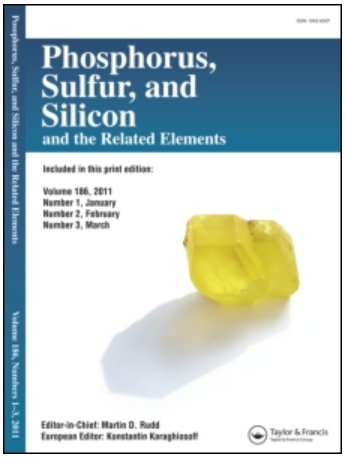

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1,1-Bis(Methylthio)-2-Nitroethene, a Versatile Synthon for the Synthesis of Oximinoorthothioesters

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1,1-BIS(METHYLTHIO)-2-NITROETHENE, A VERSATILE SYNTHON FOR THE SYNTHESIS OF OXIMINOORTHOTHIOESTERS.

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Abstract 1,1-bis(methylthio)-2-nitroethene gives a stable hydroxynitrilium ion in trifluoromethanesulfonic acid. This cation can be trapped by various nucleophiles to yield α-oximinoorthothioesters.

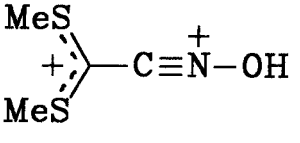
INTRODUCTION

Nitroderivatives and nitronates are polyprotonated in superacidic media to give transient species which can be trapped with suitable nucleophiles such as aromatics to gives oximes[1,2]. The stereochemistry of the resulting product -in which the aryl and hydroxyl group are cis- is consistent with the intermediacy of an hydroxynitrilium ion[3,4].

$$R\text{-}CH_2\text{-}NO_2 \longrightarrow R\text{-}C{\equiv}N^{+}\text{-}OH \longrightarrow R\text{-}C(Ph)=N\text{-}OH$$

HYDROXYNITRILIUM ION

Protonation of the title compound gives transient cations and finally the sole hydroxynitrilium ion 1 which has been fully characterized by ^{1}H and ^{13}C NMR spectroscopy in TFSA at low temperature[5]. ^{13}C chemical shifts are in good agreement with what has been reported for nitrile N-oxides[6].



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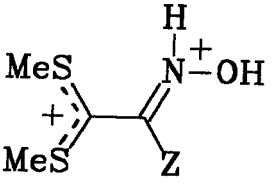
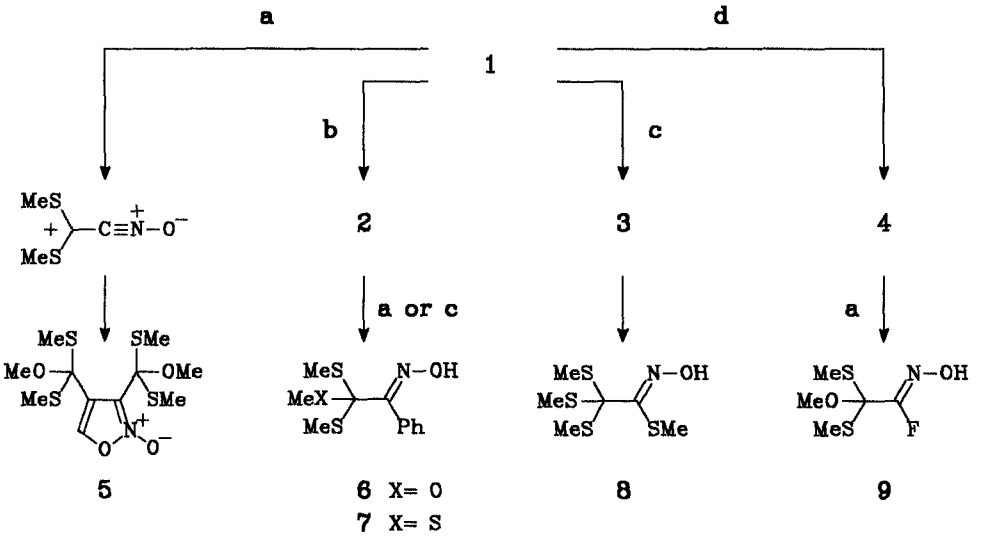


2 Z= Ph
3 Z= SMe
4 Z= F

The stabilizing effect of sulfur atom accounts for the specific reactivity of 1 compared to protonated forms of substituted nitroethylenes in TFSA[7]. Ion 1 is easily trapped on the hydroxynitrilium group to give ions2 to 4. The resulting 1,3-dithioallylic cationic system is very stable in TSFA or HF-SbF_5 and can only be trapped by nucleophiles when

the acidity is destroyed by quenching. The yield in products is good to excellent (65 to < 90%).

REACTIVITY OF HYDROXYNITRILIUM ION



a = MeOH in excess; b = PhH in excess; c = MeSH in excess; d = HF-SbF_5

Isomerization of orthothioesters in TFSA allows group exchange reaction for example 7 ionizes to 2 and trapping with methanol yields 7 (65%). All the ions described here have been fully characterized by ^{1}H and ^{13}C NMR spectroscopy at low temperature[8].

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