New Naphthalene-to-indene Ring-contraction: Synthesis of Perfluoro-2-cyanoindene *via* *N*-Chlorination of Perfluoro-2-aminonaphthalene

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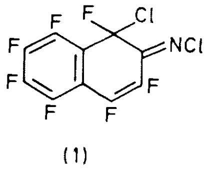
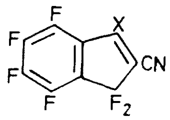
Summary Flow pyrolysis of *N*,1-dichloroperfluoro-(1,2-dihydro-2-naphthylideneamine) provides perfluoro-2-cyanoindene.



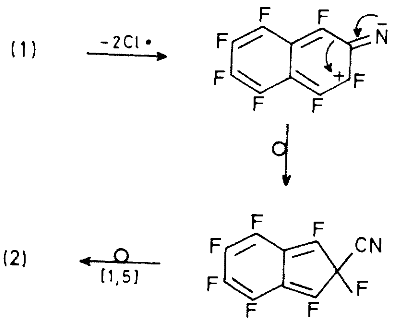
(1)



(2) X = F
(3) X = OEt
(4) X = N₃

The complex mixture produced by flow pyrolysis of the perfluorodichloronaphthylideneamine (**1**) in silica at 570 °C and <1 mmHg comprises one major component, isolable in at least 45% yield by g.l.c. This was shown by elemental and spectroscopic (mainly n.m.r.) analyses[†] to be perfluoro-2-cyanoindene (**2**). The same cyanoindene was obtained when perfluoro-2-azidonaphthalene was pyrolysed (at *ca.* 300 °C and 5 mmHg in silica), but yields were low (<5%) since experiments were prematurely terminated by explosions.

The conversion (**1**) → (**2**), speculated to occur as shown in the Scheme, is noteworthy for two reasons: (i) it completes a simple three-stage route into polyfluoroindene chemistry[1] starting from commercially available perfluoronaphthalene [→(with NH_3) $C_{10}F_7NH_2$-2 (58%)[2]→(with Bu^tOCl) (**1**) (68%)[3]]; and (ii) it provides further circumstantial support for the hypothesis[4] that *N*-chloroimines derived from fluorinated arylamines constitute a new class of nitrene precursors.



Scheme

[†] With $\nu_{max.}$ 2232 cm^{-1} (C≡N str.) and δ_F (negative values to high field of external trifluoroacetic acid) −19·2 (F-3), −39·0 (F-1), −60·5 (F-7), −61·3 (F-4), −68·3 (F-6), and −69·3 (F-5) p.p.m., and the coupling constant moduli $J_{13} = 8{\cdot}3$, $J_{14} = 3{\cdot}2$, $J_{15} \leqslant 1$, $J_{16} \leqslant 1$, $J_{17} = 4{\cdot}3$, $J_{34} = 15{\cdot}4$, $J_{35} \leqslant 1$, $J_{36} = 4{\cdot}0$, $J_{37} = 11{\cdot}5$, $J_{45} = 18{\cdot}3$, $J_{46} = 7{\cdot}2$, $J_{47} = 15{\cdot}3$, $J_{56} = 15{\cdot}2$, $J_{57} = 7{\cdot}8$, and $J_{67} = 18{\cdot}3$ Hz. The assignment follows from an analysis of the spectra of perfluoroindene and some of its derivatives, and the absence of substantial coupling of the olefinic fluorine to F-6 rules out the 3-cyano-isomer [R. S. Matthews and W. E. Preston, *Org. Magnetic Resonance*, in the press, quote the ranges $|J_{36}| = 4{\cdot}4$—$4{\cdot}9$ and $|J_{26}| = 15$ Hz (3 values)].

Previously,[5] pyrolysis of N,4-dichloroperfluorocyclohexa-2,5-dienylideneamine gave products which can be accounted for in part by initial formation of perfluorophenylnitrene; one of these was perfluoro-1-cyanocyclopentadiene (<5%), the analogue of perfluoro-2-cyanoindene (**2**). The favourable effect of annelation on the yield of the ring-contraction product in the case of the N-chloroimine (**1**) finds analogy in the hydrocarbon field, where the corresponding ring-contraction of 2-naphthylnitrene results in the formation of both 2- and 3-cyanoindene.[6]

Perfluoro-2-cyanoindene is highly susceptible to nucleophilic attack, yielding derivatives (**3**) and (**4**) with ethanol and sodium azide (in MeCN), respectively.

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[1] For details of other routes see: R. E. Banks, A. C. Harrison, and R. N. Haszeldine, *J. Chem. Soc. (C)*, 1966, 2102; W. J. Feast and W. E. Preston, *Tetrahedron*, 1972, **28**, 2805; E. P. Ivanova, V. M. Karpov, V. E. Platonova, G. P. Tataurov, G. G. Yakobson, and O. M. Yakhlakova, *Bull. Acad. Sci., U.S.S.R. Div. Chem. Sci.*, 1972, 733; V. M. Karpov, V. E. Platonov, and G. G. Yakobson, *J. Org. Chem. (U.S.S.R.)*, 1974, **10**, 663.

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[3] R. E. Banks, M. G. Barlow, and M. M. Saleh, *J. Fluorine Chem.*, 1977, **10**, 81.

[4] R. E. Banks and T. J. Noakes, unpublished work.

[5] B. Al-Saleh, R. E. Banks, M. G. Barlow, and J. C. Hornby, *J. Fluorine Chem.*, 1978, **12**, 341.

[6] C. Wentrup, *Topics in Current Chem.*, 1976, **62**, 173.