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FORMATION OF REACTIVE THIOALDEHYDES BY VACUUM GAS-PHASE DEHYDROCYANATION OF THIOCYANOHYDRINS; CHARACTERIZATION BY MS/MS SPECTROMETRY.

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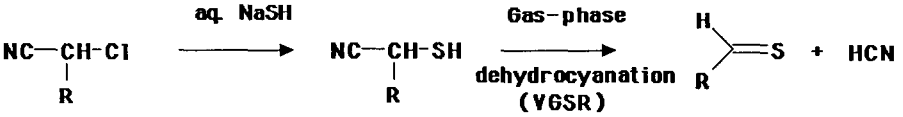
Abstract : Methanethial 2a and ethanethial 2b are obtained by a vacuum gas-phase dehydrocyanation of the corresponding thiocyanohydrins and characterized by mass spectroscopy experiments.

Most of aliphatic and aromatic thioaldehydes are too reactive species to be isolated in pure form, even at low temperature; they can be however chemically characterized in solution by cycloaddition reactions with aliphatic 1,3 dienes[1] and in gas-phase by photoelectron spectroscopy[2]. We have recently shown that α-aminonitriles and α-chloroalkylphosphines can be considered as protected imines or phosphaalkenes respectively, the corresponding HCN or HCl gas-phase elimination on solid base (Vacuum gas-solid reactions, VGSR) giving the best results.[3,4] We now report the formation of methanethial 2a and ethanethial 2b by a gas-phase dehydrocyanation of the corresponding thiocyanohydrins 1a and 1b.



Eq.1 1 2

1a,2a : R=H
1b,2b : R=CH_3

If S-substituted thiocyanohydrins have been recently used as capto-dative reagents[5], the S-unsubstituted derivatives are practically unknown. The parent compound 1a has been synthetized by treatment of chloroacetonitrile with aqueous sodium hydrosulfide (eq.1)[6]. We have prepared the C-methylated derivative 1b by the same way[7] (Eq. 1). Compounds 1 were heated in flash vacuum thermolysis (FVT) conditions or vaporized on solid base (VGSR conditions)[8]. All attempts to characterize the expected thioaldehydes by low temperature ^1H NMR were unsuccessful, polymerization occuring at a lower temperature than analysis. However, these two reactive species have been unambiguously characterized by fitting the reactor on a mass spectrometer: FVT of 1a and vaporization of 1b on solid base (K_2CO_3 or CaO at 473K) gave respectively the expected molecular ions m/z 42 and 60 characterized by high resolution measurements[9]; comparison with the mass spectrum of the corresponding thiol precursors shows that the loss of HCN occurs fewly in the ion source and mainly in the reactor (fig. 1 and 2).

The three following experiments were performed to establish the chemical structure of the molecular ion m/z 60. 1-The loss of a methyl group was observed in a CAD-MIKE spectrum (fig. 4, 5). 2-The mass spectra of the compounds obtained respectively by FVT (950K) of the anthracenic adduct 3 and by VGSR of 1b (CaO, 473K) are similar (comparison between fig. 2 and 3). Ions above m/z are some impurities and not obtained by ion-molecule reactions 3- The IR spectrum (77K) of the compound obtained by FVT of 3[10] presented the characteristic band $\nu_{C=S}$ 1068cm^{-1} [11]; no detectable $\nu_{C=C-SH}$ band was observed. From these experiments, we conclude that the formation of the more stable ethenethiol[12] which can be formed in VGSR conditions either by direct loss of HCN from 1b or by a base-catalyzed isomerization of 2b remains, if it happens, a minor process.

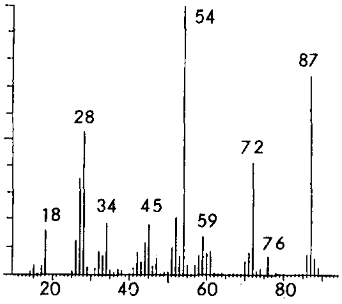


Fig.1. Mass Spectrum (MS) of 1b

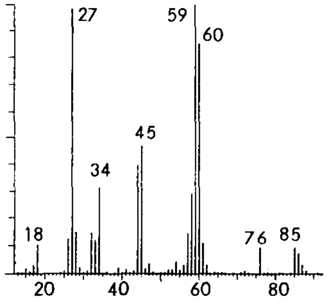


Fig.2. MS of 2b obtained from 1b by VGSR

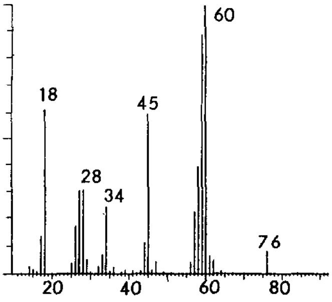


Fig.3. MS of 1b obtained from 3 by FVT

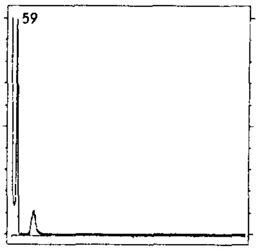


Fig.4. MIKE spectrum of m/z 60

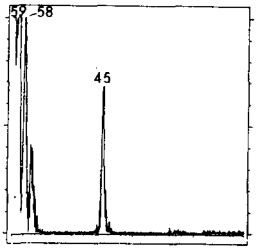
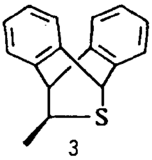


Fig.5. CAD-MIKE spectrum of m/z 60



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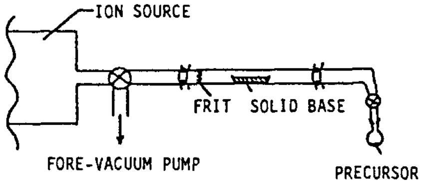
Thiocyanohydrins 1 can be considered as protected reactive thioaldehydes 2, dehydrocyanation occuring in gas-phase under mild conditions. Extention of this reaction to the preparation of reactive thioketones is under investigation.

Experimental



The VGSR-MS apparatus is represented in Scheme. The reactor consisted of a quartz tube (L 15cm, ϕ 2cm), containing a quartz cupel (L 8cm, ϕ 1cm) filled with a solid reagent. Two "O" rings assure the connection. The precursor is cooled at liquid nitrogen temperature. The line is evacuated at a pressure lower than 10^{-4} torr, then the mass spectrometer is connected. The liquid nitrogen bath is removed and the mass spectrum can be recorded when the pressure increases on heating.

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7. These two compounds should be handle with caution and kept on Amberlyst 15 (Aldrich) which acts as stabilizing agent.
8. For similar VGSR experiments see for example : B. De Corte, J.M. Denis, N. De Kimpe, J. Org. Chem., 1987, 52, 1147; J.C. Guillemin, J.M. Denis, Tetrahedron, 1988, 44, 4431.
9. High Resolution measurements: 2a (CH_2S) calcd 45.9877, found 45.9874; 2b (C_2H_4S) calcd 60.0034, found 60.0043.
10. Owing to the presence of trace of HCN, the product obtained by VGSR polymerizes on the KBr window (77K).
11. The $\nu_{C=S}$ 1147cm^{-1} given by Bock[2b] for the same compound 2b probably corresponds to the C-C band. We observe also this band.
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