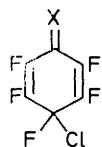


NN-Dichloroperfluoroaniline

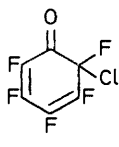
By Ronald E. Banks* and Timothy J. Noakes, Chemistry Department, The University of Manchester Institute of Science and Technology, Manchester M60 1QD

NN-Dichloroperfluoroaniline has been prepared by chlorination of perfluoroaniline with *t*-butyl hypochlorite. It oxidises iodide ion to iodine, converts anisole into a mixture of *o*- and *p*-chloroanisole, yields perfluoroazobenzene when pyrolysed, and rearranges to *N*,4-dichloropentafluorocyclohexa-2,5-dienylideneamine when treated with a catalytic quantity of iodine. The *N*-chloro-imine gives a 1 : 4 adduct with bistrifluoromethyl nitroxide and a 1 : 1 Diels-Alder adduct with cyclopentadiene, and provides 4-chloropentafluorocyclohexa-2,5-dienone and a compound believed to be 3,4-dichlorotetrafluorocyclohexa-2,5-dienone when hydrolysed with hydrochloric acid.

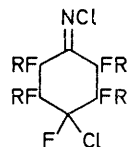
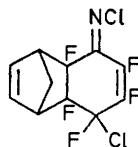
CHLORINATION of perfluoroaniline was undertaken with the objective of providing a cheaper alternative to 4-(dichloroamino)tetrafluoropyridine¹ for use in an investigation of new routes to perfluorinated aryl nitrenes.² *NN*-Dichloroperfluoroaniline was obtained, but initially proved troublesome to isolate owing to its tendency to isomerise to *N*,4-dichloropentafluorocyclohexa-2,5-dienylideneamine (1), a property that has caused the original plan to be abandoned.



(1) X=NCl



(2) X=O

(3) R=(CF₃)₂N·O

(4) R=O

increases when purification by distillation is attempted. The lemon-yellow, oily *NN*-dichloro-amine can be stored in the dark at 20 °C for several days before formation of the *N*-chloro-imine becomes noticeable; the rate of isomerization increases if the temperature is raised and formation of chlorine and perfluoroazobenzene also begins to occur. Flash pyrolysis of the *NN*-dichloro-amine at 160 °C provides perfluoroazobenzene in high yield. The pronounced positive character of the chlorine substituents in *NN*-dichloroperfluoroaniline is revealed by the ease with which the compound reacts with hydrogen iodide to yield iodine and perfluoroaniline and effects electrophilic chlorination of anisole.

The *N*-chloro-imine (1), a high-boiling pale-yellow oil, can be obtained rapidly and quantitatively by adding a small crystal of iodine to a dilute solution of *NN*-dichloroperfluoroaniline in AnalaR carbon tetrachloride. In the absence of solvent, isomerization proceeds almost explosively and the heat generated causes formation of much perfluoroazobenzene. Hexamethylphosphoramide shows a catalytic activity similar to that of iodine, and iodine-free iodo-methane or -benzene can be

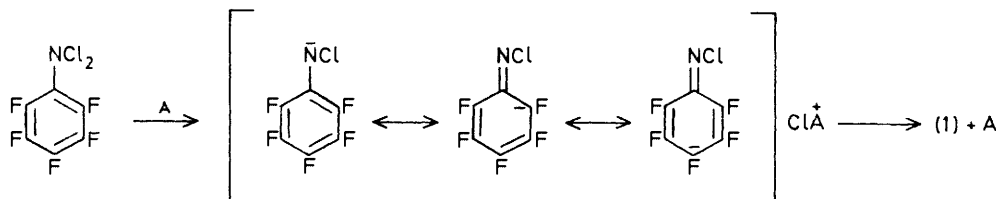
Treatment of perfluoroaniline with *t*-butyl hypochlorite in pure carbon tetrachloride at -15 to +20 °C provides *NN*-dichloroperfluoroaniline in at least 74% yield; use of laboratory-grade carbon tetrachloride or of ether or acetone as solvent gives product contaminated with the *N*-chloro-imine (1), the concentration of which

¹ R. E. Banks and T. J. Noakes, *J.C.S. Perkin I*, 1975, 1419.

² R. E. Banks and M. M. Saleh, work in progress.

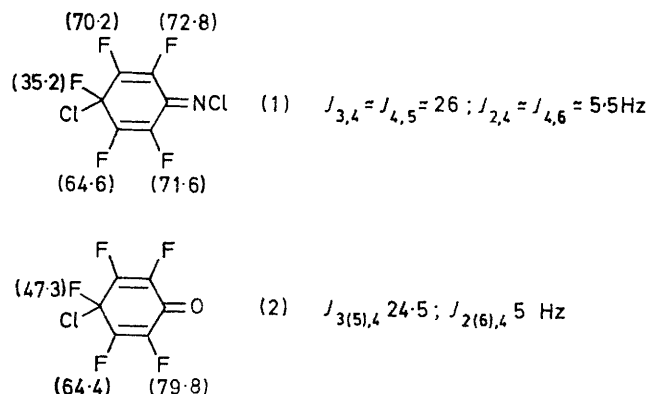
used to effect controlled rearrangement of neat *NN*-dichloroperfluoroaniline at room temperature, reaction being complete within 2 h. Detailed discussion of the mechanism of the rearrangement is deferred until work on substituted (dichloroamino)tetrafluorobenzenes is finished; the results so far are not inconsistent with a mesomeric nitranionic intermediate (see Scheme).

The structure of the *N*-chloro-imine (1) was established by i.r., u.v., and ^{19}F n.m.r. (see Figure) spectroscopy, and is consistent with the results of a gas-phase electron diffraction investigation;³ particularly helpful was the availability of spectroscopic data for the related dienone



SCHEME A(Cl⁺ acceptor) = I₂, IR (R = Me or Ph), or O : P(NMe₃)₃

(2) and its isomer (3),⁴ notably ^{19}F n.m.r. parameters. Chemically, the imine was found to contain one 'positive' chlorine per molecule (KI reaction) and two C:C bonds



^{19}F n.m.r. data [chemical shifts are upfield from $\text{CF}_3\text{CO}_2\text{H}$, those for the dienone (2) being obtained by subtracting the $\delta_{\text{C},\text{F}}$ values⁴ from 88 p.p.m.]

[treatment with bistrifluoromethyl nitroxide to give the 4:1 adduct (4)], to act as a dienophile towards cyclopentadiene [giving the Diels–Alder adduct (5)], and to undergo hydrolysis to the 2,5-dienone (2) when heated with dilute hydrochloric acid; treatment of the imine with cold concentrated hydrochloric acid provided a compound believed (from ^{19}F n.m.r. data) to be 3,4-dichlorotetrafluorocyclohexa-2,5-dienone.

EXPERIMENTAL

N.m.r. absorptions to high field of the reference are assigned negative shift values.

NN-Dichloroperfluoroaniline.—A solution of commercial (Fluorochem Ltd.) perfluoroaniline (20.0 g, 109 mmol) in carbon tetrachloride (200 cm³) was dripped slowly into a cold (−15 °C), stirred solution of *t*-butyl hypochlorite (24.0 g, 221 mmol) in AnalaR carbon tetrachloride (500 cm³). The mixture was stirred at *ca.* −15 °C for 1 h then warmed to room temperature and evaporated at water-pump pressure.

The residue (*ca.* 35 cm³) was transferred to a simple distillation unit comprising a flask attached to a vacuum system *via* a modified Dean–Stark head equipped with a cold-finger condenser and a detachable closed-end collection tube; with no coolant in the condenser, the stirred distilland was kept at 20 °C while residual carbon tetrachloride and some *t*-butyl alcohol were pumped away at *ca.* 10 mmHg; then, with no change in stillpot temperature and the receiver cooled to *ca.* −70 °C, the pressure was lowered to 0.1 mmHg to provide a mixture (4.0 g) of *t*-butyl alcohol and *NN*-dichloroperfluoroaniline, which was discarded, and *NN*-dichloroperfluoroaniline (20.4 g, 80.95 mmol, 74%) (Found: C, 28.5; Cl, 28.4; F, 37.3; N, 5.7. C₆Cl₂F₅N requires C,

28.6; Cl, 28.1; F, 37.7; N, 5.6%), a lemon-yellow liquid, m.p. *ca.* −10 °C, λ_{max} [film; fast scan otherwise bands caused by the formation of perfluoroazobenzene and the *N*-chloro-imine (1) appear] 6.62 μm (C₆F₅ nucleus; strongest absorption present), δ_{F} (56.5 MHz; neat liq.; ext. CF₃CO₂H) −66.6 (2- and 6-F), −75.4 (4-F, $J_{3,4}$ 21, $J_{2,4}$ 4 Hz), and −86.0 p.p.m. (3- and 5-F) (rel. int. 2 : 1 : 2).

Reactions of NN-Dichloroperfluoroaniline.—(a) *With iodides.* Iodine was liberated immediately when the dichloro-compound (0.2022 g, 0.8024 mmol) was dissolved in a solution of potassium iodide (0.4 g, 1.5 mmol) in 4 : 1 (v/v) acetone–water. The amount present in the mixture after it had been kept at 20 °C overnight was determined by titration against sodium thiosulphate (Found: 0.771 mmol, 48% based on NCl=I₂). The low iodine value is ascribed to isomerization of the *NN*-dichloro-amine to the *N*-chloro-imine (1).

Hydrogen iodide (2.05 g, 16 mmol) was condensed, *in vacuo*, into a cold (−196 °C) Pyrex tube (300 cm³) containing the *NN*-dichloro-compound (1.0 g, 4.0 mmol). The tube was sealed, allowed to warm to room temperature, then left for 1 h. Work-up of the iodine-containing product by standard techniques provided perfluoroaniline (0.55 g, 3.0 mmol, 75%).

(b) *Thermolysis.* An ignition tube containing *NN*-dichloroperfluoroaniline (0.2 g, 0.8 mmol) was plunged into a hot (160 °C) oil-bath. When the vigorous evolution of chlorine had ceased (30 s), the brownish-red product was cooled to 20 °C and then recrystallised from petroleum (b.p. 60–80 °C) to provide orange plates of perfluoroazobenzene (0.12 g, 0.33 mmol; 82.5%), m.p. and mixed m.p.

³ B. Beagley, A. Foord, and T. J. Noakes, in preparation.

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*, 1973, 86 (the actual n.m.r. spectra are reproduced); N. E. Akhmetova, A. A. Shtark, and V. D. Shteingarts, *J. Org. Chem. (U.S.S.R.)*, 1973, 9, 1246 (i.r. and u.v. data; see also L. Denivelle, R. Chesneau, and H. A. Hoa, *Compt. rend.*, 1970, 271, 192). The ^{19}F n.m.r. spectra of a number of 4-substituted pentafluorocyclohexa-2,5-dienones are reproduced in an earlier Russian paper [A. G. Budnik, V. D. Shteingarts, and G. G. Yakobson, *J. Org. Chem. (U.S.S.R.)*, 1970, 6, 1204], which also gives i.r. and u.v. data.

142—143 °C (lit.,⁵ 143 °C), identical (i.r. spectrum) with an authentic specimen.

(c) *Rearrangement.* A small crystal of iodine was added to a stirred solution of *NN*-dichloroperfluoroaniline (20.0 g) in AnalaR carbon tetrachloride (200 cm³). After 15 min the product was evaporated at 50—60 °C and water-pump pressure to remove most of the carbon tetrachloride. Distillation of the residual orange oil gave *N,4-dichloropentafluorocyclohexa-2,5-dienylideneamine* (19.5 g, 97.5%) (Found: C, 28.6; Cl, 28.2; F, 37.7; N, 5.7. C₆Cl₂F₆N requires C, 28.6; Cl 28.1; F, 37.7; N, 5.6%), a pale yellow liquid, m.p. ca. -13 °C, b.p. 67—69 °C at 10 mmHg, λ_{max.} (film); the spectrum of the same sample was measured four times and no changes occurred) 5.76 m and 5.93 vs μm (CF=CF str.; presumably coupled oscillators), λ_{max.} (hexane) 263 (ε 26 200) nm, δ_F (94.1 MHz; neat liq.; CF₃·CO₂H lock) -35.15 (4-F, t of t), -64.6 (3-F, d of d of t), -70.2 (5-F, d of d of d), -71.6 (2-F, d of d of d), and -72.8 p.p.m. (6-F, d of d of d) (rel. int. 1 : 1 : 1 : 1).

(d) *With anisole.* A solution of *NN*-dichloroperfluoroaniline (1.0 g, 4.0 mmol) in anisole (29.0 cm³) was stored at 20 °C for 48 h then analysed by a combination of t.l.c., g.l.c., and high-pressure liquid chromatography. Besides anisole, it contained perfluoroaniline (0.8 mmol, 20%), *p*-chloroanisole (1.1 mmol, 14% based on 1 C₆F₅NCl₂ giving 2 *p*-ClC₆H₄·OMe), *o*-chloroanisole (0.3 mmol, 4%), perfluoroazobenzene (0.8 mmol, 40%), and several unidentified products.

Reactions of the N-Chloro-imine (1).—(a) *With iodide ion.* A homogeneous mixture of the *N*-chloro-imine (0.2120 g, 0.8413 mmol), potassium iodide (1.0 g), 2*M*-hydrochloric acid (2 cm³), water (10 cm³), and acetone (60 cm³) was shaken at 20 °C for 24 h. The iodine liberated [0.8219 mmol, 98% (NCl=I₂)] was determined volumetrically (Na₂S₂O₃).

(b) *With bistrifluoromethyl nitroxide.* The nitroxide (8.66 g, 51.6 mmol) was condensed, *in vacuo*, into a cold (-196 °C) Pyrex tube (30 cm³) containing a solution of the *N*-chloro-imine (2.0 g, 7.9 mmol) in carbon tetrachloride (10 cm³). The tube was sealed and stored at 20 °C for 6 days in the absence of light. Removal of unchanged nitroxide followed by evaporation of the liquid product at 50 °C and ca. 15 mmHg to remove carbon tetrachloride provided 2,3,5,6-tetrakis(bistrifluoromethylamino-oxy)-*N,4-dichloro-2,3,4,5,6-pentafluorocyclohexylideneamine* (6.5 g, 7.0 mmol, 89%) (Found: C, 18.2; Cl, 8.3; F, 59.1; N, 7.5. C₁₄Cl₂F₂₀N₃O₄ requires C, 18.2; Cl, 7.7; F, 59.6; N, 7.6%) as an oil, λ_{max.} (film) 6.2 vμm (C:N str.), δ_F (94.1 MHz; neat liq.; *p*-CF₂Cl·S·C₆H₄Cl lock, shifts converted to ext. CF₃·CO₂H scale by addition of 50.5 p.p.m.) +11.0br (m,

CF₃), -37.2br (s, CFCl), -41.2br (s, 3- and 5-F), -45.3br (s, 2- or 6-F), and -51.3br p.p.m. (s, 6- or 2-F) (rel. int. of last four absorptions 1 : 2 : 1 : 1), which liberated iodine from potassium iodide in wet acetone at 20 °C.

(c) *With cyclopentadiene.* A mixture of the *N*-chloro-imine (3.8 g, 15 mmol) and cyclopentadiene (3.0 g, 45 mmol) in carbon tetrachloride (20 cm³) was heated at 100 °C for 4 h in the absence of air in a Pyrex ampoule. Distillation of the product afforded *N,6-dichloro-2,4,5,6,7-pentafluorotri-cyclo[6,2,1,0²,7]undeca-4,9-dien-3-ylideneamine* (1.5 g, 4.7 mmol, 31%) (Found: C, 41.5; H, 1.9; Cl, 22.0; F, 30.0; N, 4.1. C₁₁H₆Cl₂F₅N requires C, 41.5; H, 1.9; Cl, 22.3; F, 29.9; N, 4.4%), m.p. 49—51 °C [pale yellow crystals from petroleum (b.p. 60—80 °C)], b.p. 100 °C at <0.1 mmHg, λ_{max.} (melt) 5.85s μm (CF:CF str.) δ_H (100 MHz; soln. in CCl₄; ext. Me₄Si lock) +2.18 (AB pattern, CH₂, *J*_{gem} ca. 10 Hz), +3.36 (s, CH), +4.08 (s, CH), and +6.1 p.p.m. (complex, =CH) (rel. int. 2 : 1 : 1 : 2), δ_F (94.1 MHz; same soln.; ext. CF₃·CO₂H lock) -39.3 (m, CFCl), -60.5 (m, =CF), -64.0 (m, =CF), -67.6br (d, CF), and -89.6 p.p.m. (d, CF) (rel. int. 1 : 1 : 1 : 1).

(d) *Hydrolysis.* The *N*-chloro-imine (5.0 g, 20 mmol) was stirred with cold (0 °C) concentrated hydrochloric acid (20 cm³) for 3 h. The acid layer became dark yellow, then a white suspension appeared, and finally a dense colourless oil settled out. The oil was washed with water (100 cm³) and extracted with ether (2 × 100 cm³). The extract was dried (MgSO₄) and evaporated and the residual oil (4.0 g), a multicomponent mixture (by g.l.c.), was fractionated in a micro-spinning-band still to yield material (1.0 g), b.p. 25—46 °C at 0.6 mmHg, containing (ca. 75% by g.l.c.) a compound believed to be 3,4-dichloro-2,4,5,6-tetrafluorocyclohexa-2,5-dienone, δ_F (soln. in CCl₄; 94.1 MHz; ext. CF₃·CO₂H) -37.9 [d(27 Hz) of t (5.5 Hz), CFCl], -48.5 (d of t, 2-F), -53.7 (d of d of d, 5-F), and -77.2 p.p.m. ('q', 6-F).

The imine (2.0 g, 7.9 mmol) was heated under reflux for 3 h with 2*M*-hydrochloric acid (50 cm³). The product was extracted with ether (2 × 200 cm³) and the extract was dried (MgSO₄) and evaporated; short-path distillation of the product provided 4-chloropentafluorocyclohexa-2,5-dienone (2) (1.3 g, 6.0 mmol, 76%), identified spectroscopically (i.r. and ¹⁹F n.m.r.).

We thank the S.R.C. for a studentship (to T. J. N.) and Dr. M. G. Barlow for help with the n.m.r. interpretation.

[5/1109 Received, 9th June, 1975]

⁵ J. M. Birchall, R. N. Haszeldine, and J. E. G. Kemp, *J. Chem. Soc. (C)*, 1970, 449.