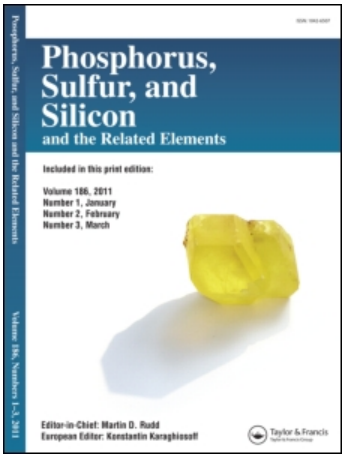


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SYNTHESIS OF HETEROCYCLIC COMPOUNDS AND NEW ROUTES FOR THE PREPARATION OF CERTAIN DITHIOCARBONATES AND SULFIDES FROM POTASSIUM CYANODITHIOIMIDOCARBONATE[1,2]

Peter G. Ruminski[a]; Lydia A. Suba[a]; John J. D'amico[a]
[a] Research Department, Monsanto Agricultural Products Company, St. Louis, Missouri

To cite this Article Ruminski, Peter G. , Suba, Lydia A. and D'amico, John J.(1984) 'SYNTHESIS OF HETEROCYCLIC COMPOUNDS AND NEW ROUTES FOR THE PREPARATION OF CERTAIN DITHIOCARBONATES AND SULFIDES FROM POTASSIUM CYANODITHIOIMIDOCARBONATE[1,2]', Phosphorus, Sulfur, and Silicon and the Related Elements, 19: 3, 335 — 344
To link to this Article: DOI: 10.1080/03086648408077598
URL: http://dx.doi.org/10.1080/03086648408077598

Phosphorus and Sulfur, 1984, Vol. 19, pp. 335–344
0308-664X/84/1903–0335/$18.50/0

SYNTHESIS OF HETEROCYCLIC COMPOUNDS AND NEW ROUTES FOR THE PREPARATION OF CERTAIN DITHIOCARBONATES AND SULFIDES FROM POTASSIUM CYANODITHIOIMIDOCARBONATE[1,2]

PETER G. RUMINSKI, LYDIA A. SUBA and JOHN J. D'AMICO*

Monsanto Agricultural Products Company, Research Department, 800 N. Lindbergh Boulevard, St. Louis, Missouri 63166

(*Received January 13, 1984*)

The reaction of potassium cyanodithioimidocarbonate with 3-chloro-2,4-pentanedione, ethyl α-chloroacetoacetate, chloroacetone, or 2,3-dichloro 1,4-napthoquinone afforded novel heterocyclic compounds (**2**), (**3**), and (**4**) and (**6**). The reaction of the potassium salt with *p*-chlorophenyl chlorothioformate, 4-chloro-3-nitro or 3,5-dinitrobenzotrifluoride or dimethylthiocarbamoyl chloride furnished new routes for the synthesis of *S,S'*-bis-*p*-chlorophenyl dithiocarbonate (**7**) and the sulfides (**8**), (**9**) and (**10**). Possible mechanisms and supporting NMR and mass spectra are discussed.

Potassium cyanodithioimidocarbonate, $(KS)_2C{=}N{-}C{\equiv}N$, was first prepared by Fleisher[3] in 1875 as an intermediate. Its structure was later established by Hantzsch and Wolvekamp[4] in 1904 by means of a convenient synthesis from cyanamide, carbon disulfide and potassium hydroxide.

$$H_2NCN + CS_2 + 2KOH \longrightarrow (KS)_2C{=}N{-}C{\equiv}N + H_2O \qquad (1)$$

In 1967, we[5] reported the synthesis of the potassium salt by modifying the procedure described by Hantzsch and Wolvekamp.[4] The dimethyl[4] and dibenzyl[6] derivatives were prepared from the silver and potassium salts, respectively. However, since 1907

$$(MS)_2C{=}N{-}C{\equiv}N + RI \longrightarrow (RS)_2C{=}N{-}C{\equiv}N \qquad (2)$$

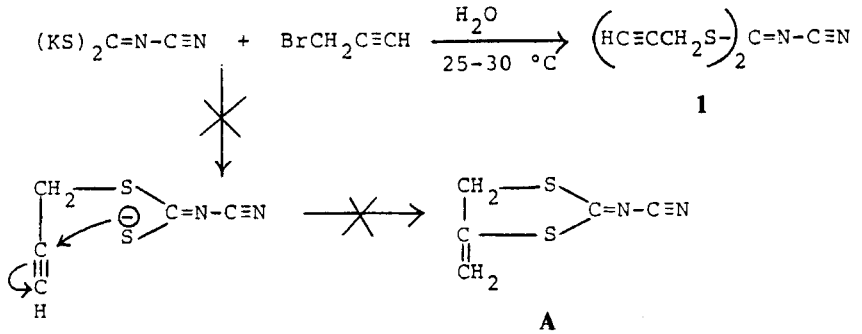
$M = Ag;\ R = -CH_3;\ M = K;\ R = -CH_2C_6H_5$

the chemistry of the salt has received comparatively little attention until 1966 when several publications appeared concerning alkyl,[5,7] acyl,[7] allyl and propynyl,[8] organotin[9] derivatives and metal complexes.[10,11] The use of the potassium salt as an intermediate in the synthesis of nitrogen and sulfur containing heterocycles has recently received moderate attention.[5,7,12–17]

In this paper we wish to report the synthesis of novel heterocyclic compounds and new routes for the preparation of certain *S,S'*-dithiocarbonates and sulfides from potassium cyanodithioimidocarbonate.

It was anticipated that the reaction of the potassium salt with 3-bromo-1-propyne would have furnished the monoalkylation product followed by cyclization to give the heterocycle **A**. However, this was not the case for the product obtained in 90% yield

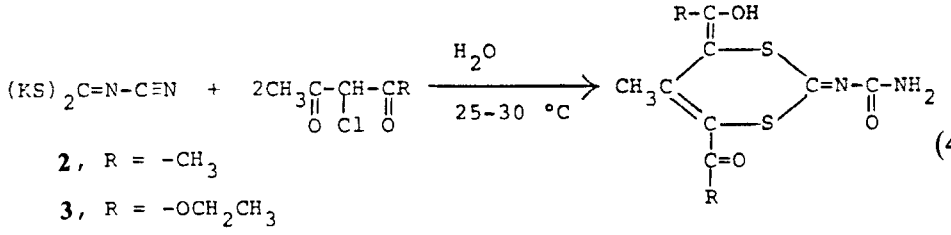
was *S,S'*-2-propynyl cyanodithioimidocarbonate (**I**).[8]



(3)

Analysis, NMR and mass spectra were in agreement for the proposed structure **1**.

The reaction of the potassium salt with 3-chloro-2,4-pentanedione, ethyl α-chloroacetoacetate and chloroacetone afforded [6-acetyl-4-(1-hydroxyethylidene)-5-methyl-4H-1,3-dithiin-2-ylidene]urea (**2**), ethyl 2-[(aminocarbonyl)imino]-4-(ethoxyhydroxymethylene)-5-methyl-4H-1,3-dithiin-6-carboxylate (**3**) and (6-acetyl-5-methyl-4H-1,3-dithiin-2-ylidene)urea (**4**), respectively (reactions (4) and (5)).



2, R = $-CH_3$

3, R = $-OCH_2CH_3$

(4)

NMR ($CDCl_3$) R = $-CH_3$ **2**

ppm

2.43; $\underline{CH_3}C$=C

2.58; $-CO\underline{CH_3}$ and $-C(=C)-\underline{CH_3}$

6.88; $-CO\underline{NH_2}$

17.60; $\underline{HO}$-C-

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

ppm

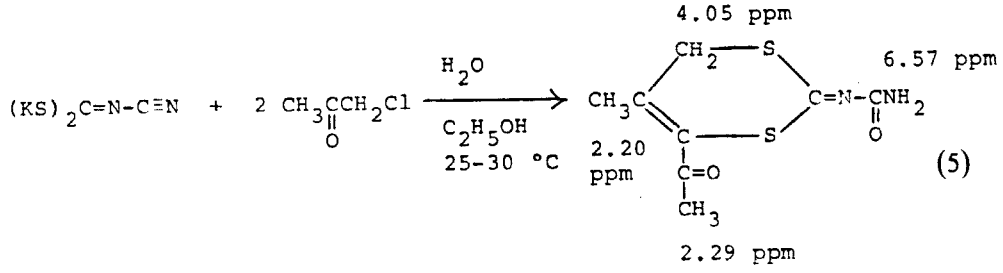
1.16 and 1.21; $-OCH_2\underline{CH_3}$

2.28; $\underline{CH_3}C$=C

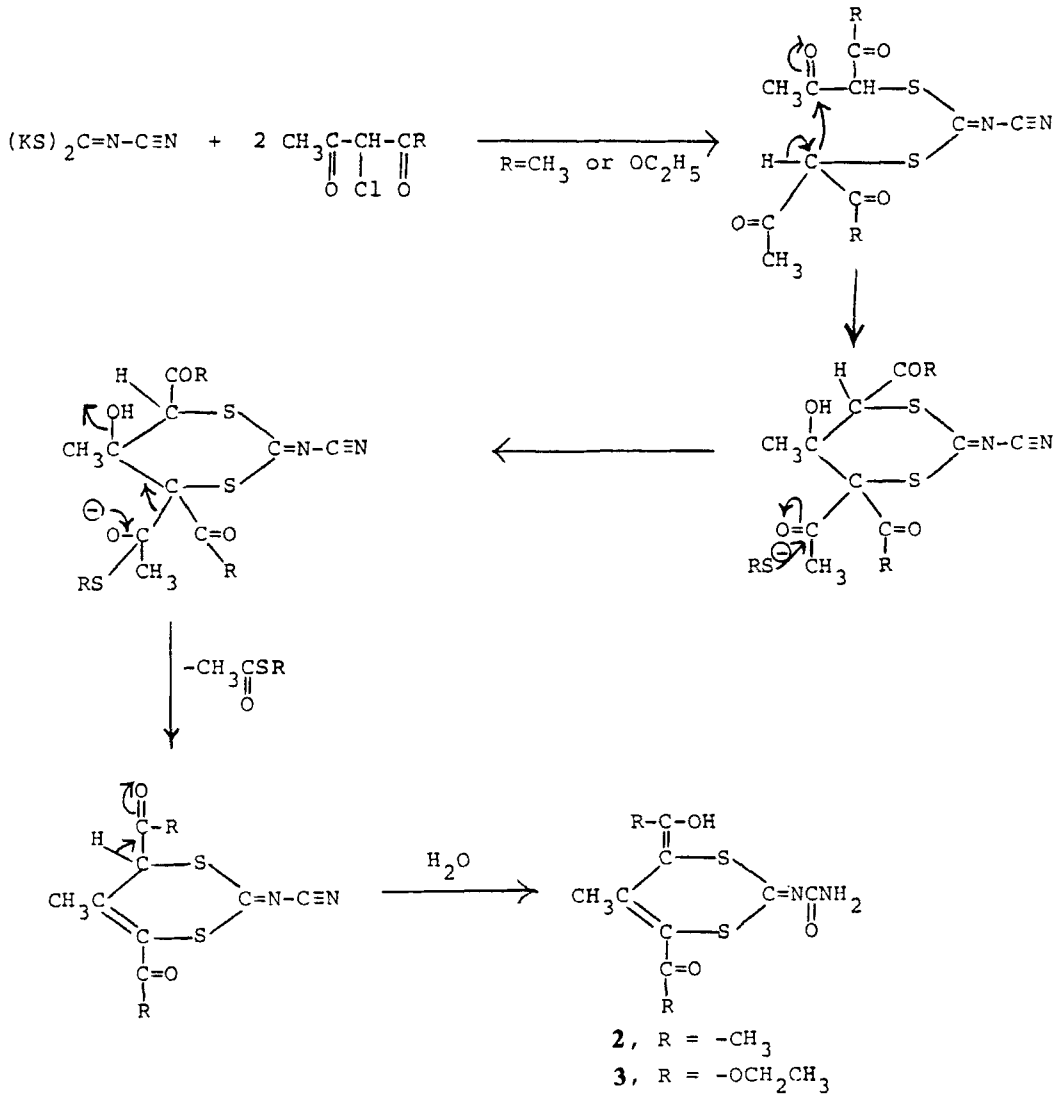
4.14 and 4.20; $-O\underline{CH_2}CH_3$

5.84; $-CO\underline{NH_2}$

14.01; $\underline{HO}$-C-



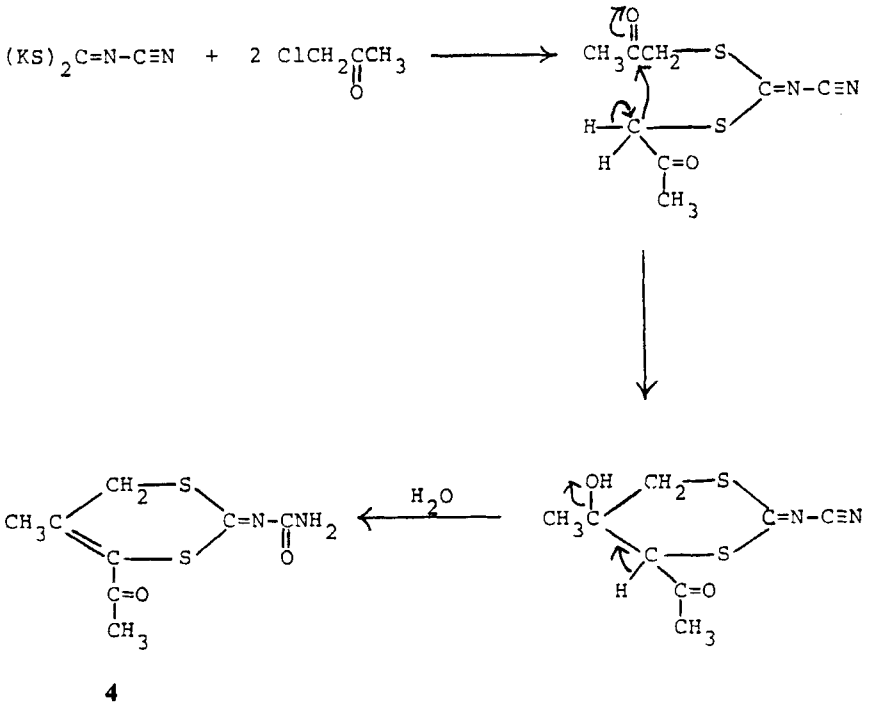
(5)



SCHEME 1

Proof of structure for **2**, **3** and **4** was based on analysis, NMR and mass spectra. Evidence for the enol structure of **2** and **3** instead of the keto structure was based on the NMR spectra data. The OH proton for **2** and **3** appeared at 17.60 and 14.01 δ, respectively. This large downfield shift in **2** and **3** is due to presence of enol form and the deshielding effect of the sulfur atom in the ring. Moreover, the hydration of the cyano (C≡N) to the amido ($CONH_2$) group was also based on the NMR data. The $CONH_2$ protons for **2**, **3** and **4** appeared at 6.88, 5.84 and 6.57 δ, respectively. The proposed mechanisms for reactions **4** and **5** are depicted in Schemes 1 and 2, respectively.

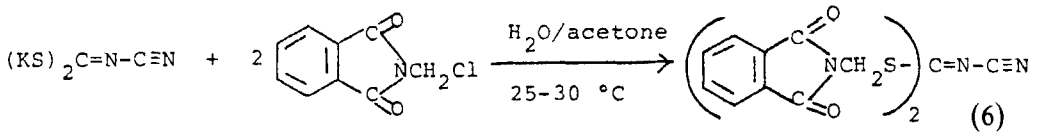
The reaction of the potassium salt with *N*-(chloromethyl)phthalimide and 2,3-dichloro 1,4-napthoquinone furnished *S,S'*-phthalimidomethyl cyanodithioimidocar-



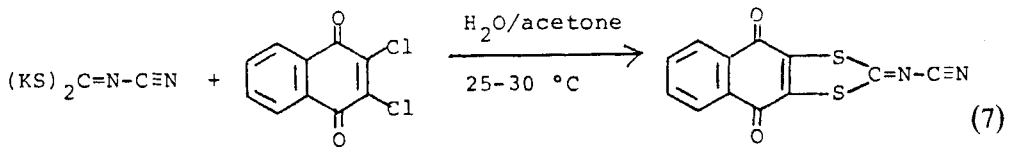
4

SCHEME 2

bonate (**5**) and (3a,4,9,9a-tetrahydro-4,9-dioxonaphtho[2,3-d]-1,3-dithiol-2-ylidene) cyanamide (**6**), respectively.



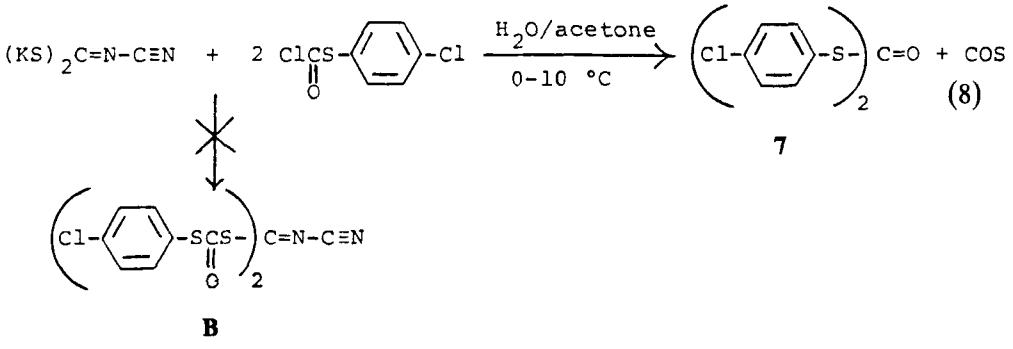
5 (6)



6 (7)

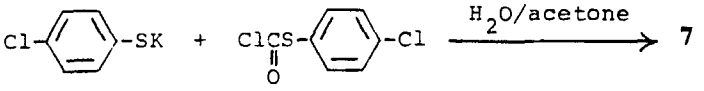
The analysis and NMR confirmed the proposed structures **5** and **6**.

The reaction of the potassium salt with *p*-chlorophenyl chlorothioformate did not afford the expected product **B** but instead furnished *S,S'*-bis-*p*-chlorophenyl dithiocarbonate (**7**) in 79% yield (Method I).



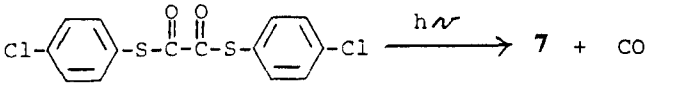
(8)

Proof of structure for **7** was established by the following conventional reaction: (Method II)



(9)

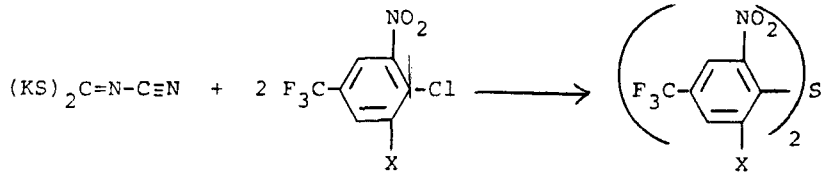
7 was first prepared by H. G. Heine and W. Metzner[18] by the photofragmentation of *S,S'*-bis-*p*-chlorophenyl dithiooxalate.



(10)

The proposed mechanism for reaction **8** is depicted in Scheme 3.

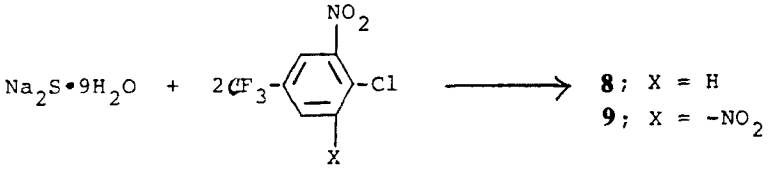
The reaction of the potassium salt with 4-chloro-3-nitrobenzotrifluoride and 4-chloro-3,5-dinitrobenzotrifluoride afforded bis(2-nitro-4-trifluoromethylphenyl) sulfide (**8**) and bis(2,6-dinitro-4-trifluoromethylphenyl)sulfide (**9**), respectively (Method I).



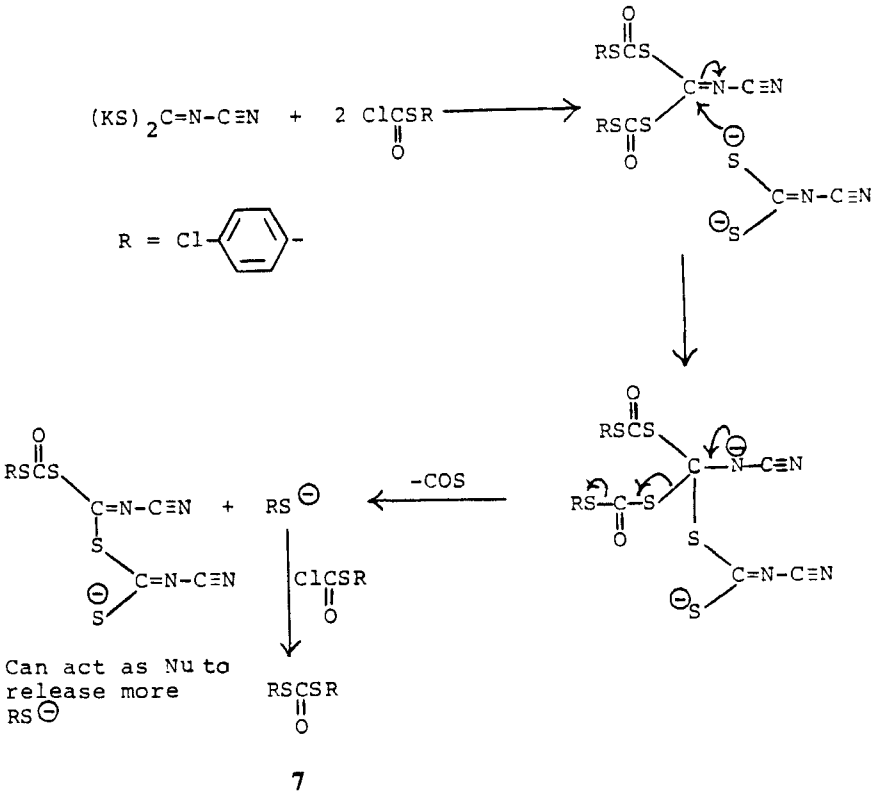
(11)

8; X = H
9; X = $-NO_2$

Proof of structure for **8** and **9** was established by the following conventional reaction: (Method II).



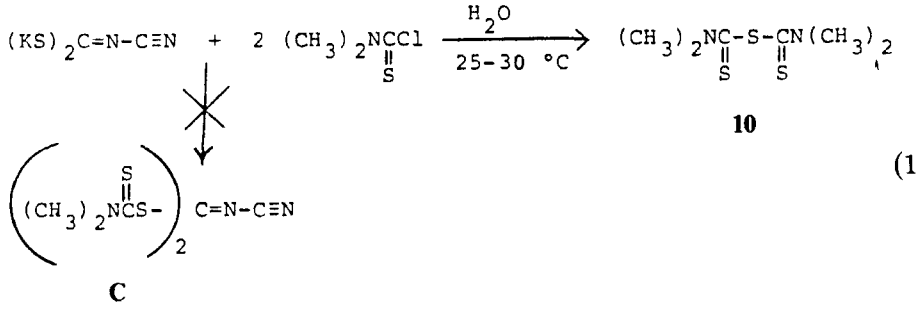
(12)



7

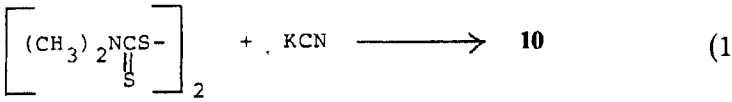
SCHEME 3

The reaction of the potassium salt with dimethylthiocarbamoyl chloride did not afford the expected product **C** but instead furnished bis(dimethylthiocarbamoyl) sulfide (**10**) (Method I).



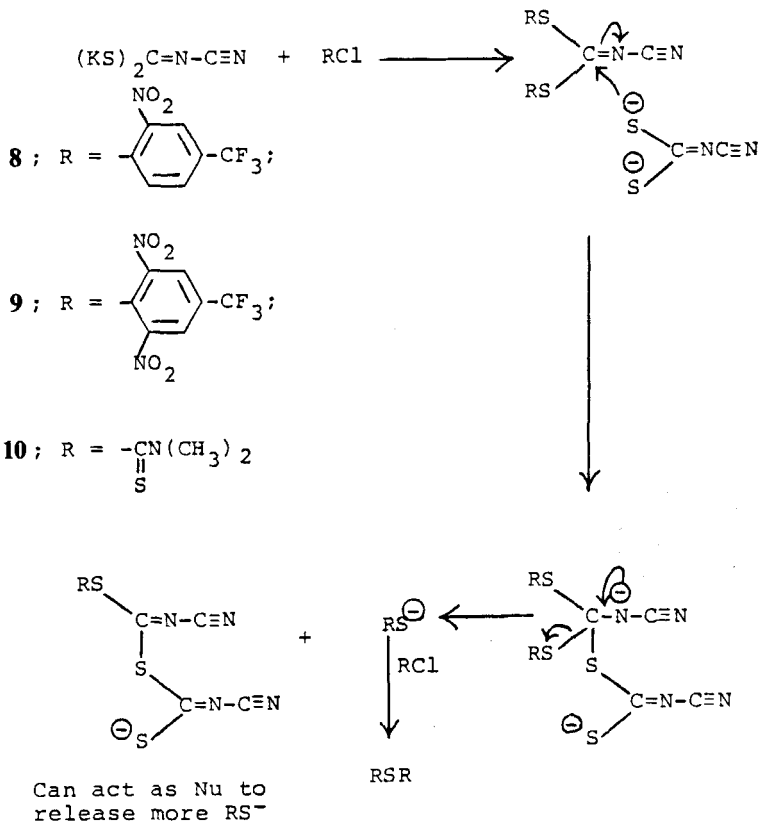
(13)

Proof of structure for 10 was obtained by the following conventional reaction: (Method II)



(14)

The proposed mechanisms for reactions 11 and 13 are depicted in Scheme 4.



SCHEME 4

EXPERIMENTAL SECTION

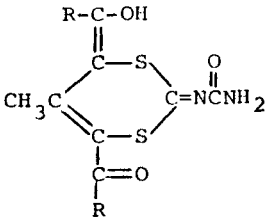
NMR spectra were obtained with a Varian T-60 NMR spectrometer. The chemical shifts are reported in δ, using tetramethylsilane as reference. All melting points were taken upon a Fisher-Johns block and are uncorrected. The electron impact mass spectra were determined with a Varian-MAT CH-7A mass spectrometer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

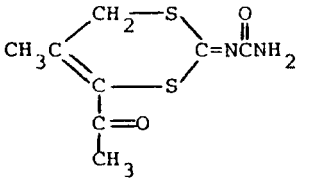
S,S'-2-Propynyl Cyanodithioimidocarbonate[8] (**1**). To a stirred solution (pH = 9.6) comprising 78.8 g (0.4 mol) of potassium cyanodithioimidocarbonate[5] in 800 mL of water was added in one portion 95.2 g (0.8 mol) of 3-bromo-1-propyne. The reaction mixture was stirred at 25–30°C for 1 day (pH = 7.4). After cooling to 0°C, the precipitate was collected by filtration, washed with water until the washings were neutral to litmus and air-dried at 25–30°C. **1**, mp 89–91°C, was obtained in 90% yield. After recrystallization from ethyl acetate **1** melted at 94–95°C; NMR (Me_2SO-d_6) δ 3.41 (m, 2, $CH_2C{\equiv}C\underline{H}$), 4.28 (s, 4, $CH_2C{\equiv}CH$); mass spectrum m/e (rel. intensity), 193 (5.5) ($M^{\cdot+}$ − 1), 155 (35) ($M^{\cdot+}$—$CH_2C{\equiv}CH$), 123 (42) (M^{+}—$SCH_2C{\equiv}CH$).

Anal. Calcd. for $C_8H_6N_2S_2$: C, 49.46; H, 3.11; N, 14.42; S, 33.01. Found: C, 49.39; H, 3.11; N, 14.39; S, 32.99.

[*6-Acetyl-4-(1-hydroxyethylidene)-5-methyl-4H-1,3-dithiin-2-ylidene)urea* (**2**), *Ethyl 2-[(aminocarbonyl)imino]-4-(ethoxyhydroxymethylene)-5-methyl-4H-1,3-dithiin-6-carboxylate* (**3**), *and (6-Acetyl-5-methyl-4H-1,3-dithiin-2-ylidene)urea* (**4**). To a stirred solution at 5°C (pH = 9.6) containing 38.9 g (0.2 mol) of potassium cyanodithioimidocarbonate[5] in 200 mL of water and 200 mL of ethyl alcohol, 0.4 mol of 3-chloro-2,4-pentanedione, ethyl α-chloroacetoacetate or chloroacetone was added in one portion. The reaction mixture was stirred at 25–30°C for 2 days (pH = 5–6). 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.

TABLE I





4

No.	R	Crude % yield	Mp °C	MR, δ (ppm) $CDCl_3$—Me_4Si	M^+ (Rel. intensity)	Empirical formula[b]
2	$-CH_3$	52	146–148[a]	2.43 (s, 3, CH_3C ) OH 2.58 (s, 6, CO $\underline{CH_3}$ and C=C—$\underline{CH_3}$) 6.88 (br s, 2, $CONH_2$) 17.60 (s, 1, HO—C)	272 (19)	$C_{10}H_{12}N_2O_3S_2$
3	$-OCH_2CH_3$	59	111–113[a]	1.16 and 1.21 (t, 6, $OCH_2\underline{CH_3}$) 2.28 (s, 3, CH_3C) 4.14 and 4.20 (q, 4, $O\underline{CH_2}CH_3$) 5.84 (br s, 2, $CONH_2$) 14.01 (s, 1, HO—C)	332 (11)	$C_{12}H_{16}N_2O_5S_2$
4	—	76	127–128[a]	2.20 (s, 3, CH_3C ) 2.29 (s, 3, $COCH_3$) 4.05 (s, 2, CH_2S) 6.57 (br s, 2, $CONH_2$)	230 (38)	$C_8H_{10}N_2O_4S_2$

[a]Recrystallization from ethyl alcohol.
[b]Satisfactory analytical data ($\pm 0.4\%$) for C, H, N and S were reported.

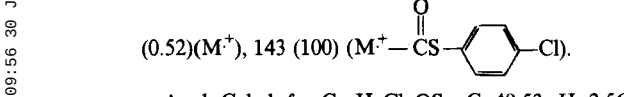
S,S'-Phthalimidomethyl cyanodithioimidocarbonate (**5**) *and* (*3a,4,9,9a-Tetrahydro-4,9-dioxonaptho*[*2,3-d*]-*1,3-dithiol-2-ylidene*)*cyanamide* (**6**). To a stirred solution (pH = 9.5) comprising 38.9 g (0.2 mol) of potassium cyanodithioimidocarbonate[5] in 400 mL of water and 400 mL of acetone, 78.4 g (0.4 mol) of *N*-(chloromethyl)phthalimide or 47.4 g (0.2 mol) of 2,3-dichloro 1,4-napthoquinone was added in one portion. An exothermic reaction set in causing a temperature rise of 25°C to about 36°C. The reaction mixture was stirred at 25–30°C for 1 day. After the addition of 1 l of water, stirring was continued at 25–30°C for 30 min. (pH = 7.3 and 7.5 for **5** and **6**, respectively). The precipitate was collected by filtration, washed with water until neutral to litmus and air-dried at 25–30°C. The crude product (**5**), mp 163–166°C, was obtained in 80% yield. After recrystallization from methyl ethyl ketone **5** melted at 177–178°C. NMR (Me_2SO-d_6) δ 5.43 (s, 4, NCH_2S), 7.91 (s, 8, 2ArH); isobutane chemical ionization mass spectrum m/e 437 $(M + 1)^+$.

Anal. Calcd. for $C_{20}H_{12}N_4O_4S_2$: C, 55.04; H, 2.77; N, 12.84; S, 14.69. Found: C, 54.99; H, 2.80; N, 12.80; S, 14.64.

The crude product (**6**), mp 228–231°C, was obtained in 90% yield. After recrystallization from DMF, **6** melted at 233–234°C. The NMR of **6** could not be obtained since it was insoluble in most solvents including DMSO.

Anal. Calcd. for $C_{12}H_{14}N_2O_2S_2$: C, 52.93; H, 1.48; N, 10.29. S, 23.55. Found: C, 53.00; H, 1.70; N, 10.02; S, 23.36.

S,S'-Bis-p-chlorophenyl dithiocarbonate (**7**)—*Method I.* To a stirred solution at 5°C (pH = 8.5) containing 19.5 g (0.1 mol) of potassium cyanodithioimidocarbonate[5] in 150 mL of acetone and 50 mL of water, 41.5 g (0.2 mol) of *p*-chlorophenyl chlorothioformate was added dropwise at 0–10°C in 30 min. The reaction mixture was stirred at 0–10°C for 5 h and 25–30°C for 1 h. After cooling to 5°C, 700 g of ice water was added and stirring continued at 0–10°C for 30 min (pH = 4). The solid was collected by filtration, washed with water until neutral to litmus and air-dried at 25–30°C. The crude product (**7**), mp 119–121°C, was obtained in 79% yield. After recrystallization from heptane **7** melted at 126–127°C. (Lit.[18] mp 125–127°C). NMR ($CDCl_3$) δ 7.51 (s, 8, ArH); mass spectrum m/e (rel. intensity) 315



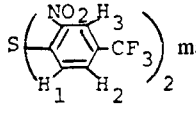
(0.52)(M^+), 143 (100) (M^+—CS—C$_6$H$_4$—Cl).

Anal. Calcd. for $C_{13}H_8Cl_2OS_2$: C, 49.53; H, 2.56; Cl, 22.49; S, 20.34. Found: C, 49.53; H, 2.58; Cl, 22.44; S, 20.34.

(**7**)—*Method II. Conventional.* To a stirred solution at 5°C comprising 28.9 g (0.2 mol) of *p*-chlorothiophenol, 13.2 g (0.2 mol) of 85% potassium hydroxide, 200 mL of acetone and 10 mL of water, 41.5 g (0.2 mol) of *p*-chlorophenyl chlorothioformate was added dropwise at 0–10°C. The reaction mixture was stirred at 25–30°C for 1 day. After the addition of 700 mL of water stirring was continued at 25–30°C for 30 min. The precipitate was collected by filtration, washed with water until neutral to litmus and air-dried at 25–30°C. Crude **7**, mp 125–126°C, was obtained in 97% yield. After recrystallization from heptane **7** melted at 126–127°C. A mixture melting point with the product obtained from Method I was not depressed and the NMR spectra of the two were identical.

Anal. Calcd. for $C_{13}H_8Cl_2OS_2$: Cl, 22.49; S, 20.34. Found: Cl, 22.15; S, 20.10.

Bis(*2-nitro-4-trifluoromethylphenyl*)*sulfide* (**8**)—*Method I.* To a stirred slurry containing 19.4 g (0.1 mol) of potassium cyanodithioimidocarbonate[5] in 200 mL of dimethylformamide, 45.2 g (0.2 mol) of 4-chloro-3-nitrobenzotrifluoride was added in one portion. An exothermic reaction set in causing a temperature rise from 20°C to 39°C over a 5 min period. The stirred reaction mixture was heated at 80–90°C for 1 day. After cooling to 5°C, 800 g of ice water was added and stirring continued at 0–10°C for 30 min. The solid was collected by filtration, washed with water until neutral to litmus and air-dried at 50°C. Crude **8**, mp 142–145°C, was obtained in 99% yield. After recrystallization from ethyl acetate **8** melted at 146–147°C. NMR (Me_2SO-d_6) δ 7.70 (d, 2, H_1); 8.00 (d, 2, H_2); 8.65 (s, 2, H_3)

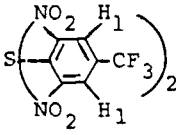


mass spectrum m/e (rel. intensity) 412 (74.2)(M^+).

Anal. Calcd. for $C_{14}H_6F_6N_2O_4S$: C, 40.79; H, 1.47; F, 27.65; N, 6.79; S, 7.78. Found: C, 40.75; H, 1.64; F, 27.52; N, 6.80; S, 7.86.

(**8**)—*Method II.* **8** was prepared as described by Roe and co-workers[19] and D'Amico *et al.*[20] A mixture melting point with the product obtained by Method I was not depressed and the NMR and mass spectra of the two were identical.

Bis(2,6-dinitro-4-trifluoromethylphenyl)sulfide (**9**)—*Method I.* To a stirred solution containing 19.4 g (0.1 mol) of potassium cyanodithioimidocarbonate[5] in 200 mL of water a solution comprising of 54 g (0.2 mol) of 4-chloro-3,5-dinitrobenzotrifluoride in 200 mL of ethyl alcohol was added in one portion. An exothermic reaction set in causing a temperature rise from 20 to 35°C over a 8 min period. The reaction mixture was stirred at 25–30°C for 3 days. After the addition of 800 mL of water stirring was continued at 25–30°C for 30 min. The product was collected by filtration, washed with water until neutral to litmus and air-dried at 25–30°C. The crude product (**9**), mp 190–196°C, was obtained in 96% yield. After recrystallization from heptane-ethyl acetate **9** melted at 203–204°C. NMR (Me_2SO-d_6) δ 8.85 (s, 4, H_1)



; mass spectrum m/e (rel. intensity) 502 (6.1) ($M^{\cdot+}$).

Anal. Calcd. for $C_{14}H_4F_6N_4O_8S$: C, 33.48; H, 0.80; F, 22.70; N, 11.15; S, 6.38. Found: C, 33.42; H, 0.87; F, 22.79; N, 11.13; S, 6.33.

(**9**)—*Method II.* **9** was prepared as described by us.[20] A mixture melting point with **9** obtained by Method I was not depressed and the NMR and mass spectra of the two were identical.

Bis(dimethylthiocarbamoyl)sulfide (**10**). To a stirred solution containing 38.8 g (0.2 mol) of potassium cyanodithioimidocarbonate[5] in 400 mL of water, 49.4 g (0.4 mol) of dimethylthiocarbamoyl chloride was added in one portion. An exothermic reaction set in causing a temperature rise from 25°C to 40°C over a 6 min period. The reaction mixture was stirred at 25–30°C for 1 day. The oily precipitate was collected by filtration, washed with water until neutral to litmus and air-dried at 25–30°C. Crude **10**, mp 76–80°C was obtained in 88% yield. After two recrystallizations from ethyl alcohol **10**, mp 105–106°C, was obtained in 36% yield. A mixture melting point with an authentic sample[21] was not depressed and NMR and mass spectra of the two were identical. NMR (Me_2SO-d_6) δ 3.42 (s, 12, $N(CH_3)_2$); mass spectrum m/e (rel. intensity) 208 (22.2) ($M^{\cdot+}$).

Anal. Calcd. for $C_6H_{12}N_2S_3$: C, 34.59; H, 5.81; N, 13.44; S, 46.16. Found: C, 34.53; H, 5.81; N, 13.39; S, 46.09.

REFERENCES AND NOTES

1. Presented at the National Meeting of the American Chemical Society, Organic Division, St. Louis, MO. April (1984).
2. The *Chemical Abstracts* preferred name for compounds **2**, **3**, **4** and **6** was kindly furnished by Dr. K. L. Loening of the Chemical Abstracts Service.
3. A. Fleisher, *Ann.*, **179**, 204 (1875).
4. A. Hantzsch and Wolvekamp, *Ann.*, **331**, 265 (1904).
5. J. J. D'Amico and R. H. Campbell, *J. Org. Chem.*, **32**, 2567 (1967).
6. E. Fromm and D. Von Gonez, *Ann.*, **335**, 196 (1907).
7. R. J. Timmons and L. S. Wittenbrook, *J. Org. Chem.*, **32**, 1566 (1967).
8. J. J. D'Amico, U.S. Patent 3,299,129 (Monsanto Co.), 1-17-67.
9. R. Seltzer, *J. Org. Chem.*, **33**, 3896 (1968).
10. F. A. Cotton and J. A. McCleverty, *Inorg. Chem.*, **6**, 229 (1967).
11. J. P. Fackler, Jr., and D. Coucouvanis, *J. Am. Chem. Soc.*, **88**, 3913 (1966).
12. J. J. D'Amico and R. H. Campbell, U.S. Patent 3,525,752 (Monsanto Co.), 8-25-70.
13. W. A. Thaler and J. R. McDivitt, *J. Org. Chem.*, **36**, 14 (1971).
14. J. J. D'Amico, U.S. Patent 3,652,256 (Monsanto Co.), 3-28-72.
15. J. J. D'Amico, K. Boustany, A. B. Sullivan and R. H. Campbell, *Int. J. Sulfur Chem., Part A*, Vol. 2, 37 (1972).
16. L. S. Wittenbrook, G. L. Smith and R. J. Timmons, *J. Org. Chem.*, **38**, 465 (1973).
17. L. S. Wittenbrook, *J. Heterocycl. Chem.*, **12**, 37 (1975).
18. H. G. Heine and W. Metzner, *Liebigs Ann. Chem.*, **724**, 223–225 (1969).
19. A. Roe, J. A. Montgomery, W. A. Yarnall and V. A. Hoyle, Jr., *J. Org. Chem.*, **21**, 28 (1956).
20. J. J. D'Amico, C. C. Tung, W. E. Dahl and D. J. Dahn, *J. Org. Chem.*, **41**, 3564 (1976).
21. (a) A. D. Cummings and H. E. Simmons, *Ind. Eng. Chem.*, **20**, 1173 (1928); (b) J. V. Braun and F. Stechele, *Ber.*, **36**, 2275 (1903).