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

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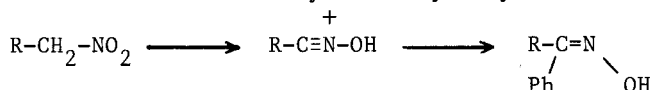
1,1-BIS(METHYLTHIO)-2-NITROETHENE, A VERSATILE SYNTHON FOR THE SYNTHESIS OF OXIMINOORTHOTHIOESTERS.

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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.

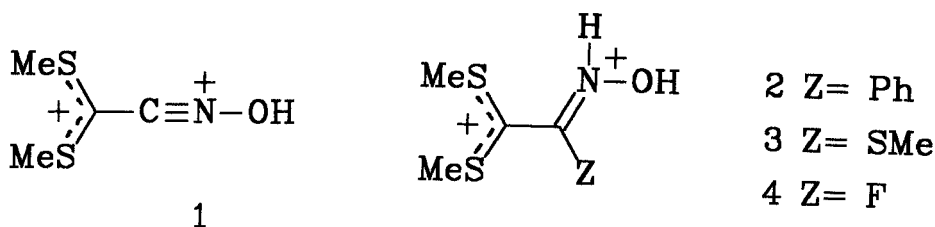
INTRODUCTION

Nitroderivatives and nitronates are polyprotonated in superacidic media to give transient species which can be trapped with suitable nucleophiles such as aromatics to give 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}.



HYDROXYNITRILIUM ION

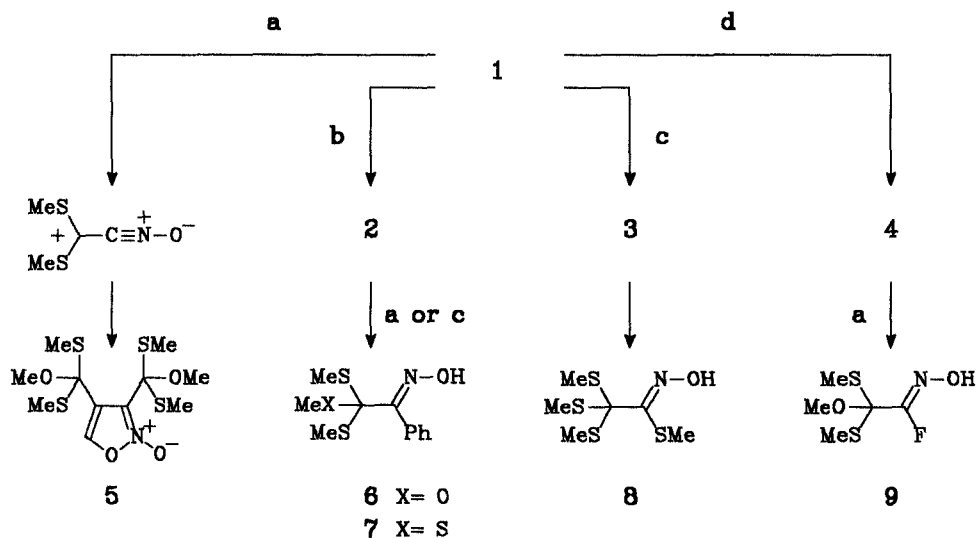
Protonation of the title compound gives transient cations and finally the sole hydroxynitrilium ion 1 which has been fully characterized by ¹H and ¹³C NMR spectroscopy in TFSA at low temperature⁵. ¹³C chemical shifts are in good agreement with what has been reported for nitrile N-oxides⁶.



The stabilizing effect of sulfur atom accounts for the specific reactivity of 1 compared to protonated forms of substituted nitroethylenes in TFSA⁷. Ion 1 is easily trapped on the hydroxynitrilium group to give ions 2 to 4. The resulting 1,3-dithioallylic cationic system is very stable in TSFA or HF-SbF₅ 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-SbF₅. 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 ¹H and ¹³C NMR spectroscopy at low temperature⁸.

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5. All chemical shifts are relative to TMS in acetone D₆. ¹³C NMR : 22.32 (Me), 23.42 (Me), 30.7 (C≡), 201.3 (>C-). ¹H NMR : 2.38 (Me) and 2.51 (Me).
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