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FLUORINATION WITH CONCOMITANT CYCLIZATION OF $CCl_2N=CCl_2CCl_2=NCCl_2$ WITH SbF_5 AND MOLECULAR STRUCTURE OF A 2-IMIDAZOLIDINONE DERIVATIVE

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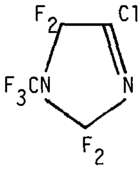
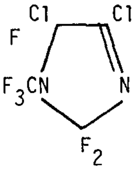
SUMMARY

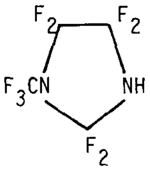
The perchlorodiazahexadiene $Cl_2C=NCCl_2CCl_2N=CCl_2$ undergoes fluorination with concomitant ring closure to yield the 4-chloro and 4,5-dichloro-3-imidazoline derivatives (VII) and (VIII) upon treatment with stoichiometric amounts of SbF_5 in SO_2. Ring closure of $CF_3NHCF_2CF_2NHCF_3$ is achieved by catalytic amounts of SbF_5, and (XV) and its hydrolysis product (XVI) were prepared in high yield. The Cl atom in (VII) has been substituted by OC_6H_5 and $N(C_2H_5)_2$ groups.



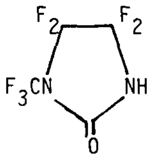
(VII)



(VIII)



(XV)



(XVI)

The crystal structure determination shows that (XVI) possesses a planar ring and nitrogen atoms with coplanar bonds. Comparison of the bond lengths of (XVI) with those of nonfluorinated imidazolidinones reveals significant fluorine substitution effects.

INTRODUCTION

It has been reported that by nucleophilic cyclization of $CF_3N=CFCF=NCF_3$ (I) with CsF at 220 °C the isomers (II) and (III) were formed with a yield of 16 and 65%, respectively [1]. The diazadiene (I) can be obtained

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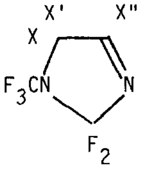
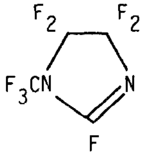
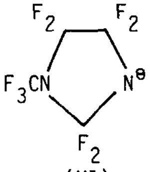


X=X'=X"=F (II)
X=X'=F,X"=Cl (VII)
X=F,X'=X"=Cl (VIII)
X=X'=X"=Cl (IX)
X=X'=F,X"=OC_6H_5 (X)
X=X'=F,X"=$N(C_2H_5)_2$ (XI)



(III)



(VI)

by treating $Cl_2C{=}NCCl_2CCl_2N{=}CCl_2$ (IV) with HF and subsequent dehydrofluorination of the reaction product $CF_3NHCF_2CF_2NHCF_3$ (V) with NaF at 70 °C [2]. Both imidazolines (II) and (III) add $F^{\ominus}$ to form the anion (VI). The chemistry of (VI) has been studied extensively [3,4].

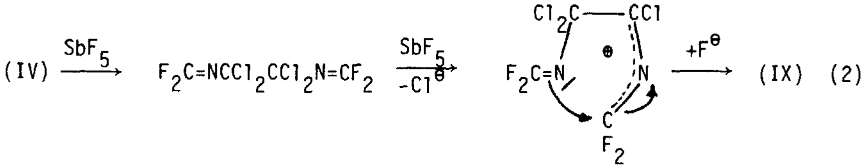
Following our observation that $CF_3N{=}CF_2$ can be trimerized both to a cyclic and non-cyclic derivative by SbF_5, we have studied the reaction of (IV) and compound (V) with SbF_5. The aim of the present investigation is to provide a one-step synthesis instead of the previous multistep route of the five-membered ring system starting from the easily available educt (IV).

RESULTS

The reaction of (IV) with a stoichiometric amount of SbF_5 in SO_2 as a solvent proceeded smoothly at room temperature, and (VII) was obtained in a yield of 82%, eqn. (1):

$$(IV) + 7/5\ SbF_5 \longrightarrow (VII) + 7/5\ SbCl_5 \qquad (1)$$

If the reaction was carried out with less than the amount of SbF_5 required by eqn. (1), major quantities of (VIII) along with a minor yield of (IX) were obtained. From the distribution of products we conclude that initially the 1,6 chlorine atoms of (IV) are substituted by F and that ring closure occurs according to eqn. (2) before the 3,4 chlorine atoms are substituted:



(2)

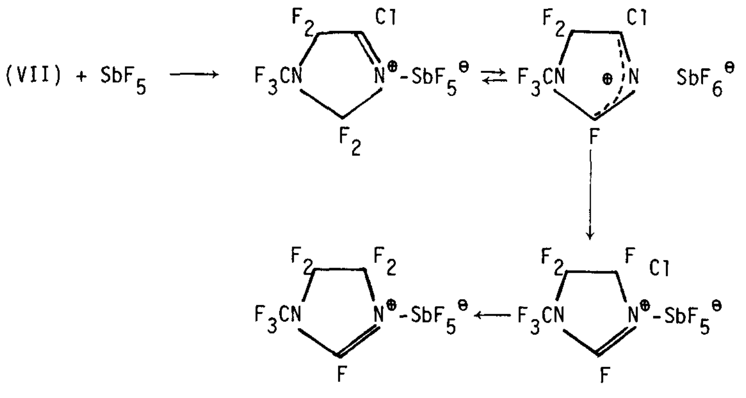
Though (VII) may be converted to the perfluoro dervative (II) with $F^{\ominus}$ in a suitable solvent, (VII) itself is a valuable precursor for 4-substituted derivatives. Thus, selective replacement of the Cl atom by OC_6H_5 or

$N(C_2H_5)_2$ was readily achieved with almost quantitative yields according to eqn. (3) and (4):

$$\text{(VII)} + C_6H_5OH + N(C_2H_5)_3 \longrightarrow \text{(X)} + [HN(C_2H_5)_3]Cl \qquad (3)$$

$$\text{(VII)} + 2\ HN(C_2H_5)_2 \longrightarrow \text{(XI)} + [H_2N(C_2H_5)_2]Cl \qquad (4)$$

On the other hand, the perfluoro compound (II) was not obtained even with SbF_5 in excess because a stable 1:1 complex was formed, eqn. (5):

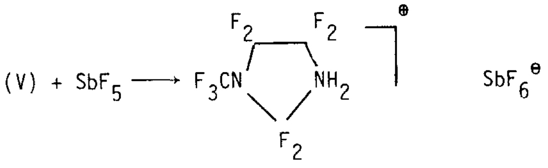


(XIII) (XII) (5)

In neat SbF_5, this complex slowly isomerized at 60°C with formation of the 2-imidazoline derivative (XII). Reaction (5) can be followed by ^{19}F NMR spectroscopy, (XII) being easily monitored by the signal of the AB spin system of the CF_2 group.

After one week at 60°C, the NMR signals of (XII) had completely disappeared. Chlorine/fluorine exchange had occurred, and the only species present was assigned the constitution (XIII).

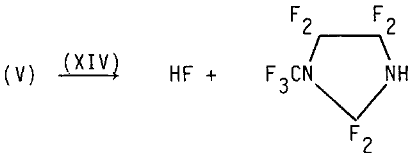
The fluorination with concomitant cyclization of (IV) according to (1) has the disadvantage that stoichiometric quantities of SbF_5 are consumed. If a completely fluorinated species (e. g., a derivative of (VI)) rather than a 4-chloro derivative is desired, then an alternative route starting with compound (V) may be taken. We have found that (V) and SbF_5 react according to eqn. (6) to yield the 1:1 complex (XIV):



(XIV)

(6)

Complex (XIV), which dissociates into (XV) and HF/SbF_5, catalyzes the elimination of HF from (V) with formation of the imidazolidine (XV), eqn. (7):

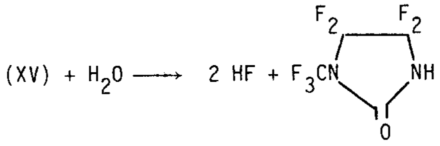


(XV)

(7)

Thus, (V) may be converted to (XV) by catalytic amounts of SbF_5.

As was observed for the perfluoro-1,3-dimethylimidazolidine [5], the fluorine substituents of (XV) in the 2-position are very reactive. HF is easily eliminated, and the 2-imidazoline (III) is formed. With water or in contact with glass, (XIV) and (XV) are hydrolyzed to yield the urea derivative (XVI), eqn. (8):



(XVI)

(8)

CHARACTERIZATION OF COMPOUNDS

The physical properties of all new compounds have been determined, and their constitution has been confirmed by their ^1H and ^{19}F NMR spectra (Table 1), IR and Raman spectra, mass spectra (Table 2), elemental analyses and a single crystal X-ray examination of (XVI).

TABLE 1

Physical properties and NMR spectra of compounds (VII)-(XIII), (XV) and (XVI)

Compound	(VII)	(VIII)	(IX)	(X)	(XI)	(XII)	(XIII)	(XV)	(XVI)
mp [°C]									58
bp [°C/Torr]	67/760	93/760		104/43	130/92				
^{1}H [a]									
δNH [ppm]								5.1	8.2
$\delta CH_3/CH_2$ [ppm]					1.27/3.53				
δC_6H_5 [ppm]				7.4					
^{3}J (HH) [Hz]					7.13				
^{19}F [b]									
δCF_3 [ppm]	-57.2	-56.6	-56.0	-57.4	-57.4	-54.0	-54.0	-56.7	-57.9
δ(2-C)F [ppm]	-70.6	-64.5 -71.9	-65.8	-68.5	-63.1	-46.8	-44.3	-59.4	—
δ(5-C)F [ppm]	-94.4	-73.3	—	-90.5	-83.3	-80.7 -91.6	-94.8	-93.2	-97.4
δ(4-C)F [ppm]						-85.4	-91.0	-88.2	-93.2
^{2}J(FF) [Hz]		161.5				153.0			

[a] At 90 MHz, int. std. TMS. [b] At 84.67 MHz, int. std. CF_3COOCH_3 = -76.2 ppm.

TABLE 2

EI mass spectra, m/e arranged in the order of decreasing intensity[a]

(VII)	111/113 $(CF_2NCCl)^+$, 69 $(CF_3)^+$, 130/132 $(CF_3NCCl)^+$, 114 $(CF_3NCF)^+$, 183 $(M - ClCN)^+$, 225/227 $(M - F)^+$
(VIII)	225/227 $(M - Cl)^+$, 130/132 $(CF_3NCCl)^+$, 69 $(CF_3)^+$, 111/113 $(CF_2NCCl)^+$ 85/87 $(CF_2Cl)^+$, 199/201 $(M - ClCN)^+$, 241/243/245 $(M - F)^+$
(IX)	241/243/245 $(M - Cl)^+$, 85/87 $(CF_2Cl)^+$, 69 $(CF_3)^+$, 146/148/150 $(CF_2NCCl_2)^+$, 111/113 $(CF_2NCCl)^+$, 130/132 $(CF_3NCCl)^+$, 215/217/219 $(M - ClCN)^+$
(X)	77 $(C_6H_5)^+$, 302 $(M)^+$, 141 $(C_6H_5NCF_2)^+$, 143 $(C_6H_5OCF_2)^+$, 51 $(C_4H_3)^+$ 119 $(C_6H_5OCN)^+$, 114 $(CF_3NCF)^+$, 69 $(CF_3)^+$
(XI)	238 $(M - C_3H_7)^+$, 252 $(M - C_2H_5)^+$, 273 $(CF_3NCFCH_2NCF)^+$, 281 $(M)^+$, 266 $(M-CH_3)^+$, 262 $(M - F)^+$, 218 $(CF_3NCFC(NCH_2)NCF_2)^+$, 114 $(CF_3NCF)^+$, 69 $(CF_3)^+$
(XVI)	134 $(CF_3NHCF_2)^+$, 69 $(CF_3)^+$, 92 $(CF_2NCO)^+$, 187 $(CF_3NCFCFNCO)^+$ 114 $(CF_3NCF)^+$, 65 $(CF_2NH)^+$, 73 $(FCNCO)^+$, 226 $(M)^+$

[a] Varian MAT 311 A, 70 eV.

The ^{19}F NMR spectra are not of first order and were not completely analyzed. Therefore not all coupling constants are quoted in Table 1. The observed chemical shifts are in agreement with those quoted in [3] for related molecules.

X-RAY STRUCTURE ANALYSIS

Crystal data. Compound (XVI), $C_4HF_7N_2O$, M_r = 226.05, orthorhombic, space group $P2_12_12_1$, a = 4.9404(6) Å, b = 8.003(1) Å, c = 18.504(5) Å, D_c = 2.052 g/cm^3, Zr-filtered MoKα (λ = 0.71073 Å), sin Θ/λ (max.) = 0.650, 1019 unique reflections, 810 with $F \geq 4\sigma(F)$, μ(MoKα) = 2.5 cm^{-1}, transmission = 0.904-0.980, R = 0.044, R_w = 0.065, $w = (\sigma^2(F) + 0.0009\ F^2)^{-1}$, 131 parameters, Δρ (max.) = 0.23 e/Å^3.

The cell constants and intensity data were obtained as described previously [6] with a Siemens AED 1 diffractometer. Conventional techniques were used to solve and refine the structure which is displayed with bond lengths in Fig. 1 [7].

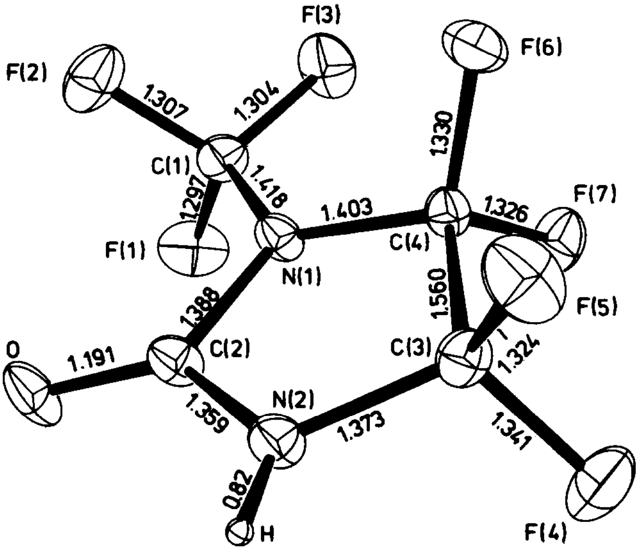


Fig. 1. View of (XVI) with bond distances (Å), σs between 0.004 and 0.005 Å.

The structure of (XVI) roughly obeys C_s symmetry. The ring atoms deviate by no more than 0.016(4) Å from planarity, and the substituent atoms O, C(1) and H lie within ±0.05 Å of this plane. This planarity contrasts to the shallow envelope conformations reported for 1-carbamoyl-2-imidazolidinone-4,5-diol (XVII) [8] and 1-(5-nitro-1,3-thiazol-2-yl)-2-imidazolidinone (XVIII) [9], which appear to be the only other structurally characterized imidazolidinones. Furthermore, the C(1)-F(3) and N(1)-C(4) bonds in (XVI) exhibit a synplanar orientation as has previously been found for CF_3 groups bonded to $N(CF_2)C{=}O$ fragments [10].

Both endocyclic bonds of N(1) are longer than those of N(2). For the N(1)-C(2) and N(2)-C(2) bonds, the difference (0.029(6) Å) is approximately half as large as in (XVII) (0.060 Å [8]) and (XVIII) (0.077(7) Å[9]). In (XVII) and (XVIII), the N(1)-C(4) and N(2)-C(3) bond lengths are equal, and their average value, 1.460 (8) Å, is appreciably longer than either of these distances in (XIV). On the other hand, the N(2)-C(2) bond in (XVI) is 0.036(7) Å longer than that in (XVIII) [9]. Thus fluorination of the ring atoms appears to shorten the N-C(sp^3) distances markedly while lengthening the N-C(sp^2) valencies. Furthermore, both types of bonds are longer when formed by a CF_3N fragment rather than by a HN moiety.

The N-CF_3 bond length in (XVI) doesn't differ significantly from those in $(CF_3)_3N$ (1.426(2) Å [11]) or $C_4N_2[N(CF_3)_2]_4$ (1.40(3) Å [6]) but is probably shorter than those found in a fluorinated hexahydrotriazinedione (1.446(9) and 1.465(9) Å [10]).

Interestingly, C_s rather than C_{3V} symmetry is found for the CF_3 group; that is, the cross-plane F(1)-C(1)-F(2) angle (106.9(4)°), is significantly smaller than the other two angles (mean 108.3(3)°). However, differences in the C(1)-F distances have not been resolved. Even after corrections for CF_3N librations [12], the in-plane C(1)-F(3) bond (1.337(5)Å) remains insignificantly shorter than the mean of the other two distances (1.345(9)Å).

Hydrogen bonding links the molecule into infinite chains. The N(2) atom donates its H atom to the O' atom of a screw-related molecule (N(2)...O', 2.835(4) Å; N(2)-H-O', 167(4)°). No other short intermolecular contacts are formed.

EXPERIMENTAL

1-Trifluoromethyl-2,2,5,5-tetrafluoro-4-chloro-3-imidazoline (VII) and 1-Trifluoromethyl-2,2,5-trifluoro-4,5-dichloro-3-imidazoline (VIII)

To 55.8 g (160 mmol) (IV) in a glass cylinder equipped with a Teflon valve was added a solution of 48.5 g (224 mmol) SbF_5 in 65 g SO_2 at -35°C. The reaction mixture was allowed to warm to 20 °C and kept for 3 days. (VII) was isolated by trap to trap distillation, collected at 70 °C and purified by distillation over a slit tube column, yield 82%. When a ratio SbF_5:(IV) = 1.25 was chosen and the reaction interrupted after 1 day, (VII), (VIII) and (IX) were formed in a 9:89:2 ratio. From this mixture (VIII) was isolated by fractional distillation, yield 73%.

(VII) $C_4ClF_7N_2$. Required/found; %Cl, 14.50/14.7; %F, 54.39/54.0. IR/Raman (cm^{-1}): 1657 s/1650 m (ν(C=N)), 1387 s/-, 1340 vs/-, 1251 vs/-, 1213 vs/- (ν(CF)).

(VIII) $C_4Cl_2F_6N_2$. Required/found; %Cl, 27.17/27.6; %F, 43.68/44.1. IR/Raman (cm^{-1}): 1653 s/1646 m (ν(C=N)), 1366 vs/-, 1318 vs/-, 1204 vs/-, (ν(CF)).

1-Trifluoromethyl-2,2,5,5-tetrafluoro-4-phenoxy-3-imidazoline (X)

4 g (16 mmol) (VII) and 20 ml dry CH_2Cl_2 were mixed, cooled to -65 °C, and a solution of 1.4 g (15 mmol) C_6H_5OH in 10 ml CH_2Cl_2 and then 2.5 g

(25 mmol) $N(C_2H_5)_3$ added. The mixture was stirred at room temperature for 30 min, filtered and (X) isolated by trap to trap distillation, yield 86%.
$C_{10}H_5F_7N_2O$. Required/found; %C, 39.75/40.0; %H, 1.67/1.7; %F, 44.01/43.9.
IR/Raman (cm^{-1}): 1686 s/1685 m (ν(C=N)), 1335 vs/-, 1320 vs/-, 1180 vs/-, (ν(CF)).

1-Trifluoromethyl-2,2,5,5-tetrafluoro-4-diethylamino-3-imidazoline (XI)

3.6 g (49 mmol) $HN(C_2H_5)_2$ was slowly added to a mixture of 6.03 g (25 mmol) (VII) and 20 ml CH_2Cl_2 at -65 °C, the precipitate filtered off and (XI) isolated by trap to trap distillation, yield 91%.
$C_8H_{10}F_7N_3$. Required/found; %C, 34.17/34.5; %H, 3.56/3.5; %F, 47.29/46.0.
IR/Raman (cm^{-1}): 1663 vs/1664 m (ν(C=N)), 1370 vs/-, 1305 vs/-, 1172 vs/- (ν(CF)).

1-Trifluoromethyl-2,2,4,4,5,5-hexafluoro-imidazolidine (XV) and 1-Trifluoromethyl-4,4,5,5,-tetrafluoro-2-imidazolidinone (XVI)

4.4 g (20 mmol) (V) were reacted with 9.4 g (35 mmol) SbF_5 in a Teflon cylinder at room temperature for 12 h, 4.4 g of volatile products were removed in vacuo and identified as a mixture of HF and (XV). The non-volatile residue consisted of 20 mmol (XIV). This residue converted another 4 g of (V) quantitatively to HF and (XV). By treatment of the residue with an excess of H_2O, (XVI) was formed as a colourless solid, yield 84%.
Similarly, (XVI) was formed when (XV) was stored in a glass vessel.
(XVI) $C_4HF_7N_2O$. Required/found; %F, 58.83/59.1; %N, 12.39/12.5.
IR/Raman (cm^{-1}): 3280 w/- (ν(NH)), 1830 vs/1830 w, 1791 vs/1790 s (ν(CO)), 1380 vs/-, 1311 vs/-, 1200 vs/- (ν(CF)).

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REFERENCES

1 R.N. Barnes, R.D. Chambers, M.J. Silvester, C.D. Hewitt and E. Klauke, J. Fluorine Chem., 24 (1984) 211.
2 H.J. Scholl and E. Klauke, Ger. Offen. 2 013 433 (1971).
3 R.N. Barnes, R.D. Chambers, C.D. Hewitt, M.J. Silvester and E. Klauke, J. Chem. Soc. Perkin Trans. I, (1985) 53.
4 R.D. Chambers, C.D. Hewitt, M.J. Silvester and E. Klauke, J. Fluorine Chem., 32 (1986) 389.
5 H. Bürger, R. Köplin and G. Pawelke, J. Fluorine Chem., 24 (1984) 457.
6 D.J. Brauer, H. Bürger and G. Pawelke, J. Fluorine Chem., 23 (1983) 339.
7 Further crystallographic details may be obtained from Fachinformationszentrum Energie - Physik - Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, F. R. G., on submission of the deposit number CSD 52 161 the literature reference and the names of the authors.
8 J.L. Flipper, Acta Crystallogr., B 29 (1973) 1756.
9 O.M. Peeters, N.M. Blaton and C.J. De Ranter, Acta Crystallogr., C 40 (1984) 1748.
10 H. Bürger, R. Köplin, G. Pawelke and C. Krüger, J. Fluorine Chem., 22 (1983) 175.
11 H. Bürger, H. Niepel, G. Pawelke and H. Oberhammer, J. Mol. Struct., 54 (1979) 159.
12 V. Schomaker and K.N. Trueblood, Acta Crystallogr., B 24 (1968) 63.