An Unusual Photochemical Rearrangement of a Ketone

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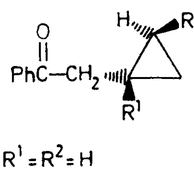
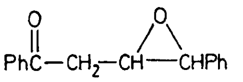
Summary Ultraviolet irradiation of a benzene solution of *trans*-1-phenyl-2-phenacylcyclopropane caused equilibration with the *cis*-isomer, and cyclization to 4-phenyl-3,4-methano-1-tetralone.

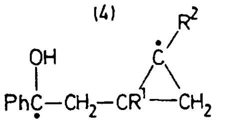
Recently we had prepared the cyclopropylcarbinyl phenyl ketones (**1**)—(**3**) in connection with another investigation, and it seemed of interest to examine their behaviour under u.v. irradiation. Analogy with earlier work on the *trans*-epoxide (**4**)[1] suggested that type II fragmentation in (**1**)—(**3**) (which would give highly strained cyclopropenes) would be inefficient, and that closure of the type II biradicals (**5**) might therefore afford bicyclopentanol derivatives (**6**).



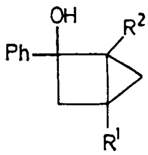
(1); R^1 = R^2 = H
(2); R^1 = Ph; R^2 = H
(3); R^1 = H; R^2 = Ph



(4)



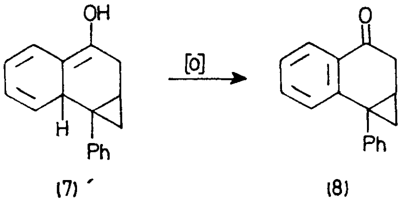
(5)



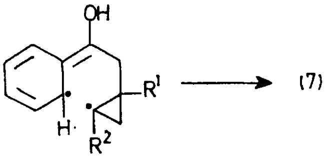
(6)

Prolonged irradiation of (**1**) and (**2**) in benzene† gave no detectable chemical change. However, under comparable conditions compound (**3**)‡§ was equilibrated with its *cis*-isomer,§ and further irradiation led to the appearance of a third compound (itself photolabile), identified as the benzobicycloheptenone (**8**).§ There was no detectable formation either of acetophenone (<*ca.* 1%) or of products identifiable as the expected bicyclopentanols.

Although normal type II photoreactions[2] were therefore not observed, the most straightforward rationalisation of the formation of both (**8**) and the *cis*-isomer of (**3**) would be in terms of the biradical (**5**; R^1 = H, R^2 = Ph) which could revert to (**3**) (or to its *cis*-isomer), or could cyclise to (**7**) which may then be oxidised (by ketone triplets or adventitious oxygen?) to (**8**). Consistent with this is the predominance of the *cis*-isomer in the pseudo-photostationary state, since in the *cis*-isomer the γ-hydrogen is less accessible to carbonyl oxygen than it is in (**3**). On the other hand, that the γ-hydrogen is accessible at all in the *cis*-isomer seems surprising, and the possibility of alternative epimerisation mechanisms involving electronic or vibrational[3] excitation of the phenylcyclopropane grouping cannot yet be excluded. Even more surprising is that apparently the only alternative route available for the decay of the intermediate biradical should involve cyclisation to a six-membered rather than to a four-membered ring. Six-membered ring formation has been encountered in type II photoreactions when there is δ,ε-unsaturation,[2,4] but in the extensive literature on photochemistry of alkyl aryl ketones we have been unable to find any precedent for cyclisation on to the benzene ring, although it is a mechanistically reasonable result (*cf.* **5a**). It is not clear why this particular type II biradical should collapse preferentially by this route, particularly in view of epoxycyclobutanol formation on irradiation of (**4**).[1]



(7)′ (8)



(5a) (R^1 = H; R^2 = Ph)

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† Irradiations were carried out using a medium pressure mercury arc, with a water-cooled Pyrex jacket, immersed in the benzene solutions (at *ca.* 20 °C) which were continuously purged with nitrogen.

‡ Prepared by homologation of *trans*-2-phenylcyclopropanecarboxylic acid and reaction of the acid chloride with diphenylcadmium (m.p. 75—76 °C).

§ New compounds had spectroscopic and analytical or accurate mass data in accord with the assigned structures. The n.m.r. spectrum of (**6**) (m.p. 79—81 °C) was of particular interest; a key feature was the single high-field aromatic proton (δ 6·81) adjacent to the phenyl substituent, but the α-methylene protons at δ 2·97 were almost isochronous as were the bridgehead and the *exo*-cyclopropane protons at δ 1·86. Full analysis of the aliphatic region was possible following decoupling experiments at 220 MHz, and comparison of the spectra obtained with the spectrum of unsubstituted benzobicyclo[4.1.0]hept-2-en-3-one where these coincidences are absent.

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[2] P. J. Wagner, *Accounts Chem. Res.*, 1971, **4**, 168.
[3] T. R. Darling, N. J. Turro, R. H. Hirsch, and F. D. Lewis, *J. Amer. Chem. Soc.*, 1974, **96**, 434.
[4] K. H. Schulte-Elte and G. Ohloff, *Tetrahedron Letters*, 1964, 1143; N. C. Yang, A. Morduchowitz, and D. H. Yang, *J. Amer. Chem. Soc.*, 1966, **88**, 1245.