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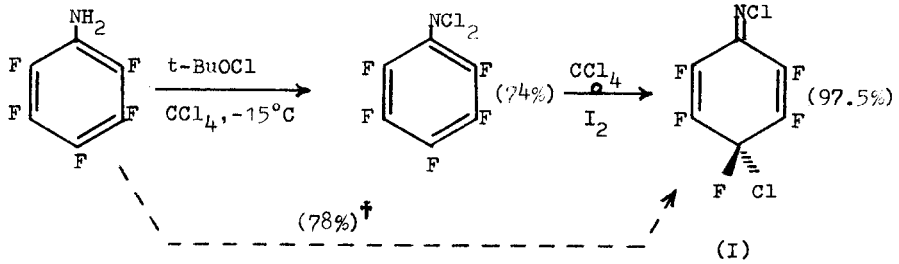
PRELIMINARY NOTE

Thermolysis of N,4-Dichloroperfluorocyclohexa-2,5-dienylideneamine

B. AL-SALEH, R. E. BANKS*, M. G. BARLOW, and J. C. HORNBY

Chemistry Department, The University of Manchester Institute of Science & Technology, Manchester M60 1QD (Great Britain)

Re-consideration of the possibility that NN-dichloroperfluoroaniline might be a useful source of perfluorophenylnitrene [1] led to the work described below which both possesses inherent mechanistic interest and points to a new strategy for the synthesis of polyfluorinated N-heteroaromatics.



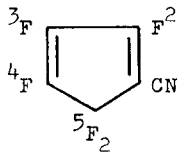
SCHEME 1

† It is not necessary to isolate the NN-dichloroperfluoroaniline [2].

N,4-Dichloroperfluorocyclohexa-2,5-dienylideneamine (I), which is quite easy to prepare (see Scheme 1) [1], resists thermal decomposition when subjected to flow pyrolysis at ca. 1 mmHg pressure in silica (100 x 1 cm tube, heated length 50 cm) at 300 °C. At 550 °C, however, passage of 10.0 g of (I) through the tube during 2.5 h effects its complete conversion [3] into an oil (6.5 g) coloured orange-red by perfluoroazobenzene plus a gas containing chlorine. In addition to the

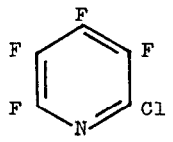
* To whom enquiries should be addressed.

azo-compound, the oil contains at least eleven components (by g.l.c. analysis) only eight (II-IX) of which have been identified owing to isolation problems. From the nature of these products, we conjecture that some of the conversions involved are those shown in Scheme 2. In



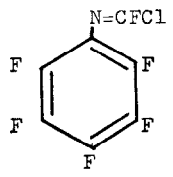
(II)

$\lambda_{max.}$ 4.60 (CN str), 5.70 (CF=CF str), 5.99μm (CF=CCN str); *δ_2 28.0, δ_3 76.3, δ_4 73.0, δ_5 54.6 p.p.m., J_{23} 9.0, J_{24} 2.0, J_{25} 8.3, J_{34} 14.2, J_{35} 5.5, J_{45} 8.6 Hz; m/e 181 (M^+, 100%).



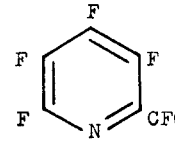
(III)

δ_3 63.1, δ_4 59.8, δ_5 82.3, δ_6 7.7 p.p.m., J_{34} 17.6, J_{35} 4.2, J_{36} 25.6, J_{45} 17.0, J_{46} 15.7, J_{56} 22.2 Hz [5].



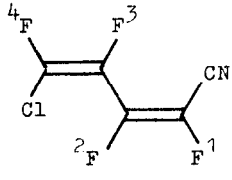
(IV)

δ_{CFCl} -73.8, $\delta_{2,6}$ 75.4, $\delta_{3,5}$ 87.1, δ_4 83.8 p.p.m. [6]; m/e 247 ($C_7F_6N^{35}Cl^+$, 98), 212 ($C_7F_6N^+$, 100%).



(V)

δ_2 -17.8, δ_3 60.9, δ_4 58.6, δ_5 74.6, δ_6 4.9 p.p.m., J_{23} 29.8, J_{34} 17.6, J_{35} 9.3, J_{36} 26.8, J_{45} 16.4, J_{46} 17.5, J_{56} 23.0 Hz [7]; m/e 251 ($C_6F_5N^{35}Cl_2^+$, 16.8), 216 ($C_6F_5N^{35}Cl^+$, 100%).

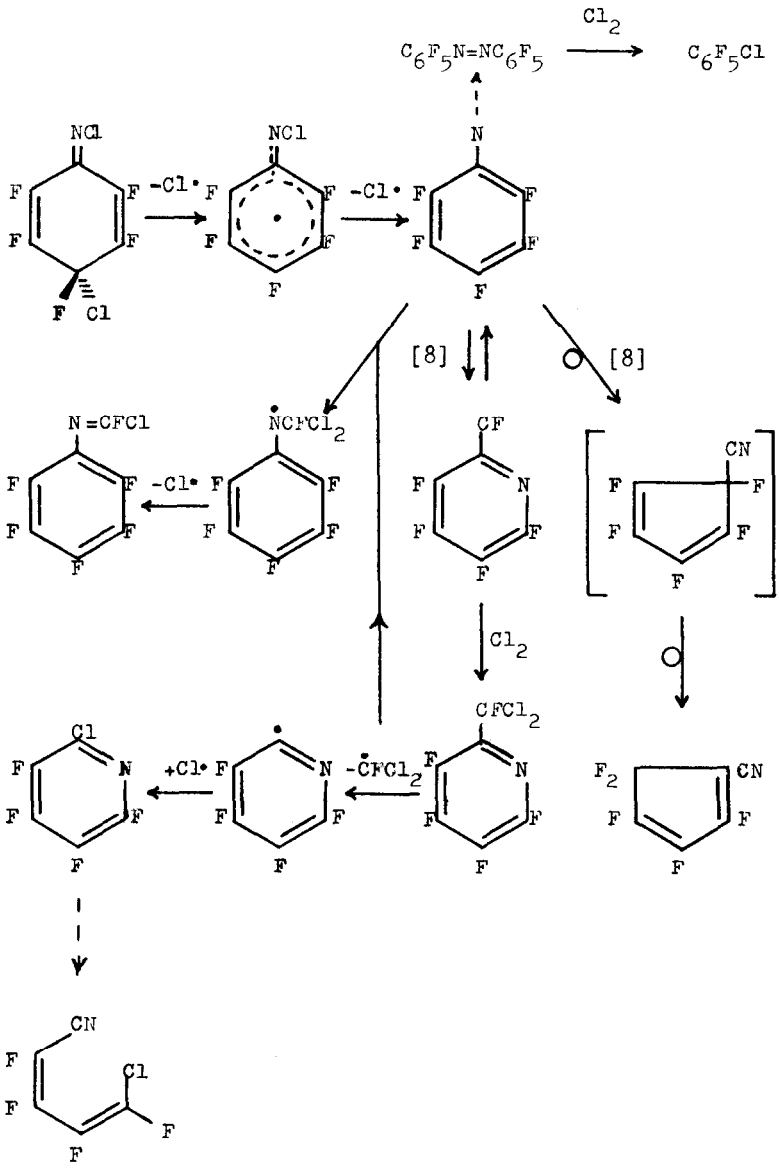


(VI)

δ_1 63.2, δ_2 96.1, δ_3 68.5, δ_4 8.4 p.p.m., J_{12} 10.6, J_{13} 3.2, J_{14} 13.6, J_{23} 38.4, J_{24} 3.4, J_{34} 11.2 Hz.

Known compounds: hexafluorobenzene (VII), chloropentafluorobenzene (VIII), and pentafluoropyridine (IX).

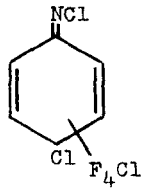
*Positive values of chemical shifts are to high field of trifluoroacetic acid, and magnitudes of coupling constants are quoted.



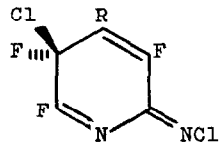
SCHEME 2

support of the suggestion that perfluoroazobenzene functions as a source of chloropentafluorobenzene (the major product), co-pyrolysis of the azo-compound with chlorine at 550 °C/1 mmHg has been shown to produce the perhalogenobenzene in at least 50% yield. Further information

is being sought [4] through study of (i) the pyrolysis of 2-chlorotetrafluoropyridine, (ii) thermolysis of N,4-dichloroperfluorocyclohexa-2,5-dienylideneamine over copper, and (iii) thermal conversions of compounds of type (X) and (XI).



(X)



[R = F,Cl, or $(CF_3)_2CF$]

(XI)

REFERENCES

1 R. E. Banks and T. J. Noakes, J.C.S. Perkin Trans. I, (1976) 143.

2 Dropwise addition of perfluoroaniline (40.0 g, 219 mmol) in AnalaR carbon tetrachloride (300 cm^3) to a cold (-23 °C), stirred solution of t-butyl hypochlorite (48.0 g, 442 mmol) in the same solvent (700 cm^3) followed, after 1 h, by the addition of a small crystal of iodine to the mixture provides N,4-dichloroperfluorocyclohexa-2,5-dienylidene amine in 78% yield (43.0 g, 171 mmol).

3 Only 80% conversion was achieved at 450 °C.

4 B. Al-Saleh, R. E. Banks, M. G. Barlow, G. R. Lomax, and M. Mamaghani, work in progress.

5 Cf. R. D. Chambers, D. Close, W. K. R. Musgrave, J. S. Waterhouse, and D. L. H. Williams, J.C.S. Perkin Trans. II, (1977) 1774.

6 Typical C_6F_5 absorptions; cf. the chemical shifts for $C_6F_5N{=}CCl_2$: T. I. Savchenko, T. D. Petrova, V. E. Platonov, and G. G. Jakobson, J. Fluorine Chem., 9 (1977) 505.

7 Cf. the parameters for perfluoro-(2-methylpyridine): J. Lee and K. G. Orrell, J. Chem. Soc., (1965) 582.

8 For a recent review of interconversions of nitrenes and carbenes, see C. Wentrup, Top. Curr. Chem., 62 (1976) 173.