Photochemically-allowed [3,5] Sigmatropic Rearrangements

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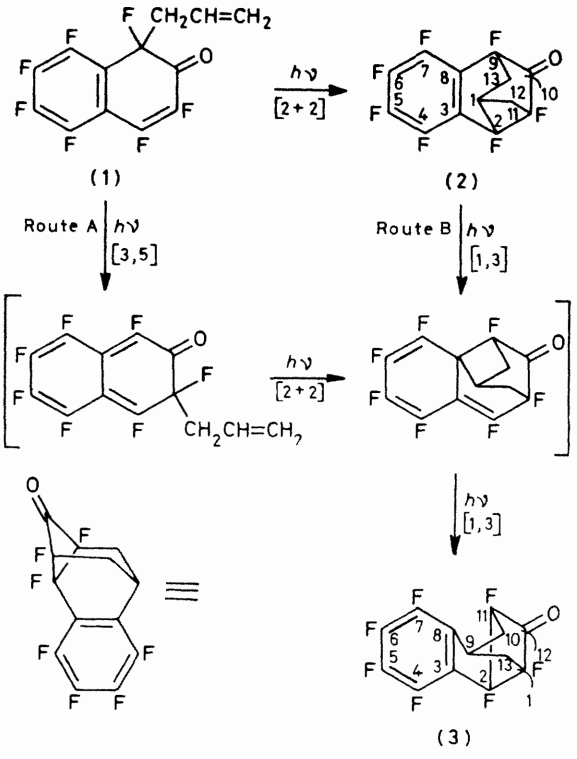
Summary The photolysis of 1,3,4,5,6,7,8-heptafluoro-1-(prop-2-enyl)naphthalen-2-one (**1**) gives 1,2,4,5,6,7,11-heptafluorotetracyclo[7.3.1.$0^{2,11}$.$0^{3,8}$]trideca-3(8),4,6-trien-12-one (**3**) *via* an initial [3,5]sigmatropic rearrangement, and an expected [2 + 2] adduct, 2,4,5,6,7,9,11-heptafluorotetracyclo[7.3.1.$0^{2,11}$.$0^{3,8}$]trideca-3(8),4,6-trien-10-one (**2**).

ONLY one example of a reaction involving a photochemically-allowed [3,5] sigmatropic rearrangement proceeding suprafacially on both components[1] has been described in the literature[2] (1953). We now report a reaction involving the second example.

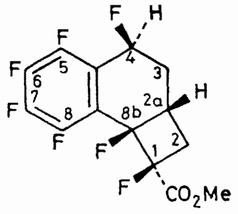
1,3,4,5,6,7,8-Heptafluoro-1-(prop-2-enyl)naphthalen-2-one (**1**) on photolysis in acetonitrile at 350 nm over 21 h undergoes complete conversion into a mixture of two isomers: (**2**) (3 parts), an expected [2 + 2] allowed adduct; and (**3**) (1 part). The unexpected formation of (**3**) can be rationalised on the basis of two possible mechanisms involving photochemically allowed reactions (Scheme). However, we have discounted Route B since no reaction occurs when (**2**) is photolysed under the conditions used to convert (**1**) into (**2**) and (**3**). Consequently, we propose Route A, involving an initial [3,5] shift as the reaction pathway to (**3**).

The naphthalenone (**1**) (m.p. 57—59 °C) was prepared by the thermal isomerisation of 1,3,4,5,6,7,8-heptafluoro-2-naphthyl prop-2-enyl ether (b.p. 83·5 °C at 0·01 mmHg) in boiling xylene over 2·5 h, the ether itself being obtained from 1,3,4,5,6,7,8-heptafluoro-2-naphthol[3] and prop-2-enyl bromide. That the prop-2-enyl group had migrated to the 1-position and not the 3-position (which is the product of the [3,5] shift in the Scheme) was clearly shown by the presence of only one large *peri*-F–F coupling constant ($J_{F(4)-F(5)}$ 75·7 Hz) in the ^{19}F n.m.r. spectrum.



SCHEME

Only one of the two possible [2+2] adducts was formed from (**1**). This compound (m.p. 137—139 °C) was shown to have the structure (**2**) by converting it into compound (**4**) by a haloform type cleavage with caustic soda, acidification, and methylation with CH_2N_2. Broad band decoupling of all the hydrogen atoms other than the geminal C*H*F identified the highest absorption in the ^{19}F n.m.r. spectrum of (**4**) at δ 180·8 p.p.m. as F(1), (t, $J_{F(1)-H(2)}$ *syn* = $J_{F(1)-H(2)}$ *anti* = 25 Hz, collapsing to a singlet); the absorption at δ 161·9 p.p.m. as F(4β) (td, $J_{gem\ FH}$ 50 Hz; $J_{F(4\beta)-H(3\alpha)}$ 50 Hz; $J_{F(4\beta)-H(3\beta)}$ 20 Hz, collapsing to a doublet, $J_{gem\ FH}$ 50 Hz); and the absorption at 140·3 p.p.m. as F(8bβ) (t, $J_{F(8b\beta)-H(2a\beta)}$ 20 Hz; $J_{F(8b\beta)-F(8)}$ 20 Hz, collapsing to a doublet $J_{F(8b\beta)-F(8)}$ 20 Hz). Compound (**3**) (m.p. 122–123 °C) is the 3,4-(tetrafluorobenzo)analogue of (**5**) which had been prepared previously.[4] Significantly, the absorption centred at δ 185·1 p.p.m. which accounted for two fluorines, was a doublet and not two separate absorptions, since the separation did not increase when the spectrum was run in turn at 56·4 and 84·67 MHz. This showed that the molecule contained two magnetically equivalent fluorine atoms in positions related through a plane of symmetry and identified them as F-1 and F-11.



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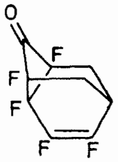

(5)

All of the compounds had acceptable elementary analyses.

We thank the S.R.C. for financial support (to N. S. R.).

(*Received*, 30*th November* 1979; *Com.* 1251.)

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[2] R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Verlag Chemie/Academic Press, 1970, p. 127.

[3] B. Gething, C. R. Patrick, and J. C. Tatlow, *J. Chem. Soc.*, 1962, 186.

[4] G. M. Brooke, D. H. Hall, and H. M. M. Shearer, *J.C.S. Perkin I*, 1978, 780.