

## Some Novel Cyclisations through Benzophenone Carbanions

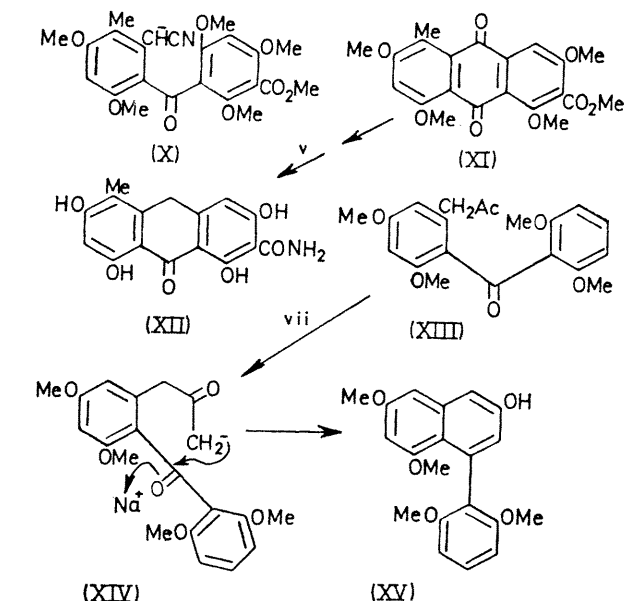
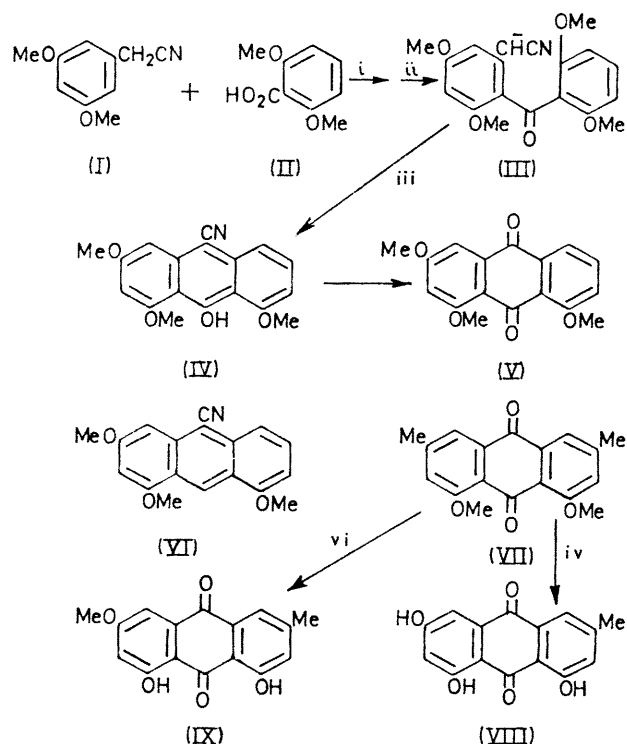
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**Summary** Anthraquinones, including emodin and physcion, and an amide related to the tetracyclines, have been synthesised in high yield through appropriately substituted 2-cyanomethyl-2'-methoxybenzophenones.

As an extension of an earlier investigation,<sup>1</sup> we have established that the anthraquinones (V), emodin (VIII), physcion (IX), and the amide (XII), which is an analogue of the pretetramids, biosynthetic precursors of tetracyclines,<sup>2</sup> may be synthesised in high yield through the related benzophenones. These benzophenones were prepared very

A similar reaction sequence gave tri-*O*-methylemodin (VII) which was converted into physcion (IX) and into emodin (VIII) by demethylation processes. The amide (XII) was prepared through the appropriate carbanion (X) by a sequence involving conversion of the anthraquinone (XI) into the corresponding amide which was demethylated with hydriodic acid in phenol. In one experiment using sodium hydride-dimethylformamide at 100° to generate the carbanion (III), rather than the sodium methoxide-dimethylformamide (or dimethyl sulphoxide) which was used for the other syntheses, the reduction product (VI) was obtained.



(i)  $(\text{CF}_3\text{CO})_2\text{O}$ . (ii)  $\text{NaOMe-HCONMe}_2$ . (iii)  $\text{NaH-HCONMe}_2$  at 100°. (iv)  $\text{C}_6\text{H}_5\text{N}_2\text{HCl}$ . (v)  $\text{HI-PhOH}$ . (vi)  $\text{HBr-HOAc}$ . (vii)  $\text{NaOMe-MeOH}$ .

readily by the action of a suitably substituted 2-methoxybenzoic acid such as (II) on 1-cyanomethyl-3,5-dimethoxybenzene (I) in the presence of trifluoroacetic anhydride. In a typical case, intramolecular elimination of the 2'-methoxy-group from the carbanion (III) gave an excellent yield of the nitrile (IV), which was converted into the corresponding anthraquinone, quantitatively, by oxidation.

When the benzophenone (XIII) was used as an alternative to the nitrilo-derivative (III), the base-catalysed ring closure took a different course. There was an excellent yield (95%) of the naphthalene derivative (XV) [ $^1\text{H}$  n.m.r. signals:  $\tau$  2.82 (tr), 3.24 (d), 3.44 (d), 3.53 (d), 3.82 (d), 3.41 (observed) all integrating for 7H; 6.22 (s, 3H), 6.42 (s, 6H), 6.65 (s, 3H); 5.0 (br band, OH)]. Evidently, in this case, the alternative carbanion (XIV) was an intermediate.

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<sup>1</sup> J. S. Davies, V. H. Davies, and C. H. Hassall, *J. Chem. Soc. (C)*, 1969, 1873.

<sup>2</sup> J. R. D. McCormick in "Biogenesis of Antibiotic Substances," Czechoslovak Academy of Sciences, Prague, 1965, p. 73.