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PHOTOCYCLISATION OF AN AROYLCYCLOHEXENE

THE SYNTHESIS OF *CIS*-1,2,3,4,4*a*,9*a*-HEXAHYDRO-1-METHYL-6-METHOXY-9-OXOFLUORENE-1-CARBOXYLIC ACID[1]

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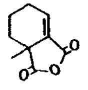
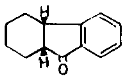
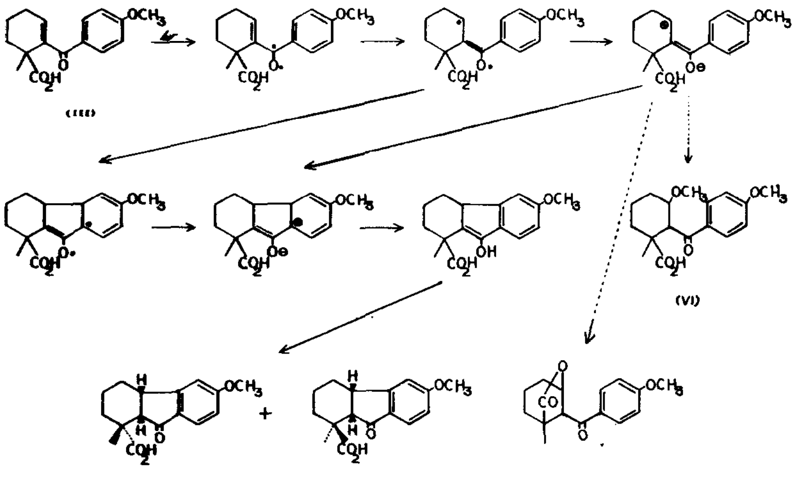
The *cis*-1,2,3,4,4*a*,9*a*-Hexahydro-1-methyl-6-methoxy-9-oxofluorene-1-carboxylic acids (I) and (II), potential intermediates in the synthesis of gibberellins have been prepared in high yield by a novel photocyclisation. The photolysis (500 watt Hanovia medium pressure lamp with Pyrex filter) of the anisoylcyclohexene (III), prepared from the Friedel-Crafts reaction between 1-methyl-2-cyclohexene-1,2-dicarboxylic anhydride (IV)[2] and anisole [82% yield; colourless crystals (ex EtOAc); m.p. 154-5°; ν_{max}(KCl disc), 1710, 1640, 1600, 1575, 1505, 840, 810 cm^{-1}; λ_{max}(EtOH), 287 (ϵ 4,600), 280 (ϵ 5,300), 270 (ϵ 6,100), 246 (ϵ 3,900), 218 (ϵ 1,800) mμ] gave a mixture of (I) and (II) in nearly quantitative yield. The epimer (I) was obtained from the crude mixture by crystallisation from ethyl acetate [50% yield; colourless crystals; m.p. 222-223.5°; ν_{max}(KCl disc), 1700, 1600, 1500, 870, 830 cm^{-1}; λ_{max}(EtOH), 292 (ϵ 4,800), 287 (ϵ 4,800), 267 (ϵ 7,200), 222 (ϵ 7,700) mμ; nmr of methyl ester ($CDCl_3$), τ2.37, 3.15, 3.15 [$AA'X$ system, H(8), H(5), H(7), respectively], τ6.10 (OMe), τ6.22 (OMe), τ6.66 [H(4*a*), double triplet $\underline{J}_{4\underline{a},9\underline{a}} = 6.4$; $\underline{J}_{4\underline{a},3(\underline{a})} \geq 11.5$; $\underline{J}_{4\underline{a},3(\underline{e})} \leq 5.8$ Hz;] τ6.99 [H(9a), doublet, $\underline{J} = 6.4$ Hz], τ7.8 - 8.5 (6H, complex multiplet), τ8.53 (1-Me, singlet). Although the second isomer (II) could not be obtained in a pure form its only contaminant appeared to be (I) and its nmr



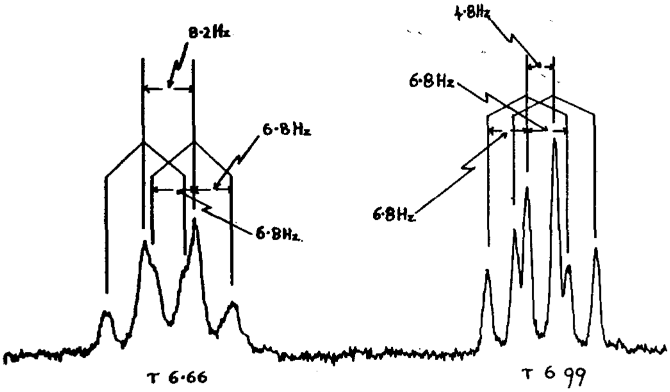
(IV)



(V)



(III) (VI) (I) (II) (VII)



spectrum could be inferred from that of the mixture. In this isomer both H(9a) and H(4a) absorb near τ6.6 and the C-Me at τ8.37. Apart from these differences, the spectra are very similar indicating that (I) and (II) have the same gross structure [the mass spectra of (I) and the mixture are virtually identical].

In both epimers, the 9a-proton undergoes base catalysed exchange in D_2O without isomerization proving that both have the thermodynamically more stable stereochemistry for the A/B ring junction. This is assigned as cis by analogy with cis-1,2,3,4,4a,9a-hexahydrofluorenone (V) for which the stereochemistry has been firmly established and which also is the more stable isomer.[3] We have examined the nmr spectrum of (V) and the absorptions of the 4a- and 9a- protons are shown in the Figure. $J_{4a,9a}$ is seen to be 6.8 Hz. The assignment of configuration at C(1) rests on less secure evidence. The presence of two substituents at C(1) ensures that ring A adopts a quasi-chair conformation. Models then indicate that the 1-methyl group in (II) lies in the plane of the 9-carbonyl group and in close proximity to the oxygen atom. It should therefore be abnormally deshielded.[4] Similarly, the axial carbomethoxy group of this epimer will most probably adopt the conformation in which the 9a-proton bears a similar relation to the ester carbonyl group and will therefore be deshielded with respect to the analogous proton in (I). Thus the stereochemistry of (I) is assigned to the acid, m.p. 222-223.5°, in which both the 1-methyl and 9a-proton absorb at higher fields.

Photocyclisation of an aryl enone, such as (III) has not been previously reported. Chalcones[5] and β-benzoylacrylic acid[6] undergo cis - trans isomerization and photodimerization, and the latter suffers the addition of methanol when photolysed in that solvent.[7] β-Benzoyl-α-methacrylic acid also undergoes cis - trans isomerization as well as rearranging to the β,γ-isomer. Evidently, the two geminal substituents in (III) inhibit dimerization and, possibly orient the aromatic ring such that ring closure by radical attack or, after electron demotion, electrophilic attack occurs in preference to completing reactions. If electron demotion occurs prior to cyclisation, the ether (VI) or even the lactone (VII)[8] might have formed but their presence in the crude reaction mixture could not be detected.

This cyclisation is, of course, formally analogous to the well documented photocyclisations of cross conjugated cyclohexadienones.[9]

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†† All new compounds reported here gave satisfactory analyses.

1. This work constitutes a portion of the Ph.D. Thesis of HCY.
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