

PRELIMINARY NOTE

Iodine-catalyzed Rearrangement of Polyfluorinated
2-(Dichloroamino)pyridines

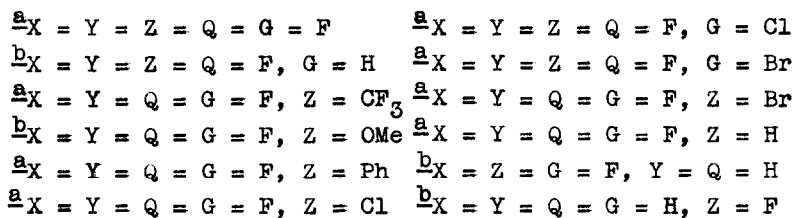
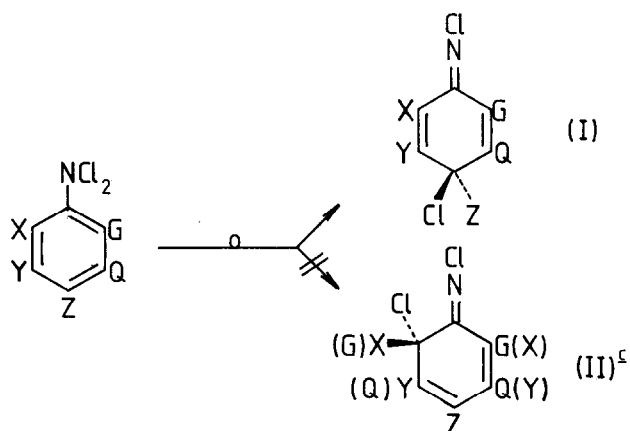
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Numerous examples of iodine-catalyzed or 'spontaneous' rearrangement of fluorine-containing NN-dichloroanilines to N,4-dichlorocyclohexadienylideneamines have been studied [1-4], and in each case formation of only one [viz. the 2,5-isomer (I)] of the two possible chloriminocyclohexadienes has been observed (see Scheme 1). N-Chlorination of 2-aminoheptafluoronaphthalene [6] appeared to provide only the corresponding N-chloro-imine containing a 2,4-dienic moiety [as in (II)], which is not unexpected since 'para-migration' of an N-chloro substituent would have disrupted the aromatic sextet in ring A (see Scheme 2). In the pyridine series, attempts to force 4-(dichloroamino)tetrafluoropyridine [7] or 3-chloro-4-(dichloroamino)trifluoropyridine [3] to isomerize led to the formation of the corresponding azo-compounds.

As part of an investigation of skeletal rearrangements which occur when N,4-dichlorocyclohexa-2,5-dienylideneamines are thermolyzed [8], work aimed at the synthesis of aza-analogues of the 2,5-dienes (I) was undertaken. This has provided the first examples of iodine-catalyzed rearrangement of monocyclic dichloroaminoarenes to chloriminocyclohexa-2,4-dienes (see Scheme 3). A single attempt to isolate

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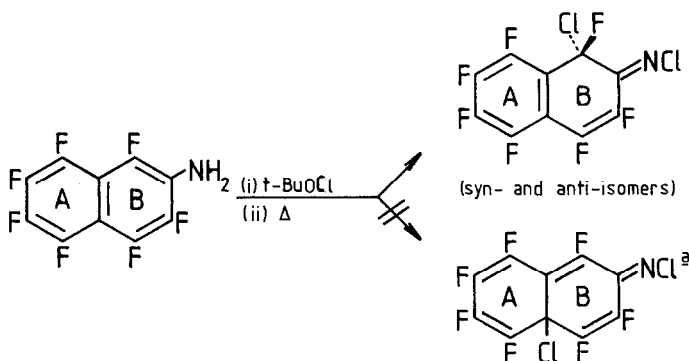


SCHEME 1 [5]

^aIodine-catalyzed.

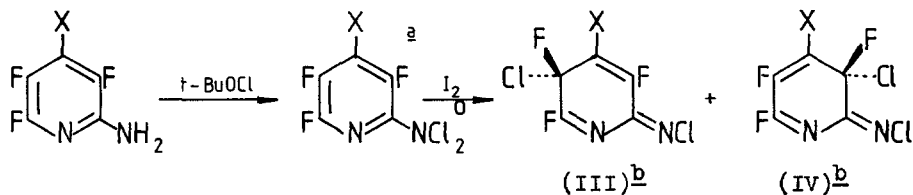
^b'Spontaneous' rearrangement occurs during attempted isolation.

^cNone detected by ¹⁹F n.m.r.



SCHEME 2

^aNone detected by ¹⁹F n.m.r.



X = H, (III) : (IV) = 94 : 6^c

X = Cl, (III) ; (IV) = 90 : 10^c

X = CF(CF₃)₂, (III) : (IV) = 60 : 40^c

SCHEME 3

^aYields: X = H, 96%; X = Cl, 82%; X = CF(CF₃)₂, 77%

^bCombined yields of (III) + (IV): X = H, 86%; X = Cl, 87%;
X = CF(CF₃)₂, 60%

^cRatios determined by ¹⁹F n.m.r.

2-(dichloroamino)-3,5,6-trifluoro-4-methylpyridine following treatment of the corresponding NH₂-compound with t-butyl hypochlorite failed, removal of solvent (CCl₄) at the end of the reaction providing a mixture of the 2,5-diene (III; X = Me) and, through attack on that product by adventitious moisture, the amide (V). Treatment of the mixtures (III + IV) where X = H or Cl with water rapidly gave amides (VI) and (VII), the corresponding products derived from nucleophilic displacement of the imidoyl fluorine from the *minor* isomer (IV) in each case not being detected by ¹⁹F n.m.r. spectroscopy.

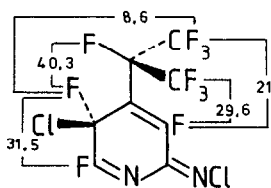


(V) X = Me

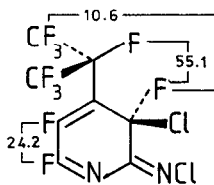
(VI) X = H

(VII) X = Cl

The structures of the 6-chlorimino-1-azacyclohexadienes (III) and (IV) [$X = H, Cl, \text{ or } CF(CF_3)_2$] were determined by ^{19}F n.m.r. spectroscopic examination of their mixtures* [only in the case of the 4-chloro system was it possible to isolate (by g.l.c.) a pure sample of the major isomer (III; $X = Cl$)]. Interestingly, the 4-heptafluoroisopropyl-compounds (III) and (IV) [$X = CF(CF_3)_2$] are judged to be 'locked' conformationally [see (VIII) and (IX)] with non-equivalent CF_3 groups in each isomer and substantial 'through space' coupling of the tertiary fluorine to the adjacent olefinic fluorine; this can be ascribed to the buttressing effect of the chlorines of the adjacent $CFC1$ groups.



(VIII)



(IX)

(N.m.r. coupling constants in Hz)

Further work is in progress to determine the factors affecting the ratio of 'ortho' (\rightarrow -chloriminocyclohexa-2,4-dienes) to 'para' (\rightarrow -chloriminocyclohexa-2,5-dienes) migration of N-chlorine substituents during iodine-catalyzed rearrangements of NN-dichloroamino-arenes and -hetarenes.

REFERENCES

- 1 R.E. Banks and T.J. Noakes, J.C.S. Perkin Trans. I, (1976) 143.
- 2 R.E. Banks, M.G. Barlow, and T.J. Noakes, J. Fluorine Chem., 10 (1977) 45.

*Correct elemental analyses were obtained for the mixtures and for all the other new compounds encountered in this work.

- 3 R.E. Banks, M.G. Barlow, T.J. Noakes, and M.M. Saleh, J.C.S. Perkin Trans. I, (1977) 1746.
- 4 R.E. Banks, M.G. Barlow, J.C. Hornby, and T.J. Noakes, J. Fluorine Chem., 13 (1979) 179.
- 5 Russian workers [Yu.G. Shermolovich, O.M. Polumbrik, L.N. Markovskii, E.P. Saenko, G.G. Furin, and G.G. Yakobson, J. Org. Chem. U.S.S.R., 13 (1977) 2404] have checked our [1] observations on the iodine-catalyzed rearrangement of NN-dichloroperfluoroaniline and, independently (cf. [3]), studied the analogous rearrangement of NN-dichloroperfluoro-p-toluidine; they too failed to detect the formation of the corresponding 2,4-dienes (II; X = Y = Z = Q = G = F; X = Y = Q = G = F, Z = CF₃).
- 6 R.E. Banks, M.G. Barlow, and M.M. Saleh, J. Fluorine Chem., 10 (1977) 81.
- 7 R.E. Banks and T.J. Noakes, J.C.S. Perkin Trans. I, (1975) 1419.
- 8 B. Al-Saleh, R.E. Banks, M.G. Barlow, and J.C. Hornby, J. Fluorine Chem., 12 (1978) 341.