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The Decomposition Product of Ethyl 2-Cyano-3-mercapto-3-methylthioacrylate

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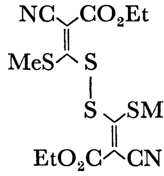
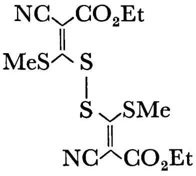
2-Cyano-3-mercapto-3-methylthioacrylamide is stable but the 2-cyano-3-mercapto-3-methylthioacrylic acid ethyl ester (**1**) obtained as colorless needles has been found to be unstable and to change easily into a stable yellow material after being left standing for several hours at room temperature.[1] The present work was undertaken in order to determine the structure of the yellow material derived from **1**.

It was found that heating solution (in EtOH or CS_2) of **1** gave yellow material (**2**), which was also synthesized by adding hydrogen sulfide to disulfide (**3**) prepared by oxidizing **1** with ammonium persulfate.

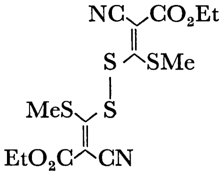
Structural assignments of **2** and **3** were made on the basis of elemental analysis, IR and NMR spectra. The NMR spectrum (DMSO-d_6) of **3** showed two signals due to two methylthio groups at δ 2.77 and δ 2.63, two quartet signals at δ 4.25 and δ 4.23, and two triplet signals at δ 1.27 and δ 1.25 which were assignable to the two ethyl groups. The following three structures can be considered for **3**.



A



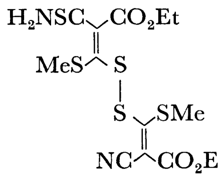
B



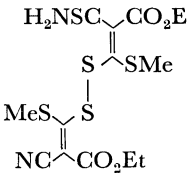
C

It was demonstrated by tlc that **3** was not a mixture of geometrical isomers. The above results supported the view that **3** has the structure of B, for only B has nonequivalent methylthio and ethyl groups. Hence, the structure of **3** was determined to be diethyl (1*Z*, 5*E*)-1,6-dicyano-2,5-bis(methylthio)-3,4-dithia-1,5-hexadiene-1,6-dicarboxylate.

In the IR spectrum (KBr) of **2**, the absorptions of 3305, 3190, 3150, and 2195 cm^{-1} suggested the presence of the amino group and the conjugated cyano group. The NMR spectrum (DMSO-d_6) of **2** showed two broad amino signals (δ 10.70 and 9.68) disappearing on deuterium exchange and two sharp singlet singlas (δ 2.87 and 2.33) due to two methylthio groups. The spectroscopic evidence revealed the presence of the two nonequivalent thiocarbamoyl groups. The result of tlc revealed that **2** existed as two geometrical isomers (see Experimental). Hence, the decomposition products were tentatively assigned to the structures of diethyl (1*E*, 5*E*)-6-cyano-2,5-bis(methylthio)-1-thiocarbamoyl-3,4-dithia-1,5-hexadiene-1,6-dicarboxylate (**2a**) and diethyl (1*Z*, 5*Z*)-6-cyano-2,5-bis(methylthio)-1-thiocarbamoyl-3,4-dithia-1,5-hexadiene-1,6-dicarboxylate (**2b**).



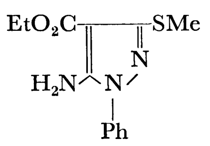
2a



2b

Compounds **2a** and **2b** were not separated.

Pyridine cleaved both **2** and **3** to give pyridinium salt of **1** (**5**). Compounds **1**, **2**, and **3**, treated with phenylhydrazine, gave 5-amino-4-ethoxycarbonyl-3-methylthio-1-phenyl-1,2-pyrazole (**4**). The chemical reactivities also supported the structure of **2**.



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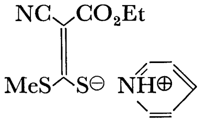

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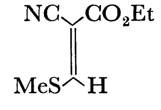

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The decomposition reaction of **1** could not be carried out in a sealed tube *in vacuo* without the irradiation of an ultraviolet ray (234 nm). On the other hand, the reaction could be depressed by the addition of hydroquinone as a radical trapping reagent. A small amount of ethyl (*E*)-2-cyano-3-methylthioacrylate (**6**) was isolated as a by-product of the decomposition reaction of **1**. This suggests that **1** is degraded by a radical mechanism.

Experimental

Compound **1** was prepared according to the method of Gompper and Töpfel.[2] The NMR spectra were recorded with a JNM-4H-100 MHz spectrometer, using tetramethylsilane as an internal standard. The IR, UV and mass spectra were recorded with Nihon Densi 403 G, Hitachi EPS-3T, and Hitachi Double Focus RMU-6E, respectively. Microanalyses were carried out at the Institute of Physical and Chemical Research.

*Preparation of **2a** and **2b**.* A mixture of **1** (7.55 g) and carbon disulfide or ethanol (100 ml) was refluxed for 1 hr. The crude material was collected by filtration, washed with ethanol and recrystallized from ethanol to give 1.40 g of yellow needles: yield 17%; mp 136—138°C; UV max (99% EtOH) 224 nm (log ε 4.25), 240 (sh, 4.16), 294 (sh, 4.14), 334 (4.53); NMR (DMSO-d_6) δ 10.70, 9.68 (br, 2, NH_2), 4.40, 4.38, 3.98, 3.96 (q, 2, $C\underline{H}_2$, J=7.5 Hz), 2.89, 2.87, 2.33, 2.30 (s, 3, $SC\underline{H}_3$), 1.35, 1.32, 1.15, 1.12 (t, 3, $C\underline{H}_3$, J=7.5 Hz).

Found: C, 38.02; H, 4.15; N, 6.35; S, 36.52%; mol wt (Rast), 440. Calcd for $C_{14}H_{18}N_2S_5O_4$: C, 38.33; H, 4.15;

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[1] M. Yokoyama, This Bulletin, **44**, 1610 (1971).

[2] R. Gompper and W. Töpfel, *Chem. Ber.*, **95**, 2861 (1962).

N, 6.38; S, 36.55%; mol wt, 438.62.

Compound **2** also was obtained when an ultraviolet light of 234 nm was irradiated on a sealed tube *in vacuo* containing **1** for 16 hr by using a minerallight UVSL-25 (Ultraviolet Products Inc. 13.8 W).

When **2** was examined by tlc with methanol and benzene (1 : 3) as a developing solvent, two spots (R_f: 0.72, 0.70) could be recognized.

*Conversion of **3** into **2**.* Compound **3** was prepared by the method of Gompper and Töpfel[2]: **1** (9.2 g, 45 mmol) was dissolved in 100 ml of 2% sodium hydroxide solution. To the resulting mixture was added aqueous ammonium persulfate solution (10.3 g of ammonium persulfate in 50 ml of water) dropwise under stirring. Stirring was continued for several minutes after the addition was complete. The solid product was collected and recrystallized from ethanol to give 3.5 g of colorless plates: yield 38%; mp 125—126°; UV max (99% EtOH) 255 nm (log ε 4.23), 335 (4.61); NMR (DMSO-d_6) δ 4.25, 4.23 (q, 2, $C\underline{H}_2$, J= 2.5 Hz), 2.77, 2.63 (s, 3, $SC\underline{H}_3$), 1.27, 1.25 (t, 3, $C\underline{H}_3$, J= 2.5 Hz).

Into a 200 ml acetone solution containing **3** (4.75 g) was gently passed hydrogen sulfide for 1 hr with stirring at room temperature. The whole was shaken for an additional 1 hr. The yellow crystals were collected and recrystallized from ethanol to give 2.8 g of yellow needles; yeild 54.2%. The IR spectrum coincided with that of **2**.

*Preparation of **4**.* A mixture of **3** (3.2 g, 8 mmol), phenylhydrazine (1.58 ml, 15.8 mmol), and ethanol (25 ml) was refluxed for 45 min. The colorless product was collected and recrystallized from ethanol-water to give 0.41 g of colorless needles; mp 98°C; UV max (99% EtOH) 248 nm (log ε 4.78); IR (KBr) 3440, 3340 (s), 3050 (w), 2985, 2920 (m), 1668 (vs), 1605 (vs), 1525 cm^{-1} (vs); NMR (DMSO-d_6) δ 7.50 (m, 5, $C_6\underline{H}_5$), 6.30 (br, 2, $N\underline{H}_2$), 4.20 (q, 2, $C\underline{H}_2$, J= 6 Hz), 2.38 (s, 3, $SC\underline{H}_3$), 1.25 (t, 3, $C\underline{H}_3$, J=6 Hz).

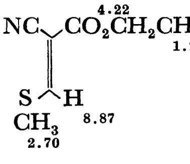
Found: C, 56.24; H, 5.44; N, 15.28; S, 11.52%; mol wt (Rast), 276. Calcd for $C_{13}H_{15}N_3SO_2$: C, 56.27; H, 5.49; N, 15.15; S, 11.56%. mol wt, 277.4.

*Preparation of **5**.* 11.35 g of **5** was obtained as yellowish prisms by dissolving **1** (9.75 g, 50 mmol) in pyridine, followed by the addition of ether. Compound **5** decomposed at 120—130°C; UV max (99% EtOH) 223.5 nm (log ε 4.73), 289 (4.57), 343.8 (5.06); IR (KBr) 3240, 3180 (m), 3080 (s), 2200 (vs), 1640 (vs), 1530 cm^{-1} (vs); NMR (DMSO-d_6) δ 8.65 (t, 2, C(2,6)$\underline{H}$, J=8 Hz), 8.10 (t, 3, C(3,4,5)$\underline{H}$, J= 8 Hz), 7.35 (br, 1, $N\underline{H}^{\oplus}$), 4.02 (q, 2, $C\underline{H}_2$, J=6 Hz), 2.38 (s, 3, $SC\underline{H}_3$), 1.18 (t, 3, $C\underline{H}_3$, J=6 Hz). The signal of δ 7.35 disappeared on deuterium exchange. Compound **1** was recovered by adding dilute hydrochloric acid to the aqueous solution of **5**. Compound **5** was also obtained by the above method from **2** and **3** in yields of 98% and 48%, respectively.

*Isolation of Ethyl (E)-2-cyano-3-methylthioacrylate (**6**).* A mixture of **1** (1.36 g) and 50 ml of ethanol was refluxed for 20 min. 0.82 g of **2** was filtered off and the resulting filtrate was evaporated with a vacuum evaporator to give a red oil, which was then extracted by shaking with two 50 ml portions of ether. A small amount of yellow crystal was obtained from the extracted ether and recrystallized from *n*-hexane to give yellowish plates; mp 68—69°C; UV max (99% EtOH) 304 nm (log ε 4.21); IR (KBr) 3005 (m), 2980, 2919 (m), 2210 (s), 1705 (vs), 1538 cm^{-1} (vs).

Found: C, 49.33; H, 5.02; N, 8.06; S, 18.63%; mol wt (mass spectrum) 171. Calcd for $C_7H_9NOS_2$: C, 49.11; H, 5.32; N, 8.18; S, 18.73%; mol wt, 171.23. A vinyl proton at δ 8.87 is just in the range expected for one of the *E*-form.[3]

*Geometrical Structure of **1**.* The NMR spectrum of **6** showed a singlet signal due to methylthio group at δ 2.70. The two singlet signals due to the two methylthio groups of ethyl 2-cyano-3,3-bis(methylthio)acrylate were observed at δ 2.72 and 2.52, which seem assignable to the *cis* methylthio group and the *trans* methylthio group with respect to the cyano group, respectively. This supports the conclusion that **1** in DMSO-d_6 can exist only in **1a** because the NMR spectrum of **1** shows a singlet signal at δ 2.70. The chemical shifts are summarized as follows:



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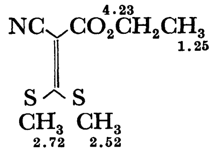

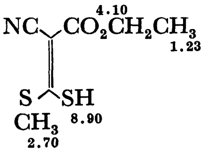

1a

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3) V. E. Matter, C. Pascual, E. Pretsch, A. Pross, W. Simon, and S. Sternhell, *Tetrahedron*, **25**, 691 (1969).