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TETRAHEDRON

1-Amino-2-Nitroethene Derivatives in Triflic Acid: NMR Study and Triflates Formation from their Hydroxynitrilium Ions

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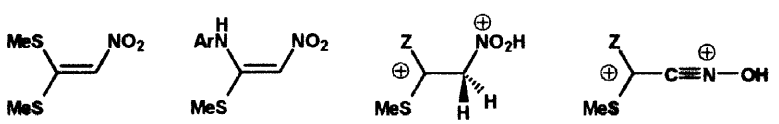
Abstract: In triflic acid, 1-amino-2-nitroene derivatives undergo a *C,O*-diprotonation followed by the loss of (protonated) water, to form the >C=N$^{\oplus}$< conjugated hydroxynitrilium ions that can react, in a competitive way, either with TfO$^{\ominus}$ or with added C_6H_6. The resulting phenylated dications can be selectively reduced by $NaBH_4$ at the iminium bond moiety. A protonated nitroso derivative was also isolated as its triflate salt. Structure, reactivity and mechanism of these reactions are discussed.

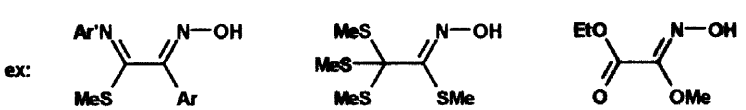
INTRODUCTION

In previous papers were described the behavior and reactivity of 1,1-bis(methylthio)-2-nitroethene **1** and 1-arylamino-1-methylthio-2-nitroethene derivatives **2** in superacidic media HF-SbF_5 and triflic acid.[1,2] It was shown that these compounds are firstly *C,O*-diprotonated, cations **3**, then transformed into conjugated hydroxynitrilium ions **4** which are fair electrophiles that react with aromatic rings, methanethiol or methanol to yield aromatic oximes **5**, *S*-methylthiohydroxyimidate **6** or *O*-methylhydroxyimidates **7** respectively.



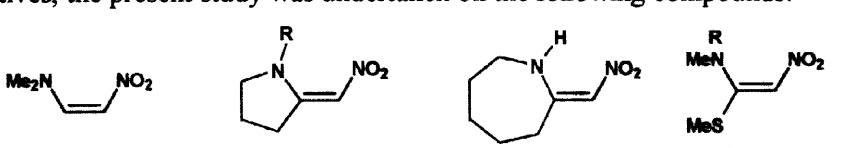
1 **2** **3** **4**

The general feature of these compounds is that they all have the entering group (Ph, MeS or MeO) and the OH of the hydroxyimino group, in the *syn* configuration, as deduced from ^{1}H- and ^{13}C-NMR studies of their neutral and diprotonated forms, or from X-ray crystallographic analysis.[3]



5 **6** **7**

As a way to have a better understanding of the reactivity of non-aromatic 1-aminosubstituted-2-nitroethene derivatives, the present study was undertaken on the following compounds:



8 **9** R = H **10** R = Me **11** **12** R = H **13** R = Me

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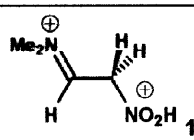
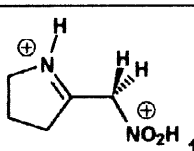
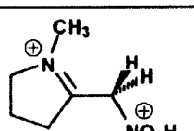
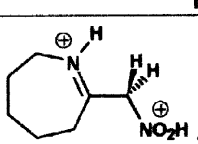
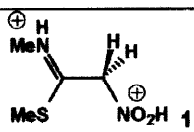
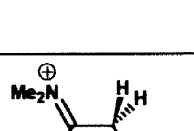
Compound **8** was prepared from reaction of dimethylformamide dimethyl acetal and nitromethane[4a,b] or from one-pot synthesis from orthoesters.[4c] The others compounds were prepared by conventional methods, i) either using nitromethane as a synthon for the 2-nitroene moiety and reaction with the corresponding *O*-methyllactim, compounds **9** and **11**,[4a,5] or α-di-*O*-methylacetal, compound **10**,[5] ii) or by nucleophilic substitution of one MeS group of 1,1-bis(methylthio)-2-nitroethene by one molar equivalent of $MeNH_2$ or Me_2NH, compounds **12** and **13**.[6a,b]

RESULTS AND DISCUSSION

C,O-diprotonated cations:

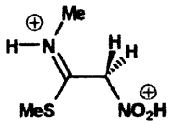
These compounds were dissolved in triflic acid at temperatures close to 273 K with ultrasonic stirring. NMR study at room temperature or lower temperature (NMR variable temperature probe) allows observation of generally short lived species and monitoring of the reaction. *C,O*-diprotonation of compounds **8-13** leads respectively to kinetic cations **14-19** of which spectra are reported Table 1. The kinetic *C,O*-diprotonated cations are generally observed as short lived species with a half-live of some minutes at room temperature, with the exception of cations **18** and **19** which are stable for hours under these experimental conditions.

Table 1: NMR of kinetic *C,O*-diprotonated cations in triflic acid.

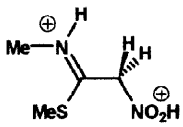
Cation #	^{1}H-NMR (δ_H ppm)	^{13}C or DEPT135-NMR (δ_C ppm)
 **14**	T=275 K, ref TMS acetone-d_6 3.00 (s, 3H, CH_3); 3.26 (s, 3H, CH_3); 5.11 (b.s, 2H, $CH_2NO_2H^+$); 8.20 (b.s, $h_{1/2}$= 5 Hz, 1H, =C-H)	44.5 (CH_3); 72.08 ($CH_2NO_2H^+$)
 **15**	T= 250 K, ref. TMS/MeOH-d_4 1.84 (b.s, 2H, CH_2); 2.58 (b.s, 2H, CH_2); 3.66 (b.s., 2H, CH_2); 5.29 (s, 2H, $CH_2NO_2H^+$); 10.66 (b.s, $=NH^+$)	T= 250 K ref TMS in MeOH-d_4 19.12; 37.92; 56.31; 71.62 ($CH_2NO_2H^+$); 186.88 (C=N<).
 **16**	T = 250 K ref TMS in MeOH-d_4 1.85 (m, 2H, CH_2); 2.83 (m, 2H, CH_2); 3.00 (s, 3H, CH_3); 3.79 (m, 2H, CH_2); 5.21 (s, 2H, CH_2)	T = 250 K ref TMS in MeOH-d_4 20.04; 40.75; 41.13; 61.90; 71.65 ($CH_2NO_2H^+$); 181.39 (>C=N<).
 **17**	1.28 (b.s, 4H, 2 x CH_2); 1.44 (b.s, 2H, CH_2); 2.40 (b.s, 2H, CH_2); 3.52 (b.s, 2H, CH_2); 5.09 (s, 2H, $CH_2NO_2H^+$); 10.04 (b.s., 1H, $\geq N^+$-H)	21.14; 23.56; 29.03; 34.13; 51.31; 75.44 ($CH_2NO_2H^+$)
 **18**	Ref: TMS in acetone-d_6: 2.18 (s, 3H, SCH_3); 2.57 (d, J= 5.8 Hz, 3H, NCH_3); 4.98 (s, 2H, CH_2); 8.82 (b.s, N-H) minor ion: (1/5): 2.00 (s, 3H, SCH_3); 2.44 (d, J=5 Hz 3H ,NCH_3); 4.93 (s, 2H $CH_2NO_2H^+$); 8.32 (b.s, 1H, NH)	Ref.: C_6H_6 at 128.50 in TFSA (R.T.) 14.71 (SCH_3); 35.19 (NCH_3); 73.30 ($CH_2NO_2H^+$)
 **19**	2.32 (s, 3H, SCH_3);3.05 (s, 3H, NCH_3); 3.16 (s, 3H, NCH_3); 5.30 (s, 2H, $CH_2NO_2H^+$) Stable for hours at RT.	17.01 (CH_3S), 46.79, 47.26 71.95 ($J_{13C-14N}$ = 1.5 Hz, $CH_2NO_2H^+$) 181.55 (>C=N<)

These cations are all characterized by a deshielded methylene next to the protonated nitro group in the range δ_H 4.98 to 5.30 and δ_C 71.6 to 75.4, values close to the previously observed ones for cations **3**.[1,2] The proton on the nitro group was not observed because of its very rapid exchange rate with the medium, as previously reported.[7] Starting materials **8-11** and **13** can afford only one *C,O*-diprotonated form, respectively cations **14-17** and **19**, but for product **12**, two protonated forms can be observed. The configuration of the major isomer

is probably the same as the one of the starting compound **12**, with the MeS and MeN in the *s-cis* configuration, as observed by X-ray crystallographic analysis in the same series[8a] or in solution in other series.[8b] In agreement with such an assumption are the deshielding of MeS and CH_2 groups and shielding of MeN proton in ion **(Z)-18**, because of steric interactions. The amount of the minor *E* isomer seems to depend upon the way in which compound **12** is dissolved in triflic acid. It represents less than 1/5 of both cations, and is probably due to a further isomerization of the major cation, as previously observed with aromatic derivatives.[2]



(*E*)-18

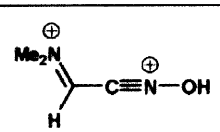
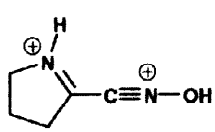
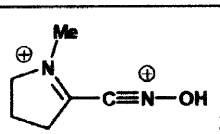


(*Z*)-18

Hydroxynitrilium ions:

The *C,O*-diprotonated cations are transformed into conjugated hydroxynitrilium ions. The transformation can be monitored by NMR. However, observation of the hydroxynitrilium ions cannot always be possible because some of them are either too slowly formed at low temperature or too highly reactive at higher temperature, even with triflate anion (*vide supra*). The species **20**, **21** and **22**, shown in table 2, were observed. Hydroxynitrilium ion **20** is nearly quantitatively formed and was observed as a single ion in the medium (figure 1). It is stable enough for hours near 273 K allowing easy NMR characterization. Its nice spectra show that both methyl protons resonate as a singlet at δ_H 3.23 and the vinylic proton as a broad singlet at δ_H 7.62, however, the methyl carbons have different chemical shifts and appeared as two signals at δ_C 47.7 and 49.4. Iminium carbon resonates at δ_C 150.9 ppm with an apparent coupling constant of $^2J_{13C=14N}$ = 12 Hz, a value in the range of what is usually encountered for an sp^2 carbon. The most interesting feature is the hydroxynitrilium carbon that appears as a weak and partially resolved triplet at δ_C 27.7 with an apparent coupling constant of $^2J_{13C\equiv14N}$ = 37 Hz. The latter chemical shift and coupling constant values are close to the values observed with various nitrile oxides.[9a,b] Quadripolar relaxation of ^{14}N acts as a decoupling mechanism on ^{13}C-^{14}N coupling and causes a broadening of the signals.The hydroxynitrilium carbons in cations **21** and **22** resonate as very weak and broad signals respectively at δ_C 25.6 and 24.7, probably in connection with nitrogen substitution. The influence of nitrogen substitution is more sensitive on the iminium carbon with δ_C value 168.33 and 165.10 ppm, respectively.

Table 2: NMR of some hydroxynitrilium ions

Cation #	^{1}H-NMR (δ_H ppm)	^{13}C-NMR (δ_C ppm)
 **20**	3.18 (s, 6H, 2 C<u>H</u>$_3$); 7.59 (s, 1H, =C-<u>H</u>).	27.74 (t, $J_{13C-14N}$ =37 Hz,-C≡N$^+$-OH) 47.69; 49.37 150.93 (b.s, $J_{13C-14N}$ =12 Hz,-C=N<)
 **21**	T= 250 K, ref.: TMS in MeOH-d_4 1.84 (m, 2H, CH_2); 2.69 (m, 2H, CH_2); 3.68 (m, 2H, CH_2); 9.96 (b.s, 1H, NH)	T= 250 K, ref.: TMS in MeOH-d_4. 20.06; 25.6 (broad & weak signal - C≡N$^+$-OH); 40.66; 55.67; 168.33 (C=N<)
 **22**	Not very reactive. No reaction at 250 K in the medium, colorless solution. Ref.: TMS in MeOH-d_4 at 250 K 1.85 (m, 2H, CH_2); 2.83 (m, 2H, CH_2); 3.07 (s, 3H, CH_3); 3.66 (m, 2H, CH_2)	T= 250 K, ref.: TMS in MeOH-d_4 18.48; 24.7 broad & weak signal - C≡N$^+$-OH); 39.00 (CH_3); 39.44; 64.96; 165.10 (C=N<).

The hydroxynitrilium **20** is relatively stable at temperature close to 273 K but cation **22** and to a greater extent cation **21**, are prone to add triflate anion at this temperature. The hydroxynitrilium ions **21** and **22** were observed along with their precursor cations **15** and **16** respectively. A rough reactivity scale can be established taking into account the relative *in situ* reaction rate of hydroxynitrilium ions with benzene *vs.* triflate anion. Ion **20** reacts only with C_6H_6 but ratio of 9/1 and 7/3 were observed for hydroxynitrilium ions **22** and **21**

respectively. The even more reactive and not observed hydroxynitrilium ion derived from azaheptacyclic derivative **11**, affords more than 50% of triflate derivative *(vide supra)*. From these observations, it may be concluded that a full alkyl substitution of amino nitrogen and a lack of alkyl substituent on C1 are stabilizing factors and that an azaheptacyclic ring is a destabilizing factor for hydroxynitrilium ions. It is noteworthy that thioderivative **12** is easily *C,O*-diprotonated into cation **18** which is very stable in the medium and of which transformation into the corresponding hydroxynitrilium ion is very slow: reaction with C_6H_6 needs to operate at more than 50°C for three hours.

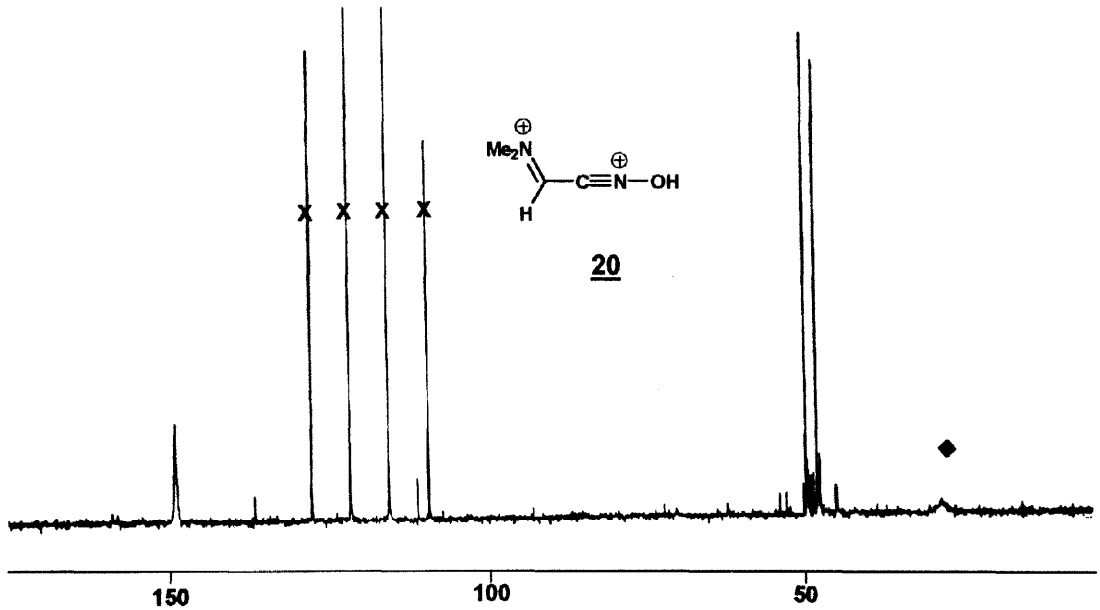
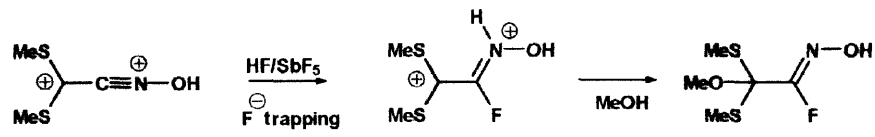


Figure 1: ^{13}C-NMR spectra (50 MHz) of hydroxynitrilium ion **20** at 275 K (x: triflic acid & ♦: -C≡N$^+$-OH)

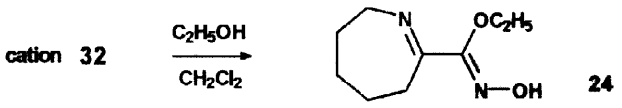
In situ hydroxynitrilium ion reactivity:

When a solution of hydroxynitrilium ion is left at room temperature for some hours, or when a solution of compound **12** is heated for about one hour at 40 to 45° C, a new species is formed by a clean reaction. The NMR spectra of these cations show, along with methyl and methylene signals, i) the presence of an iminium carbon at δ_C 174.0 to 180.6 and, ii) a usually stronger signal in the field δ_C 137.0 to 156.2 along with, iii) a weak CF_3 quadruplet in the vicinity of the triflic acid signals ($\Delta\delta_C$ = 0.05 to 0.30 ppm) having a slightly higher coupling constant ($^1J_{CF}$ = 319.5 to 320.7 Hz *vs.* 316 Hz for triflic acid). Such analogous signals and coupling constants were previously described for ketone enol triflates e.g. δ_C 143 to 149 and $^1J_{CF}$ = 319 to 322 Hz [11b]. From these observations, it may be postulated that these cations are triflate derivatives formed by nucleophilic addition of triflate anion to the -C≡N- triple bond of hydroxynitrilium ions. The signal in the range δ_C 137.0 to 156.2 corresponds to the resonance of the carbon bearing the triflate group. This behavior may also be compared to that previously observed in HF-SbF_5 when cation **25** was trapped by fluoride anion to afford the subsequent fluoro ion **26**, then compound **27** after quenching with methanol.[1]

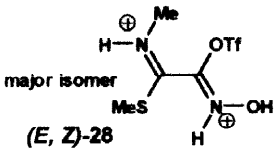


25 **26** **27**

The formed species does not react with benzene *in situ*, even at 50°C for some hours. When the acidity is destroyed with water, they afford soluble products not otherwise identified in the present study.[10,11a] The azaheptacyclic cation **32** can be quenched with ethanol in dichloromethane to afford, by a clean reaction, the *O*-ethylhydroxyimidate derivative **24**, a usually stable compound but apparently sensitive to decomposition on silica gel.



Two isomeric cations **28** were observed: the iminium carbon of the minor isomer resonates at higher field than the iminium carbon of the major isomer: δ_C 175.83 and δ_C 179.85 respectively. Usually to the more crowded *Z* isomer corresponds the more shielded iminium carbon. Such a feature was also previously observed in another series and confirmed by X-ray crystallographic analysis of trapping product (PhN instead of MeN and Ph instead of OTf).[3] The hydroxyiminium carbons of the both cations are not very different ($\Delta\delta_C$ 0.29 ppm) and because the course of the nucleophilic addition on the -C≡N-O triple bond occurs in such a way that the entering group and OH are in the *cis* configuration in the resulting product[14], the configuration of both C=N< hydroxyiminium bonds must be the same and in the present case (*Z*)-configured. From these considerations, it may be concluded that the major cation must be ***(E, Z)*-28** and the minor cation ***(Z, Z)*-28**. Triflate derivatives are described table 3.



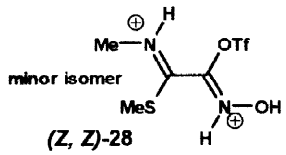
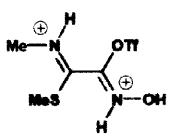
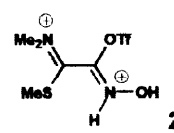
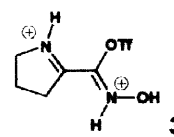
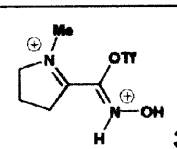
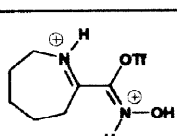
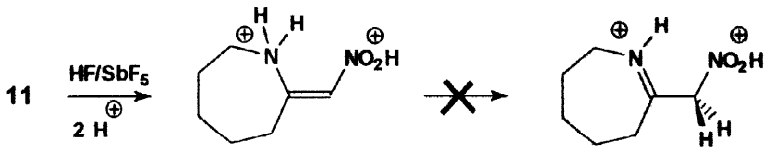


Table 3: NMR chemical shifts of triflated cations in triflic acid.

Cation #	^{1}H-NMR (δ_H ppm)	^{13}C- or DEPT135-NMR (δ_C ppm)
 **28**	two isomers: minor: 2.33 (s, 3H, CH_3S); 3.03 (d, *J*=5.6 Hz, 3H, NCH_3); 9.15 (b.s, NH) major: 2.37 (s, 3H, SCH_3); 2.90 (d, *J*=5.6 Hz, 3H, NCH_3); 9.93 (b.s, NH)	two isomers: minor 18.02; 35.82; 156.22 & 175.83 major: 16.80; 37.00; 119.08 (q, $^1J_{CF}$= 319.5 Hz, OTf); 155.93 (C-hydroxyimino); 179.85 (C-imino);
 **29**	2.30 (s, 3H, SCH_3); 3.04 (s, 6H, $(CH_3)_2N$=]; TFSA, RT, *In situ* no C_6H_6 trapping. Slow formation	17.11; 49.01; 48.59; 119.03 (q, $^1J_{CF}$= 321.3 Hz, OTf); 155.96 (C-hydroxyimino); 177.09 (C-imino).
 **30**	1.88 (m, 2H, CH_2); 2.91 (m, 2H, CH_2); 3.73 (m, 2H, CH_2); 9.82 (b.s, NH)	19.92; 35.35; 56.43; 119.28 (q, $^1J_{CF}$= 320.7 Hz, OTf); 137.04 (C-hydroxyimino); 180.01 (C-imino)
 **31**	1.82 (m, 2H, CH_2); 2.90 (m, 2H, CH_2); 3.15 (s, 3H, NCH_3); 3.84 (m, 2H, NCH_2) Slow formation. No reaction *in situ* with C_6H_6	18.47; 38.57; 41.85(Me); 66.89; 119.28 (q, $^1J_{CF}$= 320 Hz, OTf); 137.04 (C-hydroxyimino); 173.95 (C imino)
 **32**	1.27 m 2H (CH_2); 1.48 m 2H (CH_2); 2.77 m 2H (CH_2); 3.52 m 2H (CH_2); 10.03 b.s. (N-H) No reaction *in situ* with C_6H_6	20.24; 22.98; 28.41; 29.34; 50.35(CH_2-N=); 118.25 (q, $^1J_{CF}$= 320.65 Hz, OTf); 138.42 (C-hydroxyimino); 180.57(C-imino)

Following these results, it was tempting to prepare the corresponding fluoro derivatives in superacid HF-SbF_5. The fluoro derivatives are much less reactive than the triflates[10,11a] and should be easily recovered. A very exothermic reaction occurred when **11** was dissolved in HF-SbF_5. After one hour reaction time at 0-5°C followed by quenching with water/$NaHCO_3$, the starting product was nearly quantitatively recovered. Such a decrease in reactivity was previously observed, however to a lesser extent, with 1-arylamino-1-methylthio-2-nitroethene in HF-SbF_5.[2] This presently observed lake of reactivity may account for the strong basicity of the aminonitrogen atom -no aromatic ring conjugation- of which strong protonation must prevent any further

deprotonation leading to ion **17**, the key intermediate species on the way to the corresponding hydroxynitrilium ion.



This assumption implies that a very fast kinetic *N,O*-diprotonation firstly occurred in HF-SbF_5. Deprotonation of this species, e.g. by quenching with water/$NaHCO_3$, leads to the starting material. Such a fast heterodiprotonation was previously observed with 1,1-bis(methylthio)-2-nitroethene in triflic acid at low temperature: the very first step of the reaction is a *S,O*-diprotonation that affords the same kind of heterodiprotonated cation.[1]

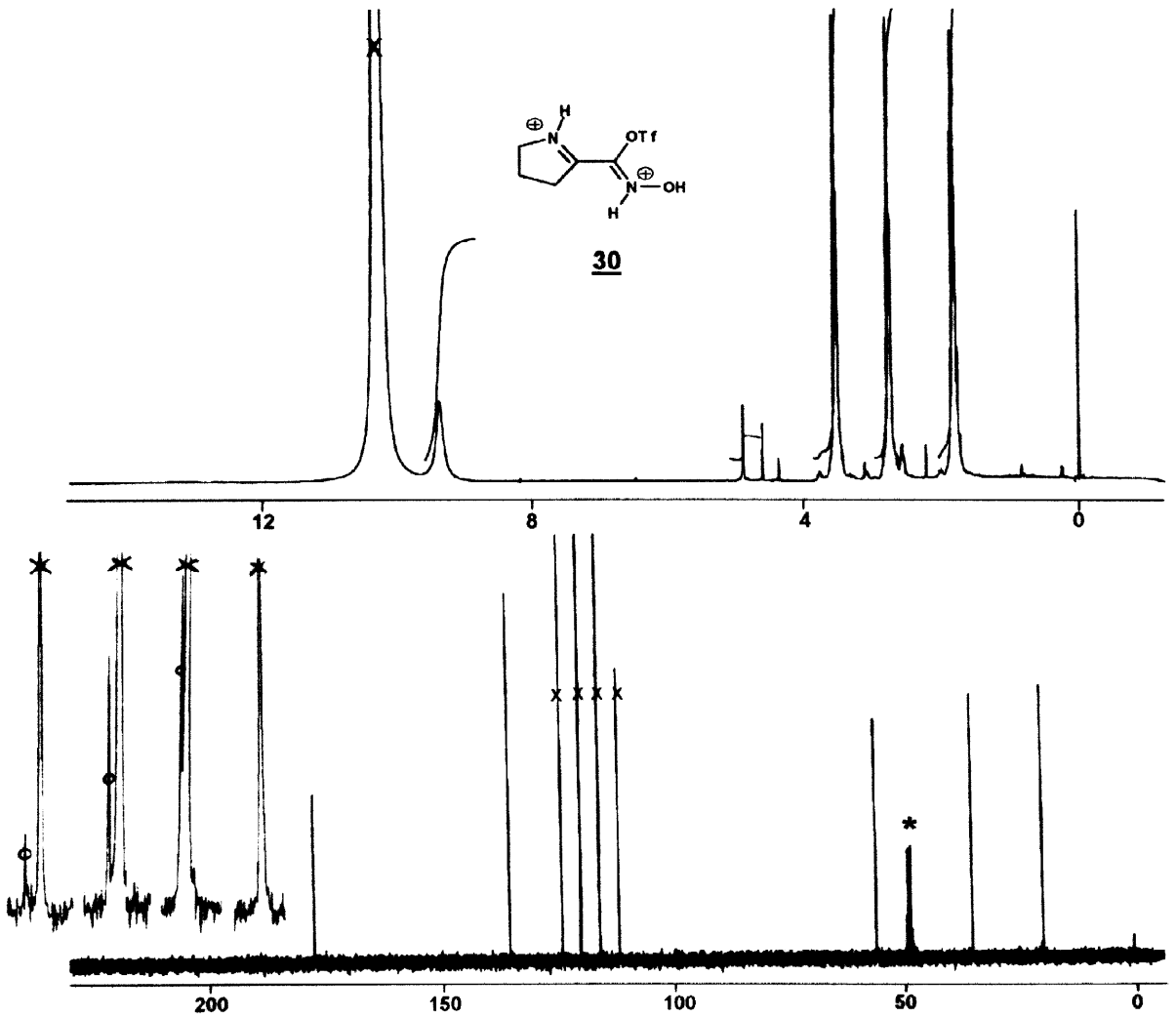


Figure 2: ^{1}H- and ^{13}C-NMR spectra of cation **30** in triflic acid (x: triflic acid, o: triflate and * methanol-d_4)

In situ benzene trapping

Compounds **8-13** can be dissolved in a mixture of triflic acid and benzene to afford respectively cations **33-37**. These reactions can be monitored by means of NMR spectroscopy.

The reactions proceeded smoothly until formation of the final cation by electrophilic addition of hydroxynitrilium ion onto the benzene ring. However, with starting products **9**, **10** and **13** that are transformed into reactive hydroxynitrilium ions, a competitive reaction occurred because of triflate anion trapping.

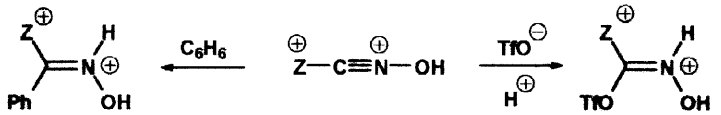
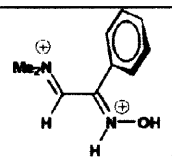
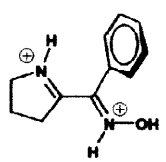
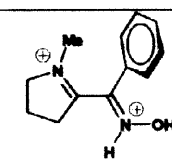
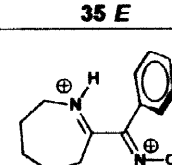
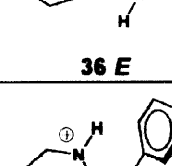
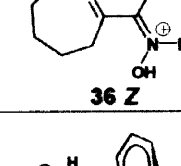
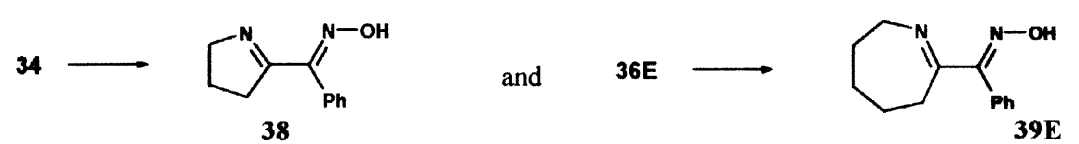


Table 4: NMR of cations resulting from benzene trapping in triflic acid.

Cation #	^{1}H-NMR (δ_H ppm)	^{13}C or DEPT135-NMR (δ_C ppm)
 **33**	2.97 (d, *J*= 1.1 Hz, 3H, CH_3); 3.49 (s, 3H, CH_3); 7.15 (dd, *J*= 8 & 8 Hz, 2H *m*-); 7.36 (dd, *J*= 8 & 8 Hz, 1H *p*-); 7.52 (d, *J*= 8 Hz, 2H *o*-); 8.43 (b.t, *J*= 1.5 Hz, 1H, =NH) in TFSA / benzene	Ref.: PhH at 128.5 ppm in TFSA. 47.42; 53.09; 126.96 (C-Ipso); 131.40; 133.43; 141.03; 149.40 (C-hydroxyimino); 164.57 (C-imino).
 **34**	2.14 (m, 2H, CH_2); 3.30 (m, 2H, CH_2); 4.00 (m, 2H, CH_2); 7.16 (m, 2H *m*-); 7.34 (m, 3H *o*- & *p*-), 10.67 (s, 1H, =NH). Stable for more than 5 days at RT without decomposition. *In TFSA saturated with benzene(RT) competitive trapping between benzene & TfO⁻ with 7:3 ratio*	Ref. TMS in MeOH-d_4/RT. 20.49; 39.08; 58.76; 120.89 (C-Ipso); 131.41 & 132.66 (C *o*- & *m*-); 139.80 (C-*p*); 151.62 (C-hydroxyimino); 182.24 (C-imino).
 **35 *E***	1.83 (m, 2H, CH_2); 2.74 (s, 3H, NCH_3); 2.86 (m, 2H, CH_2); 3.73 (m, 2H, CH_2); 6.98 (dd, *J*= 8 & 8 Hz, 2H *m*-); 7.15 (t, *J*=8 Hz,1H *p*-) 7.25 (d, *J*=8 Hz, 2H -*o*). in TFSA/benzene and with about 10% of triflated cation **31**.	Ref. PhH: 128.50 ppm in TFSA 19.20; 41.05 ($\underline{C}H_3$); 42.63; 65.99; 120.56 (Ipso); 131.52; 133.35; 141.03; 150.06 (C-hydroxyimino); 178.93 (C-imino).
 **36 *E***	Ref.: TMS in MeOH-d_4, TFSA & Benzene (RT) 0.94 (b.s., 2H); 1.55 (m, 2H); 2.49 (b.s, 2H).; 4.45 (b.s. 2H); 7.08 (dd, *J* = 7.8 & 7.8 Hz, 2H *m*-); 7.24 (t, *J* = 7.8 Hz, 1H *p*-); 7.29 (d, *J* = 7.8 Hz, 2H *o*-).	Ref. PhH: 128.50 ppm in TFSA 21.85; 23.28; 28.54; 36.16; 54.33; 119.98; 131.16; 133.44; 140.34; 155.77 (C-hydroxyimino); 185.67 (C-imino)..
 **36 *Z***	1.31 (m, 6H); 2.68 (m, 2H); 3.57 (m, 2H) 6.94 (m, 4H); 7.23 (m, 1H) 10.47 (s, 1H, $=NH^+$) very stable in TFSA	Ref.: TMS in acetone-d_6 21.81; 23.48; 28.40; 35.47; 54.17; 119.97; 130.48; 131.59; 140.49; 158.64 (C-hydroxyimino); 185.75 (C-imino)..
 **37 *E***	1.79 (s, 3H, SCH_3); 2.82 (d, J= 5.5 Hz, 3H, NCH_3) ; 7.08 (dd., *J*= 8 & 8 Hz, 2H *m*-); 7.27 (t, *J*= 8 Hz, 1H *p*-); 7.47 (dd., *J*= 8,8 Hz, 2H *o*-); 9.50 (b.s, 1H, NH imino) From C_6H_6 trapping of ion **20** in TFSA. A sole isomer probably with a *Z*-configured iminium bond.	Ref. PhH: 128.50 ppm in TFSA/RT 16.48 (CH_3S); 37.10 (CH_3N); 120.61 (C-Ipso); 131.71 & 133.95 (C *m*- & *o*-); 141.71 (C *p*-); 151.71 (C-hydroxyimino); 182.61 (C-thioimidate).

Quenching the solution with water generally affords the corresponding phenylhydroxyimino derivatives of which yields depend upon the extent of the competitive triflate trapping reaction. For instance, azapentacyclic compound **9** leads to triflated cation **30** and phenylated cation **34** in a 3/7 relative ratio. Quenching with water/$NaHCO_3$ affords phenylhydroxyimino derivative **38** (from **34**) with 55% isolated yield after extraction and crystallization.



Azaheptacyclic derivative **11** leads to less than 50% phenylated cation **36E** and no more than 38% of phenylhydroxymino derivative **39E** after quenching and extraction followed by flash-chromatography.

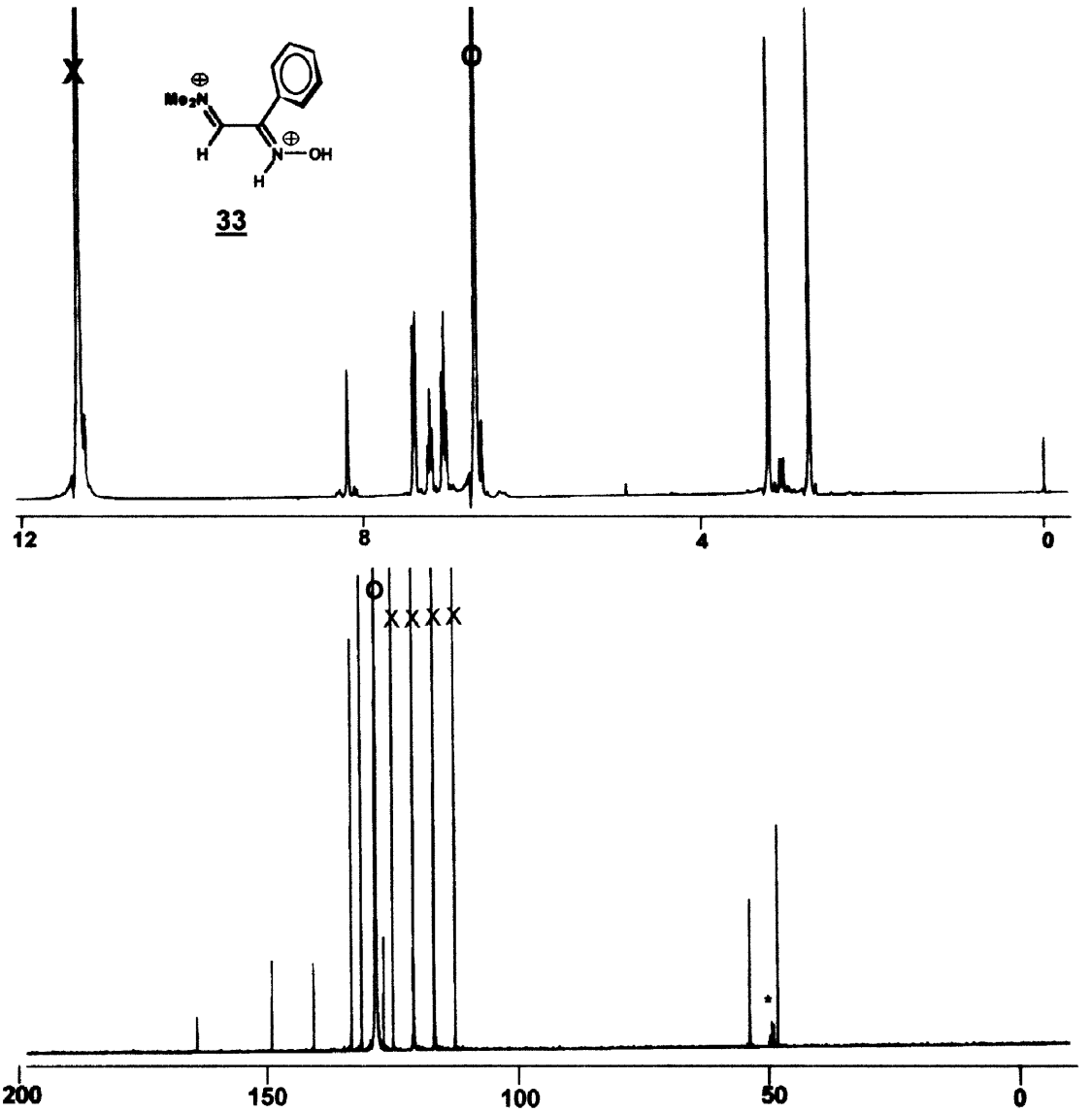
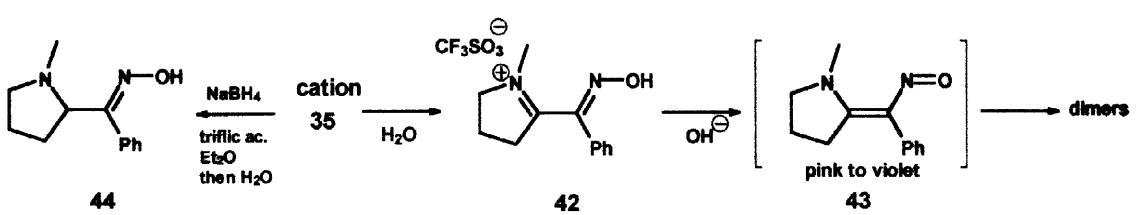


Figure 2: ^{1}H- and ^{13}C-NMR spectra of cation **33** in triflic acid (x: triflic acid, o: benzene and * methanol-d_4)

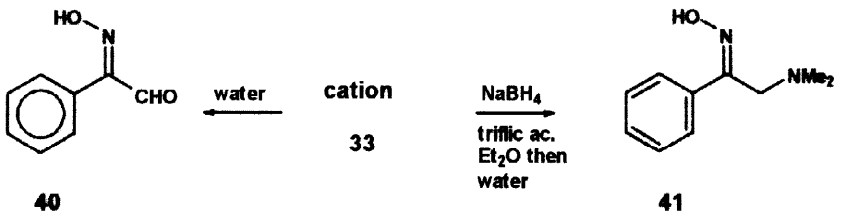
The competitive trapping reaction by triflate anion explains why the yield of phenyl derivative is sometimes poor.

Ion **35** is interesting because it affords, after hydrolysis and extraction from the acidic aqueous phase, the nitroso derivative as the triflate salt **42**. Basification of the aqueous phase leads to the formation of the nitroso derivative with a pink-violet color that fades because of its dimerization into a mixture of isomers, a usual behavior for nitroso derivatives.[13]

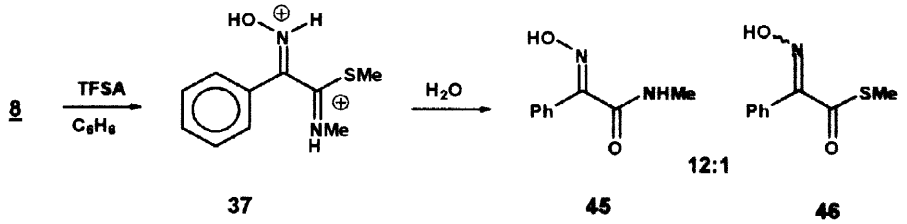


Hydrolysis of the iminium bond (e.g. with dilute KOH) was not attempted in the present study. However, direct reduction of this same cation **35** in triflic acid with $NaBH_4$ in anhydrous ether and at 0°C under a nitrogen atmosphere, as described by Olah *et al.*,[12] led to a selective reduction of the iminium bond to form the *N*-methylazacyclopentane derivative **44** (69% recovered yield).

Quenching the solution with water can also be complicated by hydrolysis reaction: cation **33** underwent deprotonation and hydrolysis of its imino bond to afford the corresponding carbonyl derivative **40.** However, interestingly, direct reduction of this same cation **33**, in triflic acid with $NaBH_4$ in anhydrous ether and at 0°C, under nitrogen, led to the selective reduction of the iminium bond to afford crystallized hydroxyimino derivative **41**.



Concerning cation **37** from thioderivative **8**, two sites for hydrolysis are possible, either the iminium bond, or the C-SMe bond. Both reactions were observed and afforded respectively products **45** and **46** [1] in a 12:1 relative ratio, indicating that the iminium bond is less prone to hydrolysis than the C-SMe bond.



Hydroxyiminium bond configuration

Configuration of the C=N hydroxyiminium bond in the kinetic product was previously shown to have the phenyl ring and OH in the *cis* configuration.[2,3] This result is in full agreement with an expected addition on a CN triple bond.[14] This configuration is generally preserved in the neutral product after usual work up. Retention of configuration can be checked, when ever possible, by dissolving the recovered neutral product in triflic acid and recording ^1H- and ^{13}C-NMR spectra, with special emphasis on the chemical shifts of aromatic protons and iminium/hydroxyiminium carbons. In the present study, isomerization was not generally observed for the kinetic cations in triflic acid, even after days at room temperature or hours at temperatures >40°C. The very strong protonation of the nitrogen atoms may account for this behavior, in agreement with previously observed results: the strong acidity of the medium causes complete protonation of the hydroxyiminium nitrogen atom and so prevents any isomerization of the CN double bond *via* the unprotonated form.[15]

The special case of cation **36E** is particularly interesting because of its corresponding neutral iminooxime **39E** isomerizes in acetone to afford quantitatively compound **39Z**. When compound **39Z** was dissolved in triflic acid, it afforded cation **36Z**, stable for days at room temperature. Cations **36E** and **36Z** have nearly the same nmr spectra excepted that, i) the aromatic protons present a different pattern and, ii) both iminium carbons have nearly the same chemical shift δ_c 185.7, but differ at the level of the hydroxyiminium carbon with δ_c 158.64 *vs.* 155.77 respectively. This difference value of $\Delta\delta_c = 2.87$ ppm is usually related to *Z-E* isomers of oximes[15] and indicates that both the cations **36E** and **36Z** are respectively the *E* and *Z* isomers of the cation resulting from benzene trapping of hydroxynitrilium ion derived from the azaheptacyclic starting product **11**.

From all these observations and by comparisons with previously reported results on nucleophilic addition on CN triple bonds, it may be concluded that all these kinetic cations have their hydroxyiminium groups with the phenyl ring and the OH in the *cis*-configuration.

CONCLUSION

In triflic acid, 1-amino-2-nitroene derivatives undergo a *C,O*-diprotonation followed by a loss of (protonated) water, to form >C=N$^{\oplus}$< conjugated hydroxynitrilium ions. These latter ions are reactive enough to add triflate anion by a clean reaction to yield the corresponding diprotonated triflates, even in presence of C_6H_6. Trapping by C_6H_6 affords only one isomer in which the aromatic ring and the OH of the hydroxyimino group are in the *cis* configuration. The phenylated dications can be selectively reduced by $NaBH_4$ at the iminium bond moiety to afford the corresponding amino oxime. When the amino group is fully substituted and part of a ring conjugated with the C(1)=C(2) double bond of the starting compound, it was possible to isolate the triflate salt of the protonated conjugated nitroso derivative resulting from C_6H_6 trapping in TfOH. Concerning the reactivity of the formed hydroxynitrilium ions, the least reactive observed ion possesses a H-C(1) carbon bearing a Me_2N group. Other interesting results in this field will be published soon.

AKNOWLEDGEMENTS

Thanks to Pr J.C. Jacquesy for a nice suggestion. Thanks also to Janie Joffre for low resolution mass spectra, to Sophie Schneider for elemental analysis and to CNRS for financial support.

EXPERIMENTAL PART

Melting points were determined with a Büchi 510 apparatus using capillary tube (temperature rate 2°C/mn) and are not corrected. A Brüker WP 200 SX NMR spectrometer or a Brüker DPX 300, equipped with a low temperature probe, were used for ^{1}H and ^{13}C spectra recorded respectively at 200 MHz / 50 MHz or 300.13 MHz / 75.47 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, but from experiment to experiment, small scale shifts were also observed depending probably of the NMR cell used, concentration of the analytes and, of course, temperature. However NMR chemical shifts were given with two decimal points in a way to allow comparison between different signals of the same cation or for comparison between two cations in the same solution. Electron impact ionization (70 eV) mass spectra were obtained with a Finnigan Incos 500 instrument. HRMS were performed at the CNRS analytical service and microanalysis were performed with a **N.A. 2000** Analyzer. 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 described below, and performed with a Waters 600 pump equipped with Rheodyne 7125 injector valve (20 µl loop) and an Applied Biosystem 785 A programmable or Waters 486 UV detector, column 250x4 mm I.D., 5 µm Spherisorb silica. Triflic acid came from Acros and was used without further purification. No attempt was made to optimize the yields of the recovered products.

Ethyl *N*-hydroxy-(1-azacyclohept-1-en-2-yl)carboximidate [24]
Compound **11** (214 mg, 3.3 mmol.) was dissolved in triflic acid (4.6 ml, 52 mmol). After 16 hours reaction time, this solution was poured over a stirred mixture of CH_2Cl_2 (50 ml)-ethanol (10 ml) at -60 °C. When temperature was around 0°C, brine (20 ml) and $NaHCO_3$ were added in a way to bring the pH to a value around 7-8. Extraction with $CHCl_3$ (2x150 ml) and usual workup afforded an oil (384 mg), homogeneous by TLC and ^{1}H-NMR. Purification by PTLC on silica gel ($CHCl_3$: EtOH 95:5 saturated with NH_4OH) afforded **24** (111 mg, 34%). Extensive decomposition seemed to occurred during PTLC. **^{1}H-NMR** ($CDCl_3$) δ_H1.27 (t, 3H, *J* = 7Hz); 1.70 (m, 4H); 1.70 (m, 2H); 2.55 (m, 2H); 3.40 (m, 2H), 4.11 (q, 2H *J* = 7Hz). **^{13}C-NMR** ($CDCl_3$) δ_C 14.39 (CH_3); 23.83; 28.69; 30.33; 36.65; 44.26; 60.90 (O<u>C</u>H$_2$); 164.24 (C-hydroxyimino); 177.06 (C-imine). **MS**: 184 [M$^+$, 17]; 156 [M-(C_2H_4), 10]; 139 [M-(OEt), 85] 112 [100]. **HRMS** $C_9H_{16}N_2O_2^+$ calc. 184.1212 found 184.1217

(*E*)-(1-azacyclopent-1-en-2-yl)phenylketone oxime [38]
Compound **9** (212 mg, 1.65 mmol) and benzene (1 ml, 11.3 mmol) were added under stirring to triflic acid (4.3 ml, 48 mmol) and let to react for 14 hours at 5°C. Quenching over ice/$NaHCO_3$/$CHCl_3$ and usual workup of the organic phase (3x120 ml $CHCl_3$) afforded a white crystallized product. Crystallization from CH_2Cl_2 afforded the title compound **38** (171 mg; 55%). **m.p.°** 180-1°C (white crystal). **^{1}H-NMR** (DMSO-*d*$_6$/$CDCl_3$) δ_H1.86 (m, 2H); 2.85 (m, 2H); 3.86 (m, 2H); 7.33 (m, 5H); 11.81 (s, 1H). **^{13}C-NMR** (DMSO-*d*$_6$/$CDCl_3$) δ_C 21.83; 34.51; 61.26; 127.17; 127.83; 129.17; 131.87; 153.52; 172.10. **MS** 188 [M$^+$,43] 187 [M-H, 45] 171 [M-(OH), 100]; 158 [M-(NO), 53]. **Analysis** for $C_{11}H_{12}N_2O$ found: C 70.16, H 6.25, N 14.84 calc.: C 70.19, H 6.43, N 14.88 .

(*E*)-(1-azacyclohept-1-en-2-yl)phenylketone oxime [39E] *kinetic product*
Compound **11** (312 mg, 2 mmol.) was added under stirring to a mixture of C_6H_6 (1.5 ml, 17 mmol.) and triflic acid (5 ml, 56.5 mmol.) at 0°C. The reaction lasted for 16 hours during which temperature was let to rise to RT. Quenching was performed on ice (80 g) and $CHCl_3$ (120 ml). Na_2CO_3 was added in a way to bring the pH of the solution to 8 -9.The organic phase was isolated and two further $CHCl_3$ extraction (2x120 ml) were performed. Organic phase was washed

with water then brine and finally dry over $MgSO_4$. Elimination of the solvent under reduced pressure afforded an oil (237 mg) that was purified by PTLC on silica gel ($CHCl_3$-MeOH 95/5 saturated with concentrated NH_4OH) to afford an oily compound **39E** (130 mg, 38%).This compound eventually may undergo an easy Z/E isomerization in organic solvents (e.g. nmr cell). **^{1}H-NMR** ($CDCl_3$) 1.52 m 4H; 1.79 m 2H; 2.86 m 2H; 3.74 m 2H; 7.16d, 2H; 7.31 m 3H, 9.80 b.s. =N-OH. **^{13}C-NMR** ($CDCl_3$)23.31; 25.94; 28.84; 31.25; 52.23; 127.59; 128.24; 129.29; 131.53 (C-ipso); 157.34 (C-oxime); 174.34 (C-imine). **MS** 216 [M^+, 83]; 199[M-(OH), 85]; 185 [M-(NOH), 85]; 171 [63]; 157 [42]; 96 [$C_6H_{10}N$, 100]. **HRMS:** $C_{13}H_{16}N_2O^+$: calc. 216.12626 and found: 216.1261

(*Z*)-(1-azacyclohept-1-en-2-yl)phenylketone oxime [39Z] *isomerized product*
Isomerization of **39E** in organic solvent e.g. $CDCl_3$ (acidic catalysis ?) afforded **39Z**.
m.p. 164-5°C (crystallized from acetone). **^{1}H-NMR** ($CDCl_3$/DMSO-d_6) δ_H 1.48 m; 1.77 m; 2.80 (m, 2H); 3.70 (m, 2H); 7.16 (dd, J = 8Hz, 8Hz 2H, *m*-); 7.26 (m, 3H, *o*-, *p*-); 9.67 (b.s., 1H, oxime).**^{13}C-NMR** δ_C 22.28; 25.93; 30.52; 34.07; 51.67; 126.20; 126.65; 127.83; 128.34; 156.59 (C-oxime); 171.92 (C-imine). **MS**: 216 [M^+, 58]; 199 [M-(OH), 63]; 185 [M-(NOH), 48]; 171 [20]; 96 [$C_6H_{10}N^+$, 100]. **HRMS** $C_{13}H_{16}N_2O^+$ calc:216.12626 and found: 216.12560

(*E*)-phenylglyoxal α-monooxime. [40]
Compound **8** (151 g, 1.30 mmol.) was dissolved in a mixture of triflic acid (3 ml, 34 mmol.) and benzene (1.0 ml, 11.2 mmol.) at 0-5°C. The temperature was let to reach room temperature and the reaction lasted for 15 hour. After neutralization with ice/Na_2CO_3/ether (50 ml) and further extraction with ether (3x100 ml) then drying of the organic phase with $MgSO_4$ and vacuum distillation of the solvent, the residual product was crystallized and flash-chromatographic (CH_2Cl_2: acetone 8: 2) to afford compound **40** (124 mg, 64% yield). Some *(E)-(Z)* isomerization was observed during purification of **40**. **m.p.** 116-7°C **^{1}H-NMR** ($CDCl_3$) 7.35 m 5H; 9.61 s (CH=O). **^{13}C-NMR** (DMSO-d_6/$CDCl_3$) δ_C 126.67; 127.65; 128.35; 129.21; 155.46 (C-oxime); 190.88 (CH=O). **MS**: 149 [M^+, 22], 120 [M-(HCO), 20], 119 [M-(H_2CO), 92], 103 [PhCN, 35], 77 [C_6H_5, 100]. **Analysis** for $C_8H_7NO_2$: found C 64.43, H 4.89, N 9.12, calc. C 64.43, H 4.70, N 9.40.
The corresponding phenylglyoxime can be directly prepared by addition of a 15 to 20 time molar excess of NH_3OHCl to the aqueous phase during neutralization ($NaHCO_3$) and 20 mn reaction time at about 45°C. Mainly, one isomer was observed. Extraction with $CHCl_3$:EtOH 85:15 then crystallization, afforded phenylglyoxime (59-63% yield) m.p. 174-6 °C litt 178-180° for the *anti*-phenyl-*amphi*-glyoxime.[16]

(*E*)-1-phenyl-2-dimethylaminoethanone oxime. [41]
Compound **8** (382 mg, 3.3 mmol.) was added to a cold (ice/water bath) stirred mixture of triflic acid (4.2 ml, 47 mmol) and benzene (1.6 ml, 18 mmol). After 6 hours reaction time from 0° to 12°C, the solution was carefully injected, with the help of a syringe through a septum, to a stirred suspension of $NaBH_4$ (475 mg, 12.5 mmol.) in stirred anhydrous Et_2O (30 ml) under nitrogen at 0-5°C. After one hour reaction time at 0-5°C, the mixture was hydrolyzed[12] and extracted with $CHCl_3$ (3x100 ml.). Purification by PTLC on silica gel ($CHCl_3$-MeOH 95/5 saturated with NH_4OH) afforded compound **41** (427 mg, 72%).**m.p.**: 75.2-76.3°C (very long needles from cyclohexane), litt 87-89°C[17a] or 80-83°C[17b], **Picrate**: m.p.: 159°C (yellowish crystals from ethanol). **MS**: 178 [M^+, 3]; 161 [M-(OH), 6]; 103 [$PhCNO^+$, 30]; 58 [$C_3H_8N^+$, 100]. **^{1}H-NMR** ($CDCl_3$) δ_H 2.23 (s, 6H); 3.35 (s, 2H); 7.30 (m, 3H); 7.51 (m, 2H); 9.5 (b.s. =N-OH), **^{13}C-NMR** ($CDCl_3$) δ_C 45.20 (CH_3); 62.78 (CH_2); 128.14 &128.52 (*ortho* & *meta*); 128.93 (*para*); 132.92 (*ipso*); 153.55 (C-oxime)

α-(N-methylcyclopent-2-enyl)-α-nitrosotoluene triflic acid salt. [43]
Compound **10** (244 mg, 1.72 mmol) was added to a stirred mixture of triflic acid (5 ml, 56.5 mmol.).) and benzene (1 ml, 11.2 mmol). After 14 hours reaction time from 0°C to 17°C, the acidic medium was quenched over ice/CH_2Cl_2 (120 ml). $NaHCO_3$ (about 4.5 g) was added in such a way that the aqueous phase stayed always acidic (both organic and aqueous phases are colorless). Further extraction of the aqueous phase with CH_2Cl_2: EtOH 90: 10 (3x120 ml) was performed and the recombined organic phases were dry over Na_2SO_4. Vacuum distillation of the solvent afforded a crude whitish crystallized compound (574mg,). After washing with Et_2O, white prisms of **43** were isolated (267 mg; 49% yield). **m.p.**: 113.5-116°C. **H-NMR** (acetone-d_6) δ_H 2.33 (q J= 7.8 Hz 2H); 3.44 (s 3H MeN^+); 3.47 (t J= 7.8Hz 2H); 4.50 (t J= 7.8 Hz 2H); 7.48 (m. 5H); 12.86(s. =N-OH). **^{13}C-NMR** (acetone-d_6) δ_C 18.95; 39.71; 40.89 (CH_3); 65.73 (CH_2); 121.95 (q $^1J_{CF}$= 320.0 Hz CF_3); 127.62; 129.71; 129.97;131.24; 150.24; 180.41. **MS** (probe: 300°C): 202 [$C_{12}H_{14}N_2O_1$ for M^+, 20]; 184 [M-(H_2O), 100]; 169 (15); 156 (20) 129 (25). **Picrate: m.p.** 186 °C (dec.) yellow needles from ethanol and analysis for $C_{18}H_{17}N_5O_8$: found C 50.34, H 3.99, N 15.86 calc. C 50.12, H 3.94, N 16.24.

(*E*)-(*N*-methyl-1-azacyclopentan-2-yl)phenylketone oxime. [44]
Compound **10** (306 mg, 2.16 mmol) was added to a stirred mixture of triflic acid (4 ml, 45 mmol) and benzene (1.6 ml, 18.mmol). After 14 hours reaction time from 0°C to 7-9°C, the acidic medium was carefully added with the help of a

syringe to a stirred suspension of $NaBH_4$ (300 mg, 7.9 mmol) in anhydrous ether (30 ml) and under dry nitrogen. After one hour reaction time at 0-5°C (ice/water bath), the reaction medium was neutralized and extracted.[12]
Preparative thin layer chromatography (CH_2Cl_2: EtOH 95: 5 saturated with concentrated NH_4OH) afforded compound **44** (305 mg, 69 %). **m.p.** 86.5-88 °C. **^{1}H-NMR** δ_H 1.65 (m, 3H); 1.90 (m, 1H); 2.20 (dd, 1H); 2.39 (s, 3H, m); 3.08 (m, 2H). **^{13}C-NMR**: δ_C 27.77; 29.22; 40.42; 56.51; 69.90; 127.72; 128.36; 128.44; 132.35; 157.89. **MS**: 204 [M^+, <1] 187 [M-(OH), 28]; 159 [M-(CH_3NO), 15]; 103 [PhCNO, 48]; 84 [$C_5H_{10}N$, 100]. **Analysis** for $C_{12}H_{16}N_2O$: found C 70.36, H 7.83, N 13.55 calc. C 70.59, H 7.84, N 13.72.

(*E*)-α-hydroxyiminophenylglyoxalic acid *N*-methylamide [45]
Compound **12** (182 mg, 1.23 mmol.) was added to cold (ice-water bath) triflic acid (3 ml, 34 mmol) and benzene (1 ml, 11.2 mmol). After 13 hours reaction time at R.T., this solution was quenched over a mixture of ice/$NaHCO_3$/$CHCl_3$ Usual workup of the organic phase (3x120 ml $CHCl_3$) afforded a white crystallized product. Flash chromatography (eluent CH_2Cl_2: AcOEt 97: 3) allowed the separation of starting material **12** (23 mg, 12%) from compound **46** [1] (12 mg, 5%), eluent CH_2Cl_2: acetone 95:5 afforded compound **45** (140 mg, 64 %). **m.p.**° 190-1°C. **^{1}H-NMR** ($CDCl_3$/ DMSO-d_6) δ_H 2.83 (d, 3H J = 5 Hz MeNH); 7.35-7.53 (m, 5H); 13.68 (s, 1H). **^{13}C-NMR** (acetone D_6) δ_C 26.23; 128.22; 129.63; 130.60; 131.08; 152.18; (oxime); 164.93 (C=O). **SM** 178 (M^+,50) 161 (M-OH, 8) 134 (10) 119 (13) 104 (100) 77 (60) 58 (97) **HRMS** $C_9H_{10}N_2O_2^+$ cal. 178.07422 found 178.07417 **Analysis** for $C_9H_{10}N_2O_2$ calc. C 61.10, H 5.86, N 15.10 calc. C 60.67, H. 5.66, N 15.72.

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