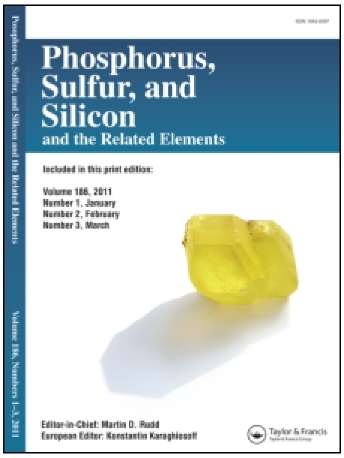

## Phosphorus, Sulfur, and Silicon and the Related Elements

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# SYNTHESIS OF HETEROCYCLIC COMPOUNDS FROM DIPOTASSIUM 1,1-DIMERCAPTO-2,2-DICYANOETHYLENE

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# SYNTHESIS OF HETEROCYCLIC COMPOUNDS FROM DIPOTASSIUM 1,1-DIMERCAPTO-2,2-DICYANOETHYLENE[1,2]

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The reaction of dipotassium 1,1-dimercapto-2,2-dicyanoethylene with 3-bromo-1-propyne, 3-chloro-3-methyl-1-propyne, 3-chloro-2,4-pentanedione, ethyl α-chloroacetoacetate or chloroacetone afforded novel heterocyclic compounds (**1–5**). Possible mechanisms and supporting NMR and mass spectra are discussed.

Dipotassium-1,1-dimercapto-2,2-dicyanoethylene was first prepared in 1950 by Edwards and Tendall[3] but was not isolated. Brown[4] in 1962 reported an elegant synthesis for this salt and also established its structure.

$$CH_2(CN)_2 + CS_2 + 2KOH \xrightarrow{C_2H_5OH} (KS)_2C{=}C(CN)_2 \qquad (1)$$

The chemistry of this salt has received comparatively little attention until 1962 when several publications appeared.[5–15] This is surprising in view of the potential of this salt as a low-cost chemical intermediate.

We wish to report the synthesis of novel heterocyclic compounds derived from dipotassium-1,1-dimercapto-2,2-dicyanoethylene.

The reaction of the dipotassium salt with 3-bromo-1-propyne or 3-chloro-3-methyl-1-propyne afforded the monoalkylation product followed by cyclization to give (4-methylene-1,3-dithiolan-2-ylidene)propanedinitrile (**1**) and 2-cyano-2-(4-methyl-5-methylene-1,3-dithiolan-2-ylidene)acetamide (**2**), respectively. However, based on only elemental analysis and molecular weight data the six-membered heterocycle **A** had to be considered. The presence of the exocyclic methylene group in **1** and **2** was confirmed by the NMR spectral data and thus ruled out structure **A**. Moreover, the hydration of one of the cyano to amido group for **2** was also confirmed by the NMR data.

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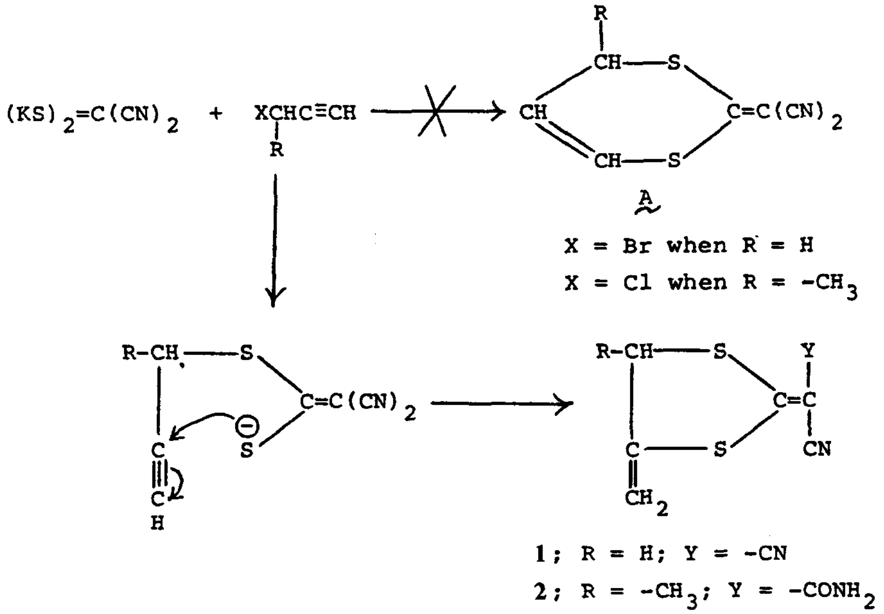
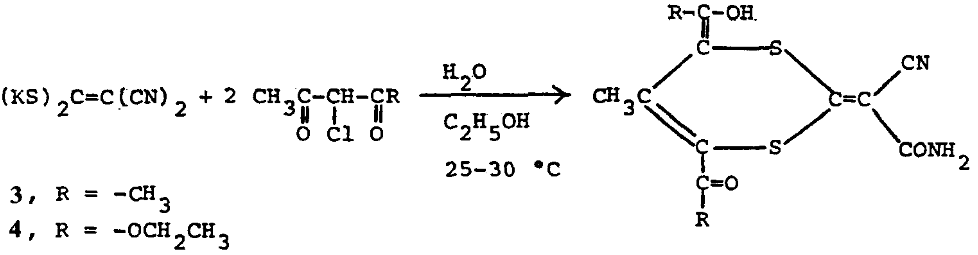


(2)

Moreover, the mass spectra data were in agreement for the proposed structures **1** and **2**.

The reaction of the dipotassium salt with 3-chloro-2,4-pentanedione, ethyl α-chloroacetoacetate and chloroacetone afforded 2-[6-acetyl-4-(1-hydroxyethylidene)-5-methyl-4*H*-1,3-dithiin-2-ylidene]-2-cyanoacetamide (**3**), ethyl 2-(2-amino-1-cyano-2-oxoethylidene)-4-(ethoxyhydroxmethylene)-5-methyl-4*H*-1,3-dithiin-6-carboxylate (**4**) and 2-(6-acetyl-5-methyl-4*H*-1,3-dithiin-2-ylidene)-2-cyanoacetamide (**5**), respectively. [Reactions (3) and (4).]



NMR ($CDCl_3$), R = $CH_3$, **3**

ppm

2.28; $\underline{CH_3}C\begin{smallmatrix}\diagup C\\ \diagdown\diagdown\end{smallmatrix}$

2.42; $CO\underline{CH_3}$ and $-\underset{\underset{C}{\|}}{C}-\underline{CH_3}$

6.71; $CO\underline{NH_2}$

17.43; $\underline{H}O-C$

NMR ($CDCl_3$), R = $-OCH_2CH_3$, **4** (3)

ppm

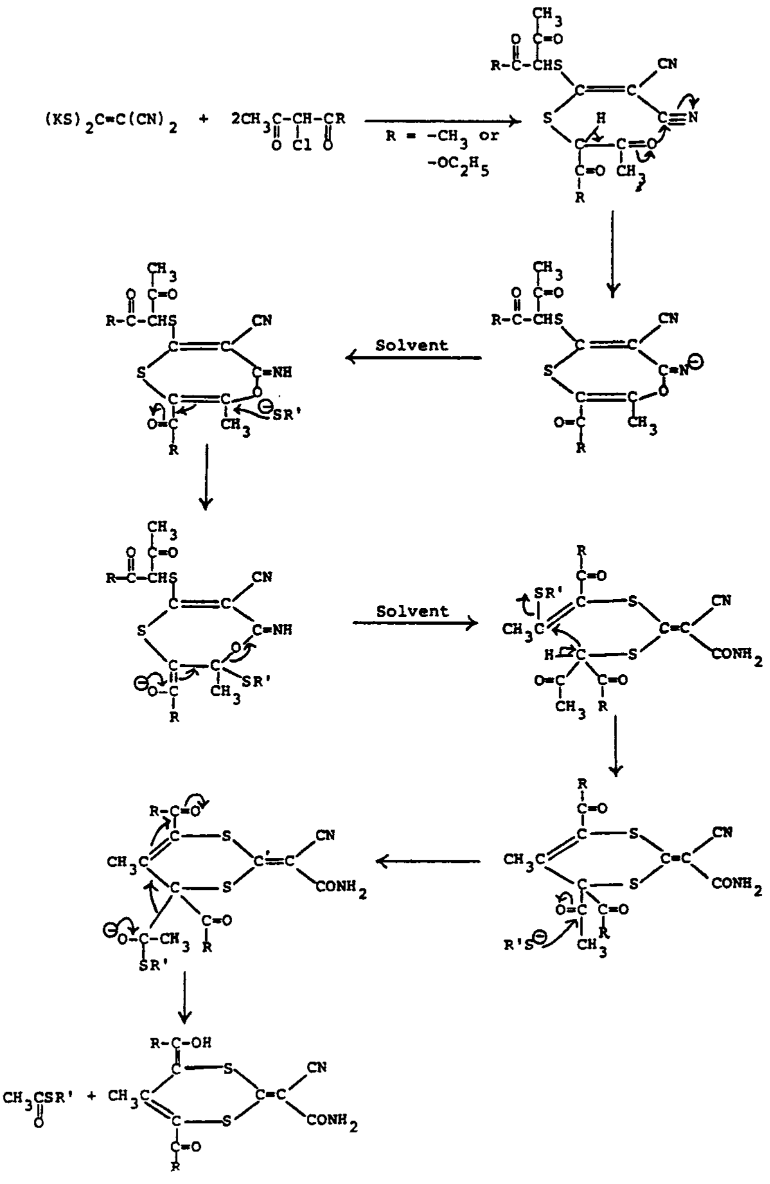
1.26 and 1.30; $-OCH_2\underline{CH_3}$

2.36; $\underline{CH_3}C\begin{smallmatrix}\diagup C\\ \diagdown\diagdown C\end{smallmatrix}$

4.27; $-O\underline{CH_2}CH_3$

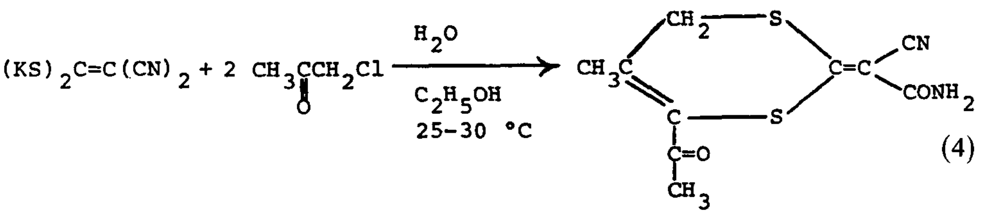
5.80; $-CO\underline{NH_2}$

14.00; $\underline{H}O-C-$



3 R = $-CH_3$
4 R = $-OCH_2CH_3$

SCHEME 1

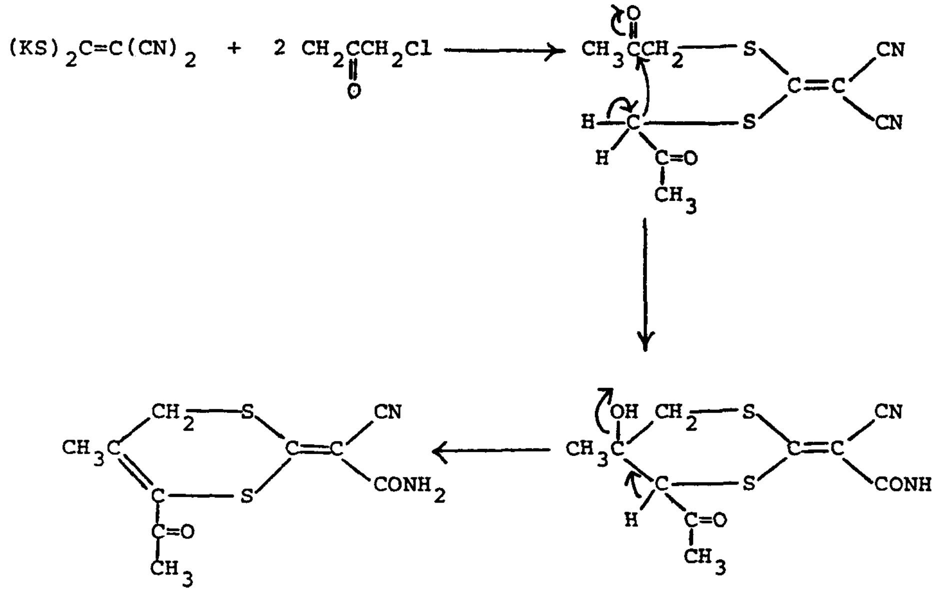


(4)

5

$M^{+\cdot}$ - 254 (39.28)

The analysis, NMR and mass spectra were in agreement for the proposed structures **3**, **4**, and **5**. The presence of the O$\underline{\text{H}}$ protons in **3** and **4** at 17.43 and 14.00 $\delta$, respectively furnished evidence for the enol form instead of the keto structure. This large downfield shift in **3** and **4** is due to the presence of enol form and the deshielding effect of the sulfur atom in the ring. Moreover, the hydration of one of the cyano (C≡N) to the amido ($CONH_2$) group for **3** and **4** was also based on the NMR data. The CO$\text{N}\underline{\text{H}}_2$ protons for **3** and **4** appeared at 6.71 and 5.80 $\delta$, respectively. The proposed mechanisms for reactions **3** and **4** are depicted in Schemes 1 and 2, respectively. It is noteworthy that for reaction (2) monoalkylation is followed by cyclization whereas for reactions (3) and (4) dialkylation is followed by cyclization. In proposed Scheme 1, after dialkylation the addition of the carbonyl to the nitrile group furnished the heterocyclic anion. After protonation of this anion the nucleophilic attack of the R′S⁻ anion occurred followed by ring opening and the



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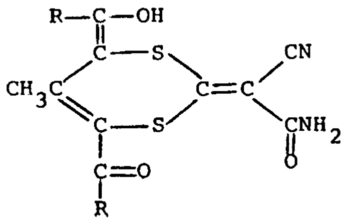
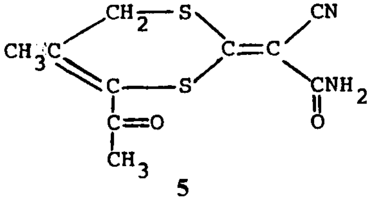
SCHEME 2

TABLE I





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| No. | R | Crude % Yield | Mp °C | NMR, δ(ppm) $\mathrm{CDCl_3—Me_4Si}$ | $\overset{+}{\mathrm{M}}{}^{\bullet}$ (Rel. intensity) | Empirical formula[c] |
|---|---|---|---|---|---|---|
| 3 | $—\mathrm{CH_3}$ | 78 | 182–183[a] | 2.28 (s, 3, $\mathrm{CH_3C}\begin{smallmatrix}\diagup \mathrm{C}\\ \diagdown\!\!\diagdown\end{smallmatrix}$<br>2.42 (s, 6, $\mathrm{CO\underline{CH}_3}$ and $\mathrm{C{=}\overset{OH}{\overset{\vert}{C}}—\underline{CH}_3}$<br>6.71 (br s, 2, $\mathrm{CONH_2}$)<br>17.43 (s, 1, HO—C) | 296 (15) | $\mathrm{C_{12}H_{12}N_2O_3S_2}$ |
| 4 | $—\mathrm{OCH_2CH_3}$ | 58 | 114–115[b] | 1.26 and 1.30 (t, 6, $\mathrm{OCH_2\underline{CH}_3}$)<br>2.36 (s, 3, $\mathrm{CH_3C}\begin{smallmatrix}\diagup \mathrm{C}\\ \diagdown\!\!\diagdown \mathrm{C}\end{smallmatrix}$)<br>4.27 (q, 4, $\mathrm{O\underline{CH}_2CH_3}$)<br>5.80 (br s, 2, $\mathrm{\overline{CONH}_2}$)<br>14.00 (s, 1, HO—C) | 356 (10) | $\mathrm{C_{14}H_{16}N_2O_5S_2}$ |
| 5 | — | 73 | 220–222 | Insoluble in all solvents even DMSO | 254 (39) | $\mathrm{C_{10}H_{10}N_2O_2S_2}$ |

[a] Recrystallization from methyl ethyl ketone.
[b] Recrystallization from ethyl alochol.
[c] Satisfactory analytical data (±0.4%) for C, H, N and S were reported.

conversion of one of the cyano to the amido group. The second cyclization occurred and is followed by the addition of the R'S$^-$ anion to the carbonyl group. The elimination of the thioester $(CH_3\underset{\underset{O}{\|}}{C}SR')$ followed by the formation of the enol form afforded **3** and **4**. In proposed Scheme 2, after dialkylation cyclization occurred by the addition of the alpha methylene group to the carbonyl group. The hydration of one of the cyano to the amido group followed by the loss of water furnished **5**.

## EXPERIMENTAL SECTION

NMR spectra were obtained with a Varian T-60 NMR spectrometer. The chemical shifts are reported in $\delta$, using tetramethylsilane as reference. All melting points were taken upon a Fisher-Johns block and are uncorrected. The electron impact mass spectra were determined with a Varian-MAT CH-7A mass spectrometer operating at an ionizing potential of 70 eV using the direct insertion probe technique with a source temperature of 250 °C.

*(4-Methylene-1,3-dithiolan-2-ylidene)propanedinitrile* (**1**) *and 2-Cyano-2-(4-methyl-5-methylene-1,3-dithiolan-2-ylidene)-acetamide* (**2**). To a stirring solution comprising 43.7 g (0.2 mol) of dipotassium 1,1-dimercapto-2,2-dicyanoethylene[4] in 800 mL of water, 0.4 mol of 3-bromo-1-propyne or 3-chloro-3-methyl-1-propyne was added in one portion. The reaction mixture was stirred at 25–30 °C for 4 days. After the addition of 200 mL of ethyl ether stirring was continued for 15 min. The solid was collected by filtration, washed with water until neutral to litmus and air-dried at 50 °C. **1**, mp 127–128 °C, and **2**, mp 143–147 °C, were obtained 44 and 50% yield, respectively. **1** melted at 129–130 °C and **2** melted at 163–164 °C after recrystallization from ethyl acetate and isopropyl alcohol, respectively. **1**, NMR ($CDCl_3$) $\delta$ 4.48 (m, 2, $CH_2S$); 5.53 and 5.71 (2 m, 2 $C{=}CH_2$); mass spectrum m/e (rel. intensity) 180 (49.10)($M^{\overset{+}{\cdot}}$).

Anal. Calcd for $C_7H_4N_2S_2$: C, 46.64; H, 2.24; N, 15.54; S, 35.28. Found: C, 46.65; H, 2.24; N, 15.51; S, 35.51. **2**, NMR ($Me_2SO$-$d_6$) $\delta$ 1.51 (d, 3, CH—$\underline{CH}_3$); 4.76 (q, 1, $\underline{CH}$—$\underline{CH}_3$); 5.48 (m, 2, $C{=}CH_2$); 7.47 (br s, 2, $CONH_2$); mass spectrum m/e (rel. intensity) 212 (22.45) ($M^{\overset{+}{\cdot}}$).

Anal. Calcd for $C_8H_8N_2OS_2$: C, 45.25; H, 3.79; N, 13.19; S, 30.20. Found: C, 45.28; H, 3.82; N, 13.15; S, 30.14.

*2-[6-Acetyl-4-(1-hydroxyethylidene)-5-methyl-4H-1,3-dithiin-2-ylidene]-2-cyanoacetamide* (**3**); *Ethyl 2-(2-amino-1-cyano-2-oxoethylidene)-4-(ethoxyhydroxymethylene)-5-methyl-4H-1,3-dithiin-6-carboxylate* (**4**); *2-(6-Acetyl-5-methyl-4H-1,3-dithiin-2-ylidene)-2-cyanoacetamide* (**5**). To a stirred solution (pH = 9) containing 43.7 g (0.2 mol) of dipossium 1,1-dimercapto-2,2-dicyanoethylene[4] in 160 mL of water and 140 mL of ethyl alcohol, 0.4 mol of 3-chloro-2,4-pentanedione, ethyl $\alpha$-chloroacetoacetate or chloroacetone was added in one portion. An exothermic reaction set in causing a temperature rise from 25 ° to about 53 °C. The reaction mixture was stirred at 25–30 °C for 3 days (pH = 4–5). After the addition of 150 mL of ethyl ether, the reaction mixture was stirred at 0–10 °C for 30 min. The solid was collected by filtration, washed with water until neutral to litmus and air-dried at 25–30 °C. The data are summarized in Table I.

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