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NEW SYNTHETIC METHOD OF THIOALDEHYDES FROM β-IMINO-NITRILES AND DITHIOFORMATE

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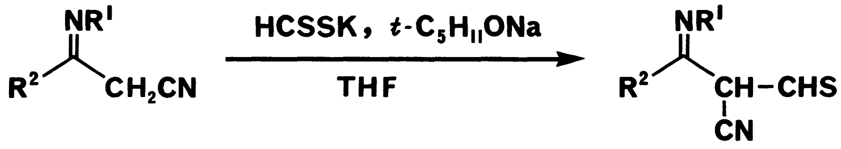
A series of stable monomeric α-cyano-β-imino-thioaldehydes were synthesized from β-imino-nitriles and potassium dithioformate.

There have been numerous challenges that aim at the preparation of simple thioaldehydes so far. The products obtained, however, were cyclic or linear polymers instead of the expected monomeric thioaldehydes. Exceptionally, a few thioaldehydes have been prepared when the thioformyl group is stabilized by conjugation. Woodward and his co-workers first synthesized the stable monomeric thioaldehyde, 5-thioformyldipyrrylmethane derivative, in the course of Woodward's synthesis of chlorophyll-a.[1)] McKenzie and Reid established the first general method of preparation of thioaldehydes, which involves a novel application of Vilsmeier salt.[2-5)] In addition, the following three other preparative methods are now available; (1) from 1,2-dithiole-3-thiones and acetylenedicarboxylate,[6)] (2) from 1,2-dithiolium salt and ω,ω'-diamines,[7,8)] and (3) from phosphorous ylides and ethyl thionoformate.[9)]

The development of an effective method for the synthesis of stable thioaldehydes is of particular interest. We wish to report a new synthetic method of the thioaldehydes, which involves an application of dithioformate.

Potassium dithioformate, when treated with β-imino-nitriles in an aprotic solvent such as tetrahydrofuran in the presence of sodium 1,1-dimethylpropanolate, gave the expected monomeric thioaldehydes. Polar aprotic solvents were unsuitable for this reaction. α-Cyano-β-imino-thioaldehydes were prepared as follows: A mixture of freshly prepared β-imino-butyronitrile or β-aryl-β-imino-propiononitrile (10.4 mmol), potassium dithioformate (1.20 g, 10.3 mmol), sodium 1,1-dimethylpropanolate (2.72 g, 24.7 mmol), and tetrahydrofuran (80 ml) was stirred at room temperature for 24 h. After the addition of water (100 ml), the aqueous solution was acidified with 2N-hydrochloric acid to pH ca. 2, the resulting red oil which



	R^1	R^2		R^1	R^2
1	H	CH_3	**5**	H	β-$C_{10}H_7$
2	H	p-$CH_3C_6H_4$	**6**	CH_3	p-$CH_3C_6H_4$
3	H	m-$CH_3C_6H_4$	**7**	CH_3	m-$CH_3C_6H_4$
4	H	p-$CH_3OC_6H_4$			

Scheme 1

separated was dissolved in ether, and the ether solution was dried over magnesium sulfate. The ether was removed under diminished pressure to leave red oil, which solidified on addition of the mixed solvent of toluene and hexane. The resulting solid was collected, washed with hexane, and dried. Recrystallization from aromatic hydrocarbon or ethanol-water gave orange or yellow needles.

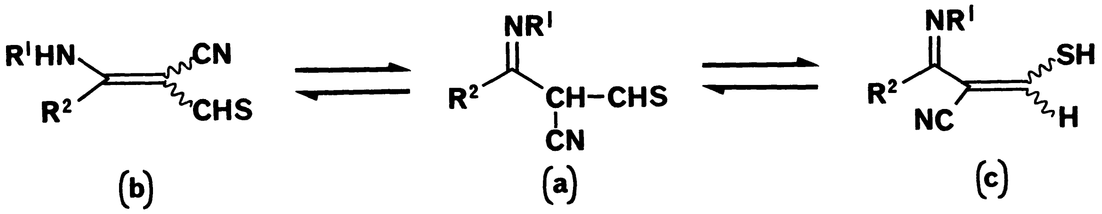
All the thioaldehydes synthesized here are exceedingly stable and have definite melting points. The observed molecular weights (osmometry) revealed that these thioaldehydes exist in monomeric state (see Table 1).

Table 1. α-Cyano-β-imino-thioaldehydes **1** – **7**[a]

Compd	Mp (°C) (solvent)	Yield (%)	Appearances	Mw[b] (osmometry)[c]
1	131 – 132 (C_6H_6-C_6H_{12})	23	Dark red prisms	126.7 (126.18)
2	155 – 156 (C_6H_6)	96	Orange needles	203.7 (202.27)
3	109 – 111 (EtOH-H_2O)	64	Orange needles	200.0 (202.27)
4	181 – 182 (toluene)	73	Dark orange needles	217.1 (218.27)
5	166 – 167 (xylene)	64	Orange prisms	239.4 (238.31)
6	125 – 126 (EtOH-H_2O)	45	Yellow needles	216.5 (216.30)
7	120.5-121 (EtOH-H_2O)	37	Yellow needles	214.0 (216.30)

[a] All the compounds had satisfactory microanalyses. [b] Mass spectrum also had M^+ (M^+– 1; 100%) in each case. [c] Acetone used as solvent and theoretical molecular weight in parentheses.

It was strongly supported that compounds **1** – **7** are not thioformamides but thioaldehydes from their spectral properties.[10] The IR, UV, and visible spectra resembled closely with those of α-cyano-β-imino-dithiocarboxylic acids.[11] It was confirmed by the NMR spectra that compounds **1** – **7** are of thioaldehydes. For example, in the NMR spectrum of **2** in hexadeuterioacetone, there appear two singlet peaks corresponding to thioformyl proton at δ 10.58 and 10.16 (total 1H) which are well in agreement with those of thioaldehydes reported.[4,6,8] Further, two very broad singlet peaks at δ 13.26 (0.45H) and 8.50 (1.4H) due to the amino protons in the enamino form of **2** (**2b**), which disappeared on addition of heavy water, indicate that compounds **1** – **7** are to be undoubtedly of thioaldehyde structure. A amall singlet peak at δ 9.39 is attributable to an SH proton of tautomeric thioenol (**2c**). The vinylic proton in tautomer (**1c**) is observed at fairly low field (δ ca. 7.3).



Scheme 2

N-Methyl-β-imino-β-(p-tolyl)- and N-methyl-β-imino-β-(m-tolyl)-propiononitriles in this reaction likewise gave respective thioaldehydes. NMR spectrum of **7** also had two very broad peaks at δ 14.0 and 8.33 (total 0.8H) due evidently to an imino proton of the enamino form of **7**.

Synthesis of another type of thioaldehydes by the reaction of dithioformate towards other conjugation-stabilized carbanions and the applicability of the thioaldehydes mentioned above for organic synthesis are at present under progress.

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10) The spectral data of the β-imino-thioaldehydes **1** – **7** are as follows (in the NMR spectra, merely NH_2, NH, CHS, SH, vinylic and methine protons were described): **1**; $\nu_{max.}$(KBr) 3230, 2205, 1650, 1605, 1443, 1242 cm^{-1}; $\lambda_{max.}$(EtOH) 247 (log ε 3.91), 364.5 nm (4.18); δ (CD_3COCD_3) 13.02 and 9.40 (all br. s, 1.8H, NH_2), 10.49 and 10.21 (all s, 1H, CHS), 9.12 (s, 0.15H, SH), and 7.31 ppm (s, 0.15H, =CH-); **2**; $\nu_{max.}$(KBr) 3290, 2206, 1631, 1449, 1240, and 1000 cm^{-1}; $\lambda_{max.}$(EtOH) 265 (log ε 3.90) and 378 nm (4.36); δ (CD_3COCD_3) 13.26 and 8.50 (all br. s, 1.8H, NH_2), 10.58 and 10.16 (all s, 1H, CHS), 9.39 (s, 0.2H, SH), and 2.24 ppm (s, trace, C$\underline{H}$CNCHS); **3**; $\nu_{max.}$(KBr) 3270, 2205, 1631, 1460, 1260, and 1008 cm^{-1}; $\lambda_{max.}$(EtOH) 261 (log ε 3.88) and 376 nm (4.35); δ (CD_3COCD_3) 13.30 and 8.60 (all br. s, 2H, NH_2), 10.59 and 10.14 (all s, 1H, CHS),9.38 (s, trace, SH), and 2.69 ppm (s, trace, C$\underline{H}$CNCHS); **4**; $\nu_{max.}$(KBr) 3295, 2205, 1640, 1604, 1450, 1260, 1184, 1020, and 1000 cm^{-1}; $\lambda_{max.}$(EtOH) 266 (log ε 3.74), 297 (3.74), and 381 nm (4.43); δ (CD_3COCD_3) 13.20 and 8.66 (all br. s, 2H, NH_2), 10.54 and 10.21 (all s, 1H, CHS), 9.38 (s, 0.05H, SH), and 2.27 ppm (s, 0.05H, C$\underline{H}$CNCHS); **5**; $\nu_{max.}$(KBr) 3296, 3200, 2206, 1621, 1480, 1442, 1237, and 1000 cm^{-1}; $\lambda_{max.}$(EtOH) 250 (log ε 4.09), 265 (4.11), and 381 nm (4.41); δ (CD_3COCD_3) 13.38 and 8.78 (all br. s, ca. 2H, NH_2), 10.66 and 10.23 (all s, 1H, CHS), 9.46 (s, 0.05H, SH), and 2.31 ppm (s, 0.05H, C$\underline{H}$CNCHS); **6**; $\nu_{max.}$(KBr) 3215, 2206, 1602, 1442, 1426, 1403, 1305, 1150, and 1052 cm^{-1}; $\lambda_{max.}$(EtOH) 261 (log ε 3.86) and 379 nm (4.38); δ (CD_3COCD_3) 14.46 and 8.49 (all br. s, 0.5H, NH), 10.41 and 10.14 (all s, 1H, CHS), 9.83 (s, 0.1H, SH), and 3.62 ppm (s, 0.15H, C$\underline{H}$CNCHS); **7**; $\nu_{max.}$(KBr) 3240, 2208, 1570, 1380, 1295, 1144, 1045, and 992 cm^{-1}; $\lambda_{max.}$(EtOH) 258 (log ε 3.79) and 378 nm (4.36); δ (CD_3COCD_3) 14.00 and 8.33 (all br. s, 0.8H, NH), 10.17 and 9.92 (all s, 1H, CHS), 9.53 (s, 0.2H, SH), and 3.51 ppm (s, 0.2H, C$\underline{H}$CNCHS).

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