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UNSATURATED NITROGEN COMPOUNDS CONTAINING FLUORINE. PART 7[1]. THE REACTION OF 2,5-DICHLORO-1,1,1,6,6,6-HEXAFLUORO-3,4-DIAZAHEXA-2,4-DIENE WITH PHENYL-LITHIUM

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SUMMARY

Treatment of the title azine (**1**) with phenyl-lithium results in initial replacement of chlorine by phenyl to give the monophenylazine (**4**) and then the diphenylazine (**5**), but this is followed by successive replacement of fluorine in one CF_3 group to afford first the 3,4-diazahexa-1,3-diene $CF_3CPh_2N{=}NCPh{=}CXY$ (**6**) (X=Y=F), then (**7**) (X=F,Y=Ph) and finally (**8**) (X=Y=Ph).

INTRODUCTION

It has been reported previously that treatment of the dichloroazine (**1**) with N- and O-centred nucleophiles results in displacement of chloride ion to afford the mono- or di-substituted azines, (**2**) and (**3**), respectively, depending on the reactant ratio employed and the reaction conditions [2].

RESULTS AND DISCUSSION

In a preliminary investigation of carbanion attack on azine (**1**) it was observed that reaction involving an excess of phenyl-lithium gave orange red crystalline material the mass spectrum of which indicated that it contained a pentaphenyltrifluoromethyl compound, but this was not isolated pure and positively identified [3].

This prompted a detailed investigation of the reaction of azine (**1**) with phenyl-lithium, the results of which are summarized in the Table.

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The mono- and di-phenylazines **(4)** and **(5)**, respectively, are formed by addition of phenyl carbanion to a ClC=N linkage followed by elimination of chloride ion. Use of a 1:1 reactant ratio in dilute or in concentrated solution did not result in exclusive or near exclusive formation of the monosubstituted azine as found with *N*- and *O*-centred nucleophiles, *i e.* the second ClC=N linkage was not deactivated appreciably to further carbanion attack. This is presumably because mesomeric electron release from a phenyl group is much less effective than release from a lone pair on nitrogen or oxygen. Such mesomeric release increases the electron density at carbon in the remaining ClC=N linkage, i.e $CF_3CCl{=}N{-}N{=}C(CF_3){-}\ddot{X}(R)_n$ $\longleftrightarrow$ $CF_3\overset{-}{C}Cl{-}N{=}N{-}C(CF_3){=}\overset{+}{X}(R)_n$ (where X=N, n=2 and X=O, n = 1) and so nucleophilic attack on this linkage leading to the disubstituted azine is less favourable than initial attack on azine **(1)**

It was considered probable that the tetraphenyl- and pentaphenyl-compounds, **(7)** and **(8)**, respectively, were formed via the diphenylazine **(5)**. This was proved by reaction of azine **(1)** with two equivalents of phenyl-lithium at -78 °C followed by treatment of the resulting product mixture [comprising mainly diphenylazine **(5)**] with a further three equivalents of phenyl-lithium at room temperature to afford mainly **(7)** (29%) and **(8)** (55%). The yields of these products were identical to those obtained by treatment of azine **(1)** with five equivalents of phenyl-lithium at room temperature.

The products are therefore considered to be formed by the pathway outlined in the Scheme. This is the first report of a nucleophilic displacement of fluoride ion from a trifluoromethyl group in a disubstituted azine of type **(2)** and may be attributed to (i) high electron deficiency at the azine carbons in the diphenylazine **(5)** due to -I electron withdrawal by CF_3 and N not being counterbalanced to any extent by +M electron release by phenyl and (ii) the nucleophilic strength of phenyl-lithium. The substitution is also noteworthy in that it involves loss of fluoride ion from an atom five removed from that attacked by the nucleophile

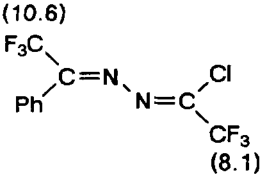
The difluorovinyl compound **(6)** was not detected in the products indicating that,as expected, it was more reactive towards nucleophilic attack than the other products. The ^{13}C and ^{19}F n.m.r. spectra of the tetraphenyl compound **(7)** indicated that it was formed as a single isomer, but the stereochemistry was not established.

One experiment, using a 1:1 ratio of reactants at -78 °C, was carried out in air and not under nitrogen and a proportion of the phenyl-lithium was converted into lithium phenoxide. This resulted in the formation of a mixture of monophenylazine **(4)** (*ca*. 25%), monophenoxyazine **(9)** (*ca*. 12%) and diphenylazine **(5)** (19%) Compound **(9)** was identified by an accurate mass measurement and by a

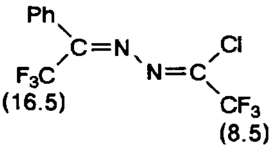
$CF_3CCl{=}N{-}N{=}CClCF_3$ **(1)**

$CF_3CR{=}N{-}N{=}CClCF_3$ **(2)**

$CF_3CR{=}N{-}N{=}CRCF_3$ **(3)**



(4a)



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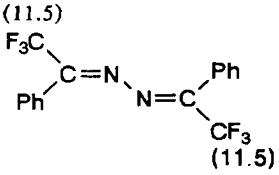


(5)

TABLE

Reaction of phenyl-lithium with azine (1) in diethyl ether [a]

Molar Ratio	Temp.	Products (%) [b]			
PhLi : (1)	(°C)	(4) [c]	(5)	(7)	(8)
1 : 1	- 78 [d]	41	20	-	-
1 : 1	- 78 [e]	43	24	-	-
2 : 1	- 78	5	58	4	7
5 : 1	ca. + 20	-	-	29	55
2 : 1	- 78	-	4.5	29	55
3 : 1	ca. + 20				

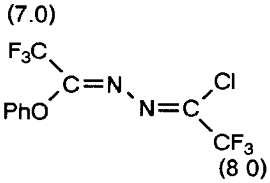
[a] Reactions carried out under nitrogen.

[b] Isolated yields based on reactant azine (1); biphenyl was also isolated from product mixture.

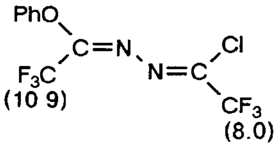
[c] Mixture of two isomers (4a) and (4b) in the ratio 18 : 1.

[d] Solvent volume 200 cm^3.

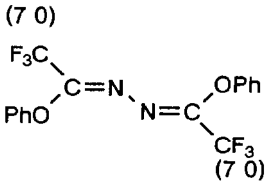
[e] Solvent volume 30 cm^3.



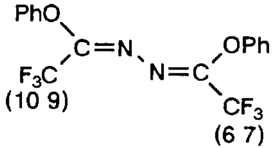
(9a)



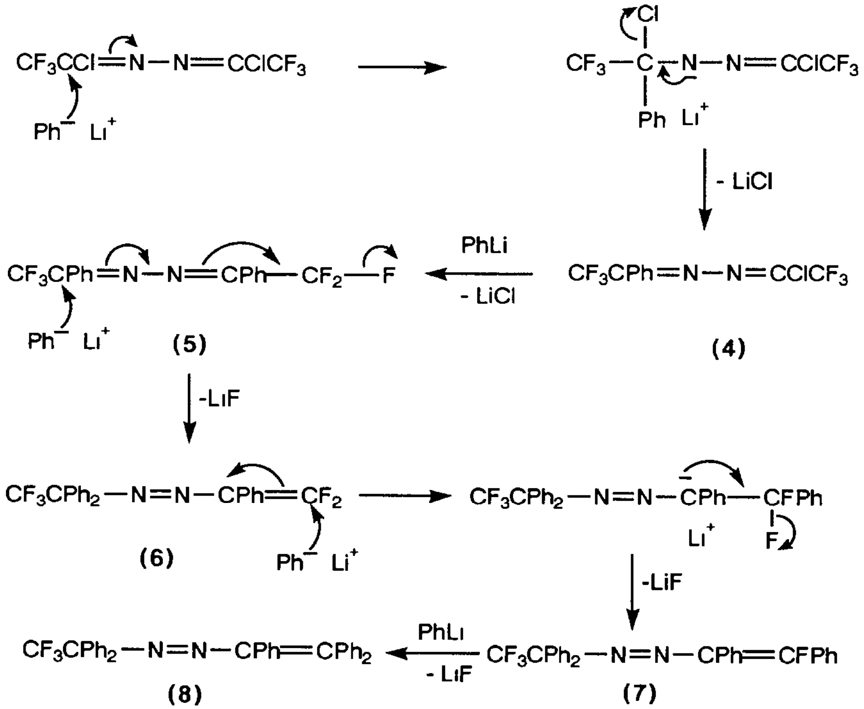
(9b)



(10a)



(10b)



Scheme.

comparison of the ^{13}C and ^{19}F n.m.r. spectra of a mixture of compounds **(4)** and **(9)** with those of a pure sample of **(9)** synthesized in 73% yield by reaction of azine **(1)** with lithium phenoxide (1:1 molar ratio) in ether.

The azine **(9)** consisted of two isomers in the ratio 4:5:1.0 (^{19}F n.m.r.); cf. the diphenoxyazine **(10)** formed in 61% yield [from treatment of azine **(1)** with phenol (1:2 molar ratio) in the presence of triethylamine] as a mixture of two isomers in the ratio 7:4 [4]. The monophenylazine **(4)** was also formed as a mixture of two isomers.

The diphenylazine **(5)** has the (EE)-configuration as shown by an X-ray crystal study [5] and on steric grounds it is considered that the $CF_3CCl{=}N$ linkage in dichloroazine **(1)** and the monosubstituted azine isomers has the (Z)-configuration. The major isomers are therefore assigned structures **(4a)**, **(9a)** and **(10a)** and are shown together with the observed ^{19}F n.m.r. chemical shifts (in parentheses) It is noteworthy that a syn-CF_3 group (anti to the nitrogen lone pair) absorbs to lower field than an anti-CF_3 group.

EXPERIMENTAL

Starting Materials

The dichloroazine **(1)** was synthesized from trifluoroacetic acid by the procedure reported [2] and phenyl-lithium [2.0M solution in cyclohexane and ether (70.30 v/v)] was purchased [Aldrich-Chemical Co. Ltd.].

General Techniques

Reactions involving phenyl-lithium were carried out under a nitrogen atmosphere in round-bottomed flasks fitted with either a cold finger (-78 °C) or a water-cooled condenser with dropwise addition of the phenyl-lithium in anhydrous diethyl ether to a stirred solution of dichloroazine **(1)** in the same solvent at either -78 °C or room temperature. The resulting precipitate was filtered off at room temperature and the solvent was removed in vacuo from the filtrate at -20 °C to give crude product which was examined by TLC (SiO_2, eluant C_6H_{14}:CH_2Cl_2 4:1 v/v) and the components then separated by dry column flash chromatography (DCFC) using silica (Fluka 60 GF_{254} and a 30:1 w/w ratio of SiO_2: product; eluant as above). Separated components were examined by i.r. (Perkin-Elmer 783 instrument) and n.m r {(solutions in $CDCl_3$); ^{1}H [Perkin-Elmer R32 (90 MHz), Perkin-Elmer R34 (220 MHz) or Bruker AC 300 (300 MHz spectrometers using TMS as external reference], ^{19}F [Perkin-Elmer R32 (84.6 MHz) instrument with TFA as external reference and ^{13}C [Bruker WP80 (20.1 MHz) or AC 300 (75.0 MHz) spectrometers with broad band proton decoupling, D_2O as deuterium lock signal and TMS as external reference] with chemical shifts to low field of reference designated positive} spectroscopy and mass [Kratos MS25 instrument for low resolution spectra using electron impact (e.i.) or chemical ionisation (c i , NH_3) and Kratos Concept IS instrument for accurate mass measurement (e.i)] spectrometry

Reaction of Dichloroazine (1) with Phenyl-lithium

(a) Molar ratio 1:1

The addition of phenyl-lithium (5.75 cm^3, 11.50 mmol) in ether (50 cm^3) to the azine **(1)** (3.00 g, 11.49 mmol) in ether (150 cm^3) at -78 ^oC over one hour followed by stirring at -78 ^oC for a further hour and then warming to room temperature gave lithium chloride (0.42 g, 10.0 mmol, 87%) and a dark yellow oil (3.01 g) the three components of which were separated (DCFC) and identified as (i) 2-chloro-5-phenyl-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene **(4)** (nc) (R_F 0.60) (1.43 g, 4.73 mmol, 41%) (Found: C, 39.6; H, 1.9; N, 9.1; F, 37.4%; $\underline{M}^+$, 304 and 302. $C_{10}H_5ClF_6N_2$ requires C, 39.7; H, 1.7; N, 9.3, F, 37.7%; $\underline{M}$, 302.5) as two isomers in the ratio 18:1; $\nu_{max.}$ 3075 w(arom. C-H str), 1630s (C=N str.), 1200-1150s (C-F str.), 760s (CF_3 def.) and 740 and 710s (C-H out of plane def) cm^{-1}, δ_H 7.0 to 8.0 (mult., Ph); δ_F (major isomer) + 8.1 (CF_3CCl) and +10.6 (CF_3CPh) p.p m. and δ_F(minor isomer) + 8.5 (CF_3CCl) and +16.5 (CF_3CPh), p.p.m.; δ_C 148.4 (q, Ph$\underline{C}$=N, ^2J 34.9 Hz), 131.8 (q, ClC=N, ^2J 36.0 Hz), 129.8 (s, ipso-Ph), 131.7, 128.9 and 127.7 (o-, m- and p-Ph), 119.7 (q, $\underline{C}F_3$-CPh, ^1J 277.0Hz) and 116.9 (q, $\underline{C}F_3CCl$, ^1J 275.3 Hz) p.p.m.; m/z (e.i.) 304 and 302 (35.7%, $\underline{M}^+$), 267 [16.3; $(\underline{M}\text{-}Cl)^+$], 247 [22.4, $(\underline{M}\text{- }HFCl)^+$], 235 and 233 [53.0, $(\underline{M}\text{-}CF_3)^+$], 197 (43.4, $C_9H_4F_3N_2^+$), 172 (49.5, $C_8H_5F_3N^+$), 140 and 138 (59.2, $C_7H_5ClN^+$), 103 (85.8, $PhCN^+$), 77 (100, $C_6H_5^+$) and 69 (98.7, CF_3^+), (ii) biphenyl (R_F=0.54) (0.21 g, 1 36 mmol) (Found: $\underline{M}^+$, 154. Calc. for $C_{12}H_{10}$ $\underline{M}$, 154), m.p and mixed m.p 69-70 ^oC and (iii) 2,5-diphenyl-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene **(5)** (nc) (R_F 0.47) (0.78 g, 2.26 mmol, 20%) (Found: C, 56.1; H, 3.1; N, 7.8; F, 32.9%; $\underline{M}^+$, 344. $C_{16}H_{10}F_6N_2$ requires C, 55.8; H, 2.9; N, 8.1; F, 33.1%; $\underline{M}$, 344), m.p. 40-42 ^oC, $\nu_{max.}$ 3110-3080w (arom. C-H str.), 1615s (C=N str.), 1200-1130s (C-F str.), 765s

(CF_3 def.) and 735 and 700s (C-H out of plane def.) cm^{-1}; δ_H 7.0 to 8.0 (mult., Ph) p.p.m.; δ_F + 11.5 (2 x CF_3) p.p.m.; δ_C 144.2 (q, C=N, ^2J 34.5 Hz), 129.7 (ipso-Ph), 131.2, 128.7 and 128.1 (o-, m- and p-Ph), and 119.8 (q, CF_3, ^1J 276.7 Hz) p.p.m., m/z (e.i.) 344 (2.5%, $M^{+\cdot}$), 275 [74.8, (M-CF_3^+)], 172 (17.7, $C_8H_5F_3N^+$), 103 (41.8, $PhCN^+$), 77 (100, $C_6H_5^+$) and 69 (42.1 (CF_3^+).

A second reaction, carried out under the same conditions except that the total solvent volume was reduced to 30 cm^3, gave azine **(4)** (1.50 g, 4.97 mmol, 44%), azine **(5)** (0.95 g, 2.75 mmol, 24%) and biphenyl (0.20 g).

For a third reaction carried out at room temperature in ether (50 cm^3) the ^{19}F n.m.r. spectrum of the product mixture showed the presence of azines **(4)** and **(5)** and two components identified (see below) as the tetraphenyldiaza-1,3-diene **(7)** and the pentaphenyldiaza-1,3-diene **(8)** in the ratio 60:14:8:2.

(b) Molar ratio 1:2

The addition of phenyl-lithium (7.70 cm^3, 15.40 mmol) in ether (15 cm^3) to azine **(1)** (2.00 g, 7.66 mmol) in ether (50 cm^3) at -78 °C over 30 minutes followed by stirring for two hours and then warming to room temperature gave a mixture (0.64 g) of lithium chloride and lithium fluoride and a yellow oil (2.51 g) the five components of which were separated (DCFC) and identified as (i) azine **(4)** (0.21 g, 0.39 mmol, 5%), (ii) biphenyl (0.25 g), (iii) azine **(5)** (1.53 g, 4.45 mmol, 58%), (iv) 1,2,5,5-tetraphenyl-1,6,6,6-tetrafluoro-3,4-diazahexa-1,3-diene **(7)** (nc) (R_F 0.38) (0.13 g, 0.28 mmol, 4%) (Found: C, 73.2; H, 4.3; N, 5.8; F, 16.6%, $M^{+\cdot}$, 460 $C_{28}H_{20}F_4N_2$ requires C, 73.0; H, 4.4; N, 6.1; F, 16.5%, M, 460), m.p. 70-71 °C, $\nu_{max.}$ 3090-3040w (arom. C-H str.),1620s (C=C str.), 1575w (N=N str.), 1200-1130, 1080 and 1070s (C-F str.), 780s (CF_3 def.) and 730 and 700s (C-H out of plane def.) cm^{-1}; δ_H 7.0-8.0 (mult., Ph) p.p.m., δ_F + 11.9 (s, 3F, CF_3) and -16.0 (s, 1F, =CF), p.p.m., δ_C 164.5 (d, = CF, ^1J 259.6Hz), 140.4 (d, $>\underline{C}$=CF, ^2J 33.4 Hz), 138.3 to 127.8 (Ph), 125.0 (q, CF_3, ^1J 286.7 Hz) and 84.5 (q, $\gtrdot$C-N, ^2J 23.2 Hz) p.p m ; m/z (c.i.) 460 ($M^{+\cdot}$), (e.i.) 236 (18.4%, $CF_3CHPh_2^+$), 235 (21.2, $CF_3CPh_2^+$), 216 (28.7, $CF_2CPh_2^+$), 215 (25.3, $C_{14}H_9F_2^+$), 198 (44.9, $C_{14}H_{11}F^+$), 197 (100, $C_{14}H_{10}F^+$), 178 (36.6, $C_{14}H_{10}^+$), 167 (38.6 $C_{13}H_{11}F^+$), 165 (38.6, $C_{13}H_9^+$), and (v) 1,1,2,5,5-pentaphenyl-6,6,6-trifluoro-3,4-diazahexa-1,3-diene **(8)** (nc) (R_F 0.32) (0.27 g, 0.52 mmol, 7%), (Found. C, 78.5; H, 4.8; N, 5.4; F, 11.5%. $C_{34}H_{25}F_3N_2$ requires C, 78.7; H, 4.8; N, 5.4; F, 11.0%), m.p. 125 -127 °C, $\nu_{max.}$ 3080-3040w (arom. C-H str.), 1600w (C=C str.), 1580w (N=N str.), 1200-1100s (C-F str.), 770m (CF_3 def.), and 730 and 700s (C-H out of plane def.) cm^{-1} ; δ_H 7.0-8.0 (mult. Ph) p.p.m.; δ_F + 12.0 (CF_3) p.p.m.; δ_C 151.7 (s, N-C=), 151.1 (s, $Ph_2\underline{C}$=), 140.8 to 126.9 (Ph), 125.2 (q, CF_3 ^1J 286.6 Hz) and 83.7 (q, →C-N, ^2J 23 0 Hz) p.p m ; *m/z* (e.i) 490 [43.9%, (*M*-N_2)$^+$], 470 (21.3, $C_{34}H_{24}F_2^+$), 256 (76.5, $Ph_3C_2H^+$), 255 (100, $Ph_3C_2^+$) and 235 (18.7, $CF_3CPh_2^+$).

(c) Molar ratio 1.5

The addition of phenyl-lithium (19.16 cm^3, 38.32 mmol) in ether (10 cm^3) to azine **(1)** (2.00 g, 7.66 mmol) in ether (15 cm^3) at room temperature over a period of 40 minutes followed by stirring for sixteen hours gave a mixture (1.50 g) of lithium chloride and lithium fluoride and a dark orange solid (3.64 g) the three components of which were separated (DCFC) and identified as (i) biphenyl (0.35 g), (ii) compound **(7)** (1.01 g, 2 19 mmol, 29%) and (iii) compound **(8)** (2.21 g, 4.24 mmol, 55%).

In a second experiment addition of phenyl-lithium (3 83 cm^3, 7.66 mmol) in ether (15 cm^3) to azine **(1)** (1.00 g, 3.83 mmol) in ether (50 cm^3) during thirty minutes at -78 °C followed by stirring at -78 °C for two hours and then warming to room temperature gave a mixture of compounds **(4)**, **(5)**, **(7)** and **(8)**. The mixture was treated with a further quantity of phenyl-lithium (5.74 cm^3, 11.49 mmol) in ether (10 cm^3) during thirty minutes at room temperature and stirring was continued for sixteen hours. Work-up afforded a mixture (0.72 g) of lithium chloride and lithium fluoride and a dark orange solid (1.85 g) separation (DCFC) of which gave azine **(5)** (0.06 h, 0.17 mmol, 4.5%), biphenyl (0.15 g), compound **(7)** (0.52 g, 1.13 mmol, 29%) and compound **(8)** (1.10 g, 2.12 mmol, 55%).

(d) Molar ratio 1:1 in air

Dropwise addition of phenyl-lithium (5.75 cm^3, 11.50 mmol) in ether (15 cm^3) to azine **(1)** (3.00 g, 11.49 mmol) in ether (20 cm^3) at -78 °C in air during fifty minutes and stirring continued at -78 °C for one hour gave lithium chloride (0.40 g, 9.5 mmol, 83%) and a dark yellow oil (2.53 g) separation (DCFC) of which gave (i) a mixture (1.35 g) of azine **(4)** (Found: *M*$^+$, 302.0053. Calc. for $C_{10}H_5{}^{35}ClF_6N_2$: *M*, 302.0045) and 2-chloro-5-phenoxy-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene **(9)** (Found: *M*$^+$, 317.9989 Calc. for $C_{10}H_5{}^{35}ClF_6N_2O$: *M*,317.9995 in the ratio 2.3·1.0 (^{19}F n.m.r.), (ii) biphenyl (0.21 g) and (iii) azine **(5)** (0.75 g, 2.18 mmol, 19%).

Reaction of Dichloroazine (1) with Lithium Phenoxide

Dropwise addition of an ethereal solution of lithium phenoxide [prepared from treatment of phenol (0.50 g, 5.31 mmol) in anhydrous diethyl ether (5 cm^3) at 0 ^oC with n-butyl-lithium (3.4 cm^3, 1.6M, 5.44 mmol) in ether (5 cm^3)] to a stirred solution of azine (**1**) (1.40 g, 5.36 mmol) in ether (50 cm^3) at -78 ^oC for half an hour, gave a precipitate of lithium chloride (0 21 g, 5.0 mmol, 93%). Removal of the solvent from the filtrate at -20 ^oC *in vacuo*, followed by purification (DCFC) of the residue afforded 2-chloro-5-phenoxy-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene (**9**) (nc) (R_F 0.60) (1.24 g, 3.89 mmol, 73%) (Found: C, 38.0; H, 1.8, N, 8.8%; *M*$^+$, 320 and 318. $C_{10}H_5ClF_6N_2O$ requires C, 37.7; H, 1.6; N, 8.8%; *M*, 318.5) as a mixture of two isomers in the ratio 4.5:1.0; $\nu_{max.}$ 3060w (arom C-H str.), 1670s (C=N str.), 1590 and 1480m (arom. C=C str.), 1290s (C-O str.), 1210-1125s (C-F str.) and 740s (arom. C-H out of plane def.) cm^{-1}; δ_H 6.8 (mult. 2H, *o*-C_6H_5) and 7.2 (mult., 3H, *m*- and *p*-C_6H_5) p.p.m.; δ_F (major isomer + 7.0 [s, $CF_3C(OPh)=$] and +8.0 (s, $CF_3CCl=$) p.p.m. and δ_F (minor isomer),+ 8.5 (s, $CF_3CCl=$) and +10.9 [s, $CF_3C(OPh)=$] p.p.m.; δ_C (major isomer) 152.8 (s, *ipso*-C_6H_5), 139.8 (q, $PhO\underline{C}=N$, ^2J 39.4 Hz), 130.8 (q, $Cl\underline{C}=N$, ^2J 38.6 Hz), 116.9 (q, CF_3, ^1J 276.5 Hz) and 116.65 (q, CF_3, ^1J 275.2 Hz) p.p.m. and δ_C (minor isomer) 151.5 (s, *ipso* -C_6H_5), 150.4 (q, $PhO\underline{C}=N$, ^2J *ca*. 40 Hz), 133.9 (q, $Cl\underline{C}=N$, ^2J *ca*. 40 Hz), 117.3 (q, CF_3 ^1J 275.4 Hz) and 116.2 (q, CF_3, ^1J 284.1 Hz) p.p.m. (*o*-, *m*- and *p*-C_6H_5 carbon absorptions for both isomers appeared between 129.8 and 119.5 p.p.m.); *m/z* (e.i.) 320 and 318 (22.0%; *M*$^+$), 283 [86.1, (*M*-Cl)$^+$], 251 and 249 [22.8, (*M*-CF_3)$^+$], 227 and 225 [44.7, (*M*-PhO)$^+$], 77 (70.7, $C_6H_5^+$) and 69 (100, CF_3^+).

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