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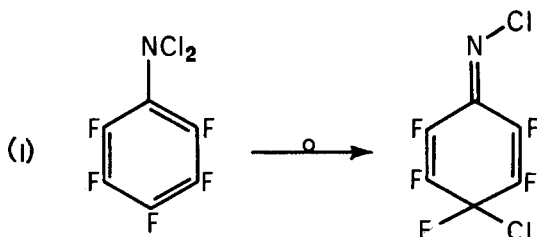
SHORT COMMUNICATION

N-Halogeno-compounds. Part IV [1]. N-Chlorination of
2-Aminoheptafluoronaphthalene

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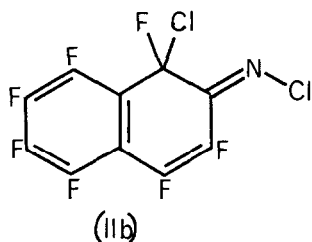
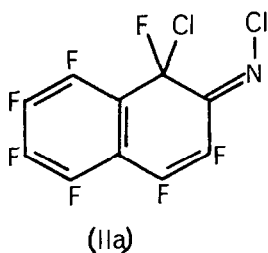
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Electrophilic chlorination of pentafluoroaniline with *t*-butyl hypochlorite yields NN-dichloropentafluoroaniline (I), isolation of which requires care if loss of material via the rearrangement



is to be avoided [2]. Similar rearrangement of the fused-ring analogue of (I), 2-(dichloroamino)heptafluoronaphthalene, appears to occur with ease since only a product comprised mainly of a 50:50 mixture of the isomeric N-chloroimines (IIa) and (IIb) could be isolated following treatment of 2-aminoheptafluoronaphthalene with *t*-butyl hypochlorite.

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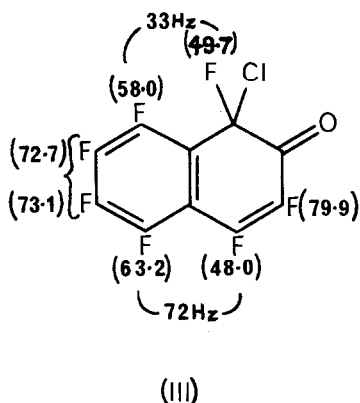


Short-path distillation (bath temp., 30°C; pressure, ca. 0.02 mmHg) of the oily brown residue left after evaporation (at 10°C and ca. 0.2 mmHg) of the solution obtained by adding 2-aminoheptafluoronaphthalene (1.03 g, 3.82 mmol) in AnalaR chloroform (60 cm³) to a cold (ca. -15°C) stirred solution of t-butyl hypochlorite (1.0 g, 9.2 mmol) in Analar carbon tetrachloride (50 cm³) provided a tan-coloured oil (0.89 g, 2.6 mmol, 68%) { Found: C, 35.6; 'positive' Cl (iodometric detn. [2]), 10.5; F, 39.6; N, 4.4. Calc. for C₁₀Cl₂F₇N: C, 35.5; Cl, 21.1; F, 39.3; N, 4.1% } , which was examined (as a solution in CCl₄) by ¹⁹F n.m.r. spectroscopy (at 56.46 and 94.1 MHz). Apart from bands caused by small amounts of unidentified material, the absorptions in the highly complex spectrum fell in three regions, all to high field of external CF₃.CO₂H : (i) 37.3 (d, 46 Hz) and 37.5 (d, 32 Hz) p.p.m. (CFC1 groups); (ii) 54.5 (d, 70 Hz), 55.0 (br., complex), 56.4 (br., complex d, 44 Hz), 57.7 (d, 72 Hz), 61.5 (br. d, 68 Hz), and 63.0 (br. d, 70 Hz) p.p.m.; and (iii) 71-73 (highly complex, probably 5 fluorine nuclei) and 73.8 (br.) p.p.m. These observations are consistent with the presence of approximately equal amounts of the syn and anti isomers of the hitherto unreported perfluoro-(4,5-benzo-N,6-dichlorocyclohexa-2,4-dienylideneamine) (IIa, b).

The fluorines of the CFC1 groups in these isomers show substantial coupling to the pseudo-peri fluorines, which absorb at 55.0 and 56.4 p.p.m. The bands at 54.5

and 57.7 p.p.m. are caused by the olefinic fluorines (at C3, one in each isomer) coupled to the peri-fluorines at 61.5 and 63.0 p.p.m. One of the remaining olefinic (C2) fluorines absorbs at 73.8 p.p.m., and the corresponding band for the other isomer occurs in the 71-73 p.p.m. region together with the absorptions for the remaining aromatic fluorines (two for each isomer).

Substantial (60-70 Hz) coupling, mainly of 'through-space' origin, occurs between peri-fluorines in fluoronaphthalenes [3], and it is noteworthy that a similar interaction exists with respect to the CFC1 fluorines of the N-chloroimines (IIa) and (IIb) despite the non-coplanar (*i.e.* pseudo-peri) situation. Since the chlorine of the =NCl group in isomer (IIa) should exert a buttressing effect on the fluorine of the adjacent CFC1 group, the absorption (at 37.3 p.p.m.) associated with the pseudo-peri coupling of higher magnitude (46 Hz) is ascribed to that isomer; in support of this, the related dienone (III) exhibits a corresponding coupling of 33 Hz [4], *i.e.* of value close to that (32 Hz) now ascribed to the pseudo-peri coupling in isomer (IIb). The expected similarities exist between the other spectral parameters of the dienone (III) and those of the N-chloroimines (IIa) and (IIb).



(The chemical shifts are in p.p.m. upfield from $\text{CF}_3\text{CO}_2\text{H}$ and obtained by subtracting the $\delta_{\text{C}_6\text{F}_6}$ values in the literature [4] from 88.0 p.p.m.)

- 1 Part III, R.E. Banks, M.G. Barlow, T.J. Noakes and M.M. Saleh, submitted for publication in J.C.S. Perkin Trans. I.
- 2 R.E. Banks and T.J. Noakes, J.C.S. Perkin Trans. I, (1976) 143.
- 3 R.A. Fletton, R.D. Lapper and L.F. Thomas, J.C.S. Chem. Comm., (1969) 1049.
- 4 N.E. Akhmetova, N.G. Kostina, V.I. Mamatyuk, A.A. Shtark and V.D. Shteingarts, Izvest. Sibirsk. Otdel. Akad. Nauk, Ser. Khim. Nauk (U.S.S.R.), (1973) 86 . The actual ^{19}F n.m.r. spectrum of the bromo-analogue of the chloro-compound (III) is reproduced in this paper.