PRELIMINARY NOTE
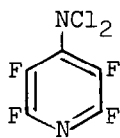
Vacuum Pyrolysis of 4-(Dichloroamino)tetrafluoropyridine
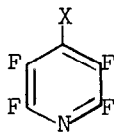and Related Compounds

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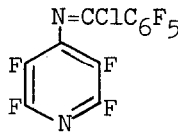Institute of Science and Technology, Manchester M60 1QD
(Great Britain)

Russian investigators [1] have reported recently
that co-pyrolysis of 4-(dichloroamino)tetrafluoropyridine
(I) with pentafluoro(trichloromethyl)benzene in a stream of
nitrogen at 510-520 °C and atmospheric pressure in silica
gives a mixture comprising chloropentafluorobenzene [2],
twelve unidentified compounds, 4-chlorotetrafluoropyridine
(II), and the imidoyl chloride (III) [3]. This prompts
us to disclose knowledge gleaned to-date through work on
the low-pressure flow pyrolysis of the dichloroamino-
compound (I), and of related heterocycles, carried out
as part of a wide-ranging study aimed at providing knowledge
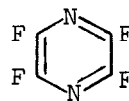about arylnitrenes of the fluorocarbon and chlorocarbon
classes [4].

(I)   (II) X = Cl   (III)   (V)
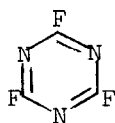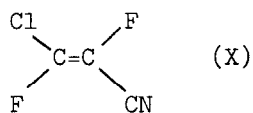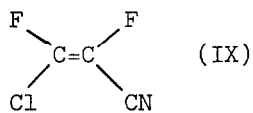   (IV) X = F

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$$
\begin{array}{ccc}
\text{(VI)} & \text{CFCl}_3 & \text{CF}_2\text{=CClCN} \\
 & \text{(VII)} & \text{(VIII)}
\end{array}
$$

(IX)

(X)
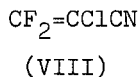
Owing to the nature and complexity [at least 12 components, each of low abundance except one (vide infra)] of the volatile material collected following flow pyrolysis of 4-(dichloroamino)tetrafluoropyridine (I) at 550 °C and ca. 2 mmHg in silica, we have managed to identify only eight products, viz. (II) and (IV)-(X) [6]. The major entity by far is 4-chlorotetrafluoropyridine (II) (estimated yield at least 75%), formation of which is suggested to occur as outlined in Scheme 1. At lower temperatures perfluoro-4,4'-azopyridine (XI) can be detected in the pyrolysate, and, in a separate experiment, this azo-compound has been shown to yield 4-chlorotetrafluoropyridine (II) when co-pyrolysed with chlorine at 550 °C and ca. 1 mmHg in silica [7].

(I) $\xrightarrow[-\text{Cl}\cdot]{\Delta}$ $\qquad \longleftrightarrow \qquad \longleftrightarrow$ etc.

$|||$

(XV) $\quad \text{py}_F\ddot{\text{N}}\colon \;\rightleftharpoons\; \text{py}_F\dot{\text{N}}\colon \;\xleftarrow{-\text{Cl}\cdot}\; \text{py}_F\dot{\text{N}}\text{Cl}$ (XIV)

dimerization $\qquad\qquad$ dimerization

$\text{N}_2 + 2\text{py}_F\text{Cl} \xleftarrow[\Delta]{2\text{Cl}\cdot} \text{py}_F\text{N=Npy}_F \xleftarrow{-2\text{Cl}\cdot} (\text{py}_F\text{NCl})_2$

$\quad$ (II) $\qquad\qquad$ (XI)
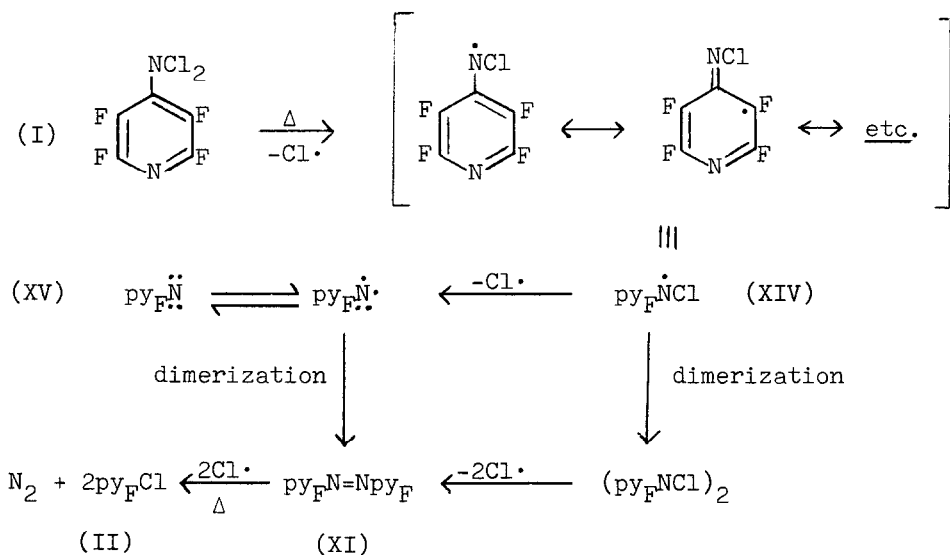
SCHEME 1 [5]

The traces of pentafluoropyridine formed during pyrolysis of the dichloroamine (I) are assumed to have arisen _via_ attack on the major product (II) by fluoride ion at the walls of the silica pyrolysis tube. If the tetrafluoro-pyrazine (V) originated in like manner, _i.e._ fluoride attack on 2-chlorotrifluoropyrazine (XII) formed first, then the situation parallels the production of 2-chlorotetrafluoro-pyridine and pentafluoropyridine, inter alia, by vacuum pyrolysis (550 °C) of N,4-dichlorohexafluorocyclohexa-2,5-dienylideneamine (XIII)[8], a substrate which is arguably a source of the resonance-stabilized nitrogen-centred radical $C_6F_5\overset{\bullet}{N}Cl$ [_cf_. radical (XIV) in Scheme 1] and, subsequently, pentafluorophenylnitrene. Acceptance of this line of argument culminates in the mechanistic proposal formulated in Scheme 2. Further circumstantial evidence for the incursion of tetrafluoro-4-pyridylnitrene (XV) is provided by the formation of the fragmentation products (IX) and (X), and hence of the sym-triazine (VI) (see Scheme 2).
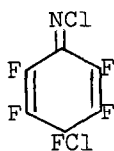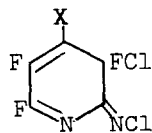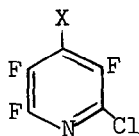

(XIII)
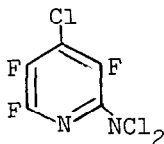
(XVI)
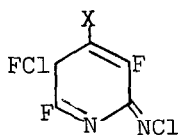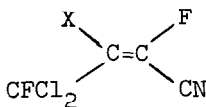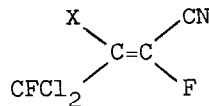
(XVII) X = Cl
(XVIII) X = H

(XIX) X = Cl
(XX) X = H

(XXI) X = Cl
(XXII) X = H

(XXIII) X = Cl
(XXIV) X = H

(XXV) X = Cl
(XXVI) X = H

SCHEME 2 [10,11]

Ring cleavage also occurs during pyrolysis (550 °C and ca. 1 mmHg) in silica of N-chloro-compounds (XVI)-(XVIII) { the last two were contaminated with small amounts (10 and 6%, respectively) of their positional isomers (XIX) and (XX) [12] }. The major product in each case is the corresponding chloropyridine [(XVI) and (XVII) $\longrightarrow$ (XXI) (50 and 54%, respectively); (XVIII) $\longrightarrow$ (XXII) (45%)], and work so far on the remainder of each highly complex pyrolysate has established the presence of the cyanopropenes [(XXIII)-(XXVI)] expected [13] from ring-opening of α-pyridylnitrenes [(XXVII), X = Cl or H] followed, or accompanied, by loss of FCN and coupling reactions involving atomic chlorine (see Scheme 3).

Owing to separation problems, only the major products [(II), (XXI) and (XXII)] were isolated in a pure state and subjected to elemental as well as spectroscopic analysis. All the other products were identified by a combination of i.r., g.l.c.-i.r., n.m.r. (^{19}F), m.s. and g.l.c.-m.s. techniques.
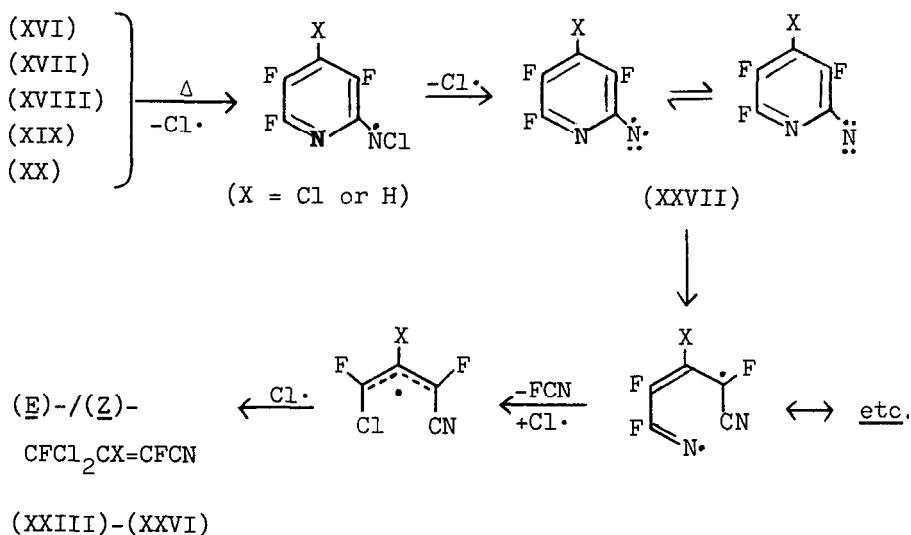
SCHEME 3

1   T.I. Savchenko, T.D. Petrova, V.E. Platonov, and
    G.G. Yakobson, J.Org.Chem. U.S.S.R. (Engl.Transl),
    <u>15</u> (1979) 915.

2   We have observed that flow pyrolysis of $C_6F_5CCl_3$ alone
    at 550 $^{\circ}C$ and <u>ca.</u> 1 mmHg in silica yields $C_6F_5Cl + CCl_4$.

3   The same authors [T.I. Savchenko, T.D. Petrova,
    V.E. Platonov, and G.G. Yakobson, J.Org.Chem. U.S.S.R.
    (Engl. Transl.), <u>15</u> (1979) 909] have also reported on
    the co-pyrolysis of (I) with aliphatic carbene and/or
    radical sources to yield (A) + (II)   [from (I) + $CHCl_3$
    (at 650 $^{\circ}C$) or $CHFCl_2$ (at 700 $^{\circ}C$)] and (B) [from (I) +
    CHF_2Cl or C_2F_4 (both at 740 $^{\circ}C$)] (the other products
    were not defined); co-pyrolysis of (I) with CCl_4 apparently
    gave unidentified products like those obtained using $C_6F_5CCl_3$.
    No mechanisms relevant to our work were presented in either
    paper.

(A)

(B)
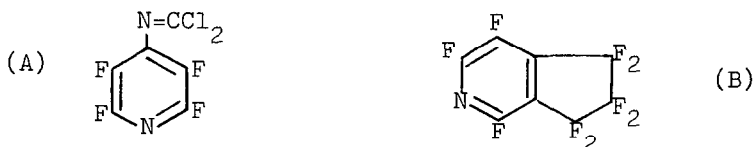
4   See, for example, R.E. Banks, T.A. Hamor, and
    N.D. Venayak, J.Chem.Soc., Chem. Commun., (1980)
    900; R.E. Banks, M.G. Barlow, and N.D. Venayak, <u>ibid.</u>,
    p.151; R.E. Banks, A. Prakash, and N.D. Venayak, J. Fluorine
    Chem., <u>16</u> (1980) 325; and references cited therein.

5   This scheme is adapted from that proposed to account
    for the formation of $4-F_3CC_6F_4N=NC_6F_4CF_3-4'$ and
    $4-F_3CC_6F_4Cl$ <u>via</u> vacuum pyrolysis of $4-F_3CC_6F_4NCl_2$; the
    pyrolysate in this case also contains, <u>inter alia</u>,
    perfluoro-(2-dichloromethyl-4-methylpyridine) and per-
    fluoro(1-cyano-4-methylcyclopenta-1,3-diene), formation
    of which provides evidence for the initial generation of
    perfluoro-<u>p</u>-tolylnitrene [B.A. Al-Saleh, R.E. Banks, and
    M.G. Barlow, J.Chem.Soc., Chem. Commun., in the press].
    More work is required on the complex pyrolysate to
    determine the nature of the fragmentation products.

6   Identification of all 12 (or more) components has been thwarted by the difficulty of the g.l.c. separation required.

7   B.A. Al-Saleh, R.E. Banks, and M.G. Barlow, unpublished results (see, however, ref. 8). The sequence $Ar_F F \longrightarrow$ (with NH_3 aq.) $Ar_F NH_2 \longrightarrow$ (with t-BuOCl) $Ar_F NCl_2 \longrightarrow$ (ca. 160 °C) $Ar_F N=NAr_F \longrightarrow$ (with Cl_2 at 550 °C and 1 mmHg) $Ar_F Cl$ has been carried through for the cases where Ar_F = C_6F_5 (67% yield of $Ar_F Cl$ in the final stage), $4-F_3CC_6F_4$ (92%), $2,3,5,6-F_4C_5N$ (59%), and $4-Cl-3,5,6-F_3C_5N$ (68%).

8   B.A. Al-Saleh, R.E. Banks, M.G. Barlow, and J.C. Hornby, J. Fluorine Chem., 12 (1978) 341.

9   In support of this proposal, formation of C_6F_5Cl has been observed to occur when $C_6F_5CFCl_2$ is co-pyrolysed with Cl_2 at 550 °C and ca. 1 mmHg [7].

10   The arylnitrene $\rightleftharpoons$ arylcarbene interconversion shown here is certainly not without precedent [C. Wentrup, Top.Curr.Chem., 62 (1976) 173; idem, 'Reactive Intermediates', ed. R.A. Abramovitch, Plenum Press, N.Y. and London, 1980, Vol.1, p.263]; and sound evidence has been discovered for ring-expansion of pentafluoro-phenylnitrene to the corresponding 2-azepinylidene [R.E. Banks, T.A. Hamor, and N.D. Venayak, J.Chem.Soc., Chem. Commun., (1980) 900].

11   No decision has been reached yet about the origin of the isomer of (IX) and (X), $CF_2=CClCN$ (VIII).

12   R.E. Banks, M.G. Barlow, J.C. Hornby and M. Mamaghani, J.Chem.Soc., Perkin Trans. I, (1980) 817. As can be seen from Scheme 3, each of the isomers is expected to yield the same products.

13   C. Wentrup, Top.Curr.Chem., 62 (1976) 173.