Stereospecific 2+2 Photoaddition of Indene and 1,2-Dihydronaphthalene to Hexafluorobenzene

By Boris Šket and Marko Zupan*

(*Department of Chemistry and Jožef Stefan Institute, Ljubljana,* 61000 *Ljubljana, Yugoslavia*)

Summary Photoaddition of indene or 1,2-dihydronaphthalene to hexafluorobenzene in cyclohexane solution results in the formation of *cis-syn-cis*-2+2-cycloadducts.

Benzene and substituted benzenes undergo several types of cycloaddition reactions with olefins,[1] but the corresponding reactions of hexafluorobenzene have received much less attention. Bryce-Smith and his co-workers[2] established the formation of seven 1 : 1 photoadducts by irradiation in the presence of *cis*-cyclo-octene. They suggested many pathways leading to the products.

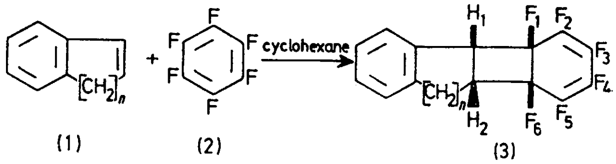
Table

	Chemical shift δ in p.p.m.[a]							
Adduct	F–1	F–6	H–1	H–2	F–2, F–5		F–3, F–4	
	ddd	ddd	ddd	m	m	m	br s	
(**3a**)	156·4	178·5	4·05	3·7	156·4	158·6	157·5	162·4
(**3b**)	160·5	171·0	4·05	3·18	157·5	159·0	161·4	162·4

[a] Upfield of internal $CFCl_3$ in CCl_4 solution.

We now report that under photochemical conditions hexafluorobenzene (**2**) readily reacts with indene (**1a**) or 1,2-dihydronaphthalene (**1b**), to form only one 1 : 1 adduct. A cyclohexane solution of (**1b**) (5 mmol) and hexafluorobenzene (**2**) (10 mmol) was irradiated at λ 253·7 nm for 60 h. The structure of the product (**3b**) formed in 45% yield (m.p. 63–64·5 °C) was established on the basis of its n.m.r., i.r., and mass spectral data. In its ^{19}F n.m.r. spectrum the product shows six signals (Table) and in its ^{1}H n.m.r. spectrum two low-field resonances (Table) together with CH_2 resonances at δ 2·0 (m) and 2·8 (t). The mass spectrum shows the following major fragments: (*m/e* calc. for $C_{16}H_{10}F_6$, 316·0687, found *m/e* 316·0699), *m/e* 316 (M^+, 5%), 186 (64), 131 (73), 130 (100), 129 (93), 128 (77), 127 (61), 117 (40), 115 (83), and 102 (28). On the basis of the three-bond coupling constants[3] J[H(1)–F(1)] = J[H(2)–F(6)] = 25 (F and H are in *cis* positions) J[F(1)–F(6)] = 50, J[H(1)–H(2)] = 12, and J[H(1)–F(6)] = 4 Hz, we have assigned the structure of (**3b**) as a *cis-syn-cis*-2 + 2-cycloadduct.

The reaction with indene (**1a**) under similar conditions also results in the formation of one product (m.p. 88—90 °C, yield 35%), whose n.m.r. data are given in the Table. The mass spectrum shows the following major fragments: (*m/e*: calc. for $C_{15}H_8F_6$, 302·0530, found *m/e* 302·0524), *m/e*: 302 (M^+, 2%), 224(24), 223(98), 222(100), 221(55), 186(10), 118(15), 117(35), 116(97), 115(68), 104(14), and 91(32). The similarity of the i.r., n.m.r., and mass spectral data to those of (**3b**) led us to the conclusion that the *cis-syn-cis*-2 + 2-cycloadduct (**3a**) was formed.



(1) (2) (3)

a; $n = 1$

b; $n = 2$

The photocycloaddition of (**1b**) was completely quenched by piperylene and resulted in a complex mixture of piperylenehexafluorobenzene products. The reaction of 1,4-dihydronaphthalene under the same conditions as above resulted in a complex mixture of products.

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[1] W. Hartmann, 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. Gilbert, *Tetrahedron*, 1976, **32**, 1309.

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

[3] R. Fields, 'Annual Reports on NMR Spectroscopy,' Vol. 5A, Academic Press, London, 1972, p. 99. On the basis of *X*-ray analysis of a similar cyclobutane derivative we have established that ^3J(F – H) of the *syn* isomer is greater than that of the *anti* one (25 and 12 Hz, respectively).