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ACID-CATALYSED REACTION OF 1-(2,5-DIKETO-1-METHYLCYCLOPENTYL)-3-(4-METHOXYPHENYL)-5-METHYLHEXA-2,4-DIENE. STRUCTURE OF A NOVEL PRODUCT.

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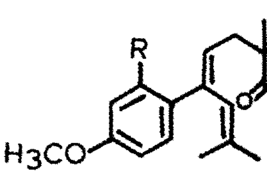
We have described[1] the novel acid-catalysed (CH_2Cl_2-H_2SO_4) cyclisation of the intermediate (Ia) to the B-norsteroid derivative (IIa). We now report the unusual reaction of the intermediate (Ib), under similar conditions.

Grignard reaction of 4-methoxyphenyl- Δ^4-isovalerophenone with vinylmagnesium bromide followed by condensation with 2-methylcyclopentane-1,3-dione afforded the seco-dione (IIb)[2,3] (M^+ 312), NMR(CCl_4): δ 0.96, 1.06 (3H,CH_3), 1.33-1.9 [6H,HC=C-($C\underline{H}_3)_2$], 3.73 (3H,ar-OCH_3), 5.2-5.8 (2H,HC=C<) and 6.5-7.2 (4H,ar-H). The seco-dione (Ib) on treatment with conc.H_2SO_4 in CH_2Cl_2 at 0° followed by intensive purification of the crude product gave three compounds, A, B and C. Compound A[4] (5%) (M^+ 200), m.p. 136°, IR(nujol): 1615 and 1585 cm^{-1}, UV: $\lambda_{max.}$ 274 nm (ε 11,000), NMR($CDCl_3$): δ 1.4 [d,J=1.5 Hz,3H,HC=C-$C\underline{H}_3$], 2.0-2.14 (m,2H), 2.44 (s,2H), 3.82 (3H, ar-OCH_3), 5.94, 6.1 (2H,HC=C<) and 6.8,7.38 (2d,J=9 Hz,4H,ar-H), was assigned the structure (III). Compound B (10%) was the expected pentaenone (IIb) (M^+ 296), m.p. 142°, NMR(CCl_4): 1.1 (3H,CH_3), 1.32,1.38 (6H, <u>gem</u> dimethyl), 3.84 (3H,ar-OCH_3), 5.82 (1H,HC=C<) and 6.66-7.14 (3H,ar-H). Compound C was an amorphous solid[5] softening at 85° (M^+ 512), IR(nujol): 3570 and 1748 cm^{-1}, UV: $\lambda_{max.}$ 267 nm (ε 10,560), NMR(CCl_4): δ 1.08 (3H,CH_3), 1.2-1.4 (4s,12H,4CH_3), 1.7-3.0 (m,∽14-15H), 3.78-3.80 (6H,ar-OCH_3), 5.86, 6.2 (2H,HC=C<) and 6.64-7.4 (∽6-7H,ar-H). The UV absorption maximum and the chemical shifts of the olefinic protons are comparable to those of (III). The $^{13}C\{^1H\}$ spectrum of compound C suggested the presence of 34 C atoms. The aforementioned spectral data could be explained on the basis of two alternate structures, (IV) and (V), with a molecular formula[6] $C_{34}H_{40}O_4$. The off-resonance decoupled ^{13}C NMR spectrum exhibited 9 singlets and 8 doublets in the region δ_C[7] 100-220 which ruled out structure (IV) for the hydroxy ketone C.

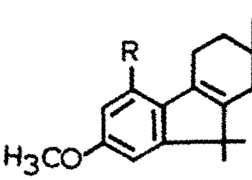
The probable mechanism of formation of (III) and (V) could be as shown in the Chart. Similar acid-catalysed elimination of the enol (VI) is documented in literature[8].

Further work on the acid-catalysed reaction of related seco-diones is in progress.

a: R = OCH_3
b: R = H



I



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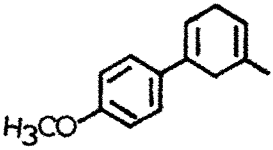
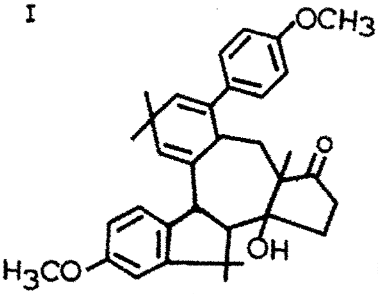
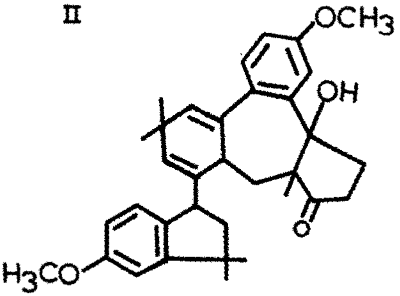


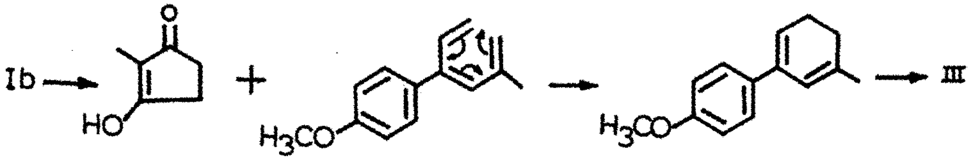
III



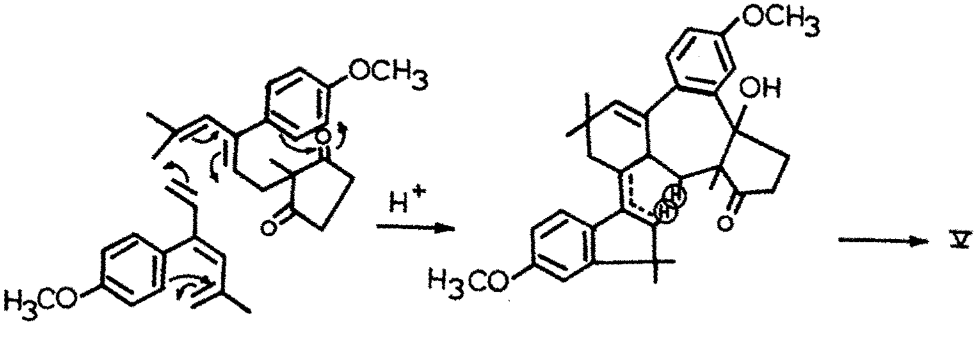
IV



V



VI VII



REFERENCES AND NOTES

1) T.R.Kasturi, E.M.Abraham and R.S.Prasad, Tetrahedron Letters, 971 (1974).
2) All new compounds gave satisfactory elemental analyses.
3) Compound (Ib) was a mixture of E and Z isomers.
4) Compound (III) was also obtained during distillation of seco-dione (Ib).
5) Compound C was chromatographically (TLC and HPLC) homogeneous.
6) Elemental analysis indicated molecular formula $C_{34}H_{40}O_4 \cdot 2H_2O$.
7) δ_C ppm from TMS.
8) J.S.Baran, D.D.Langford, I.Laos and C.D.Liang, Tetrahedron, <u>33</u>, 609 (1977).

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