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SHORT COMMUNICATION

N-Halogeno-compounds. Part VI [1]. N-Chlorination of 4-Fluoro-, 2,4,6-Trifluoro-, and 2,3,5,6-Tetrafluoro-aniline, and Tetrafluoro-p-phenylenediamine

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The acquisition of samples of 2,4,6-trifluoroaniline, 2,3,5,6-tetrafluoroaniline, and tetrafluoro-*p*-phenylenediamine has enabled us to extend previous work [2–4] on the electrophilic chlorination of polyfluorinated arylamines with t-butyl hypochlorite.

2,3,5,6-Tetrafluoroaniline behaved like pentafluoroaniline [2] and yielded an isolable *NN*-dichloro-derivative (I) which underwent smooth iodine-initiated rearrangement to the corresponding *N*-chloro-imine (II) (see Scheme 1). 2,4,6-Trifluoroaniline resembled 2,3,4,5-tetrafluoroaniline [4] in that attempts to isolate *NN*-dichloro-2,4,6-trifluoroaniline failed owing to its 'spontaneous' isomerization to *N*,*4*-dichloro-2,4,6-trifluorocyclohexa-2,5-dienylideneamine (III) when the solvent used in the chlorination was removed (see Scheme 2).

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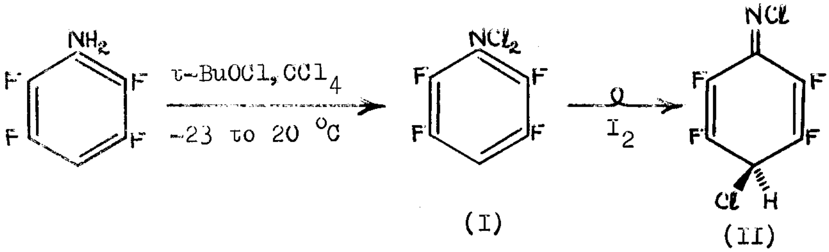
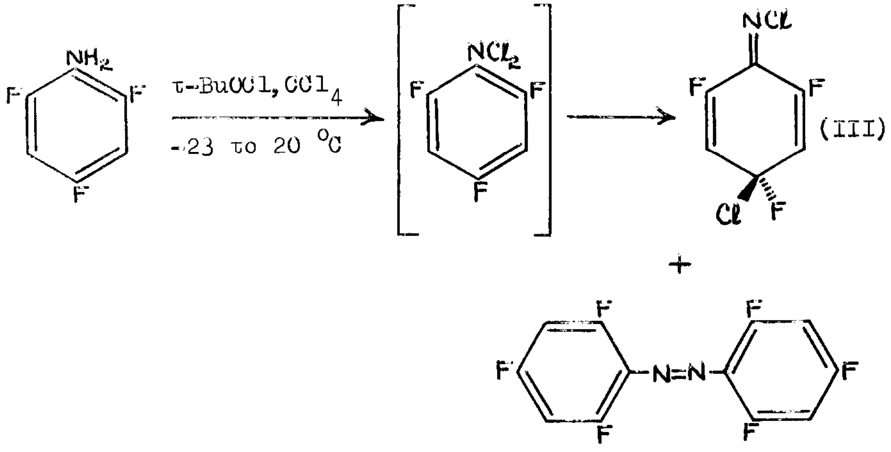


SCHEME 1



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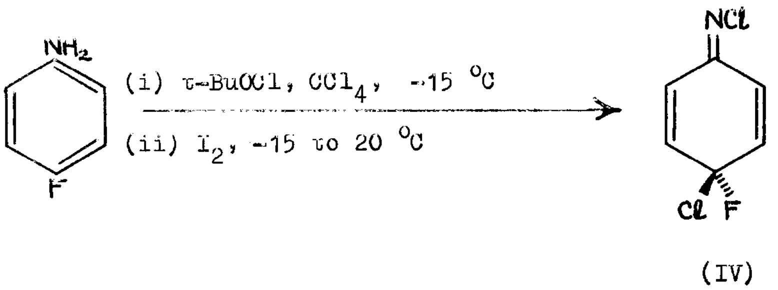
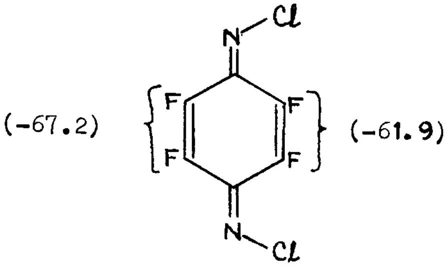


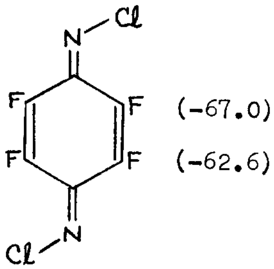
SCHEME 3

Also unsuccessful was an attempt to isolate *NN*-dichloro-4-fluoroaniline following treatment of 4-fluoroaniline with t-butyl hypochlorite in cold carbon tetrachloride: the product of chlorination decomposed violently, leaving behind a black tar, when the solvent was removed by evaporation at room temperature. The same problem was experienced following similar chlorination of aniline [5] and *p*-toluidine, the initial products (presumably $C_6H_5NCl_2$ and *p*-$MeC_6H_4NCl_2$, respectively) undergoing decomposition to black tars with even greater violence [6]. Smooth *in situ* rearrangement of the presumed *NN*-dichloro-4-fluoroaniline to *N*,4-dichloro-4-fluorocyclohexa-2, 5-dienylidenamine (IV) (see Scheme 3) was achieved, however; no attempts were made to deal with the initial products of chlorination of aniline and *p*-toluidine in this manner.

Tetrafluoro-*p*-phenylenediamine, the first fluorinated diaminobenzene to be studied [*cf.* ref.4], reacted rapidly with t-butyl hypochlorite in carbon tetrachloride at -15 °C to yield, not unexpectedly, a *ca.* 2:3 mixture of the *syn*- and *anti*-isomers of *NN'*-dichlorotetrafluoro-*p*-benzoquinonedi-imine (Va and b). Both isomers gave deceptively simple ^{19}F n.m.r. spectra of the $AA'XX'$-type, one showing two broadened doublets ($|J_{AX} + J_{AX'}|$ = 4 Hz) at -61.9 and -67.2 p.p.m., and the other two triplets ($|J_{AX}| + |J_{AX'}|$ = 10 Hz) at -62.6 and -67.0 p.p.m. In *N*-chloropolyfluorocyclohexa-2,5-dienylideneamines [3], the absorption of the fluorines *anti* to the *N*-chloro substituent are more shielded than the respective *syn*-fluorines, and this is most pronounced for the 5-fluorine, where a difference of *ca.* 6 p.p.m. is



(Va)



(Vb)

observed. If similar effects operate when two =NCl groups are present, then the _syn_-isomer (Va), which has a pair of fluorines _anti_ to both chlorines, should show the biggest difference in chemical shifts. The assignments shown then follow.

EXPERIMENTAL

N.m.r. Spectroscopy

Chemical shifts were measured relative to external CF_3CO_2H (δ_F) or Me_4Si (δ_H), downfield shifts being assigned positive values. Nuclei are labelled according to systematic nomenclature (_cf_. ref. 3).

Chlorination of Amines

(a) 2,3,5,6-Tetrafluoroaniline

A solution of the amine (7.55 g, 45.8 mmol) in AnalaR carbon tetrachloride (50 cm^3) was added dropwise during 15 min to a cold (_ca_. -23 °C) stirred solution of t-butyl hypochlorite (11.2 g, 103 mmol) in the same solvent (150 cm^3). The mixture was stirred at _ca_. -23 °C for 1 h then allowed to warm to room temperature and evaporated at water-pump pressure. Distillation of the residual red oil (as described for NN-dichloropentafluoroaniline [2], provided NN-dichloro-2,3,5,6-tetrafluoroaniline (nc) (8.00 g, 34.2 mmol, 75%) (Found: C, 30.8, H, 0.2; Cl, 30.1; F, 32.4; N, 6.0. $C_6HCl_2F_4N$ requires C, 30.8; H, 0.4; Cl, 30.3; F, 32.5; N, 6.0%), δ_F (neat liq.) -60.9 (3,5-F) and -66.2 p.p.m. (2,6-F) and δ_H 7.09 p.p.m. The assignment of fluorines is based upon the magnitude of the HF-coupling constants ($|^3J|>|^4J|$) and the observation that fluorines ortho to an NCl_2 group are more shielded than those ortho to a hydrogen atom [4]. Analysis of the spectra indicated that the meta F,F-coupling constants had the same sign, and together with the previously obtained substituent contributions [4] for the NCl_2 group, yielded the following parameters:

$J_{23} = -20.5$; $J_{25} = +11.4$; $J_{26} = -7.4$; $J_{35} = -1.1$;
$|J_{2H}| = 7.1$; and $|J_{3H}| = 9.5$ Hz.

(b) 2,4,6-Trifluoroaniline

Experiment (a) above was repeated, using 10.3 g (70.1 mmol) of 2,4,6-trifluoroaniline (in 100 cm^3 of CCl_4) and 17.2 g (158 mmol) of t-butyl hypochlorite (in 200 cm^3 of CCl_4). The dark red oil obtained by evaporation of the reaction mixture decomposed almost at once, with the evolution of heat and the formation of free chlorine, leaving a solid suspended in a dark brown oil. This mixture was extracted with cold petroleum ether (b.p. 30-40 °C) and the insoluble solid was crystallized from petroleum ether (b.p. 60-80 °C) to afford red needles of 2,2',4,4',6,6'-hexafluoroazobenzene (nc) (0.5 g, 2 mmol, 6%) (Found: C, 49.4; H, 1.2; F, 39.0;

N, 10.0. $C_{12}H_4F_6N_2$ requires C, 49.7; H, 1.4; F, 39.3; N, 9.7%), m.p. 143–144 °C, *m/e* 290 ($\underline{M}^{+\bullet}$, 44.5), 159 ($C_6H_2F_3N_2^{+}$, 77) and 131 ($C_6H_2F_3^{+}$, 100%), δ_F –29.6 (4-F) and –37.8 p.p.m. (2,6-F), and δ_H 6.74 p.p.m. Analysis and assignment of coupling constants to their appropriate ranges yielded the following parameters: $\underline{J}_{23} = \pm 11.1$; $\underline{J}_{25} = \mp 2.4$; $|\underline{J}_{26}| = 0.8$; $|\underline{J}_{35}| = 2.3$, ; $\underline{J}_{24} \simeq 0$; $|\underline{J}_{34}| = 8.7$ Hz. Distillation of the extract provided *N*,4-dichloro-2,4,6-trifluorocyclohexa-2,5-dienylideneamine (nc) (3.8. g 1.76 mmol, 25%)(Found: C,33.0; H, 0.8; Cl, 33.3; F, 25.9; N, 6.2. $C_6H_2Cl_2F_3N$ requires C, 33.3; H, 0.9, Cl.32.9, F, 26.4; N, 6.5%), $\lambda_{max.}$(film) 5.92 and 6.08 µm (CH=CF str.; presumably coupled oscillators), δ_F – 14.1 (4-F), –42.7 (2-F, *syn* to the *N*-chlorine [3]), and –45.5 p.p.m. (6-F), and δ_H *ca.* 6.15 p.p.m. (3,5-H, complex).

(c) 4-Fluoroaniline

A solution of 4-fluoroaniline (8.9 g, 80 mmol) in AnalaR carbon tetrachloride (100 cm^3) was added slowly to a cold (*ca.* – 15 °C) stirred solution of t-butyl hypochlorite (19.0 g, 175 mmol) in the same solvent (200 cm^3). After 1 h, a sample (5 cm^3) of the cold reaction mixture was evaporated at 20 °C and water pump pressure so that the progress of the reaction could be assessed by measuring the i.r. spectrum of the residue; however, when nearly all the carbon tetrachloride had been removed, the material decomposed with explosive violence, leaving a black tar. A crystal of iodine was added to the remainder of the cold (*ca.* –15 °C) reaction mixture, which was then stirred at the same temperature for 30 min, warmed to room temperature, and evaporated at water-pump pressure. The dark-coloured oily residue was distilled in the apparatus used to purify <u>NN</u>-dichloroperfluoroaniline [2] to provide <u>N</u>,4-dichloro-4-fluorocyclohexa-2,5-dienylideneamine (nc) (6.3 g, 35 mmol, 44%) (Found: C, 39.5; H, 2.2; Cl, 39.8; F, 10.5; N, 7.7. $C_6H_4Cl_2FN$ requires C, 40.0; H, 2.2; Cl, 39.4; F, 10.6%), a pale-yellow, sweet-smelling oil, m.p. <u>ca.</u> 9 °C, δ_F −16 p.p.m. (4-F), and δ_H 6.5 (2H), 6.7 (1H), and 7.04 p.p.m. (1H), which rapidly liberated iodine from potassium iodide in wet acetone and darkened rapidly when stored at room temperature.

<u>(d) Tetrafluoro-p-phenylenediamine</u>

A solution of tetrafluoro-<u>p</u>-phenylenediamine (5.0 g, 28 mmol) in AnalaR carbon tetrachloride (100 cm^3) was dripped slowly into a cold (<u>ca.</u> −15 °C) solution of t-butyl hypochlorite (16.0 g, 147 mmol) in AnalaR carbon tetrachloride (250 cm^3); a dark green colour that developed where each drop entered the chlorinating agent quickly disappeared if the addition was stopped. The final yellow reaction mixture was warmed to <u>ca.</u> 50 °C, evaporated at water pump pressure until the volume reached <u>ca.</u> 50 cm^3, then allowed to cool to 20 °C. The yellow crystalline solid that precipitated was shown by n.m.r. spectroscopy to be a <u>ca.</u> 3:2 mixture of <u>syn</u>- and <u>anti</u>-<u>NN'</u>-dichlorotetrafluoro-<u>p</u>-benzoquinonedi-imine (2.5 g, 10 mmol, 36%) (Found: C, 29.3; Cl, 28.9; F, 30.2; N, 10.9. Calc. for $C_6Cl_2F_4N_2$: C, 29.1; Cl, 28.7; F, 30.8; N, 11.3%), $\lambda_{max.}$ (melt) 5.91w, 6.13s, 7.37s, 7.53s (d), 8.94vw, 9.10w, 10.03s μm, $\lambda_{max.}$ (hexane) 218 (ε 4,940), 304 (ε 47, 860), 317 (ε 59,430) nm, fractional recrystallization of which from petroleum (b.p. 60 − 80 °C) gave a sample of the *syn*-isomer, m.p. 178 °C, δ_F (94.1 MHz; soln. in $CHCl_3$) -61.9 and -67.2 (rel. int. 1:1). The mother liquor from evaporation of the reaction mixture was worked-up by standard methods to yield 1.5 g (total 4.0 g, 16 mmol, 57%) of dark-yellow crystalline material, recrystallization of which from petroleum-carbon tetrachloride gave a *ca.* 1:3 mixture of the *syn*- and *anti*-isomers (0.4 g), m.p. 131 °C, δ_F (94.1 MHz; soln. in $CHCl_3$) -62.6 and -67.0. p.p.m. (*anti*-isomer; rel. int. 1:1), and -62.0 and -67.2.p.p.m. (*syn*-isomer; rel. int. 1:1).

Rearrangement of *NN*-Dichloro-2,3,5,6-tetrafluoroaniline

A small crystal of iodine was added to a stirred solution of *NN*-dichloro-2,3,5,6-tetrafluoroaniline (4.5 g, 19 mmol) in AnalaR carbon tetrachloride (100 cm^3). After 2 h, the solvent was removed at *ca.* 50 °C and water-pump pressure, and the residue (red oil) was distilled to give *N*,4-dichloro-2,3,5,6-tetrafluorocyclohexa-2,5-dienylideneamine (nc) (40 g, 17 mmol, 89%) (Found: C, 31.1; H, 0.4; Cl, 30.2; N, 6.0. $C_6HCl_2F_4N$ requires C, 30.8; H, 0.4; Cl, 30.3; N, 6.0%), a pale yellow oil, b.p. 38 °C at *ca.* 0.2 mmHg, $\lambda_{max.}$ (film) 5.78m and 5.95s μm (CF=CF str.), δ_F -50.6 (3-F), -56.9 (5-F), -70.4 (2-F), and -72.3 p.p.m. (6-F), and δ_H 4.48 p.p.m. The assignment is based upon that of other cyclohexadienylideneamines [3], and 2-F and 3-F are *syn* to the *N*-chlorine. Analysis of the first-order spectrum yielded the following non-zero magnitudes of coupling constants: $|J_{23}| = 4.1$; $|J_{25}| = 1.2$, $|J_{26}| = 1.2$; $|J_{35}| = 3.2$; $|J_{56}| = 8.6$; $|J_{2H}| = 6.3$, $|J_{3H}| = 3.3$; $|J_{5H}| = 3.3$; and $|J_{6H}| = 6.3$ Hz.

It is notable that for the HF–coupling constants, unlike the corresponding FF–coupling constants, $\left|{}^{3}\underline{J}\right| < \left|{}^{4}\underline{J}\right|$.

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