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Halogen exchange reactions of perhalo-3-azaalkenes and their subsequent dehalogenation to form hetero-1,3-dienes

Michael I. Cook and Darryl D. Desmarteau*

H. L. Hunter Chemistry Laboratory, Clemson University, Clemson, South Carolina 29634-1905 (U.S.A.)

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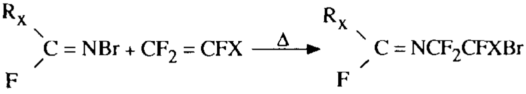
Abstract

Treatment of the perhalogenated azaalkenes, $R_xCF{=}NCF_2CFXBr$ ($R_x = CF_3$, C_2F_5, $ClCF_2$; $X = F$, CF_3) with $AlCl_3$ readily produces new imines of the type $R_xCCl{=}NCCl_2CFXBr$ and $R_xCCl_2N{=}CClCFXBr$. Dehalogenation of these new imines using activated zinc dust affords a series of novel hetero-1,3-dienes ($R_xCCl{=}NCCl{=}CFX$).

Introduction

Studies of the reaction chemistry of *N*-bromoperhalo-1-alkanimines ($R_xCF{=}NBr$) have so far shown that they react quite readily under thermal conditions with halogenated olefins to form 1,2-addition products [1]. The addition to a majority of unsymmetrical olefins was found to be highly regioselective, where during the addition the $R_xCF{=}N–$ group adds preferentially to the end of the olefin which would result in the formation of the most stable radical. As a result the reaction between $R_xCF{=}NBr$ and $CF_2{=}CFX$ affords perhalo-3-azaalkenes of the structure shown in eqn. (1).



$$\overset{R_x}{\underset{F}{>}}C{=}NBr + CF_2{=}CFX \xrightarrow{\Delta} \overset{R_x}{\underset{F}{>}}C{=}NCF_2CFXBr \quad (1)$$

$R_x = CF_3$, C_2F_5, $ClCF_2$; $X = Br$, Cl, F, CF_3

Recently our studies have concentrated on the reaction chemistry of the perhalo-3-azaalkenes and, in particular, their use as synthetic intermediates in the preparation of hetero-1,3-dienes.

Novel 1,3-dienes of the type $R_xC(O)N{=}CFCF_2Br$ can easily be prepared by hydrolysis of the perhalo-azaalkenes, followed by dehydrofluorination of perhaloacidamides, $R_xC(O)N(H)CF_2CF_2Br$, with KF [2].

We now report the synthesis of another series of hetero-1,3-dienes having the structure $R_xCCl{=}NCCl{=}CFX$.

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*Author to whom correspondence should be addressed.

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Experimental

General methods

All work was carried out in a Pyrex vacuum system equipped with glass–Teflon valves. Pressures were measured with a Wallace Tiernan series 1500 differential pressure gauge. Quantities of reactants and products were measured by direct weighing or by PVT measurements. Temperatures were measured by using a digital-indicating iron–constantan thermocouple.

Infrared spectra were recorded using a Perkin–Elmer 1430 spectrometer with a Model 3600 data station, using a 10-cm glass cell fitted with KCl windows. NMR spectra were recorded using a JEOL FX-90Q spectrometer using various deuterated media as both solvent and internal lock, and ~1% $CFCl_3$ as the internal reference. Chemical shifts are negative upfield from $CFCl_3$. Mass spectra were recorded using a Hewlett–Packard 5985B instrument at 70 eV for electron-impact (EI) and chemical ionization [(CI), CH_4)] spectra. Samples were introduced by direct gas injection.

Boiling points were determined using Siwoloboff's method [11] and are uncorrected.

Reagents

Aluminum chloride ($AlCl_3$) and zinc dust were obtained from commercial sources; $AlCl_3$ was freshly sublimed before use and zinc dust was activated by treatment with 2 N HCl, followed by washing with H_2O and then dried *in vacuo*. The compounds $CF_3CF{=}NCF_2CF_2Br$, $C_2F_5CF{=}NCF_2CF_2Br$, $ClCF_2CF{=}NCF_2CF_2Br$ and $CF_3CF{=}NCF_2CFBrCF_3$ were prepared using methods reported earlier [1].

General procedure for the reaction between $R_xCF{=}NCF_2CFXBr$ and $AlCl_3$

The imine (2–4 mmol) was condensed onto a five-fold excess of freshly sublimed $AlCl_3$ cooled to −196 °C in a 140 ml glass reactor. The flask was warmed to room temperature and the mixture magnetically stirred for a period of ~16 h. The volatiles were then pumped off from the solid and collected in a −196 °C trap. Purification was carried out by a series of trap-to-trap distillations to afford the product in 65–70% yield. Characterizations of the new imines are described below.

$CF_3CCl{=}NCCl_2CF_2Br$ and $CF_3CCl_2N{=}CClCF_2Br$

(2:3 mixture), glass at −90 °C to −88 °C. IR (gas): 1698 (vs) (C=N), 1283 (vs), 1228 (vs), 1185 (vs), 1065 (vs), 1021 (vs), 954 (m), 929 (s), 865 (vs), 838 (w), 803 (w), 774 (s), 673 (w), 609 (m) cm^{-1}. MS: (CI, major *m/z*): 346/344/342 $[(M+1)^+]$, 310/308/306 $[(M-Cl)^+$, 100%], 216/214/212 $[(M-CF_2Br)^+]$, 215/213/211 ($CCl_2CF_2Br^+$), 155/153/151 ($CF_3CCl_2^+$). (EI, major *m/z*): 310/308/306 $[(M-Cl)^+]$, 276/274/272 $[(M-CF_3)^+]$, 216/214/212 $[(M-CF_2Br)^+]$, 155/153/151 ($CF_3CCl_2^+$), 69 (CF_3^+, 100%). ^{19}F NMR (C_6D_6): $CF_3^ACCl{=}NCCl_2CF_2^BBr$, δA −72.6, δB −62.2; $CF_3^CCCl_2N{=}CClCF_2^DBr$, δC −83.0, δD −56.8; $J_{AB}=J_{CD}=0$ Hz.

$CF_3CF_2CCl{=}NCCl_2CF_2Br$ *and* $CF_3CF_2CCl_2N{=}CClCF_2Br$

(10:1 mixture), glass flowing slowly at −76 °C to −74 °C, vap. press. ~1.5 Torr at 25 °C. IR (liquid film): 1690 (vs) (C=N), 1345 (s), 1329 (s), 1228 (vs), 1209 (vs), 1185 (s), 1160 (vs), 1081 (s), 1067 (s), 1007 (vs), 987 (s), 874 (s), 767 (s), 744 (m), 695 (w), 656 (w) cm^{-1}. MS (CI, major *m/z*): 396/394/392 $[(M+1)^+]$, 306/358/356 $[(M-Cl)^+$, 100%], 266/264/262 $[(M-CF_2Br)^+]$, 215/213/211 $(CCl_2CF_2Br^+)$, 205/203/201 $(C_2F_5CCl_2{}^+)$, 131/129 (CF_2Br^+), 119 $(C_2F_5{}^+)$. (EI, major *m/z*): 360/358/356 $[(M-Cl)^+]$, 266/264/262 $[(M-CF_2Br)^+]$, 69 $(CF_3{}^+$, 100%). ^{19}F NMR (C_6D_6): $CF_3{}^ACF_2{}^BCCl{=}NCCl_2CF_2{}^CBr$, δA −81.4, δB −114.4, δC −62.4; $CF_3{}^DCF_2{}^ECCl_2N{=}CClCF_2{}^FBr$, δD −75.8, δE −120.6, δF −56.8; all J values ≈0 Hz.

$ClCF_2CCl{=}NCCl_2CF_2Br$ *and* $ClCF_2CCl_2N{=}CClCF_2Br$

(1:1 mixture), glass flowing slowly at −86 °C to −84 °C, vap. press. ~1 Torr at 25 °C. IR (liquid film): 1688 (s) (C=N), 1275 (w), 1225 (vs), 1170 (vs), 1163 (s), 1029 (s), 1000 (vs), 863 (s), 793 (vs), 764 (vs), 688 (m), 665 (w), 640 (m), 606 (m) cm^{-1}. MS (CI, major *m/z*): 326/342/332 $[(M-Cl)^+$, 100%], 276/274/272 $[(M-CF_2Cl)^+]$, 232/230/228 $[(M-CF_2Br)^+]$, 213/211 $(CCl_2CF_2Br^+)$, 171/169/167 $(CCl_2CF_2CCl^+)$. (EI, major *m/z*): 131/129 (CF_2Br^+), 99/97 (CF_2CCl^+), 87/85 (CF_2Cl^+). ^{19}F NMR (C_6D_6): $ClCF_2{}^ACCl{=}NCCl_2CF_2{}^BBr$, δA −59.7, δB −62.1; $ClCF_2{}^CCCl_2N{=}CClCF_2{}^DBr$, δC −67.5, δD −56.5; $J_{AB}=J_{CD}=0$ Hz.

$CF_3CCl_2N{=}CClCFBrCF_3$

Glass flowing slowly at −81 °C to −79 °C. IR (liquid film): 1691 (vs) (C=N), 1278 (vs), 1209 (vs), 1166 (s), 1089 (m), 1057 (s), 932 (s), 903 (vs), 852 (s), 813 (m), 739 (w), 719 (m), 647 (w) cm^{-1}. MS (EI, major *m/z*): 360/358/356 $[(M-Cl)^+$ 100%], 326/324/322 $[(M-CF_3)^+$, 279/277 $[(M-BrCl)^+]$, 181/179 (CF_3CFBr^+), 155/153/151 $(CF_3CCl_2{}^+)$, 69 $(CF_3{}^+)$. ^{19}F NMR (C_6D_6): $CF_3{}^ACCl_2N{=}CClCF^BBrCF_3{}^C$, δA −83.3, δB −127.3 (q), δC −76.3 (d); $J_{BC}=8.8$ Hz.

General procedure for the dehalogenation of $R_xCCl{=}NCCl_2CFXBr$ *and* $R_xCCl_2N{=}CClCFXBr$

The isomeric mixture of the imine (3.0 mmol) was condensed onto a mixture of activated zinc dust (1.0 g) and sulfolane (5.0 ml), and cooled to −196 °C whilst contained in a 140 ml glass reactor. After warming to room temperature, the contents of the vessel were magnetically stirred for ~1 h and the volatiles were then pumped off and collected in a −196 °C trap. Purification was achieved by vacuum-line fractionation to give the corresponding hetero-1,3-dienes $(R_xCCl{=}NCCl{=}CFX)$ in approximately 80% yield. The compounds were characterized as described below.

$CF_3CCl{=}NCCl{=}CF_2$

Boiling point, 89.5 °C. IR (gas): 1708 (vs) (C=N), 1668 (w) (C=C), 1343 (vs), 1291 (vs), 1233 (vs), 1180 (vs), 1030 (vs), 946 (s), 760 (s), 737 (w) cm^{-1}. MS (CI, major m/z): 232/230/228 [$(M+1)^+$], 231/229/227 [M^+], 210/208 [$(M-F)^+$], 194/192 [$(M-Cl)^+$, 100%], 160/158 [$(M-CF_3)^+$]. (EI, major m/z): 231/229/227 [M^+], 210/208 [$(M-F)^+$], 194/192 [$(M-Cl)^+$, 100%], 118/116 (CF_3CCl^+), 99/97 (CF_2CCl^+). ^{19}F NMR (C_6D_6): $CF_3{}^ACCl{=}NCCl{=}CF^BF^C$, δA −71.9, δB −72.8 (d), δC −82.3 (d); $J_{BC}=22$ Hz, $\Delta\delta_{BC}=797$ Hz. Mol. wt.: calcd 227.9, found 228.6.

$CF_3CF_2CCl{=}NCCl{=}CF_2$

Boiling point, 111 °C. IR (gas): 1704 (vs) (C=N), 1664 (m) (C=C), 1344 (vs), 1290 (w), 1219 (vs), 1157 (s), 1073 (s), 1028 (vs), 884 (s), 853 (vs), 750 (s), 721 (s), 670 (w) cm^{-1}. MS (CI, major m/z): 281/279/277 [M^+, 100%], 262/260/258 [$(M-F)^+$], 244/242 [$(M-Cl)^+$], 162/160/158 [$(M-C_2F_5)^+$]. (EI, major m/z): 281/279/277 [M^+], 244/242 [$(M-Cl)^+$], 119 ($C_2F_5{}^+$), 99/97 (CF_2Cl^+), 69 ($CF_3{}^+$, 100%). ^{19}F NMR (C_6D_6): $CF_3{}^ACF_2{}^BCCl{=}NCCl{=}CF^CF^D$, δA −81.5, δB −113.9, δC −72.2 (d), δD −81.5 (d); $J_{CD}=24.9$ Hz, $\Delta\delta_{CD}=784$ Hz. Mol. wt.: calcd. 277.9, found 279.3.

$ClCF_2CCl{=}NCCl{=}CF_2$

Boiling point, 115–117 °C. IR (gas): 1707 (vs) (C=N), 1669 (w) (C=C), 1341 (vs), 1292 (w), 1237 (vs), 1187 (s), 1155 (s), 1130 (w), 1098 (w), 1035 (vs), 957 (w), 932 (w), 865 (s), 826 (m), 796 (w), 716 (m), 644 (w) cm^{-1}. MS (CI, major m/z): 248/246/244 [$(M+1)^+$], 228/226/224 [$(M-F)^+$], 210/208 [$(M-Cl)^+$, 100%], 168/158 [$(M-CF_2Cl)^+$]. (EI, major m/z): 247/245/243 [M^+], 210/208 [$(M-Cl)^+$], 160/158 [$(M-CF_2Cl)^+$, 100%], 99/97 (CF_2CCl^+), 87/85 (CF_2Cl^+). ^{19}F NMR (C_6D_6): $ClCF_2{}^ACCl{=}NCCl{=}CF^BF^C$, δA −57.9, δB −73.2 (d), δC −82.5 (d); $J_{BC}=22.0$ Hz, $\Delta\delta_{BC}=785$ Hz. Mol. wt.: calcd 244.5, found 247.3.

$CF_3CCl{=}NCCl{=}CFCF_3$

(Mixture of E and Z isomers, ratio ~1:9), b.p., 109.5 °C. IR (gas): 1703 (s) (C=N), 1669 (s) (C=C), 1353 (vs), 1288 (vs), 1235 (vs), 1220 (vs), 1188 (vs), 1174 (vs), 1132 (m), 1096 (m), 1061 (w), 970 (vs), 906 (w), 874 (s), 822 (w), 763 (s), 724 (vs), 648 (s) cm^{-1}. MS (CI, major m/z): 281/279/277 [M^+, 100%], 262/260/258 [$(M-F)^+$, 244/242 [$(M-Cl)^+$, 210/208 [$(M-CF_3)^+$]. (EI, major m/z): 281/279/277 [M^+], 210/208 [$(M-CF_3)^+$], 149/147 (CF_3CFCCl^+), 69 ($CF_3{}^+$). ^{19}F NMR (C_6D_6): Z-$CF_3{}^ACCl{=}NCCl{=}CF^BCF_3{}^C$, δA −72.4, δB −123.2 (q), δC −66.1 (d); $J_{BC}=9.4$ Hz; E-$CF_3{}^DCCl{=}NCCl{=}CF^ECF_3{}^F$, δD −71.0, δE −127.0 (q), δF −64.9 (d); $J_{EF}=8.8$ Hz.

Results and discussion

Halogen exchange reaction

The fact that the addition reactions of N-bromoimines to unsymmetrical olefins is highly regioselective creates a problem in trying to use these perhalo-azaalkenes as precursors to hetero-1,3-dienes. Ideally one would like the reverse addition to take place as this would give rise to compounds of the type $R_xCF{=}NCFXCF_2Br$, where $X{=}Br$, Cl. A 1,2-dehalogenation could then be achieved by a variety of methods to afford the desired perhalogenated dienes, $R_xCF{=}NCF{=}CF_2$. Unfortunately this is not the case, since the addition always occurs in such a manner that the heaviest halogens are attached to the same terminal carbon. Alternatively, the reaction of *N*-bromoimines with symmetrical halogenated olefins $XCF{=}CFX$ other than $CF_2{=}CF_2$ was unsuccessful and no addition products were observed. As a result, formation of perhalo-3-azaalkenes containing a halogen other than fluorine on the carbon adjacent to nitrogen via these routes had to be abandoned.

α,α,α'-Trichloro(perfluoro)azaalkenes that contain all three chlorine atoms centered around the imine group ($CCl{=}NCCl_2^-$) have been prepared previously by treating the corresponding perfluorinated tertiary amine with $AlCl_3$ [3–5]. In most cases the reaction gives rise to an isomeric mixture (eqn. (2)]:

$$(CF_3CF_2)_2NCF_2R_f \xrightarrow{AlCl_3} CF_3CCl{=}NCCl_2R_f + CF_3CCl_2N{=}CClR_f \tag{2}$$

The reaction is believed to proceed via the intermediate perfluoroazaalkene $CF_3CF{=}NCF_2R_f$, which in the presence of $AlCl_3$ undergoes a series of halogen-exchange reactions to give the observed products. The perhalo-azaalkenes used in our study all have the basic structure $R_xCF{=}NCF_2CFXBr$ ($R_x{=}CF_3$, C_2F_5, $ClCF_2$, $X{=}F$ or CF_3), and each of these compounds contains three fluorine atoms centered around the imine group. We therefore decided to use this procedure to see if similar trichloro-azaalkenes to those already reported could be prepared.

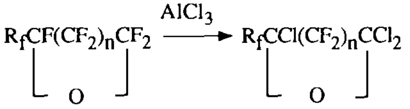
The reaction conditions employed were rather mild: the alkanimines were stirred with an excess of dry $AlCl_3$ at room temperature for a period of approximately 16 h and the products formed were identified as those given in Table 1. In all cases the three fluorine atoms centered around the imine functionality were exchanged by chlorine and in all but one example ($R_x{=}CF_3$, $X{=}CF_3$) a mixture of isomeric imines were formed. The ratio of each isomer was determined from their ^{19}F NMR spectra.

Previous work has shown that $AlCl_3$ can readily be used for replacing fluorine by chlorine. Perfluorocyclic ethers of the type shown below can easily be converted to their α,α,α'-trichloro analogs with $AlCl_3$ [6] [eqn. (3)]:

TABLE 1

Reaction of $R_xCF{=}NCF_2CFXBr$ with $AlCl_3$

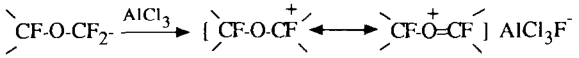
Azaalkene	Products (isomer ratio)
$CF_3CF{=}NCF_2CF_2Br$	$CF_3CCl_2N{=}CClCF_2Br$, $CF_3CCl{=}NCCl_2CF_2Br$ (3:2)
$C_2F_5CF{=}NCF_2CF_2Br$	$C_2F_5CCl_2N{=}CClCF_2Br$, $C_2F_5CCl{=}NCCl_2CF_2Br$ (1:10)
$ClCF_2CF{=}NCF_2CF_2Br$	$ClCF_2CCl_2N{=}CClCF_2Br$, $ClCF_2CCl{=}NCCl_2CF_2Br$ (1:1)
$CF_3CF{=}NCF_2CFBrCF_3$	$CF_3CCl_2N{=}CClCFBrCF_3$ (one isomer)



$$R_fCF(CF_2)_nCF_2 \xrightarrow{AlCl_3} R_fCCl(CF_2)_nCCl_2$$

(3)

The mechanism proposed for this conversion involves the formation of an aluminum complex by the abstraction of an α-fluorine, *i.e.*



$$>CF\text{-}O\text{-}CF_2\text{-} \xrightarrow{AlCl_3} [>CF\text{-}O\text{-}\overset{+}{C}F< \longleftrightarrow >CF\text{-}\overset{+}{O}{=}CF<]\ AlCl_3F^-$$

Exchange is then completed by abstracting a chloride ion from $AlCl_3F^-$ by the carbocation intermediate. The process is repeated a further two times until the trichloro derivative is finally formed.

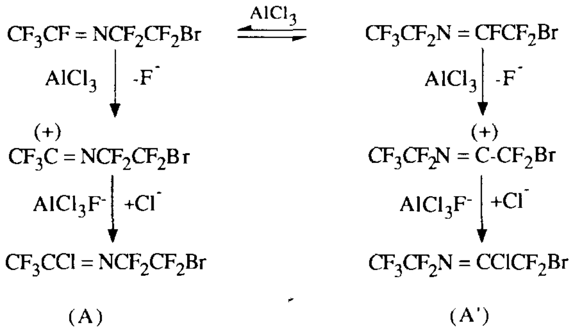
In an attempt to obtain more information with regard to the mechanism of the halogen exchange, a series of reactions were carried out on the 3-azaalkene, $CF_3CF{=}NCF_2CF_2Br$, using varying quantities of $AlCl_3$. Our results showed that before halogen exchange occurs, the imine undergoes isomerization [eqn. (4)] similar to the equilibrium that has also been observed when the imine is treated with active KF.

$$CF_3CF{=}NCF_2CF_2Br \xleftrightarrow{AlCl_3} CF_3CF_2N{=}CFCF_2Br \qquad (4)$$

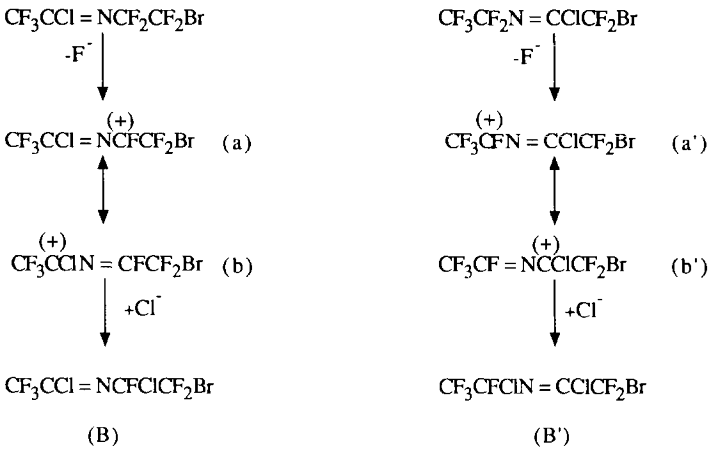
The next step is probably similar to that already described, in that an anionic aluminum complex is formed by the abstraction of the α'-fluorine (CF=N) from each of the isomeric imines. This will then give rise to the carbonionic intermediates shown in Scheme 1.

Chlorination then occurs to afford the two monochloro-imines (A) and (A'). A mixture of these isomers (1A:3A') was successfully isolated in a 3:1 reaction of $CF_3CF{=}NCF_2CF_2Br$ with $AlCl_3$ and identified by ^{19}F NMR spectroscopy [$CF_3{}^ACCl{=}NCF_2{}^BCF_2{}^CBr$, δA -73.2 (s), δB -99.8 (t), δC -69.0 (t); $J_{BC} = 6.0$ Hz; $CF_3{}^ACF_2{}^BN{=}CClCF_2{}^CBr$, δA -86.0 (s), δB -103.2 (s), δC -57.4 (s)].

The next step would entail the removal of an α-fluorine from the N–CF_2 group of each of the two isomers. This then gives rise to a series of resonance-stabilized intermediates shown in Scheme 2.

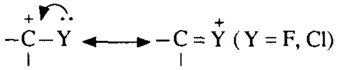


Scheme 1.



Scheme 2.

The canonical forms (a, a′) and (b, b′) are also further stabilized by the effect of a mesomeric interaction which occurs between an empty orbital on carbon and an unshared pair of electrons on the adjacent halogen



$$\overset{+}{-\text{C}}-\text{Y} \longleftrightarrow -\text{C}=\overset{+}{\text{Y}} \quad (\text{Y} = \text{F, Cl})$$

The (+M) effect of the fluorine is stronger than that of chlorine [7], thus fluorine should bestow a greater degree of stability on the canonical forms (a) and (a′). This is also coupled with the fact that chlorine has a greater stabilizing effect on the imine (C=N) bond than does fluorine. Therefore if we consider these intermediates to be the predominant ones, the addition of chloride ion will afford the dichloro-compounds (B) and (B′). Unfortunately all attempts at isolating the dichloro derivatives have so far proved unsuccessful. The process is further repeated until the α,α,α'-trichloro analogs are finally formed.

The ratio of the isomers formed cannot be easily explained. It may arise from the initial step of isomerisation of the unreacted imine, although we have no clear evidence that the ratio of the final products is related to the ratio of the unreacted imine isomers. We could base our observations on steric grounds. After abstraction of the third fluorine the following stabilized cation is formed:

$$\text{R}_x\overset{(+)}{\text{C}}\text{Cl-N} = \text{CClR}_y \longleftrightarrow \text{R}_x\text{CCl} = \text{N-}\overset{(+)}{\text{C}}\text{ClR}_y$$

R_x=CF_3, C_2F_5, $ClCF_2$, R_y=CF_2Br, -$CFBrCF_3$

In the case where $R_x = ClCF_2$ and $R_y = BrCF_2$, these two groups are of similar size; hence Cl^- should show an equal preference to attach at either carbon adjacent to the two groups. As a result we would expect the products to be a 1:1 mixture of isomers, which is in agreement with the result observed.

When $R_x = CF_3$, $R_y = CFBrCF_3$, R_y is bulkier than R_x, thus on steric grounds we would expect Cl^- to attach preferentially at the position adjacent the group R_x. This would give rise to $CF_3CCl_2N{=}CClCFBrCF_3$ as the major isomeric product. In this case the steric effect must be extremely predominant as no trace of the other isomer $CF_3CCl{=}NCCl_2CFBrCF_3$ was detected.

The identity of the new compounds is strongly supported by the data given in the experimental section. In most cases, molecular ions MH^+ are observed and all exhibit a base peak corresponding to $(M-Cl)^+$ in the CI mass spectra.

The effect of exchanging the fluorine atoms around the imine group by chlorine should result in a shift of the $C{=}N$ stretching frequency, which usually occurs in the region of 1780 cm^{-1} for the unreacted imines, to a much lower wavenumber. This is observed and each new imine shows a strong $C{=}N$ absorption near 1690 cm^{-1} in the infrared spectra.

Dehalogenation of $R_xCCl_2N{=}CClCFXBr{:}R_xCCl{=}NCCl_2CFXBr$

The conversion of the $-CF{=}NCF_2^-$ group to $-CCl{=}NCCl_2^-$ provides a series of highly halogenated azaalkenes that should readily undergo dehalogenation to afford hetero-dienes. Although there are a variety of methods one could use to accomplish this [8], zinc dust in sulfolane proved very effective. Sulfolane proved to be an excellent solvent since not only was it unreactive towards the imines, but its high boiling and low volatility meant that the products could easily be separated from the reaction mixture by vacuum line fractionation. The products isolated were all identified as those listed in Table 2.

It is interesting to note that in all cases elimination of BrCl occurs in such a manner that only 1,3-dienes are formed [eqn. (5)]:

$$\left.\begin{array}{l} R_xCCl_2N=CClCFXBr \\ R_xCCl=NCCl_2CFXBr \end{array}\right\rangle \xrightarrow[\text{Sulfolane}]{\text{Zn}} R_xCCl=NCCl=CFX \qquad (5)$$

$R_x = CF_3,\ C_2F_5,\ ClCF_2,\ X = F,\ CF_3$

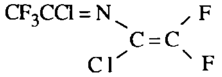
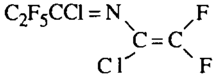
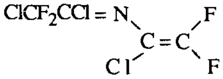
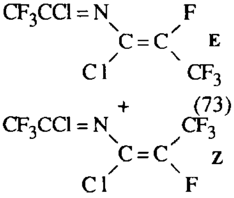
In order for this to occur each of the isomers must undergo dehalogenation via slightly different routes. The isomer $R_xCCl_2N{=}CClCFXBr$ dehalogenates by a 1,4-elimination of BrCl. The first step in this metal-induced process is probably nucleophilic attack by the zinc on the electrophilic bromine. Loss of $ZnBr^+$ results in the formation of a short-lived carbonionic intermediate [9, 10], which very rapidly, via the shift of the imine $(C{=}N)$ bond, eliminates Cl^- from the 4-position (Scheme 3).

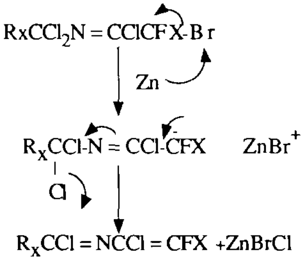
The other isomer, $R_xCCl{=}NCCl_2CFXBr$, undergoes a 1,2-elimination of BrCl from the *N*-alkyl side-chain where the imine group plays no part in the elimination process. There is also the possibility that the isomer R_x-$CCl_2N{=}CClCFXBr$ can undergo a 1,2-elimination to form a 1,2-diene (ketenimine) of the type $R_xCCl_2N{=}C{=}CFX$. However, no such products were observed in any of the dehalogenation reactions.

All the new dienes were identified by interpreting the data given in the experimental section. Molecular ions MH^+ or M^+ were observed for each

TABLE 2

Dehalogenation of $R_xCCl_2N{=}CClCFXBr{:}R_xCCl{=}NCCl_2CFXBr$

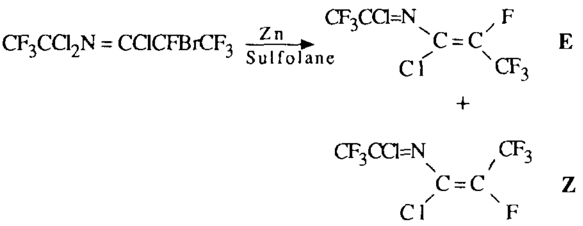
Azaalkene	Conditions	Products (% yield)
$CF_3CCl_2N{=}CClCF_2Br$ $CF_3CCl{=}NCCl_2CF_2Br$	Zn/sulfolane 22 °C, 1 h	 (76)
$C_2F_5CCl_2N{=}CClCF_2Br$ $C_2F_5CCl{=}NCCl_2CF_2Br$	Zn/sulfolane 22 °C, 1 h	 (70)
$ClCF_2CCl_2N{=}CClCF_2Br$ $ClCF_2CCl{=}NCCl_2CF_2Br$	Zn/sulfolane 22 °C, 1 h	 (83)
$CF_3CCl_2N{=}CClCFBrCF_3$	Zn/sulfolane 22 °C, 30 min	 ratio $E:Z \sim 1:9$



Scheme 3.

compound in either the CI or EI mass spectra and all exhibited a strong absorption at ~1705 cm^{-1} [ν(C=N)] and a weak absorption at ~1668 cm^{-1} [ν(C=C)] in the infrared.

The ^{19}F NMR spectra were straightforward, those containing the $-C{=}CF_2$ moiety exhibiting a classic AB pattern where $J_{AB} \sim 22$ Hz and $\Delta\delta_{AB} \sim 790$ Hz. In all of these examples only one isomer was observed, the stereochemistry of which could not be determined from the data available. For the diene $CF_3CCl{=}NCCl{=}CFCF_3$, a mixture of *E* and *Z* isomers was detected, with the *Z* isomer being the major one formed [eqn. (5)]:



(5)

ratio *E*:*Z* ~ 1:9.

Conclusion

To summarize, the reaction between α,α,α'-trifluoro-perhaloazaalkenes with $AlCl_3$ provides a facile route to the formation of the corresponding α,α,α'-trichloro analogs. The practical use of the trichloro derivatives to prepare a variety of highly halogenated hetero-1,3-dienes in good yields has also been demonstrated. Further studies of the reaction chemistry of these dienes and other related compounds are currently in progress.

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References

1 B. A. O'Brien and D. D. DesMarteau, *J. Org. Chem.*, *49* (1984) 1467; *Rev. Chem. Miner.*, *23* (1986) 621.
2 M. I. Cook and D. D. DesMarteau, *J. Org. Chem.*, *56* (1991) 5256.
3 V. S. Plashkin, L. N. Pushkina and S. V. Sokolov, *Zh. Org. Khim.*, (1974) 1215; *J. Org. Chem.*, *10* (1974) 1225.
4 S. V. Sokolov and S. A. Mazolov, *Dokl. Akad. Nauk SSSR*, *162* (1965) 1071.
5 For a review and references cited therein, see *Perfluorohalogeno-organo Compounds, Gmelin's Handbuch der Anorganische Chemie*, 8th edn., Springer-Verlag, Berlin, 1981, part 9, p. 134.
6 G. V. D. Tiers, *J. Am. Chem. Soc.*, *77* (1955) 4837.
7 R. D. Chambers, *Fluorine in Organic Chemistry*, Wiley, New York, 1973, p. 73.
8 For monographs on dehalogenation reactions, see W. H. Saunders and A. F. Cockerill, *Mechanisms of Elimination Reactions*, Wiley, New York, 1973, p. 332.
9 D. V. Barthorpe, *Elimination Reactions*, Elsevier, Amsterdam, 1963.
10 W. M. Schubert, B. S. Rabinovitch, N. R. Larson and V. A. Sims, *J. Am. Chem. Soc.*, *74* (1952) 4590.
11 D. L. Pavia, *Introduction to Organic Laboratory Techniques*, W. B. Saunders, Philadelphia, PA, 1976, p. 537.