Carbene Photocycloelimination from a Vinyl-cyclopropane[1]

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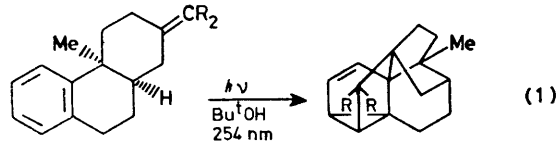
Summary A novel photochemical fragmentation of a vinyl-cyclopropane to give a carbene derived product is reported.

THERE have been surprisingly few reports on the photochemistry of the simple vinyl-cyclopropane chromophore; these reactions apparently take place *via* homolytic fission

of one of the cyclopropane bonds.[2] During the course of another study, we prepared a rigid vinyl-cyclopropane for which such homolytic fission should be unproductive and find that this molecule undergoes a new, ready photochemical extrusion *via* a carbene intermediate.[3]

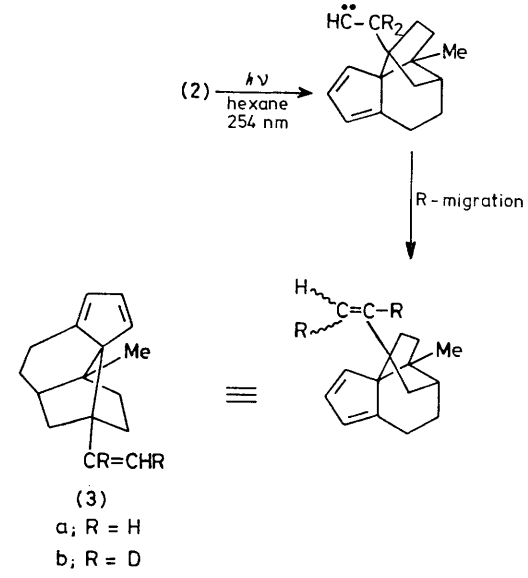


(1) (2) (1)

a; R = H
b; R = D

Photolysis of the tricyclic aryl-olefin (**1a,b**) leads to single primary photoproducts (**2a,b**) *via* an intramolecular 1,3-cycloaddition analogous to that observed for 6-phenylhex-2-ene[4] [equation (1)]. Compound (**2a**) takes up 2 equiv. of hydrogen to give a tetrahydro-derivative, yet shows only two vinyl carbons at δ 128·68 (d) and 130·39 (d) in its ^{13}C n.m.r. spectrum. The ^{1}H n.m.r. spectrum in $CDCl_3$ shows signals at δ 5·80—5·65 (1H, dd, *J* 2·0 and 5·5 Hz, olefinic H), 5·60—5·45 (1H, d, *J* 5·5 Hz, olefinic H), and 2·3—0·8 (16H, complex m, which includes a singlet at δ 0·98). Pyrolysis of (**2a**) induces the 1,5-hydrogen shift characteristic of such vinyl-cyclopropanes.[4]

Photolysis of (**2a**) results in a single product (**3a**). The structure of (**3a**) derives from its 1H n.m.r. and u.v. spectra. The cyclopentadiene resonances (δ 6·35, 6·09, and 5·98) and coupling constants (5·6, 2·0, and 1·4 Hz) match quite well with those of 1-methylcyclopentadiene (δ 6·25, 6·07, and 6·00; 5·4, 1·9, and 1·4 Hz).[5] The u.v. transition [λ_{max} (hexane) 264 nm, ϵ 2520] is likewise consistent with a cyclopentadiene chromophore.[6] The vinyl group appears as an ABX pattern: δ 5·8—5·4 (1H, q, J_{AX} 18, J_{BX} 9 Hz) and 5·0—4·6 (2H, J_{AB} 2 Hz). The remaining signals are at δ 2·6—2·4 (2H, t), 2·3—1·4 (9H, m), and 0·67 (3H, s). Photolysis of (**2b**) gives (**3b**). The product clearly results from a carbene cycloelimination followed by a 1,2-hydrogen shift (Scheme).



(3)
a; R = H
b; R = D

SCHEME

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[1] For previous paper in the series 'Organic Photochemistry,' see D. D. Neidigk and H. Morrison, *J.C.S. Chem. Comm.*, in the press.

[2] P. J. Kropp, *J. Amer. Chem. Soc.*, 1967, **89**, 1126.

[3] Carbene formation from photolysis of aryl-cyclopropanes is well documented (G. W. Griffin, *Angew. Chem. Internat. Edn.*, 1972, **10**, 537). There is a possibility of such a reaction for a vinyl-cyclopropane having a conjugated ester (M. J. Jorgensen and C. H. Heathcock, *J. Amer. Chem. Soc.*, 1965, **87**, 5264), and an example involving a conjugated diene has recently been reported (R. G. Weiss and G. S. Hammond, *ibid.*, 1978, **100**, 1172).

[4] W. Ferree, Jr., J. Grutzner, and H. Morrison, *J. Amer. Chem. Soc.*, 1971, **93**, 5502.

[5] V. A. Korenevsky and N. M. Sergeyev, *J. Amer. Chem. Soc.*, 1972, **94**, 8586.

[6] *E.g.*, a 1,1,2-trialkylcyclopentadiene is reported to have λ_{max} (MeOH) 256 nm (ϵ 3850): L. L. Barber, O. L. Chapman, and J. D. Lassila, *J. Amer. Chem. Soc.*, 1969, **91**, 3664.