N-Chlorosulfenyl-aziridines

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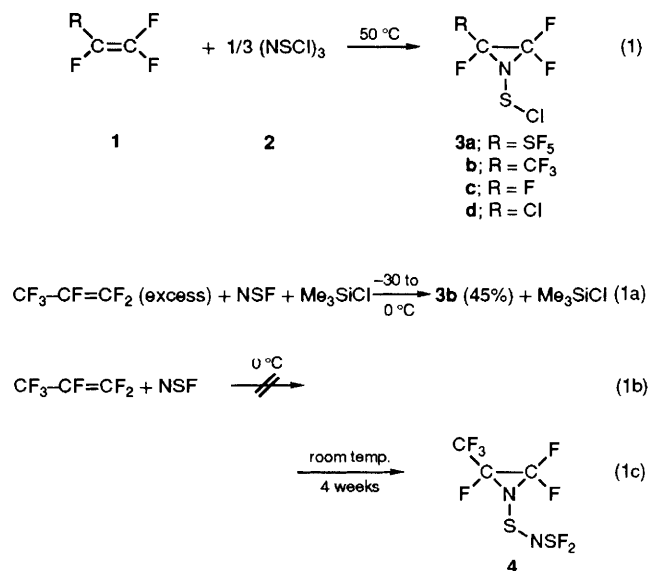[b] Department of Chemistry, Portland State University, Portland, OR 97207-0751, USA
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Monomeric NSCl adds to the C=C double bond of highly fluorinated alkenes $R-CF=CF_2$ (R = F, CF_3, SF_5, Cl), to give the corresponding chlorosulfenylaziridines.

Atkinson and Judkins have demonstrated that S-arylthiazynes, prepared from $Ar-S-NH_2$ and $Pb(OAc)_4$, add in situ to alkenes with formation of N-arylsulfenylaziridines.[1] For reactions of the S-perfluoroalkylthiazynes R_fSN[2,3] and aminothiazynes R_2NSN,[4] probably formed as intermediates, and of halothiazynes XSN (X = F[5] and Cl[6]), the isolated products might be explained by a sulfenylnitrene pathway. We have found that (NSCl) provides a simple route to perhalogenated N-chlorosulfenylaziridines (Scheme 1). The reactive intermediate is the monomeric NSCl, which is generated either from the cyclic trimer by heating to 50 °C or by metathesis from NSF and Me_3SiCl at low temperatures. NSF does not react with hexafluoropropene under the conditions of reactions (1a) or (1b), but after 4 weeks at room temperature 4 (50%) is isolated. This product was obtained earlier from the photolysis of NSF and $CF_3CF=CF_2$.[4b]

These results unequivocally show that NSCl will react in a nitrene type fashion with highly fluorinated alkenes. The addition mechanism is of some interest, although it is not yet fully understood.

A preliminary MNDO calculation (Fig. 1) for the addition of NSCl to tetrafluoroethene in the singlet state, including minimal configuration interaction (CI) using the HOMO and the LUMO, indicates a two-step reaction: the educts I react

$$\begin{array}{ccc}
\underset{F}{\overset{R}{>}}C=C\underset{F}{\overset{F}{<}} & + \ 1/3\ (NSCl)_3 & \xrightarrow{50\ °C} \end{array}$$ (1)

1   2   3a; R = SF_5
  b; R = CF_3
  c; R = F
  d; R = Cl

$$CF_3-CF=CF_2\ (\text{excess}) + NSF + Me_3SiCl \xrightarrow[0\ °C]{-30\ to} 3b\ (45\%) + Me_3SiCl\ (1a)$$

$$CF_3-CF=CF_2 + NSF \xrightarrow{0\ °C} \!\!\!\!\not\,\,$$ (1b)

$$\xrightarrow[4\ weeks]{room\ temp.}$$ (1c)

4

Scheme 1 3a, b.p. 45–46 °C at 10 mmHg, 65% yield; 3b, b.p. 85 °C, 78% yield; 3c, b.p. ca. 50 °C, 46% yield; 3d, b.p. 66 °C, 41% yield
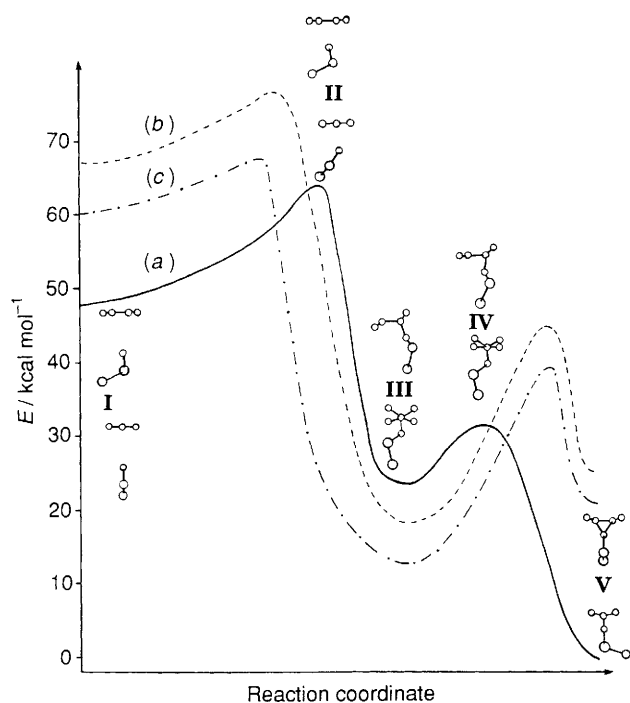
Fig. 1 MNDO calculated reaction pathway for the addition of NSCl to tetrafluoroethene in the singlet state (a) RHF (restricted Hartree–Fock) and in the triplet state (b) RHF, (c) UHF (unrestricted HF); the singlet optimized structures of the educts I, the product V, the transition states II and IV and the intermediate III are shown in two different ways: in the lower one the CC axis lies perpendicular to the plane of the paper, whereas in the upper one the plane formed by the two carbon atoms and the nitrogen atom lies in the plane of the paper. This leads in some cases to a superposition of the atoms above and below the paper plane. 1 cal = 4.184 J.

via the transition state II, which is about 18 kcal mol^{-1} higher in energy than I, to give the intermediate III, which is about 23 kcal mol^{-1} more stable than I. III reacts with an activation barrier of about 8 kcal mol^{-1} via the transition state IV to give the product V; V is about 48 kcal mol^{-1} more stable than I. The optimized transition states as well as the intermediate indicate a highly unsymmetrical approach of the nitrene towards one of the two carbon atoms, which is not unexpected because the symmetrical concerted approach is forbidden,† as confirmed by simple orbital arguments. MNDO calculations for the triplet state, however, suggest the possibility that there might be an intersection between the energy surfaces of the singlet and the triplet state, the latter being more stable in the region of both the singlet transition states II and IV and the singlet intermediate III. If there were indeed two intersystem crossings involved in the reaction with F_3C–CF=CF$_2$, the heavy atom effect could be the reason for the observed higher reactivity of NSCl as compared with NSF. (*Ab initio* calculations are presently being used to answer this question which was raised by MNDO calculations.) With C_2F_4 NSF already reacts below 0 °C, but by a different mechanism. Several isomers of 2NSF·C_2F_4 are formed, among them the product which is analogous to 4.

While compounds 3a and 3b are distillable stable yellow liquids, 3c and 3d decompose at room temperature. All new compounds were characterized by mass, IR and NMR spectra, and elemental analyses.

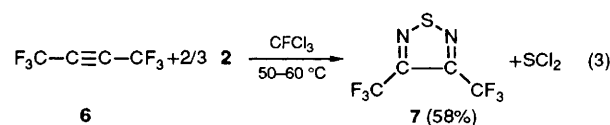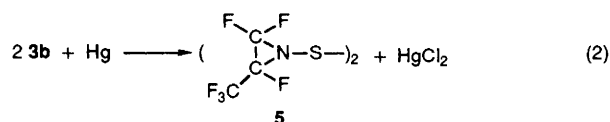In the ^{19}F NMR spectrum (Table 1) for 3a, 3b and 3d, a characteristic ABX pattern is found for the fluorine atoms

† As suggested by one of the referees calculations for the concerted one-step reaction were performed, resulting in a transition state which is unexpectively only 3.5 kcal mol^{-1} higher in energy than transition state II in Fig. 1.

Table 1 ^{19}F Chemical shifts (δ in ppm from CFCl$_3$) and coupling constants (J in Hz) of 3a–3d

R	3a R = SF$_5$	3b R = CF$_3$	3c R = F	3d R = Cl
F(1)	—^{a}	-75.2		
F(2)	-110.95	-114.2 ⎤	-119.5	⎰ -124.45
F(3)	-118.14	-123.1 ⎦		⎱ -121.28
F(4)	-144.13	-176.1		-106.55
$^3J_{1,4}$	⎰ 5.8 (A) ⎱ 13.3 (B)	5.5		
$^4J_{1,2}$	11.1 (B)	7.5		
$^4J_{1,3}$		0.6		
$^2J_{2,3}$	68.85	81.0		72.4
$^3J_{2,4}$	18.41	19.8		18.0
$^3J_{3,4}$	16.3	15.6		12.0

^{a} AB$_4$ Spin system, δ_A 66.0, δ_B 50.88, J_{AB} 146.9 Hz.

$$2\ 3b + Hg \longrightarrow (\ \underset{F_3C}{\overset{F}{\text{C}}}\underset{}{\text{N–S–}})_2 + HgCl_2 \qquad (2)$$

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$$F_3C–C\equiv C–CF_3 + 2/3\ 2 \xrightarrow[50–60\ °C]{CFCl_3} \underset{F_3C}{\overset{}{}} \overset{S}{\underset{}{}} \underset{CF_3}{\overset{}{}} + SCl_2 \qquad (3)$$

6   7 (58%)

bonded to the aziridine ring, while for 3c only a singlet is observed. As reported for other sulfenylaziridines,[6] inversion at the nitrogen is not restricted even at low temperatures (−80 °C).

Preliminary investigations show that an extensive chemistry with the chlorosulfenylaziridines might be possible; e.g. 3b reacts with mercury to give the disulfide 5 [reaction (2)]; with silylamines nucleophilic exchange of the chlorine bonded to sulfur is possible. From the alkyne 6 and 2 3,4-bis(trifluoromethyl)-1,3,5-thiadiazole 7 was isolated as a yellow liquid, b.p. 98 °C [reaction (3)]. This compound has been observed among the products of the reaction of NSF and 6;[7] it was also isolated in low yield from S$_4$N$_4$ and CF$_3$–C≡C–CF$_3$.[8] The formation of 7 can be explained by addition of 2NSCl to the triple bond and loss of SCl$_2$.

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