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THIOCYANOHYDRINS, A NEW CLASS OF COMPOUNDS, PRECURSORS OF UNSTABILIZED THIOCARBONYL DERIVATIVES[1].

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ABSTRACT : Mono- and dialkylated thiocyanohydrins are prepared by alkylation of the parent compound **2** ($NCCH_2SH$) under mild conditions. Some examples of the reactivity of this new class of compounds are also given.

INTRODUCTION

Unstabilized thiocarbonyl compounds such as thioaldehydes or thioketones are very reactive species and consequently interesting synthetic intermediates. However, unless sterically or electronically stabilized, they show a pronounced tendency to oligo or even polymerize[2]. For some 10 years, a vast array of methods[3] which range from pyrolytic techniques[4] to photochemically induced Norrish II type cleavage of phenacyl sulfide[5], elimination reactions from appropriate sulfides[6] and direct conversion of carbonyl compounds[7], has been described in the literature for the generation of such unstable species. As part of our investigation on unstabilized carbon-heteroatom double bond chemistry[8], we were interested in generating thioaldehydes and thioketones. It occured to us that thiocyanohydrins could be considered as good precursors of these compounds, if the vacuum gas-phase dehydrocyanation could be easily run. To the best of our knowledge and with the exception of the parent derivative[9], no thiocyanohydrins were described in the literature. We now report herein a convenient, general and mild synthesis of this new class of compounds and also provide some examples of their reactivity.

RESULTS AND DISCUSSION

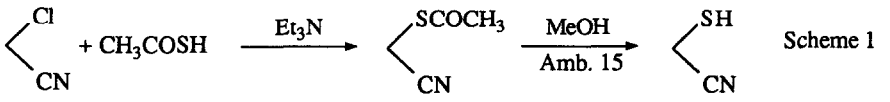
Synthesis of the parent compound : thioacetonitrile **2**

A procedure for the formation of the parent compound **2** was proposed by Mathias and Shimanski[9]. The method involves treatment of chloroacetonitrile **1** with aqueous sodium hydrosulfide (Eq.1).

$$\underset{\mathbf{1}}{NCCH_2Cl} + \text{aq.NaSH} \longrightarrow \underset{\mathbf{2}}{NCCH_2SH} \qquad \text{Eq. 1}$$

However, this transformation suffers from some disadvantages which limit the scope of application. Compound **2** is not very stable in this media and a sudden vigorous polymerization with gas evolution may

ensue. Furthermore the reaction cannot be run on a preparative scale. Therefore, we searched for a safe and preparative synthetic method. We developed a two-step procedure starting from chloroacetonitrile **1** (Scheme 1).

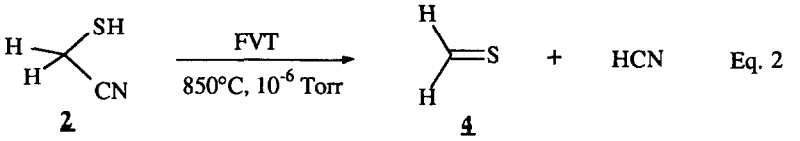


1 **3** **2** Scheme 1

Thioester **3**, prepared from chloroacetonitrile **1** and thiolacetic acid in the presence of triethylamine, reacts with methanol and a catalytic amount of Amberlyst® 15, to afford thioacetonitrile **2**. The overall yield of this sequence is higher than 80%. Thioacetonitrile **2**, thus generated, is pure enough to be used without further purification (purity > 95%). This transformation proceeds smoothly under mild conditions and is easily run on a molar scale. Furthermore, **2** can be kept for several months in the refrigerator without decomposition by using a catalytic amount of Amberlyst® 15.

Formation of reactive methanethial **4**

Methanethial **4**, which has already been described by Bock[4f], was obtained by dehydrocyanation of thioacetonitrile **2** under Flash Vacuum Thermolysis (FVT) conditions. Compound **4** has been unambiguously characterized by real time analysis of the gaseous flow, the device consisting in fitting the FVT reactor on the ion source of a mass spectrometer. The best conditions for dehydrocyanation (850°C, 10^{-6} Torr) were determined by real time analysis. At this temperature, loss of HCN is nearly complete (>90%). The expected molecular ion m/z 46 was characterized by high resolution measurements ($CH_2S^{+\cdot}$: Calcd 45.9877, Found 45.9874) (Eq. 2). Unfortunately, all attempts to characterize **4** by low temperature ^1H NMR were unsuccessful, polymerization occuring at a lower temperature than analysis.



2 **4** Eq. 2

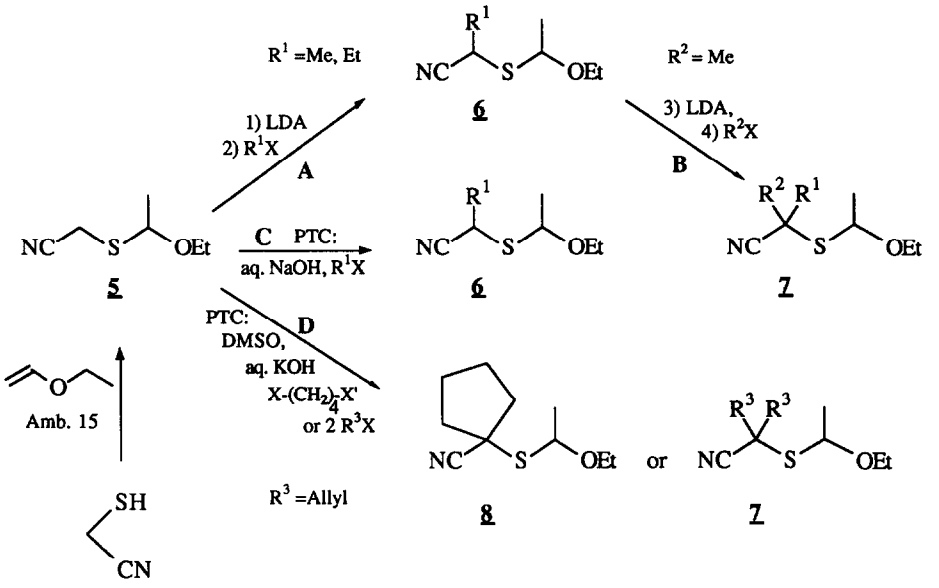
Consequently, thioacetonitrile **2** can be considered as protected reactive methanethial **4**: dehydrocyanation occuring in the gas-phase. To extend the scope of this methodology and to generalize this route, we searched after a general approach to C-alkylated thiocyanohydrins.

Alkylation of thioacetonitrile **2**

We first tried the direct alkylation of thioester **3** by different ways but never observed the expected product. Consequently, we reasoned that the procedure described by Stork and Maldonado[10] for alkylation of cyanohydrins might also be a favourable process affording C-alkylated thiocyanohydrins. This method consists in the protection of the thiol group before the alkylation. Protection of **2** with ethylvinylether proceeds under mild conditions in the presence of a small amount of Amberlyst® 15 and gives in excellent yield (>85%) the hemithioacetal **5**. The following alkylation which proceeds either with lithium diisopropylamide, or by Phase

Transfer Catalysis (PTC), leads selectively to the formation of a variety of mono- and dialkylated protected thiocyanohydrins (Scheme 2). The main results are summarized in Table 1.

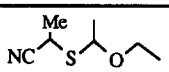
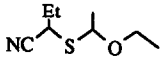
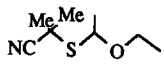
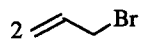
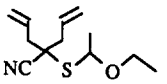
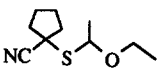
In pathway **A**, the hemithioacetal **5** is added dropwise at -78°C to a solution of freshly prepared lithium diisopropylamide (1 eq.) followed by the quenching of the resulting anion with alkylhalide (1.1 eq.). These conditions only allow the formation of monoalkylated compounds **6**. The dialkylated derivatives **7** can be generated in the same pot, by adding another equivalent of lithium diisopropylamide and quenching of the second anion with alkylhalide (pathway **B**).



Scheme 2

Alkylation reaction can also be achieved (pathway **C**) by vigorously stirring **5** and the alkylating agent under liquid/liquid conditions using NaOH/toluene and tetrabutylammonium iodide as a phase tranfer catalyst. This reaction is selective and only monoalkylated compounds are obtained. The effects of solvent, alkylating agent, reaction time and catalyst were investigated: the results presented in Table 1 give the optimized conditions. Dialkylated and cyclic compounds **7** and **8** are prepared by PTC, according to the Kabachnik procedure[11] (pathway **D**) by stirring **5** with an alkylhalide (2.5 eq.) or with a bromo-chloroalkane (1.2 eq.) and KOH (8 eq.) in DMSO. Alkylation procedures presented above allow the obtention of a wide variety of compounds with reasonable yields ranging from 50 to 70%.

Table 1 : Selective Mono- and Dialkylation of Hemithioacetal **5**

Alkylating Agent	Conditions (a)	Reaction Time (°C)	Product (b)		bp (°C/ 0.03 Torr)	Yield(c) %
Me I	A	-		**6a**	58-60	61
$(MeO)_2SO_2$	C	24h (25)			"	55
EtBr	A	-		**6b**	75	51
"	C	48h (25)			"	50
2 MeI	B	-		**7a**	(d)	50
2 	D	24h (25)		**7b**	102	70
Br $(CH_2)_4Cl$	D	24h (40)		**8a**	90	65

(a) conditions : **A** 1) LDA (1 eq.), 2) R^1X (1.1 eq.) in THF -78°C; **B** 3) LDA (1 eq.), 4) R^2X (1.1 eq.) in THF -78°C; **C** 50% aq. NaOH (10 eq.), R^1X (1.1 to 1.5 eq.), $Bu_4N^+I^-$ in toluene at RT; **D** DMSO, 50% aq. KOH (8 eq.), RX (1.2 eq. or 2.5 eq.). (b) all new compounds were fully characterized spectrally and had elemental composition established by high resolution mass spectroscopy. (c) isolated yield. (d) purified on a silica column

Deprotection of the C-alkylated thiocyanohydrins **6**, **7** and **8**

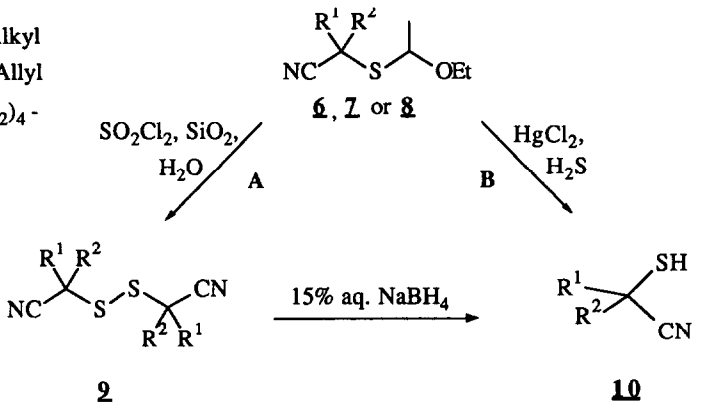
Cleavage of the carbon sulfur bond represents an important type of reaction in organic synthesis[12]. Since divalent oxygen is a hard base and divalent sulfur a soft base, it is expected that the carbon sulfur bond in O-S-acetal could be selectively cleaved. Two methodologies were investigated for the displacement of the protecting group (Scheme 3).

Method **A**, described by Hojo[13] for deprotection of dithioacetals uses mild conditions : on treatment of hemithioacetal **6** with sulfuryl chloride in the presence of a small amount of wet silica gel, the carbon-sulfur bond is selectively cleaved to afford the corresponding disulfide **9**. This compound is then reduced with a 15% aqueous or ethanolic $NaBH_4$ solution to give the expected thiocyanohydrin **10** (Scheme 3). The overall yield is higher than 50%. However, this method is not of a general applicability : the reduction reaction does not occur with the disubstituted protected thiocyanohydrins **7** or **8**.

Some remarks must be made concerning the formation of disulfide **9** : we never detected the sulfoxide intermediate mentioned in the literature[13]. However, on the basis of our observations, the reaction may be viewed as proceeding via the formation of sulfenyl chloride **11** and chloroalkylether **12** ; the highly reactive sulfenyl halide leads to disulfide **9** in the presence of water (Scheme 4). This mechanism would be in agreement with the the Benneche proposal[12b]. Furthermore, the same disulfide **9** was also observed as a by-product by treatment of thioacetonitrile **2** with N-chlorosuccinimide (NCS), the main product being the expected sulfenyl chloride **16**[14] (see Scheme 5).

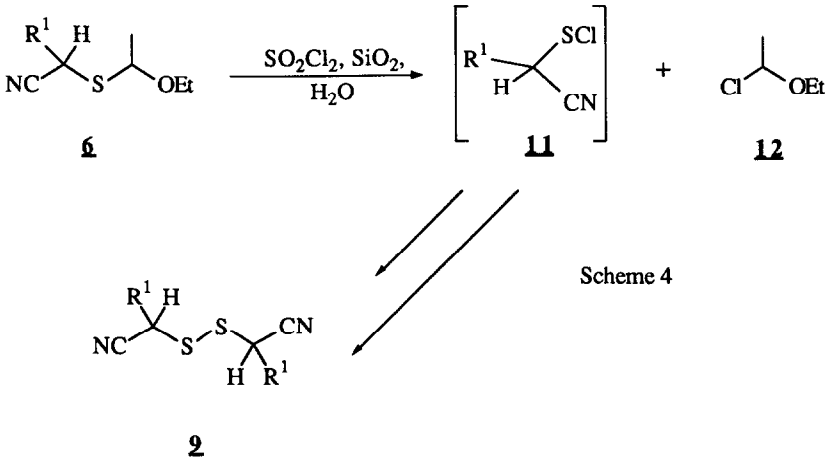
The second pathway (**B**) which is related to Block's method[12c] for cleavage of thioacetals, uses mercury (II) chloride. This metal usually forms a sparingly soluble complex with hemithioacetal **7** or **8** which is displaced in reasonable yield (50 to 70%) to afford the expected thiocyanohydrin **10** when treated with hydrogen sulfide (Scheme 3). This reaction is quite general and can be applied either to mono- or dialkylated thiocyanohydrins.

6, **9** : R^2=H, R^1=Alkyl
7 : R^1, R^2=Alkyl, Allyl
8 : R^1, R^2 = - $(CH_2)_4$ -



Scheme 3

10a :R^1= Me, R^2= H; **10b**: R^1 = Et, R^2= H;
10c : R^1,R^2= Me; **10d**: R^1, R^2= Allyl; **10e**: R^1, R^2 =-$(CH_2)_4$-

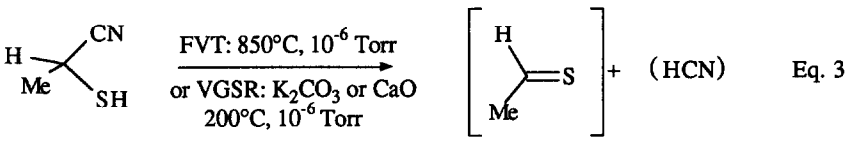


Scheme 4

After deprotection, alkylated thiocyanohydrins can be distilled under vacuum, but due to their tendency to polymerize, they were used without purification.

Gas-phase dehydrocyanation: access to reactive thiocarbonyl compounds **13a**, **13c**, **13e**

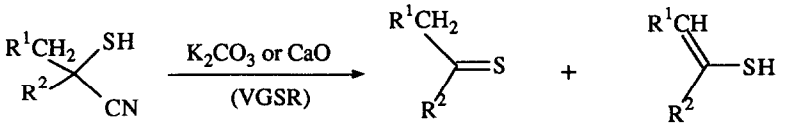
Since gas-phase dehydrocyanation of thioacetonitrile **2** led to the expected methanethial **4**[1], we anticipated that a similar HCN-elimination of alkylated thiocyanohydrins should lead to thiocarbonyl derivatives. Compounds **10a** (R^1=Me, R^2=H), **10c** (R^1=R^2=Me), **10e** (R^1, R^2=-$(CH_2)_4$-) were chosen as representative examples and submitted to HCN gas-phase elimination. FVT reaction of **10a** is performed under the same conditions as applied to the parent compound **2** (FVT/MS sequence) and allows the formation of the expected ethanethial **13a**. However this reaction is less selective than the previous one : H_2S elimination is also observed. A selective dehydrocyanation is performed by using a Vacuum Gas-Solid Reaction (VGSR)[15] with K_2CO_3 or CaO as solid base (Eq. 3). The best conditions (K_2CO_3 or CaO, 200°C, 10^{-6} Torr) for the formation of ethanethial **13a** were determined by direct analysis of the gaseous flow in a VGSR/MS sequence[1].



10a **13a** Eq. 3

The mass spectrum shows the expected molecular ion m/z 60 (high resolution measurements : $C_2H_4S^{+\cdot}$: Calcd 60.0034, Found 60.0037). In mass spectroscopy, the loss of a methyl group which is observed in a CAD-MIKE spectrum characterizes unambiguously the ethanethial **13a** and shows the lack of the more stable enethiol tautomer[16]. This result was confirmed by IR spectroscopy (77 K) . the characteristic band $\nu_{C=S}$ 1068 cm^{-1} was observed but no $\nu_{C=C-SH}$ band was detected.

In the same way, VGSR (K_2CO_3 or CaO, 200°C, 10^{-3} Torr) of **10c** and **10e** gives the expected thioketone **13c**,**13e** (Eq. 4).



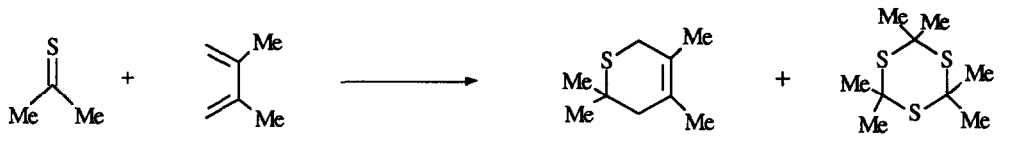
10 **13** **14**

10c , **13c**, **14c**: R^1= H, R^2 = Me

10e, **13e**, **14e**: R^1, R^2 = -(CH_2)$_3$- Eq. 4

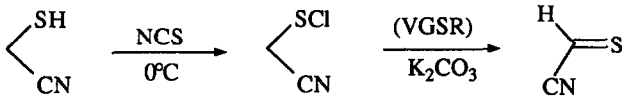
However, in these conditions the reaction is not selective : the enethiol tautomer **14** is also observed. The ratio depends on the substituents. For propanethione **13c**, only 10% of enethiol **14c** was detected by NMR spectroscopy; on the other hand the cyclopentenethiol **14e** is the major product; the expected cyclopentanethione **13e** only represents 35% of the mixture. This result is not very surprising, due to the fact that aliphatic thioketones bearing a hydrogen atom adjacent to the C=S bond, exist in equilibrium with their more stable enethiol tautomer[16]. The thioketo- and thioenol forms are not separated, but are characterized by infrared and

NMR spectroscopy. In the IR spectrum, the enethiol tautomer can be recognized by characteristic absorptions in the region of $\nu_{C=C}$ (1640 cm^{-1}), ν_{SH} (2540-2550 cm^{-1}). In the ^1H NMR spectrum, the olefinic protons are clearly distinguishable about ca. 5.5 ppm. The thioketones **13** are characterized by their low temperature (-30°C) ^1H and ^{13}C NMR spectra and comparison with literature data[17]. Propanethione **13c** presents a characteristic singlet in ^1H NMR at 2.70 ppm and in particular an heptuplet ($^2J_{C-H}$ = 5.8 Hz) at 255 ppm for the sp_2 carbon atom in ^{13}C NMR. The ^1H NMR spectra of cyclopentanethione **13e** exhibits a multiplet at 2.6-2.9 ppm. In ^{13}C NMR we observe a multiplet at 270 ppm characteristic of the thiocarbonyl sp_2 carbon atom. Furthermore **13c** was trapped by Diels-Alder cycloaddition to the dimethylbutadiene (Eq. 5). We also observed in the crude mixture , the presence of the corresponding trimeric product **16** as a minor product. The cycloadduct **15** (75%) was separated from the trimeric product (25%) by Gas Chromatography and characterized by ^1H, ^{13}C NMR and high resolution mass spectroscopy.



13c Eq. 5 **15** **16**

Finally, we must mentioned another application of thiocyanohydrins[14] : thioformylcyanide **18**, a possible interstellar species, was prepared by a VGSR HCl-elimination of the sulfenyl chloride **17** and characterized by on-line millimeter wave spectroscopy (Scheme 5).



2 **17** **18** Scheme 5

CONCLUSION

This study describs a general and convenient synthesis of a new class of compounds: thiocyanohydrins. Thus, mono- and dialkylated compounds were prepared by a protection-alkylation-deprotection sequence starting from a key compound: hemithioacetal **5**. The foremost synthetic application of this class of compounds was found in its dehydrocyanation which afforded the corresponding unstable thioaldehydes and thioketones. Furthermore, thioacetonitrile **2** was found to be a good precursor of thioformyl cyanide **18**, a possible interstellar derivative. Other investigations must be undertaken in order to have a more thorough knowledge of their reactivity.

EXPERIMENTAL SECTION

All reactions were carried out under dried nitrogen. All glassware was flamed prior to use. Diethylether and tetrahydrofuran were distilled from sodium/benzophenone, dichloromethane and pentane from phosphorus pentoxide. Other solvents and reagents were purified by standard procedures as necessary. Amberlyst® 15 was dried for 12 hours at 150°C under vacuum, K_2CO_3 for 12 hours at 250°C and CaO.for 3 hours at 900°C. ^1H NMR and ^{13}C NMR spectra were recorded using respectively WP 80 CW, WP 80 DS and AC 300P Bruker spectrometers. Chemical shifts are reported in parts per million (ppm) relative to the appropriate reference signals. The spectra were recorded in deuterochloroform ($CDCl_3$) using the tetramethylsilane signal (δ= 0.0) as reference for ^1H and ^{13}C NMR. Multiplicities of signals are given as: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintuplet; hept, heptuplet; m, multiplet and coupling constants are measured in Hertz. High resolution mass spectra were recorded on a Varian MAT 311 spectrometer. Thiocyanohydrins and thiocarbonyl derivatives are too reactive to be characterized by combustion analysis, but the mass spectra confirm their identities. Products were purified by bulb-to-bulb distillation.

Acetylthioacetonitrile **3**: Over a period of approximately two hours, triethylamine (38.3 g; 0.378 mol) was added dropwise to a cold (-30°C) stirred solution of chloroacetonitrile **1** (23.9 g; 0.316 mol) and thiolacetic acid (24.0 g; 0.316 mol) in dichloromethane (200 mL). The solution was stirred at -30°C for 5 min and then allowed to warm slowly to room temperature. The solution first turned yellow-orange and then brown. Water (10 mL) was added to the reaction mixture and the organic layer was washed with 10% diluted acetic acid (2 x 30 mL) and water (2 x 30 mL). The combined extracts were dried over $MgSO_4$ and solvent was evaporated under vacuo. The orange oil was transferred into a 50 mL round bottom flask equipped with a 1 x 10 cm distillation column packed with glass-helices, to afford 32.6 g (90%) of the yellow title compound (bp 53°C/0.1 Torr). **^1H NMR** ($CDCl_3$, 80 MHz) δ: 3.70 (s, 2H, $C\underline{H}_2$-S), 2.50 (s, 3H, $C\underline{H}_3CO$). **^{13}C NMR** ($CDCl_3$, 20 MHz) δ: 192.0 (q, ^2J = 3.7 Hz, $\underline{C}O$-S), 118.0 (t, ^2J = 8.5 Hz, N$\underline{C}$-C), 30.0 (q, ^1J = 131 Hz, $\underline{C}H_3CO$), 15.0 (t, ^1J = 149.5 Hz, $\underline{C}H_2$-S). **IR** (film): 2230 cm^{-1} (ν_{CN}), 1715 cm^{-1} ($\nu_{C=O}$). **Anal.** Calcd for C_4H_5NOS: C 41.72, N 12.16, Found C 41.52, N 12.07. **M.S.**: Mass Calcd for $C_4H_5NOS^+$: 115.0092, Found 115.009.

Thioacetonitrile **2**: Acetylthioacetonitrile **3** (29.0 g; 0.252 mol), methanol (300 mL) and dried Amberlyst® 15 (8.7 g) were introduced into a dried flask equipped with a reflux condenser, a magnetic stirrer bar and a nitrogen gas-inlet. The mixture was refluxed under magnetic stirring for 20 hours. After filtration, a new catalytic amount of Amberlyst® 15 (0.5 g) was added to stabilize **2**, then the solvent was evaporated in vacuo without heating. Thioacetonitrile **2**, thus prepared in 95% yield was pure enough to be used without further purification. Nevertheless, it can be purified by distillation but the yield is lower than 50% (bp: 22°C/ 0.02Torr). **^1H NMR** ($CDCl_3$, 80 MHz) δ: 3.35 (A_2B system, 2H, ^3J = 7.8 Hz, $C\underline{H}_2$-S), 2.35 (A_2B system, 1H, ^3J = 7.8 Hz, C-S$\underline{H}$). **^{13}C NMR** ($CDCl_3$, 20 MHz) δ: 118.0 (t, ^2J = 8.3 Hz, N$\underline{C}$-C), 9.5 (t, ^1J = 148 Hz, $\underline{C}H_2$-S). **IR** (film): 2560 cm^{-1} (ν_{SH}), 2220 cm^{-1} (ν_{CN}). **M.S.**: m/z (%) 73 (M^+, 21), 46 (16), 45 (100), 44 (29). Mass Calcd for $C_2H_3NS^+$: 72.9986, Found 72.9984.

CAUTION: *Thioacetonitrile* **2**, *which has an unpleasant odor, is unstable and can vigorously polymerize or be oxidized to the disulfide at ambient temperature or under basic conditions. However, we never observed polymerization when utilizing a small amount of Amberlyst® 15. Thioacetonitrile* **2** *can be kept in these conditions for several months in a refrigerator without decomposition*

2-Thioethyl (1'-ethoxy) acetonitrile **5**: Thioacetonitrile **2** (17.5 g; 0.239 mol) and a catalytic amount of Amberlyst® 15 (0.5 g) were placed into a dried two-necked flask fitted with a nitrogen gas-inlet, a rubber

septum and a dropping funnel. To this stirring mixture, diethylether (100 mL) was transferred via a flex-needle through the septum. After cooling to 0°C, freshly distilled ethylvinylether (34.4 g; 0.478 mol) was added dropwise and the reaction mixture was allowed to warm slowly to room temperature. The solution was filtered to remove the catalyst, then the solvent was evaporated under vacuo. The pure product was isolated by distillation under reduced pressure (bp 70-71°C/2 Torr) in a yield higher than 90%. **^{1}H NMR** ($CDCl_3$, 80 MHz) δ = 4.85 (q, 1H, ^3J = 6.3 Hz, O-C<u>H</u>-S), δ_{Ha} 3.74, δ_{Hb} 3.52 (ABX_3 system, 2H, ^3J = 7.0 Hz, $^2J_{HaHb}$ = 9.3 Hz, $CH_3C\underline{H}_2$-O), δ_{Ha} 3.33, δ_{Hb} 3.28 (AB system, 2H, $^2J_{HaHb}$ = 17.1 Hz, $C\underline{H}_2$-S), 1.62 (d, 3H, ^3J = 6.3 Hz, $C\underline{H}_3CH$), 1.25 (t, 3H, ^3J = 7.0 Hz, $C\underline{H}_3CH_2$). **^{13}C NMR** ($CDCl_3$, 20 MHz) δ: 117.7 (t, ^2J = 9.9 Hz, N<u>C</u>-C), 81.0 (dq, ^1J = 158.7Hz, ^2J = 4.1 Hz, O-<u>C</u>H-S), 63.1 (tquint, ^1J = 141.6 Hz, $^3J \approx {}^2J$ = 4.3 Hz, $CH_3\underline{C}H_2$-O), 22.0 (qd, ^1J = 129 Hz, ^2J = 2.4 Hz, <u>C</u>H_3CH), 14.8 (qt, ^1J = 125.8 Hz, ^2J = 2.5 Hz, <u>C</u>H_3CH_2), 12.3 (td, ^1J = 147 Hz, ^3J = 4.1 Hz, <u>C</u>H_2CN). **IR** (film): 2220 cm^{-1} (ν_{CN}). **Anal.** Calcd for $C_6H_{11}NOS$: C 49.65, N 9.65, S 22.07, Found C 49.72, N 9.42, S 22.07. **M.S.**: Mass calcd for $(C_6H_{11}NOS\text{-}OC_2H_5)^+$: 100.0221, Found 100.022.

2-Thioethyl (1'-ethoxy) propionitrile **<u>6a</u>** (Pathway A) : Diisopropylamine (0.308 mL; 2.2 mmol) and freshly distilled tetrahydrofuran (3 mL) were introduced into a three-necked flask fitted with a dropping funnel, a nitrogen gas-inlet, a rubber septum and a thermometer. The stirred reaction mixture was cooled to 0°C and n-butyllithium (1.6 M solution in hexane, 1.4 mL, 2.2 mmol) was added. The solution was allowed to warm to room temperature, and then cooled to -78°C in dry ice-acetone. To this cooled mixture, a solution of 2-thioethyl (1'-ethoxy) acetonitrile **<u>5</u>** (0.3 g; 2.1 mmol) in dry tetrahydrofuran (2 mL) was added dropwise with vigorous stirring. After stirring for an additional 5 min, methyl iodide (0.174 mL, 2.8 mmol) was added dropwise (5-10 min). Stirring was continued for another 2 hours in the cold and 1 hour at room temperature. After cooling the mixture to -20°C, addition of water, extraction with dichloromethane, the combined extracts were dried over $MgSO_4$, followed by the removing of solvents under vacuo. The product was purified by distillation under reduced pressure. 2-Thioethyl (1'-ethoxy) propionitrile **<u>6a</u>** was obtained in 61% yield as a mixture of the two expected diastereoisomers which were analysed without separation (bp 58-60/0.03 Torr). **^{1}H NMR** ($CDCl_3$, 80 MHz) δ: 5.15 (q, 1H, ^3J = 6.5 Hz, <u>C</u>H-O), 4.0-3.4 (m, 3H, $C\underline{H}_2CH_3$,C<u>H</u>-CN), 1.60 (d, 3H, ^3J = 6.5 Hz, $C\underline{H}_3$CH-S), 1.56 (d, 3H, ^3J = 6.5 Hz, $C\underline{H}_3$CH-O), 1.21 (t, 3H, ^3J = 7 Hz, $CH_2C\underline{H}_3$). δ: 4.97 (q, 1H, ^3J = 6.4 Hz, <u>C</u>H-O), 4.0-3.4 (m, 3H, $C\underline{H}_2CH_3$,C<u>H</u>-CN), 1.64 (d, 3H, ^3J = 6.4 Hz, $C\underline{H}_3$CH-S), 1.61 (d, 3H, ^3J = 7.8 Hz, $C\underline{H}_3$CH-O), 1.22 (t, 3H, ^3J = 7 Hz, $CH_2C\underline{H}_3$). **^{13}C NMR** ($CDCl_3$, 20 MHz) δ: 121.2 (m, N<u>C</u>-CH), 82.1 (d, ^1J = 156.2Hz, O-<u>C</u>H-S), 62.9 (tq, ^1J = 141.9 Hz, ^2J = 3.9 Hz, <u>C</u>H_2CH_3), 36.6, 24.0, 22.7, 14.9. δ: 120.5 (s, N<u>C</u>-CH), 81.2 (d, ^1J = 158.7Hz, O-<u>C</u>H-S). 62.7 (tquint, ^1J = 141.6 Hz, $^2J \approx {}^3J$ = 3.9 Hz, <u>C</u>H_2CH_3), 36.6, 23.2, 22.1, 14.9. **IR** (film): 2220 cm^{-1} (ν_{CN}). **M.S.**: m/z (%) 159 (0.14), 114 (3), 78 (26), 73 (91), 45 (100), 29 (11). Mass Calcd for $(C_7H_{13}NOS\text{ - }OC_2H_5)^+$: 114.0377, Found 114.037.

2-Thioethyl (1'-ethoxy) butyronitrile **<u>6b</u>** was prepared according to the procedure described above for **<u>6a</u>** (pathway A) and was obtained in 51% yield as a mixture of the two expected diastereoisomers which were analysed without separation (bp 75°C/0.03 Torr). **^{1}H NMR** ($CDCl_3$, 80 MHz) δ: 4.95 (q, 1H, ^3J = 6.3 Hz, $CH_3C\underline{H}$-O), 3.9-3.4 (m, 3H, $CH_3C\underline{H}_2$-O, CH_3CH_2-C<u>H</u>-S), 2.1-1.6 (m, 2H, $CH_3C\underline{H}_2CH$-S), 1.57 (d, 3H, ^3J = 6.3 Hz, $C\underline{H}_3$CH-O), 1.22 (t, 3H, ^3J = 7.0 Hz, $C\underline{H}_3CH_2$-O), 1.1-0.9 (m, 3H, $C\underline{H}_3CH_2$-CH). δ: 4.82 (q, 1H, ^3J = 6.4 Hz, $CH_3C\underline{H}$-O), 3.9-3.4 (m, 3H, $CH_3C\underline{H}_2$-O, CH_3CH_2-C<u>H</u>-S), 2.1-1.6 (m, 2H, $CH_3C\underline{H}_2CH$-S), 1.66 (d, 3H, ^3J = 6.4 Hz, $C\underline{H}_3$CH-O), 1.2 (t, 3 H, ^3J = 7.0 Hz, $C\underline{H}_3CH_2O$), 1.1-0.9 (m, 3H, $C\underline{H}_3CH_2$-CH). **^{13}C NMR** ($CDCl_3$, 20 MHz) δ: 120.5 (dt, $^2J \approx {}^3J$ = 6 Hz, N<u>C</u>-CH), 82.0 (dm, ^1J = 156.0Hz, $CH_3\underline{C}H$-S). 62.9 (tq, ^1J = 141.6 Hz, ^2J = 4.3 Hz, O<u>C</u>H_2CH_3), 31.1, 27.4, 22.9, 14.9, 11.6. δ: 119.85 (dt, $^2J \approx {}^3J$ = 6 Hz, N<u>C</u>-CH), 81.9 (dm, ^1J = 155.0 Hz, $CH_3\underline{C}H$-S). 62.7 (tq, ^1J = 141.6 Hz,

^2J = 4.3 Hz, O$\underline{C}H_2CH_3$), 30.2, 26.5, 21.7, 14.9, 11.6. **IR** (film): 2220 cm^{-1} (ν_{CN}). **M.S.**: m/z (%) 173 (M^+,1.18), 73 (100), 45 (80), 29 (17.3). Mass Calcd for $C_8H_{15}NOS^+$: 173.0874, Found 173.088.

2-Thioethyl (1'-ethoxy) propionitrile **6a** (pathway C): 2-Thioethyl (1'-ethoxy) acetonitrile **5** (0.96 g; 6.6 mmol), toluene (15 mL), 50% aqueous NaOH solution (10 eq.), tetrabutylammonium iodide (0.27 g; 0.7 mmol) and freshly distilled dimethylsulfate (0.23 mL; 7.9 mmol) were introduced into a flask fitted with a mechanical stirrer. The reaction mixture was vigorously stirred for 48 hours. Water (40 mL) and dichloromethane (60 mL) were added. The extracts were dried over $MgSO_4$ and solvents evaporated under vacuo. The title compound was obtained in 55% yield after distillation under reduced pressure (see spectroscopic data above).

2-Thioethyl (1'-ethoxy) butyronitrile **6b** (pathway C) was prepared according to the procedure described above for **6a** and was obtained in 50% yield as a mixture of the two expected diastereoisomers (see spectroscopic data above).

2-Methyl-2-thioethyl (1'-ethoxy) propionitrile **7a** (pathway B): Diisopropylamine (0.308 mL; 2.2 mmol), and freshly distilled tetrahydrofuran (3 mL) were placed into a three-necked flask fitted with a dropping funnel, a nitrogen gas-inlet, a rubber septum and a thermometer. The stirred reaction mixture was cooled to 0°C and n-butyllithium (1.6M solution in hexane, 2.2 mmol, 1.4 mL) was added. The solution was allowed to warm to room temperature and then cooled to -78°C in dry ice-acetone. To this cooled mixture, a solution of 2-thioethyl (1'-ethoxy) acetonitrile **5** (0,3g; 2.1 mmol) in dry tetrahydrofuran (2 mL) was added dropwise with vigorous stirring. After stirring for an additional 5 mın, methyl iodide (0.174 mL, 2.8 mmol) was added dropwise (5-10 min). Stirring was continued for another 2 hours in the cold and 1 hour at room temperature. This solution was added dropwise with a flex-needle through a septum to a flask which contained a cooled (-78°C) freshly prepared lithium diisopropylamide solution (2.2 mmol). After stirring for 10 min (formation of the anion), methyl iodide (0.174 mL, 2.8 mmol) was added dropwise. Stirring was continued for another 2 hours in the cold and 1 hour at room temperature. After cooling the mixture to -20°C, addition of water, extraction with dichloromethane, the combined extracts were dried over $MgSO_4$, followed by the removing of solvents under vacuo. The product was purified by chromatography on silica gel (eluent: benzene/pentane 1/1).The yield was ca. 50%. **^{1}H NMR** ($CDCl_3$, 80 MHz) δ: 5.13 (q, 1H, ^3J = 6.4 Hz, S-C$\underline{H}CH_3$), 3.64 (q, 2H, ^3J = 7.0 Hz, O-C$\underline{H}_2CH_3$), 1.7, 1.65 (2 s, 3H, 3H, (C$\underline{H}_3$)$_2$C-CN), 1.59 (d, 3H, ^3J = 6.4 Hz, C$\underline{H}_3$CH-O), 1.21 (t, 3H, ^3J = 7 Hz, $CH_2C\underline{H}_3$). **^{13}C NMR** ($CDCl_3$, 20 MHz) δ: 122.7 (hept, ^3J = 5.2 Hz, C-$\underline{C}$N), 82.0 (dm, ^1J = 158.7 Hz, $CH_3\underline{C}H$-S), 61.5 (t quint, ^1J = 141.6 Hz, $^2J \approx {}^3J$ = 4.5 Hz, O-$\underline{C}H_2CH_3$), 36.7 (dhept, ^2J = 4.3 Hz, (CH$_3$)$_2\underline{C}$-S), 29.3 (qq, ^1J = 131.6 Hz, ^3J = 4.9 Hz, $\underline{C}H_3$-C-CH$_3$), 28.5 (qq, ^1J = 131.2 Hz, ^3J = 4.9 Hz, CH$_3$-C-$\underline{C}$H$_3$), 22.1 (q, ^1J = 127.8 Hz, $\underline{C}H_3CH$), 14.9 (q, ^1J = 126.5 Hz, $\underline{C}H_3CH_2$). **IR** (film): 2220 cm^{-1} (ν_{CN}). **M.S.**: m/z (%) 173 (M^+, 0.6), 128 (3), 73 (83), 45 (100). Mass Calcd for $C_8H_{15}NOS^+$: 173.0874, Found 173.087

4-Cyano-4-thioethyl (1'-ethoxy) hepta-1,6-diene **7b** (pathway D): 2-thioethyl (1'-ethoxy) acetonitrile **5** (1g; 6.9 mmol) and dimethyl sulfoxide (17 mL) were placed into a two-necked flask fitted with a dropping funnel. A 50% aqueous potassium hydroxyde solution (55.2 mmol, 8 eq.) was added to the stirred reaction mixture and then allyl bromide (1.5 mL, 17.25 mmol) was added dropwise. After stirring 24 hours at room temperature, the mixture was diluted with water and extracted with pentane. The extracts were washed with water, dried with $MgSO_4$ and solvent was distilled off under vacuo. The residue was distilled under vacuo (bp 102°C/0.03 Torr) to afford the title compound in 70% yield. **^{1}H NMR** ($CDCl_3$, 80 MHz) δ: 6.0-5.80 and 5.30-5.15 (m, 6H, (C$\underline{H}_2$=C$\underline{H}$-CH$_2$)$_2$), 5.20 (q, 1H, ^3J = 6.5 Hz, CH$_3$-C$\underline{H}$), 3.65 (q, 2H equivalent (deceptively simple spectrum), ^3J =7 Hz, OC$\underline{H}_2$CH$_3$), 2.80-2.50 (m, 4H, (CH$_2$=CH-C$\underline{H}_2$)$_2$), 1.60 (d, 3H, ^3J = 6.5 Hz, C$\underline{H}_3$-CH), 1.22 (t, 3H, ^3J = 7 Hz, O-CH$_2$C$\underline{H}_3$). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ: 131.0,

130.7 (2 dm, ^1J = 155.5, ^1J = 155.0, (CH_2=$\underline{C}$H-CH_2)$_2$), 120.8, 120.7(2 dm, ^1J = 155.0, 154.6 Hz, $^1J'$ = 160.3, 159.0 Hz, ($\underline{C}H_2$=CH-CH_2)$_2$), 120.3 (quint, ^3J = 4.9 Hz, C-$\underline{C}$N), 81.8 (dq, ^1J = 159.2 Hz, ^3J = 4.5 Hz, $CH_3\underline{C}$H-O), 61.4 (tquint, ^1J = 141.7 Hz, $^2J \approx {}^3J$ = 4.6 Hz, $CH_3\underline{C}H_2$-O), 45 (m, $\underline{C}$-CN), 42.5, 41.5 (2 tm, ^1J = 132.3 Hz, ^1J = 131.9 Hz, (CH_2=CH-$\underline{C}H_2$)$_2$), 22.0 (qt, ^1J = 128.5 Hz, ^3J = 2.2 Hz, $\underline{C}H_3$CH-O), 14.9 (qt, ^1J = 126.4 Hz, ^3J = 2.9 Hz, $\underline{C}H_3CH_2$-O). **IR** (film): 2220 cm^{-1} (ν_{CN}), 1650 cm^{-1} ($\nu_{C=C}$). **M.S.**: m/z (%) 180 (0.33), 73 (100), 45 (83), 41 (12), 29 (4), 28 (10.5). Mass Calcd for ($C_{12}H_{19}NOS$ - OC_2H_5)$^+$: 180.0847, Found 180.086.

1-Cyano-1-thioethyl (1'-ethoxy) cyclopentane **8** (pathway **D**) was prepared according to the procedure described above for **7b**, but only 1.2 equivalent of 1-bromo-4-chlorobutane was used (bp 90°C/0.03 Torr, 65% yield) **^{1}H NMR** ($CDCl_3$, 80 MHz) δ: 5.10 (q, 1H, ^3J = 6.4 Hz, S-C$\underline{H}$-CH_3), δHa 3.62, δHb 3.56 (ABX_3 system, 2H, ^3J = 7.0Hz, $^2J_{HaHb}$ = 6.8 Hz, O-C$\underline{H}_2$CH3), 2.6-1.7 (m, 8H, ($\underline{C}H_2$)$_4$), 1.62 (d, 3H, ^3J = 6.4 Hz, S-CH-C$\underline{H}_3$), 1.23 (t, 3H, ^3J = 7 Hz, O-CH_2-C$\underline{H}_3$). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ: 122.6 (t, ^3J = 5.1 Hz, C-$\underline{C}$N), 82.4 (dm, ^1J = 158.2 Hz, S-$\underline{C}$H-CH_3), 61.9 (tquint, ^1J = 141.7 Hz, $^2J \approx {}^3J$ = 4.6 Hz, O-$\underline{C}H_2$-CH_3), 44.7 (m, (CH_2)$_2\underline{C}$-S), 41.0, 39.9 (2 tm, ^1J = 136.6 Hz, ^1J = 134.7 Hz, ($\underline{C}H_2$)$_2$C-S), 29.2 (qd, ^1J = 128.4 Hz, ^2J = 2.15 Hz, $\underline{C}H_3$-CH), 23.9, 23.6 (2 tm, ^1J = 132.3 Hz, ^1J = 130.8 Hz, $\underline{C}H_2$-$\underline{C}H_2$-CH_2-C), 14.9 (q, ^1J = 126.4 Hz, $\underline{C}H_3$-CH_2-O). **IR** (film): 2220 cm^{-1} (ν_{CN}). **M.S.**: m/z (%) 199 (M^+, 1.8), 154 (1.4), 73 (100), 67 (7), 45 (77), 43 (6), 29 (6), 28 (45.5). Mass Calcd for $C_{10}H_{17}NOS^+$: 199.1030, Found 199.103.

2-Thiol propionitrile **10a** was prepared according to the Hojo and Masuda modified procedure[13] (pathway **A**): A solution of sulfuryl chloride (0.162g; 1.2 mmol) in dichloromethane (3 mL) was added dropwise, under nitrogen, at room temperature to a stirred mixture containing wet silica gel (0.2-0.5g of silicic acid, Mallinckrodt 100 mesh and 0.2-0.5g of water) and 2-thioethyl (1'-ethoxy) propionitrile **6a** (1.0 mmol) in dichloromethane (6mL). After stirring for 1.5 hours at room temperature, finely powdered anhydrous potassium carbonate (0.3-0.6g) was added to the reaction mixture and stirring was continued for another 1.5 hours. Filtration and evaporation of the solvent in vacuo gave the intermediate disulfide **9**. Dichloromethane (6 mL) was added to the residue and the mixture was cooled to 0°C. A freshly prepared 15% aqueous or ethanolic sodium borohydride solution was added dropwise for ca. 0.5 hour. Immediate gas evolution was observed upon mixing the reagents and a cream yellow suspension was obtained. The reaction mixture was allowed to warm to room temperature and then stirred for 1 hour. The organic layer was washed with water (5 mL) and the combined water extracts were acidified with a 33% aqueous HCl solution. Dichloromethane (10 mL) was added and the organic layer washed with water until pH reached 6, and then dried over $MgSO_4$. The crude product, stabilized with Amberlyst® 15 (0.1g) was obtained in 60% yield and was pure enough to be used without further purification. However, it can be distilled under reduced pressure, but the yield is unsatisfactory (bp 55°C/7 Torr). **^{1}H NMR** ($CDCl_3$, 80 MHz) δ: 3.70 (dq, 1H, ^3J = 7.8 Hz, ^3J = 7.0 Hz, $CH_3C\underline{H}$-SH), 2.6 (d, 1H, ^3J = 7.8 Hz, CH_3CH-S$\underline{H}$), 1.7 (d, 3H, ^3J = 7.0 Hz, $\underline{C}H_3$CH-SH). **^{13}C NMR** ($CDCl_3$, 20 MHz) δ: 121.1 (m, CH_3CH-$\underline{C}$N), 22.9 (qt, ^1J = 132.2 Hz, $^2J \approx {}^3J$ = 4.9 Hz, $\underline{C}H_3CHCN$), 20.8 (dq, ^1J = 147.5 Hz, ^2J = 3.9 Hz, $CH_3\underline{C}$H-CN). **IR** (film): 2560 cm^{-1} (ν_{SH}), 2220 cm^{-1} (ν_{CN}). **M.S.**: m/z (%) 87 (M^+, 93), 72 (45), 54 (100), 33 (4), 28 (43), 15 (34). Mass Calcd for $C_3H_5NS^+$: 87.0143, Found 87.014.

2-Thiol butyronitrile **10b** was prepared in 55% yield according to the procedure described above for **10a**. **^{1}H NMR** ($CDCl_3$, 80 MHz) δ: 3.8-3.2 (m, 1H, CNC$\underline{H}$-SH), 2.42, (d, 1H, ^3J = 8.0 Hz, CNCH-S$\underline{H}$), 2.0-1.75 (m, 2H, $CH_3C\underline{H}_2$-CH), 1.17 (td, 3H, ^3J = 7.4 Hz, ^3J = 3 Hz, $\underline{C}H_3CH_2$-CH). **^{13}C NMR** ($CDCl_3$, 20 MHz), δ: 120.0 (m, CH-$\underline{C}$N), 34.4 (tm, ^1J = 130.8 Hz, CH-$\underline{C}H_2CH_3$), 27.6 (dm, ^1J = 146 Hz, $\underline{C}$H-CH_2CH_3), 11.3 (qm, ^1J = 127.0 Hz, CH-$CH_2\underline{C}H_3$). **IR** (film): 2560 cm^{-1} (ν_{SH}), 2220 cm^{-1} (ν_{CN}).

2-Methyl-2-thiol propionitrile **10c** (pathway **B**). A solution of 2-methyl, 2-thioethyl (2'-ethoxy) propionitrile **7a** (0.5g; 2.89 mmol) in methanol (5 mL) was added dropwise at 25°C to a well stirred solution of mercuric (II) chloride (0.85g; 3.18 mmol) in acetonitrile (6mL). After stirring for 1 hour at this temperature, methanol was evaporated in vacuo. Chloroform (20 mL) was added to the residue and the suspension thus obtained cooled to 0°C and treated with a moderate stream of H_2S for 10 min. Water (10 mL) was added to the homogeneous reaction mixture and the organic layer was washed with water (5 mL) and then dried over $MgSO_4$. Solvents were evaporated under vacuo. The title compound was obtained in 73% yield and was pure enough to be used without further purification. However, it can be distilled under reduced pressure (bp 44°C/12 Torr) but the yield is lower. **^{1}H NMR** ($CDCl_3$, 80 MHz) δ: 3.48 (hept, 1H, ^4J = 0.6 Hz, C-S**H**), 1.80 (d, 6H, ^4J = 0.6 Hz, (C**H**$_3$)$_2$C). **^{13}C NMR** ($CDCl_3$, 20 MHz) δ: 123.6 (m, C-**C**N), 32.4 (m, **C**-CN), 31.4 (q quint, ^1J = 131.5 Hz, $^3J_{C\text{-}CH_3} \approx {}^3J_{C\text{-}SH}$ = 4.5 Hz, (**C**H$_3$)$_2$-C). **IR** (film): 2560 cm^{-1} (ν_{SH}), 2220 cm^{-1} (ν_{CN}). **M.S.**: m/z (%) 101 (M^+, 53), 41 (100) 68 (68) 42 (14), 33 (2). Mass Calcd for $C_4H_7NS^+$: 101.0299, Found 101.029.

4-Cyano-4-thiol hepta-1,6-diene **10d** was prepared from **7b** in 50% yield according to the procedure described above for **10c** (pathway **B**). **^{1}H NMR** ($CDCl_3$, 80 MHz) δ: 6.08-5.84 and 5.44-5.25 (m, 6H, (C**H**$_2$=C**H**-CH$_2$)$_2$), 2.85-2.42 (m, 4H, (CH$_2$=CH-C**H**$_2$)$_2$), 2.75 (s, 1H, C-S**H**). **^{13}C NMR** ($CDCl_3$, 20 MHz) δ: 130.7 (dm, ^1J = 155.4 Hz, (CH$_2$=**C**H-CH$_2$)$_2$), 121.7 (tm, ^1J = 157.Hz, (**C**H$_2$=CH-CH$_2$)$_2$), 121.1 (m, C-**C**N), 45.1 (tm, ^1J = 134 Hz, (CH$_2$=CH-**C**H$_2$)$_2$), 41.1 (m, **C**-CN). **IR** (film): 2560 cm^{-1} (ν_{SH}), 2220 cm^{-1} (ν_{CN}), 1650 cm^{-1} ($\nu_{C=C}$).

1-Cyanocyclopentanethiol **10e** was prepared from **8** in 60% yield according to the procedure described above for **10c** (pathway **B**). **^{1}H NMR** ($CDCl_3$, 80 MHz) δ: 2.7 (s, 1H, C-S**H**), 2.5-2.0 and 2.0-1.7 (m, 2H, m, 6H, cyclopentyle C**H**$_2$). **^{13}C NMR** ($CDCl_3$, 20 MHz) δ: 123.5 (m, C-**C**N), 43 (tm, ^1J = 136 Hz, (**C**H$_2$)$_2$C-SH), 39.7 (m, **C**-SH), 24 (tm, ^1J = 134 Hz, (**C**H$_2$)$_2$-CH$_2$-C-SH). **IR** (film): 2560 cm^{-1} (ν_{SH}), 2220 cm^{-1} (ν_{CN}) **M.S.**: m/z (%) 127 (M^+, 39), 94 (28), 93 (23), 86 (18), 85 (16), 67 (100), 33 (3). Mass Calcd for $C_6H_9NS^+$: 127.0456, Found 127.045.

Methanethial **4**: Detection of methanethial **4** was performed in a FVT/MS sequence (Flash Vacuum Thermolysis / Mass Spectroscopy) by connecting the thermolysis reactor to the ion source of a mass spectrometer. The apparatus consists in a quartz tube (L = 40 cm, i.d. = 1.2 cm) surrounded with an external resistance and fitted to the ionisation chamber The scheme of this apparatus was given in the preliminary communication[1]. Optimum conditions for dehydrocyanation (850°C, 10^{-6} Torr) were determined by real time analysis of the gaseous flow. Thioacetonitrile **2** (0.1g, 1.4 mmol) was slowly vaporized through the quartz FVT tube heated to 850°C (P = 10^{-6} Torr) M.S.: m/z (%) 78 (183), 76 (20.6), 73 (6.8), 72 (2 6), 48 (4.2), 47 (6.3), 46 (M^+, 95.8), 45 (100), 44 (29.1). Mass Calcd for CH_2S^+: 45.9877, Found 45.987.

Ethanethial **13a** : Detection of ethanethial **13a** was performed under vacuum gas-solid conditions by connecting the VGSR reactor to the ion source of a mass spectrometer. The apparatus consists in an empty quartz tube (L = 80 cm, i.d. = 3.5 cm) half-filled with a dried finely powdered solid base (K_2CO_3 or CaO, 100 g) heated (200°C) and degassed (10^{-3} Torr for two hours). This reactor was directely fitted to the ionisation chamber[18]. Optimum conditions for dehydrocyanation (200°C, 10^{-6} Torr) were determined by real time analysis of the gaseous flow. 2-Thiol propionitrile **10a** (0.1g, 1.15 mmol) was slowly vaporized through the VGSR reactor heated to 200°C (P = 10^{-6} Torr). **M.S.**: m/z (%) 60 (M^+,86), 59 (100), 58 (29.5), 57 (14.8), 45 (47), 44 (39.5), 34 (31.6), 27 (98), 26 (12.8). Mass Calcd for $C_2H_4S^+$: 60.00337, Found 60.0037

Propanethione **13c** was prepared by VGSR dehydrocyanation. The VGSR reactor (pyrex tube, L = 90 cm, i.d.= 3.5 cm) was half-filled with dried finely powdered K_2CO_3 (100g), heated and degassed to 200°C for

two hours. 2-Methyl-2-thiol propionitrile **10c** was slowly vaporized on the solid base. Propanethione **13c** was trapped on a cold finger (liquid nitrogen) and analysed by low temperature ^{1}H and 13C NMR. **^{1}H NMR** ($CDCl_3$, 80 MHz, -30°C) δ: 2.7 (s, 6H, $(C\underline{H}_3)_2C$). **^{13}C NMR** ($CDCl_3$, 20 MHz, -30°C) δ: 255 (hept, ^2J = 5.8 Hz, $\underline{C}$=S), 42.5 (qq, ^1J = 128 Hz, ^3J = 3.7 Hz, $(\underline{C}H_3)_2C$).

Cyclopentanethione **13e** was prepared from **10d** according to the procedure described above for **13c**. **^{1}H NMR** ($CDCl_3$, 80 MHz, -30°C) δ: 2.6-2.9 (m, 8H, $C\underline{H}_2$). **^{13}C NMR** ($CDCl_3$, 20 MHz, -30°C) δ: 270 (m, $\underline{C}$=S), 53 (t, ^1J = 130 Hz, $(\underline{C}H_2)_2C$), 27 (t, ^1J = 128 Hz, $(\underline{C}H_2)_2CH_2$-C).

3,4,6,6-Tetramethyl-1-thiacyclohex-3-ene **15**: Propanethione **13c** prepared as described above was condensed on a cold finger (liquid nitrogen) and then collected with diethylether as solvent. The mixture was cooled to 5°C and a large excess of dimethylbutadiene was added. The mixture was stirred for two days at 5°C, then the solvent was evaporated under vacuo. The cycloadduct **15** (75%) was separated from the trimeric product **16** (25%) by Gas Chromatography (GC). **^{1}H NMR** ($CDCl_3$, 80 MHz) δ: 3.09 (q, 2H, ^4J = 1.7 Hz, $C\underline{H}_2$-S), 2.13 (m, $C\underline{H}_2$-C(CH3)$_2$), 1.74, 1.66 (2 m, 6H, $C\underline{H}_3$-C=C-$C\underline{H}_3$), 1.29 (s, 6H, C-$(C\underline{H}_3)_2$). **^{13}C NMR** ($CDCl_3$, 20 MHz) δ:126.3 (m, C=$\underline{C}$-CH_2-S), 121.5 (m, $\underline{C}$=C-CH_2-S), 47.6, 29.1, 29.0. **M.S.**: m/z (%) 156 ($M^{+\cdot}$, 58), 141 (23), 123 (31), 113 (27), 106 (44), 74 (100), 67 (37), 59 (94). Mass Calcd for $C_9H_{16}S^+$, 156.0972, Found 156.098.

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