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PRELIMINARY NOTE

Chlorination of Perfluorodiazines

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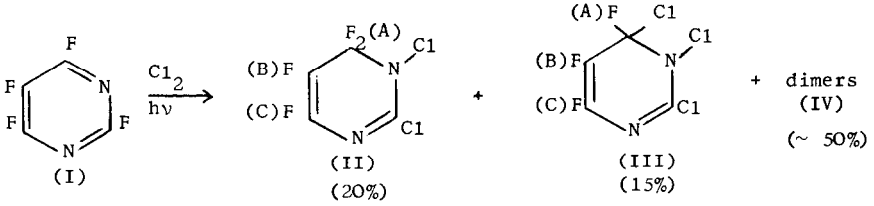
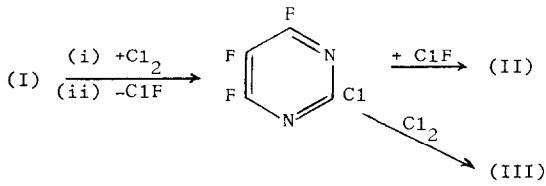
Chlorination of pentafluoropyridine[1] and fluorinations of perfluorodiazines[2] with cobalt trifluoride have been reported. Here we describe some novel products obtained in preliminary experiments involving reactions of tetrafluoro-pyrimidine and -pyrazine with chlorine.

Fluorination of tetrafluoropyrimidine gave a dimer[2] whereas photochemical chlorination gives a mixture of monomeric and dimeric products. The structure

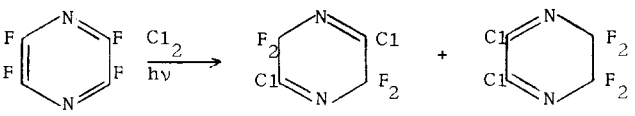


of (II) follows from the ^{19}F n.m.r. spectrum and analysis and is unexpected. The ^{19}F n.m.r. spectrum of (II) shows a prominent AA' system at 89·9 and 95·9 p.p.m. (from $CFCl_3$), $J_{AA'}$ = 205 Hz, which indicates that inversion of the >N-Cl centre is prevented; F_B occurs as a sharp triplet, 143·3 p.p.m. J_{AB} = 15, $J_{A'B}$ = 15 Hz, while F_C occurs as a broadened singlet 29·6 p.p.m. although it could not contain a J value > 5 Hz. Formation of the CF_2 group in (II) seems more likely to occur via production of ClF and then addition, as indicated below, rather than a mechanism involving fluorine atom migration.



The structures of the dimers (IV) have not been established, but g.l.c./m.s. indicates a mixture of $C_8N_4F_{10}Cl_2$, $C_8N_4F_8Cl_6$ and $C_8N_4F_9Cl_5$, presumably formed by coupling through nitrogen, in a process similar to that observed in fluorination of (I).[2] Structure assignment of (III) was made by comparison on the ^{19}F n.m.r. spectrum with data obtained for (II), 98·8(A); 130·1(B); 34·3 p.p.m., J_{A_1B} = 16 Hz.

Tetrafluoropyrazine gave mainly the di-imine (VI), whose structure follow from analysis, m.s. and a singlet ^{19}F n.m.r. spectrum at 78·2 p.p.m. ($CFCl_3$);



(V) (VI) (~50%) (VII) (~10%)

also, the u.v. showed no absorption at all above 220 nm. whereas (VII) showed bands at 215 and 325 nm. Compound (VII) showed a singlet at 98·6 p.p.m. in the ^{19}F n.m.r. spectrum. The formation of the difluoromethylene groups in (VI) a (VII) may be accounted for in a mechanism, involving ClF, similar to that described above for reactions involving tetrafluoropyrimidine.

Tetrafluoropyridazine did not appear to react with chlorine under similar conditions.

1. R.E. Banks, W.M. Cheng, R.N. Haszeldine, and G. Shaw, J. Chem. Soc. (C), (1970) 55.

2. R.D. Chambers, D.T. Clark, T.F. Holmes, W.K.R. Musgrave, and I. Ritchie, J. Chem. Soc. Perkin I, (1974) 114.