomer (XXXIV) with resonance contributions from (XXXV). On the basis of Table 1 the band at 1620 cm.$^{-1}$ in 7,12-dihydro-1-hydroxypleiadene-7,12-dione might be assigned to the chelated carbonyl in (XXXIV), with the band at 1653 cm.$^{-1}$ representing the 7-carbonyl (values for chloroform solutions). The classical structure of the 1-methoxy-compound (I; R = OMe) is known by unambiguous synthesis.[8] In this, both bands are at higher frequency and it seems reasonable that the one at 1653 cm.$^{-1}$ should be raised to 1671 cm.$^{-1}$ [polar resonance contributions due to (XXXV) not present in (I; R = OMe, R′ = H)] and the band formerly at 1620 cm.$^{-1}$ replaced by one at 1649 cm.$^{-1}$ [diarylketone, not chelated]. This interpretation does not hold for information accumulated in Table 1 for model compounds.

Table 1

Carbonyl frequencies (cm.$^{-1}$)

		($CHCl_3$)	(Mull)
7,12-*Dihydropleiadene*-7,12-*diones* (I)			
1-Hydroxy	(R = OH, R′ = H)	1653, 1620	1645, 1620
1-Methoxy	(R = OMe, R′ = H)	1671, 1649	1675, 1643
1,6-Dihydroxy	(R = R′ = OH)	1608	1620
1,6-Dimethoxy	(R = R′ = OMe)	1673, 1663	1680, 1668
7,12-*Dihydropleiaden*-7-*ones* (XXIX)			
1-Hydroxy	(R = OH, R′ = H)	1647	1639
1-Methoxy	(R = OMe, R′ = H)	1645	1643
1,6-Dihydroxy	(R = R′ = OH)	1616	1611
1,6-Dimethoxy	(R = R′ = OMe)	1661	1662
6-Hydroxy-1-methoxy	(R = OMe, R′ = OH)	1613	1609

The 7-carbonyl absorption is at 1647 and 1645 cm.$^{-1}$ in 7,12-dihydro-1-hydroxy- and -1-methoxy-pleiaden-7-one [(XXIX; R = OH, R′ = H) and (XXIX; R = OMe, R′ = H)] so that in 7,12-dihydro-1-methoxypleiadene-7,12-dione (I; R = OMe, R′ = H) the band at 1649 cm.$^{-1}$ is reasonably assigned to the 7-carbonyl and that at 1671 cm.$^{-1}$ to the 12-carbonyl. In support of this frequency rise due to the *o*-methoxyl, is the rise

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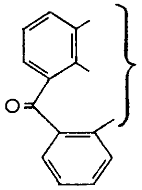
[7] G. L. Buchanan, *Chem. and Ind.*, 1952, 855; G. L. Buchanan and D. R. Lockhart, *J.*, 1959, 3586.

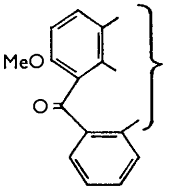
[8] L. F. Fieser and M. Fieser, *J. Amer. Chem. Soc.*, 1933, **55**, 3010.

from 1647 cm.$^{-1}$ on passing from 7,12-dihydro-1-methoxypleiaden-7-one (XXIX; R = OMe, R′ = H) to 1661 cm.$^{-1}$ in 7,12-dihydro-1,6-dimethoxypleiaden-7-one (XXIX; R = R′ = OMe). The carbonyl groups in 7,12-dihydro-1,6-dimethoxypleiadene-7,12-dione (I; R = R′ = OMe) give a mean frequency of 1668 cm.$^{-1}$ and are probably doubled because of vibrational interaction. Compounds (XXIX; R = R′ = OH), (XXIX; R = OMe, R′ = OH), and (I; R = R′ = OH) all have carbonyl bands at lowered frequency, consistent with their chelated character. Correlations for this series are:



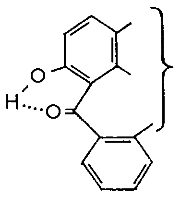
$\nu_{max.}$ ~ 1647 cm.$^{-1}$

(A)



$\nu_{max.}$ ~ 1660 – 1670 cm.$^{-1}$

(B)



$\nu_{max.}$ ~ 1610 – 1620 cm.$^{-1}$

(C)

Structure (XXXIII) is thus supported by the infrared evidence, the absorption at 1653 cm.$^{-1}$ being due to feature (A) and that at 1620 cm.$^{-1}$ being due to (C), and there is no reason for favouring the tautomer (XXXIV).

In the p.m.r. spectra of 7,12-dihydro-1-hydroxypleiadene-7,12-dione (XXXIII) and the corresponding 1-methoxy-compound there occurs a difference which suggests a difference in fine structure. The spectrum of the 1-methoxy-compound has a characteristic low-field double doublet arising from one proton and showing *o*- and *m*-splittings (J = 7 and 1·5 c./sec.). Since the four benzenoid protons in phthaloyl derivatives give rise to a comparatively narrow band (*e.g.*, covering 0·3 p.p.m. near τ 2·15 in bromoethylphthalimide) [9] the low-field double doublet is assigned to the naphthalenic 6-hydrogen, deshielded by the 7-carbonyl. This characteristic double doublet appears in the spectra of 7,12-dihydro-1-hydroxy- and -1-methoxypleiaden-7-one and, as required by the assignment, is absent in those of 7,12-dihydro-1,6-dimethoxypleiadene-7,12-dione and the corresponding pleiaden-7-one. In 7,12-dihydro-1-hydroxypleiadene-7,12-dione (XXXIII) however, the low-field double doublet is absent, all nine aromatic protons covering the broad region τ 1·6—2·8. A possible explanation is that in this case the chelate ring may be resisting the flexing about the 7,12-axis which in the other cases brings the 6-proton into

TABLE 2

Ultraviolet absorptions

	R	R′		$\lambda_{max.}$ (mμ) (ε)	
7,12-*Dihydropleiadene*-7,12-*diones* (I)					
1-Hydroxy	OH	H	240 (36,100)	325 (10,000)	380 (13,100)
1-Methoxy	OMe	H	244 (32,700)	324 (6200)	374 (9700)
1,6-Dihydroxy	OH	OH	218sh (23,900)	327 (37,000) 362 (13,600)	349sh (23,700) 398 (12,800)
1,6-Dimethoxy	OMe	OMe	232 (39,600)	250 (30,900)	372 (13,000)
7,12-*Dihydropleiadene*-7-*ones* (XXIX)					
1-Hydroxy	OH	H	225 (37,600)	262 (16,900)	331sh (3500) 383 (7700)
1-Methoxy	OMe	H	225 (40,000)	258 (27,700)	337sh (4500) 374 (8600)
1,6-Dihydroxy	OH	OH	236 (35,600)	282 (6800)	386 (11,300)
1,6-Dimethoxy	OMe	OMe	235 (44,200)	296 (14,200)	356 (10,200)
6-Hydroxy-1-methoxy	OMe	OH	239 (41,300)	288 (7700)	398 (12,800)

sh = Shoulder.

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[9] N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, Nuclear Magnetic Resonance Spectra Catalog, Varian Associates, Palo Alto, 1962, Spectrum 246.

the maximum deshielding region of the 7-carbonyl. Hence, the 6-proton resonance is less clearly distinguishable from other aryl protons. The spectrum of Fieser's compound supports this explanation. As mentioned earlier, the 7-carbonyl must be kept permanently out of the plane of the 6-hydrogen and the low-field double doublet is absent from the spectrum.

Ultraviolet data for some of the compounds discussed are summarised in Table 2.

EXPERIMENTAL

Except where otherwise stated, the following apply. Ultraviolet spectra were determined for ethanol solutions: ε in parenthesis follows $\lambda_{max.}$ and i denotes an inflexion. Infrared spectra were determined for chloroform solutions (unless otherwise stated) with sodium chloride optics. Molecular weights were determined by the vapour-pressure osmometric method (Mechrolab equipment). In chromatographic work the letter A together with a numeral refers to acid alumina of the numbered Brockmann grade. Evaporation signifies evaporation under reduced pressure and drying refers to the use of anhydrous magnesium sulphate. P.m.r. spectra were measured at 60 Mc./sec. on 5—10% solutions containing a trace of tetramethylsilane.

7,12-Dihydro-1-hydroxypleiadene-7,12-dione (I; R = OH, R′ = H).—This compound was prepared by the method of Fieser.[10] It crystallised from ethanol as yellow needles, m. p. 205—206° (lit.,[10] 198°), τ ($CDCl_3$) 2·8—1·7 (complex, 9 aryl protons), −5·15 (singlet, 1-OH, chelated).

7,12-Dihydro-1-methoxypleiadene-7,12-dione (I; R = OMe, R′ = H).—This compound, best prepared by refluxing 7,12-dihydro-1-hydroxypleiadene-7,12-dione (I; R = OH, R′ = H) (1 g.) in anhydrous benzene (16 ml.) with anhydrous potassium carbonate (2·17 g.) and dimethyl sulphate (1·46 g.) for 24 hr., formed pale yellow crystals (700 mg.), m. p. 211—212° from ethanol (lit.,[11] 205°) (Found: C, 79·45; H, 4·4. Calc. for $C_{19}H_{12}O_3$: C, 79·15; H, 4·2%); τ ($CDCl_3$) 5·97 (singlet, 1-OMe), 2·73—1·88 (complex, 8 aryl protons), 1·47 (double doublet, J_o = 7·5 c./sec., J_m = 1·75 c./sec., 6-H).

Fieser's Compound (VI).—The preparation [1] using a two-fold excess of diazomethane gave a product contaminated with starting material. By using a seven-fold excess of reagent, pure product was obtained (30—40%). It crystallised from ethanol as pale yellow needles, m. p. 209·5—211·5° (lit.,[1] 208°) (Found: C, 79·25; H, 4·85%; *M*, 316. Calc. for $C_{20}H_{14}O_3$: C, 79·45; H, 4·65%; *M*, 302), $\lambda_{max.}$ 355 (5390), 370 mμ (6580); $\nu_{max.}$ 1677 cm.$^{-1}$ (C=O) and, with a Unicam S.P. 100 spectrophotometer, $\nu_{max.}$ (Nujol mull) 1684, 1679 cm.$^{-1}$ (C=O); τ ($CDCl_3$) 5·97 (singlet, 1-OMe), 5·68, 5·40 (AB quartet, J = 14·5 c./sec., 13-methylene), 2·75—1·65 (complex, 9 aryl protons).

The *2,4-dinitrophenylhydrazone* crystallised from methanol–dioxan as yellow needles, m. p. 272—273°, $\nu_{max.}$ (Nujol mull) 1678 cm.$^{-1}$ (C=O) (Found: C, 64·6; H, 3·9; N, 11·5. $C_{26}H_{18}N_4O_6$ requires C, 64·7; H, 3·75; N, 11·6%).

Action of Hydriodic Acid on Fieser's Compound.—A solution of Fieser's compound (200 mg.) in glacial acetic acid (10 ml.) was refluxed for 90 min. with hydriodic acid (2 ml., sp. gr. 1·68—1·71). The solution was poured into water, and the precipitate extracted into ether. The ethereal solution was washed with sodium thiosulphate solution, sodium hydrogen carbonate solution, and finally with water, and was dried and evaporated. The residual solid was chromatographed (A III). Elution with benzene and crystallisation from acetone gave creamy-white needles of the *compound* (XI; R = OH, R′ = H), m. p. 169° which gave no colour with ethanolic ferric chloride. (Found: C, 83·45; H, 4·6%; *M*, 284. $C_{19}H_{12}O_2$ requires C, 83·8; H, 4·4%; *M*, 272), $\lambda_{max.}$ 211, (37,630), 233·5 (39,780), 249i (23,250), 287 (15,950), 299 (16,400), 338i (9436), 348 mμ (11,000); $\nu_{max.}$ 3360 (O–H), 1690 cm.$^{-1}$ (C=O). The peak at 233·5 mμ shifted to 246 mμ in ethanolic potassium hydroxide solution (0·01N). The infrared spectrum in carbon tetrachloride (0·00043M, quartz cells, path 2 cm.) had $\nu_{max.}$ 3390 cm.$^{-1}$ (intramolecularly bonded O–H). The p.m.r. spectrum ($CDCl_3$) showed resonances at τ 5·27, 4·84 (AB quartet, J = 6·5 c./sec., 7- and 13-H), 2·875—2·115 (complex, 9 aryl protons plus 1-OH). The *acetate* crystallised from methanol, needles, m. p. 181—182° (Found: C, 79·9; H, 4·6. $C_{21}H_{14}O_3$ requires C, 80·25; H, 4·45%), $\nu_{max.}$ 1757 (acetate), 1712 cm.$^{-1}$ (C=O); τ ($CDCl_3$) 7·74 (singlet,

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[10] L. F. Fieser, *J. Amer. Chem. Soc.*, 1931, **53**, 3546.

[11] W. Knapp, *Monatsh.*, 1932, **60**, 189.

acetate), 5·125, 4·675 (AB quartet $J = 6$ c./sec., 7- and 13-H), 2·835—2·115 (complex, 9 aryl protons). The *methyl ether* (XI; R = OMe, R′ = H), prepared with diazomethane or dimethyl sulphate, crystallised from acetone, m. p. 154—155° (Found: C, 83·9; H, 5·15%; *M*, 283. $C_{20}H_{14}O_2$ requires C, 83·9; H, 4·9%; *M*, 286), $\lambda_{max.}$ 210 (40,610), 236 (59,950), 252i (13,750), 291 (10,600), 301 (10,150), 340i (5409), 352 mμ (5941); $\nu_{max.}$ 1712 cm.$^{-1}$ (C=O); τ ($CDCl_3$) 5·98 (singlet, 1-OMe), 5·125, 4·705 (AB quartet, $J = 6·5$ c./sec., 7- and 13-H), 2·78—2·09 (complex, 9 aryl protons). The 2,4-*dinitrophenylhydrazone* of (XI; R = OMe, R′ = H) crystallised from acetone as yellow needles, m. p. >360°, $\nu_{max.}$ (Nujol mull) 3311 (N–H), 1616 cm.$^{-1}$ (aryl) (Found: N, 12·0. $C_{26}H_{18}N_4O_5$ requires N, 12·0%).

Action of Pyridine Hydrochloride on Fieser's Compound.—Pyridine hydrochloride (3 g.) was fused, allowed to resolidify, and Fieser's compound (100 mg.) was added. The two compounds were fused together until a homogeneous brown melt was obtained. On solidification the melt was treated with water and the resulting brown precipitate was filtered off, washed with water, and dried by suction. Chromatography (A III) from benzene gave a solid which crystallised from ethanol to give silky black needles of the *ketone* (X; R = OMe) (47 mg.), m. p. 196° (Found: C, 84·6; H, 4·2%; *M*, 303 (at 0·016M), 329 (at 0·0255M), 388·5 (at 0·029M). $C_{20}H_{12}O_2$ requires C, 84·5; H, 4·25%; *M*, 284), $\lambda_{max.}$ 225 (46,690), 266 (40,560), 355 (11,790), 435 (8652), 534 mμ (1346); $\nu_{max.}$ (Nujol mull) 1705 cm.$^{-1}$ (C=O); τ ($CDCl_3$) 5·97 (singlet, 1-OMe), 2·82—1·83 (complex, 9 aryl protons). Elution with benzene–chloroform (1 : 1) yielded compound (X; R = OH) as stout purple-red needles, m. p. 205° from ethanol; $\lambda_{max.}$ 213 (39,190), 218 (39,280), 223 (41,010), 265 (30,810), 357 (10,380), 437 mμ (7114); $\nu_{max.}$ (Nujol mull) 3255 (O–H), 1678 cm.$^{-1}$ (C=O). It sublimed as black-brown needles and gave no colour with ethanolic ferric chloride. Methylation of the compound (X; R = OH) with dimethyl sulphate gave the expected ether (X; R = OMe) as fine black needles, m. p. and mixed m. p. 195° (identified also by infrared spectroscopy). On hydrogenation in glacial acetic acid with Adams catalyst, the ether (X; R = OMe) took up one mol. of hydrogen to give (XI; R = OMe, R′ = H) (mixed m. p. and infrared spectrum).

Action of Alkali on Fieser's Compound.—A solution of Fieser's compound (200 mg.) in aqueous 2N-potassium hydroxide (20 ml.) and ethanol (20 ml.) was heated under reflux for 2 hr. and the resulting brown-black solution was cooled, acidified with hydrochloric acid (2N), and extracted with ether. Chromatography (A III) from benzene solution gave black needles, m. p. 194° from ethanol, shown by mixed m. p. and infrared spectrum to be the ether (X; R = OMe).

Action of Boron Tribromide on Fieser's Compound.—A solution of Fieser's compound (200 mg.) in dry methylene chloride (10 ml.) was cooled to −80°. Freshly distilled boron tribromide (3·5 ml.) was chilled and added rapidly. The deep red solution was kept at −80° for 0·5 hr. and then allowed to warm up to room temperature over 16 hr. The solvent was boiled down and the residue was treated with methanol (3 × 3 ml.) and evaporated to dryness after each addition. The product was chromatographed (A III). Elution with benzene containing chloroform (10% by volume) yielded stout purple-red needles (65 mg.), m. p. 205° from methanol. It was identical with the pyridine hydrochloride product (X; R = OH) (mixed m. p. and infrared spectrum).

Action of Boron Trichloride on Fieser's Compound.—Treatment of Fieser's compound with freshly distilled boron trichloride, using the conditions of the boron tribromide reaction, and chromatography of the product (A III) from benzene, gave the ether (X; R = OMe). Continued elution with benzene–chloroform (3 : 1 by volume) gave compound (X; R = OH).

Oxidation of Fieser's Compound.—Fieser's compound (400 mg.) was refluxed for 90 min. with sodium dichromate (800 mg.) in glacial acetic acid (15 ml.). The solution was poured into water and the precipitate in benzene was chromatographed (A III) to give three products. The first, present in small amount, which formed black needles from ethanol, m. p. 195°, was (X; R = OMe) (mixed m. p. and infrared spectrum). The second was the *lactone* (XIV) (10 mg.), obtained as white needles from methanol, m. p. 236—238° (Found: C, 75·65; H, 4·05%; *M*, 310. $C_{20}H_{12}O_4$ requires C, 75·95; H, 3·8%; *M*, 316), $\nu_{max.}$ (Nujol mull) 1774 (α,β-unsaturated δ-lactone), 1745 cm.$^{-1}$ (5-membered-ring C=O); τ ($CDCl_3$) 5·65 (singlet, 1-OMe), 2·74—1·73 (complex, 9 aryl protons). The third product, isolated in small amount, was a pale yellow crystalline solid, m. p. 198—204°, $\nu_{max.}$ (Nujol mull) 3480 (O–H), 1697 (C=O), 1260vs cm.$^{-1}$ (–OMe). This may be the aldol (XI; R = OMe, R′ = OH), the intermediate in the formation of (X; R = OMe) and (XIV) from Fieser's compound, because an attempt to prepare the acetate, using anhydrous sodium acetate and acetic anhydride, yielded a black solid with an infrared spectrum identical with that of (X; R = OMe).

Reduction of Fieser's Compound with Zinc Dust and Acetic Acid.—The reduction was carried out by Fieser's method.[1] The pale yellow *hemi-ketal* (XVIII) crystallised from ethanol, m. p. 246° (decomp.) (lit.,[1] 245°) (Found: C, 78·6; H, 5·6. $C_{20}H_{16}O_3$ requires C, 78·9; H, 5·3%), $\lambda_{max.}$ 235 (49,550), 289 (6162), 300 (6418), 340 mμ (3286); $\nu_{max.}$ (Nujol mull) 3328 (O–H), 1610i, 1595 cm.$^{-1}$ (aryl) and, under high resolution in carbon tetrachloride, $\nu_{max.}$ 3595 cm.$^{-1}$ (tertiary O–H). The p.m.r. spectrum (Me_2SO) showed resonances at τ 6·14 (singlet, 1-OMe), 6·63, 5·89 (AB quartet, *J* = 18 c./sec., 13-methylene), 3·63 (singlet, 7-H), 3·10—2·05 (complex, 9 aryl protons plus 12-OH). The derived acetate crystallised from ethanol (lit.,[1] m. p. 184°) (Found: C, 76·3; H, 5·3. Calc. for $C_{22}H_{18}O_4$: C, 76·3; H, 5·25%), $\nu_{max.}$ (Nujol mull) 1750 (acetate), 1612i, 1600 cm.$^{-1}$ (aryl); τ ($CDCl_3$) 7·83 (singlet, acetate), 6·16 (singlet 1-OMe), 6·16, 5·59 (AB quartet, *J* = 17 c./sec., 13-methylene), 3·50 (singlet, 7-H), 3·10—2·15 (complex, 9 aryl protons). The reduction product (XVIII) was recovered unchanged after being shaken in acetone with active manganese dioxide for 48 hr., or after being shaken in pyridine with bispyridinechromium(VI) oxide for 48 hr.

Preparation of the Diol (XX).—A solution of Fieser's compound (955 mg.) in anhydrous benzene (20 ml.) was added dropwise to a slurry of lithium aluminium hydride (252 mg.) in anhydrous ether (20 ml.) and the mixture heated under reflux for 2 hr. The excess of reagent was destroyed (ethyl acetate) and the mixture poured into water. Isolation with ether gave the *diol* (XX) (580 mg.) which formed needles from ethanol, m. p. 212·5° (decomp.) (Found: C, 78·3; H, 6·05. $C_{20}H_{18}O_3$ requires C, 78·4; H, 5·9%). $\nu_{max.}$ (Nujol mull) 3425, 3330, (O–H), 1620, 1600 cm.$^{-1}$ (aryl). A solution of this diol (36 mg.) in acetone (4 ml.) was shaken for 24 hr. with active manganese dioxide (600 mg.). The reagent was filtered off and washed with acetone, and the combined filtrate and washings were concentrated and monitored by thin-layer chromatography. Preparative thin-layer chromatography of the component with R_F identical with that of Fieser's compound yielded pure Fieser's compound (mixed m. p. and infrared spectrum).

Preparation of the Ether (XXI).—Fieser's compound (200 mg.) was reduced with lithium aluminium hydride (140 mg.) and the product was poured into sulphuric acid (50 ml.; 20%). The aqueous layer was separated, extracted with ether, and the extracts were washed, dried, and evaporated. The *ether* (XXI) (120 mg.) crystallised from ethanol as needles, m. p. 216·5° (decomp.) (Found: C, 82·85; H, 5·45. $C_{20}H_{16}O_2$ requires C, 83·3; H, 5·6%), $\nu_{max.}$ 1610w, 1595 cm.$^{-1}$ (aryl); τ ($CDCl_3$) 6·21 (singlet, 1-OMe), 6·38 (double doublet, J_1 = 18 c./sec., J_2 = 5 c./sec.) 5·97 (double doublet, J_1 = 18 c./sec., J_3 = 2 c./sec.), 4·29 (double doublet, J_2 = 5 c./sec., J_3 = 2 c./sec.) (AMX pattern, $ArCH(O){\cdot}CH_2Ar'$), 3·71 (singlet, 7-H), 3·16—2·29 (complex, 9 aryl protons). The cyclic ether (XXI), identical with the above specimen, was also prepared by boiling the diol (XX) (20 mg.) in methanol (5 ml.) containing concentrated sulphuric acid (1 drop).

Action of Lithium Aluminium Hydride and Aluminium Trichloride on Fieser's Compound.—A slurry of Fieser's compound (1 g.) in dry tetrahydrofuran (25 ml.) was added to a slurry of aluminium trichloride (3·08 g.) and lithium aluminium hydride (440 mg.) in dry tetrahydrofuran. The mixture was refluxed for 30 min., excess of reagent destroyed with ethyl acetate, and the mixture poured into water. The aqueous layer was separated off and extracted with ether, and the combined organic layers were dried and evaporated. The solid product (160 mg.) crystallised from ethanol as needles, m. p. and mixed m. p. 216°, and infrared spectrum identical with that of the cyclic ether (XXI).

7,12-*Dihydro*-7,12-*dihydroxy*-1-*methoxypleiadene* (XXII; R = OH).—A slurry of lithium aluminium hydride (200 mg.) in anhydrous ether (50 ml.) was added to 7,12-dihydro-1-methoxypleiadene-7,12-dione (I; R = OMe, R′ = H) (500 mg.) in dry benzene (50 ml.) and the mixture was refluxed for 2 hr. The excess of reagent was destroyed with ethyl acetate and the mixture was poured into water and worked up with ether. From ethyl acetate, 7,12-*dihydro*-7,12-*dihydroxy*-1-*methoxypleiadene* (216 mg.) had m. p. 182° (decomp.) (Found: C, 77·65; H, 5·25. $C_{19}H_{16}O_3$ requires C, 78·0; H, 5·45%), $\nu_{max.}$ (Nujol mull) 3500 (O–H), 1616w, 1595w cm.$^{-1}$ (aryl).

7,12-*Dihydro*-1,7,12-*trimethoxypleiadene* (XXII; R = OMe).—7,12-Dihydro-7,12-dihydroxy-1-methoxypleiadene (80 mg.) was dissolved in methanol (10 ml.) and concentrated sulphuric acid (2 drops) was added. The solution was brought to the boil, poured into water, and extracted with ether. The organic layer was washed with water, dried, and evaporated to give 7,12-*dihydro*-1,7,12-*trimethoxypleiadene* (32 mg.), m. p. 157—158° from methanol (Found: C, 78·3; H, 6·3. $C_{21}H_{20}O_3$ requires C, 78·7; H, 6·3%), $\nu_{max.}$ (Nujol mull) 1619w, 1604w cm.$^{-1}$ (aryl); τ ($CDCl_3$) 6·58 (singlet, OMe), 6·33 (singlet, OMe), 6·01 (singlet, OMe), 3·8 (singlet, ArCH(OR)Ar′), 3·14 (singlet, ArCH(OR)Ar′), 2·97—2·03 (complex, 9 aryl protons).

7,12-*Dihydro*-1-*methoxypleiadene* (XXII; R = H).—7,12-Dihydro-1-methoxypleiadene-7,12-dione (500 mg.) in dry benzene (50 ml.) was refluxed for 2 hr. with a slurry of lithium aluminium hydride (254 mg.) and aluminium trichloride (1·78 g.) in anhydrous ether (50 ml.), and then the mixture was poured into 20% sulphuric acid (80 ml.). The aqueous layer was extracted with ether to give 7,12-*dihydro*-1-*methoxypleiadene* (41 mg.), m. p. 163·5—164° from ethanol (Found: C, 87·2; H, 6·3. $C_{19}H_{16}O_6$ requires C, 87·65; H, 6·2%), $\nu_{max.}$ (Nujol mull) 1616w, 1600w cm.$^{-1}$ (aryl); τ ($CDCl_3$) 6·10 (singlet, OMe), 5·56 (broad band, methylene), 5·40 (singlet, methylene), 2·99—2·34 (complex, 9 aryl protons).

7,12-Dihydro-1,6-dihydroxypleiadene-7,12-dione (I; R = R′ = OH was prepared by the method of Rieche *et al.*[12]. The crude product was heated on a steam-bath with dilute hydrochloric acid for 16 hr., filtered off, washed with hot water, and then digested with a saturated solution of sodium hydrogen carbonate. The product was collected, washed with cold water, and dried at 100°. Chromatography of a solution in chloroform on acid alumina [Spence Type " H " (400 g.), treated with acetic acid (20 ml.; 10%)] yielded yellow needles of 7,12-dihydro-1,6-dihydroxypleiadene-7,12-dione, m. p. 264·5—265·5° from benzene (lit.,[12] 267°). The dimethyl ether (I; R = R′ = OMe) was best prepared by adding dimethyl sulphate (5 ml.) to a hot solution of 7,12-dihydro-1,6-dihydroxypleiadene-7,12-dione (700 mg.) in 4N-potassium hydroxide solution (50 ml.). Yellow 7,12-*dihydro*-1,6-*dimethoxypleiadene*-7,12-*dione* (400 mg.) had m. p. 254—255° from ethanol (Found: C, 75·35; H, 4·55. $C_{20}H_{14}O_4$ requires C, 75·45; H, 4·45%), τ ($CDCl_3$) 5·96 (singlet, 1- and 6-OMe), 2·72, 2·05 (AB quartet J = 9 c./sec., 2-, 3-, 4-, and 5-H), 2·41 (singlet, 8-, 9-, 10-, and 11-H).

Action of Diazomethane on 7,12-*Dihydro*-1,6-*dihydroxypleiadene*-7,12-*dione*.—The dione was treated with ethereal diazomethane, using the method described for the preparation of Fieser's compound. The ring expansion *product* (XXVI) (160 mg.) crystallised from ethanol as pale yellow needles, m. p. 213—215° (Found: C, 76·15; H, 5·0%; *M*, 336. $C_{21}H_{16}O_4$ requires C, 75·9; H, 4·85%; *M*, 332), $\lambda_{max.}$ 239 (61,100), 356 (5451), 386 mμ (4323); $\nu_{max.}$ (Nujol mull) 1679 cm.$^{-1}$ (C=O); τ ($CDCl_3$) 6·01 (singlet, OMe), 5·99 (singlet, OMe), 5·59, 5·275 (AB quartet, J = 14·5 c./sec., 13-methylene), 2·93—1·87 (complex, 8 aryl protons).

7,12-Dihydro-1-hydroxypleiaden-7-one (XXIX; R = OH, R′ = H) prepared by Fieser's method, crystallised from aqueous ethanol as yellow needles, m. p. 228·5—230·5° (lit.,[8] 232°), which gave no colour with ethanolic ferric chloride, τ (acetone) 5·60 (singlet, 12-methylene), 2·77—1·85 (complex, 8 aryl protons), 1·72 (double doublet, J_o = 7·0 c./sec., J_m = 1·75 c./sec., 6-H), 0·90 (singlet, 1-OH). Treatment of a solution of 7,12-dihydro-1-hydroxypleiaden-7-one in tetrachloroethane with excess of ethereal diazomethane, and crystallisation of the product from ethanol, yielded yellow needles, m. p. 156°, shown to be 7,12-dihydro-1-methoxypleiaden-7-one (XXIX; R = OMe, R′ = H), by mixed m. p. and infrared spectrum.

7,12-Dihydro-1-methoxypleiaden-7-one crystallised from ethanol as golden yellow needles, m. p. 157—159° (lit.,[8] 160°), τ ($CDCl_3$) 5·99 (singlet, 1-OMe), 5·63 (singlet, 12-methylene), 2·90—1·93 (complex, 8 aryl protons), 1·64 (double doublet, J_o = 7·5 c./sec., J_m = 1·8 c./sec., 6-H).

7,12-Dihydro-1,6-dihydroxypleiaden-7-one (XXIX; R = R′ = OH) crystallised from benzene as yellow needles, m. p. 229—230° (lit.,[13] 233°), τ (acetone) 5·82 (broad band 12-methylene), 3·09—1·96 (complex, 8 aryl protons, plus 1-OH), −5·17 (singlet, 6-OH).

7,12-*Dihydro*-6-*hydroxy*-1-*methoxypleiaden*-7-*one* (XXIX; R = OMe, R′ = OH).—A solution of 7,12-dihydro-1,6-dihydroxypleiaden-7-one (1 g.) in tetrachloroethane (30 ml.) was treated with ethereal diazomethane (110 ml.; from 11 g. of nitrosomethylurea) and set aside overnight. The ether was distilled off at reduced pressure and the tetrachloroethane was removed by steam-distillation. The residue crystallised from ethanol to give 7,12-*dihydro*-6-*hydroxy*-1-*methoxypleiaden*-7-*one* as yellow needles (255 mg.), m. p. 181—182°, which gave a dark brown colour with ethanolic ferric chloride (Found: C, 78·5; H, 5·05. $C_{19}H_{14}O_3$ requires C, 78·6; H, 4·85%), τ ($CDCl_3$) 6·06 (singlet, 1-OMe), 5·92 (broad band, 12-methylene), 3·08—2·15

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[12] A. Rieche, H. Sauthoff, and O. Müller, *Ber.*, 1932, **65**, *B*, 1371.

[13] L. F. Fieser, *J. Amer. Chem. Soc.*, 1933, **55**, 4977.

(complex, 8 aryl protons), —5·4 (singlet, 6-OH). A solution of 7,12-dihydro-6-hydroxy-1-methoxypleiaden-7-one (255 mg.) in tetrachloroethane (10 ml.) slowly reacted with ethereal diazomethane (10 ml.; from 1 g. of nitrosomethylurea) in the presence of lithium chloride (5 mg.) in methanol (1 ml.). The solution was kept overnight at 20° and was then evaporated. Chromatography of the residue (A III) and elution with benzene gave 7,12-dihydro-1,6-dimethoxypleiaden-7-one (XXIX; R = R′ = OMe). Continued elution with 1 : 1 (v/v) benzene–chloroform gave starting material and no ring-expanded product was detected.

7,12-Dihydro-1,6-dimethoxypleiaden-7-one (XXIX; R = R′ = OMe) crystallised from ethanol, m. p. 202°, as pale yellow needles, (lit.,[13] 201°), τ ($CDCl_3$) 6·01 (singlet, OMe), 5·98 (singlet, OMe), 5·66 (singlet, 12-methylene), 2·92—2·08 (complex, 8 aryl protons).

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