The Photoisomerization of 2-Cyclopropyl-1-phenylethylene

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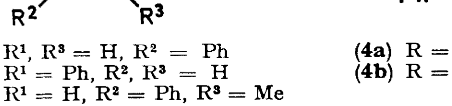
Summary The photoisomerizations of several vinylcyclopropanes to cyclopentenes have been described and their photochemical reactivity roughly correlated with their ground state conformations.

THE photochemical reactions of vinylcyclopropanes have been the subject of several recent investigations[1] but these studies have mostly involved compounds in which the vinylcyclopropane moiety is constrained as part of a bicyclic system. Of the few examples of monocyclic vinylcyclopropanes studied[2–4] only one of these, β-cyclopropylacrylic acid,[2] affords cyclopentenes and these results have been interpreted on the basis of the ground state conformations of the vinylcyclopropane moiety. We describe our results on a relatively simple and conformationally mobile model, the 2-cyclopropyl-1-phenylethylene (**1**) system.



(**1a**) R^1, R^3 = H, R^2 = Ph
(**1b**) R^1 = Ph, R^2, R^3 = H
(**2a**) R^1 = H, R^2 = Ph, R^3 = Me
(**2b**) R^1 = Ph, R^2 = H, R^3 = Me
(**3a**) R^1 = Pr^i, R^2 = Ph, R^3 = H
(**3b**) R^1 = Ph, R^2 = Pr^i, R^3 = H

(**4a**) R = H
(**4b**) R = Me

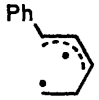
Irradiation of either (**1a**) or (**1b**) in hexane proceeded with the initial formation of the other isomer. Prolonged irradiation resulted in the formation of a single additional monomeric product in 40% yield (estimated by g.l.p.c.). The product was identified as 3-phenylcyclopentene (**4a**) on the basis of the following spectral data: ν_{max} (neat) 3054, 754, and 696 cm^{-1}; τ (CCl_4) 2·87 (5H, aromatic), 4·20 (m, 2H, vinyl), 6·18 (m, 1H, benzylic), and 7·48—8·65 (m) 4H, methylene). In addition hydrogenation of (**4a**, (Pt/C–HOAc) afforded phenylcyclopentane.

Similarly irradiation of a mixture of (**2a**) and (**2b**) proceeded with the generation of a single new monomeric product, 2-methyl-3-phenylcyclopentene (**4b**), in 31% yield The structure of (**4b**) follows from its spectral properties ν_{max} (neat) 3020, 750, and 695 cm^{-1}, τ (CCl_4) 2·85 (5H, aromatic), 4·49 (br s, 1H, vinyl) 6·43 (br m, 1H, benzylic), 7·31—8 40 (m, 4H, methylene), and 8 47 (d, 3H, methyl, J 1·0Hz)

In contrast with the preceding results, prolonged irradiation of either (**3a**) or (**3b**) resulted only in the formation of the other isomer and the slow disappearance (polymerization) of starting material

The conformations of vinylcyclopropanes have usually been analysed[5] on the basis of an *s-trans* (θ = 180°)† and a pair of gauche (θ = 60°) conformers The recently determined vicinal coupling constants, J (3′,4′) for these two conformations in vinylcyclopropane[6] allows the calculation‡ of % *s-trans* conformer and gives values of 75% for (**1a**) and 85% for (**1b**), (**3a**), and (**3b**) Franck–Condon excitation should generate the excited states (**5**) or (**6**) as a function of the populations of these ground state conformations Presumably[2] only (**6**) (from the gauche conformer) can lead to cyclopentenes Obviously there is little correlation between the n m r and photochemical results


(5)


(6)


(7)

The u v spectra of (**1a**) and (**1b**) suggest that these data from simple vinylcyclopropanes do not accurately reflect the situation in more complex molecules There is a distinct hypsochromic shift in going from (**1a**) [λ_{max} 261 nm (ϵ 19,000)] to (**1b**) [λ_{max} 250 nm (ϵ 13,700)] That this is not due to a "preferred" orientation of the cyclopropane ring is apparent from the spectra of *cis-* and *trans*-3-methyl-1-phenylbut-1-ene which show maxima at 250 nm (ϵ 20,000) and 241 nm (ϵ 12,600) respectively We ascribe this shift to the benzene ring twisting out of co-planarity[7,8] with the double bond

Since the electronic demands for coplanarity are more stringent for the benzene ring than are the orientational requirements[9] for a cyclopropane ring, it is probable that the latter also assumes an orientation which minimizes unfavourable steric interactions § Models indicate that there should be a pair of *s*-transoid (θ = 160°) conformations[2] which are of minimum energy Application of the Karplus equation [for θ = 160° and J (3,4) 10·6 Hz[6] at θ = 180°] gives values of *ca* 100% for the population of these *s*-transoid conformations for (**1b**), (**3a**), and (**3b**), entirely consistent with the photochemical results

It has been reported[3] that irradiation of a 2-phenylvinylcyclopropane leads to the formation of bicyclo[2,1,0]-pentanes but no cyclopentenes, and it was suggested that this might be due to the generation of diradical (**7**) with exclusive transoid geometry The absence of bicyclic products from the present work suggests that, although geometry is of importance (*vide supra*), there must be additional factors (*i e* electronic) which influence the partition to bicyclo[2,1,0]pentanes and cyclopentenes

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† Where θ is the dihedral angle between 3-H and 4-H

‡ The coupling constants (apparent) are 8 5, 9 5, 9 4, and 9 5 Hz for (**1a**), (**1b**), (**3a**), and (**3b**) respectively

§ The preferred orientation of the cyclopropane ring for electronic interaction is the *s-trans* (θ = 180°) arrangement

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