Stereochemistry of 2 + 2 Photoaddition of Cyclopentene to Hexafluorobenzene

By Boris Šket and Marko Zupan*

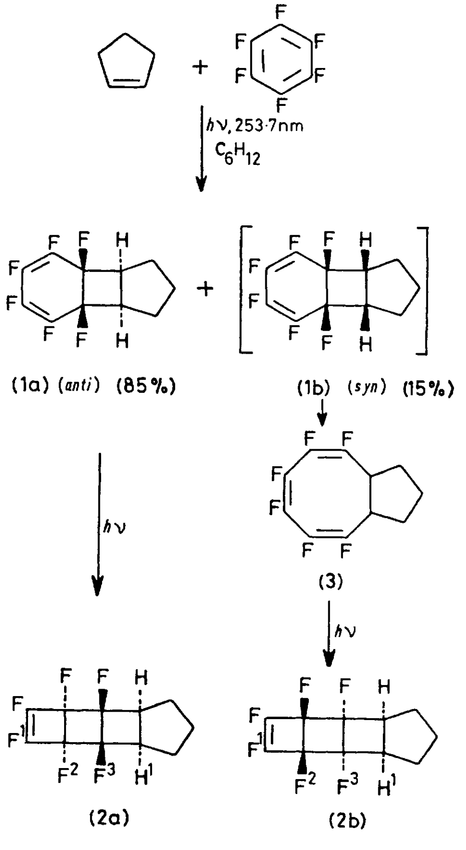
(*Department of Chemistry and 'J. Stefan' Institute, University of Ljubljana, Yugoslavia*)

Summary 2 + 2 photoaddition of cyclopentene to hexafluorobenzene in cyclohexane solution proceeds predominately *via anti* (85%) rather than *syn* attack (15%).

Benzene and substituted benzenes undergo several types of cycloadditions with olefins.[1] Recently, we have observed that photoaddition of indene or 1,2-dihydronaphthalene to hexafluorobenzene results in *cis-syn-cis*-2+2-cycloadducts.[2] Bryce-Smith and his co-workers[3] had earlier established the formation of seven 1 : 1 cycloadducts upon irradiation of hexafluorobenzene in the presence of *cis*-cyclo-octene. They found that the major products formed arose from 1,3-addition of hexafluorobenzene to olefin and suggested several pathways leading to the products.

We now report an investigation of the stereochemistry of 2 + 2 photoaddition of cyclopentene to hexafluorobenzene. A cyclohexane solution of cyclopentene (5 mmol) and hexafluorobenzene (10 mmol) was irradiated at 253·7 nm for 3 h. The crude mixture was separated by preparative g.l.c. or t.l.c., and three products in relative yields of 59% (**1a**), 26% (**2a**), and 15% (**3**) (determined by n.m.r. spectroscopy) were isolated. The structures of the products were established on the basis of n.m.r., mass, and i.r. spectra. Upon further irradiation, (**1a**) was quantitatively transformed into (**2a**), while further irradiation of (**3**) resulted in (**2b**). Products (**2a**) and (**2b**) were transformed by heating at 150 °C for 5 min into a mixture of compounds (**1a**) and (**3**).

Products (**2a**) and (**2b**) have similar mass spectra, but with differences in intensities of the peaks: *m/e* 254 (M^+), 226, 213, 199, 169, 121, 119, 117, 99, 85, 81, 68, and 67. In their ^{19}F n.m.r. spectra both products show three multiplets. The major product (**1a**) shows three ^{19}F n.m.r. signals [δ −161·5 (m), −165 (br s), and −189·75 p.p.m. (m), and two ^{1}H n.m.r. multiplets [δ 3·1 (m, 2H, $^{3}J_{FH}$ 7·5 Hz) and 2



Scheme

TABLE. N.m.r. data for (**2a**) and (**2b**)

	δ/p.p.m.				^3J/Hz		
	F^1	F^2	F^3	H^1	F^3–H^1	F^2–F^3	F^1–F^2
(**2a**)	−124·5	−196·5	−183·75	3·2	7·5	18	9
(**2b**)	−126·5	−190·5	−163·1	3·4	24	18	4·5

(m, 6H)] and the following fragments in its mass spectrum: *m/e* 254 (M^+), 186 (C_6F_6) 117, 99, 93, and 68 (cyclopentene). Product (**3**) also shows three ^{19}F n.m.r. multiplets [δ −158·3 (m, $^3J_{FF}$ 12 Hz), −160·5 (br s), and −167·3 p.p.m. (m)], and two ^{1}H n.m.r. multiplets [δ 3·5 (m, 2H, $^3J_{FH}$ 27 Hz) and 2 (m, 6H)] and in its mass spectrum fragments different from those observed for compounds (**1a**), (**2a**), or (**2b**): *m/e* 254 (M^+, 22%), 212(40), 211(27), 99(33), 68(75), 67(58), 58(40), 43(73), and 42(100).

On the basis of comparison of the n.m.r., mass, and i.r. data of the products (**1a**), (**2a**), (**2b**), and (**3**) with the literature data[3] and chemical transformations of (**1a**), (**2a**), and (**2b**), we suggest the pathway in the Scheme: hexafluorobenzene reacted with cyclopentene with *anti*-attack (85%) predominating over *syn-attack* (15%). However, product (**1b**) proved to be very unstable at room temperature, undergoing ring opening to the cyclo-octatriene derivative (**3**). Product (**3**) was then stereospecifically converted into the tetracyclic system (**2b**) with the stereochemistry outlined in the Scheme: the coupling constants in the Table show that F^2 and F^3 are *trans* and F^2 and H^1 are *cis*. Product (**1a**), formed by *anti* attack of hexafluorobenzene or by heating (150 °C) of products (**2a**), (**2b**), or (**3**), undergoes rapid photocyclisation, thus forming product (**2a**), with the stereochemistry outlined in the Scheme: F^2 and F^3 are again *trans* and F^3 and H^1 are *trans* also.

Photoaddition of hexafluorobenzene to cyclopentene at 350 nm and also in the presence of benzophenone sensitizer did not occur. The photocycloaddition was also quenched by piperylene resulting in a complex mixture of piperylene–hexafluorobenzene products.

(*Received*, 15*th March* 1977; *Com.* 251.)

---

[1] W. Hartman, H. G. Heine, and L. Schrader, *Tetrahedron Letters*, 1974, 3101; D. Bryce-Smith, R. R. Deshpande, and A. Gilbert, *ibid.*, 1975, 1627; J. Berridge, D. Bryce-Smith, and A. Gilbert, *J.C.S. Chem. Comm.*, 1974, 964; H.-G. Heine and W. Hartmann, *Angew. Chem.*, 1975, **87**, 708; D. Bryce-Smith and A. Gillbert, *Tetrahedron*, 1976, **32**, 1309.

[2] B. Šket and M. Zupan, *J.C.S. Chem. Comm.*, 1976, 1053.

[3] D. Bryce-Smith, A. Gilbert, and B. H. Orger, *Chem. Comm.*, 1969, 800.