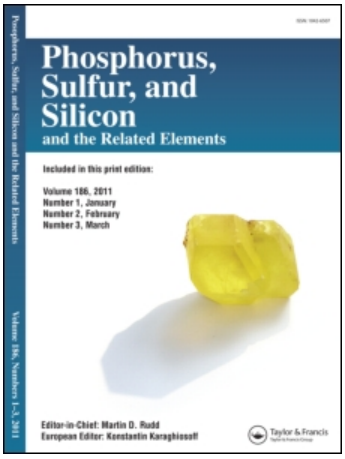

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SYNTHESIS OF ALKYL *N*-CYANO-*N*-SUBSTITUTED CARBAMATES AND *N,N*-DISUBSTITUTED CYANAMIDES[1]

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SYNTHESIS OF ALKYL *N*-CYANO-*N*-SUBSTITUTED CARBAMATES AND *N*,*N*-DISUBSTITUTED CYANAMIDES[1]

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The reactions of S,S′ methyl cyanodithioimidocarbonate with potassium hydroxide in alkyl or benzyl alcohol furnished the O-alkyl and benzyl O-potassium cyanoimidocarbonates (**1–5**). The reaction of the potassium salts (**1**, **3**, or **4**) with a 10% excess of alkyl, allyl or benzyl halides afforded the unknown titled carbamates (**6–17**). The reaction of **2** with 10% excess benzyl bromide or **5** with 10% excess methyl iodide gave the same product, *N*-benzyl-*N*-methyl cyanamide (**18**). The reactions of **2** with 10% and 55% excess allyl bromide afforded *N*-allyl-*N*-methyl cyanamide (**19**) and *N*,*N*-diallyl cyanamide (**20**), respectively. The reaction of **3** with 28% excess of allyl iodide furnished *N*-allyl-*N*-propyl cyanamide (**21**).

Possible mechanisms and supporting NMR, IR and mass spectra data are discussed.

In the preceding paper in this issue,[2] we reported the synthesis of O-potassium S-alkyl cyanothioimidocarbonates by the reaction of S,S′ alkyl cyanodithioimidocarbonate with potassium hydroxide in an *acetone* medium. Moreover, the reaction of the potassium salts with alkyl, allyl or benzyl halides afforded alkyl *N*-cyano-*N*-substituted thiolcarbamates.

We now wish to report that replacing the above potassium salts with O-alkyl and benzyl O-potassium cyanoimidocarbonate afforded the synthesis of the previously unknown titled carbamates of the *N*,*N*-disubstituted cyanamides.

By replacing acetone with methyl, ethyl, propyl, butyl or benzyl alcohol as a solvent, the reaction of S,S′ methyl cyanodithioimidocarbonate[3] with potassium hydroxide furnished the unexpected key intermediates, O-alkyl and benzyl O-potassium cyanoimidocarbonates (**1–5**).

$$(CH_3S)_2C{=}N{-}C{\equiv}N + ROH \xrightarrow{KOH} \begin{matrix} KO \\ RO \end{matrix}\!\!>C{=}N{-}C{\equiv}N + 2CH_3SH \qquad (1)$$

1, R = $-C_2H_5$; **2**, R = $-CH_3$; **3**, R = $-C_3H_7$; **4**, R = $-C_4H_9$; **5**, R = $-CH_2C_6H_5$

Analysis, infrared (neat), and NMR spectra were in agreement for the proposed structures of **1–5**. Based on elemental analysis and NMR spectra the alternate carbamate structure NC—N(K)—C(=O)—OR had to be considered in Reaction 1. However, the carbamate structure was ruled out on the basis of the infrared spectral data. In **1** the presence of C≡N and C=N absorption bands at 2170 and 1580

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cm^{-1}, respectively and the absence of the C=O absorption band at 1700–1755 cm^{-1} furnished conclusive evidence for the proposed structures **1–5**.

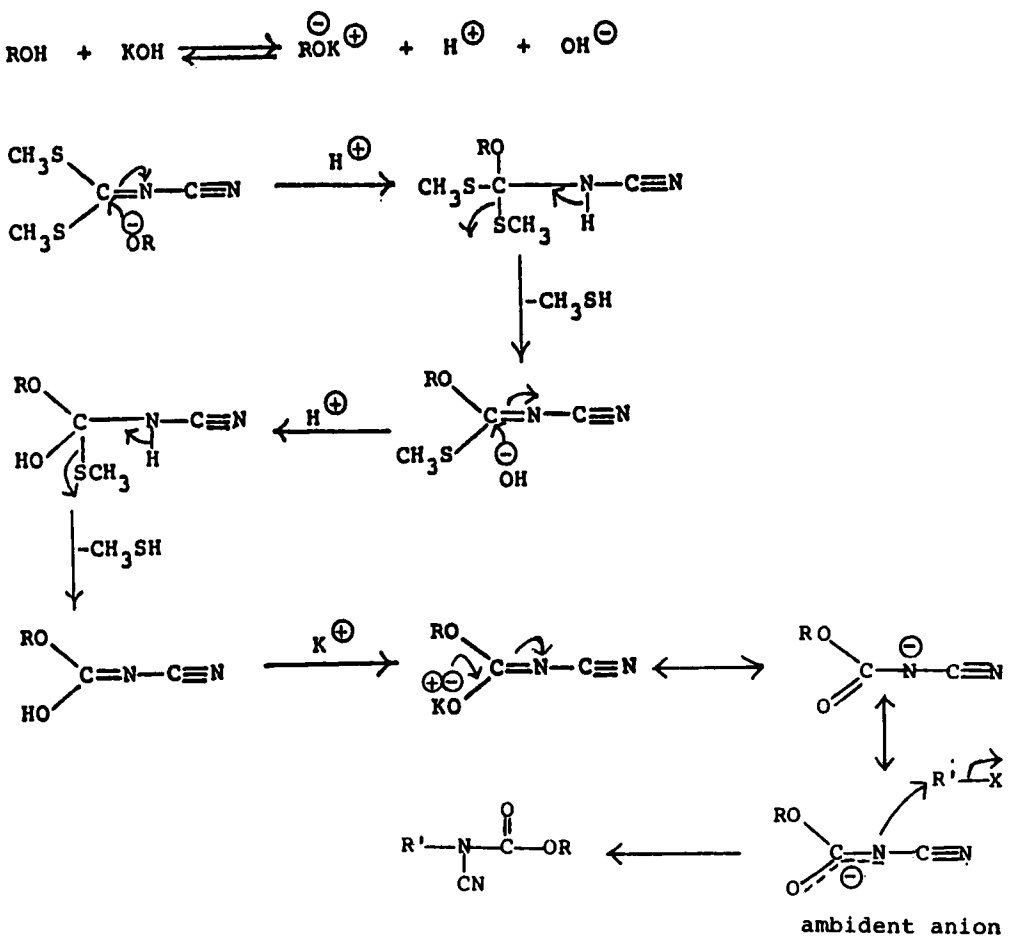
The reaction of the potassium salts (**1**, **3** or **4**) with a 10% excess of alkyl, allyl or benzyl halides in dimethylformamide at 80–90°C afforded the titled carbamates (**6–17**).

$$\begin{matrix}KO\\RO\end{matrix}\!\!>C{=}N{-}C{\equiv}N + R'X \xrightarrow[80\text{–}90^{\circ}C]{DMF} R'{-}\underset{\underset{CN}{|}}{N}{-}\overset{\overset{O}{\|}}{C}{-}OR \qquad (2)$$

10% excess

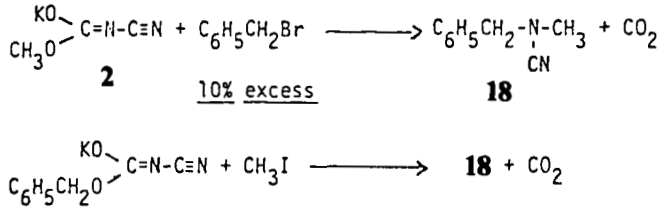
R and R′ as shown in Table II

Analysis, infrared, NMR and mass spectra were in agreement for the proposed structure of **6–17**. The proposed mechanisms for Reactions 1 and 2 are depicted in Scheme I.



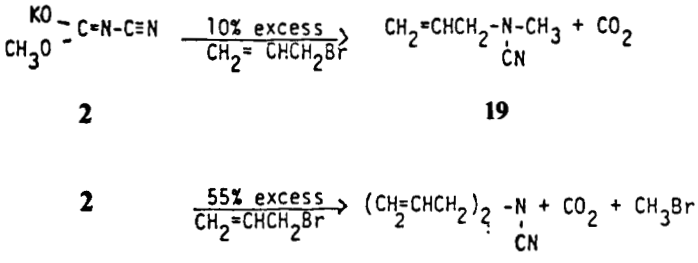
SCHEME 1

The reaction of **2** with 10% excess benzyl bromide or **5** with 10% excess methyl iodide gave the same product, *N*-benzyl-*N*-methyl cyanamide (**18**).



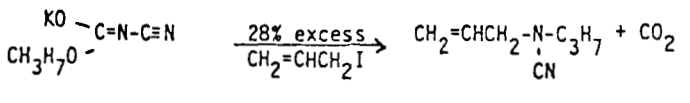
(3)

The reaction of **2** with 10% and 55% excess allyl bromide afforded *N*-allyl-*N*-methyl cyanamide (**19**) and *N*,*N*-diallyl cyanamide (**20**), respectively.



(4)

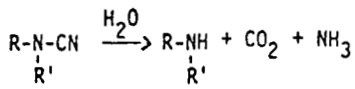
The reaction of **3** with 28% excess of allyl iodide gave *N*-allyl-*N*-propyl cyanamide (**21**).



(5)

The proposed mechanisms for the formation of **18**, **19**, **20** and **21** are shown in Scheme 2.

The determination of the optimum conditions for the synthesis of the unsymmetrical cyanamides similar to **18**, **19** and **21** by our novel method (Reactions 3, 4 and 5) would be very desirable. The hydrolysis of these mixed cyanamides would provide a useful synthesis of secondary mixed amines (Reaction 6) which is not possible by Vliet's method[4] (Reaction 7) which affords only secondary symmetrical amines.



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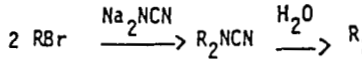

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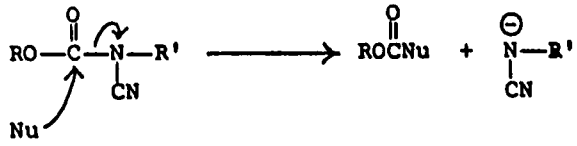
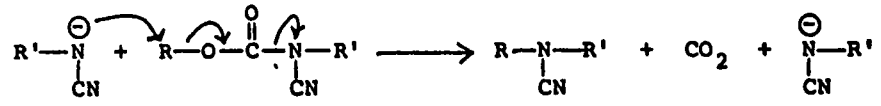
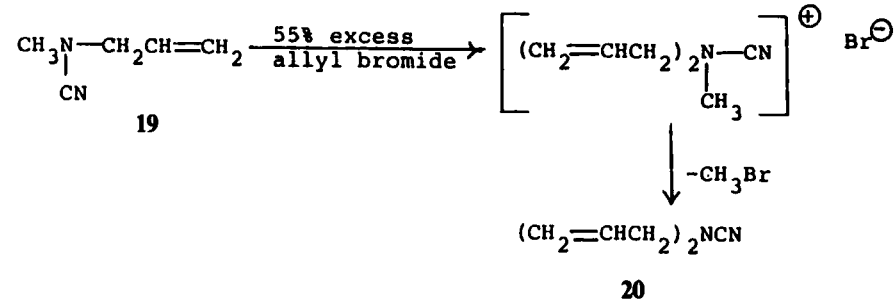




No.	R	R'	excess Halide
18	$-CH_3$	$-CH_2C_6H_5$	10%-Benzyl bromide
	$-CH_2C_6H_5$	$-CH_3$	10%-Methyl iodide
19	$-CH_3$	$-CH_2CH=CH_2$	10%-Allyl bromide
21	$-C_3H_7$	$-CH_2CH=CH_2$	28%-Allyl iodide



SCHEME 2

In summary, depending on reaction condition, we have described a novel and versatile direct synthesis of alkyl *N*-cyano-*N*-substituted carbamates or *N*,*N*-disubstituted cyanamides. The required intermediates can be prepared in good yields from cyanamide, carbon disulfide, potassium hydroxide, alkyl or benzyl alcohols and alkyl or benzyl halides which are readily available and inexpensive.

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. The infrared spectra were obtained with a Beckman IR-12 spectrophotometer.

O-Alkyl and benzyl O-potassium cyanoimidocarbonates **1–5**. To a stirred solution at 25°C containing 19.8 g (0.3 mol) of 85% potassium hydroxide in 300 mL of methyl, ethyl, propyl, butyl or benzyl alcohol,

TABLE I

O Alkyl and benzyl O potassium cyanoimidocarbonates

$$(CH_3S)_2C{=}N{-}C{\equiv}N + ROH \xrightarrow{KOH} \begin{matrix} KO \\ RO \end{matrix}\!\!>C{=}N{-}C{\equiv}N + 2CH_3SH$$

No.	R	Mp °C (dec.)	Heating period Hrs.	Heating period T °C	% Yield	NMR, δ (ppm) $Me_2SO d_6$—Me_4Si	Empirical formula
1[a]	$-C_2H_5$	196–7[b]	6	75–80	87	1.05 (t, 3, $CH_2\underline{CH_3}$) 3.80 (q, 2, $\underline{CH_2}CH_3$)	$C_4H_5KN_2O_2 \cdot \frac{1}{2}H_2O$[c]
2	$-CH_3$	238–9	6	50–60	68	3.40 (2, 3, $\overline{CH_3}$)	$C_3H_3KN_2O_2$[d]
3	$-C_3H_7$	159–61	22	54–58	65	—	$C_5H_7KN_2O_2$[f]
4	$-C_4H_9$	153–5[e]	48	78–80	79	—	$C_6H_9KN_2O_2$[f]
5	$-CH_2C_6H_5$	229–31[e]	48	80–90	99	5.1 (s, 2, CH_2) 7.4 (s, 5, C_6H_5)	$C_9H_7KN_2O_2 \cdot \frac{1}{4}H_2O$[f]

[a] IR (CsI): 3000 (aliph C—H), 2170 (C≡N), and 1580 cm^{-1} (C=N).
[b] Recrystallization from ethanol.
[c] Calcd: C, 29.80; H, 3.75; K, 24.75; N, 17.38; O, 24.81
Found: C, 30.17; H, 3.78; K, 24.48; N, 16.98; O, 24.44.
[d] Calcd: C, 26.08; H, 2.19; K, 28.30; N, 20.27
Found: C, 26.02; H, 2.13; K, 28.19; N, 20.10.
[e] Recrystallization from methanol.
[f] Analytical data (±0.4%) for C, H and N were reported.

43.9 g (0.3 mol) of S,S′ methyl cyanodithioimidocarbonate[3] was added in one portion. An exothermic reaction set in causing a temperature rise from 25° to about 45°C and the formation of a precipitate over a 10–15 minute period. The stirred reaction mixture was heated at 50° to 90°C for the time period specified in Table I and at 25–30°C for 24 hours. During this period methyl mercaptan was liberated (*Hood*). After cooling to 0°C, 400 mL of heptane was added and stirring continued at 0–10°C for 30 minutes. The solid was collected by filtration and air-dried at 50°C. The data are summarized in Table I.

Alkyl N-cyano-N-substituted carbamates—**6–17**. To a stirred solution containing 0.3 mol of **1**, **3** or **4** in 200 mL of dimethylformamide, 0.33 mol (10% excess) of the alkyl, allyl or benzyl halide was added in one portion. The stirred reaction mixture was heated at 80–90°C for the time period specified in Table II. 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 80°C at 10–12 mm. The crude product was distilled *in vacuo*. The data are summarized in Table II.

N-Benzyl-N-methyl cyanamide, method I—**18**. To a stirred solution containing 27.6 g (0.2 mol) of **2** in 200 mL of dimethylformamide, 37.6 g (0.22 mol—10% excess) of benzyl bromide was added in one portion. The stirred reaction mixture was heated at 80–90°C for 22 hours. 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 rest of the procedure was identical as described for **6–17**. **18**, bp 105–112°C/0.65 mm, N_D^{25} = 1.5287, was obtained in 39% yield NMR ($CDCl_3$) δ 2.63 (s, 3, NCH_3); 4.02 (s, 2, NCH_2); 7.28 (s, 5, C_6H_5). IR (CsI): 2240 (C≡N) and 739 and 704 cm^{-1} (C_6H_5).

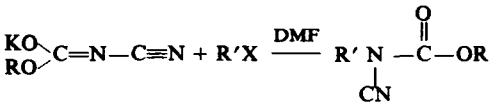
Mass spectrum m/e (rel. intensity): 146 (7) (M^+). *Anal.* Calcd. for $C_9H_{10}N_2$: C, 73.94; H, 6.89; N, 19.16. Found: C, 73.88; H, 7.02; N, 18.82.

Method II—**18**. The procedure was identical as described in Method I except 43.7 g (0.2 mol) of **5** and 31.2 g (0.22 mol—10% excess) of methyl iodide was substituted for **2** and benzyl bromide, respectively. **18**, 96–98°C/0.5 mm. N_D^{25} = 1.5277, was obtained in 48% yield. The analytical data (NMR, IR, mass spectra and elemental analyses) were comparable to that reported in Method I.

N-Allyl-N-methyl cyanamide—**19**. To a stirred solution containing 27.6 g (0.2 mol) of **2** in 200 mL of dimethylformamide, 0.22 mol—(10% excess) of allyl bromide or iodide was added in one portion. The stirred reaction mixture was heated at 80–90°C for 72 hours. The rest of the procedure was the same as described for **6–17**. **19**, bp 36–40°C/0.8 mm, N_D^{25} = 1.4432 (Lit.[5] bp 74–5°C/15 mm), was obtained in

TABLE II

Alkyl *N*-substituted carbamates



No.	R	R'	X	Reaction time days	bp °C/mm	% yield	NMR, δ (ppm) $CDCl_3$—Me_4Si	IR (cm^{-1}) neat	M^+ (Rel. intensity)	Empirical formula
6	$-C_2H_5$	$-CH_2C_6H_5$	Br	2	122–5/0.7 N_D^{25} = 1.5149	30	1.20 (t, 3, $OCH_2\underline{CH_3}$) 4.18 (q, 2, $O\underline{CH_2}CH_3$) 4.55 (s, 2, NCH_2) 7.33 (s, 5, C_6H_5)	2250 (C≡N) 1750 (C=O)	204 (15)[b]	$C_{11}H_{12}N_2O_2$[a]
7	$-C_2H_5$	$-CH_2CH=CH_2$	I	2	53–5/0.3 N_D^{25} = 1.4532	41	1.30 (t, 3, $OCH_2\underline{CH_3}$) 4.07 (d, 2, $N\underline{CH_2}CH=CH_2$) 4.27 (q, 2, $O\underline{CH_2}CH_3$) 5.03–6.20 (m, 3, $CH_2\underline{CH=CH_2}$)	2250 (C≡N) 1755 (C=0)	154(7)[b]	$C_7H_{10}N_2O_2$[a]
8	$-C_2H_5$	$-C_2H_5$	Br	1	79–81/3.2 N_D^{25} = 1.4355	46	1.33 (t, 6, $OCH_2\underline{CH_3}$ and $NCH_2\underline{CH_3}$) 3.57 (q, 2, $N\underline{CH_2}CH_3$) 4.27 (q, 2, $O\underline{CH_2}CH_3$)	2245 (C≡N) 1750 (C=O)	142(12)[b]	$C_6H_{10}N_2O_2$[a]
9	$-C_2H_5$	$-C_3H_7$	Br	3	66–8/0.8 N_D^{25} = 1.4389	41	0.97 (t, 3, $NCH_2CH_2\underline{CH_3}$) 1.30 (t, 3, $OCH_2\underline{CH_3}$) 1.70 (q, 2, $NCH_2\underline{CH_2}CH_3$) 3.47 (t, 2, $N\underline{CH_2}CH_2CH_3$) 4.25 (q, 2, $O\underline{CH_2}CH_3$)	2240 (C≡N) 1750 (C=O)	156(3)[b]	$C_7H_{12}N_2O_2$[a]
10	$-C_2H_5$	$-CH_3$	I	1	42/0.4 N_D^{25} = 1.4393	27	1.30 (t, 3, $OCH_2\underline{CH_3}$) 3.17 (s, 3, NCH_3) 4.25 (q, 2, $O\underline{CH_2}CH_3$)	2250 (C≡N) 1755 (C=O)	128(8)[b]	$C_5H_8N_2O_2$[a]
11	$-C_3H_7$	$-CH_3$	I	1	74–6/1.4 N_D^{25} = 1.4332	41	0.92 (t, 3, $O(CH_2)_2\underline{CH_3}$) 1.70 (q, 2, $OCH_2\underline{CH_2}CH_3$) 3.18 (s, 3, NCH_3) 4.14 (t, 2, $O\underline{CH_2}CH_2CH_3$)	2210 (C≡N) 1755 (C=O)	142(10)[b]	$C_6H_{10}N_2O_2$[a]

12	$-C_3H_7$	$-C_2H_5$	Br	1	81/1.6 N_D^{25} = 1.4375	48	1.0 (t, 3, $O(CH_2)_2\underline{CH_3}$) 1.32 (t, 3, $NCH_2\underline{CH_3}$) 1.73 (q, 2, $OCH_2\underline{CH_2}CH_3$) 3.6 (q, 2, $N\underline{CH_2}CH_3$) 4.2 (t, 2, $O\underline{CH_2}CH_2CH_3$)	2210 (C≡N) 1755 (C=O)	156(10)[b]	$C_7H_{12}N_2O_2$[a]
13	$-C_3H_7$	$-C_3H_7$	Br	1	90/1.6 N_D^{25} = 1.4385	67	0.98 (t, 6, $O(CH_2)_2\underline{CH_3}$ and $N(CH_2)_2\underline{CH_3}$) 1.73 (q, 4, $OCH_2\underline{CH_2}CH_3$ and $NCH_2\underline{CH_2}CH_3$) 3.55 (t, 2, $N\underline{CH_2}CH_2CH_3$) 4.2 (t, 2, $O\underline{CH_2}CH_2CH_3$)	2210 (C≡N) 1755 (C=O)	170(7)[b]	$C_8H_{14}N_2O_2$[a]
14	$-C_3H_7$	$-CH_2C_6H_5$	Br	1	144–5/1.2 N_D^{25} = 1.5093	41	0.85 (t, 3, $O(CH_2)_2\underline{CH_3}$) 1.63 (q, 2, $OCH_2\underline{CH_2}CH_3$) 4.15 (t, 2, $O\underline{CH_2}CH_2CH_3$) 4.68 (s, 2, $N\underline{CH_2}$) 7.3 (s, 5, $C_6\underline{H_5}$)	2210 (C≡N) 1755 (C=O)	218(8)[b]	$C_{12}H_{14}N_2O_2$[a]
15	$-C_4H_9$	$-C_3H_7$	Br	1	78–9/0.5 N_D^{25} = 1.4361	71	0.93 (m, 6, $N(CH_2)_2\underline{CH_3}$ and $O(CH_2)_3\underline{CH_3}$) 1.1–1.9 (m, 6, $NCH_2\underline{CH_2}CH_3$) and $OCH_2(\underline{CH_2})_2CH_3$) 3.23 (t, 2, $N\underline{CH_2}CH_2CH_3$) 4.1 (t, 2, $O\underline{CH_2}(CH_2)_2CH_3$)	2250 (C≡N) 1755 (C=O)	185[c]	$C_9H_{16}N_2O_2$[a]
16	$-C_4H_9$	$-C_2H_5$	Br	1	76–8/0.8 N_D^{25} = 1.4348	57	0.85 (m, 3, $O(CH_2)_3\underline{CH_3}$) 1.05–1.95 (m, 7, $NCH_2\underline{CH_3}$ and $OCH_2(\underline{CH_2})_2CH_3$) 3.5 (q, 2, $N\underline{CH_2}CH_3$) 4.15 (t, 2, $O\underline{CH_2}(CH_2)_2CH_3$)	2250 (C≡N) 1750 (C=O)	171[c]	$C_8H_{14}N_2O_2$[a]
17	$-C_4H_9$	$-CH_3$	I	1	68–71/0.9 N_D^{25} = 1.4351	19	0.9 (m, 3, $O(CH_2)_3\underline{CH_3}$) 1.1–1.8 (m, 4, $O(\underline{CH_2})_2CH_2CH_3$) 3.2 (t, 3, $N\underline{CH_3}$) 4.2 (t, 2, $O\underline{CH_2}(CH_2)_2CH_3$)	2250 (C≡N) 1765 (C=O)	157[c]	$C_7H_{12}N_2O_2$[a]

[a] Satisfactory analysis (±0.4%) were reported for C, H and N.
[b] Electron impact mass spectra.
[c] Chemical ionization mass spectra $(M + 1)^+$.

37% yield. NMR ($CDCl_3$) δ 2.85 (s, 3, NCH_3); 3.63 (d, 2, $NCH_2CH{=}CH_2$); 5.13–6.37 (m, 3, $NCH_2CH{=}CH_2$). IR: 2210 (C≡N) cm^{-1}. Mass spectrum m/e (rel. intensity): 96 (45) (M^+). *Anal.* Calcd for $C_5H_8N_2$; C, 62.47; H, 8.39; N, 29.14. Found: C, 62.28; H, 8.40; N, 29.04.

N,N-Diallyl cyanamide—**20**. To a stirred solution containing 82.8 g (0.6 mol) of **2** in 350 mL of dimethylformamide, 111 g (0.93 mol—55% excess) of allyl bromide was added in one portion. The stirred reaction mixture was heated at 80–90°C for 72 hours. The rest of the procedure was the same as described for **6–17**. **20**, bp 74–9°C/4.2 mm, N_D^{25} = 1.4610 (Lit.[4] bp 105–110°C/18 mm) was obtained in 27% yield. NMR ($CDCl_3$) δ 3.65 (d, 4, $NCH_2CH{=}CH_2$); 5.2—6.4 (m, 6, $NCH_2CH{=}CH_2$). IR: 2235 (C≡N) cm^{-1}. Chemical ionization mass spectrum: 123 $(M + 1)^+$. *Anal.* Calcd. for $C_7H_{10}N_2$: C, 68.82; H, 8.25; N, 22.93. Found: C, 68.16; H, 8.48; N, 23.16.

N-Allyl-N-propyl cyanamide—**21**. To a stirred solution containing 47 g (0.28 mol) of **3** in 200 mL of dimethylformamide, 60.5 g (0.36 mol—28% excess) of allyl iodide was added in one portion. The stirred reaction mixture was heated at 80–90°C for 48 hours. The rest of the procedure was the same as described for **6–17**. **21**, bp 53–6°C/0.9 mm, N_D^{25} = 1.4534, was obtained in 20% yield. NMR ($CDCl_3$) δ 0.92 (t, 3, $N(CH_2)_2CH_3$); 1.3–2.0 (m, 2, $NCH_2CH_2CH_3$); 2.9 (t, 2, $NCH_2CH_2CH_3$); 3.5 (d, 2, $NCH_2CH{=}CH_2$); 5.1–6.2 (m, 3, $NCH_2CH{=}CH_2$). IR: 2220 (C≡N) cm^{-1}. Mass spectrum m/e (rel. intensity): 124 (10) (M^+). *Anal.* Calcd. for $C_7H_{12}N_2$: C, 67.70; H, 9.74; N, 22.56. Found: C, 67.50; H, 9.73; N, 22.50.

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