Tetrahedron Letters No. 32, pp 2811 - 2814, 1977. Pergamon Press. Printed in Great Britain.

Stereochemistry of 2+2 Photoaddition of Norbornadiene to Hexafluorobenzene

Boris Šket and Marko Zupan*

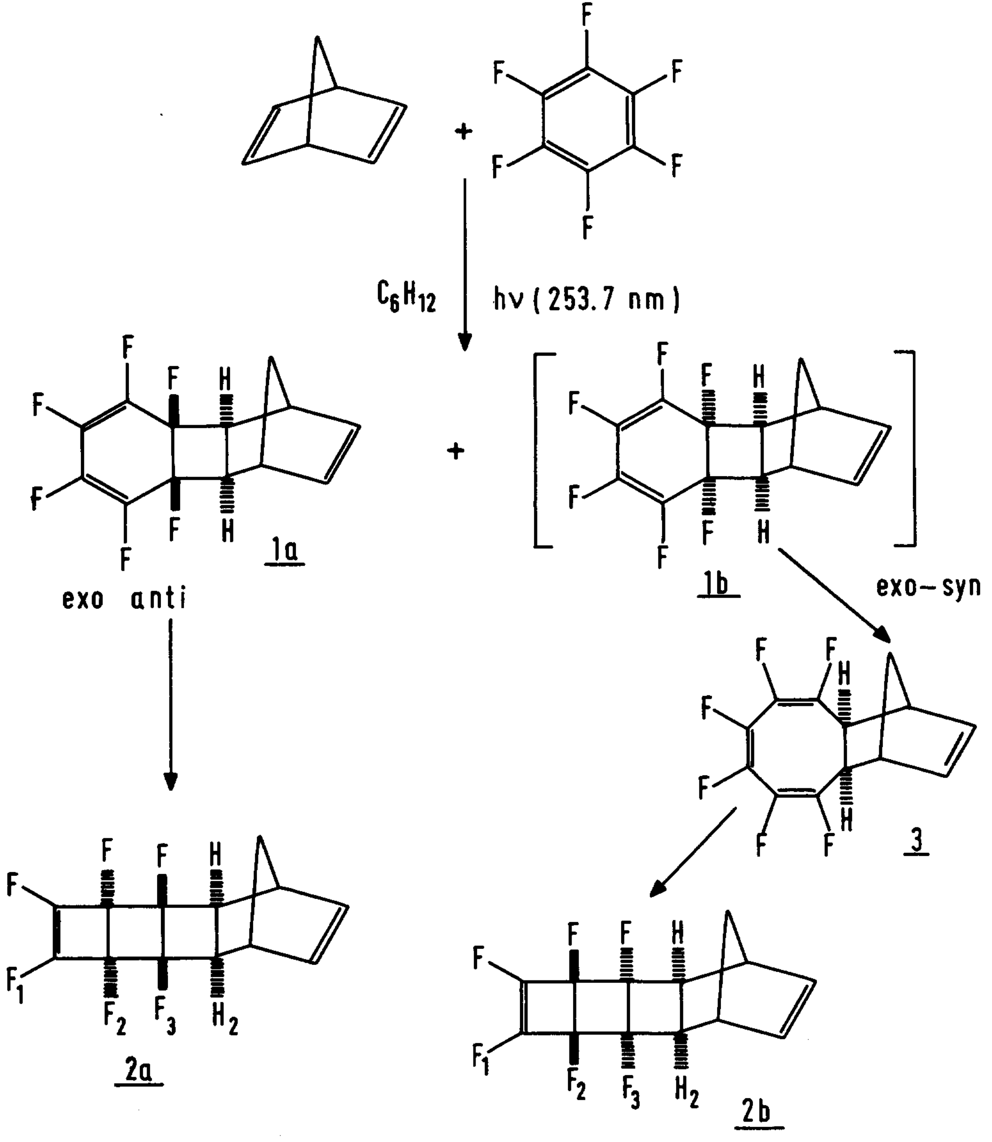
Department of Chemistry and "J.Stefan" Institute, University of Ljubljana, Ljubljana, Yugoslavia

(Received in UK 8 June 1977; accepted for publication 20 June 1977)

Benzene and substituted benzenes undergo several types of cycloaddition reactions with olefins[1]. Recently, we have found that photoaddition of indene or 1,2-dihydronaphthalene to hexafluorobenzene results in the formation of cis-syn-cis-2+2-cycloadducts[2]. On the other hand, Bryce-Smith and his coworkers[3] established the formation of seven 1:1 photoadducts by irradiation of hexafluorobenzene in the presence of cis-cyclooctene. 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 hexafluorobenzene to norbornadiene. There are four possible primary 2+2 attacks: exo-syn, exo-anti, endo-syn, endo-anti. A cyclohexane solution of norbornadiene (5 mmol) and hexafluorobenzene (10 mmol) was irradiated at λ = 253.7 nm for 60 hrs. The crude reaction mixture was separated by preparative tlc. and glc. and three products in relative yields of 47% (3), 33% (2b) and 20% (2a) (determined by nmr) were isolated. The structures of the products were established on the basis of their nmr, ir, mass and x-ray spectra. Products 2a and 2b have very similar mass spectra with differences in intensities of peaks: m/e 278(M^+), 237, 232, 97, 92, 91, 79, 67, 66 (basic peak for both products). In their ^{19}F nmr spectra, both products show three multiplets (Scheme 1). The major product formed (3) shows in its ^{19}F nmr spectrum three signals with δF: -159 ppm(m), -161.25 ppm (broad singlet), -168 ppm(m) and in its ^1H spectrum four signals with δH: 6.3 ppm (broad singlet), 3.09 ppm (broad singlet), 2.7 ppm(m), 1.5 ppm(m) with coupling constants $^3J_{F,H}$ = 26 Hz, $^3J_{F,F}$ = 13 Hz, and the following fragments in its mass spectrum: m/e 278(M^+, 9%) 232(16), 97(22), 92(32), 91(40), 66(100). Product 3 was quantitatively transformed by further irradiation to product 2b (Scheme 2). On the other hand, by heating product 3 (T = 150°C) a mixture of the starting material and a newly formed compound 1a resulted. Product 1a was isolated by preparative glc. and shows in its ^{19}F nmr three multiplets with δF: -162.3 ppm(m), -163.9 ppm (broad singlet) and -188.62 ppm(m) and in its ^1H nmr four signals with δH: 6.12 ppm (broad singlet), 3.36 ppm (broad singlet), 2.34 ppm(m), 1.35 ppm (m) with the coupling constant $^3J_{F,H}$ = 7.5 Hz, and in its mass spectrum fragments, different from those observed for compounds 2a, 2b or 3: m/e 278(M^+,6), 232(43), 186(71, hexafluorobenzene species), 117(50), 92(83), 91(100, C_7H_8 species). Product 1a was rapidly transformed by irradiation into product 2a (Scheme 2). Products 2b and 2a were transformed by heating at T = 150°C for 5 min into a mixture of compounds 3 and 1a.

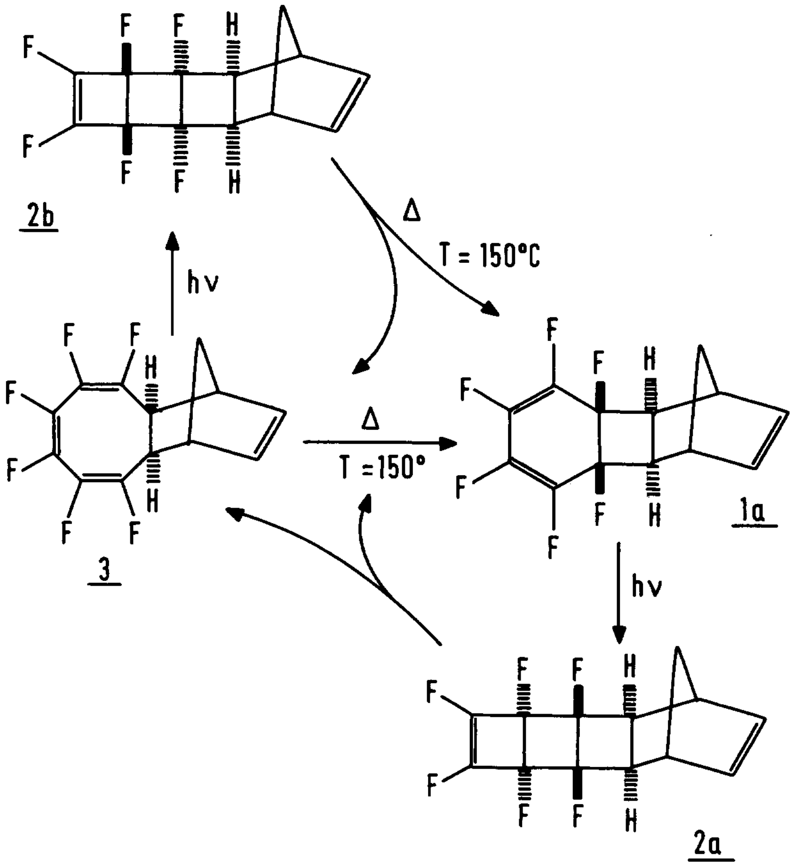
SCHEME 1



NMR DATA FOR 2a and 2b

	δF_1	δF_2	δF_3	δH_2	δH_7	$^3J_{F_3H_2}$	$^3J_{F_2F_3}$	$^3J_{F_1F_2}$
2a	−123.75	−180.75	−194.25	2.55	3.24	7.5	15	9
2b	−125.25	−180	−164.25	2.7	3.18	24	15	4.5

SCHEME 2



By reducing the irradiation time from 60 hrs to 3 hrs we have observed only 15 % conversion of starting materials with the formation into 22 % of 1a and 78 % of 3 (relative yields determined by ^{19}F nmr). On the basis of a comparison of nmr, mass and ir data of products 1a, 2a, 2b and 3 with the literature ones[3], chemical transformations of products 1a, 2a, 2b and 3 and x-ray analysis[4] of that product, formed by irradiation of norbornene and hexafluorobenzene, which has similar nmr data (δF: -124.5 ppm, -158.25 ppm and -179.25 ppm) to product 2b, we suggest the following reaction pathway (Scheme 1): hexafluorobenzene reacted exclusively exo with norbornadiene, with syn attack (80 %) predominating over anti attack (20 %). However, product 1b proved to be very unstable at room temperature undergoing the ring - opening process, thus resulting in cyclooctatriene derivative

(3). Product 3 was then stereospecifically converted to hexafluoropentacyclic system (2b) with the stereochemistry outlined in Scheme 1; F_2 and F_3 are in trans-position ($^3J_{F_2,F_3}$ = 15 Hz) and F_3 and H_2 are in cis-position ($^3J_{F_3,H_2}$ = 24 Hz) (the structure of a product with similar stereochemistry was also established by x-ray analysis[4]). Product 1a, formed by exo-anti attack of hexafluorobenzene, and which was isolated only when a shorter reaction time was used or by heating (T = 150°C) products 2a, 2b, or 3, undergoes rapid photocyclization, thus forming product 2a, with the stereochemistry outlined in Scheme 1: F_2 and F_3 are again in trans-position ($^3J_{F_2,F_3}$ = 15 Hz) and F_3 and H_2 are in trans-position ($^3J_{F_3,H_2}$ = 7.5 Hz).

The photoaddition reaction of hexafluorobenzene and norbornene at λ = 350 nm and also in the presence of benzophenone sensitizer did not occur. The photocycloaddition was also completely quenched by piperylene and resulted in a complex mixture of piperylene-hexafluorobenzene product.

The effect of the structure of the olefin and the effect of the substituents in polyfluorobenzene on photoaddition reactions is now under investigation.

References:

1. W.Hartman, H.G. Heine and L.Schrader, Tetrahedron Letters, 3101, 1974, D.Bryce-Smith, R.R.Deshpande and A.Gilbert, Tetrahedron Letters, 1627, 1975, J.Berridge, D.Bryce-Smith and A.Gilbert, J.Chem.Soc., Chem.Commun. 964, 1974, H.-G.Heine and W.Hartmann, Angew.Chem., 87, 708 (1975), D.Bryce-Smith and A.Gilbert, Tetrahedron, 32, 1309 (1976).
2. B.Šket and M.Zupan, Chem.Comm., 1976, 1053.
3. D.Bryce-Smith, A.Gilbert and B.H.Orger, Chem.Comm., 1969, 800.
4. I.Leban and L.Golič, unpublished observation.