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Sigmatropic isomerizations in 2-aza-allylic systems. Part X★. Prototropic and chlorotropic rearrangements in fluoroalkyl-substituted 1,3-dichloro-imines★★

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Abstract

The photochemical chlorination of *N*-benzylimidoyl chlorides $RC(Cl)=NCH_2Ph$ ($R=CF_3$, $CFCl_2$, C_3F_7, ^tBu, Ar) results in $RC(Cl)=NCH(Cl)Ph$ or its mixture with isomeric $RCCl_2N=CHPh$ depending on the nature of the substituent R. 1,3-Prototropic and 1,3-chlorotropic rearrangements in the chlorination products have been observed and investigated.

Keywords: Sigmatropic isomerization; 2-Aza-allylic systems; Prototropic rearrangements; Chlorotropic rearrangements; NMR spectroscopy; IR spectroscopy

1. Introduction

We have found previously that trifluoromethyl-substituted 2-aza-allylic systems undergo characteristic 1,3-transfers of a proton [2,3], sulfur-containing groups [1,3,4] and, to a somewhat lesser extent, phosphorus-containing groups [3]. The triethylamine-catalyzed isomerization of *N*-benzylidene-1-chloro-2,2,2-trifluoroethylamine, i.e. $CF_3CH(Cl)N=CHPh \rightarrow CF_3CH_2N=C(Cl)Ph$ [5], is presumed to involve a similar 1,3-migration of chlorine in a C=N−C triad. Such rearrangements in fluorinated *N*-(α-chloroalkyl)imidoyl chlorides are of particular interest since the products may prove to be important synthons for the preparation of various cyclic and acyclic nitrogen compounds with fluorine-containing substituents [6].

In the present study, the photochemical chlorination of the *N*-benzylimidoyl chlorides, $R_FC(Cl)=NCH_2Ph$ ($R=CF_3$, $CFCl_2$, C_3F_7), is described and the feasibility of 1,3-rearrangement for the dichlorides produced is considered. For comparison, the chlorination of some non-fluorinated analogues $RC(Cl)=NCH_2Ph$ ($R=^tBu$, Ph, 4-$O_2NC_6H_4$) has also been performed.

*For Part IX, see Ref. [1].

**Dedicated to Professor L.M. Yagupolskii on the occasion of his 70th birthday.

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2. Experimental details

^1H and ^{19}F NMR spectra were recorded on a Bruker WP-200 instrument (at operating frequencies of 200 and 188 MHz, respectively) in $CDCl_3$ solutions, using Me_4Si (^1H) and $CFCl_3$ (^{19}F) as internal standards, unless otherwise indicated. Downfield shifts were designated positive. IR spectra for solutions in CCl_4 were obtained on a UR-20 spectrophotometer.

2.1. Preparation of N-benzyldichlorofluoroacetimidoyl chloride (1b)

To a solution consisting of 60 mmol of methyl dichlorofluoroacetate [7] in 60 ml of diethyl ether cooled to 10–15 °C was added dropwise 60 mmol of benzylamine. After 24 h, the solvent was removed under reduced pressure and the residue crystallized from a mixture of benzene and petroleum ether (1:1) to afford *N*-benzyldichlorofluoroacetamide in 90% yield, m.p. 71–72 °C. ^1H NMR (CCl_4, $(Me_3Si)_2O$ external) δ: 4.72 (2H, d, $^3J_{CH_2NH}=6$ Hz, CH_2); 7.52 (5H, s, Ph) ppm. ^{19}F NMR δ: −66.31 ppm. IR (cm^{-1}): 1730 (C=O); 3350, 3450 (NH). Analysis: Calc. for $C_9H_8Cl_2FNO$: Cl, 30.04; N, 5.93%. Found: Cl, 30.01; N, 6.08%.

A mixture consisting of 0.1 mol of the amide and 0.1 mol of PCl_5 was heated at 90–120 °C for ca. 3 h until evolution of gas had ceased and then distilled in

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vacuum to give the desired product in 68% yield, b.p. 67–69 °C/0.06 mmHg. ^{1}H NMR (CCl_4, $(Me_3Si)_2O$ external) δ: 5.06 (2H, s, CH_2); 7.54 (5H, s, Ph) ppm. ^{19}F NMR δ: −57.57 ppm. IR (cm^{-1}): 1690 (C=N). Analysis: Calc. for $C_9H_7Cl_3FN$: Cl, 41.79; N, 5.50%. Found: Cl, 39.99; N, 5.52%.

N-Benzylperfluorobutanimidoyl chloride (**1c**) was also obtained as described above starting from *N*-benzylperfluorobutyramide and pentachlorophosphorane. Yield 56%, b.p. 49–51 °C/0.1 mmHg. ^{1}H NMR δ: 4.73 (2H, s, CH_2); 7.20 (5H, s, Ph) ppm. IR (cm^{-1}): 1715 (C=N). Analysis: Calc. for $C_{11}H_7ClF_7N$: Cl, 11.02; N, 4.35%. Found: Cl, 10.33; N, 4.57%.

2.2. General procedure for the photochemical chlorination of imidoyl chlorides 1a–e and α-chloroimine (5)

A mixture consisting of 80 mmol of an appropriate imidoyl chloride and 80 mmol of chlorine in 60 ml of dry carbon tetrachloride was placed in a quartz flask and irradiated with a DRT-230 mercury lamp with water cooling for 0.5–2.5 h until the chlorine colour had disappeared. The solvent was then evaporated and the residue distilled. The ratio of isomers **2** and **3** was determined before and after distillation from the integral intensities of their CHCl and CH=N ^{1}H NMR signals. In the case of **2a,b** and **3a,b**, comparison was also made using the ^{19}F NMR signals of the isomers. Both methods gave identical results.

N-(α-Chlorobenzyl)trifluoroacetimidoyl chloride (**2a**) and *N*-benzylidene-1,1-dichloro-2,2,2-trifluoroethylamine (**3a**) (**2a/3a** = 1:2.5): yield 15%, b.p. 101–105 °C/14 mmHg. ^{1}H NMR δ: 6.60 (s, CHCl in **2a**); 8.77 (s, CH=N in **3a**); 7.2–7.9 (5H, m, Ph) ppm. ^{19}F NMR δ: −72.20 (**2a**); −81.20 (**3a**) ppm. IR (cm^{-1}): 1655, 1695 (C=N in **3a** and **2a**, respectively). Analysis: Calc. for $C_9H_6Cl_2F_3N$: Cl, 27.69; N, 5.47%. Found: Cl, 27.52; N, 5.56%. Measurements of the ^{19}F NMR spectra for a 10% chlorobenzene solution of the isomer mixture in the temperature range from 20 °C to 100 °C revealed no significant changes in the relative intensities of the two signals.

According to the ^{19}F NMR spectra, the fraction with b.p. 113–119 °C/14 mmHg contains, in addition to **2a** and **3a** (approximately 85%), about 15% of the trichloride $CF_3CCl_2N{=}C(Cl)Ph$ (**4**), δ_F −83.2 ppm. The latter is always present in the raw reaction mixture. With two equivalents of chlorine, the trichloride was obtained as the main product [**4**/(**2a** + **3a**) = 86:14]: yield after distillation 20%, b.p. 123–125 °C/11 mmHg. Compound **4** was not isolated in a pure state and the isomeric structure $CF_3C(Cl){=}NCCl_2Ph$ cannot be excluded for it.

2.3. Preparation of N-(α-chlorobenzyl)dichlorofluoroacetimidoyl chloride (2b) and N-benzylidene-1,1,2,2-tetrachloro-2-fluoroethylamine (3b) (2b/3b = 2:1)

Chlorine was bubbled through a solution consisting of 6 mmol of azadiene **8** in 6 ml of anhydrous carbon tetrachloride cooled to 10–15 °C until the solution was yellow in colour. The mixture was then warmed to 20 °C and chlorine was further bubbled up to saturation. The mixture was left to stand overnight, then the solvent was evaporated and the residue distilled in vacuum. Yield 59%, b.p. 102–103 °C/0.18 mmHg. ^{1}H NMR δ: 6.59 (s, CHCl in **2b**); 8.80 (s, CH=N in **3b**); 7.3–8.0 (5H, m, Ph) ppm. ^{19}F NMR δ: −58.7 (**2b**); −64.4 (**3b**) ppm. IR (cm^{-1}): 1655, 1690 (C=N in **3b** and **2b**, respectively). Analysis: Calc. for $C_9H_6Cl_4FN$: Cl, 49.08; N, 4.85%. Found: Cl, 49.59; N, 4.82%.

Photochemical chlorination of imidoyl chloride **1b** gave the same ratio of isomers **2b** and **3b**; however, in this case, they were difficult to separate from the starting material **1b** and a more chlorinated product.

N-(α-Chlorobenzyl)perfluorobutanimidoyl chloride (**2c**): Yield 61%, b.p. 52–54 °C/0.05 mmHg. ^{1}H NMR δ: 6.64 (1H, s, CHCl); 7.3–7.8 (5H, m, Ph) ppm. ^{19}F NMR δ: −80.7 (3F, t, J_{FF} = 9 Hz, CF_3); −111.9 (2F, q, $^3J_{FF}$ = 9 Hz, CF_2CF_3); −125.5 (2F, s, $CF_2C{=}$) ppm. IR (cm^{-1}): 1687 (C=N). The product contained ca. 2% of isomer **3c**, $\delta_{CH=N}$ 8.78 ppm. Analysis: Calc. for $C_{11}H_6Cl_2F_7N$: Cl, 19.91; N, 3.95%. Found: Cl, 19.64; N, 3.99%.

N-(α-Chlorobenzyl)-2,2-dimethylpropanimidoyl chloride (**2d**): Yield 15%, b.p. 77–85 °C/0.07 mmHg. ^{1}H NMR δ: 1.30 (9H, s, ^{t}Bu); 6.64 (1H, s, CHCl); 7.3–7.7 (5H, m, Ph) ppm. IR (cm^{-1}): 1694 (C=N). Analysis: Calc. for $C_{12}H_{15}Cl_2N$: Cl, 29.04; N, 5.74%. Found: Cl, 29.39; N, 5.86%.

N-(α-Chlorobenzyl)benzimidoyl chloride (**2e**): Yield 36%, b.p. 118–140 °C/0.05 mmHg. The product was identified by comparison of its ^{1}H NMR spectrum with that of an authentic sample obtained according to Ref. [8].

N-(α-Chlorobenzyl)-4-nitrobenzimidoyl chloride (**2f**): Yield 86%, m.p. 92–94 °C (diethyl ether). ^{1}H NMR δ: 6.86 (1H, s, CHCl); 7.4–7.9 (5H, m, Ph); 8.29 (4H, s, $O_2NC_6H_4$) ppm. IR (cm^{-1}): 1353, 1532 (NO_2); 1655 (C=N). Analysis: Calc. for $C_{14}H_{10}N_2O_2Cl_2$: Cl, 22.94; N, 9.06%. Found: Cl, 22.78; N, 8.80%.

N-(1-Chloro-2,2,2-trifluoroethyl)benzimidoyl chloride (**7a**): Yield 48% (from **5**), 15% (from **6**), b.p. 103–106 °C/13 mmHg. ^{1}H NMR δ: 5.94 (1H, q, $^3J_{HF}$ = 4.9 Hz,

CHCl); 7.3–8.1 (5H, m, Ph) ppm. ^{19}F NMR δ: −78.1 (d, $^3J_{FH}$ = 5 Hz) ppm. Analysis: Calc. for $C_9H_6Cl_2F_3N$: Cl, 27.69; N, 5.47%. Found: Cl, 27.41; N, 5.50%.

2.4. Preparation of N-benzylidene-1,2-dichloro-2-fluoroethenylamine (8)

To a solution of 40 mmol of *N*-benzyldichlorofluoroacetimidoyl chloride (**1b**) in 20 ml of anhydrous benzene was added dropwise a solution of 44 mmol of triethylamine in 10 ml of benzene. After 24 h, the precipitate was filtered, the filtrate evaporated and the residue distilled to give **8**. Yield 70%, b.p. 56–57 °C/0.05 mmHg. ^{1}H NMR δ: 7.4–7.8 (5H, m, Ph); 8.25 (0.22H, s, CH=N); 8.38 (0.78H, s, CH=N) ppm. ^{19}F NMR: δ_1 −79.16; δ_2 −82.08 ppm; δ_1/δ_2 = 3.5. The presence of two CH=N proton signals and two fluorine signals with the same intensity ratios in the ^{1}H and ^{19}F NMR spectra suggests that azadiene **8** is formed as a mixture of *E*- and *Z*-isomers. Analysis: Calc. for $C_9H_6Cl_2FN$: Cl, 32.52; F, 8.71; N, 6.42%. Found: Cl, 32.53; F, 8.37; N, 6.47%.

2.5. Isomerization of equilibrium mixtures of 2a–c and 3a–c to 1,3-dichloroimines 7a–c

To a solution of 0.1 g of a mixture of **2a–c** and **3a–c** in 1 ml of dry benzene or toluene was added 3–4 drops of triethylamine. After 24 h, the small quantity of precipitate formed was filtered off and the solvent and triethylamine evaporated. The dichlorides obtained were identified by ^{1}H NMR and ^{19}F NMR spectroscopies. In the case of **2b–3b**, 1,4-dehydrochlorination leading to **9** (**7b**/**9** = 1:2) proceeded in parallel with isomerization.

N-(1,2,2-Trichloro-2-fluoroethyl)benzimidoyl chloride (**7b**) and *N*-(1,2-dichloro-2-fluoroethenyl)benzimidoyl chloride (**9**): ^{1}H NMR δ: 6.10 (0.33H, d, $^3J_{HF}$ = 5 Hz, CHCl in **7b**); 7.4–8.1 (5H, m, Ph) ppm. ^{19}F NMR: δ_1 −64.8 (d, $^3J_{FH}$ = 5 Hz) (**7b**); δ_2 −86.4 (s); δ_3 −92.5 (s) (**9**) ppm; $\delta_1/(\delta_2+\delta_3)$ = 1:2); δ_2/δ_3 = 1:2.8. The presence of two fluorine signals for azadiene **9** indicates that it is formed as a mixture of *E*- and *Z*-isomers (cf. the ^{19}F NMR spectrum of compound **8**).

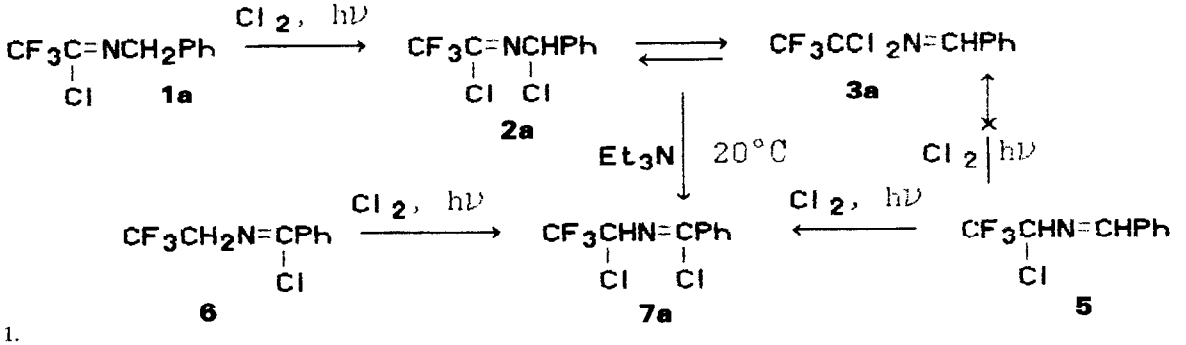
N-(1-Chloro-2,2,3,3,4,4,4-heptafluorobutyl)benzimidoyl chloride (**7c**): ^{1}H NMR δ: 6.15 (dd, J_{HF} = 12 and 6 Hz, CHCl); 7.4–8.1 (m, Ph) ppm.

3. Results and discussion

The photochemical chlorination of *N*-benzyltrifluoroacetimidoyl chloride (**1a**) with an equimolar quantity of chlorine proceeds under mild conditions (CCl_4, 15–20 °C) and results in the predominant formation of a mixture of isomeric dichlorides **2a** and **3a** in the ratio 1:2.5 (see Scheme 1). Since, under these reaction conditions, a secondary chlorination leading to the trichloride $CF_3CCl_2N{=}C(Cl)Ph$ (**4**) (or its chlorotropic isomer) takes place to a partial extent, some starting imidoyl chloride **1a** is preserved unreacted in the raw reaction mixture. The ratio of isomers **2a** and **3a** remained constant over a number of experiments. It also did not change after distillation and presumably was close to the equilibrium value (cf. Refs. [9,10]). Most likely the chlorination of **1** results initially in the 1,3-dichloride **2** which then undergoes 1,3-migration of a chlorine atom in the triad C=N−C to give **3**.

The route involving a prototropic isomerization of **1** and subsequent chlorination of the resulting isomer **5** (**1** → **5** → **3**) could be regarded as an alternative mechanism. However, our experimental data reject such a reaction pathway as α-chloroimine **5** on chlorination under similar conditions gave no **3** and/or **2** (Scheme 1). Instead, the isomeric dichloride *N*-(1-chloro-2,2,2-trifluoroethyl)benzimidoyl chloride (**7a**) was obtained, i.e. in this case selective substitution of a benzylidene hydrogen atom occurred. Compound **7a** was also formed on chlorination of benzimidoyl chloride **6** (Scheme 1).

As ^{19}F NMR measurements have shown, the ratio **2**/**3** in chlorobenzene solution remained almost constant over the wide temperature range 20–100 °C. Nevertheless, the following chemical observations are indicative of the reversible chlorotropic nature of the conversion **2** ⇄ **3**. Formation of **3** on chlorination of **1** (Scheme 1) suggests the involvement of a chlorotropic shift **2** → **3**. In the presence of triethylamine, under mild conditions (benzene, 20 °C), the mixture of isomers **2**



Scheme 1.

and **3** was completely converted into 1,3-dichloroimine **7a** (Scheme 1), presumably through two consecutive shifts – chlorotropic and prototropic: $\mathbf{3a} \xrightarrow{1,3\text{-Cl}} \mathbf{2a} \xrightarrow{1,3\text{-H}} \mathbf{7a}$. It is believed that the irreversible prototropic isomerization **2a** → **7a** disturbs the chlorotropic equilibrium **2a** ⇄ **3a**, but the latter can be re-established owing to the reverse chlorine shift **3a** → **2a**.

It should be noticed that a similar rearrangement for **7a**, i.e. **7a** → $PhCCl_2N{=}CHCF_3$, was never observed but for a trichloromethyl analogue of compound **2a** the reversible 1,3-transfer of a chlorine atom has been confirmed experimentally [9]. Thus, chlorotropic 1,3-shifts are sensitive to substituents at a terminal carbon atom in an aza-allylic triad. To clarify the effects of substituents at an imidoyl carbon atom on possible 1,3-chlorotropic shifts, we performed the photochemical chlorination of the *N*-benzylimidoyl chlorides **1b–f** (Eq. (1)). The reaction was carried out under the same conditions as in chlorination of **1a**. It was found that compounds **1b,c** gave both chlorotropic isomers, **2b,c** and **3b,c**, while in the case of **1d–f** only the 1,3-dichloro derivatives **2d–f** were formed:

$$\underset{\textbf{(1b–f)}}{RC(Cl){=}NCH_2Ph} \xrightarrow{Cl_2,\ h\nu} \underset{\textbf{(2b–f)}}{RC(Cl){=}N{-}CHPh(Cl)} \rightleftharpoons \underset{\textbf{(3b,c)}}{RCCl_2N{=}CHPh} \quad (1)$$

b: R = $CFCl_2$; **c**: R = $CF_3CF_2CF_2$; **d**: R = ^{t}Bu; **e**: R = Ph; **f**: R = *p*-$O_2NC_6H_4$

The isomeric dichlorides **2b** and **3b** were prepared independently by the addition of chlorine to azadiene **8**:

$$\underset{\textbf{(1b)}}{CFCl_2C(Cl){=}NCH_2Ph} \xrightarrow[-Et_3N\cdot HCl]{-Et_3N} \underset{\textbf{(8)}}{CFCl{=}CClN{=}CHPh} \xrightarrow{Cl_2,\ CCl_4} \mathbf{2b} \rightleftharpoons \mathbf{3b} \quad (2)$$

The ratio of chlorotropic isomers (**2b**/**3b** = 67:33) obtained by the routes depicted in Eqs. (1) and (2) was the same and, obviously, reflects their relative stability.

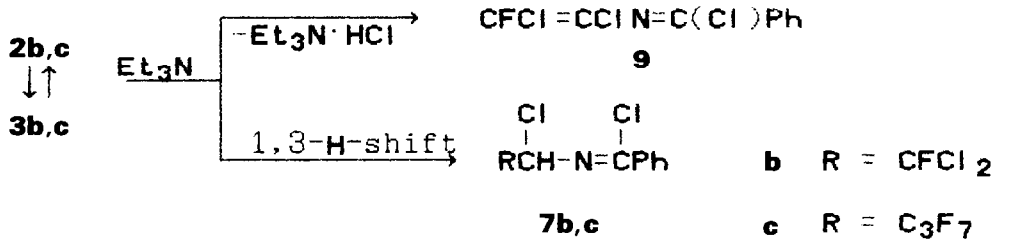
As is evident from Eq. (2), in the same way as *N*-benzyltrichloroacetimidoyl chloride [9], imidoyl chloride **1b** undergoes dehydrochlorination on treatment with triethylamine. Under similar reaction conditions, along with dehydrochlorination, in 1,3-dichloride **2b** a 1,3-prototropic shift leading to **7b** occurs (Scheme 2). A similar prototropic isomerization is also characteristic for dichloride **2c**.

Note that the triethylamine-catalyzed prototropic isomerizations **2a–c** → **7a–c** are almost irreversible. It is readily seen that in these transformations a proton moves within an aza-allylic triad to the carbon atom bearing the stronger electron-accepting substituent R. Conjugation of a benzene ring with the C=N bond is believed to be an additional factor stabilizing structure **7**.

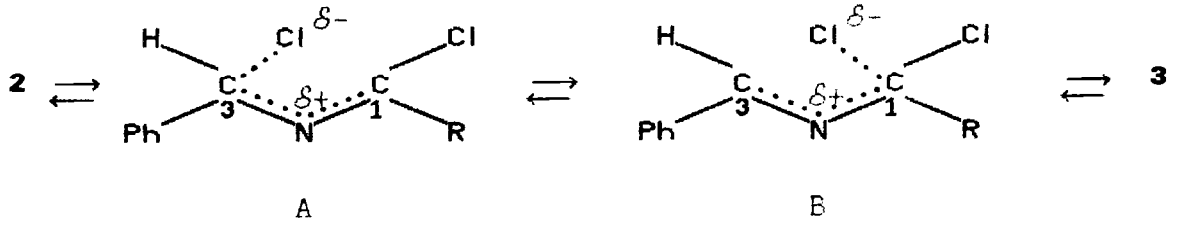
Let us now consider the factors determining the relative stability of chlorotropic isomers **2** and **3**. As follows from the data presented in Table 1, the ratio of the isomers in the series studied varied over a wide range – from the preferential formation of a 1,1-dichloro derivative **3** (with R = CF_3) to the exclusive production of a 1,3-dichloride **2** (R = ^{t}Bu, Ar). Analysis of the tabulated data leads to the conclusion that this ratio depends on both the electronic and steric properties of the substituents R. The inductive constants σ_I for the halogen-containing substituents listed in Table 1 (CF_3, $CFCl_2$, CCl_3, C_3F_7) vary only slightly. It is believed that the considerable changes in the **2/3** ratio observed in this series are mainly due to steric effects of the substituents R. Indeed, although the σ_I values for the CF_3 and C_3F_7 groups are nearly identical, the **2/3** ratios for these groups are 0.4 and 49, respectively, i.e. steric hindrance suppresses formation of the 1,1-dichloride **3**. On the other hand, isomer **3** completely disappears from the reaction products for R = ^{t}Bu though the steric constant E_s for ^{t}Bu is intermediate in magnitude between those for the CF_3 and C_3F_7 groups. In this case, a substituent inductive effect is present. The σ_I values in the sequence ^{t}Bu, CCl_3, CF_3 increase from 0.0 to 0.42 with a concurrent increase in the relative content of isomers **3** from 0% to 71%, thus indicating that electron-withdrawing substituents R are likely to stabilize form **3**.

The results obtained can be explained in the framework of Scheme 3 for chlorotropic isomerization. Transfer of a chloride anion most likely proceeds over the aza-allyl cation plane through intermediates A and B. As the electronegativity of R increases, the positive charge at the C_1 atom in both A and B also increases and facilitates addition of a Cl anion and the formation of **3**. Bulky R groups hinder the addition. With R = Ph, XC_6H_4, additional steric hindrance arises as a result of interaction between the migrating chlorine atom and the *ortho*-hydrogen atoms of the aryl ring [11]. Furthermore, the most favourable conditions for conjugation and charge delocalization in A and B are created when the aryl substituent is coplanar with the aza-allylic system. As the Cl anion approaches the C_1 centre, the coplanarity will be disturbed which results in a rise in the activation barrier. As a consequence, even with a sufficiently strong electron-withdrawing group, R = *p*-$NO_2C_6H_4$ (σ_I 0.28), isomerization of **2** to **3** does not take place.

In conclusion, the aza-allylic compounds with fluorine-containing substituents are suitable models for studying 1,3-chlorotropic and prototropic shifts. The indicated



Scheme 2.



Scheme 3.

Table 1
Effect of inductive and steric constants of substituents R on the ratio of isomers RC(Cl)=NCH(Cl)Ph (2) and $RCCl_2N=CHPh$ (3)

R	σ_I	E_s	2	3
CF_3	0.42	−1.16	29	71
$CFCl_2$	(0.34)[a]	(−1.8)[a]	67	33
CCl_3	0.30	−2.06	80[b]	20[b]
C_3F_7	(0.40)[c]	–	98	2
^{t}Bu	0.0	−1.54	100	–
Ph	0.15	−2.48	100	–
4-$O_2NC_6H_4$	0.28	–	100	–

[a]Rough estimate assuming the additivity of σ_I and E_s variations on substituting F for Cl.
[b]Data from Ref. [9].
[c]Average of σ_I values for $R=C_2F_5$ (0.41) and $R=C_4F_9$ (0.39).

rearrangements proceed in these systems with reasonable facility and the presence of fluorine-containing groups enables reliable identification of isomers and estimation of their ratio using ^1H and ^{19}F NMR spectral data. In particular, the chlorotropic isomers **2** and **3** show characteristic chemical shifts of protons at the sp^3- or sp^2-hybridized carbon atoms of the C=N–C triad (~6.6 and ~8.8 ppm, respectively). The prototropic isomers **2** and **7** differ primarily in signal multiplicity. Thus, in the ^{19}F NMR spectra of the 1,3-dichlorides **2a,b**, the fluorine nuclei are present as singlets (δ −72.2 and −81.2 ppm, respectively), whereas in the isomeric compounds **7a,b** they exhibit doublets (δ −78.1 and δ −64.8 ppm, respectively, $J_{FH}=5$ Hz). In the ^1H NMR spectra of **7a,b** the CHCl group can be observed as a quartet (**7a**) or a doublet (**7b**) with the same J_{HF} constants. In the case of the dichloride **7c**, this group appears in the ^1H NMR spectra as a double doublet (δ 6.15 ppm, $J=12$ Hz and 6 Hz) due to differential coupling with the diastereotopic fluorines in the CF_2 group.

In the IR spectra of the isomers **2a–d** and **3a–c** containing alkyl or fluoro(chloro)alkyl substituents at a C=N bond, the valence-vibrational band of the latter appears at ~1690 or ~1650 cm^{-1} respectively (see Experimental details). This distinction is likely to be caused by the fact that in the isomers **3** the carbon atom of the azomethine group is linked with a phenyl substituent capable of conjugation. In the diaryl derivatives **2e,f** possessing an ArC(Cl)=N– moiety, the C=N bond absorption band (~1695 cm^{-1}) is close to that for compounds **3a–c**.

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