

1,2-, 1,3- and 1,4-Photocycloaddition Modes on the Naphthalene Ring

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The photochemical reaction of octafluoronaphthalene and indene results in all three cycloaddition modes, *i.e.*, 1,2-, 1,3- and 1,4-cycloaddition take place.

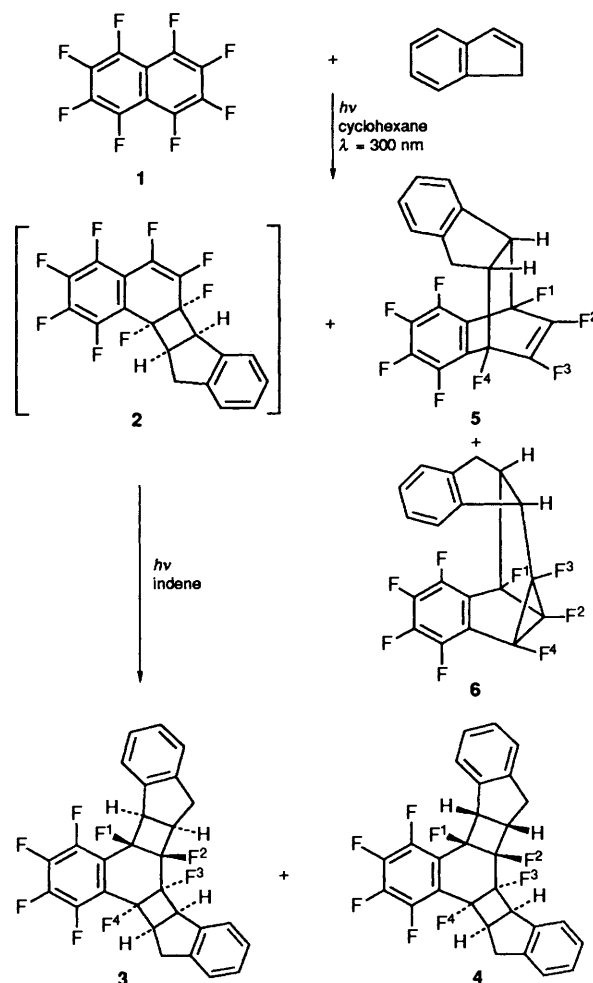
The photochemistry of benzene involves photorearrangement and photosubstitution, as well as 1,2-, 1,3- and 1,4-photocycloaddition reactions, and it has been studied and reviewed in detail.¹ The photochemical behaviour of naphthalene is quite different from benzene. Simple naphthalenes do not photorearrange to Dewar naphthalene or naphthvalene. The 1,2- and 1,4-photocycloaddition reactions are preferred reaction modes in the case of photochemical reactions of naphthalenes and alkenes, but 1,3-additions of alkenes, so important in benzene photochemistry, are seldom observed with naphthalenes.² Very few publications relating to photocycloaddition reactions of octafluoronaphthalene have appeared, in which only reactions with conjugated dienes have been studied.³ Photocycloaddition reactions of naphthalene and some acetylene derivatives result in the 1,2- and 1,4-cycloaddition modes followed by a secondary rearrangement or intramolecular cycloaddition leading to the final products.⁴

Previously, we have found that photoaddition of indene and hexafluorobenzene results in the formation of the *cis-syn-cis* [2 + 2] cycloadduct.⁵ We now report that under photochemical conditions, octafluoronaphthalene reacts with indene forming the corresponding 1,2-, 1,3- and 1,4-cycloadducts.

A cyclohexane solution of indene and octafluoronaphthalene was irradiated at 300 nm for 70 h. The crude reaction mixture was analysed by ¹⁹F NMR spectroscopy and it was determined that the conversion of the initial naphthalene was 78% with the formation of four products in the relative ratio of 3:4:5:6 being 39:16:10:35 (Scheme 1). The mixture was separated by column chromatography (neutral Al₂O₃, W 200), and the crude isolated products were crystallised from methanol. The structure of the products was determined on the basis of their spectroscopic data and, for compound 3, also by X ray analysis.⁷ The mass spectrum of product 3 [*m/z* 504 (M⁺), 388 (M⁺ - C₉H₈), 272 (M⁺ - 2 × C₉H₈) and base peak at *m/z* 116 (C₉H₈)] indicates that the 2:1 adduct of indene and octafluoronaphthalene was formed. The adduct shows no IR absorption in the region of 1700–1760 cm⁻¹ which means that no isolated -CF=CF- group is present and that both indene rings are bound to the same ring of the octafluoronaphthalene by [2 + 2] cycloaddition. The stereochemistry of adduct 3 was determined by ¹H and ¹⁹F NMR spectra using also the results of COSY and HETCOR experiments. The ¹⁹F NMR spectrum shows, in addition to signals corresponding to the fluorine atoms bonded to the aromatic carbon atoms, also signals at δ -196.3 and -177.6, indicating an *anti* disposition of fluorine and hydrogen atoms in the cyclobutane ring,⁶ while the signals at δ -152.0 and -150.0 correspond to *syn* oriented fluorine and hydrogen atoms in the second cyclobutane ring⁵ (Table 1). The signals in the ¹H NMR spectrum of the compound 3 at δ 4.0 and 4.2, containing also the coupling constants *J* 16.5 and 22 Hz, corresponding to the coupling of a fluorine and a hydrogen atom in a *syn* position, and the signals at δ 3.0 and 3.9, containing also a small coupling constant (less than 3 Hz), corresponding to the coupling of a fluorine and a hydrogen atom in an *anti* position, also indicate a *syn* orientation of the fluorine and hydrogen atoms in one

cyclobutane ring and an *anti* orientation of the fluorine and hydrogen atoms in another. The structure of product 3 was also confirmed by COSY and HETCOR experiments and by X ray analysis.⁷

Product 4 (Scheme 1) shows the same molecular peak and very similar fragmentations in the mass spectrum as product 3. The absence of the vibration of an isolated -CF=CF- group in its IR spectrum indicates that the structure of product 4 must be closely related to product 3. The ¹H NMR spectrum of compound 4 shows two signals at δ 4.0 and 4.3, which are nearly the same as the signals in the ¹H NMR spectrum of compound 3, *i.e.*, signals that correspond to the hydrogen atoms in the cyclobutane ring having a *syn* orientation to the fluorine atoms bonded in the same ring.⁵ Instead of the signals at δ 3.6 and 3.9 observed in the ¹H NMR spectrum of compound 3, there are two signals in the ¹H NMR spectrum of compound 4, at δ 3.4



Scheme 1

Table 1 ^{19}F NMR spectroscopy data for the photoproducts of octafluoronaphthalene and indene

Compound	Chemical shift (ppm)*
3	-196.3 (m, 1 F, F-2), -177.6 (m, 1 F, F-1), -158.1 (m, 1 F, aromatic F), -150.7 (m, 1 F, aromatic F), -137.3 (m, 1 F, aromatic F), -136.2 (m, 1 F, aromatic F), -152.0 (tm, 1 F, F-3) and -150.0 (m, 1 F, F-4)
4	-175.1 (m, 1 F, F-3), -172.2 (m, 1 F, F-2), -152.4 (m, 2 F, aromatic Fs), -136.5 (m, 1 F, aromatic F), -131.5 (m, 1 F, aromatic F), -149.1 (m, 1 F, F-1) and -146.7 (m, 1 F, F-4)
5	-196.5 (d, 1 F, F-1), -195.1 (dd, 1 F, F-4), -154.7 (m, 2 F, aromatic Fs), 154.7 (m, 2 F, aromatic Fs) and -148.4 (m, 2 F, F-2, F-3)
6	-222.4 (m, 1 F, cyclopropyl F), -209.1 (m, 1 F, cyclopropyl F), -190.3 (m, 1 F, cyclopropyl F), -159.9 (d, 1 F, F-1), -152.7 (m, 1 F, aromatic F), -150.9 (m, 1 F, aromatic F), -144.9 (m, 1 F, aromatic F) and -141.4 (m, 1 F, aromatic F)

* Solvent, CDCl_3 ; internal reference, CFCl_3 .

and 4.5, showing also the coupling constant 16 Hz which again indicates a *syn* orientation of hydrogen and fluorine atoms in the second cyclobutane ring of product **4**. The chemical shifts and coupling constants observed in the ^{19}F NMR spectrum of compound **4** (Table 1) (no signals for fluorine atoms in an *anti* position with hydrogen atoms were observed) also demonstrate the *syn* orientation in both cyclobutane rings. The structure of compound **5** was also determined on the basis of its spectroscopic data. In the mass spectrum, the molecular peak m/z 388 corresponds to a 1:1 adduct of octafluoronaphthalene and indene. IR absorption (ν_{max} 1755 cm^{-1}) indicates the presence of a $-\text{CF}=\text{CF}-$ double bond which is not in a conjugate position to the aromatic system. The signals at δ 4.3 and 3.5 show a coupling constant (J 10 Hz), which indicates their *cis* position to each other, as well as through space coupling with the fluorine atoms bonded to the double bond (J_{FH} 10 Hz). This demonstrates that product **5** (Scheme 1) is a 1,4-cycloadduct with an *endo* orientation of the indan ring. The 1,4-addition mode can also be determined on the basis of the ^{19}F NMR spectrum of compound **5** in which were observed, in addition to signals for aromatic fluorine atoms, two signals at δ -196.5 and -195.1 corresponding to the fluorine atoms bonded to saturated carbon atoms, and a signal at δ -148.4 of the two fluorine atoms at the double bond (Table 1).⁸ The ^{13}C , COSY and HETCOR measurements were also in accordance with the structure proposed.

Compound **6** has a molecular peak at m/z 388 (1:1 adduct), but the fragmentations are different from those of compound **5**. There is no vibration of the isolated $-\text{CF}=\text{CF}-$ group in the IR spectrum of compound **6**, but in its ^{19}F NMR spectrum, there are three signals in addition to others, at δ -222.4, -209.1 and -190.3 corresponding to the fluorine atoms bonded to the saturated carbon atoms of the cyclopropane ring (Table 1).^{8,9} On the basis of the data mentioned and from COSY and HETCOR measurements, it was proposed that product **6** is a 1,3-adduct of octafluoronaphthalene and indene. To determine if the 1,3-adduct is formed as a primary photochemical product or by a rearrangement from the 1,4-adduct, a cyclohexane solution of product **5** was irradiated under the same reaction conditions as mentioned. No transformation into 1,3-adduct was observed.

From the results obtained it was concluded that 1,2-*endo*-, 1,3-*endo*- and 1,4-*endo*-adducts were the primarily formed products. The *endo* attack can be explained by maximum overlapping of the π -systems of the reactants and was determined by X ray analysis⁷ of product **3** and from ^1H and ^{19}F NMR spectra of product **5**. The compounds **3** and **4** were formed from the

primarily formed [2 + 2] *endo* adduct **2** by an *endo* or *exo* attack of an indene molecule to the double bond in this dihydronaphthalene derivative (**2**, Scheme 1). It is, as far as we know, the first example observed in reactions of naphthalene ring and alkene in which 1,2-, 1,3- and 1,4-cycloaddition takes place.

The photochemical reactions of octafluoronaphthalene with some other cycloalkenes (such as 1,2-dihydronaphthalene, cyclopentene and norbornene) and some substituted acetylenes (such as 1-phenylprop-1-yne and dimethyl acetylenedicarboxylate) were also studied. It was determined that in all cases the conversion of octafluoronaphthalene was very low (less than 5%) which made it impossible to isolate any products formed.

From the results obtained, it can be concluded that the ΔIP rule which is based on the difference between the ionisation potentials of arene and olefin, as proposed by Bryce-Smith *et al.*,¹⁰ as well as the correlations between the selectivities and the free enthalpies of electron transfer (the ΔG rule)¹¹ cannot be used to predict the mode of photochemical reaction in octafluoronaphthalene.

Experimental

Octafluoronaphthalene (1 mmol) and indene (2 mmol) were dissolved in cyclohexane (16 cm^3). The solution was irradiated at room temperature for 70 h with 300 nm lamps in a Rayonet Photochemical Chamber reactor. The solvent was evaporated under reduced pressure and methanol (2 cm^3) was added to the crude reaction residue. The white crystalline compound that precipitated was filtered off and recrystallised from methanol to give compound **3** (m.p. 243–244 °C) (Found: M^+ , 504.110. Calc. for $\text{C}_{28}\text{H}_{16}\text{F}_8$: M , 504.1124; m/z 504 (M^+ , $10^{-2}\%$), 272 (31×10^{-2}), 117 (11), 116 (100) and 115 (18).

The filtrate which contained octafluoronaphthalene and compounds **4**, **5** and **6** was separated using column chromatography (Al_2O_3 W 200, neutral, mobile phase light petroleum) and the crude products were crystallised from methanol. Compound **4**, m.p. 194–197 °C (Found: M^+ , 504.113. Calc. for $\text{C}_{28}\text{H}_{16}\text{F}_8$: M , 504.1124; m/z 504 (M^+ , 0.6%), 272 (10), 117 (11), 116 (100) and 115 (18). Compound **5** m.p. 148–150 °C (Found: M^+ , 388.050. Calc. for $\text{C}_{19}\text{H}_8\text{F}_8$: M , 388.0498; m/z 388 (M^+ , 2×10^{-2}), 272 (5), 117 (11), 116 (100) and 115 (27). Compound **6** m.p. 133–135 °C (Found: M^+ , 388.050. Calc. for $\text{C}_{19}\text{H}_8\text{F}_8$: M , 388.0498; m/z 389 (M^+ + 1, 0.5%), 388 (M^+ , 2), 272 (8), 148 (10), 147 (86), 146 (14), 145 (23), 117 (11), 116 (100) and 115 (27).

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