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One-step synthesis of diazadihydroacenaphthylene derivatives with an isoxazoline ring, starting from 1-benzylamino-1-methylsulfanyl-2-nitroethenes

Yaya Soro,[a] Fanté Bamba,[b] Sorho Siaka[a] and Jean-Marie Coustard[b,*]

[a]*Laboratoire des Procédés Industriels de Synthèse et d'Environnement, Institut National Polytechnique Félix Houphouët-Boigny, BP 991 Yamoussoukro, Cote d'Ivoire*
[b]*Laboratoire 'Synthèse et Réactivité des Substances Naturelles', UMR CNRS 6514 40, Avenue du Recteur Pineau, F-86022 Poitiers Cedex, France*

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Abstract—At low temperature in trifluoromethanesulfonic acid, 1-benzylamino-1-methylthio-2-nitroethene derivatives form hydroxynitrilium ions (or O-protonated nitrile oxides) observed by NMR. Quenching with water leads to the formation of a reactive nitrile oxide, dipole which undergoes an unexpected INOC reaction leading to new 3-methylsulfanyl-8a,8b-dihydro-5*H*-1-oxa-2,4-diazaacenaphthylenes.

1. Introduction

Isoxazoline derivatives are an important class of heterocyclic compounds and their chemical properties have been studied over the years.[1] They are versatile scaffolds for the synthesis of a wide variety of complex natural products[2] and important pharmacophore in therapeutic chemistry.[3,4]

Isoxazoline derivatives are also known to exhibit interesting biological activities in the agricultural field[5] and possess medicinal properties including anticancer, antibiotic[6] or antiviral and anti-HIV activities.[7]

One of the most general methods used to prepare isoxazoline derivatives involves 1,3-dipolar cycloaddition between nitrile oxides and olefins.[8] Nitrile oxide can be prepared from primary nitro compounds with phenylisocyanate/triethylamine (Et_3N),[9] or by deshydrohalogenation of oximinoyl halides[10] (Huisgen procedure) obtained from the reaction of aldoximes with NCS, NBS, halogens and chlorobenzotriazole or from direct aldoxime oxidation with hypochlorite. Nitrile oxides can either be prepared in situ, or prepared in advance in the case of the more stable derivatives, for example, substituted phenylnitrile oxide.

Recently, Corsaro et al.[11] reported the dipolarophilic reactivity of polycyclic aromatic hydrocarbons and their aza-analogues in 1,3-dipolar cycloadditions, which gave mainly monocycloadducts with partial destruction of the aromaticity.

In previous papers,[12–14] the observation of stable hydroxynitrilium ions from 1-heterosubstituted-2-nitroethene in trifluoromethanesulfonic acid at low temperature was reported. In the particular case of 1,1-bis(methylthio)-2-nitroethylene **1** and its derivatives **2** and **3**, the corresponding hydroxynitrilium ions **4** were characterized by their NMR spectra in superacid. Cation **4** may either react in situ as an electrophilic species or during quenching as a new source of nitrile oxide **5** (Scheme 1).

In the present letter, the use of trifluoromethanesulfonic acid (or triflic acid) and 1-benzylamino-1-methylsulfanyl-2-nitroethenes is reported to prepare the corresponding 3-methylsulfanyl-8a,8b-dihydro-5*H*-1-oxa-2,4-diazaacenaphthylenes, a new class of oxazoline

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* Corresponding author. Tel.: +33 0549 454 100; fax: +33 0549 453 501; e-mail: jean.marie.coustard@univ-poitiers.fr

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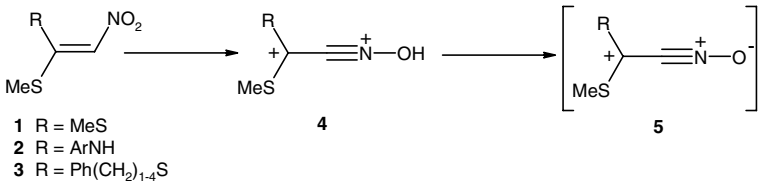


Scheme 1. Formation of nitrile oxide from 1-substituted-2-nitroethene derivatives.

derivatives. The observed reaction is an unusual intramolecular nitrile oxide cyclization (INOC reaction) that occurs on a single phenyl ring with the full loss of aromaticity of the molecule. This is, to our best knowledge, the first example reported of a direct addition of nitrile oxide on a monosubstituted monoaromatic phenyl ring.

2. Results and discussion

2.1. Starting compounds

The starting 1-benzylamino-2-nitroethylenes **7a**–**d** were prepared by nucleophilic substitution between the corresponding *para*-substituted benzylamine **6a**–**d** and 1,1-bis(methylthio)-2-nitroethylene **1** (1.1 molar equivalent) in refluxing 95% ethanol[15] (Scheme 2).

The yields of **7a**–**d** vary from 65% to 75% with no particular influence from the *para*-substituent on the aromatic ring (Table 1). Some N,N-disubstituted derivatives were also formed as by-products during the reaction.

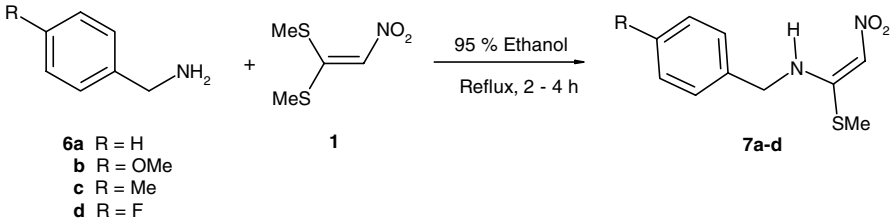
Compounds **7a**–**d** were characterized from their ^{1}H and ^{13}C NMR spectra, with vinylic protons in the range of δ_H 6.58–6.60 ppm and the C-1 and C-2 carbons at δ_C 164.8–165.9 and 107.0–107.2 ppm, respectively. A single set of signals was observed for each benzylaminonitroethene **7a**–**d**, which may imply that a sole isomer was present in the solution. This is probably the (*E*)-isomer as previously reported for 1-arylamino-1-methylsulfanyl-2-nitroethene **2**.[16] This configuration allows the formation of an intramolecular hydrogen bond between the N–H and one of the oxygen atoms of the planar $-NO_2$ group.

In the present study, the reactions were carried out in trifluoromethanesulfonic acid at low temperature (−30 to −10 °C) and under nitrogen atmosphere. The molar ratio of trifluoromethanesulfonic acid/benzylaminonitroethenes **7a**–**d** was 50:1. The starting material was fully transformed within 0.5–6.25 h of reaction time, depending on the substituent. At the end of the reaction, the acidic solution was poured onto a mixture of ice (10 g) and anhydrous Na_2CO_3 (6 g) and the extraction was carried out promptly at approximately 0 °C with dichloromethane (3×20 mL).[17] These reactions were clean, except for the fluoro compound **7d**. The observed reaction is reported in Scheme 3.

The formed 3-methylsulfanyl-8a,8b-dihydro-5*H*-1-oxa-2,4-diazaacenaphthylenes **8a**–**d** were separated by column chromatography and purified by crystallization. The yields are in the range of 41–57% as indicated in Table 1, with the lowest being that for the fluoro compound (R = F).

The NMR spectra of cyclized compounds **8a**–**d** are characterized by two kinds of protons, in the range of 4.19–4.38 ppm and 5.19–5.66 ppm, for H-8b and H-8a, respectively. The $^{3}J_{HH}$ coupling constants are close to 15 Hz, a value which is characteristic of a cis configuration and in agreement with previously reported values for isoxazolines of this kind.[11] Vinylic protons resonate between 5.19 and 5.91 ppm and the C–H carbons of the oxazolidine ring at δ_C 47.1–51.4 ppm and 77.2–82.0 ppm (C-8b and C-8a, respectively) and close to previously reported values (Table 1).[11]

When dissolved in triflic acid, 1-heterosubstituted-2-nitroethene derivatives undergo a double protonation: one occurs on the oxygen of the nitro group, with a fast proton exchange[18], and the second on carbon 2 with double bond migration to form a CH_2 group. This transient dication undergoes prototropic rearrangements, and the loss of a molecule of water, to afford the hydroxynitrilium group (or O-protonated nitrile oxide). Such hydroxynitrilium cations were previously observed with 1,1-heterodisubstituted-2-nitroethylene derivatives using NMR.[12–14] They are electrophilic species, which can react in situ either with nucleophilic anions ($CF_3SO_3^-$ in triflic acid [14a] or F^- in HF-SbF_5[12]) or with aromatic rings.



Scheme 2. Synthesis of monosubstituted products **7a**–**d**.

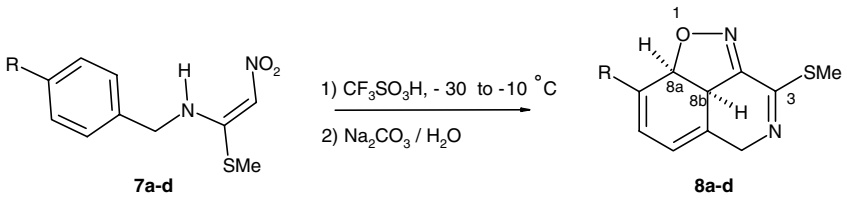
Table 1. Yields and data for compounds **7a–d** and cyclized products **8a–d**

Compd	R	Yield[a] (%)	^{1}H NMR ($CDCl_3$, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm), J (Hz)	Mp (°C)	HRMS ([M$^+$])
7a	H	75	^{1}H NMR: 2.41 (s, 3H, CH_3), 4.61 (d, $J = 5.9$ Hz, 2H, CH_2), 6.58 (s, 1H, vinylic H), 7.28–7.31 (m, 2H, Ar), 7.32–7.36 (m, 2H, Ar), 7.37–7.38 (m, 1H, Ar), 10.76 (broad s, NH) ^{13}C NMR: 14.9 (SCH_3), 48.7 (CH_2), 107.1 (=CH–NO_2), 127.8 (Ar CH), 129.5 (Ar CH), 135.9 (*ipso*-C), 165.1 (–NH–C=)	122.4	$C_{10}H_{12}N_2O_2S$, calcd 224.0619, found 224.0621
7b	OMe	72	^{1}H NMR: 2.35 (s, 3H, SCH_3), 2.44 (s, 3H, CH_3), 4.59 (d, $J = 5.9$ Hz, 2H, CH_2), 6.60 (s, 1H, vinylic H), 7.19 (m, 4H, Ar), 10.70 (broad s, NH) ^{13}C NMR: 14.9 (SCH_3), 21.6 (CH_3), 48.5 (CH_2), 106.9 (=CH–NO_2), 127.8 (Ar CH), 130.1 (Ar CH), 132.8 (*ipso*-C-Me), 138.54 (*ipso*-C), 165.08 (–NH–C=)	94.9	$C_{11}H_{14}N_2O_2S$, calcd 238.0776, found 238.0765
7c	Me	65	^{1}H NMR: 2.44 (s, 3H, SCH_3), 3.81 (s, 3H, CH_3), 4.56 (d, $J = 5.9$ Hz, 2H, CH_2), 6.60 (s, 1H, vinylic H), 6.89 (d, $J = 2.1$ Hz, 1H, Ar), 6.92 (d, $J = 2,2$ Hz, 1H, Ar), 7.22 (d, $J = 2.2$ Hz, 1H, Ar), 7.25 (d, $J = 2.1$ Hz, 1H, Ar), 10.73 (broad s, 1H, NH) ^{13}C NMR: 14.9 (SCH_3), 48.3 (CH_2), 55.7 (OCH_3), 106.9 (=CH–NO_2), 114.8 (Ar CH), 127.8 (Ar CH), 129.3 (*ipso*-C), 160.0 (*ipso*-C OMe), 164.8 (–NH–C=)	93.3	$C_{11}H_{14}N_2O_3S$, calcd 254.0725, found 254.0734
7d	F	69	^{1}H NMR: 2.45 (s, 3H, SCH_3), 4.61 (d, $J = 5.9$ Hz, 2H, CH_2), 6.60 (s, 1H, =CH–NO_2), 7.04–7.10 (ct, $J_{app} = 8.6$ Hz, 2H, Ar), 7.26–7.30 (m, 2H, Ar), 10.71 (broad s, 1H, NH) ^{13}C NMR: 14.9 (SCH_3), 48.0 (CH_2), 107.2 (=CH–NO_2), 116.4 (d, $^2J_{CF} = 21.9$ Hz, Ar CH), 129.7 (d, $^3J_{CF} = 8.2$ Hz, Ar CH), 131.7 (d, $^4J_{CF} = 3.3$ Hz, *ipso*-C), 162.9 (d, $^1J_{CF} = 247.0$ Hz, *ipso*-C-F), 164.9 (–NH–C=)	119.9	$C_{10}H_{11}FN_2O_2S$, calcd 242.0525, found 242.0527
8a	H	57	^{1}H NMR: 2.39 (s, 3H, SCH_3), 4.19 (d, $J = 14.9$ Hz, 1H, H-8b), 4.50 (s, 2H, CH_2), 5.62 (dd, $J = 14.9$ and 4.3 Hz, 1H, H-8a), 5.89 (m, 2H, vinylic H), 6.19 (dd, $J = 9.8$ and 5.9 Hz, 1H, vinylic H) ^{13}C NMR: 11.7 (SCH_3), 47.1 (C-8b), 58.0 (CH_2), 77.7 (C-8a), 117.0 (=CH), 120.3 (=CH), 126.5 (=CH), 126.8 (quaternary C, C-5a), 151.8 (>C=N–O–), 155.0 (–S–C=N–)	108.8	$C_{10}H_{10}N_2OS$, calcd 206.0514, found 206.0507
8b	OMe	44	^{1}H NMR: 2.39 (s, 3H, SCH_3), 3.66 (s, 3H, OCH_3), 4.25 (d, $J = 14.6$ Hz, 1H, H-8b), 4.46 (m, 2H, CH_2), 5.19 (d, $J = 6.7$ Hz, 1H, vinylic H), 5.52 (d, $J = 14.6$ Hz, 1H, H-8a), 5.83 (d, $J = 6.7$ Hz, 1H, vinylic H) ^{13}C NMR: 12.1 (SCH_3), 49.8 (C-8b), 55.7 (OCH_3), 58.3 (CH_2), 79.2 (C-8a), 95.6 (=CH, C-7), 117.6 (=CH, C-6), 119.8 (quaternary C, C-5a), 152.6 (*ipso* OMe, C-8), 153.2 (>C=N–O–), 155.2 (–S–C=N–)	120.1	$C_{11}H_{12}N_2OS$, calcd 220.0670, found 220.0680
8c	Me	44	^{1}H NMR: 2.01 (s, 3H, CH_3), 2.39 (s, 3H, SCH_3), 4.23 (d, $J = 14.9$ Hz, 1H, H-8b), 4.47 (s, 2H, CH_2), 5.46 (d, $J = 14.9$ Hz, 1H, H-8a), 5.81 (d, $J = 7.1$ Hz, 1H, vinylic H), 5.84 (d, $J = 7.1$ Hz, 1H, vinylic H) ^{13}C NMR: 12.0 (SCH_3), 21.1 (CH_3), 48.0 (C-8b), 58.4 (CH_2), 82.0 (C-8a), 117.8 (=CH, C-6), 121.7 (=CH, C-7), 124.8 (quaternary C, C-5a), 130.4 (C *ipso* Me, C-8), 152.6 (>C=N–O–), 155.4 (–S–C=N–)	132.5	$C_{11}H_{12}N_2O_2S$, calcd 236.0619, found 236.0619
8d	F	41	^{1}H NMR: 2.40 (s, 3H, CH_3), 4.38 (d, $J = 14.94$ Hz, 1H, H-8b), 4.51 (m, 2H, CH_2), 5.66 (dd, $J = 14.9$ and 4.95 Hz, 1H, H-8a), 5.81 (m, 2H, vinylic H) ^{13}C NMR: 12.2 (SCH_3), 51.4 (d, $^3J_{CF} = 8.2$ Hz, C–H, C-8b), 58.1 (CH_2, C-5), 77.2 (d, $^2J_{CF} = 27.6$ Hz, C–H, C-8a), 105.5 (d, $^2J_{CF} = 19.2$ Hz, C–H, C-7), 115.9 (d, $^3J_{CF} = 6.0$ Hz, C–H, C-6), 123.8 (d, $^4J_{CF} = 6.0$ Hz, quaternary C, C-5a), 152.1 (d, $^4J_{CF} = 2.2$ Hz, >C=N–O–), 155.1 (S–C=N–), 156.3 (d, $^1J_{CF} = 266.7$ Hz, C *ipso* F, C-8)	98.7	$C_{10}H_9FN_2OS$, calcd 224.0420, found 224.0425

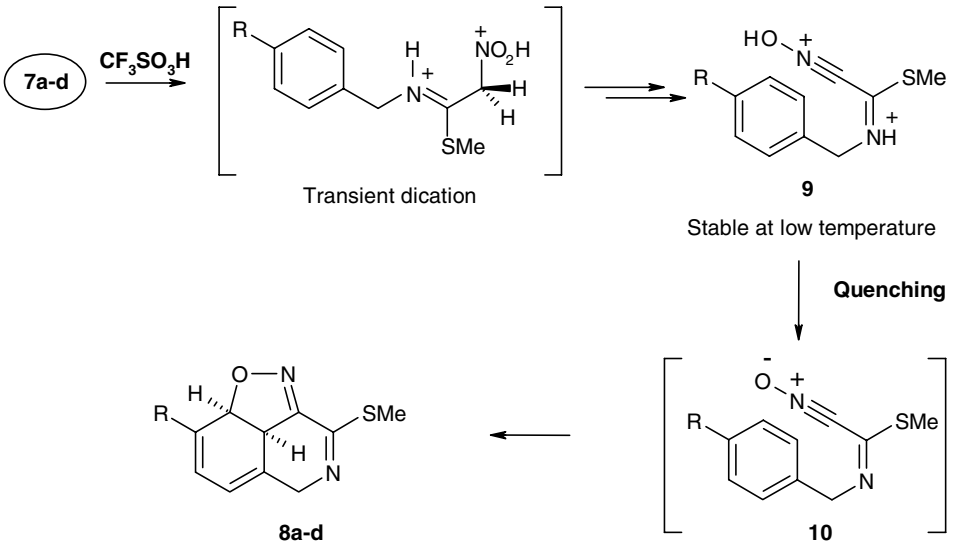
[a] Yields after crystallization/Ar was used for aromatic.

In the present case, nitro derivatives **7** are transformed into hydroxynitrilium ion **9** which do not react, even by an intramolecular process, probably because of the excessively high activation energy of the reaction at this low temperature. Indeed, NMR spectroscopic analysis indicates that nitro derivative **7a** affords ion **9a** as the sole species in trifluoromethanesulfonic acid, in a few minutes at 255 K. This species is mainly characterized by the hydroxynitrilium carbon, which resonates at 24.9 ppm as a broad and very weak signal,[19] in agreement with previously reported values.[12–14] The broadening and weakening of the carbon signal is firstly due to coupling with ^{15}N, but secondly, mainly to a quadrupolar relaxation with ^{14}N, the most abundant isotope.[20]

By quenching with water, the high acidity is destroyed and the hydroxynitrilium ion **9** is transformed into a reactive nitrile oxide **10**, which undergoes an intramolecular



Scheme 3. Cyclization of compounds **7a–d** in trifluoromethanesulfonic acid.



Scheme 4. Suggested mechanism for the formation of compounds **8a–d**.

1,3-dipolar cycloaddition (INOC reaction) to afford the cyclized products **8a–d**. The suggested reaction pathway is depicted in Scheme 4.

3. Conclusion

A novel methodology has been developed for the syntheses of tricyclic 3-methylsulfanyl-8a,8b-dihydro-5*H*-1-oxa-2,4-diazaacenaphthylenes with an isoxazoline ring from 2-nitroethene derivatives, using trifluoromethanesulfonic acid. The mechanism of the reaction implies the formation of a stable hydroxynitrilium ion (or O-protonated nitrile oxide) in superacid, the quenching of which leads to a reactive nitrile oxide. An intramolecular 1,3-dipolar cycloaddition (INOC) with the phenyl ring affords tricyclic non-aromatic isoxazoline. To the best of our knowledge, it is the first time that is reported the reaction of a nitrile oxide with a monosubstituted phenyl ring to form isoxazoline, with a full loss of aromaticity.

The 3-methylsulfanyl-8a,8b-dihydro-5*H*-1-oxa-2,4-diazaacenaphthylenes can be used as synthons and further work is in progress in this field.

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15. Typical procedure for nitroethene derivatives **7**: 1,1-bis(methylthio)-2-nitroethene (2.2 g, 13.32 mmol) and benzylamine **6a** (1.35 mL, 12.36 mmol) were heated together in refluxing 95% ethanol (75 mL) under nitrogen atmosphere. The reaction was followed by thin-layer chromatography (CH_2Cl_2). After disappearance of the benzylamine (4 h) and cooling, the mixture was concentrated under reduced pressure and the resulting oily product was purified by flash chromatography with dichloromethane and then crystallized from CH_2Cl_2/petroleum ether to afford **7a** (2.07 g, 75%) as yellow crystals.
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17. Typical procedure for isoxazoline derivatives **8**: 1-benzylamino-1-methylthio-2-nitroethene **7a** (220 mg, 0.982 mmol) was dissolved in trifluoromethanesulfonic acid (4 mL, 45 mmol) at −26 to −23 °C under nitrogen atmosphere. The reaction was monitored as follows: one or two drops of the reacting medium were quenched over ice (about 1 g)/Na_2CO_3 and extracted with CH_2Cl_2 (0.5 mL). The organic phase extract was analyzed by TLC (Silica gel on aluminum sheet 'Alugram® Sil G/UV_{254} für die DC', Art.-Nr. 818 133 from Macherey-Nagel, eluent CH_2Cl_2:MeOH 99/1). NMR at low temperature was also used as an alternative method (external reference: TMS in acetone-d_6 or methanol-d_4 in a sealed capillary tube inside the NMR cell). After disappearance of the starting compound (≈0.5 h), the solution was poured into 80 mL of CH_2Cl_2/MeOH (87:13) at −60 to −40 °C. The resulting mixture was poured over ice (10 g) and Na_2CO_3 and extracted with CH_2Cl_2 (3 × 20 mL). The organic phase was dried over $MgSO_4$ and the solvent evaporated under reduced pressure. The crude product was purified by flash chromatography with dichloromethane and then crystallized from CH_2Cl_2/petroleum ether to afford **8a** (116 mg, 57%) as light white crystals.
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19. NMR spectra of cation **9a** in triflic acid at 255 K: ^{1}H NMR (reference: TMS in external acetone-d_6): δ_H 2.07 (s, 3H, S-CH_3); 3.85 (d, $^3J_H = 5.4$ Hz, 2H, –CH_2-Ph); 6.27–6.35 (broad multiplet, 5H, aromatic H), 8.91 (broad triplet, $^3J_H = 5.4$ Hz, 1H, $=N^+$–H); ^{13}C NMR (reference: external acetone-d_6): δ_C 16.83 (–S–CH_3), 24.9 (weak and broad signal from 23.9 to 25.9, –$C{\equiv}N^+$–OH), 53.47 (–CH_2–); 128.56 and 129.06 (*o*- and *m*-aromatic *C*H), 129.28 (*IPSO* aromatic C), 129.69 (*p*-aromatic CH), 166.82 ($>C{=}NH^+$–CH_2–).
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