

A SERENDIPITOUS ROUTE TO THE BENZIDENE NUCLEUS.  
STRUCTURAL ELUCIDATION BY NOEDS.

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and

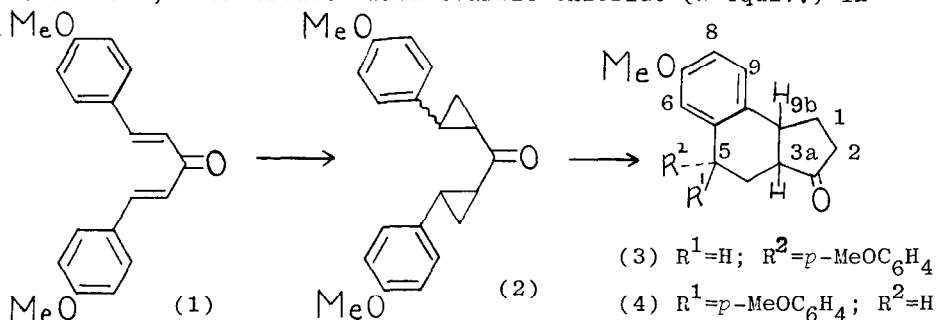
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The epimeric indenones (3) and (4) are readily synthesised and rapidly formed by treating bis(*p*-methoxyphenylcyclopropyl) ketone (2) with stannic chloride in nitromethane. The structure of (3) was determined by X-ray crystallography and that of (4) by NOEDS.

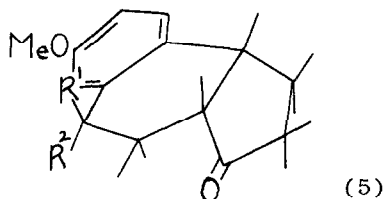
Following on our discovery of the acid catalysed rearrangement of aryl cyclopropyl ketones to aryl tetralones,<sup>1</sup> we have initiated a similar investigation of bis(arylcyclopropyl) ketones.

Ketone (2) was readily synthesised as a mixture of diastereomers by the reaction of (1) with dimethylsulphoxonium methylide.<sup>2</sup> Deepseated rearrangement of ketone (2)<sup>3</sup> to benzinden-3-ones (3)<sup>3</sup> and (4)<sup>3,4</sup> (1:1) (50% yield) occurred within 15 min. at 20°C, when treated with stannic chloride (1 equiv.) in nitromethane.

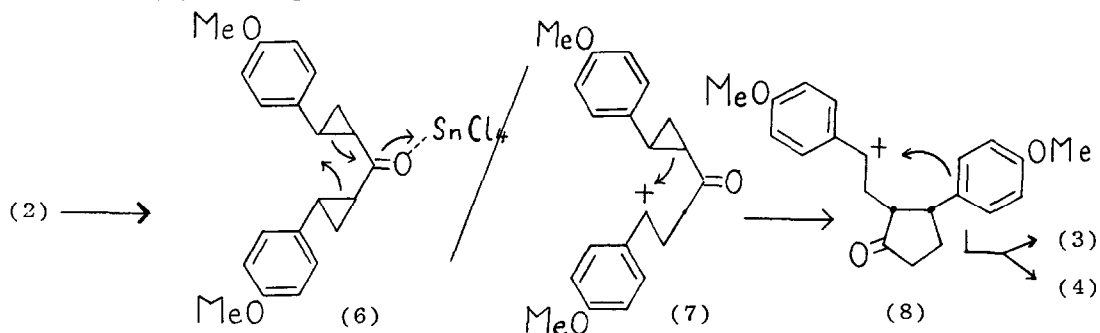


The structure of ketone (3), m.p. 141-142°C (p.t.l.c.) was indicated by its spectra  $\nu$  1735  $\text{cm}^{-1}$ ;  $M^+$  322;  $\delta_{\text{H}}$  (250 MHz)<sup>5</sup> 1.71-2.54(m 6H), 2.70(ddd, J 11.4, 7.7 and 5.1 Hz, 3a-H), 3.45(dt, J 11.4 and 7.2 Hz, 9b-H), 3.61(s, 7-3H), 3.80(s, 4'-3H), 3.91(dd, J 12.3 and 4.2 Hz, 5-H), 6.30(d, J 1.8 Hz, 6-H), 6.77(dd, J 1.8 and 8.6 Hz, 8-H), 6.97(m, 4H), and 7.18(d, J 8.6 Hz, 9-H). The assignment was confirmed by X-ray crystallography.<sup>6</sup> The structure of ketone (4), m.p. 119-122°C, was again indicated by its spectra:  $\nu$  1730  $\text{cm}^{-1}$ ;  $M^+$  322;  $\delta_{\text{H}}$  (250 MHz) 1.25-2.11 (m, 7H), 3.51(q, J 7.4 Hz, 9b-H), 3.68(s, 7-3H), 3.76(s, 4'-3H), 4.08(t, J 4.9 Hz, 5-H), 6.48(d, J 2.7 Hz, 6-H), 6.82(dd, J 2.7 and J 8.7 Hz, 8-H), 6.84(m, 4H), and 7.24(d, J 8.7 Hz, 9-H). Nuclear Overhauser difference spectroscopy (NOEDS)<sup>7</sup> of (3) was undertaken.<sup>5</sup> Double

irradiation of 5-H resulted in NOE enhancement of 3a-H(8%) and double irradiation of 3a-H effected enhancement of 9b-H(14%) and 5-H(8%). Ketone (4) was similarly treated. Double irradiation of 5-H effected no enhancement of 3a-H and double irradiation of 3a-H resulted in enhancement of 9b-H(14%) and 5-H(~1%). This confirmed *cis*-fusion and the *trans*- relationship of 5-H and 3a-H. The magnitude of the coupling constants of 5-H in each epimer showed that each adopts an identical conformation (5) in solution.



We suggest a mechanism, that is related to cyclopropyl ketone pi<sup>8</sup> and related cyclisations<sup>9</sup> and involves the formation of the intermediate (8) by a concerted (6) or stepwise route (7).



#### REFERENCES

1. W.S. Murphy and S. Wattanasin, J.C.S. Perkin Trans. 1, 1982, 1029.
2. E.J. Corey and M. Chaykovsky, J. Amer. Chem. Soc., 1965 87, 1353.
3. All new compounds had satisfactory microanalysis.
4. Variable yields of as yet uncharacterised side-products were also formed.
5. Full details of decoupling and NOESY experiments will be reported elsewhere. We wish to thank Dr. L.C. Waring, Q.U.B. for the <sup>1</sup>H n.m.r. spectra.
6. G. Ferguson and M. Parvez, in preparation.
7. See for example: D.H. Williams, M.P. Williamson, D.W. Butcher and S.J. Hammond, J. Amer. Chem. Soc., 1983, 105, 1332.
8. P.A. Grieco and R.S. Finkelhor, Tetrahedron Letters 1974, 527.
9. R.L. Danheiser, J.M. Morin, M. Yu, and A. Basak, Tetrahedron Letters, 1981, 4205 and refs. therein; G. Stork and P.A. Grieco, J. Amer. Chem. Soc., 1960, 91, 2407.

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