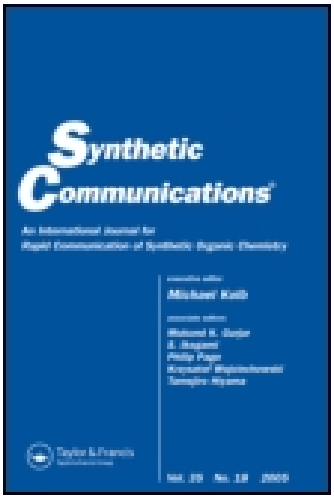

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
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Intramolecular Cyclization of 1-(ω-Phenylalkyl)-2-(nitromethylene)pyrrolidines in Triflic Acid

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Accepted author version posted online: 15 Apr 2014.Published online: 13 Jun 2014.

To cite this article: Bamba Fanté , Yaya Soro , Sorho Siaka , Jérôme Marrot & Jean-Marie Coustard (2014) Intramolecular Cyclization of 1-(ω-Phenylalkyl)-2-(nitromethylene)pyrrolidines in Triflic Acid, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 44:16, 2377-2385, DOI: 10.1080/00397911.2014.898307

To link to this article: http://dx.doi.org/10.1080/00397911.2014.898307

Synthetic Communications®, 44: 2377–2385, 2014

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397911.2014.898307

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INTRAMOLECULAR CYCLIZATION OF 1-(ω-PHENYLALKYL)-2-(NITROMETHYLENE) PYRROLIDINES IN TRIFLIC ACID

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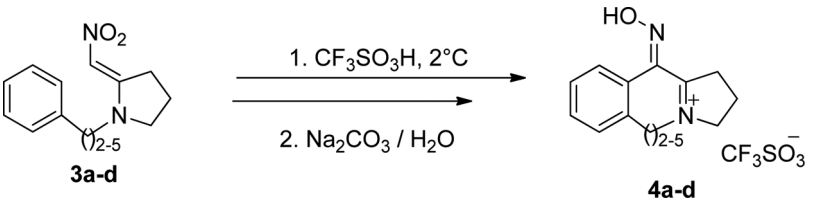
[3]*Laboratoire ILV-UVSQ-UMR 8180 CNRS, Versailles, France*
[4]*Laboratoire IC2MP-UMR 7285 CNRS, Poitiers, France*

GRAPHICAL ABSTRACT



Abstract *1-(ω-Phenylalkyl)-2-(nitromethylene)pyrrolidines in triflic acid undergo a C,O-diprotonation, followed by loss of water, to form conjugated iminium–hydroxynitrilium dications, which react with the tethered phenyl ring by electrophilic aromatic substitution to afford tricyclic iminium compounds as triflate salts. The scope and mechanism of this reaction are discussed.*

Keywords 1-(ω-Phenylalkyl)-2-(nitromethylene)pyrrolidines; cation; intramolecular cyclization; triflate salts; triflic acid

INTRODUCTION

ω-Phenylalkylaminonitroethene derivatives are useful synthons in the field of heterocyclic synthesis,[1] as they readily undergo a variety of condensation reactions.[2,3] Several compounds having a nitroenamine unit (Fig. 1) can be found on the market as drugs (ranitidine) or pesticides (nitenpyrame).[4]

Received November 6, 2013.

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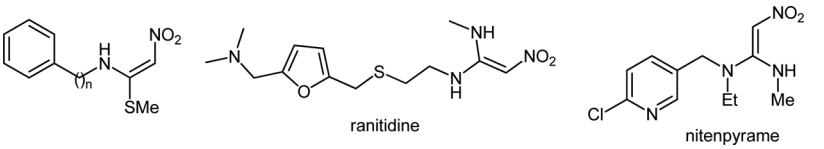


Figure 1. Some nitroenamine derivatives.

One of the most common methods of preparing nitroenamines is by the reaction of amide acetals with nitromethane. Thus dimethylformamide diethylacetal gives 1-dimethylamino-2-nitroethylene.[5] A variety of substituted amide and lactam acetals have been successfully used in this reaction (Scheme 1).[6] A simplified procedure, in some cases, makes use of the amide–dimethylsulfate complex.

It has been shown that 1-methyl-2-(nitromethylene)pyrrolidine in triflic acid formed a hydroxynitrilium ion, which can be trapped in situ with either triflate anion or benzene.[7] Following our work on the reactivity of various chemicals in superacids, the current study describes the reactivity of 1-(ω-phenylalkyl)-2-(nitromethylene)pyrrolidines in triflic acid.

RESULTS AND DISCUSSION

Starting Material

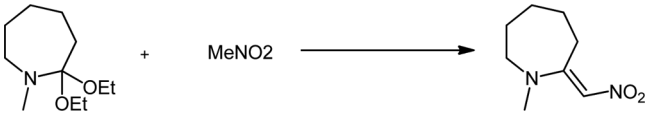
1-(ω-Phenylalkyl)pyrrolidin-2-one derivatives **1a–d** were prepared in a conventional way by alkylation[8] of pyrrolidin-2-one with the appropriate 1-bromo-ω-phenylalcane derivatives. Yields are reported in Scheme 2 without optimization.

Further treatment with dimethylsulfate followed by sodium ethoxide led to the corresponding 1-ω-phenylalkyl-2,2-diethoxypyrrolidines **2**,[9] which upon reaction with nitromethane[6] afforded the expected 1-(ω-phenylalkyl)-2-(nitromethylene) pyrrolidine derivatives **3a–d** (Scheme 2). Yields are reported in Scheme 2 without optimization.

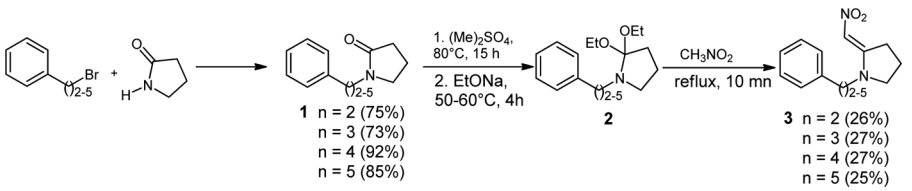
A single set of signals was observed by NMR, indicating the presence of a sole stereoisomer in solution, presumably the (*E*)-isomer, as previously reported for 1-methyl-2-(nitromethylene)pyrrolidine.[10]

Reaction in Triflic Acid

The reaction of the 1-(ω-phenylalkyl)-2-(nitromethylene)pyrrolidine derivatives **3a–d** in triflic acid was generally clean, with yields varying from 19 to 98% (Scheme 3). The yield of isolated cyclization products increases with the size of the formed ring from 85% for the seven-membered ring **4a** to 98% for the nine-membered ring **4c**.



Scheme 1. Nitrovinylamines synthesis by condensation of lactam acetals with nitromethane.



Scheme 2. Synthesis of 1-(ω-phenylalkyl)-2-(nitromethylene)pyrrolidine derivatives **3**.

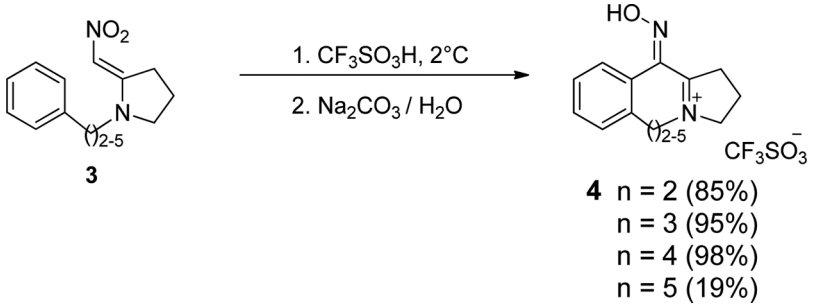
As expected for reasons of entropy,[11] the yield in intramolecular cyclization drops to 19% for the 10-membered ring product **4d**.

The structure of the molecule was further confirmed by the X-ray crystallographic analysis of **4a**[12–14] (Fig. 2). In this crystal, the hydroxyl group of the newly formed hydroxyimino group adopts a *cis* configuration relative to the aromatic ring. The torsion angle between the iminium $C{=}N^+$ and the C=N of the oxime is close to 2°, indicating that these functions are in the same plane; meanwhile, the torsion angle between the aromatic ring and the oxime is about 57°, which indicates a lack of electronic conjugation at this level.

NMR Study and Reaction Mechanism

To have a better understanding of the mechanism of the reaction, an NMR study was carried out with 1-phenethyl-2-(nitromethylene)pyrrolidine **3a** in triflic acid. The resulting solution was observed by NMR spectroscopy at 255 K. The starting material **3a** was rapidly protonated to afford the observable dication **5a** with a deshielded methylene (δ_C 71.4 and δ_H 4.37 ppm) next to the protonated nitro group (Figs. 3 and 4). These values are close to those previously observed for *C,O*-diprotonated nitroethylene derivatives in triflic acid.[7,15,16]

The arrows denote the signals of the initially formed dication, which will disappear over time in favor of other signals corresponding to the final dication. Thus, after 1 h of reaction time at 2 °C, intermediate dication **5a** was fully transformed into a stable observable dication **7a**, characterized by the presence of the hydroxyl proton at $\delta_H = 12.99$ ppm (Fig. 5) and the presence of iminium and hydroxyiminium groups respectively at $\delta_C = 173.2$ ppm and $\delta_C = 153.6$ ppm (Fig. 6).



Scheme 3. Reaction of 1-(ω-phenylalkyl)-2-(nitromethylene)pyrrolidine derivatives **3** in triflic acid.

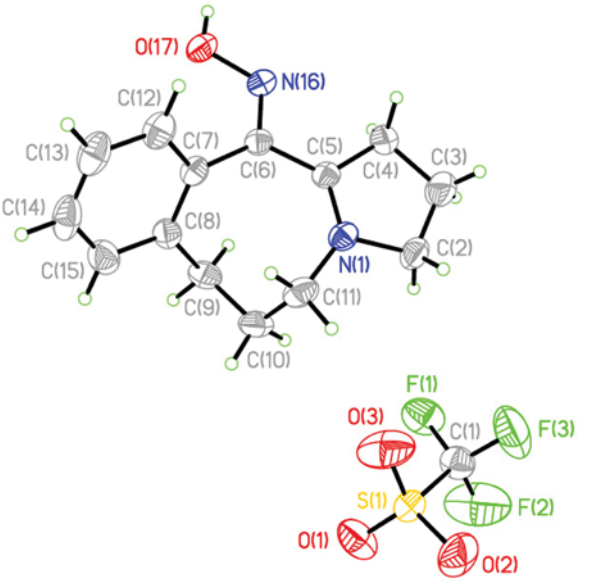


Figure 2. X-ray crystallographic analysis of **4a**.

The mechanism for the formation of cation **5a** is probably similar to the one previously reported for nitroketene aminals.[17] At the beginning of the reaction, 1-(ω-phenylalkyl)-2-(nitromethylene)pyrrolidine derivatives **3** undergo a double protonation: a C-protonation on the carbon bearing the nitro group and an *O*-protonation of the nitro group. The *O*-protonation occurs through a fast proton exchange process with the acidic medium, as observed in fluorosulfonic acid at −80 °C.[18] In this medium, the nitro group is known to be protonated but the proton is not observed because of its very rapid exchange rate with the medium.[19] Prototropic exchange and the formal loss of a molecule of water lead to the formation of the conjugated hydroxynitrilium ion **6**.[1,20] As soon as it is formed as indicated in Scheme 4, **6** reacts with the tethered phenyl ring to afford the observed stable dication **7a**.

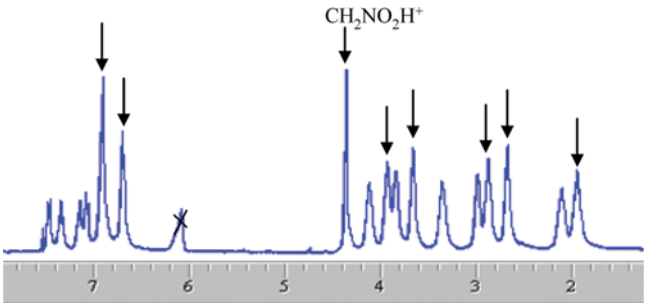


Figure 3. ^{1}H NMR spectrum of transient dication **5a** in triflic acid at 255 K (reference TMS in [D_4] methanol as external lock).

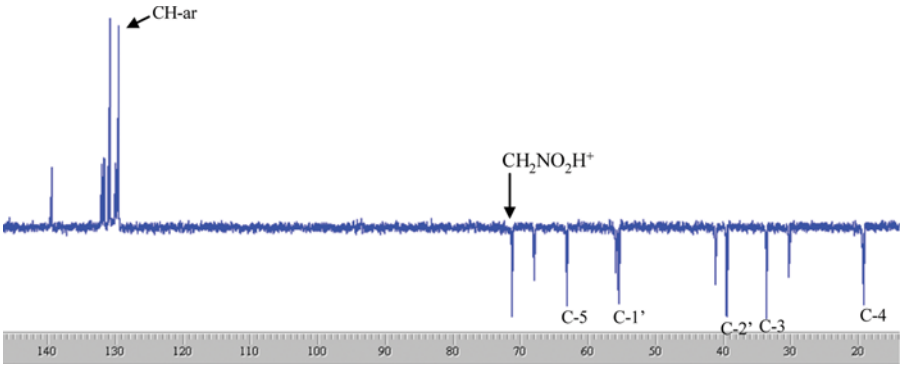


Figure 4. DEPT 135-NMR spectrum of transient dication **5a** in triflic acid at 255 K (reference TMS in [D_4] methanol as external lock).

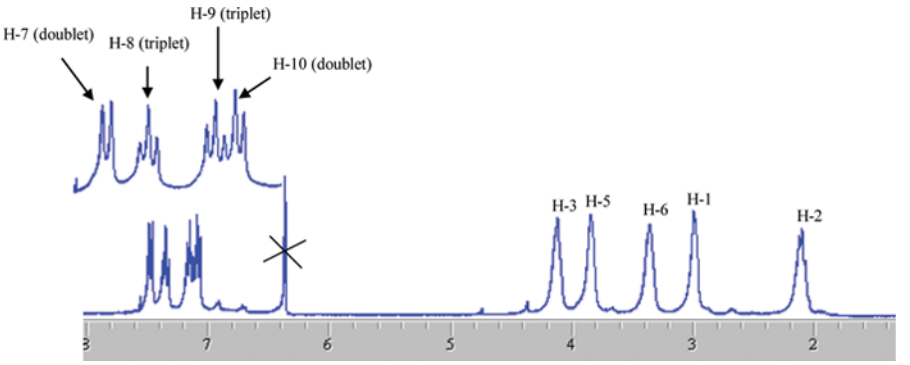


Figure 5. ^{1}H NMR spectrum of dication **7a** in triflic acid at 278 K (reference TMS in [D_4] methanol as external lock).

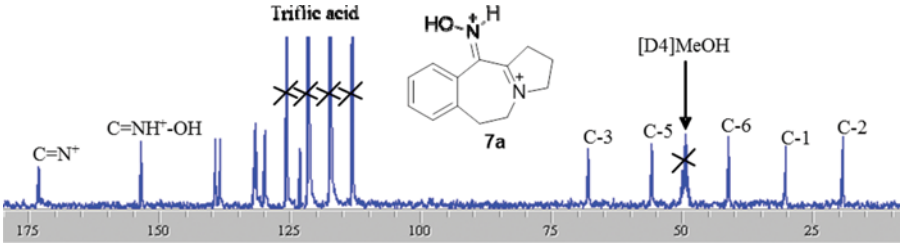
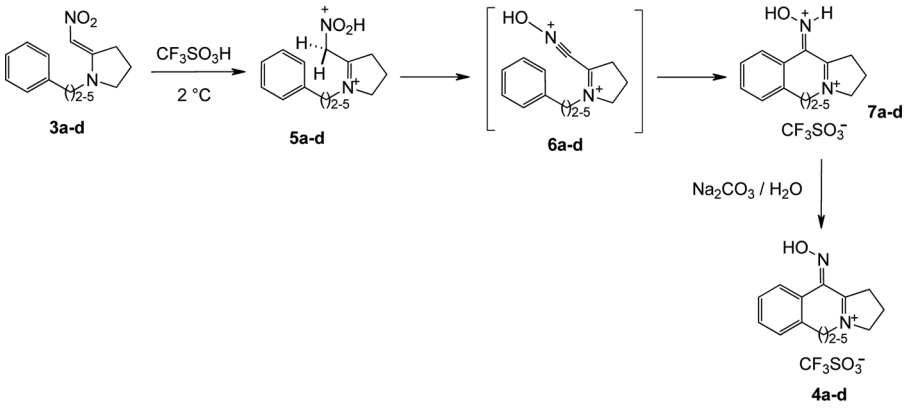


Figure 6. ^{13}C NMR spectrum of dication **7a** in triflic acid at 278 K (reference TMS in [D_4] methanol as external lock).

At the end of the reaction, the acid was quenched, and compounds **4** were isolated as triflate salts because of the presence of quaternary nitrogen in the azamacrocyclic compound structure.

The observed configuration of the oxime of **4a** is consistent with the mechanism of addition to a triple bond, as expected from a theoretical point of view[21] and in agreement with previously reported results.[15,16,17]



Scheme 4. Suggested mechanism for the formation of products **4**.

NMR spectroscopy shows a single (*E*)-oxime isomer for the seven- to nine-membered ring products **4a–c**, but two sets of signals are observed for the 10-membered ring product **4d**. These two sets of signals can be due to either (i) (*E*) and (*Z*) isomers of the oxime or (ii) to a mixture of two conformers, whose interconversion would be hampered by steric and geometric constraints of both the phenyl ring and pyrrolidine ring.[22]

CONCLUSION

This study extends previous work on the formation of hydroxynitrilium ion from heterosubstituted nitroethene derivatives and their use in the field of heterocyclic synthesis. In triflic acid, 1-(ω-phenylalkyl)-2-(nitromethylene)pyrrolidine derivatives lead to conjugated hydroxynitrilium ions, which undergo an electrophilic aromatic substitution to afford tricyclic compounds as triflate salts.

EXPERIMENTAL

Melting points were determined with a Büchi melting-point B545 apparatus using capillary tubes (temperature rate 2 °C/mn) and were not corrected. A Bruker DPX 300 spectrometer, equipped with a low-temperature probe, was used for ^{1}H, ^{9}F, and ^{13}C NMR spectra recorded at 300.13, 282.37, and 75.47 MHz, respectively. NMR spectra of cations were recorded in neat triflic acid at low temperature in the presence of methanol-d_4 contained in a sealed capillary tube placed inside the NMR tube. NMR spectra of starting compounds and products were recorded at room temperature and chemical shifts are reported relative to Me_4Si or hexafluorobenzene for fluorine. The reproducibility of ^{13}C NMR shift was about ± 0.05 ppm, depending on cell and concentration. Chemical assignments were made using distortionless enhancement polarization technique (DEPT) 135 and usual chemical shift assignments rules. Electron-impact ionization (70 eV) mass spectra were obtained with a Finnigan Incos 500 Instrument. High-resolution mass spectrometry was performed at the Faculté des Sciences–Université de Picardie Jules Verne, France, or Rennes. Flash chromatography was achieved on silica gel (20- to 45-μm particle size). Triflic acid

was purchased from Across and 1,1-bis(methylthio)-2-nitroethene was obtained from Lancaster, and both were used without further purification. No attempt was made to optimize the yields. The yields and extractions were not optimized.

Starting Material

1-(4-Phenylbutyl)pyrrolidin-2-one (1c). NaH (0.95 g, 40 mmol.) in 60% suspension in paraffin oil (1.58 g suspension) was added to a solution of pyrrolidin-2-one (3 mL; 40 mmol) in 80 mL of anhydrous toluene. After stopping the hydrogen release, the reaction mixture was heated to reflux with stirring under nitrogen atmosphere for 10 h. Then ω-phenylalkylbromide (80 mmol) dissolved in anhydrous xylene (20 mL) was added. The mixture was then refluxed for 4 h under nitrogen atmosphere. After cooling and filtration, the solvent was eliminated under reduced pressure. The viscous residue was purified by flash chromatography using CH_2Cl_2/MeOH (99/1) to give compound **1c** (7.88 g, 91%) as oil. ^{1}H NMR ($CDCl_3$): δ (ppm) = 1.57 (m, 4H, H-2′ and H-3′), 1.96 (q, J = 7.7 Hz, 2H, H-4), 2.35 (t, J = 7.9 Hz, H-3), 2.63 (t, J = 7.1 Hz, 2H, H-4′), 3.18–3.25 (quadruplet, J = 7.1 Hz and 14.2 Hz, 4H, H-5 and H-1′), 7.14–7.18 (m, 3H, aromatic *o*-H and *p*-H), 7.23–7.29 (m, 2H, aromatic *m*-H). ^{13}C NMR ($CDCl_3$): δ (ppm) = 18.21 (C-4), 27.07 (C-2′), 28.90 (C-3′), 31.42 (C-3), 35.76 (C-4′), 42.50 (C-5), 47.32 (C-1′), 126.10 (aromatic CH), 128.64 (2 aromatic CH), 128.74 (2 aromatic CH), 142.43 (aromatic C), 175.20 (C-2). MS (electrospray) $C_{14}H_{19}NONa$ ($[M+Na]^+$): calcd. 240; found 240.

Compounds **1** NMR spectra were characterized by the absence of signal corresponding to N-H and the presence of signal assigned to C=O at δ_C = 175 ppm. Compounds **1c** and **d** have not been described in the literature.

(E)-1-Phenethyl-2-(nitromethylene)pyrrolidine 3a. 1-Phenethylpyrrolidin-2-one **1a** (5.00 g, 26.45 mmol) and dimethylsulfate (2.60 mL, 27.40 mmol) were heated at 80 °C for 15 h under nitrogen atmosphere. The reaction mixture was then cooled at 50/60 °C and a solution of sodium ethoxide (0.742 g of sodium in 14 mL of ethanol) was added dropwise. The resulting mixture was stirred under nitrogen for 4 h at 50/60 °C. Then nitromethane, dried over $CaCl_2$ (3 mL, 55.0 mmol), was added, and the resulting solution was refluxed for 10 min. After cooling, the solvent was eliminated under reduced pressure. The residue was dissolved in CH_2Cl_2 and filtered, and the solvent evaporated under reduced pressure. The resulting oil was purified by column chromatography on silica gel (CH_2Cl_2/AcOEt, 99/1). Further crystallization from CH_2Cl_2/petroleum ether afforded compound **3a** (1.60 g, 26%) as crystals. Mp 113.7 °C (CH_2Cl_2/petroleum ether). ^{1}H NMR ($CDCl_3$): δ (ppm) = 1.95 (q, J = 7.5 Hz, 2H, H-4), 2.89 (t, J = 7.4 Hz, 2H, H-3), 3.33 (t, J = 7.4 Hz, 2H, H-2′), 3.45 (m, 4H, H-5 and H-1′), 6.76 (s, 1H, vinylic H), 7.16–7.19 (m, 2H, aromatic *o*-H), 7.22–7.35 (m, 3H, aromatic *p*-H and *m*-H). ^{13}C NMR ($CDCl_3$): δ (ppm) = 20.83 (C-4), 32.62 (C-3), 35.03 (C-2′), 49.29 (C-1′), 55.21 (C-5, 109.14 (vinylic CH), 127.45 (aromatic CH), 129.00 (2 aromatic CH), 129.25 (2 aromatic CH), 137.94 (aromatic C), 164.26 (C-2). HRMS for $C_{13}H_{16}N_2O_2Na$ ($[M+Na]^+$): calcd. 255.1109; found 255.1109

Starting materials **3a–d** were characterized from their NMR spectra, with the vinylic protons in the range δ_H 6.69–6.87 ppm, the carbons bearing the nitromethylene group =CH-NO_2 at δ_C 109.7–109.9 ppm, and the other ethylenic carbons >C=C at 164.5–164.7 ppm.

Tricyclic Compounds

Triflic acid (5 mL, 56.2 mmol) was placed under nitrogen in a 10-mL, round-bottom flask equipped with a three-way valve and a Teflon-coated magnetic stirrer. *Caution*: Triflic acid is a strong corrosive acid that may react violently with water. The system was cooled to ice-water bath temperature, and then the 1-(ω-phenylalkyl)-2-(nitromethylene)pyrrolidine **3** (1 mmol) was added.

11-Hydroxyimino-1,2,3,5,6,11-hexahydrobenzo[d]pyrrolo[1,2-a]azepinylium trifluoromethanesulfonate 4a. (*E*)-1-Phenethyl-2-(nitromethylene)pyrrolidine **3a** (232 mg, 1 mmol) was dissolved in triflic acid (5 mL, 56.2 mmol) at 2 °C under nitrogen atmosphere. The reaction was monitored by thin-layer chromatography (TLC; CH_2Cl_2/MeOH, 97/3). After the disappearance of the starting compound, the acidic solution was poured into 50 mL of a mixture of CH_2Cl_2/MeOH (90:10) at −60 to −40 °C and let warm. When the temperature was close to 0 °C, brine (10 mL) and anhydrous Na_2CO_3 (6 g) were added. The extraction was carried out promptly with CH_2Cl_2/MeOH, 95/5 (4 × 20 mL). The organic phase was dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. The resulting product was purified by column chromatography using CH_2Cl_2/MeOH, 95/5 as eluent, followed by precipitation from a mixture of dichloromethane/petroleum ether, to yield **4a** (309 mg, 85%) as crystals. Mp 190.9 °C (CH_2Cl_2/MeOH (95/5)/petroleum ether). ^{1}H NMR (acetone-d_6): δ (ppm) 2.29 (q, $J = 7.8$ Hz, 2H, H-2), 3.31 (m, 2H, H-1), 3.68 (m, 2H, H-6), 4.15 (s, 2H, H-5), 4.51 (t, $J = 7.33$ Hz, 2H, H-3), 7.33–7.45 (m, 3H, H-7, H-8 and H-9), 7.66–7.69 (d, $J = 7.49$ Hz, 1H, H-10). ^{13}C NMR (acetone-d_6) : δ (ppm) 18.96 (C-2), 32.15 (C-1), 40.41 (C-6), 54,79 (C-5), 66.14 (C-3), 122.34 (qd, $J_{CF} = 320.5$ Hz, $CF_3SO_3^-$), 127.96 (C-9), 129.46 (C-10a), 129.96 (C-7), 132.07 (C-10), 132.35 (C-8), 137.98 (C-6a), 149.43 (C-11), 179.98 (C-11a). ^{19}F NMR (282.37 MHz, acetone-d_6): δ (ppm) −72.45 ($CF_3SO_3^-$). HRMS for $C_{13}H_{15}N_2O$ [M-($CF_3SO_3^-$)]: calcd. 215.1184; found 215.1184.

The compounds **4a–d** were characterized by the presence of four CH aromatic carbons (DEPT 135), an oxime group (δ_C 150 ppm), and an iminium carbon (δ_C 180 ppm). The presence of a deshielded *ortho*-aromatic proton (δ_H 7.46 to 7.69 ppm) indicates that the oxime is (*E*) configured with the phenyl ring and the oxime OH in a *cis* configuration. The trifluoromethanesulfonate anion was characterized by its CF_3 group that resonates at δ_C 122.3 and δ_F − 74.3 ppm.

DEDICATION

This publication is dedicated in memory of Professor Jean-Marie Coustard, who supervised this work and passed away at the end of August 2013.

FUNDING

The authors acknowledge CNRS for financial support; Ministère des Affaires Etrangère, France, for fellowship funds (S. S. and S. Y.); and Ministère de l'Enseignement Supérieur, Ivory Coast (B. F.).

SUPPORTING INFORMATION

Full experimental detail, ^{1}H and ^{13}C NMR spectra, and X-ray data can be found via the Supplementary Content section of the publisher's website.

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