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1,1-bis(Methylthio)-2-Nitroethene in Superacids: NMR Study and Reactivity of the Formed Hydroxynitrilium Ion.

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Abstract At low temperature in superacids TFSA or HF-SbF_5, 1,1-bis(methylthio)-2-nitroethene yields a stable dication with hydroxynitrilium and bis(methylthio)carbocationic sites. The first site can be trapped *in situ* with suitable nucleophiles (aromatics, fluoride). Both sites can be trapped when the acidity is destroyed with MeOH or MeSH, to form in fair to good yield the corresponding α-hydroxyiminoorthothioester or the furoxane orthothioester.

Nitroketene S,S-acetals are useful synthesis reagents in organic chemistry[1]. They are readily prepared in a conventional way from the reaction of active methylene compounds and CS_2 with a suitable base, followed by alkylation of the resulting salt[2]. These compounds are generally stable and readily purified by crystallisation.

From a chemical point of view, nitroketene S,S-acetals have two electron donating groups on one end of the double bond, and an electron withdrawing group on the other end. These are very prone to nucleophilic addition on the acetal carbon and the adduct so formed losses easily a thioalkylgroup to give a substituted product. For instance, nitroketene S,N-acetals or N,N-acetals can be prepared by this way[1a,2]

1

Following our work on the reactivity of various chemicals in superacids, this study presents the reactivity of 1,1-bis(methylthio)-2-nitroethylene **1** in HF-SbF_5 and in trifluoromethanesulfonic acid (TFSA).

RESULTS:

Compound **1** dissolved easily in superacids at low temperature (0°C or below) to give a pale yellow solution. Quenching the solution with an excess of MeOH/CH_2Cl_2 or MeSH/CH_2Cl_2 at -40 to -60°C gave orthoesters **2b**, **3a** and **4** (table 1):

Table 1: products formed from **1** in superacids.

Reaction conditions	Isolated products	Yield (%)
i)-TFSA ii)-MeOH in excess	**2b**	91
i)-TFSA ii)-MeSH in excess	**3a**	94
i)-HF-SbF_5 ii)-MeOH in excess	**4**	70

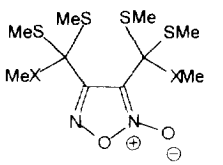
The following aromatic products were obtained when **1** was dissolved with benzene or anisole in superacids (table 2):

Table 2: aromatic compounds obtained by dissolving **1** and benzene or anisole in superacids.

Reaction conditions	Time/temperature	Products	Yield (%)
i) TFSA-Benzene			
ii) MeSH	4h./0°C	**5a**	62
or ii) MeOH	8h./ 0°C	**5b**	75-86
or ii) H_2O	20h./0°C to RT	**5a** and	30
		8	28
i) HF-SbF_5-Benzene	0-5°C / 2h	**5b**	79
ii) MeOH			
i) TFSA-Anisole	0°C to RT/10h	**6**	53 (3.5*)
ii) MeSH		**7**	7 (38*)
		3a	13 (22*)

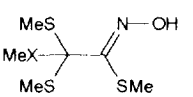
*reaction time: 3 hours, -10° to 0°C

The reaction with anisole was slower than with benzene and it was possible to isolate **7**, the 1,1,1-ter(methylthio)-2-nitroethane and the corresponding hydroxyiminoorthotrithioester **3a** after a short reaction time and quenching with MeSH. The use of water as a quenching reagent caused secondary reactions of hydrolysis, the amount of which being dependant on experimental conditions. The orthothioesters so prepared dissolve easily in TFSA and quenching with suitable nucleophiles (MeOH or MeSH) yield exchanged orthothioesters.

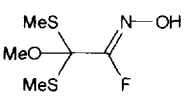


2 a,b a: X = S

b: X = O



3 a,b



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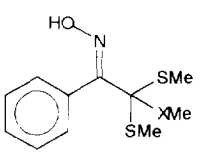
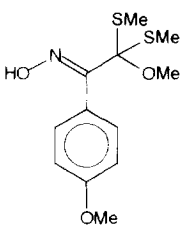


5 a,b



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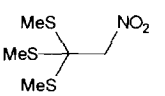


7

Structures of those various compounds were determined by NMR spectroscopy and MS analysis. With NMR, the quaternary carbons of orthotrithioesters appear near 73 ppm for aromatic derivatives **5a** and **5b** and are slightly shielded in furoxane **2a** but deshielded in **3a**. In orthodithioester, presence of an oxygen atom cause a deshielding of the quaternary carbons comparatively to the corresponding orthotrithioesters: from 22.1 ppm in **3b**, 26.42 in aromatic **5b** and 26.75/26.95 ppm in furoxane. Presence of fluorine on adjacent carbon cause a slight shielding to 93.97 ppm. Furoxanes **2a,b** exhibit a

characteristic ^{13}C pattern for the ring carbons C3 and C4 near 116 and 157 ppm, in agreement with the litterature[7]. The hydroxyiminyl carbon resonates within the range 152.55 to 156.30[3], excepted for the fluorinated product **4** at 149.65 ppm. Electronic impact ionisation mass spectra at 70 eV are characterized by a very weak if present M^+ signal and a strong [M-47] signal due to loss of MeS group. Signal corresponding to $[M-(OH)]^+$ and $[M-(MeO)]^+$ are also observed but with a much lower intensity.

The oxime stereochemistry was established from ^1H-NMR data of the protonated forms in TFSA in studying chemical shifts of aromatic protons (vide supra).

In a way to have a better understanding of these reactions, they were followed by mean of ^1H and ^{13}C-NMR spectroscopy.

NMR STUDY

When just dissolved in TFSA, **1** is protonated to give an ion with similar but shifted signals. In TFSA, nitroene compounds are known to be O,O-diprotonated but these protons were not detected because of fast exchange with the medium. The carbon bearing the nitrogroup is not affected or slightly shielded whereas the other one of the initial double bond is deshielded[4b]. In the present case such a phenomenon was observed (table 3) and two structures are possible: the O,S-protonated form **9** and the O,O-diprotonated one **22**. Structure **22** implies the presence of a bis(methylthio)carbocationic center characterized by a ^{13}C-NMR chemical shift higher than 200 ppm (vide supra) that was not observed in this case and, consequently, the most suitable structure would be **9** in which a S,O-diprotonation should cause only a slight chemical shift of both carbons.

At 0°C, cation **9** was quickly transformed into cation **10**. This cation can also be prepared cleanly by dissolving carefully 1,1,1-ter(methylthio)-2-nitroethane **7** in TFSA at low temperature. In these experimental conditions, some percent of cation **9** were also detected by NMR, probably because of equilibrium between both cations. Cation **10** was characterized by its methylene group and a bis(methylthio)carbocationic center at 222.61 ppm. Two signals for the MeS groups were also observed at 239 K probably because of different position relative to the carbocationic center. Coalescence occurred at a slightly higher temperature.

Table 3 resumes the NMR chemical shifts observed for these ions and their precursors. C-1 bears the MeS groups and C-2 the nitrogenated one.

Table 3: Chemical shifts of product **1** and related cations.

	^{13}C chemical shift			^1H chemical shift	
Specie	MeS	C 1	C 2	MeS	Others
1	15.14 17.62	164.07	125.47	2.53 ,s, 6H	7.07, s, 1H
9	18.68 19.05	171.04	116.12	2.03, s,3H 2.10, s, 3H	7.22,s, 1H
10	21.59 22.73	222.61	76.79	2.30, s, 3H 2.35, s, 3H	5.25, s, 2H
11	22.32 23.43	201.35	30.69	2.38, s, 3H 2.51, s, 3H	

*Spectra of **1** was recorded in $CDCl_3$ at room temperature. Spectra of cations **9**, **10** and **11** were recorded in TFSA near 247 K, chemical shifts are relative to $SiMe_4$ in acetone D6 in a sealed capillary tube inside the NMR cell.*

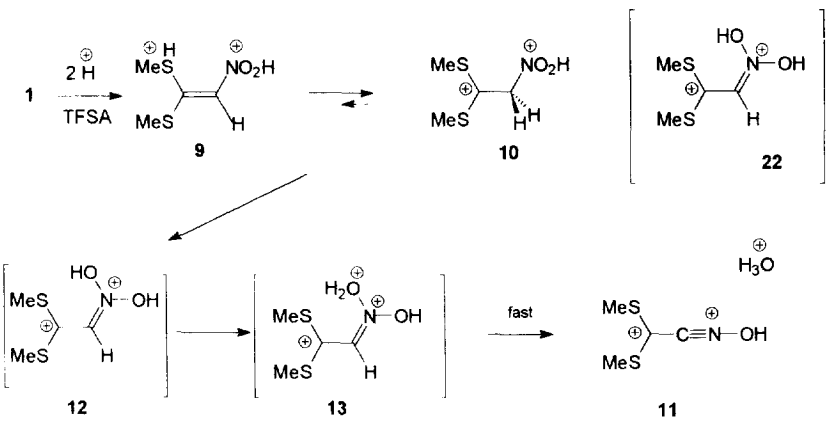
Finally, **10** was totally transformed into a stable cation **11** that shows only two signals of same intensity in ^1H NMR. These two signals are probably due to the MeS group with different conformation relative to the carbocationic center as encountered in cation **10**. The ^{13}C NMR spectrum is characterized

by a bis(methylthio)carbocationic center at 201.3 ppm and a broad and weak signal at 30.6 ppm. This latter one, by its intensity and chemical shift may be compared to the carbon of the nitrile oxide group[6] as observed for the unstable acetonitrile N-oxide[6a] prepared by flash-vacuum pyrolysis of dimethylfuroxane. Broadening and weakening of the signal is due to coupling with ^{15}N and quadripolar relaxation[6b] with ^{15}N. No other CH was detected by 2D ^{1}H ^{13}C NMR Cosy experiment. Proton on the N-hydroxynitrilium center was not observed in these experimental conditions, the acidity probably being not strong enough to prevent fast proton exchange[11]. However the presence of such a proton must be postulated to account for the great stability of cation **11** in sharp contrast with the ability to dimerization of free non aromatic nitrile oxide[5].

REACTION MECHANISM:

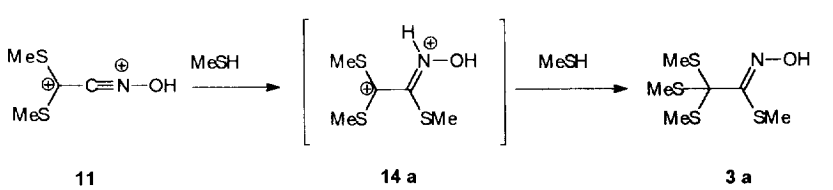
From the NMR study, the following isomerization mechanism of **1** in TFSA can be proposed (scheme 1):

Scheme 1: formation of cation **11** from **1**.



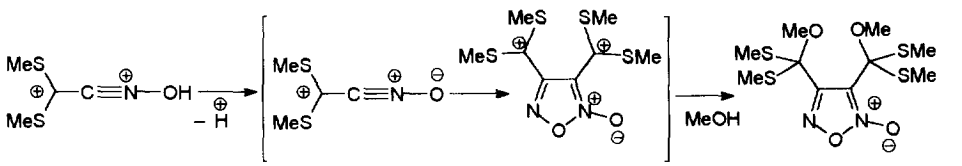
From a mechanistical point of view, hydroxynitrilium ion **11** may be formed via a transient protonated nitronic acid **12** resulting from O-protonation/S-deprotonation of **9** or from ion **10** by a O-protonation/C-deprotonation. The route from **12** to **11** may involve the formation of a protosolvated species **13**, a transient cation or a transition state. Such kind of cations, also called superelectrophiles by Olah[9] are postulated to account for an increase of reactivity of stable cations with increasing acidity of the superacid. In good agreement with this mechanism is the fact that lowering the acidity of the medium with anisole lead to accumulation of ion **10** and slow formation of hydroxynitrilium ion **11**. Cation **11** may be trapped with excess of MeSH or MeOH. Methanethiol, a good nucleophile trapped both cationic centers (scheme 2):

Scheme 2: Trapping of cation **11** by MeSH.



Meanwhile methanol, a poorer nucleophile than MeSH, first deprotonates **11** to give the nitrile oxide **15** that dimerizes easily to furoxane, the usual cyclodimerization product[5]. Only both bis(methylthio)carbocationic centers are trapped by MeOH.(scheme 3):

Scheme 3: trapping of cation **11** by methanol.

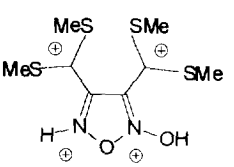


11 **15** **16** **2 b**

Ion **11** was trapped *in situ* with aromatics or fluoride anion at the hydroxynitrilium site to give cation **14**. The second cationic site: the bis(methylthio)carbocationic one was trapped only with an excess of nucleophile when acidity was destroyed. On a kinetic point of view, anisole reacts slower than benzene: for instance, at 0-5°C in TFSA the reaction with benzene was completed within three hours to give 62 % of the aromatic trapping product **5a** after quenching with MeSH whereas anisole in the same conditions leads to only 16% of aromatic trapping product, the main products being **3a** (37 %) and **7** (23 %) from trapping of cations **11** and **10** by MeSH. Formation of **7** implies that ion **10** accumulated in the medium and this behavior may be interpreted as follows: anisole is basic enough to be protonated in superacids and so causing i) a sharp decrease of the concentration of its reactive unprotonated form and ii) a decrease of the acidity of the acidic medium leading to an accumulation of cation **10** because of slow formation of **11**. The kinetic of the reaction is slow because of both concentrations of **11** and unprotonated reactive anisole are low. The hydroxynitrilium ion **11** must be a moderate electrophile because it failed to react with fluorobenzene in the same experimental conditions.

In HF-SbF_5, cation **11** was trapped by fluoride anion to give **4**, however this reaction was slower than trapping by benzene: when the starting material **1** and benzene were added at the same time in this superacid, no fluorine derivative was observed but only the trapping product by benzene **5b**.

The cations, precursors of isolated final products, and some related ones, were also observed by ^1H- and ^{13}C-NMR in TFSA at -25° to -35°C. They were prepared by carefully dissolving the corresponding orthothioester in TFSA to give a fast and clean reaction: orthodithioesters cleaved exclusively on C1-Oxygen bond to form the bis(methylthio)carbocationic center and protonated methanol, in similar way, orthotrithioesters led to the same cation and protonated methanethiol (table 4).



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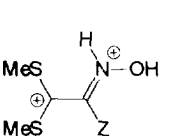
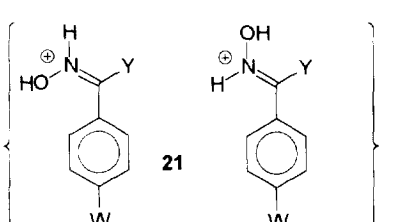


14 a,b,c,d.

a: Z = MeS, b: Z = Ph,

c: Z = pMeOPh d: Z = F



21

syn anti

W = H, MeO

Y = H, Me, $COOEt(H)^+$

Table 4 NMR spectra of cations

	^{13}C-NMR				^{1}H-NMR		
Ion	MeS (C1)	>C^{+}-	>C=N<	Others	MeS(C1)	N-H^{+}	Others
14a	28.85 24.77	212.3	167.0	15.04 MeS(C2)	2.47 s, 3H 2.59 s, 3H	11.5 b.s. 1H	1.91 s,3H MeS(C2)
14b*	23.61 24.79	217.09	153.55	120.71 130.98 133.07 140.47	2.18 s, 3H 2.66 s, 3H	10.05 s,1H	6.95 dd 2H meta J_{HH}=7.7, 7.7 Hz 7.16 dd 1H para J_{HH}=7.7, 7.7 Hz 7.30 d,2H ortho J_{HH}=7.7Hz,
14c	23.62 24.66	218.38	152.01	56.38 MeO 112.52 117.36 137.57 170.20	2.27 s, 3H 2.67 s, 3H	11.20 b.s.,1H	3.27 s, 3H, MeO 6.52 d,2H meta J_{HH}=9.2Hz 7.53 d,2H ortho J_{HH}=9.2 Hz
14d	20.65 25.69	211.49 d,$^{2}J_{CF}$= 27 Hz	148.12 d, $^{1}J_{CF}$= 327 Hz		2.27 s, 3H 2.51 s, 3H	11.30 s, 1H	

Chemical shifts relative to TMS in acetone D_6 in a sealed capillary tube inside the NMR cell
**the same cation was observed starting either from 5a or 5b*

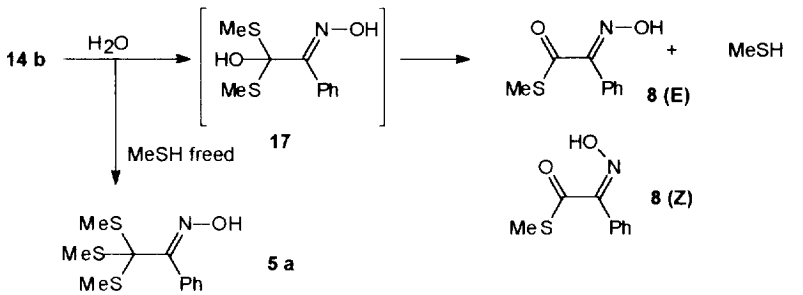
The ease of formation of these ions explains why it is possible to realize transesterification reactions. In the same way, furoxane **2a** gave ion **18** characterized by two bis(methylthio)carbocationic centers and a protonated furoxane ring causing a slight shielding of the carbon ring. Rotation around the furoxane C-ring-carbocation bonds causes a broadening of the MeS signals. O-protonation probably occurred but was not observed probably because of fast exchange with the medium.(Table 5)

Table 5: NMR spectra of protonated furoxane **18** in TFSA at 245 K.

	^{13}C-NMR				^{1}H-NMR	
Ion	MeS	>C^{+}-	C3	C4	MeS	N-H
18	24.02 b.s. 24.61 b.s.	208.17 211.62	111.78	146.42	2.43 b.s, 6H 2.60 b.s., 6H	11.47 b.s., 1H

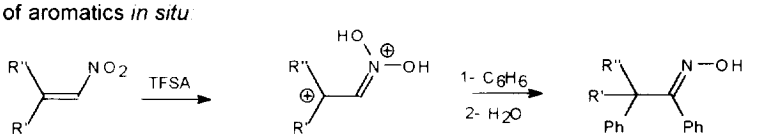
Starting from orthodithioesters and quenching with MeSH yielded nearly quantitatively the orthotrithioester e.g. the transformation of **3b** into **3a**, whereas starting from orthotrithioesters and trapping with MeOH led only to partial formation of the orthodithioester because of the reaction of MeSH freed for the formation of the cation. This is illustrated by the partial conversion of furoxane **2a** into **2b** where the concentration of MeOH was roughly 200 times that of MeSH in the final step of the reaction. A rough estimation indicates that MeSH is about 700 times more nucleophilic than MeOH for trapping the bis(methylthio)carbocationic center. The high nucleophilicity of MeSH was also observed during quenching with water of cation **14b**: water added to **14b** and the following hydrolysis reaction led to compounds **8** and the freed MeSH trapped cation **14b** to afford the corresponding othotrithioester **5a** in a near 1: 1 molar ratio (scheme 4).

Scheme 4: Secondary reactions that happen during water hydrolysis.



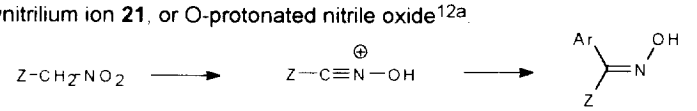
OXIME CONFIGURATION AND DISCUSSION.

Oximes were also obtained by SHUDO[4] *et al.* in studying the reactivity of alkylnitroethylene in superacids. They have shown that an O,O-diprotonation occurs to form protonated nitronic acid able to trap two moles of aromatics *in situ*.



R' R'' = alkyl, aryl, H

However, the stereochemistry of the ketoxime was not determined. At the same time, we observed that oximes formed in superacids from the reaction of aromatics and nitroalkanes or activated nitroalkanes had the entering group and the OH oxime in a *syn* configuration[12]. In TFSA at low temperature, the oxime protonated form is stable enough to allow determination of configuration[8]. The observed configuration was in agreement with what is expected on the addition on CN triple bond as shown by HEGARTY *et al.*[13] on a theoretical point of view. We concluded to the existence of a transient intermediate ion with such a triple bond, the hydroxynitrilium ion **21**, or O-protonated nitrile oxide[12a].



Z = H, alkyl, COOEt

19 **20**

Following those results, RYU *et al.*[14] prepared the same kind of intermediate by complexing an aromatic nitrile oxide with a Lewis acid. This adduct reacted with aromatics to yield diaromatic ketone oximes with the entering group and the OH oxime in the syn-configuration. The same results were also observed in TFSA during the reaction of cyclization of 1-(N-arylamino)-1-methylthio-2-nitroethylene to form 2-methylthio-3H-indole-3-one oxime[15]. Other results in the literature can be interpreted in the same way[4b].

In N-protonated aromatic oximes (or hydroxyiminium forms) the *ortho* protons are more deshielded (relative to the *meta* ones), in the *syn*-isomer than in the *anti*-isomer. Such a relation was found in protonated substituted benzaldehyde[8] or acetophenone oximes[17] and also in substituted phenylglyoxylic acid ester oximes[17] as exemplified in table 6. For instance, with a *para*-MeO group, the difference in chemical shift $\Delta\delta$ is in the range 0.53 to 0.61 for the *anti*, and 0.99 to 1.04 for the *syn* isomers. When product **6** was dissolved in TFSA at low temperature, only cation **14c** was observed with a $\Delta\delta$ = 0.88 ppm.

After more than 24 hours in freezer, some 5 to 10 % of the other isomer appeared, with a $\Delta\delta$ = 0.55 ppm. Those results shows that **14c** is really the *syn* isomer and assuming no isomerization occurs during quenching, the configuration must be retained in the final product. This configuration must be extended to the other products of those reactions.

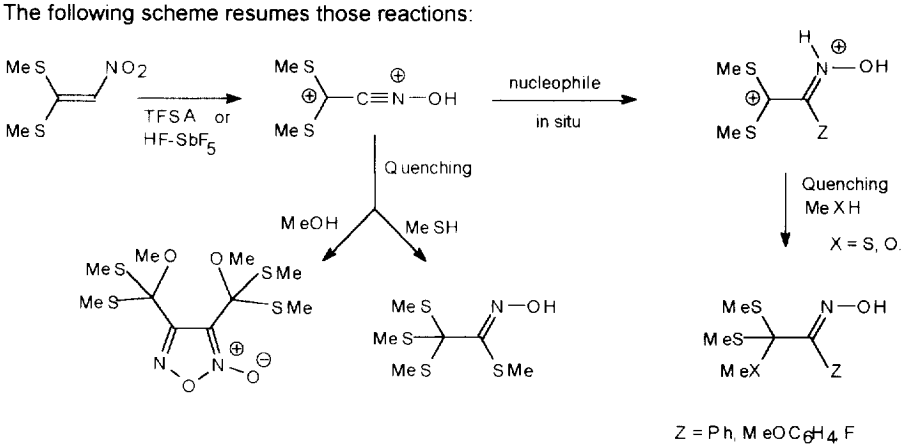
Table 6: ^{1}H NMR chemical shift of aromatic protons of hydroxyiminium ions **21** and **14b,c** in TFSA

Y →	-H§		-Me [17]		-COOEt(H)$^+$ [17]		-C$^+$(SMe)$_2$	
W ↓	*anti*	*syn*	*anti*	*syn*	*anti*	*syn*	*anti**	*syn*§§
H	6.82	6.84 m	6.80	6.82	6.80	6.85		6.95
	to	7.03	to	6.94	to	7.02		7.16
	6.99	7.43	6.98	7.15	7.04	7.22		7.30
MeO	6.42	6.44 d	6.47 d	6.50 d	6.42 d	6.43 d	6.50 d	6.52 d
	7.03	7.48 d	7.00 d	7.43 d	6.98 d	7.42 d	7.05 d	7.32 d

§ *from ref 8* §§ *from table 4, the anti isomer was slowly formed during NMR experiment.*

* *ratio syn/anti after 12 days in freezer 1/4 Other signals 2.32 and 2.64 (MeS), 3.21 (MeO).*

The following scheme resumes those reactions:



CONCLUSION:

In this study we have shown that in superacids 1,1-bis(methylthio)-2-nitroethylene forms a dication with a bis(methylthio)carbocationic center and an hydroxynitrilium group. The hydroxynitrilium group can be trapped *in situ* by various nucleophiles (aromatics, fluoride) meanwhile the other cationic center is only trapped when the acidity is destroyed.

The ions precursor of final products are stable enough in superacids to allow their direct study by ^{1}H- and ^{13}C NMR spectroscopy.

The reaction observed are generally clean and the yields of alpha hydroximinoorthothioesters or furoxane orthothioester are fair to good. The ease of transesterification reaction of the orthothioesters group extend the synthetic field of this new reaction.

Experimental part

GENERAL.

Melting points were determined with a Buchi 510 apparatus using capillary tube 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; maximum absorbance are in cm^{-1} (w= weak, s= strong, b= broad). A Bruker WP 200 SX NMR spectrometer, equipped with a low temperature probe, was used for ^1H and ^{13}C spectra recorded respectively at 200 MHz and 50 MHz. Chemical shift are relative to Me_4Si. NMR spectra of cations were recorded in TFSA at low temperature and chemical shifts are relative to Me_4Si in acetone D6 contained in a sealed capillary tube placed in the NMR cell. Electron impact ionisation (70 eV) mass spectra were obtained with a Finnigan Incos 500 instrument. MSHR and microanalysis were performed at the CNRS Service microanalyses. Flash chromatography were achieved on silica gel 20 to 45 μm particle size. Starting product **1** was purchased from Aldrich or Lancaster and flash chromatographed (hexane-AcOEt 8:2) to yield pale yellow odorless crystal. TFSA and MeSH came from Aldrich.

Beware of awful smell when handling MeSH !!

3,4-bis[(methoxybis(methylthio))methyl]furoxane. [2b]

Compound **1** (395 mg, 2.39 mmol.) was dissolved with stirring in TFSA (4 ml, 45 mmol) at 0-5°C under dry nitrogen. At the end of the reaction (2.6h. 0°C), the mixture was poured into MeOH (12 ml) in CH_2Cl_2 (100 ml) at -40 to -60°C. When the solution had warmed near to 0°C, water (30 ml) and $NaHCO_3$ were added. The organic phase was separated and the aqueous phase extracted with CH_2Cl_2 (2x30 ml). The combined organic extract was washed with a little water, then brine and dry over Na_2SO_4. Solvent was evaporated *in vacuo* to give a crystalline product that was flash chromatographed (hexane-AcOEt 9:1). Isolated yield: 340 mg, 91%.

2b: m p 108°C; **IR** 946, 1049, 1061, 1107, 1316(w), 1391, 1428, 1592 (very strong), 2828 (w), 2927, 3008.; **^1H NMR** δ 1.98 (s, 6H) 2.05 (s, 6h) 3.51 (s, 3H) 3.54 (s, 3H); **^{13}C NMR** δ 13.20 and 13.37 (MeS), 48.89 and 50.93 (MeO), 94.40 and 95.40 (C orthoester), 115.82 (C3), 157.30 (C4). **SM** 327 ([M-(MeO)]$^+$,7), 311 ([M-(MeS)]$^+$, 7), 137 ([C[$(MeS)_2$MeO]$^+$, 95); **SMHR** $C_9H_{15}N_2S_3O_4$ cal. 311.0190 found 311.01899 **analysis** cal. C 33.50 H 5.06 N 7.81 S 35.77 found C 33.54 H 5.00 N 7.71 S 35.05.

3,4-bis[ter(methylthio)methyl]furoxane. [2a]

Compound **2b** (90 mg, 0.35 mmol.) was dissolved in TFSA (2 ml, 22.5 mmol.) at 0-5°C. Ten minutes later the solution was quenched with MeSH:CH_2Cl_2 (10ml:50ml). After extraction, and crystallization in hexane afforded **2a** (78 mg, 80%).

2a: m p 143-4°C (dec.) **IR**: 888, 956, 1046, 1347, 1418, 1422, 1588 (s), 2917, 3003.; **^1H NMR** δ 2.14 (s, 9H, MeS) 2.20 (s, 9H, MeS) **^{13}C NMR** δ 14.77 and 15.46 (MeS), 67.45 and 68.65 (C-orthoester),116.50 (C3), 156.40 (C4). **SM**: 390 ([M]$^+$, 0.1), 343 ([M-(MeS)]$^+$, 80) 153 ([C$(SMe)_3$]$^+$, 100) **analysis** $C_{10}H_{18}N_2O_2S_6$ cal. C 30.74 H 4.64 N 7.17 S 49.34 found C 30.64 H 4.62 N 6.98 S 49.51.

Trimethyl (Z)-α-methylthio-α-(hydroxyimino)orthotrithioacetate. [3a]

Compound **1** (470 mg, 2.85 mmol.) was dissolved with stirring in TFSA (3.8 ml, 42.8 mmol) at 0-5°C under dry nitrogen. At the end of the reaction, the solution was poured with stirring into MeSH (8.0 g, 0.17 mol.)CH_2Cl_2 (120 ml) at -40° to -60°C. The extraction was performed as described above. Solvent was evaporated *in vacuo* to give **3a,** a crystalline product that was crystallized from hexane (562 mg, 81%).

3a: m p 137°C (hexane) **IR**: 955, 1006, 1109, 1228, 1348, 1418, 1432, 1492(w), 1599(w), 2920, 2999, 3308(b), 3555 **^1H NMR** δ 2.12 (s, 9H) 2.60 (s, 3H) 9.24 (s, 1H exchangeable with D_2O). **^{13}C NMR**: δ 14.02 (MeS orthoester), 19.91 (MeS), 76.69 (C-orthoester), 154.83 (C-hydroxyimino), **SM**: 243 [M]$^+$, 0.3), 196

([M-(MeS)]$^+$, 100), 148 ([M-(MeS)-(MeSH)]$^+$, 48) **analysis** $C_6H_{13}NOS_4$ cal. C 29.60 H 5.38 N 5.75 S 52.68 found C 29.77 H 5.36 N 5.61 S 52.59.

Trimethyl (Z)-α-methylthio-α-(hydroxyimino)orthodithioacetate. [3b]

Compound **3a** (320 mg, 1.40 mmol.) was dissolved in TFSA (4 ml, 45 mmol) at 0 -5°C for 1.5 hours. Quenching with MeOH:CH_2Cl_2 (10 ml: 70 ml) and usual work-up followed by flash chromatography (hexane: AcOEt 2:8) gave **3a** (205 mg, 64%) and **3b** (62 mg, 21%):

3b: m p 121-2°C (hexane) **IR** 923, 1066, 1430, 2828 (w), 2928, 3002, 3288 (b), 3558; **^{1}H NMR** δ 2.02 (s, 6H) 2.64 (s, 3H) 3.47 (s, 3H) 9.60 (b.s., 1H); **^{13}C NMR** δ 12.75 (MeS orthoester), 15.92 (MeS), 52.01 (MeO),101.79 (C-orthoester), 152.55 (C-hydroxyimino); **SM**: 180 ([M-(MeS)]$^+$, 100), 132 ([M-(MeS)-(MeSH)]$^+$, 67); **analysis** $C_6H_{13}NO_2S_3$ cal. C 31.70 H 5.76 N 6.12 S 42.30 found C 31.39 H 5.55 N 6.15 S 42.16.

Trimethyl (Z)-α-fluoro-α-(hydroxyimino)orthodithioacetate. [4]

Compound **1** (230 mg, 1.39 mmol) was dissolved in ice cold HF (5.5 ml, 0.27 mol.). Some minutes later SbF_5 (4.03 g, 18.6 mmol.) was carefully added. The superacidic solution was quenched 1.25 hour later with MeOH: CH_2Cl_2 (10 ml: 70 ml). After usual work-up and flash chromatography (hexane:AcOEt, 8:2), starting product **1** (41 mg, 17%) then **4** (195 mg, 70%) were isolated:

4: m p 78°C (hexane); **IR**: 916, 958, 1080 (s), 1270, 1431, 1675, 2831 (w), 2929, 3008, 3340 (b), 3570 ; **^{1}H NMR** δ 2.07 (s, 6H, MeS) 3.45(s, 3H, MeO) 8.78 (d, $^4J_{HF}$=3.7 Hz, 1 H, OH); **^{13}C NMR**: δ 12.50 (MeS), 50.95 (MeO), 93.97 (d, $^2J_{CF}$=31 Hz, C-orthoester). 149 65 (d, $^1J_{CF}$=325 Hz, C-hydroxyimino); **SM**: 168 ([M-(MeO)]$^+$, 5), 152 ([M-(MeS)]$^+$, 95), 75 (100); **analysis** $C_5H_{10}FNO_2S_2$ cal. C 30.14 H 5.06 N 7.03 F 9.53 found C 30.36 H 5.14 N 7.01 F 9.71.

Trimethyl (E)-α-(hydroxyimino)orthotrithiophenylglyoxylate. [5a]

Compound **1**(490 mg, 2.97 mmol.) was added to a stirred mixture of benzene (1.5 ml, 16.8 mmol) and TFSA (4.0 ml, 45 mmol.) at 0-5°C under dry nitrogen for 20 hours. At the end of the reaction, the mixture was poured into MeSH (10.4 g, 0.22 mol.) in CH_2Cl_2 (150 ml) at -40 to -60°C and extracted as above. Solvent was evaporated *in vacuo* to give a crystalline product (635 mg). Compound **5a** was purified by flash chromatography (hexane:AcOEt 85:15) and crystallized in hexane:CH_2Cl_2 (490 mg, 62%).

5a: m p 184-5°C; **IR**: 820, 952, 987, 1349, 1410, 1433, 1492, 1602, 2920, 3000, 3319 (broad), 3561; **^{1}H NMR** δ 2.09 (d, 9H, MeS) 7.43 (m, 5H, ar) 9.27 (s, 1H, N-OH); **^{13}C NMR** δ 13.88 (MeS), 73.13 (C-orthoester), 127.70 (C-meta), 128.82 (C-ortho), 129.15 (C-para), 131.41 (C-ipso), 156.55 (C-hydroxyimino); **SM**: 256 ([M-(OH)]$^+$, 0.5), 226 ([M-(MeS)]$^+$, 100); **analysis** $C_{11}H_{15}NOS_3$ cal. C 48.32 H 5.53 N 5.12 S 35.18 found C 48.47 H 5.58 N 4.98 S 34.79.

Trimethyl (E)-α-(hydroxyimino)orthodithiophenylglyoxylate. [5b]

The compound **5b** was prepared as describe above for **5a**, excepted that the acidic medium was quenched by dry MeOH (20 ml):CH_2Cl_2 (150 ml) at -40° to -60°C. The product **5b** was purified by flash chromatography (hexane:AcOEt 3:7) and crystallized from hexane (yield: 86%)

5b: mp 160°C (hexane); **IR**: 935,1056 (s), 1108, 1351, 1436, 1492 (w), 1602 (w), 2829 (w), 2925, 3004, 3298 (b), 3565; **^{1}H NMR** δ 2.03 (s, 6H, MeS), 3.40 (s, 3H, MeO), 7.41 (m, 3H, p+m), 7.55 (m, 2H, ortho), 9.69 (b.s.. 1H, OH); **^{13}C NMR**: δ 12.62 (MeS), 51.59 (MeO), 99.55 (C-orthoester), 127.73 (C-ortho), 129.00 (C-meta), 129.09 (para), 131.05 (C-ipso), 155.87 (C-hydroxyimino); **SM**: 210 ([M-(MeS)]$^+$, 100), 240 ([M-(MeO)]$^+$, 12); **analysis** $C_{11}H_{15}NO_2S_2$ cal. C 51.33 H 5.87 N 5.44 found C 51.66 H 5.82 N 5.29.

Trapping with anisole and quenching with MeSH;

Compound **1** (412 mg, 2.49 mmol.) was added to a stirred mixture of anisole (700 µl, 6.44 mmol.) and TFSA (4 ml, 45 mmol.) at 0-5°C under dry nitrogen. At the end of the reaction (10h. 0° to RT), the mixture was poured into a solution of MeSH (8 g, 0.17 mmol.) in CH_2Cl_2 (100 ml) at -60°C.

After usual work-up and flash chromatography with hexane-AcOEt the following compounds were isolated :**7** (38 mg, 7%) then **3a** (79 mg, 13%) and finally **6** (401 mg, 53%)

1,1,1-ter(methylthio)-2-nitroethane. [7]
m p 23-4°C; **^{1}H NMR**: δ 2.24 (s, 9H) 4.76 (s, 2H); **^{13}C NMR**: δ 13.52 (MeS), 66.08 (C-orthoester), 81.05 (CH_2-NO_2); **SM**: 213 ($[M]^+$, 0.4), 166 ($[M-(MeS)]^+$, 100), 120 ($[M-(MeS)-(NO_2)]^+$, 98); **analyse** $C_5H_{11}NO_2S_2$ cal. C 28.15 H 5.19 N 6.56 S 45.09 found C 28.10 H 5.14 N 6.48 S 45.04

Trimethyl (E)-α-hydroxyimino(para-methoxyphenyl)orthotrithioglyoxylate. [6]
m p 182-3°C; **IR** 1034, 1178, 1247 (s), 1293, 1348, 1415, 1434, 1426, 1510 (s), 1606, 2833(w), 2920, 2956 (w), 3001, 3314 (b), 3560.**^{1}H NMR** δ 2.10 (s, 9H) 3.83 (S, 3H) 6.95 (d, $^3J_{HH}$=8.7 Hz) 7.47 (d, $^3J_{HH}$=8.7 Hz) 9.16 (s, 1H); **^{13}C NMR** δ 13.90 (MeS), 55.10 (MeO), 73.60 (C-orthoester), 113.30 (C-meta), 130.28 (C-ortho), 123.38 (C-Ipso hydroxyimino), 156.30 (C-hydroxyimino), 160.23 (C-Ipso OMe); **SM**: 256 ($[M-(MeS)]^+$, 80), 75 (100); **SMHR** $C_{12}H_{17}NO_2S_3$ cal. 303.042144 found 303.042144.

In an other experiment, **1** (535 mg, 3.24 mmol.) and anisole (600 µl, 5.55 mmol) were dissolved in TFSA (4 ml, 45 mmol) at -10° to 0°C for 3 hours. Usual quenching as above and work-up led to **7** (262 mg, 37.7%), **3a** (170 mg, 21.6%), **1** (19 mg, 3.5%) and **6** (35 mg, 3.5 %).

Trapping with benzene and quenching with water:

1 (320 mg, 1.94 mmol), benzene (1400 µl) and TFSA (4 ml, 45 mmol.) were reacted during 20 hours at 0° to RT and quenched on ice water/CH_2Cl_2 (30/100 ml) and Na_2CO_3. After usual work-up, two products were isolated after flash chromatography then preparative thin layer chromatography (hexane/AcOEt: 9/1): **5(a)** (30%) and **8 (E)** (28%).

S-methyl (E)-α-(hydroxyimino)phenylthioglyoxylate. [8 (E)]
m p 123-4°C **^{1}H NMR** δ 2.39 (s, 3H), 7.47 (b.s., 5H), 8.93 (s, 1H); **^{13}C NMR** δ 11.65 (MeS), 127.81 (C-ipso), 128.08 (C-ortho), 129.44 (C-meta), 130.05 (C-para), 154.99 (C-hydroxyimino), 190.66 (C-orthoester); **SM** 195 ($[M]^+$, 17), 150, 120 ($[M-(MeSCO)]^+$, 45), 77 (100); **SMHR** $C_9H_9NO_2S$ cal. 195.0354 found 195.03547. Protonated form in TFSA (Room temperature): **^{1}H NMR** δ 1.83 (s, 3H, MeS), 6.85 (dd, *J*= 7.6, 7.6 Hz, 2H meta), 7.03 (dd, J_{HH}= 7.6, 7.6 Hz, 1H para), 7.13 (d, J_{HH}= 7.6 Hz, 2H ortho).

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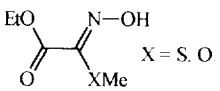
16 Such a trapping can also be observed with other compounds able to give hydroxynitrilium ion e.g. ethyl nitroacetate dissolved in TFSA at 0-5°C can be trapped after 30 mn reaction time in the same way to afford the same kind of hydroxyimino derivative in a yield of 40-60 % on isolated chromatographed products.



X = S; F°=53-5°C. ^{1}H NMR ($CDCl_3$) δ 1.37 (t,$^3J_{HH}$=7 Hz, 3H); 2.53 (s, 3H (SMe)), 4.34 (q, $^3J_{HH}$=7 Hz, 2H), 10.50 (b.s. 1H). ^{13}C NMR($CDCl_3$) δ 14.00, 14.37, 62.68, 148.60, 160.69; MS 163 (M^+, 50), 146 ([M-(OH)]$^+$, 40), 118 [M-(EtO)]$^+$, 55), 74 (100); analysis $C_5H_9NO_3S$ cal. C 36.80, H 5.56, N 8.58 found C 36.93, H 5.56, N 8.49.

X = O; F°=71.5-72°C^{1}H NMR ($CDCl_3$) δ 1.23 (t, $^3J_{HH}$= 7.2 Hz, 3H); 3.73 (s, 3H (OMe)); 4.17 (q, $^3J_{HH}$ = 7.2 Hz, 2H); 7.70 (b.s., 1H.); ^{13}C NMR ($CDCl_3$) δ 14.25, 53.08, 62.43, 151.79, 151.17; SMHR $C_5H_9NO_4$ cal. 147.05316 found 147.0529

17 Coustard, J.M. unpublished results. ^{1}H NMR of ions **21**: **(X= Me, Y= H)** *syn* isomer δ_H= 1.93 (s, 3H), 6.80 (d.d, $^3J_{HH}$= 7 Hz, $^3J_{HH}$= 7 Hz, 2H meta), 6.96 (d.d., $^3J_{HH}$= 7Hz, $^3J_{HH}$= 7Hz, 1H para), 7.25 (d, $^3J_{HH}$= 7Hz, 2H ortho); *anti* isomer δ_H= 2.05 (s, 3H), 6.80 to 9.98 (m, 5H), 10.74 (s.l., 1H, NH^+); **(X= Me, Y= MeO)** *syn* isomer δ_H= 1.90 (s, 3H), 3.35 (s, 3H), 6.50 (d, $^3J_{HH}$= 7 Hz, 2H meta), 7.43 (d, $^3J_{HH}$= 7 Hz, 2H ortho), 10.50 (b.s., 1H, NH^+); *anti* isomer δ_H= 2.03 (s, 1H), 3.30 (s, 3H), 6.47 (d, $^3J_{HH}$= 7 Hz, 2H meta), 7.00 (d, $^3J_{HH}$= 7 Hz, 2H ortho), 10.66 (b.s., 1H, NH^+); **(X= COOMe, Y= H)** *syn* isomer δ_H= 0.64 (t, $^3J_{HH}$= 7 Hz, 3H), 3.85 (q, $^3J_{HH}$= 7 Hz, 2H), 6.83 (d.d., $^3J_{HH}$= 7 Hz, $^3J_{HH}$= 7 Hz, 2H meta H), 7.00 (d.d., $^3J_{HH}$= 7Hz, $^3J_{HH}$= 7 Hz, 1H para H), 7.22 (d.d., $^3J_{HH}$= 7 Hz, $^3J_{HH}$= 7 Hz, 2H ortho H), 12.0 (b.s., 1H, NH^+); *anti* isomer δ_H= 0.65 (t, $^3J_{HH}$= 7 Hz, 3H), 3.93 (q, $^3J_{HH}$= 7 Hz, 2H), 6.80 to 7.04 (m, 5H), 11.5 (b.s., 1H, NH^+); **(X= COOMe, Y= MeO)** *syn* isomer δ_H= 0.65 (t, $^3J_{HH}$= 7 Hz, 3H), 3.25 (s, 3H,MeO), 3.83 (q, $^3J_{HH}$= 7 Hz, 2H),6.43 (d, $^3J_{HH}$= 10 Hz, 2H), 7.41 (d, $^3J_{HH}$= 10 Hz, 2H), 11.34 (braod s.,1H, NH^+); *anti* isomer δ_H= 0.65 (t, $^3J_{HH}$= 7 Hz, 3H), 3.22 (s, 3H, MeO), 3.93 (q, $^3J_{HH}$= 7 Hz, 2H), 6.42 (d, $^3J_{HH}$= 10 Hz, 2H meta), 6.98 (d, $^3J_{HH}$= 10 Hz, 2H ortho), 11.1 (b.s., 1H, NH^+).

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