

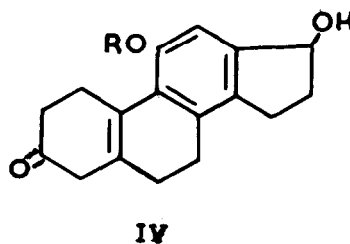
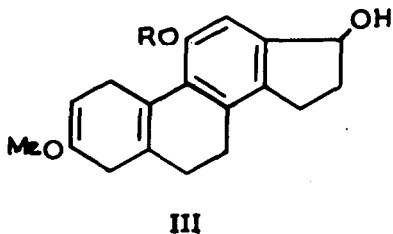
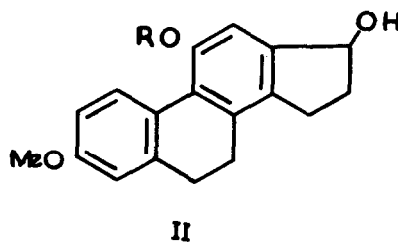
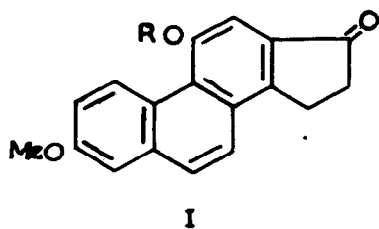
A RING-C-AROMATIC BISNORSTEROID

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The readily synthesised¹ cyclopentenophenanthrenes (I; R = Me, H) with a steroid-type oxygenation pattern do not appear to have been converted into reduced derivatives. Metal-ammonia reductions would be expected to convert the 17-carbonyl into 17-OH and to reduce initially the 6,7-double bond. The resulting system (II; R = Me) from (I; R = Me) then contains a benzyl alcohol structure and a *p*-methoxydiphenyl structure and both the 3- and 17-oxygens in these should be largely lost on further reduction.² However, using (I; R = H) formation of the phenoxide anion should prevent hydrogenolysis of the benzyl alcohol and should alter the behaviour of the ring-AC system from a diphenyl to that of one in which ring-A carries only electron-repelling substituents.³ The product expected would be (III; R = H) in which the 5(10)-double bond might also be protected from reduction by the phenoxide charge.



Reduction of (I; R = H) with excess of lithium and tert. -butanol in liquid ammonia, followed by mild acid hydrolysis gave (IV; R = H) as the chief product, m. p. 210°, λ_{max} . 279 and 285 m μ (ϵ 10,200 and 9850); ν_{max} . 3300, 1700, and 1610 cm.⁻¹, m/e 284. Diazomethane gave (IV; R = Me), m. p. 148-150°, λ_{max} . 280 and 285 m μ (ϵ 11,040 and 10,580); ν_{max} . 3300, 1710, and 1605 cm.⁻¹; τ 3.3s (1H), 6.2s (3H), and 6.8-9.0m (16H). Neither product could be isomerised to the $\alpha\beta$ -unsaturated ketone. They appear to be the first reported ring-C-aromatic compounds related to the reduced steroid hormones.

Steroid numbering has been used.

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References

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2. A. J. Birch, S. Mejer, A. J. Ryan, and G. S. R. Subba Rao, unpublished work.
3. J. F. Fried and N. A. Abraham, Tet. Lett. 3505 (1965).