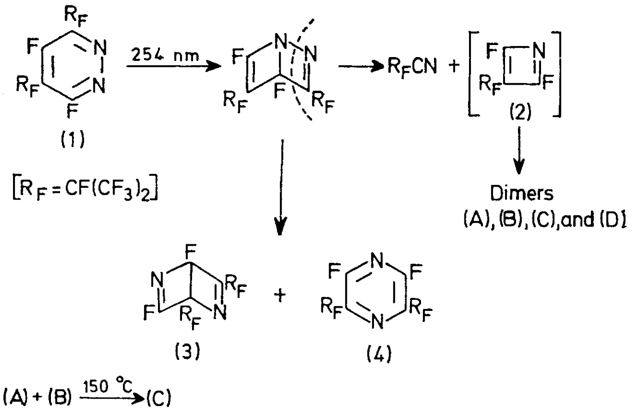
Possible Generation of a Fluorinated Azacyclobutadiene

By R. D. Chambers* and J. R. Maslakiewicz

(*University Science Laboratories, South Road, Durham City* DH1 3LE)

Summary Photolysis of a fluorinated pyridazine gives products which are dimers of a possible intermediate azacyclobutadiene (azete) derivative.

THERE are reports in the literature of the isolation of stable azacyclobutadiene derivatives[1] and here, evidence is presented for the generation of a fluorinated derivative. The isolation of valence isomers from photolysis of perfluoro-3,5-di-isopropylpyridazine has been reported previously[2] but we have now established that by-products are formed in the reaction through the intermediacy of an azacyclobutadiene derivative (**2**). Photolysis of (**1**) in a flow system gave the *para*-bonded species (**3**)[2] and corresponding pyrazine (**4**), together with a mixture which we have identified as $(CF_3)_2CFCN$, and four compounds (A)—(D), each corresponding to the molecular formula $C_{12}F_{18}N_2$.† The proportion of the isomers (A)—(D) together with $(CF_3)_2CFCN$ increased with pressure, to *ca.* 37% of the product.

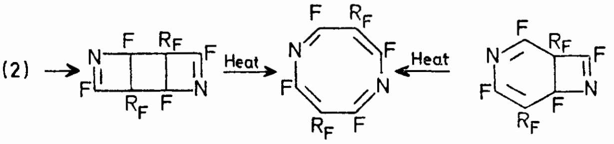


Isomers (A)—(D) were separated by g.l.c.; also, it was established that (A) and (B) gave (C) on heating. The most

---

† Satisfactory elemental analyses were obtained for compounds (A)—(D). ^{19}F N.m.r. spectra: δ $(CFCl_3)$, (A), 38·6 and 170·8; (B), 47·4, 67·6, 122·7, and 161·8; (C), 13·3 and 57·2; (D), 14·7, 29·4, and 57·4 (2F) p.p.m.

significant structural probes available for these compounds are the positions of resonance, in the ^{19}F n.m.r. spectra, of the fluorine atoms which are not part of the $CF(CF_3)_2$ groups.† Fluorine atoms attached to 'tertiary' positions lead to resonances at characteristically high-field positions, whereas when attached as in F–C=N, they lead to resonances at much lower field.[2] Isomer (A) showed both of these structural elements with absorptions at 170·8 and 38·6 p.p.m. (relative to $CFCl_3$) and each corresponding to two fluorine atoms. The presence of two 'tertiary', *i.e.* bridgehead, fluorine atoms [additional to the $CF(CF_3)_2$ groups] and hence only two fluorine atoms at unsaturated positions, clearly indicates a symmetrical tricyclic structure, *e.g.* (A).



(A) (C) (B)

In a similar way, the ^{19}F n.m.r. spectrum of isomer (B) shows only one bridgehead fluorine atom, while the spectra of (C) and (D) each indicate that no bridgehead fluorine atoms are contained. It is clear then, that (B) has a bicyclic structure while (C) and (D) have monocyclic structures and the ^{19}F n.m.r. spectra further indicate that (C) is symmetrical while (D) is unsymmetrical.

The formation of tri-, di-, and mono-cyclic isomers is consistent with the generation of the azete derivative (**2**), followed by dimerisation *etc.* Dimerisation of (**2**) could obviously occur in a number of ways and, so far, we are not able to distinguish between some of the various possibilities. The structures shown for (A)—(D) are consistent with data, although the resonance at 122·7 p.p.m. in (B) is difficult to assign, while compound (D) is one of the possible unsymmetrical monocyclic isomers of (C).

Perfluoroalkyl groups stabilise a number of small-ring compounds,[3] including valence-isomers of aromatic compounds,[2,4] but we have no evidence that (**2**) has a significant lifetime when trapped on a cold finger; the product was removed in cold solvent and examined immediately by ^{19}F n.m.r. spectroscopy but the spectrum was identical with those of samples that had been allowed to reach room temperature. Nevertheless, the products described above, are consistent with the generation of (**2**) in the vapour-phase. Similar evidence has been presented recently,[5] for the generation of tetrafluorocyclobutadiene.

(*Received*, 9*th August* 1976; *Com.* 925.)

[1] B. M. Adger, M. Keating, C. W. Rees, and R. C. Storr, *J.C.S. Chem. Comm.*, 1973, 19; C. W. Rees, R. S. Somanathan, R. C. Storr, and A. D. Woodhouse, *ibid.*, 1975, 740; G. Seybold, U. Jersak, and R. Gompper, *Angew. Chem. Internat. Edn.*, 1973, **12**, 847.

[2] R. D. Chambers, J. R. Maslakiewicz, and K. C. Srivastava, *J.C.S. Perkin I*, 1975, 1130.

[3] See *e.g.* C. W. Jefford, U. Burger, W. Broeckx, and J. C. E. Gehret, *Tetrahedron Letters*, 1973, **27**, 2483.

[4] R. D. Chambers, R. Middleton, and R. P. Corbally, *J.C.S. Chem. Comm.*, 1975, 731; M. G. Barlow, R. N. Haszeldine, and M. J. Kershaw, *Tetrahedron*, 1975, **31**, 1649; D. M. Lemal and L. H. Dunlap, *J. Amer. Chem. Soc.*, 1972, **94**, 6562; and references therein.

[5] M. J. Gerace, D. M. Lemal, and H. Ertl, *J. Amer. Chem. Soc.*, 1975, **97**, 5584.