Photochemical Isomerization of Perfluoroindene to Perfluoroisoindene. A Sigmatropic Migration of Fluorine

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Summary Perfluoroindene (I), when irradiated in the vapour phase, isomerizes *via* a sigmatropic fluorine shift to perfluoroisoindene which can be trapped as its Diels–Alder adduct with ethylene; the thermal reaction between (I) and ethylene gives the 1,2-adduct.

Thermal and photochemical isomerizations of substituted indenes have been reported by several groups.[1,3] The results have been rationalized in terms of the intermediacy of isoindenes, and in some cases the isoindenes have been trapped as their Diels–Alder adducts. These results can be accommodated within the frontier orbital approximation of the Woodward-Hoffman conservation of orbital symmetry approach. Thus, if it is assumed that the transition state for the isomerization can be constructed from an indenyl radical and a migrating group radical, then the symmetries of the HOMO (ψ_5) and LUMO (ψ_6) of indenyl shown in the Figure[4] can account for the observed reactions. As a

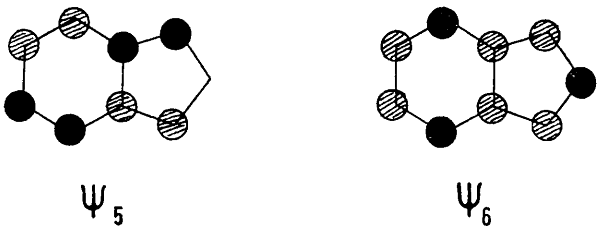
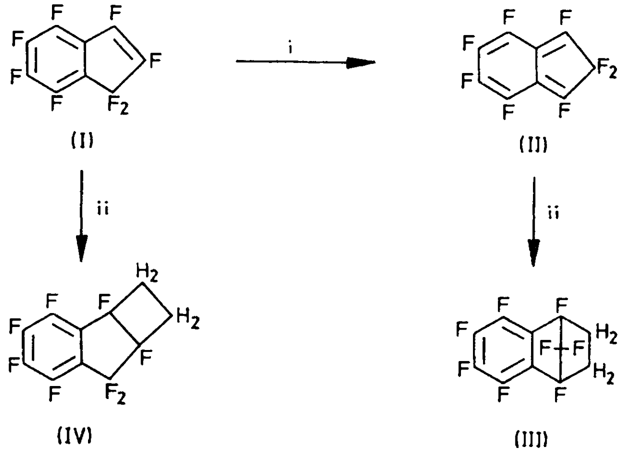


Figure 1. HOMO and LUMO for indenyl, ref. 4.

consequence of the node at C-2 in ψ_5 there is no discrimination (at this level of sophistication) between allowed and forbidden C(1) to C(2) migrations and in practice thermal migrations are observed for both hydrogen atoms and phenyl groups.[1,3] On the other hand the form of ψ_6 indicates that C(1) to C(2) migrations in the excited state will only be allowed for migrating radicals using an antisymmetric orbital; in practice phenyl migrations occur (using an orbital of *p* symmetry) whereas no evidence for hydrogen migrations could be found.[2] It is assumed that geometrical restrictions exclude antarafacial migrations.

Although sigmatropic migrations have been reported for many groups[1,3,5] the only example of a sigmatropic fluorine shift is a previous tentative suggestion of ours;[6] we now report an unambiguous example.

When perfluoroindene (I) is irradiated (λ 253·7 nm) in the gas phase in the presence of ethylene, the adduct (III) is isolated; an isomeric adduct (IV) is obtained from the thermal reaction between (I) and ethylene (Scheme). Adducts (III) and (IV) have m.p.s 42—43° and 77—78°, respectively, and their elemental analyses, and i.r., u.v. and mass spectra were consistent with the structural assignments in the Scheme which rest mainly upon their ^{19}F n.m.r. spectra. The spectrum of adduct (III) shows resonances for only one kind of tertiary fluorine at 200·3† (2F), two aromatic fluorine environments at 153·4 (2F) and 147·1 (2F), and a CF_2 group [δ_A 151·1(1), δ_B 136·6(1), J_{AB} 178 Hz], whereas in the spectrum of adduct (IV) only one tertiary fluorine can be definitely assigned on the basis of its shift at 192·4 (1F), the other being included amongst the aromatic fluorines [152·2 (1F), 148·1 (1F), 146·5 (1F), and 140·7 (2F)], the CF_2 group resonating at δ_A 113·6 (1F), δ_B 90·3 (1F), with J_{AB} 265 Hz. The chemical shifts and relative intensities distinguish clearly between structures (III) and (IV), and the J_{AB} values for the CF_2 groups are completely consistent with previous assignments in related structures.[7]



(i) $h\nu$, 253·7 nm; (ii) addition of ethylene.
Scheme

The formation of adduct (IV), a $2_\pi + 2_\pi$ addition between the double bond of perfluoroindene and ethylene, is a reaction typical of fluoro-olefins. To rationalize the formation of adduct (III) we suggest that in the photochemical process perfluoroisoindene (II) is generated by a sigmatropic shift of fluorine from C(1) to C(2) in an excited state of perfluoroindene; this very reactive compound (II) is then trapped (presumably after reaching the ground state) as its Diels–Alder adduct with ethylene. This constitutes the first unambiguous example of a sigmatropic fluorine shift; it further suggests that fluorine migrates using both lobes of a *p*-orbital.

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† Shifts quoted are in p.p.m. upfield from internal $CFCl_3$; the spectrum of (III) was recorded in Et_2O solution, and that of (IV) in CCl_4.

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