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PRELIMINARY NOTE

Perfluorobicyclobutylidine: Unusual Reactivity Arising from Angle Strain

RICHARD D. CHAMBERS,* JULIAN R. KIRK, GRAHAM TAYLOR

(University Science Laboratories, South Road, Durham City (U.K.)

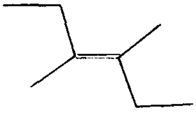
and RICHARD L. POWELL

I.C.I. Ltd., Mond Division, P.O. Box No. 8, The Heath, Runcorn, Cheshire (U.K.)

SUMMARY

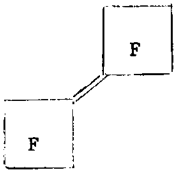
Perfluorobicyclobutylidine shows unusual reactivity in cycloaddition reactions in comparison with perfluoro-3,4-dimethylhex-3-ene. Reactions with 1,3-dienes are described giving $4\pi + 2\pi$ products; hydrogen transfer, and a copolymerisation have also been observed.

In the course of work involving formation of synthetically more sophisticated compounds from simple unsaturated fluorocarbons,[1] we have obtained the interesting fluorinated alkene (1) and perfluorobicyclobutylidine (2).



(1)

(All unmarked bonds to fluorine)



(2)

(F in the centre of a ring signifies all bonds to fluorine)

These compounds form a fascinating pair, for the purpose of illustrating the effect of strain on reactivity since, formally, both systems have four

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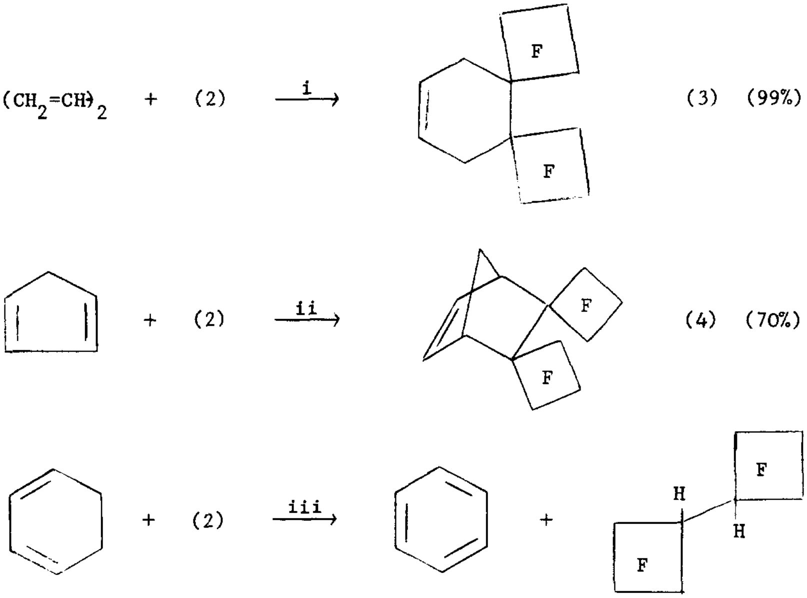
perfluoroalkyl groups attached to the double bond which will, therefore, have very similar electronic environments in (1) and (2). Compound (2) has, however, considerable angle strain and comparative addition reactions described here for (1) and (2) dramatically derive from this.

Understandably, bromine is unreactive towards the electrophilic alkene derivative (1) but in fact adds slowly to (2). We have been unable to add butadiene or other dienes to (1) but (2) undergoes a contrasting series of 4π + 2π cycloadditions under comparatively mild conditions giving e.g. the adducts (3) and (4) in high yield.



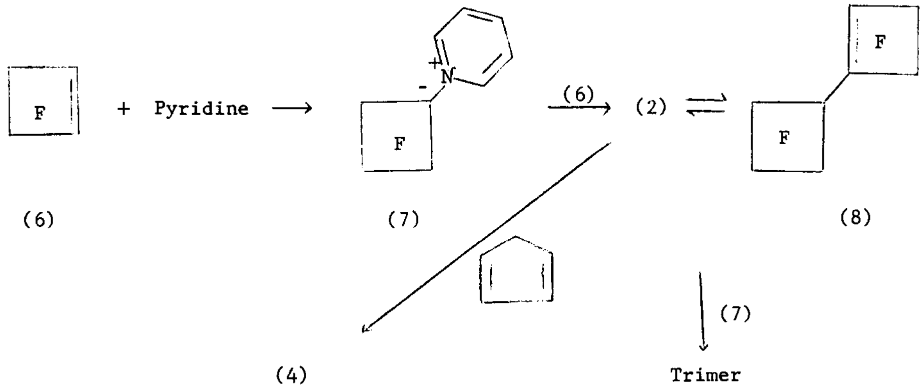
(3) (99%)

(4) (70%)

(5) (90%)

i. Cariustube 80°C, ii. 80°C, iii. 80°C

Cyclohexa-1,3-diene reacted with (2) under mild conditions but, in this case, the product was (5). Transfer of hydrogen, rather than cycloaddition, has been observed in other reactions involving cyclohexa-1,3-diene[2,3] but there is no indication on whether this transfer of hydrogen is a concerted process or involves an initial addition followed by rapid elimination of benzene. We did not observe even trace quantities of any adduct. We have now even succeeded in trapping the bicyclobutylidine derivative (2) during its formation from perfluorocyclobutene (6) in the presence of pyridine. Normally, a mixture of (2) and its isomer (8) are formed, together with a trimer as the major product.[3] The reactivity of (2) in the cycloaddition reaction is so great, however, that the reaction is completely diverted to (4).



To our surprise, compound (2) undergoes free radical co-polymerisation with butadiene (initiated by γ-rays); to form an approximately 1:1 co-polymer. No homopolymer was obtained from (2) and no corresponding co-polymer with butadiene could be obtained from (1).

All compounds show satisfactory elemental analyses and consistent mass spectra and the structures follow simply from the ^1H and ^{19}F n.m.r. spectra.

REFERENCES

1 See R.D. Chambers, J.R. Kirk and G. Taylor, J.C.S. Perkin I (1982) 673 and earlier parts of a series.

2 Y. Kobayashi, M. Honda, Y. Hanzawa, I. Kumadaki and A. Ohsawa, J.C.S. Perkin I (1979) 1743.

3 R.D. Chambers, G. Taylor and R.L. Powell, J.C.S. Perkin I (1980) 426.