*Acta Chemica Scandinavica, 1996: 50: 432–437*
*Printed in UK – all rights reserved*



ACTA
CHEMICA SCANDINAVICA
*ISSN 0904–213X*

# Sodium 2-Cyanoethylene-1,1-dithiolate Tetrahydrate: a Stable Salt of Cyanodithioacetic Acid. A New Preparative Route to 2-Cyanoketene *S,S*-, *S,N*- and *N,N*-acetals

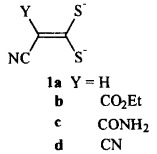
Lars Henriksen

Department of Chemistry, University of Copenhagen, The H. C. Ørsted Institute, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

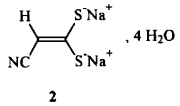
Henriksen, L., 1996. Sodium 2-Cyanoethylene-1,1-dithiolate Tetrahydrate: a Stable Salt of Cyanodithioacetic Acid. A New Preparative Route to 2-Cyanoketene *S,S*-, *S,N*- and *N,N*-acetals. – Acta Chem. Scand. 50: 432–437. © Acta Chemica Scandinavica 1996.

2-Cyanoethylene-1,1-dithiolate, the dianion of cyanodithioacetic acid, is prepared from ethyl cyanoacetate by condensation with carbon disulfide followed by hydrolysis and decarboxylation with sodium hydroxide. The anion has been isolated and characterized as a stable, tetrahydrated sodium salt (**2**) and alkylated to give 3,3-bis(alkylthio)propenonitriles (**3**) in excellent yields. Alkylation of an intermediate, unstable trianion of 2-cyano-1,1-dithiomalonic acid (**4**) gives 3,3-bis(methylthio)-2-cyanopropenic acid (**6a**) which on treatment with mono- and di-alkylamines undergoes consecutive substitution and decarboxylation to 3-amino-3-(methylthio)propenonitriles (**7**). The application of 1,2-diamines or 2-aminoethanethiol leads to cyclized products, (imidazolidin-2-ylidene)acetonitriles (**9**) and (1,3-thiazolidin-2-ylidene)acetonitrile (**10**), respectively.

2-Cyanoethylene-1,1-dithiolates (**1**) are generally prepared from nitriles with at least two α-protons, carbon disulfide and an appropriate base.[1] While these reagents are usually used *in situ* for further transformations **1b–d** have been isolated and characterized as stable sodium,[2,3] potassium[4,5] or ammonium[6,7] salts. The occurrence of the parent member of the series (**1a**) was indicated by the isolation of its *S,S'*-dialkylated derivatives (**3**) from base-induced condensations between acetonitrile and carbon disulfide[8,9] and an intractable lithium salt was obtained as an intermediate in one of these condensations.[8,9]



**1a** Y = H
**b** $CO_2Et$
**c** $CONH_2$
**d** CN

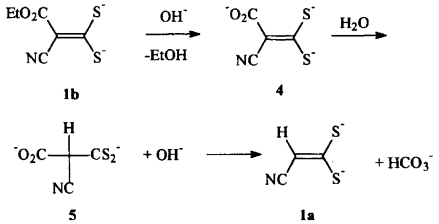


**2**

The present paper reports the formation of **1a** by alkaline (sodium hydroxide) hydrolysis and decarboxylation of the sodium salt of 2-cyano-2-ethoxycarbonylethylene-1,1-dithiolate (**1b**), the characterization of the anion as the stable, hydrated sodium salt (**2**) and some synthetic transformations of **1a** and its precursor, the trianion of 2-cyano-1,1-dithiomalonic acid (**4**).

Precursor **1b** was prepared by a modification of the Söderbäck reaction:[2] Addition of the base to a mixture of carbon disulfide and ethyl cyanoacetate in ethanol allowed the replacement of sodium ethanolate with conc. aqueous sodium hydroxide. This procedure makes the sodium salt of **1b** readily accessible in molar quantities and in >90% yield.

The conversion of **1b** into **1a** (Scheme 1) proceeds via the trianion **4** which is stable at room temperature in the presence of an excess of hydroxide ion. It was trapped by *S,S'*-dialkylation (see later) and its $^{13}C$ NMR spectrum has been recorded (Table 1). The decarboxylation of **4**



*Scheme 1.*

appears to be an electrophilic substitution with water acting as a proton source to give **5**, one of the possible tautomeric dianions of 2-cyano-1,1-dithiomalonic acid, since the process is initiated by the removal of the excess of hydroxide ion from the solution. Once started, the decarboxylation takes an autocatalytic course owing to base consumption by the liberated carbon dioxide. Thus a solution of **4** prepared from **1b** and NaOH in the molar ratio 1:2.1 (pH ~13) was unchanged over a period of 3 days. Gradual addition of sodium hydrogencarbonate caused decarboxylation to start at pH ~12.5. The pH changed to ~9.3 over a period of <5 min and only **2** (80%) and sodium carbonate were isolated from the resulting mixture.

At an elevated temperature the decarboxylation proceeds even in a strongly basic medium. In a simple preparative route to **2** sodium hydroxide and **1b** (molar ratio 2:1) were refluxed in water and most of the sodium carbonate was removed by filtration. Addition of abs. ethanol yielded a precipitate of **2** containing ca. 10% carbonate. Purification was relatively simple because **2**, like the sodium salt of **1b**,[2] forms a soluble ethanol solvate in abs. ethanol which is transformed into a sparingly soluble hydrate on addition of 5–10% of water. This procedure yielded analytically pure **2** (83%).

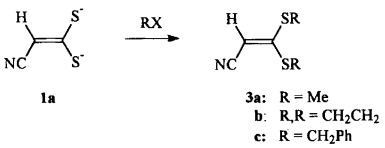
Anion **1a** is the strongest base in the series **1**. The $pK_a$ value of the corresponding acid calculated from the pH at half-neutralization and with application of Debye–Hückel correction[10] for deviations from ideality is 9.4. For comparison the analogously determined values for some known[2,3] anions **1** are: **1b**, 7.5; **1c**, 5.6; **1d**, 4.1. Compound **2** is stable and non-hygroscopic. The dry salt can be handled in air and stored for prolonged periods in a refrigerator. When moist the salt decomposes slowly, presumably by reaction with atmospheric carbon dioxide and formation of the unstable cyanodithioacetate ion (cf. Ref. 11). The IR spectrum of **2** shows the characteristic strong bands expected[12] for a cyano-stabilized 1,1-dithiolate: 2170 ($\nu_{CN}$), 1461 ($\nu_{C=C}$), and 900 ($\nu_{CSS}$) $cm^{-1}$.

Alkylation of **1a** gives 3,3-bis(alkylthio)propenonitriles (**3**) (Scheme 2). Previous approaches to this type of compound are: low-temperature lithiation of acetonitrile followed by condensation with dimethyl trithiocarbonate and alkylation[11] (40%) or with carbon disulfide and dialkylation[8] (40–53%), alkylation of the reaction mixture from acetonitrile, carbon disulfide and sodium in benzene[9] (78%), condensation of trimethylammonioacetonitrile with dialkyl trithiocarbonates[13] (50–58%) and thermal decarboxylation of 1,3-dithiolan-2-ylidenecyanoacetic acid.[14] While the alkylation of **1a** to give **3** may be carried out in homogeneous solution, e.g., in methanol, DMF or DMSO, a two-phase reaction in water with eventual addition of a phase-transfer catalyst is generally preferred. The advantages of the latter method include almost quantitative yields (>95%) of **3a–c**, improved solvent and waste economy and a simplified isolation procedure. Furthermore this technique allows the preparation of **3** from **1b** to be carried out as a one-pot operation with an unchanged overall yield.

The alkylation of trianion **4** followed by acidification (Scheme 3) yields 3,3-bis(alkylthio)-2-cyanopropenoic acids (**6**). Since the alkylation removes a strongly basic species it promotes the competing decarboxylation of **4** and makes **3** the main product in the absence of an excess of hydroxide ion. On the other hand, **6** even as the anion is electrophilic (cf., the formation of **7**, later) and an alkylthio group can be displaced by hydroxide ion. In consequence, the successful preparation of **6** requires a delicate balance between these two systematic side reactions. Optimum yields of **6a** were recorded when the hydrolysis of **1b** with two mole equivalents of sodium hydroxide at room temperature was interrupted shortly before its completion. Remaining **1b** and most of the excess hydroxide were washed out with ethanol and the aqueous phase was alkylated with dimethyl sulfate. These conditions gave **6a** (50–54%), **3a** (10–15%) and **1b**, recovered from the ethanol extract (10–20%).

With mono- and di-alkylamines 3,3-bis(methylthio)-2-cyanopropenic acid (**6a**) undergoes combined substitution and decarboxylation at room temperature to give *N*-substituted 3-amino-3-(methylthio)propenonitriles (**7**) as the main products. This reaction affords a synthetic alternative to the preparation of **7** from lithioacetonitrile and alkyl isothiocyanates.[15] The reaction requires from 1 day to more than 7 days for completion depending on the amine reactivity. Elevation of the reaction temperature only promotes the decarboxylation of **6a** to **3a**, which does not undergo substitution with amines,[11] at the expense of the substitution reaction.

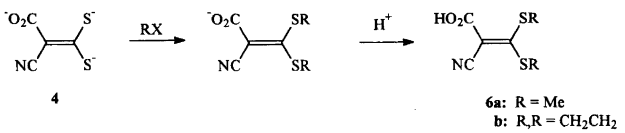
While the reaction with monoamines gives **7** rather cleanly the use of 1,2-diamines, or of 2-aminoethanthiol, leads to cyclized products, imidazolines (**9**) and 1,3-thiazolidine (**10**), respectively. These observations are in accord with the electrophilic substitution mechanism suggested in Scheme 1 for the decarboxylation. The replacement of sulfur with nitrogen on going from **3** to intermediate **8** not only lowers the rate of substitution but also renders the species more susceptible to C-protonation. Thus only the anchimerically assisted substitutions leading to **9** and **10** may compete efficiently




**1a**

**3a**: R = Me
**b**: R,R = $CH_2CH_2$
**c**: R = $CH_2Ph$

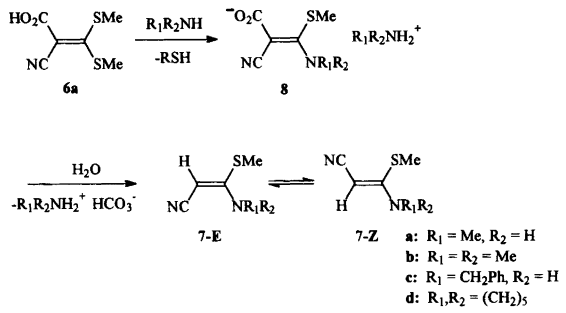
*Scheme 2.*




**4**

**6a**: R = Me
**b**: R,R = $CH_2CH_2$

*Scheme 3.*




*Scheme 4.*

with the decarboxylation to give **7**. The sequential nucleophilic substitution – electrophilic decarboxylation course shown in Scheme 4 is further substantiated by the observation by TLC of a polar intermediate, presumably **8**, and by the isolation of NC–CH=C(NHBz)$_2$ (**11**) as a by-product (3%) in the preparation of **7c**. Compounds **1–10** all are push–pull systems, i.e., species in which donor- and acceptor-substituents interact through an unsaturated carbon bridge. This interaction gives rise to some particular features in the NMR spectra. The characteristic chemical shift values are collected in Table 1. The signal from the vinylic proton in the $^1$H spectra of **1a**, **3** and **7–10** is found at relatively high field and the shielding increases with increasing donor strength: (SR)$_2$ 5.32–5.08; (S$^-$)$_2$ 4.72; (SR, NR$_2$) 4.20–3.67 and (NR$_2$)$_2$ 3.05–2.84 ppm. The $^{13}$C NMR spectra of push–pull ethylenes display a very distinct pattern. The resonances from the polarized C=C bond are widely separated, the resonance from the donor-substituted carbon occurring at high field and that from the acceptor-substituted carbon at low field, while the resonances from the remaining carbon atoms occur within their expected ranges. The previously[16] predicted dependence of the polarization upon the strength of the donor groups is supported by the present results. Thus the separation of the ethylenic carbons ($\Delta\delta$) is 67–86 for the donor combination (SR)$_2$ in **3**, 94–115 for SR, NR$_2$ in **7**, **10** and 121–133 for (NR$_2$)$_2$ in **9**, **11**. The values recorded for the salts of **1a–b**, decreases from DMSO to water showing that anion solvation moderates the donor strength of S$^-$.

The spectra of the *N*,*S*-substituted compounds, **7** and **10**, show the presence of *E*- and *Z*-forms as discrete entities on the NMR timescale. However, the ratio of the two forms in a given sample varies with the solvent indicating that the two forms equilibrate at room temperature. For example, the ratio **7a**-*Z*:**7a**-*E* is 3:1 in $CDCl_3$ and >19:1 in DMSO-$d_6$. Similar behaviour, displayed by the related 2-acylketene *N*,*S*-acetals has recently been described.[17] Crystallization may give rise to one pure form, as evidenced by the sharp melting points of **7a** and **10**, or to a mixture of *E*- and *Z*-isomers as in the case of **7c**, an analytically pure sample of which displays a melting point interval of 5 °C. The assignment of NMR signals to *E*- and *Z*-isomers of **7** and **10** is based upon the observation[11] that an *S*-methyl substituent is deshielded by a *cis* cyano-group. It is further consistent with an increase in the *Z*:*E*-ratio on going from the methylamino- (**7a**) to the more bulky dimethylamino-

*Table 1.* Characteristic NMR chemical shifts, $\delta$ in $CDCl_3$, unless otherwise specified.

| | | $^{13}$C | | | |
|---|---|---|---|---|---|
| Compound | $^1$H –CH= | =CS$_2$, =C(S)N *or* =CN$_2$ | =CH–CN *or* =C(Y) CN | C≡N | C=O |
| **1b**[a] | | 225.2 | 90.2 | 125.7 | 166.8 |
| **1b**[b] | | 222.9 | 95.9 | 129.1 | 170.0 |
| **1a**[a] | 4.7 | 205.2 | 81.9 | 128.0 | |
| **1a**[b] | [c] | 196.0 | 89.1[c] | 127.0 | |
| **3a** | 5.08 | 163.6 | 86.2 | 115.6 | |
| **3b** | 5.32 | 168.8 | 81.0 | 117.6 | |
| **3c** | 5.23 | 160.4 | 93.4 | 116.0 | |
| **4**[b] | | 200.2 | 103.9 | 130.5 | 176.0 |
| **6a** | | 179.6 | 99.6 | 116.4 | 162.9 |
| **6b** | | 184.8 | 88.2 | 116.6 | 163.6 |
| **7a**-*E* | 3.67 | 161.3 | 62.2 | 121.0 | |
| **7a**-*Z* | 4.00 | 166.7 | 57.6 | 120.2 | |
| **7b**-*E* | 3.88 | 161.7 | 67.9 | 119.6 | |
| **7b**-*Z* | 4.11 | 165.6 | 59.7 | 119.6 | |
| **7c**-*E* | 3.73 | 165.5 | 57.6 | 119.4 | |
| **7c**-*Z* | 4.14 | 159.8 | 63.8 | 120.2 | |
| **7d**-*E* | 4.08 | 167.5 | 64.6 | 119.9 | |
| **7d**-*Z* | 4.23 | 164.6 | 71.5 | 120.5 | |
| **9a** | 2.94 | 166.0 | 33.2 | 123.9 | |
| **9b** | 3.01 | 164.5 | 34.2 | 123.5 | |
| **10**-*E*[a] | 3.95 | 168.0 | 53.7 | 121.9 | |
| **10**-*Z*[a] | 4.20 | 167.0 | 51.5 | 120.0 | |
| **11** | 2.84 | 161.9 | 40.5 | 123.5 | |

[a] In DMSO-$d_6$. [b] In $D_2O$. [c] Rapid exchange of CH; additional $^{13}$CD signal at 87.8 ppm (t, $J$=77 Hz).

substituent (**7b**). In the case of **7a** and **7c** the present assignments constitute a reversal of that of Ref. 15. In addition to the *E*- and *Z*-isomers solutions of **10** contain the (4,5-dihydro-1,3-thiazol-2-yl)acetonitrile tautomer (**10′**) as the predominant constituent under non-polar conditions. The ratio **10-*Z*:10-*E*:10′** is approximately 20: 30: 50 in $CDCl_3$ and 75: 20: 5 in DMSO-$d_6$.

## Experimental

NMR spectra were recorded on a Jeol FX 90 Q instrument ($^1H$ at 90, $^{13}C$ at 22.53 MHz). Microanalyses were performed by the Microanalysis Division of this department.

*Determination of pK values.* A solution, 0.01 M each in dithiolate ion and hydrogen dithiolate ion with an ionic strength $I=0.05$, was prepared by dissolving freshly recrystallized sodium dithiolate (0.50 mmol and HCl (0.25 mmol) in degassed water (25 ml). The pH was measured with a glass electrode calibrated with standard pH 4.0 and 7.0 buffers. The $pK_A$ values were calculated using the relationship[10] $pK_A = pH - \log f^{2-} + \log f^{-}$, where activity coefficients, $f$, were calculated from $-\log f = 0.5\, I^{1/2}\, n^2\, (1+I^{1/2})^{-1}$, giving $pK_A = pH + 0.27$.

*Sodium 2-cyano-2-ethoxycarbonylethylene-1,1-dithiolate pentahydrate* (**1b**) (modification of the procedure from Ref. 2). A mixture of carbon disulfide (0.5 mol) and ethyl cyanoacetate (0.5 mol) in abs. ethanol (0.5 l) was placed in a 1 l flask equipped with an efficient mechanical stirrer and cooled to −5 °C by immersion in an efficient cooling bath. A solution of sodium hydroxide (1.0 mol) in water (40 ml) was added at a rate that maintained a reaction temperature of between 0 and −5 °C. At the end of the addition the cooling bath was removed and stirring was continued for 10 min. The product was isolated on a Büchner funnel, washed on the filter with cold 95% ethanol (2 × 200 ml) and dried in air to constant weight. Yield of **1b** 153.5 g (0.475 mol, 95%); m.p. 83–84 °C (sealed tube). $^{13}C$ NMR (22.53 MHz, DMSO-$d_6$): δ 225.2, 166.8, 125.7, 90.2, 56.8, 15.0. While apparently pure this product may not be stable over a long period owing to decomposition catalyzed by small amounts of adhered base. Recrystallization by dissolution at 50 °C in 80% methanol (1 ml $g^{-1}$) and precipitation with 3 volumes of abs. ethanol yielded a product with a considerably improved shelf life.

*Sodium 2-cyanoethylene-1,1-dithiolate tetrahydrate* (**2**). A mixture of **1b** (32.3 g, 100 mmol) and 50% w/w aqueous sodium hydroxide (16.0 g, 200 mmol) in water (20 ml) was heated to reflux for 2 h and then stirred with cooling to room temperature. Precipitated sodium carbonate was removed by suction filtration and the filter cake was washed with abs. ethanol (4 × 25 ml). The combined filtrates were diluted with abs. ethanol to a volume of 400 ml and left in a freezer overnight. Precipitated material was filtered off, washed with cold 95% ethanol (50 ml) and dried (30 °C, 1.8 kPa) to constant weight. Yield 23.0 g of a product containing 7% sodium carbonate corresponding to 92% of **2**. The crude product was dissolved at 50 °C in abs. ethanol (14 ml $g^{-1}$). After filtration water (5%) was added and the solution was cooled to 0 °C. Isolation as above yielded **2a** (19.4 g, 83%); colorless crystals, m.p. 98–99 °C (sealed tube); anal. $C_3H_9NNa_2O_4S_2$ (C,H,N,S); $^1H$ NMR (DMSO-$d_6$): δ 4.70; $^{13}C$ NMR (DMSO-$d_6$): δ 205.4, 128.0, 81.8. IR (KBr-disc) 3500–2900 (br, s), 3052 (m), 2177 (s), 1646 (m), 1635 (m), 1461 (s), 900 (s) $cm^{-1}$.

*3,3-Bis(methylthio)propenonitrile* (**3a**). *(A) (From* **2***).* Dimethyl sulfate (7.6 g, 60 mmol) was added to a stirred solution of **2** (7.0 g, 30 mmol) in water (25 ml). An exothermic reaction with temperature rise to 60 °C took place within 2 min. The stirred mixture was cooled to 0 °C. The resulting precipitated solid was filtered off, washed with water and redissolved in dichloromethane–hexane (1:1). The solution was filtered through silica gel 60 (2 g) and evaporated to give **3a** as an oil which crystallized upon cooling. Yield 4.19 g (28.9 mmol, 96%). m.p. 36–37 °C (lit. 30 °C,[8] 37 °C,[11] 36 °C[13]). $^1H$ NMR ($CDCl_3$): δ 5.08 (1 H, s), 2.57 (3 H, s), 2.46 (3 H, s). $^{13}C$ NMR ($CDCl_3$): δ 163.6, 115.6, 86.2, 16.3, 15.5.

*B (From* **1b***).* A solution containing **1b** (55 mmol) and NaOH (112 mmol) in water (25 ml) was heated to reflux for 40 min and then cooled to 15 °C. Dimethyl sulfate (112 mmol) was added and the reaction mixture was worked up according to method A. Yield of **3a** 7.05 g (88%), identical ($^1H$ NMR and m.p.) with the product from A.

*1,3-Dithiolan-2-ylideneacetonitrile* (**3b**). To a solution of **2** (5.83 g, 25 mmol) in water (15 ml) was added 1,2-dibromoethane (4.70 g, 25 mmol) and tetrabutylammonium bromide (160 mg, 0.5 mmol). The mixture was stirred at room temperature until the organic phase solidified (3 h). The product was filtered off, washed with water and dissolved in dichloromethane–hexane (1:1; 10 ml). The solution was filtered through silica gel 60 (5 g) and eluted with 30 ml of the same solvent. Concentration of the solution to 10 ml and cooling gave an oil which crystallized to give **3b**. Yield 3.44 g (24.0 mmol, 96%). M.p. 39–41 °C (lit. oil,[8,13] 32 °C[14]). Anal. $C_5H_5NS_2$ (C,H,N). $^1H$ NMR ($CDCl_3$): δ 5.32 (1 H, s), 3.60 (4 H, s); $^{13}C$ NMR ($CDCl_3$): δ 168.5, 117.3, 80.4, 39.3, 39.1.

*3,3-Bis(Benzylthio)propenonitrile* (**3c**). This was prepared analogously from **2** (25 mmol), benzyl chloride (50 mmol) and tetrabutylammonium bromide (0.5 mmol). Yield of **3c** 7.20 g (24.2 mmol, 97%). M.p. 59–60 °C. Anal. $C_{17}H_{15}NS_2$ (C, H, N). $^1H$ NMR ($CDCl_3$): δ 7.30 (10 H, s), 5.24 (81 H, s), 4.27 (2 H, s), 4.00 (2 H, s); $^{13}C$ NMR ($CDCl_3$): δ 160.4, 135,5, 134.0,

129.0, 128.8, 128.6, 128.5, 127.9, 127.5, 116.0, 93.5, 38.9, 38.5.

*Detection of trianion* (**4**). Compound **1b** (5 mmol) and sodium hydroxide (11 mmol) in $D_2O$ (4 ml) were left in a stoppered tube for 3 days at room temperature after which the $^{13}C$ NMR spectrum of the solution was recorded: δ 200.2 (=$CS_2$), 176.0 ($^-CO_2^-$), 130.5 (C≡N), 103.9 (CH) and 59.3, 19.3 (EtOH); additional EtO-signals at δ 62.3 and 16.2 indicated ca. 10% changed **1b**.

*3,3-Bis(methylthio)-2-cyanopropenic acid* (**6a**). A mixture of **1b** (16.15 g, 50 mmol) and 50% aqueous NaOH (8.2 g, 102.5 mmol) was diluted with water to a total of 50 g and stirred at ca. 40 °C for 5 h. The resulting solution of **4** was cooled to room temperature and stirred for 5 min with abs. ethanol (50 ml) to give two phases which were separated. Dilution of the upper phase with abs. ethanol (45 ml) and cooling yielded unchanged **1b** (2.8 g, 17%). The lower phase was diluted with water to 100 ml and cooled in an ice bath to 5 °C. Dimethyl sulfate (12.6 g, 100 mmol) was added and the mixture was stirred for 1 h. The resulting precipitate of **3a** (0.78 g, 5.4 mmol, 12%) was filtered off. The filtrate was acidified with 4 M HCl and precipitated material was filtered off and washed with water. For purification it was dissolved in methanol (temperature not exceeding 50 °C). If needed, the solution was decolorized with a small amount of carbon. Addition, at ca. 45 °C, of 2 volumes of water and slow cooling to 0 °C gave **6a**. Yield 4.80 g (25.4 mmol, 51%). M.p. 156–157 °C (decomp.). Anal. $C_6H_7NO_2S_2$ (C, H, N). $^1H$ NMR (DMSO-$d_6$): δ 12.3 (br, 1 H), 2.68 (s, 3 H), 2.57 (s, 3 H). $^{13}C$ NMR (DMSO-$d_6$): δ 179.6, 162.9, 116.5, 99.6, 20.2, 18.6.

*1,3-Dithiolan-2-ylidenecyanoacetic acid* (**6b**). A solution of **4** prepared as above was diluted with DMSO (1 vol.), cooled to 5 °C, stirred with 1,2-dibromoethane (60 mmol) for 2 h and then diluted with water. Neutral components were removed by extraction with dichloromethane and **6b** was precipitated with 4 M HCl, washed with water and recrystallized from methanol. Yield 4.16 g (22.2 mmol, 44%). M.p. 239–240 °C (decomp.) [lit.[13] 215 °C (decomp.)]. Anal. $C_6H_5NO_2S_2$ (C, H, N). $^1H$ NMR: (DMSO-$d_6$) δ 3.67 (s, 4 H). $^{13}C$ NMR: δ 184.6, 163.6, 116.7, 88.2, 40.4, 37.3.

*3-Methylthio-3-(di)alkylaminopropenonitriles* (**7**), *imidazolidin-2-ylideneacetonitriles* (**9**) *and 1,3-thiazolidin-2-ylideneacetonitrile* (**10**): general procedure.* Compound **6a** (5.0 mmol) was dissolved in methanol (10 ml) and stirred at room temperature with the amine mixture specified below until the disappearance of **6a** was observed (TLC: $SiO_2$; dichloromethane–10% methanol). The solvent was removed and the residue was dissolved in dichloromethane and filtered through silica gel 60 (4 g). Evaporation of the filtrate left the almost pure product. By this procedure the following were prepared.

*3-Methylamino-3-(methylthio)propenonitrile* (**7a**). With 40% aqueous methylamine (1.2 g), reaction time 24 h, crude yield 540 mg (84%). Recrystallized from water: 430 mg (67%), m.p. 66–68 °C (lit.[15] not given). $C_5H_8N_2S$ (C,H,N). $^1H$ NMR identical with Ref. 15; $^{13}C$ NMR ($CDCl_3$): δ 161.3, 121.0, 62.3, 31.3, 16.0 (*Z*-isomer); 166.7, 120.2, 56.5, 31.3, 15.1 (*E*-isomer); (*Z*/*E*-ratio 3:1).

*3-Dimethylamino-3-(methylthio)propenonitrile* (**7b**). With 40% aqueous dimethylamine (1.5 g), reaction time 2 days, crude yield 520 mg (73%). Oil, $C_6H_{10}N_2S$ (C,H,N); $M^+$ 142. $^1H$ NMR ($CDCl_3$): δ 4.11 (s, 1 H), 3.05 (s, 6 H), 2.40 (s, 3 H) (*Z*-isomer); 3.92 (s, 1 H), 3.20 (s, 6 H), 2.33 (s, 3 H) (*E*-isomer). $^{13}C$ NMR ($CDCl_3$): δ 161.7, 119.6, 67.9, 39.9, 16,5 (*Z*-isomer); 165.6, 119.5, 59.8, 41.2, 15.8 (*E*-isomer); (*Z*/*E*-ratio 8:1).

*3-Benzylamino-3-(methylthio)propenonitrile* (**7c**). With benzylamine (6 mmol) and triethylamine (6 mmol), reaction time 4 days, crude yield 980 mg (89%), recrystallization from dichloromethane–hexane gave 805 mg (78%), m.p. 67–72 °C (*E*–*Z* mixture) (lit.[15] not given). $C_{11}H_{12}N_2S$ (C, H, N). $^1H$ NMR identical with Ref. 15; $^{13}C$ NMR ($CDCl_3$): δ (phenyl signals at 137–127 not specified) 159.8, 120.2, 63.8, 48.3, 15.5 (*Z*-isomer); 165.6, 119.4, 57.6, 47.9, 14.8 (*E*-isomer); (*Z*/*E*-ratio 3:1).

Elution of the silica gel filter with dichloromethane–10% MeOH yielded 45 mg (3%) of *3,3-bis(benzylamino)propenonitrile* (**11**), m.p. 88–90 °C (dichloromethane–pentane), $C_{17}H_{17}N_3$ (C, H, N), $M^+$ 263, $^1H$ NMR (DMSO-$d_6$): δ 7.45–7.0 (m, 10 H), 6.66 (t, $J$=6 Hz, 1 H), 6.34 (t, $J$=6 Hz, 1 H), 4.42 (d, $J$=6 Hz, 2 H), 4.10 (d, $J$=6 Hz, 2 H), 2.84 (s, 1 H); $^{13}C$ NMR: δ 161.5, 139.6, 138.8, 128.2, 126.9, 126.7, 123.7, 45.4, 44.8, 37.9.

*3-(Piperidin-1-yl)-3-(methylthio)propenonitrile* (**7d**). With piperidine (5.5 mmol) and triethylamine (5.5 mmol), reaction time 7 days, yield 34%. Oil, $C_9H_{14}N_2S$ (C, H, N,); $M^+$ 182. $^1H$ NMR ($CDCl_3$: δ 4.08 (1 H, s), 3.7–3.5 (4 H, m), 2.28 (3 H, s), 1.8–1.5 (6 H, m) (*E*-isomer); 4.23 (1 H, s), 3.45–3.25 (4 H, m), 2.34 (3 H, s) 1.8–1.5 (6 H, m) (*Z*-isomer); (*Z*/*E* ratio 8:1).

*Imidazolidin-2-ylideneacetonitrile* (**9a**). With 1,2- ethanediamine (12 mmol), reaction period 24 h. Almost quantitative precipitation of the carbonate of 1,2-ethanediamine was observed. The reaction mixture was diluted with one volume of ethyl acetate and washed through the silica gel filter with the same solvent. Crude yield 510 mg (94%); recrystallized from ethyl acetate–hexane, 415 mg (76%), m.p. 106–107 °C (lit.[18] 106 °C). $^1H$ NMR (DMSO-$d_6$); δ 6.80 (br, 2 H), 3.34 (s, 4 H),

* As methanethiol is produced in these preparations a trap containing conc. sodium hydroxide was inserted into the outlet from the reaction flasks.

2.94 (s, 1 H): $^{13}$C NMR (DMSO-$d_6$): δ 166.0, 123.9, 43.3, 43.1, 33.2.

*(1,3-Dimethylimidazolidin-2-ylidene)acetonitrile* (**9b**). With *N,N'*-dimethylethanediamine (7 mmol) and triethylamine (5 mmol), reaction period 2 days. An ammonium salt of **6a** precipitated immediately and dissolved slowly during the reaction. Crude yield 476 mg (69%); recrystallized from ether–pentane, 340 mg (50%), m.p. 32–33 °C. $C_7H_{11}N_3$ (C, H, N), $M^+$ 137; $^1$H NMR ($CDCl_3$): δ 3.32 (s, 4 H), 3.17 (s, 3 H), 3.01 (s, 1 H), 2.69 (s, 3 H); $^{13}$C NMR ($CDCl_3$): δ 164.5, 123.5, 50.7, 49.2, 35.7, 34.2.

*(1,3-Thiazolidin-2-ylidene)acetonitrile* (**10**). With 2-mercaptoethylammonium chloride (5.5 mmol) and triethylamine (11 mmol), reaction period 2 days. The dichloromethane solution was washed with 0.4 M acetic acid and 6 g $SiO_2$ was used for the subsequent filtration. Yield 525 mg (83%), m.p. 39–41 °C (lit.[19] oil; b.p. 118 °C at 4 mmHg). $C_5H_6N_2S$ (C, H, N), $M^+$ 126. $^1$H NMR (DMSO-$d_6$): δ 8.03 (br, 1 H), 4.20 (s, 0.78 H [**10**-*Z*]), 3.94 (s, 0.22 H [**10**-*E*]), 3.71–3.55 (m, 2 H), 3.44–3.19 (m, 2 H); $^{13}$C NMR (DMSO-$d_6$): δ 168.0, 121.9, 53.7, 49.2, 30.6 (*Z*-isomer); 167.0, 120.0, 51.5, 49.5,30.6 (*E*-isomer); ($CDCl_3$) 160.4, 114.7, 64.6, 36.0, 25.4 (**10'**).

## References


1. Dunn, A. D. and Rudorf, W.-D. *Carbon Disulfide in Organic Synthesis*, Ellis Horwood, Chichester 1989, pp. 153–159.
2. Söderbäck, E. *Acta Chem. Scand. 17* (1963) 362.
3. Söderbäck, E. *Acta Chem. Scand. 24* (1970) 228.
4. Brown, M. *U.S.Pat.* 3,057,875 (1960); *Chem. Abstr. 58* (1963) 6873.
5. Jensen, K. A. and Henriksen, L. *Acta Chem. Scand. 22* (1968) 1107.
6. Yokoyama, M. *J. Org. Chem. 35* (1970) 283.
7. Takeshima, T., Yokoyama, M., Fukada, N. and Akano, M. *J. Org. Chem. 35* (1970) 2438.
8. Creemer, L., Bargar, T. M. and Wagner, E. R. *Synth Commun. 18* (1988) 1103.
9. Sato, T., Kimura, K. and Mizukawa, H. *Jpn. Pat.* 01,047,769 (1987); *Chem. Abstr. 111* (1989) 97234a.
10. Wiberg, K. B. *Physical Organic Chemistry*, Wiley, New York 1964, p. 263.
11. Hartke, K. and Günther, O. *Liebigs Ann. Chem.* (1973) 1637.
12. Jensen, K. A. and Henriksen, L. *Acta Chem. Scand. 24* (1970) 3213.
13. Bhattacharjee, S. S., Ila, H. and Junjappa, H. *Synthesis* (1984) 249.
14. Kendall, J. D. and Edwards, H. D. *U. S. Pat.* 2,493,071 (1950); *Chem. Abstr. 44* (1950) 7346.
15. Yokoyama, M., Watanabe, S. and Hatanaka, H. *Synthesis* (1987) 846.
16. Henriksen, L. and Eggert, H. *Acta Chem. Scand., Ser. A 32* (1978) 701.
17. Dixit, A. N., Reddy, K. V., Deshmukh, A. R. A. S., Rajappa, S., Ganguly, B and Chandrasekhar, J. *Tetrahedron 51* (1995) 1437.
18. Meyer, H. and Kurtz, J. *Liebigs Ann. Chem.* (1978) 1491.
19. Rocheville-Divorne, C., Roggero, J-P. and Mousseron, M. *C. R. Acad. Sci. Paris 285* (1977) 257.


Received June 21, 1995.