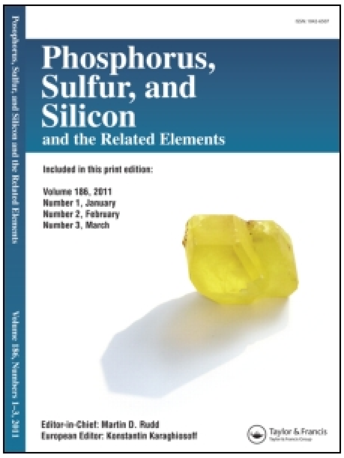

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SYNTHESIS OF ALKYL N-CYANO-N-SUBSTITUTED THIOLCARBAMATES

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SYNTHESIS OF ALKYL N-CYANO-N-SUBSTITUTED THIOLCARBAMATES[1]

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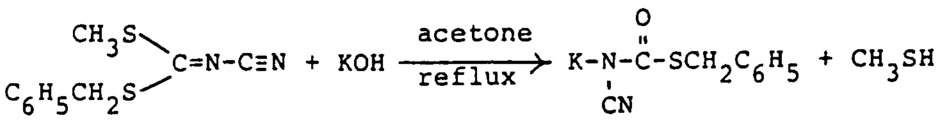
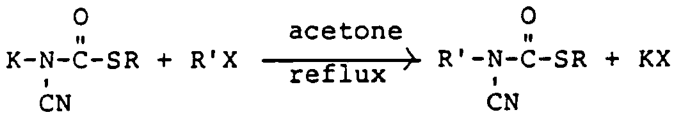
The reaction of *S,S'* alkyl and benzyl cyanodithioimidocarbonate (**1–5**) with potassium hydroxide in an acetone medium afforded the *O*-potassium *S*-alkyl and benzyl cyanothioimidocarbonates (**6–10**). The reaction of the potassium salts with alkyl, allyl or benzyl halides furnished the titled compounds (**11–29**). Possible mechanisms and supporting NMR, Ir and mass spectra data are discussed.

Kazuo Nishio and co-workers[2a,b,c] reported the synthesis of the titled compounds by the following reactions:



$$\begin{matrix}CH_3S\\C_6H_5CH_2S\end{matrix}\!>C{=}N{-}C{\equiv}N + KOH \xrightarrow[\text{reflux}]{\text{acetone}} K{-}\underset{CN}{N}{-}\overset{O}{\overset{\|}{C}}{-}SCH_2C_6H_5 + CH_3SH$$

(1)



$$K{-}\underset{CN}{N}{-}\overset{O}{\overset{\|}{C}}{-}SR + R'X \xrightarrow[\text{reflux}]{\text{acetone}} R'{-}\underset{CN}{N}{-}\overset{O}{\overset{\|}{C}}{-}SR + KX$$

(2)

where R = alkyl, alkenyl or benzyl
R′ = alkyl, alkenyl or alkynyl

Upon reviewing the cited patents in the above reference, we would like to make the following comments: (1) in all examples the elemental analyses were not reported, (2) the % yield was reported for only three compounds, (3) the structure assignment for the potassium salt (Reaction 1) is incorrect and (4) with the exception of the infrared data (Reaction 1) which were misinterpreted, no other spectral data were reported. Furthermore we question the products obtained in Reaction 1. In our opinion Reaction 1 would yield a mixture containing both the methyl and benzyl

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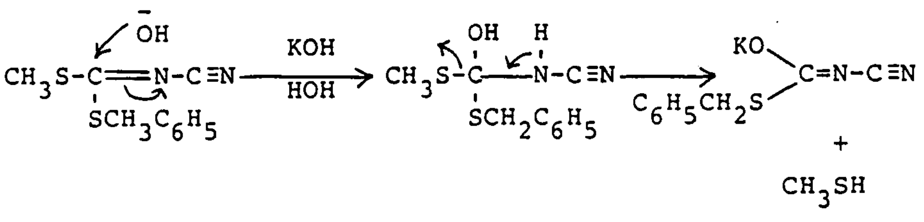
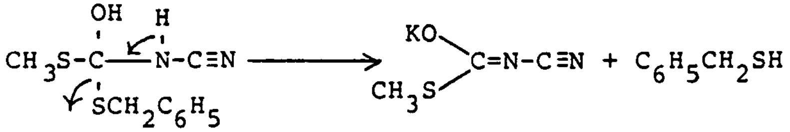
mercaptan and two potassium salts as illustrated by the following pathway:





We have published extensively concerning the synthesis of *N,N*-disubstituted thiolcarbamates[3] and moderate attention has been focused on the synthesis of compounds derived from potassium cyanodithioimidocarbonate.[4-7] Moreover, since we disagree with their proposed structure of the potassium salt in the solid state and Nishio furnished limited proof for their proposed structures, it appeared desirable to report our work in this area of chemistry.

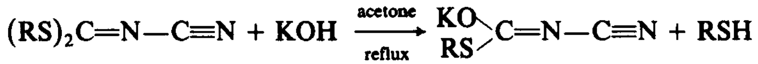
The key intermediates, *S,S'* alkyl and benzyl cyanodithioimidocarbonates (**2–5**), were prepared by the reactions of potassium cyanodithioimidocarbonate[4] with the alkyl or benzyl halides.

$$2RX + (KS)_2C{=}N{-}C{\equiv}N \xrightarrow[H_2O]{25\text{–}30°C} (RS)_2C{=}N{-}C{\equiv}N \qquad (3)$$

1,[5] $R = -CH_3$; **2**, $R = -C_2H_5$; **3**, $R = -C_3H_7$;

4, $R = -C_4H_9$; **5**,[8] $R = -CH_2C_6H_5$

The reaction of **1–5** with potassium hydroxide in an acetone medium afforded the *O*-potassium *S*-alkyl and benzyl cyanothioimidocarbonates (**6–10**) and not the structure as shown in Reaction 1.



$$(RS)_2C{=}N{-}C{\equiv}N + KOH \xrightarrow[\text{reflux}]{\text{acetone}} \begin{matrix}KO\\RS\end{matrix}\!\!>C{=}N{-}C{\equiv}N + RSH \qquad (4)$$

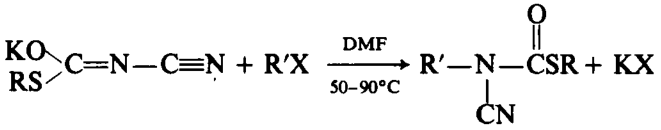
6, $R = -CH_3$; **7**, $R = -C_2H_5$; **8**, $R = -C_3H_7$;

9, $R = -C_4H_9$; **10**, $R = -CH_2C_6H_5$

Analysis, infrared (neat) and NMR spectra were in agreement for the proposed structures of **6–10**. The presence of C≡N and C=N absorption bands at 2170–2180 and 1585–1590 cm^{-1}, respectively, and the absence of the C=O absorption band at 1680–1700 cm^{-1} for **6** and **10** (Table II) furnished conclusive evidence for our structures (**6–10**) and thus ruled out their proposed structure (Reaction 1). Nishio and co-workers[2b] reported the following infrared spectral data and assignment for **10**: 2180 (C≡N) and 1580 cm^{-1} (C=O) which is comparable to our data (Table II). However, their assignment of 1580 cm^{-1} absorption band due to the presence of

C=O instead of C=N group is erroneous. Accordingly, this misinterpretation of the infrared spectrum led them to the incorrect structure (Reaction 1).

The reactions of the potassium salts (**6–9**) with alkyl, allyl or benzyl halides in dimethylformamide at 50–90°C furnished the alkyl-*N*-cyano-*N*-substituted thiolcarbamates (**11–29**).

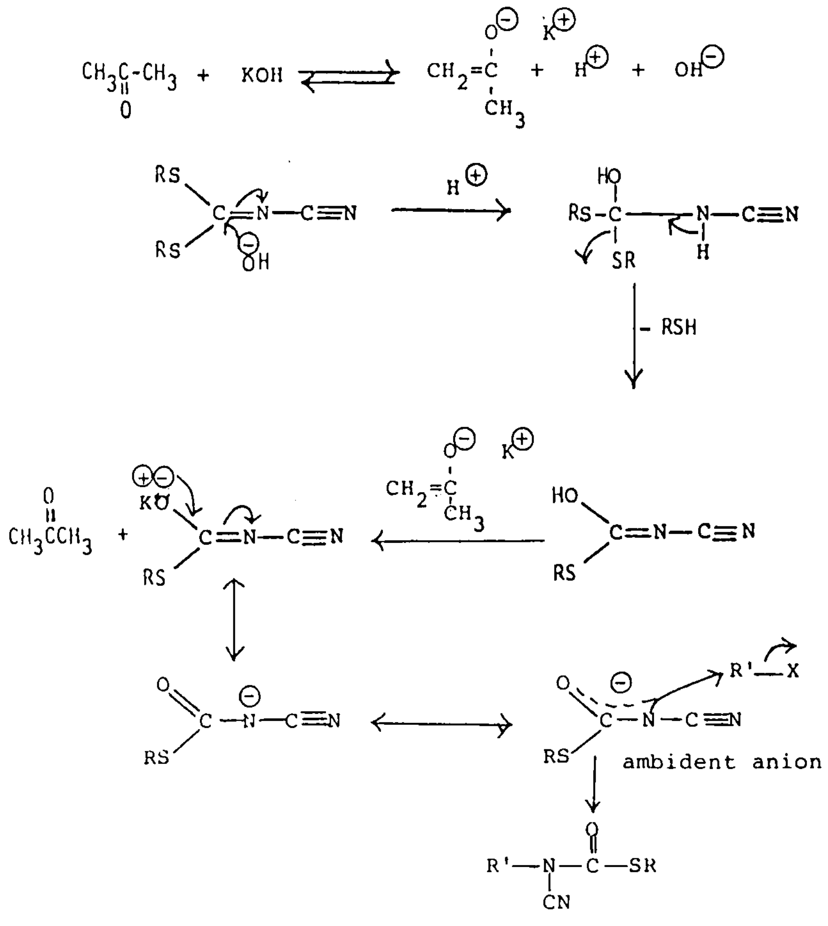


$$\mathrm{\overset{KO}{\underset{RS}{}}\!\!>C{=}N{-}C{\equiv}N + R'X \xrightarrow[50\text{-}90^{\circ}C]{DMF} R'{-}\underset{CN}{\underset{|}{N}}{-}\overset{O}{\overset{\|}{C}}SR + KX} \qquad (5)$$

R and R′ are shown in Table III.

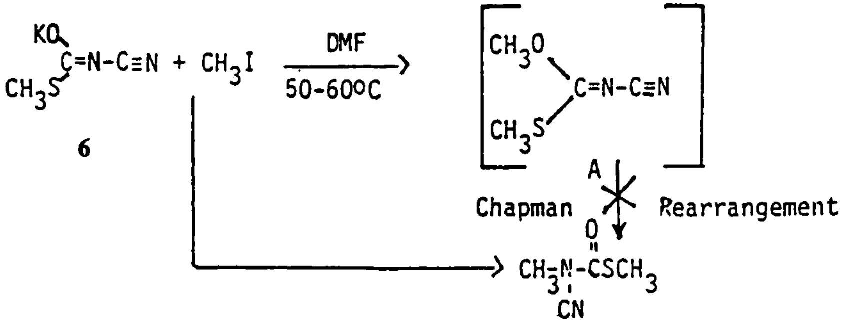
The proposed mechanisms for reactions 4 and 5 are depicted in Scheme 1. As noted, we favor addition to the conjugated system followed by elimination of the mercaptan instead of the nucleophilic displacement mechanism.

Analysis, infrared, NMR and mass spectra were in agreement for the proposed structure of **11–29**. (Table III and Scheme 2.) Initially we had anticipated that



SCHEME 1

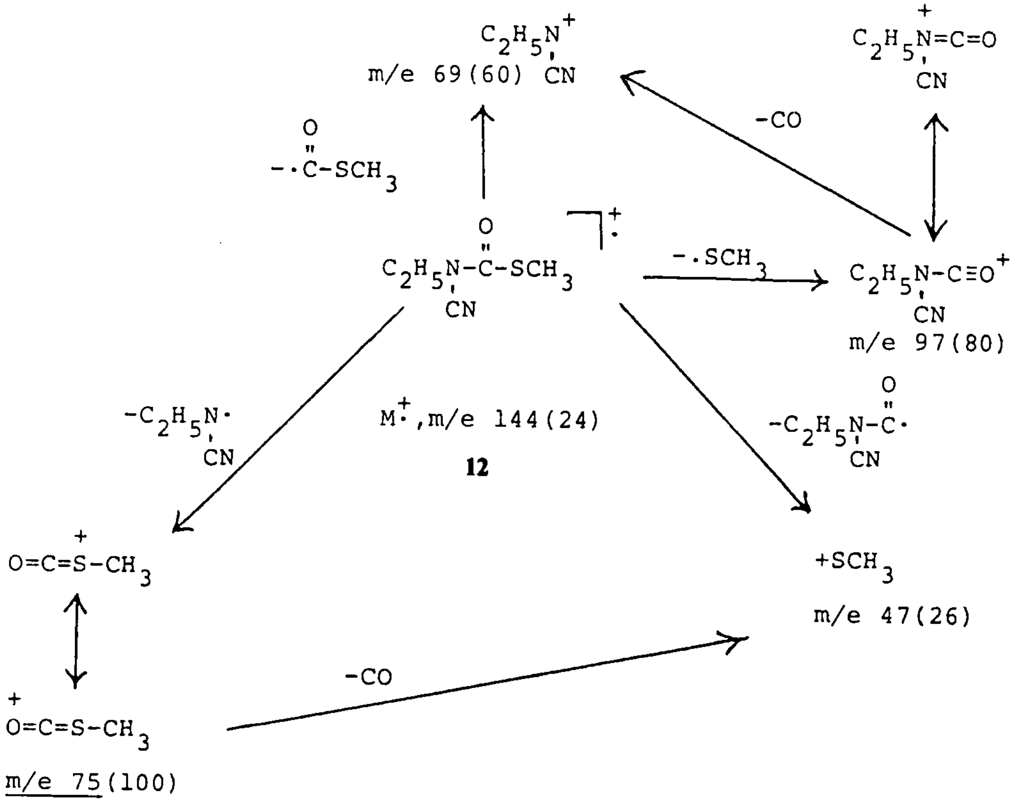
oxygen alkylation would have occurred to give the intermediate A followed by the Chapman rearrangement to give **11–29**.



11

(6)

Even when reaction 6 was conducted at low temperature no evidence was obtained for the formation of intermediate A. This conclusion was based on the examination of the analytical data of a crude sample, heated sample (100–116°C for 16 hours) and a distilled sample of **11**. All three samples furnished comparable



SCHEME 2

index of refraction, infrared and NMR spectra. (See Experimental section.) The presence of C≡N and C=O absorption bands at 2230 and 1700 cm^{-1}, respectively, and the absence of C=N absorption band at 1585 cm^{-1} for all three samples furnished conclusive evidence that no oxygen alkylation occurred but instead nitrogen alkylation resulted to give the thiolcarbamates (**11–29**).

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

TABLE I

S,S' Alkyl and benzyl cyanodithioimidocarbonates

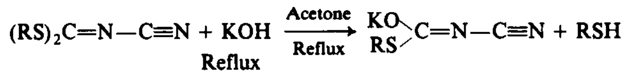
$$2RX + (KS)_2C{=}N{-}C{\equiv}N \xrightarrow[25\text{–}30°C]{H_2O} (RS)_2C{=}N{-}C{\equiv}N$$

No.	R	X	Reaction time (days)	Mp °C or (N_D^{25})	% Yield	NMR, δ (ppm) $CDCl_3$—Me_4Si	Empirical formula[a]
1[5]	$-CH_3$	I	7	55–6	84	2.64 (s, 6, CH_3)	$C_4H_6N_2S_2$
2	$-C_2H_5$	Br	7	(1.5827)	90	1.40 (t, 6, $CH_2\underline{CH_3}$) 3.20 (q, 4, $\underline{CH_2}CH_3$)	$C_6H_{10}N_2S_2$
3	$-C_3H_7$	Br	8	(1.5623)	94	—	$C_8H_{14}N_2S_2$
4	$-C_4H_9$	Br	6	(1.5484)	89	—	$C_{10}H_{18}N_2S_2$
5[8]	$-CH_2C_6H_5$	Br	1	83–4	94	4.40 (s, 4, CH_2) 7.40 (s, 10, C_6H_5)	$C_{16}H_{14}N_2S_2$

[a] Satisfactory analytical data (±0.2) for C, H, N and S were reported.

TABLE II

O-Potassium *S*-alkyl and benzyl cyanothioimidocarbonates



$$(RS)_2C{=}N{-}C{\equiv}N + KOH \xrightarrow[\text{Reflux}]{\text{Acetone}} \begin{matrix}KO\\RS\end{matrix}{>}C{=}N{-}C{\equiv}N + RSH$$

No.	R	Mp °C (dec.)	Reflux period hrs.	Yield	NMR, δ (ppm) D_2O—Me_4Si	Empirical formula
6[a]	$-CH_3$	225–7[b]	6	95	2.3 (s, 3, SCH_3)	$C_3H_3KN_2OS$[d]
7	$-C_2H_5$	220–5	1.5	56	1.2 (t, 3, $CH_2\underline{CH_3}$) 2.9 (q, 2, $\underline{CH_2}CH_3$)	$C_4H_5KN_2OS : 1.7H_2O$[e]
8	$-C_3H_7$	229–31[c]	22	69	—	$C_5H_7KN_2OS$[f]
9	$-C_4H_9$	220–2	22	62	—	$C_6H_9KN_2OS$[f]
10[g]	$-CH_2C_6H_5$	257–9[c]	72	30	4.1 (s, 2, CH_2) 7.4 (s, 5, C_6H_5)	$C_9H_7KN_2OS\frac{1}{2}H_2O$[f]

[a] IR (CsI): 2935 (aliph C—H), 2170 (C≡N) and 1585 cm^{-1} (C=N).

[b] Recrystallization from ethanol-water. (c) Recrystallization from methanol.

[d] Calcd: C, 23.36; H, 1.96; K, 25.35; N, 18.16; O, 10.37; S, 20.79.
Found: C, 23.57; H, 1.88; K, 25.28; N, 17.88; O, 10.68; S, 20.51

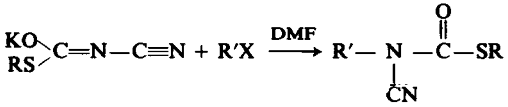
[e] Calcd: N, 14.00; S, 16.10; K, 19.60.
Found: N, 14.10; S, 16.12; K, 19.60.

[f] Satisfactory analytical data (±0.4%) for C, H, N and S were reported.

[g] IR (KBr): 2950 (aliph C—H), 2180 (C≡N) and 1590 cm^{-1} (C=N).

TABLE III

Alkyl-*N*-cyano-*N*-substituted thiolcarbamates



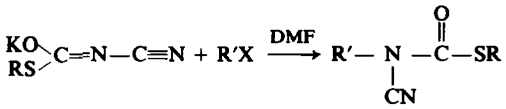
$$\begin{matrix}KO\\RS\end{matrix}\!\!>C{=}N{-}C{\equiv}N + R'X \xrightarrow{DMF} R'{-}\underset{\displaystyle CN}{N}{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}SR$$

No.	R	R′	X	Reaction conditions Temp. °C	Reaction conditions Time (days)	Bp °C/mm	% Yield	NMR, δ (ppm) CDCl$_3$—Me$_4$Si	IR (cm^{-1}) neat	Empirical formula	M$^{+\cdot}$ rel. intensity
11[a]	—CH$_3$	—CH$_3$	I	50–60	1	66/0.3 N_D^{25} = 1.5050	37	2.50 (s, 3, SCH$_3$) 3.32 (s, 3, NCH$_3$)	2230 (C≡N) 1700 (C=O)	C$_4$H$_6$N$_2$OS[c]	130 (23)
12[a]	—CH$_3$	—C$_2$H$_5$	Br	50–60	2	74–5/0.55 N_D^{25} = 1.4950	37	1.38 (t, 3, $\underline{CH_3}CH_2N$) 2.50 (s, 3, CH_3S) 3.75 (q, 2, $CH_3\underline{CH_2}N$)	2230 (C≡N) 1700 (C=O)	C$_5$H$_8$N$_2$OS[b]	144 (24)
13	—CH$_3$	—C$_3$H$_7$	Br	80–90	2	83–4/0.3 N_D^{25} = 1.4902	44	1.00 (t, 3, $N(CH_2)_2\underline{CH_3}$) 1.80 (sextet, 2, $NCH_2\underline{CH_2}CH_3$) 2.50 (s, 3, SCH$_3$) 3.70 (t, 2, $N\underline{CH_2}CH_2CH_3$)	2220 (C≡N) 1680 (C=O)	C$_6$H$_{10}$N$_2$OS[b]	158 (18)
14	—CH$_3$	—CH$_2$C$_6$H$_5$	Cl	80–90	2	150–2/0.5 N_D^{25} = 1.5645	45	2.40 (s, 3, SCH$_3$) 4.70 (s, 2, $N\underline{CH_2}$) 7.40 (s, 5, C$_6$H$_5$)	2230 (C≡N) 1670 (C=O)	C$_{10}$H$_{10}$N$_2$OS[b]	206 (12)
15	—CH$_3$	—C$_5$H$_{11}$	Br	80–90	2	87–9/0.5 N_D^{25} = 1.4859	63	0.7–1.1 (m, 3, $N(CH_2)_4\underline{CH_3}$) 1.1–2.1 (m, 6, $NCH_2(\underline{CH_2})_3CH_3$) 2.45 (s, 3, SCH$_3$) 3.67 (t, 2, $N\underline{CH_2}$)	2235 (C≡N) 1690 (C=O)	C$_8$H$_{14}$N$_2$OS[b]	186 (5)
16	—CH$_3$	—C$_4$H$_9$	Br	80–90	2	64–5/0.2 N_D^{25} = 1.4873	51	0.8–1.1 (m, 3, $N(CH_2)_3\underline{CH_3}$) 1.1–2.0 (m, 4, $NCH_2(\underline{CH_2})_2CH_3$) 2.45 (s, 3, SCH$_3$) 3.63 (t, 2, $N{-}\underline{CH_2}$)	2238 (C≡N) 1685 (C=O)	C$_7$H$_{12}$N$_2$OS[b]	172 (15)
17	—CH$_3$	—CH$_2$CH=CH$_2$	I	80–90	2	100–7/3.6 N_D^{25} = 1.5113	45	2.45 (s, 3, SCH$_3$) 4.20 (d, 2, $N\underline{CH_2}$) 5.13–6.30 (m, 3, $NCH_2\underline{CH}{=}\underline{CH_2}$)	2240 (C≡N) 1695 (C=O)	C$_6$H$_8$N$_2$OS[b]	156 (16)

TABLE III continued

18	$—C_2H_5$	$—CH_2C_6H_5$	Br	80–90	1	137–40/0.8 $N_D^{25} = 1.5537$	43	1.20 (t, 3, $\underline{CH_3}CH_2$) 2.87 (q, 2, $\underline{CH_2}CH_3$) 4.60 (s, 2, $\underline{NCH_2}$) 7.23 (s, 5, $\underline{C_6H_5}$)	2240 (C≡N) 1690 (C=O)	$C_{11}H_{12}N_2OS^b$	220 (20)
19	$—C_2H_5$	$—CH_2CH{=}CH_2$	I	80–90	1	85–8/1.0 $N_D^{25} = 1.5011$	33	1.33 (t, 3, $\underline{CH_3}CH_2$) 3.03 (q, 2, $\underline{CH_2}CH_3$) 4.23 (d, 2, $\underline{NCH_2}$) 5.13–6.33 (m, 3, $NCH_2\underline{CH}{=}\underline{CH_2}$)	2240 (C≡N) 1690 (C=O)	$C_7H_{10}N_2OS^b$	170 (25)
20	$—C_2H_5$	$—C_3H_7$	I	80–90	1	96/2.0 $N_D^{25} = 1.4869$	28	1.0 (t, 3, $\underline{CH_3}CH_2CH_2$) 1.33 (t, 3, $SCH_2\underline{CH_3}$) 1.73 (sextet, 2, $CH_2\underline{CH_2}CH_3$) 3.00 (q, 2, $S\underline{CH_2}CH_3$) 3.62 (t, 2, $N\underline{CH_2}CH_2CH_3$)	2240 (C≡N) 1690 (C=O)	$C_7H_{12}N_2OS^b$	172 (17)
21	$—C_2H_5$	$—C_2H_5$	Br	80–90	1	89–90/2.2 $N_D^{25} = 1.4892$	40	1.35 (t, 6, $SCH_2\underline{CH_3}$ and $NCH_2\underline{CH_3}$) 3.02 (q, 2, $S\underline{CH_2}CH_3$) 3.70 (q, 2, $N\underline{CH_2}CH_3$)	2240 (C≡N) 1690 (C=O)	$C_6H_{10}N_2OS^b$	158 (7)
22	$—C_2H_5$	$—CH_3$	I	70–80	1	55/0.3 $N_D^{25} = 1.4968$	41	1.33 (t, 3, $SCH_2\underline{CH_3}$) 3.00 (q, 2, $S\underline{CH_2}CH_3$) 3.27 (s, 3, $N\underline{CH_3}$)	2240 (C≡N) 1690 (C=O)	$C_5H_8N_2OS^b$	144 (10)
23	$—C_3H_7$	$—CH_3$	I	70–80	1	83–6/0.55 $N_D^{25} = 1.4928$	38	0.92 (t, 3, $S(CH_2)_2\underline{CH_3}$) 1.63 (q, 2, $SCH_2\underline{CH_2}CH_3$) 2.95 (t, 2, $S\underline{CH_2}CH_2CH_3$) 3.23 (s, 3, $N\underline{CH_3}$)	2240 (C≡N) 1690 (C=O)	$C_6H_{10}N_2OS^b$	158 (2)
24	$—C_3H_7$	$—C_2H_5$	Br	80–90	1	79–81/0.5 $N_D^{25} = 1.4881$	46	0.8–1.9 (m, 8, $CH_2\underline{CH_2CH_3}$ and $\underline{CH_3}CH_2N$) 2.98 (t, 2, $S\underline{CH_2}CH_2CH_3$) 3.70 (q, 2, $N\underline{CH_2}CH_3$)	2230 (C≡N) 1685 (C=O)	$C_7H_{12}N_2OS^b$	172 (7)
25	$—C_3H_7$	$—C_3H_7$	Br	80–90	1	96–9/0.9 $N_D^{25} = 1.4855$	34	1.0 (t, 6, $S(CH_2)_2\underline{CH_3}$ and $N(CH_2)_2\underline{CH_3}$) 1.48–2.08 (m, 4, $SCH_2\underline{CH_2}CH_3$ and $NCH_2\underline{CH_2}CH_3$) 3.0 (t, 2, $S\underline{CH_2}CH_2CH_3$) 3.63 (t, 2, $N\underline{CH_2}CH_2CH_3$)	2240 (C≡N) 1690 (C=O)	$C_8H_{14}N_2OS^b$	186 (14)

TABLE III continued



$$\begin{matrix}\mathrm{KO} \\ \mathrm{RS}\end{matrix}\!\!>\!C{=}N{-}C{\equiv}N + R'X \xrightarrow{\text{DMF}} R'{-}\underset{\displaystyle CN}{\underset{|}{N}}{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}SR$$

No.	R	R′	X	Reaction conditions Temp. °C	Time (days)	Bp °C/mm	% Yield	NMR, δ (ppm) $CDCl_3$—Me_4Si	IR (cm^{-1}) neat	Empirical formula	$M^{+\cdot}$ rel. intensity
26	—C_3H_7	—$CH_2CH{=}CH_2$	Br	80–90	1	78–9/0.2 N_D^{25} = 1.4969	51	1.0 (t, 3, $S(CH_2)_2\underline{CH_3}$) 1.74 (q, 2, $SCH_2\underline{CH_2}CH_3$) 3.02 (t, 2, $S\underline{CH_2}CH_2CH_3$) 4.2 (d, 2, N—$CH_2$) 5.2–6.2 (m, 3, $\underline{CH{=}CH_2}$)	2240 (C≡N) 1690 (C=O)	$C_8H_{12}N_2OS^b$	184 (10)
27	—C_3H_7	—$CH_2C_6H_5$	Br	80–90	1	155/0.9 N_D^{25} = 1.5476	46	0.9 (t, 3, $S(CH_2)_2\underline{CH_3}$) 1.53 (q, 2, $SCH_2\underline{CH_2}CH_3$) 2.90 (t, 2, $S\underline{CH_2}CH_2CH_3$) 4.63 (s, 2, NCH_2) 7.3 (s, 5, C_6H_5)	2240 (C≡N) 1690 (C=O)	$C_{12}H_{14}N_2OS^b$	234 (5)
28	—C_4H_5	—C_2H_5	Br	80–90	2	88–90/0.6 N_D^{25} = 1.4857	52	0.8–2.15 (m, 10, $NCH_2\underline{CH_3}$ and $SCH_2(\underline{CH_2})_2\underline{CH_3}$) 3.0 (t, 2, SCH_2) 3.7 (q, 2, N—CH_2)	2230 (C≡N) 1695 (C=O)	$C_8H_{14}N_2OS^b$	186 (28)
29	—C_4H_9	—$CH_2CH{=}CH_2$	Br	80–90	1	110–2/1.0 N_D^{25} = 1.4970	22	0.9 (br. t, 3, $S(CH_2)_3\underline{CH_3}$) 1.08–1.9 (m, 4, $SCH_2(\underline{CH_2})_2CH_3$) 3.0 (t, 2, $S\underline{CH_2}$) 4.08 (d, 2, $N\underline{CH_2}CH{=}CH_2$) 5.08–6.1 (m, 3, $CH_2\underline{CH{=}CH_2}$)	2240 (C≡N) 1690 (C=O)	$C_9H_{14}N_2OS^b$	198 (5)

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[a] Mass spectrum M/e (rel. intensity).
11, 130(23) ($M^{+\cdot}$), 84(4), 83(100), 77(3), 76(2), 75(75), 73(3), 58(5), 56(5), 47(39) and 45(14).
12, 144(24) ($M^{+\cdot}$), 98(4), 97(80), 75(100), 69(60), 47(26), 46(5) and 45(9).

[b] Satisfactory analytical data (±0.4%) for C, H, N and S were reported.

[c] Calcd: C, 36.91; H, 4.65; N, 21.52; O, 12.29; S, 24.64.
Found: C, 36.82; H, 4.69; N, 21.46; O, 12.10; S, 24.54.

spectrometer operating at an ionizing potential of 70 eV using the direct insertion probe technique with a source temperature of 250°C. The infrared spectra were obtained with a Beckman IR-12 spectrophotometer.

S,S′ Alkyl and Benzyl Cyanodithioimidocarbonates. (*Intermediates*) **1–5**. Compound 1 was prepared by the procedure described in our previous communication.[5] **2–5**. To a stirred solution containing 389 g (2.0 mol) of potassium cyanodithioimidocarbonate[4] in 1.5 L of water, 4 mol of the appropriate alkyl or benzyl halide was added in one portion. The stirred reaction mixture was held at 0–15°C for 1 hour and at 25–30°C for the time period specified in Table I. For **2**, **3** and **4**, 500 mL of ethyl ether was added and stirring continued at 25–30°C for 15 minutes. The separated ether layer was washed with water until neutral to litmus and dried over sodium sulfate. The ether was removed *in vacuo* at a maximum temperature of 80°C at 1–2 mm. For **5**, the solid was collected by filtration, washed with water until the washings were neutral to litmus and air-dried at 25–30°C. **5**, m.p. 82°C, was first prepared by E. Fromm and D. von Gonez.[8] Attempts to distill **2**, **3** and **4** *in vacuo* resulted in decomposition. The data are summarized in Table I.

O-Potassium S-Alkyl and Benzyl Cyanodithioimidocarbonates **6–10**. Upon stirring a mixture containing one mol of **1**, **2**, **3**, **4**, or **5**, 66 g (1.0 mol) of 85% potassium hydroxide and 500 mL of acetone, a temperature drop from 25° to 15°C was noted. The stirred mixture was heated at reflux for the time period specified in Table II and for all compounds except **7** at 25–30°C for 24 hours. A precipitate formed after 10 to 20 minutes at reflux (Hood-RSH). After the addition of 1500 mL of heptane, stirring was continued at 0–10°C for 30 minutes. The precipitate was collected by filtration and air-dried at 50°C. The data are summarized in Table II.

Alkyl-N-Cyano-N-Substituted Thiolcarbamates **11–29**. To a stirred solution containing 0.4 mol of **6**, **7**, **8** or **9** in 200 mL of dimethylformamide, 0.5 mol of the alkyl, allyl or benzyl halide was added in one portion resulting in a temperature rise of 25° to about 60°C over a 5 minute period. The stirred reaction mixture was heated at 50–60°C, 70–80°C or 80–90°C for time period specified in Table III. After cooling to 25°C, 500 mL of water and 500 mL of ethyl ether were added and stirring was continued for 15 minutes. The separated ether layer was washed with water until neutral to litmus and dried over sodium sulfate. The ether was removed *in vacuo* at a maximum temperature of 60°C at 10–12 mm. The crude product was distilled *in vacuo*. The data are summarized in Table III.

Stability of **11** *to Heat.* 10 g of crude **11** was heated at 100–116°C (760 mm) for 16 hours. This sample of **11** was distilled to give 8 g, bp 66°C/3 mm.

	Analytical data			
Sample	N_D^{25}	IR (cm^{-1}) neat	NMR, δ (ppm) $CDCl_3$—Me_4Si	$M^{+\cdot}$
Crude (before heating)	1.5102	2230 ($C\equiv N$) 1690 ($C=O$)	2.53 (s, 3, SCH_3) 3.39 (s, 3, NCH_3)	130
Crude (after heating)	1.5109	2225 ($C\equiv N$) 1695 ($C=O$)	2.52 (s, 3, SCH_3) 3.37 (s, 3, NCH_3)	130
Distilled product	1.5050	2230 ($C\equiv N$) 1700 ($C=O$)	2.50 (s, 3, SCH_3) 3.32 (s, 3, NCH_3)	130

The crude sample **11** gave the following analysis:

Calcd for $C_4H_6N_2OS$: C, 36.91; H, 4.65; N, 21.52; O, 12.29; S, 24.64. Found: C, 37.06; H, 4.58; O, 12.10; S, 24.49.

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