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1-Arylamino-1-Methylthio-2-Nitroethene in Superacids: NMR Study and Reactivity of the Formed Hydroxynitrilium Ions.

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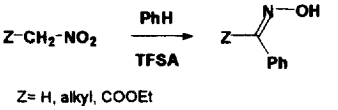
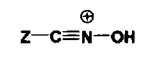
Abstract: *At low temperature in triflic acid, 1-arylamino-1-methylthio-2-nitroethylenes give firstly C,O-protonated species then a conjugated dication with aryliminium and hydroxynitrilium sites. The last one was trapped in situ with aromatic or quenched with MeOH or MeSH to form aryliminohydroxyimino derivatives. Intramolecular reaction occurs when temperature rises. Effect of aromatic ring substituant, acidity (HF-SbF_5 5:1) and Z/E imine configuration are also discussed.*

INTRODUCTION.

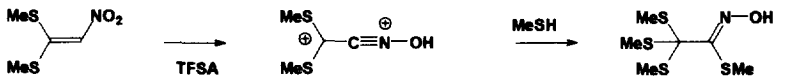
Nitroene derivatives are useful synthons in organic chemistry which can be used, for instance in heterocyclic chemistry[1]. In superacids, they are polyprotonated to yield multicharged species that can be trapped by suitable nucleophiles[2,3]. To explain electrophilic reaction with aromatics and mainly the configuration of formed aromatic oximes, we postulated the existence of a transient hydroxynitrilium ion on which reaction lead to the predicted oxime configuration[3]. Later it was shown that 1,1-bis(methylthio)-2-nitroethylene **1** dissolved in TFSA at low temperature, led quantitatively to the stable hydroxynitrilium ion **2**. Trapping this ion by suitable nucleophiles gives α-hydroxyiminoorthothioesters or furoxane orthothioesters[4].



Z= H, alkyl, COOEt



Hydroxynitrilium ion



1 **2**

The present study was undertaken with the purpose to assess existence of other stable hydroxynitrilium ions, 1-arylamino-1-methylthio-2-nitroethylene derivatives **3a-c** were studied because they were reported to give cyclic oximes in TFSA at room temperature[5].

NMR STUDY.

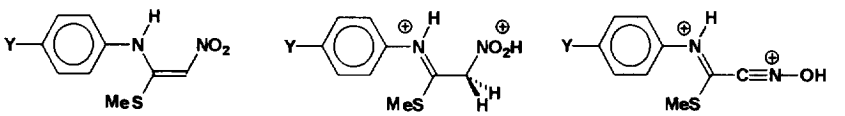
Starting materials were prepared on a conventional way[5,6] by reacting 1,1-bis(methylthio)-2-nitroethylene with one molar equivalent of a substituted aniline in acetonitrile. Resulting compounds **3a-c** dissolved easily in TFSA at 0-5°C to give a colored solution. By quickly lowering the temperature it was possible to monitor the reaction and to study the formed cations. Starting material quickly disappeared (no vinylic proton observed) to give cation **4** characterized by a methylene group that resonates near δ_H= 5.4 ppm and δ_C= 75 ppm. Those chemical shifts are of the same order of magnitude as those reported for C,O-

protonated forms of **1** in TFSA. Protonation of the nitro group was not observed by NMR in those experimental conditions probably because of a fast exchange process with the medium, but must be postulated because of the acidity of the medium. This kind of protonation is known to be fast even at temperature as low as -80°C in the more acidic medium[7] HSO_3F and is only postulated indirectly in TFSA by its influence on chemical shifts or by cryometry[2]. The iminium NH protons resonate near δ_H= 10.5 ppm and the iminium carbons in the range of δ_C= 183.8 to 187.8 ppm. NMR spectral data of ions **4a-c** are reported in table 1.

Table 1: NMR spectra of cations **4a,b,c** in TFSA at 255 °K

	^1H NMR				^{13}C NMR			
Cation		>CH_2	H ar.	NH^+		>CH_2	C ar.	>C=N
Y= H **4a**	2.15 s, MeS	5.36 s	6.8 m, 2H 6.9 m, 3H	10.27 s	15.80 SMe	73.76	123.44; 124.39; 133.39; 135.77	184.80
Y= F **4b**	2.41 s, MeS	5.36 s	6.65 m, 2H 6.86 m, 2H	10.22 s	15.81 SMe	74.52	118.15 d,^2J= 24 Hz 126.45 d,^3J= 9 Hz 132.12 d,^4J= 3 Hz 164.88 d,^1J=253 H	187.79
Y= MeO *(Z)*-**4c**	2.32 s, MeS 3.62 s, MeO	5.44 s	6.78 d,*J*= 9Hz 2H 7.02 d,*J*= 9Hz 2H	10.79 s	16.24 MeS 59.24 MeO	75.07	118.24; 127.46 130.00; 158.94	183.79
Y= MeO *(E)*-**4c**	2.50 s, MeS 3.64 s, MeO	5.10 s	6.82 d,*J*= 9Hz 2H 6.91 d,*J*= 9Hz 2H	10.15 s	16.58 MeS 59.44 MeO	74.45	118.19; 128.45 130.44; 158.83	187.32

Y: a= H, b= F, c= MeO



3a,b,c **4 a,b,c** **5a,b,c**

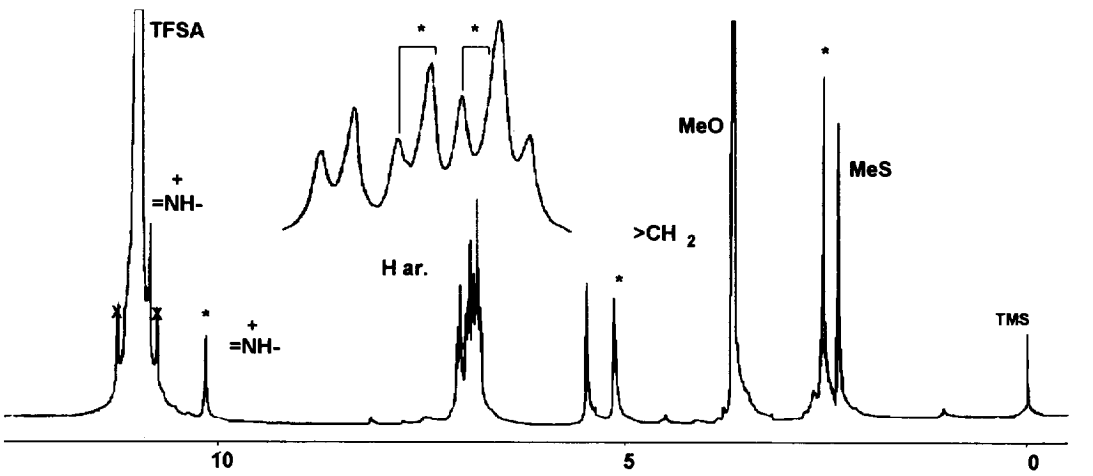


Figure 1: ^1H NMR (200 MHz/Ref. TMS in methanol-d_4) of ions *(Z)*-**4c** and *(E)*-**4c** (with *) at 255 °K in TFSA/$CDCl_3$

Only the *Z* isomer was observed, however, the methoxy derivative isomerized in TFSA/$CDCl_3$ at temperature slightly above 273° K to give a final 1:1 mixture of both *Z* and *E* isomers (Figure 1). The slowly formed *(E)*-**4c** isomer is mainly characterized by i) shielding of the methylene group ($\Delta\delta_H$= 0.34 and $\Delta\delta_C$=

0.62 ppm) and ortho aromatic protons ii) deshielding of the MeO ($\Delta\delta_H$ = - 0.02 and $\Delta\delta_C$ = - 0.20 ppm), MeS ($\Delta\delta_H$= -0.18 and $\Delta\delta_C$= -0.34 ppm) and iminium carbon ($\Delta\delta_C$ = - 3.53 ppm).

At low temperature, cations **4** are slowly transformed into ions **5**. Using ^{1}H NMR, this reaction can be monitored by following disappearance of the methylene signal. The NMR spectra of ions **5** exhibit, along with MeS and aromatic signals, an iminium carbon that resonates upfield in the region δ_C= 166.08 to 169.56 ppm because of conjugation. However, the main feature in ^{13}C NMR was a broad and weak signal near 26.5 ppm. This signal, by its shape, chemical shift and intensity is very similar to the one observed for hydroxynitrilium **2** derived from 1,1-bis(methylthio)-2-nitroethene[4] and close to values found for substituted aromatic nitrile oxides[8]. Broadening and weakening of the signal is due to coupling with ^{15}N but mainly to quadripolar relaxation with ^{14}N, the most abundant isotope[8d,9]. Ion **5a** exists as a sole *(E)* isomer (Figures 2 and 3), meanwhile **5b** gives both the *(Z)* and *(E)* isomers in a 2:1 ratio.

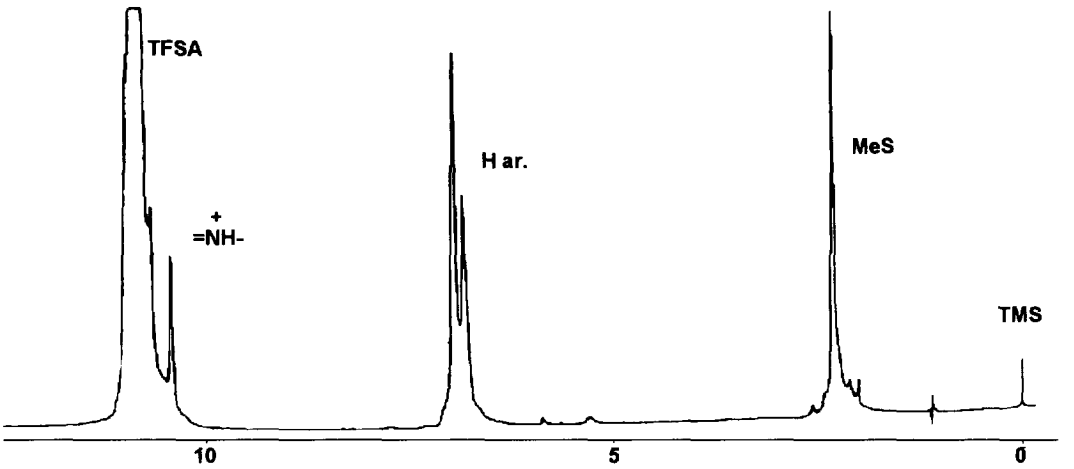


Figure 2: ^{1}H NMR spectrum (200 MHz/Ref. TMS in methanol-d_4) of hydroxynitrilium ion **5a** in TFSA at 255 K

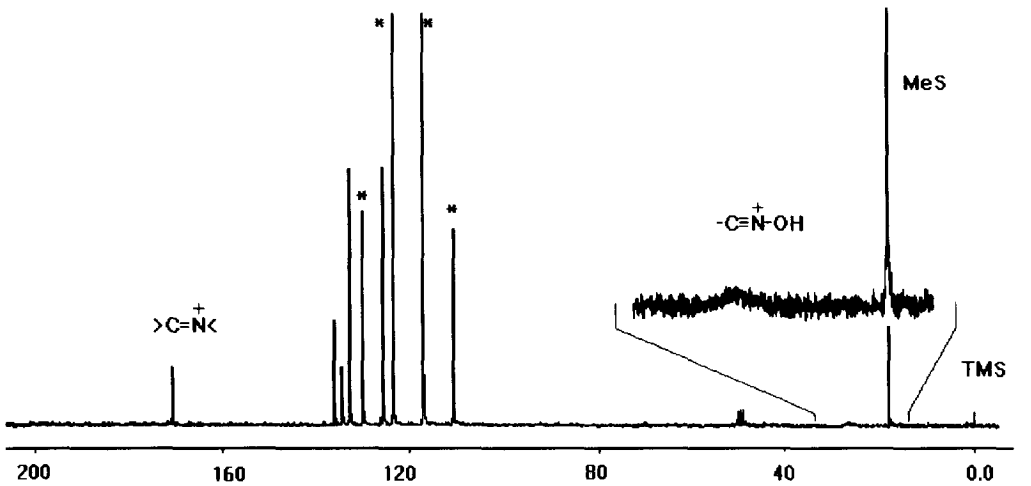


Figure 3: ^{13}C NMR (50 MHz/Ref. TMS in methanol-d_4) spectra of ion **5a** in TFSA at 255 °K (* : TSFA signals)

The major difference between *(E)* and *(Z)* structures lies in the chemical shift of the iminium carbon $\Delta\delta_C$ = 3.48 ppm, value found in other iminium systems[10]. A weak difference is also observed for the MeS group ($\Delta\delta_H$ = 0.14 and $\Delta\delta_C$= 0.80 ppm).

Table 2: NMR spectra of hydroxynitrilium ions **5** in TFSA.(200/50 Mhz; MeOD-d_4/TMS) at 254°K

	^{1}H NMR			^{13}C NMR			
Ion	**MeS**	H-ar.	$=N^+$-H	**MeS**	**-C=N^+-OH**	C-ar.	**>C=N^+**
Y = H *(E)*-**5a**	2.31 s	6.83 m, 2H 6.95 m, 3H	10.35 s	18.07	26.4*	124.13 (C-3,5), 131.19 (C-2,6), 132.80 (C *ipso* NH), 134.40 (C-4)	168.59
Y = F *(E)*-**5b**	2.34 s	6.67 m, 2H 6.87 m, 2H	10.28 s	18.04	26.5*	118.40 d, ^2J= 24 Hz (C-3,5) 126.95 d, ^3J= 9 Hz (C-2,6) 130.31 d, ^4J= 3 Hz (C *ipso* NH) 164.80 d, ^1J= 253 Hz (C-4)	169.56
Y = F *(Z)*-**5b**	2.20 s	6.67 m, 2H 6.87 m, 2H	10.48 s	17.24	26.5*	118.47 d, ^2J= 24 Hz (C-3,5) 127.13 d, ^3J= 9 Hz (C-2,6) 130.21 d,, ^4J= 3 Hz (C *ipso* NH) 164.88 d, ^1J= 253 Hz (C-4)	166.08

*broad signal.

REACTIVITY OF IONS 5.

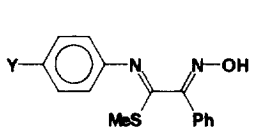
Ions **5** can also be trapped *in situ* with aromatic or quenched with excess MeOH or MeSH. The reaction occurs on the carbon bearing initially the nitro group to give an oximino derivative.

i) *In situ* trapping with benzene: When **3a-c** are dissolved with benzene in TFSA, *in situ* trapping occurred to yield products **6a-c** isolated after quenching on CH_2Cl_2 /ice-water/$NaHCO_3$ and flash-chromatography

Table 3: Trapping hydroxynitrilium ion **5** with C_6H_6

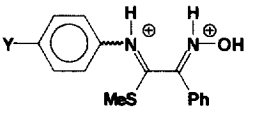
Compounds	Experimental conditions	Product	Yield (%)
3a	3.5 h./ -20° to 12°C	**6a**	77
3b	9 h./ -20° to 12°C	**6b**	83
3c	6.5 h./ 0-5°C	**6c** **11c**	36 51

In the case of the methoxy derivative **3c**, trapping with benzene competes with intramolecular reaction leading to the cyclic product **11c**.

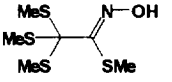


Y
a =H
b = F
c = OMe

6a-c



7a-c



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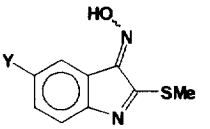


11a-c

Compounds **6** were characterized from their mass spectra that show three main peaks at M^+, $[M-(MeS)]^+$, a conventional fragment, and $[ArNCH]^+$ with increasing order of intensity. The NMR spectra in usual solvent like $CDCl_3$ are complicated because of equilibrium occurring in solution: two equilibrating isomers were generally observed as indicated by the number of MeS signals and broadening of all NMR signals. Compound **6a** gives rise to broad aromatic and to two broad MeS signals in a 3:2 ratio, the stronger

one being the more deshielded. The same phenomenon occurred with **6c** (3:2 ratio) and **6b** (3:2 ratio). However, when directly dissolved in the strongly protonating medium TFSA, isomerization was prevented and a sole cation **7a** or **7b** was formed. Hydroxyiminium and iminium carbons resonate, respectively, close to 155 and 178 ppm (Table 4). The downfield shift of the iminium carbons must be attributed to heavy atom effect of the MeS group[10c].

However, for the oily product **6c** in TFSA, two ions were observed with MeS signals at δ_H = 2.70 and 2.12 ppm, δ_C= 17.92 and 17.80 ppm, iminium δ_C= 178.34 and 177.69 ppm and hydroxyiminium carbon: δ_C= 154.17 and 155.19 ppm. The same phenomenon also occurred when **6a** or **6b** were first dissolved in the minimum amount of $CDCl_3$ then diluted with excess TFSA (Figure 4).

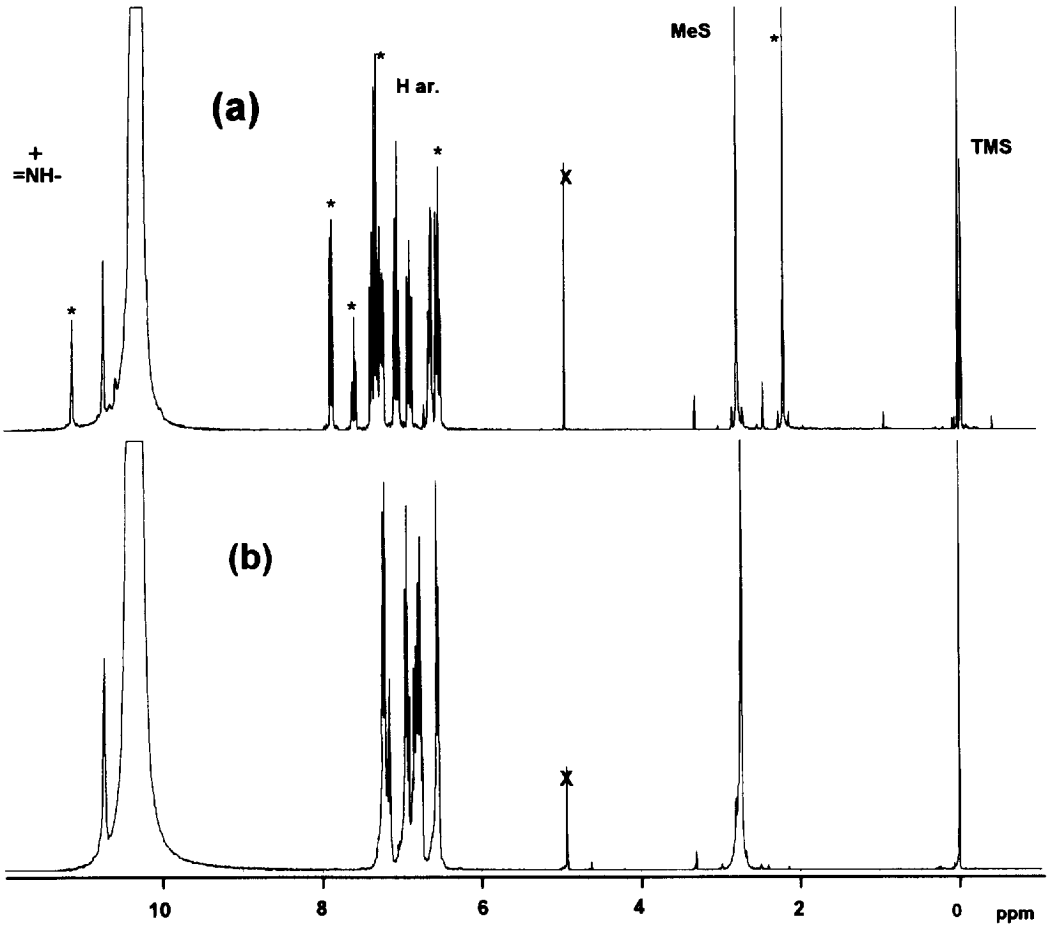


Figure 4: ^{1}H NMR (300 MHz/RT)of ions **7b**: (a) from a solution of **6b** in $CDCl_3$ dissolved in excess TFSA (minor ion with *); (b) from **6b** dissolved in TFSA.

Structure of compounds **6a-c** was further confirmed by their partial hydrolysis that led to the corresponding *para*-substituted aniline and S-methyl α-hydroxyiminophenylthioglyoxylate **8**.

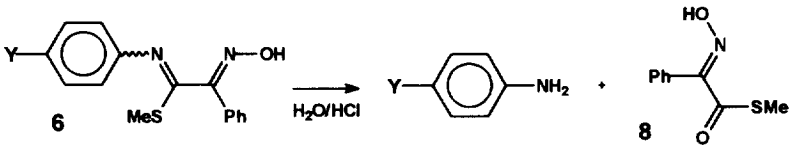


Table 4: NMR spectra of ions **7** in TFSA at room temperature*

Ion	^{1}H NMR*	^{13}C NMR
7a	2.74 s, (MeS) 6.55 d, $^3J_{HH}$= 8 Hz (2H *o*-imino.) 6.76 t, $^3J_{HH}$= 8 Hz (2H *m*-imino) 6.84 t, $^3J_{HH}$= 8 Hz (2H *p*-imino.) 6.93 dd, $^3J_{HH}$=8; 8 Hz (1H *m*- hydroxyimino.) 7.16 t, $^3J_{HH}$= 8 Hz (1H *p*-hydroxyimino.) 7.22 d, $^3J_{HH}$= 8 Hz (2H *o*-hydroxyimino.) 10.73 s, =NH$^+$-OH	19.94 (MeS); 121.24; 124.75; 130.99; 131.50; 132.84; 133.39; 134.98; 140.17; 155.19 (hydroxyiminium); 178.69 (iminium)
7b	2.72 s. (MeS) 6.45 dd, $^3J_{HH}$= 8, $^3J_{HF}$= 8 Hz (2H *m*-imino.) 6.57 dd, $^3J_{HH}$= 8, $^4J_{HF}$= 4 Hz (2H *o*-imino.) 6.96 dd, $^3J_{HH}$= 8; 8 Hz (2H *m*-hydroxyimino. 7.18 t, $^3J_{HH}$= 8 Hz (1H *p*-hydroxyimino.) 7.24 d,$^3J_{HH}$= 8 Hz (2H *o*-hydroxyimino.) 10.67 s, =NH$^+$-OH	18.24 (MeS); 119.22 d, $^2J_{CF}$= 25 Hz (*ortho* fluoro); 121.42; 126.94 d, $^3J_{CF}$= 10 Hz (*meta* fluoro); 130.89 d, $^4J_{CF}$= 4 Hz (*para* fluoro); 131.32; 132.92; 140.62, 154.83 (hydroxyiminium); 164.58 d, $^1J_{CF}$= 258 Hz (*ipso* fluoro); 178.88 (iminium)

**300 MHz; δ relative to TMS/MeOD-d_4.*

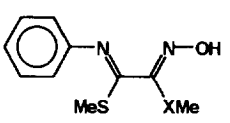
ii) Quenching with MeSH or MeOH. Ions **5a** in TFSA was also quenched with excess MeSH to afford the corresponding derivative **9b** (62%) along with some hydroxyiminiorthotrithioester **10** (18%). Quenching with methanol in somewhat different experimental conditions led to **9a** (50%) along with cyclization product **11a** (14%). The NMR spectrum of compound **9b** is complicated probably by some kind of equilibrium, as aforementioned in $CDCl_3$ or acetone-d_6 solution, that gives unusual signals: for instance ^{13}C NMR spectrum shows weak and broad signals along with a sharp and strong one. However, dissolving crystals of **9a,b** in TFSA lead only to ions **12a,b** that can be easily observed (table 5).

Table 5: NMR spectra of products **9a,b** and their protonated forms **12a,b** in TFSA at room temperature

Cation	^{1}H NMR	^{13}C NMR
9a*	2.40 s, (MeS); 3.77 s, (MeO) 7.25 to 7.43 m, 5H ar.; 11.33 bs, 1H. (N-OH)	13.87 (MeS); 52.55 (MeO); 126.29; 127.60; 129.14; 136.56; 162.84 hydroxyimino; 173.95 imine
12a**	1.97 s, (MeS), 3.32 s, (MeO) 6.71 bs, 2H; 6.87 bs, 3H) 8.05 s, (=N$^+$H- iminium); 11.03 s, [=N$^+$H(OH)]	13.44 (MeS); 56.07 (MeO); 126.62; 130.80; 131.64; 133.34; 154.13 (hydroxyiminium); 174.83 (iminium)
9b	2.13 s, (MeS); 2.50 s, (MeS) 6.92 m, 2H; 7.08 m, 1H 7.28 m, 2H; 11.95 bs, (=N-OH)	13.40 MeS§; 122.11; 125.43 ortho; 129.58; 150.30; 150.90
12b***	2.15 s, (MeS); 2.73 s, (MeS) 6.88 d, *J*= 8 Hz. 2H; 7.17 complex d, *J*= 8 Hz 3H	16.72 (MeS); 18.25 (MeS); 124.12; 132.50; 134.49; 134.75; 167.32 (hydroxyiminium); 174.66 (iminium)

**$CDCl_3$ solution . ** solution in TFSA, reference: methanol d_4 in a sealed capillary tube inside the NMR cell, at 255 K.*
****TFSA/$CDCl_3$ at room temperature. § only one signal was observed in $CDCl_3$*

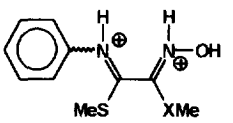
NMR spectra of ions **12a,b** are characterized by chemical shifts of their MeS and MeO groups, hydroxyiminium and iminium carbon. Both iminium carbons resonate at very close values (174.66 and 174.83 ppm respectively for **12a** and **12b**) meanwhile the hydroxyiminium carbons appear at different values because of heavy atom effect of sulfur (154.13 vs. 167.32 ppm respectively for **12a** and **12b**). This last value (δ_C= 167.32 ppm) is also very close to the one reported for ion **13** (δ_C= 167.0 ppm)[4].



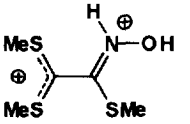
9a,b

a: X = O

b: X = S



12a,b



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DISCUSSION.

Protonation of nitrogen atoms in superacids are known to be strong enough to "freeze" the configuration of aromatic oximes[11a]. In the present case, the observed configurations in TFSA must be the same as those in the neutral forms, either in the crystal when products are directly dissolved in TFSA, or in the liquid state for oily products or solutions in organic solvents. For instance, **6a** or **6b** exist as equilibrating mixtures (broadening of the signals) of two isomers in $CDCl_3$ solution, further dissolution with large excess of TFSA "freezed" both configurations and allowed observation of two ions with well resolved signals. Those solutions are stable for days at room temperature. By contrast, the same compounds directly dissolved in TFSA led to a sole cation.

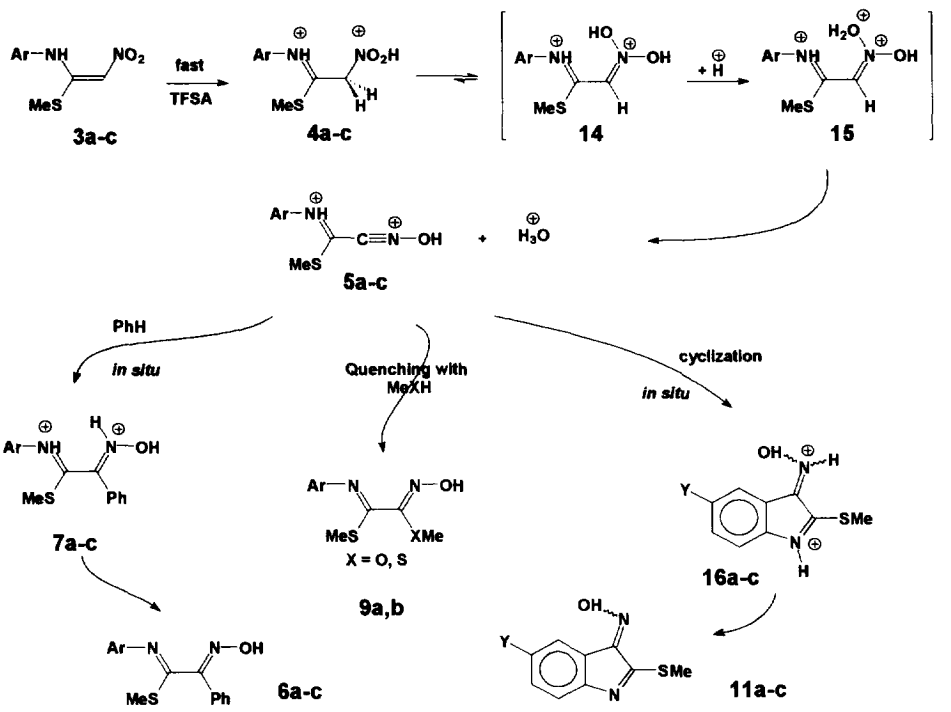
When compounds **3a-c** are dissolved in TFSA, cations **4a-c** are probably the kinetic products of the reaction because only one isomer was observed. A second one appeared only slowly in the case of the methoxy derivative because of the ability of methoxy group to share a non negligible part of the positive charge, thus lowering the C=N double bond character of the iminium group and so, its barrier to rotation[13]. In this case, the observed configuration in TFSA solution must be the same as the existing one for **3a-c** in the crystalline state which was "frozen" upon protonation immediatly on dissolution.

Configuration assignment to the C=N bond in ions **4** was made from differences in chemical shifts. Generally, the *Z* configuration is associated (e.g. imine, oxime and their N-protonated forms) with both the more shielded iminium carbon and the more deshielded α-carbon in the anti-position[10]. In ion *(Z)*-**4c** the iminium carbon resonates at δ_c = 183.8 *vs.* 187.33 ppm, a $\Delta\delta_c$ in the range of what was observed for aromatic protonated oximes in TFSA[11]. In both ions **4c**, the iminium nitrogen and the protonated nitro group should be as far as possible from each other because of coulombic repulsion, so causing a stretching of the chain; the aromatic ring must be out of the plane of the iminium bond because of steric repulsions as encountered in various imines and related compounds[12]. Because of aromatic ring anisotropic effects, the methylene group would be expected to be more shielded in *(E)*-**4c** than in *(Z)*-**4c**. Assuming that the anisotropic effect of the nitro group on the methylene should be quite equivalent in both isomers, the *(E)*-**4c** methylene would resonate upfield, in agreement with the observed values δ_H = 5.10 vs. 5.44 ppm. Other features concern aromatic protons: in N-protonated aromatic oximes or their C-substituted derivatives, the $\Delta\delta_H$ of *para* methoxy substituted aromatic ring is greater in the *Z* isomer than in the *E* one because of steric interaction between *ortho* proton and the gamma substituent: $\Delta\delta_H$=0.24 *vs.* 0.05 ppm.

(E)-4c **(Z)-4c**

The same analysis may be applied to ions **5** to determine the imine configuration. The main feature for the *Z* isomer would be a shielding of C-iminium carbon and MeS group. The iminium carbon of *(Z)*-**5b** resonates at δ_C= 166.08 *vs.* 169.56 ppm and MeS at δ_H=2.20 *vs.* 2.34, δ_C= 17.24 *vs.* 18.04 ppm. It can be concluded that the *(Z)/(E)*-**5b** isomer ratio is 2/1 and that **5a** is the *E* isomer.

The following reaction scheme may be postulated to explain the observed ions and their reactivity:



Ion **5** is formed probably through the protonated nitronic acid form **14**, as observed by Shudo[2] with different substrates in the same medium, then **15**, a kind of protosolvated species as postulated by Olah[16], that leads to **5**. The hydroxynitrilium site is electrophilic and reacted with suitable nucleophiles to form the hydroxyimino derivatives, meanwhile the iminium site did not react *in situ* and was only deprotonated into imine when the acidity was reduced. Methanol and methanethiol led to the quenching products **9a,b**. Some hydroxyiminoorthotrithioester **10** was also formed by nucleophilic substitution during quenching with MeSH. Aromatic electrophilic substitutions occurred through an intermolecular pathway with benzene or by intramolecular reaction when temperature rises. No attempt was made to determine the configuration of oxime and imine groups in the final products because of isomerization occurring in organic solvent solutions.

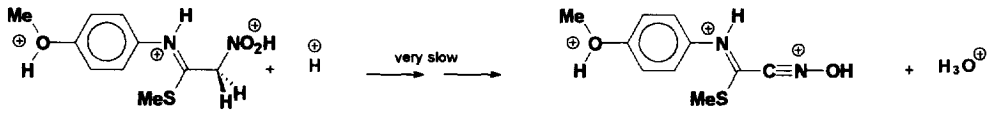
It was interesting to compare cyclization capability in the stronger acidic medium HF-SbF_5. In this medium, dissolution of **3a-c** is very exothermic even at low temperature. To prevent this drawback, **3a-c** were first dissolved in HF and then SbF_5 was carefully added at low temperature with vigourous stirring. A quite fast cyclization was observed for **3a,b** but a slower one for the methoxy derivative **3c** (Table 6).

Table 6: Cyclization of **3a-c** in HF-SbF_5

Starting material	Reaction conditions	Products (%)
3a	-30 to 5°C/ 2.5 h.	**11a** (53) and **3a** (41)
3b	-20 to 0-5°C/ 1.5 h.	**11b** (37) and **3b** (50)
3c	-30 to 0-5°C/ 4.5 h.	**11c** (24) and **3c** (60)

This behavior may be explained by the fact that HF-SbF_5 is much more acidic than TFSA as indicated by their Hammett acidity function H_0. A value of H_0 = -13.6 was reported[14b] for neat TFSA meanwhile a much lower one: H_0 < -20 was determined[14a] in HF-SbF_5 with a 95:5 molar ratio. In those last media, for instance,

complete *O*-protonation of α-substituted *para*-methoxy benzylic cations were observed by SOMMER *et al.* and this property was used to determine H_0 by mean of NMR spectroscopy[14a]. In the presently reported reaction the molar ratio of HF-SbF_5 was near 5:1 and the acidity function H_0 may be estimated to be much lower than -21 in the neat medium, however, addition of organic compounds lower the acidity but not enough to prevent a third protonation occurring, e.g. *O*-methoxyprotonation[14a,15], causing slow formation of the electrophilic species: the corresponding hydroxynitrilium ion. The slow isomerization rate may be explained by the fact that a further protonation must be needed, as previously postulated[4], to achieve formation of hydroxynitrilium ion and H_3O^+. Because of the existence of polyprotonated species, the activation energy must be high and the addition rate low. The following reaction may be postulated, e.g.:



19 20

Such an hypothesis was exemplified by trapping with benzene in comparable temperature and reaction time conditions: in TFSA formation of hydroxynitrilium occurred faster than in HF-SbF_5 and yield benzene trapping product **6c**, along with the intramolecular cyclization product **11c** because of the temperature. In HF-SbF_5 no cyclization occurred and recovery of starting material **3c** was high (Table 7).

Table 7: Comparative trapping reactions in TFSA and HF-SbF_5

	acidic media	temperature/time	products (yield %)
3c	C_6H_6/TFSA	0-5°C/ 6.5 h	**6c** (36) **11c** (51)
3c	C_6H_6/HF-SbF_5	0-5°C/ 7 h.	**6c** (16) starting material (55)

CONCLUSION.

This study extends the previous one concerning formation of hydroxynitrilium ion from 1,1-bis(methylthio)-2-nitroethylene. In superacids, 1-arylamino-1-methylthio-2-nitroethylenes are firstly *O,C*-protonated before leading to a conjugated hydroxynitrilium ion stable at low temperature, that may undergo intra- or intermolecular electrophilic reaction. From a synthesis point of view, starting materials are readily available, the observed reactions are generally clean and easy to carry on. Other work is in progress in this field and will be published soon.

EXPERIMENTAL PART.

Melting points were determined with a Büchi 510 apparatus using capillary tube (temperature rate 2°C/mn) and are not corrected. Infra-red spectra were recorded with a Bomem Easy Fourrier transform spectrometer, in $CHCl_3$ solution with a NaCl windows cell; absorbance in cm^{-1} (w= weak, str= strong, b= broad), spectra of insoluble products in this solvent were taken dispersed in KBr powder and reflective technic. A Bruker WP 200 SX NMR spectrometer or a Bruker DPX 300, equipped with a low temperature probe, were used for ^1H and ^{13}C spectra recorded respectively at 200 MHz / 50 MHz or 300 MHz / 75 MHz. NMR spectra of cations were recorded in TFSA at low temperature or at room temperature, and chemical shifts are relative to Me_4Si in methanol-d_4, contained in a sealed capillary tube placed inside the NMR cell. The reproducibility of ^{13}C NMR shifts was about 0.05 ppm. Electron impact ionization (70 eV) mass spectra were obtained with a Finnigan Incos 500 instrument. HRMS and microanalysis were performed at the CNRS Service microanalyses. Flash chromatography were achieved on silica gel 20 to 45 µm particle size. HPLC was used to check purity or identity of the various compounds describe below, and performed with a Gynkotek 480 pump equipped with Rheodyne 7125 injector valve (20 µl loop) and an Applied Biosystem 785 A programmable UV detector, mobile

phase AcOEt/hexane, flow rate 1500µl/mn, column 250X4 mm I.D., 5 µm silica. TFSA and MeSH came from Aldrich. 1,1-bis(methylthio)-2-nitroethylene from which starting products were prepared, was purchased from Lancaster.

Beware of hellish smell when handling MeSH !!

1. Reaction with benzene in TFSA. Typical procedure.

Starting product **3c** (297 mg, 1.27 mmol) was dissolved in benzene (1.00 ml, 11.2 mmol) and TFSA (3.7 ml, 42 mmol) at 0-5°C (ice water bath). The strongly colored acidic solution was quenched 6.5 hours later with ice/Na_2CO_3/CH_2Cl_2. After extraction and reduce pressure solvent elimination, the crude product was flash chromatographed (hexane/ethyl acetate : 9/1) to yield **6c** (135 mg, 36.4%) as a viscous oil, then a strongly red-orange product **11c** (140 mg, 51.1%).

S-methyl α-(hydroxyimino)-*N*-(4-methoxyphenyl)phenylthioglyoxyimidate. [6c]

oil, **I.R.** 831, 895, 931, 988, 1034, 1109, 1180, 1203, 1242 (str.), 1289, 1353, 1440, 1465, 1502 (str.), 1603, 2837, 3006, 3267, 3562. **^{1}H NMR** (200 MHz, $CDCl_3$) mixture of isomers. 2.22 s: 2.54 s (1:2) MeS; 3.66 s: 3.78 s (2: 1) MeO; 6.57 s. 3H; 6.88 m. 1H; 7.17, 7.29,7.44 and 7.91 m. 5H; 9.82 b.s.: 9.90 b.s. (2: 1) 1H. **^{13}C NMR** (50 MHz, $CDCl_3$) 13.67; 55.80; 106.15; 120.65; 128.42; 129.18; 129.42; 130.35; 135.30; 137.83; 143.24; 151.11; 155.90; 161.05. **MS**: 300 (M^+, 20), 253 ([M-MeS]$^+$, 70), 134 ([$MeOC_6H_5NCH$]$^+$, 100) **HRMS**: $C_{16}H_{16}N_2O_2S$ cal. 300.093249 found 300.09310

5-methoxy-2-methylthio-3*H*-indol-3-one 3-oxime. [11c]

m.p. 200-2°C (dec.) lit.: 210-1°C[5a] **^{1}H NMR** (200 MHz, $CDCl_3$/DMSO-d_6) 2.56 s. MeS; 3.77 s. MeO; 6.90 dd. J= 3 Hz,J= 8 Hz, (H-6); 7.21 d. J= 8Hz, (H-7); 7.50 d. J= 3Hz, (H-4); 13.43 s. (OH). **^{13}C NMR**(50 MHz, $CDCl_3$/DMSO-d_6) 11.75 (MeS); 55.80 (MeO); 112.64; 115.73; 118.46; 122.64; 149.23; 152.56; 157.08; 167.95 (C2). **MS** 222 (M^+, 84) 205 (M-[OH], 100) 190 (M-[MeOH], 99), 175 (M-[MeS], 54).

S-methyl α-(hydroxyimino)-*N*-phenylphenylthioglyoxyimidate. [6a]

Reaction time: 3.5 h and temperature from -20 to 12°C. Yield: 77 %. **m.p.** 114.5-115°C (Petroleum ether); **I.R.** 883, 909, 927, 987, 1112, 1221, 1354 (w), 1485, 1592 (str.), 3007, 3018, 3029, 3281, 3561.; **^{1}H NMR** (300 MHz, $CDCl_3$, mixture of isomers) 2.28: 2.60 (2:3 ratio) MeS; 6.56; 6.91; 7.06; 7.22; 7.30; 7.52; 7.95; 9.64: 9.66 (3: 2 ratio) NH. **MS** 270(M^+, 20), 253 (M-[OH], 8), 223 ([M-MeS]$^+$,75), 104 ($C_6H_5NCH^+$, 100); **Analysis** calc. C 66.65 H 5.22 N 10.37 S 11.84 found C 66.81 H 5.05 N 10.59 S 11.63

Minor ion **[7a]**, **^{1}H NMR** (300 MHz, $CDCl_3$/TFSA; R.T.) 2.14 s, 3H (MeS); 7.15 s, 5H; 7.30 t, J= 7.5 Hz. 2H; 7.52 J= 7.5 Hz. 1H; 7.83 d, J= 7.5 Hz. 1H; 11.10 s, 1H (NH). (For major ion, see text).

S-methyl α-(hydroxyimino)-*N*-(4-fluorophenyl)phenylthioglyoxyimidate. [6b]

Reaction time 9 hours and temperature from -20 to 12°C. Yield 83%. **m.p.** 117-118°C (acetone-petroleum ether); **I.R.** 832, 897, 934, 987, 1012, 1114, 1151, 1198, 1229, 1354, 1425, 1498 (str.), 1599, 3005, 3014, 3028, 3277, 3561; **^{1}H NMR** ($CDCl_3$, mixture of isomers) 2.19 s: 2.53 s (2: 3), MeS; 6.64 and 6.67 m. 3H; 6.97, 7.15, 7.26, 7.43 and 7.89 broad singulets 6H; 10.18 b.s.: 10.40 b.s. (3: 2). **^{13}C NMR** ($CDCl_3$, mixture of isomers) 13.93 (broad) MeS; 115.10 d, $^2J_{CF}$ = 23 Hz; 122.05 d, $^3J_{CF}$ = 8 Hz, 157.73 $^1J_{CF}$ = 242 Hz; 129.10; 129.58, 129.77; 154.03; 145.60 (oxime); 165.00 (imine).; **MS**. 288(M^+, 15), 241 ([M-MeS]$^+$, 42), 207 (18), 122 (58); **HRMS** $C_{15}H_{13}FN_2OS$ cal. 288.0732 found 288.0727.

Minor ion **[7b]**, **^{1}H NMR** (300 MHz, $CDCl_3$/TFSA; R.T.). 2.20 s: MeS; 6.87 dd, $^3J_{HH}$, $^3J_{HF}$ = 8.4, 7.7 Hz, (2H *meta* imino); 7.20 dd, $^3J_{HH}$, $^4J_{HF}$ = 8, 4 Hz (2H *para* imino); 7.34 t, $^3J_{HH}$ = 8 Hz, (2H *meta* hydroxyimino); 7.56 t, $^3J_{HH}$, = 8 Hz (1H *para* hydroxyimino); 7.84 d, $^3J_{HH}$ = 8 Hz (2H *ortho* hydroxyimino); 11.53 s. 1H, =NH$^+$OH. **^{13}C NMR** (75 MHz, $CDCl_3$/TFSA, R.T.) 18.15 (MeS); 119.01 d, $^2J_{CF}$.= 24 Hz; 127.39 d, $^3J_{CF}$ = 10 Hz; 127.34; 130.39 d, $^4J_{CF}$ = 3.6 Hz; 132.50; 134.82; 142.60; 152.73 (hydroxyiminium); 179.32 (iminium). (For major ion, see text).

2. Trapping with methanol.

Starting product **3a** (480 mg, 2.28 mmol) was dissolved with stirring in TFSA (4 ml, 0.2 mol) at -30°C to 10°C for 6 hours. The acidic solution was poured into CH_2Cl_2:MeOH (60:10 ml/ml) at -60°C and let to warm at room temperature. When temperature reached about 0°C, water (15 ml) and $NaHCO_3$ were added and extraction proceeded with dichloromethane. The resulting products were flash chromatographed (CH_2Cl_2/Acetone) to yield **9a**: (223 mg, 49.7 %) then a yellow product **11a** (58 mg, 14.3 %) and finally starting material (42 mg, 8.7 %)

2-(O-methyl)-1-(S-methyl) 1-N-phenylimino-2-hydroxyimidodithiooxalate. [9a].

m.p. 66-7°C (Pet. Et.), I.R. 746, 754, 788, 889, 937, 1054, 1255 (str.), 1262 (str.), 1314, 1360 (str.), 1439 (str.), 1495, 1560 (str.), 1591, 1641, 2951, 3007, 3033.^{1}**H NMR** ($CDCl_3$) 2.40 (MeS); 3.77(MeO); 7.2-7.5 m, 5H; 11.33 (=N-OH). ^{13}**C NMR** ($CDCl_3$) 13.87 (MeS); 52.55 (MeO); 126.29; 127.60; 129.14; 136.56; 162.84 (C-oximino); 173.95 (C-imino).**MS**: 224 (M^+, 35), 192([M-(MeOH)]$^+$, 20), 177 ([M-MeS], 55), 150 (40), 118 (50), 77 (100); **HRMS**: $C_{10}H_{12}N_2O_2S$ cal. 224.06195 found 224.06193.

2-methylthio-3*H*-indol-3-one 3-oxime. [11a]

mp. 198-9°C (dec.) lit.: 183-5°C[5a]. ^{1}**H NMR** ($CDCl_3$: DMSO-d_6; 200 MHz) 2.60 s, (MeS); 7.11-7.18 m, 1H; 7.29-7.41 m, 2H; 7.93 d, J= 7 Hz, 1H; 13.0 b.s. 1H. ^{13}**C NMR** ($CDCl_3$: DMSO-d_6; 50 MHz) 12.05; 118.29; 121.89; 125.01; 126.12; 131.53; 152.72; 155.47; 170.57 (C-2). **M.S.** 192 (M^+, 32), 175 (M-[OH], 77), 160 (M-[MeOH], 41), 145 (M-[MeS], 12). **HRMS** $C_9H_8N_2O_5$ calc. 192.03573 found. 192.03565.

Protonated form **[16a]** in TFSA (a very stable solution at room temperature). ^{1}**H NMR** (TFSA, Ref: TMS/acetone-d_6) 2.68 s. MeS; 6.96 d, J= 8 Hz, 1H; 7.12 t, J= 8 Hz, 1H; 7.42 t, J= 8 Hz, 1H; 7.82 t, J= 8 Hz; 10.95 s, 1H. ^{13}**C NMR** (TFSA, Ref.:TMS/acetone-d_6) 17.03; 115.05; 116.75; 130.82; 135.50; 142.89; 144.64; 148.52; 173.69.

3. Trapping with methanethiol.

Starting product **3a** (430 mg; 2.05 mmol) was dissolved with stirring in TFSA (3 ml; 34 mmol) at -30°C. After 2.5 hours, the acidic solution was poured into CH_2Cl_2:MeSH (60:4 ml/ml) at -60°C and let to warm at room temperature. When temperature reached about 0°C, water (15 ml) and $NaHCO_3$ were added and extraction proceeded. The white crystalline product so obtained was flash chromatographed (hexane/ethyl acetate: 9/1) to afford **10** (83 mg, 18%)[4] and **9b** (305 mg, 62%) as white crystals.

***bis*(S-methyl) 1-N-phenylimino-2-hydroxyimidodithiooxalate. [9b]**

m.p. 139-41°C; **I.R.** 882, 914, 963, 985, 1162 (w), 1341, 1428, 1590 (str.), 1605 (str.), 2930, 3002, 3252, 3569.^{1}**H NMR** (acetone d_6, 200 MHz) 2.13 s, (MeS); 2.50 s, (MeS); 6.92 m, 2H; 7.07 m, 1H; 7.28 m, 2H; 11.95 s, (=N-OH).^{13}**C NMR** (acetone d_6, 50 MHz) 13.40 (MeS); 122.11; 125.43; 129.58; 150.30; 150.90. **MS**. 240 (M^+, 8), 193 ([M-MeS]$^+$, 50), 77 (100). **HRMS** $C_{10}H_{12}N_2OS_2$ cal. 240.03910 found 240.0391.

4. Cyclization in HF-SbF_5. Typical Procedure.

Compound **3b** (323 mg; 1.41 mmol) was dissolved in HF (6 ml; 0.33 mol) at -30°C, then SbF_5 (4 ml, 12 g; 55 mmol.) was slowly added with effective stirring. After some minutes, the reaction medium was let to slowly warm to 0-5°C. After 1.5 h. reaction time, the acidic medium was poured into ice/Na_2CO_3/CH_2Cl_2. After extraction with CH_2Cl_2 (3X100 ml), the organic phase was washed with brine (10 ml) then dried over $MgSO_4$. Solvent was eliminated under vacuum and the resulting products flash chromatographed with CH_2Cl_2: ethyl acetate.(9:1) to afford an orange red product **11b** (120 mg; 37%) then starting material **3b** (162 mg; 50%)

5-fluoro-2-methylthio-3*H*-indol-3-one 3-oxime. [11b]

mp. 199-202°C (dec.) lit. 178-180°C[5a] ^{1}**H NMR**($CDCl_3$: DMSO-d_6; 300MHz) 2.59 s (MeS); 7.13 ddd $^3J_{HF}$=7.8 J_{HH}=2.2, 9 Hz (H6); 7.28 dd, $^4J_{HF}$= 3.7 $^3J_{HH}$=8.3 Hz (H7); 7.63 dd, $^3J_{HF}$=7.8 J_{HH}= 2.2 Hz (H4). ^{13}**C NMR** ($CDCl_3$: DMSO-d_6;75 MHz) 12.37 (MeS); 113.54 d, $^2J_{CF}$= 27 Hz (C4); 117.59 d, $^2J_{CF}$= 24 Hz (C6); 119.24 d, $^3J_{CF}$= 8 Hz (C7); 122.86 d $^3J_{CF}$= 10 Hz (C9); 150.90 m (C3);152.38 d $^4J_{CF}$= 3 Hz (C8); 159.97 d, $^1J_{CF}$= 242 Hz (C5); 170.59 m (C9). **M.S.** 210 (M^+, 57), 193 (M-[OH], 100), 178 (M-[MeOH], 88), 149 (70).

5. Trapping with benzene in HF-SbF_5.

Compound **3c** (295 mg; 1.23 mmol) was dissolved in HF (5 ml; 0.25 mol) at -30°C with benzene (1500 µl; 16.9 mmol), then SbF_5 (3.5 ml; 48 mmol.) was slowly added with effective stirring. After some minutes, the reaction medium was let to slowly warm to 0-5°C. After 7 h. reaction time, the acidic medium was poured into ice/Na_2CO_3/CH_2Cl_2 and extraction proceeded as above. Flash chromatography afforded **6c** (44 mg; 16 %) then starting material (162 mg 55%).

6. Hydrolysis: typical procedure.

Compound **6b** (168 mg; 0.56 mmol.) was dissolved in 6M HCl (5 ml) with the help of some ethanol, and heated at 70° C for 7 hours. The solution was poured over ice/sodium carbonate and extracted with CH_2Cl_2 (3 X 40ml). Organic phase

was dry over $MgSO_4$ then evaporated under vacuum to yield a residue that was flash chromatographed (hexane: AcOEt 8: 3) to afford **8** (65 mg; 57%)[4] and 4-fluoroaniline (24 mg; 39%).

I thank Mme Joffre for taking low resolution MS spectra.

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