

Arbeitsvorschriften und Meßwerte · Procedures and Data

An Alternative Synthesis of Sodium Cyanodithioformate and the Disodium Salt of *cis*-1,2-Dicyanoethylene-1,2-dithiol

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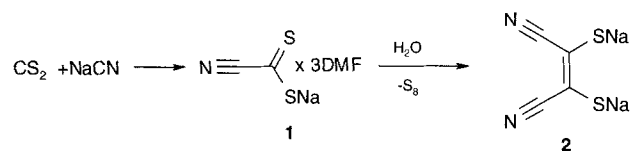
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Abstract. A new synthesis of sodium cyanodithioformate **1** and the disodium salt of *cis*-1,2-dicyanoethylene-1,2-dithiol **2** is reported. The key step involves a nucleophilic thiolation with

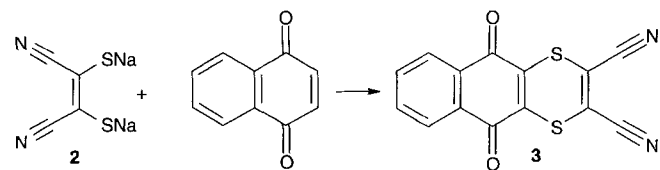
elemental sulfur starting from a substituted acetonitrile **4**. This method may serve as a cyanide- and carbondisulfide-free alternative in the preparation of the title compounds.

The sodium salts of cyanodithioformate **1** and 1,2-dicyanoethylene-1,2-dithiol **2** are very important building blocks both in the synthesis of heterocycles and in preparing chelating agents for thiophilic metals [1, 2].

Until now, these compounds have been prepared by the method of Bähr and Schleitzer by treating carbon disulfide with sodium cyanide [3, 4]. Sodium cyanodithioformate available in the first reaction step is dimerised under loss of elemental sulfur to the disodium salt of the ethylenedithiolate by various methods [5, 6].



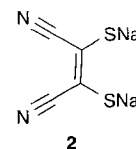
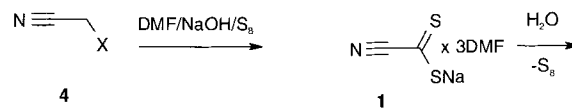
The formed *cis*-1,2-dicyanoethylene-1,2-dithiol can, for example, be used for the synthesis of the fungicide Dithianon by reaction with naphthoquinone [7].



The handling of carbon disulfide and sodium cyanide requires great care and therefore the possibility of an alternative process was explored.

In the course of our investigations into the mild thiolation of active methyl and methylene groups with elemental sulfur we tried to find a new approach to the dithiol **2** via the cyanodithioformate **1**. First attempts were made by our group some years ago [8].

By variation of the base, we were now able to prepare sodium cyanodithioformate **1** starting from a substituted acetonitrile **4**.



The yields differ depending on the leaving group. Best results were obtained by reacting chloroacetonitrile **4a** with sulfur in the presence of dry, finely powdered sodium hydroxide.

Table 1 Isolated yields of sodium cyanodithioformate **1** depending on the leaving group in **4**

| comp. 4 | X | Yield (%) |
|----------------|---|------------------|
| a | Cl | 98 |
| b | SMe | 40 |
| c | SPh | 10 ^{a)} |
| d | SCN | 51 |
| e | Py ⁺ Cl ⁻ | 58 |
| f | NEt ₃ ⁺ Cl ⁻ | 45 |

^{a)} not isolated but calculated after methylation and aqueous workup as *cis/trans*-mixture of 1,2-dicyano-1,2-dimethylthioethylene

These results were surprising, because most thiolation reactions fail when using a strong base such as *tert.*-butoxide or even dry sodium hydroxide.

The salt **1** prepared in this way gave as expected the disodium salt of *cis*-1,2-dicyanoethylene-1,2-dithiol **2**. Desulfurization occurred in water as well as in solid state.

In summary, we were able to find a cyanide-free way for the preparation of cyanodithioformate.

Even though the desulfurization process works nearly quantitative, the not readily available chloroacetonitrile makes the use of these procedure in industrial preparation prohibitive. However, the high yield of this synthesis makes these procedure an interesting alternative for laboratory use.

Experimental

Sodium Cyanodithioformate × 3DMF (**1**)

19.2 g (0.6 mol) sulfur and 24.0 g (0.6 mol) of finely powdered sodium hydroxide were dissolved in 70 ml DMF under vigorous stirring. The mixture was cooled by ice/water to confine the rise in temperature to about 50 °C. Then the mixture was cooled to 10 °C and 15.1 g (0.2 mol) chloroacetonitrile **4a** were added under vigorous stirring keeping the temperature between 15 and 20 °C. The mixture was then stirred for an additional hour at room temperature. After adding 100 ml of isobutanol, the mixture was filtered off. The filter cake was then extracted twice with 20 ml of isobutanol at a temperature of 60 °C. An equal amount of ether was added and the product was crystallized at -20 °C in a refrigerator. The product was

separated by suction filtration, washed with ether and dried over phosphorus pentoxide.

Yield 61–67 g (88–97%) brown crystals. – ¹³C NMR (300 MHz/ DMSO): δ/ppm = 117 (CN), 207.7 (CS). – IR: (identical with an authentic sample)

cis-1,2-Dicyanoethylene-1,2-dithiol Disodium Salt (aqueous solution) [9] (**2**)

3.44 g (10 mmol) sodium cyanodithioformate × 3 DMF **1** dissolved in 30 ml water were allowed to stand at room temperature for 24 h. Sulfur precipitated was collected by suction filtration and dried. The amount was nearly quantitatively (0.31 g, 97%). The yield of **2** was determined by UV-spectrophotometry and found to be 96%.

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