Tetrahedron Vol. 36, pp. 131 to 142
Pergamon Press Ltd., 1980. Printed in Great Britain

REACTIONS OF N-1(2,2-DICHLOROALKYLIDENE)AMINES WITH POTASSIUM CYANIDE: SYNTHESIS OF β-CHLORO-α-CYANOENAMINES, α-CHLOROIMIDATES AND 2-AMINO-5-CYANOPYRROLS

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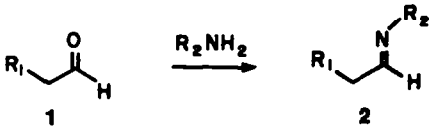
(*Received in UK 12 March 1979*)

Abstract—Reaction of N-1-(2,2-dichloroalkylidene)amines, prepared by chlorination of aliphatic aldimines with N-chlorosuccinimide, with excess of potassium cyanide in methanol gave β-chloro-α-cyanoenamines. When the reaction was carried out for a longer period, α-chloroimidates were isolated (except for N-t-Bu compounds). Reaction of the α-chloroaldimines with potassium cyanide in dimethylsulphoxide at 70° gave 1,2-dicyanoenamines while at 120° 2-amino-5-cyanopyrrols were produced via 1,3-dicyanoenamines. The reaction mechanisms are discussed.

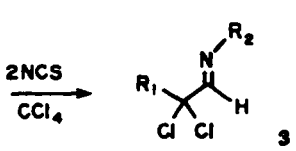
The synthesis of α- and β-substituted enamines has been a topic of continuing interest especially as useful intermediates in a variety of cycloadditions.[2-4] In the course of our studies concerning the reactivity of α-chlorinated aldimines a new synthesis of α-cyanoenamines was found by reaction of N-1-(2-chloroalkylidene)amines with potassium cyanide in methanol.[5,6] Although a number of syntheses of α-cyanoenamines (most of them are tertiary enamines) are known,[7-11] our method represents one of the most general routes to the preparation of aliphatic secundary α-cyanoenamines.

We have now studied the reactions of N-1-(2,2-dichloroalkylidene)amines 3 with potassium cyanide in various solvents and succeeded in synthesising new aliphatic β-chloro-α-cyanoenamines and α-chloroimidates.

2,2-Dichloroaldimines 3 were prepared by treatment of aliphatic aldehydes with primary amines followed by chlorination of the aldimines 2 with N-chlorosuccinimide in carbon tetrachloride at room temperature (Table 1).[12]

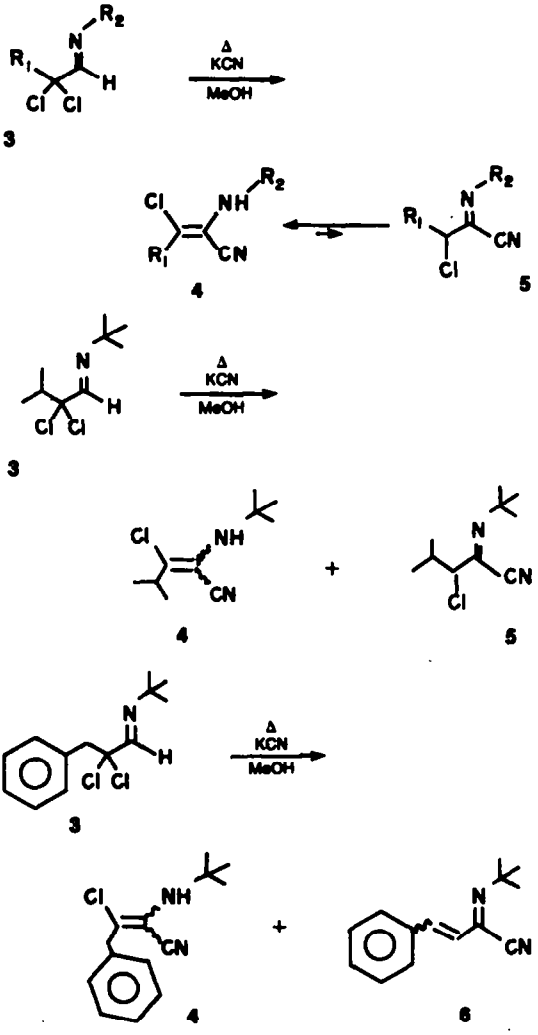


R_1 = Me, Et, Pr, i-Pr, C_6H_5, $C_6H_5CH_2$
R_2 = Me, i-Pr, s-Bu, t-Bu, cyclohex



Scheme 1.

The reaction of 2,2-dichloroaldimines 3 with potassium cyanide in methanol turned out to be strongly dependent upon the nature of both R_1 and R_2 and the time. Reaction of N-1-(2,2-dichloroalkylidene)t-butylamines (3, R_2 = t-Bu) mainly gave β-chloro-α-cyanoenamines 4. In the case of R_1 = Me, Et, Pr, C_6H_5 the compounds with Z-configuration were exclusively obtained, while when R_1 = i-Pr a mixture of E and Z isomers was isolated next



Scheme 2.

Table 1. Synthesis and spectrometric properties of N-1-(2,2-dichloroalkylidene)amines 3

R_1	R_2	Yield %	B.p. °C/mmHg	I.R. $\nu_{C=N}$ (cm^{-1})	N.M.R. δ (ppm)	Mass spectrum m/e (%)
Me	t-Bu	90	55/50	1665	1.20(9H,s,t-Bu); 2.23(3H,s,CH_3); 7.66(1H,s,N=CH)	181/83/85(M^+, 0.1); 166/68/70(5); 146/48(0.5); 131(0.6); 116/18(1); 90/92(7); 84(31); 77/79(5); 57(100) 41(14)
Et	Me	72	52- 54/20	1675	1.20(3H,t,J=7.5Hz,CH_3); 2.39(2H, q,J=7.5Hz,CH_2); 3.33(3H,d,J=2.2Hz, N-CH_3); 7.71(1H,q,J=2.2Hz,N=CH)	153/55/57(M^+, 0.1); 138/40/42(0.1); 125/27/29(0.5); 118/20(5); 104/06 (3); 68(1); 57(4); 42(100); 41(3)
Et	i-Pr	89	62- 65/16	1662	1.17(6H,d,J=6.2Hz,$(CH_3)_2$); 1.25 (3H,t,J=7.5Hz,CH_3); 2.45(2H,q, J=7.5Hz,CH_2); 3.45(1H,sept.,J= 6.2Hz,N-CH); 7.70(1H,s,N=CH)	181/83/85(M^+, 0.1); 104(2); 85(5); 70(80); 44(7); 43(100); 42(7); 41(17)
Et	s-Bu	81	66- 68/18	1670	0.85(3H,t,J=7.0Hz,CH_3); 1.19(3H, d,J=6.1Hz,CH_3); 1.23(3H,t,J=7.1Hz, CH_3); 1.50(2H,m,CH_2); 2.49(2H,q, J=7.1Hz,CH_2CCl_2); 3.17(1H,m,CH); 7.76(1H;s;N=CH)	195/97/99(M^+, 0.01); 180/82/84(0.1) 176/78/80(3); 160/62(2); 114/16(5); 99(7); 84(40); 57(100); 56(5); 55 (4); 53(4); 44(6); 42(5); 41(24)
Et	t-Bu	92	70/22	1672	1.20(9H,s,t-Bu); 1.22(3H,t,J=0.7Hz, CH_3); 2.45(2H,q,J=7.0Hz,CH_2); 7.64 (1H,s,N=CH)	195/97/99(M^+, 0.1); 180/82/84(2); 104/06(6); 99(19); 84(14); 57(100)
Et	cyclohex	78	110-114/14	1670	1.17(3H,t,J=7.2Hz,CH_3); 1.40-1.90 (10H,m,CH_2); 2.42(2H,q,J=7.2Hz, CH_2); 3.09(1H,m,=N-CH); 7.70(1H, s,N=CH)	192/94/96(0.5); 186/88(2); 125(8); 110(28); 104(39); 83(100); 55(25); 41(17); 39(4)
n-Pr	Me	81	62- 64/12	1675	0.98(3H,t,J=7.0Hz,CH_3); 1.37-2.01 (2H,m,CH_2); 2.12-2.49(2H,m,CH_2CCl_2) 3.34(3H,d,J=2.2Hz,=N-CH_3); 7.72 (1H,q,J=2.2Hz,N=CH)	167/69/71(M^+, 0.1); 138/40/42(0.1); 132/34(3); 125/27/29(4); 102/04(3); 96(2); 71(4); 53(1); 42(100); 41(2)
n-Pr	i-Pr	85	69- 73/12	1660	1.02(3H,t,J=6.8Hz,CH_3); 1.17(6H, d, J=6.7Hz,$(CH_3)_2$); 1.66-2.30(4H, m,CH_2); 3.47(1H,sept,=N-CH); 7.75 (1H,s,N=CH)	180/82/84(1); 160/62(2); 153/55/57 (4); 138/40/42(3); 118/20(3); 99(9); 70(62); 55(3); 43(100); 41(10)
n-Pr	t-Bu	91	79- 81/12	1675	1.00(3H,t,J=6.5Hz,CH_3); 1.20(9H,s, t-Bu); 1.60(2H,m,CH_2); 2.40(2H,t, J=6.9Hz,CH_2CCl_2); 7.62(1H,s,N=CH)	209/11/13(M^+, 0.1); 194/96/98(2); 174/76(0.5); 167/69/71(2); 118(4); 113(10); 98(15); 84(9); 57(100)
i-Pr	t-Bu	82	77- 80/13	1665	1.15(6H,d,J=7.0Hz,$(CH_3)_2$); 1.20 (9H,s,t-Bu); 2.77(1H,sept. J=7.0 Hz,CH); 7.58(1H,s,N=CH)	209/11/13(M^+, 0.1); 194/96/98(1); 167/69/71(1); 152/54/56(2); 118/20 (4); 111/13(5); 99(18); 84(15); 57(100)
C_6H_5	t-Bu	34	75/0.7	1675	1.21(9H,s,t-Bu); 7.25(5H,m,Ar-H); 7.75(1H,s,N=CH)	228/30/32(1); 208/10(1); 153(7); 152 (5); 117(5); 84(25); 77(4); 75(5); 58(5); 57(100); 41(13)
$C_6H_5CH_2$	t-Bu	96	M.p. 68°C	1680 1660	1.22(9H,s,t-Bu); 3.70(2H,s,CH_2); 7.29(5H,m,Ar-H); 7.65(1H,s,N=CH)	257/59/61(M^+, 0.01); 210/12(13); 172/74/76(10); 157/59(19); 129/31 (14); 100(33); 91(100); 85(41); 83 (40); 71(50); 69(49); 58(53); 57(98) 55(49); 55(43); 43(48); 41(64)

Elemental Analysis of N-1-(2,2-Dichloroalkylidene)amines 3

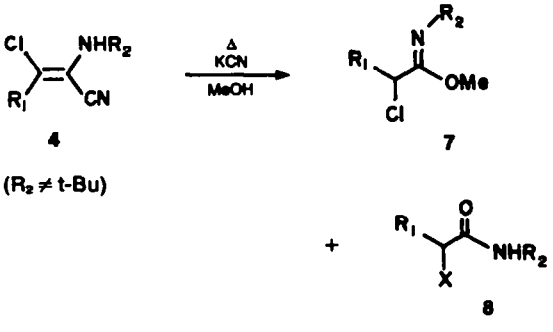
R_1	R_2	Formula	Required				Founded			
			C	H	Cl	N	C	H	Cl	N
Me	t-Bu	$C_7H_{13}Cl_2N$	46.17	7.20	38.94	7.69	46.43	7.08	38.03	7.53
Et	Me	$C_5H_9Cl_2N$	38.99	5.89	46.03	9.09	38.75	5.93	45.41	8.98
Et	i-Pr	$C_7H_{13}Cl_2N$	46.17	7.20	38.94	7.69	46.27	7.15	38.22	7.51
Et	s-Bu	$C_8H_{15}Cl_2N$	48.99	7.71	36.15	7.14	48.78	7.64	36.91	7.24
Et	t-Bu	$C_8H_{15}Cl_2N$	48.99	7.71	36.15	7.14	49.09	7.72	37.08	7.17
Et	cyclohex	$C_{10}H_{17}Cl_2N$	54.06	7.71	31.92	6.31	53.78	7.76	32.63	6.19
n-Pr	Me	$C_6H_{11}Cl_2N$	42.88	6.60	42.19	8.33	42.73	6.64	42.91	8.12
n-Pr	i-Pr	$C_8H_{15}Cl_2N$	48.99	7.71	36.15	7.14	48.71	7.76	35.44	7.23
n-Pr	t-Bu	$C_9H_{17}Cl_2N$	51.44	8.15	33.74	6.67	51.37	8.04	33.11	6.81
i-Pr	t-Bu	$C_9H_{17}Cl_2N$	51.44	8.15	33.74	6.67	51.58	8.09	34.63	6.83
C_6H_5	t-Bu	$C_{12}H_{15}Cl_2N$	59.03	6.19	29.04	5.74	58.97	6.23	29.63	5.68
$C_6H_5CH_2$	t-Bu	$C_{13}H_{17}Cl_2N$	60.48	6.64	27.46	5.43	60.15	6.71	28.31	5.51

to a minor amount of the corresponding imidoyl cyanide **5**, i.e. the imino tautomer. However on standing or on heating the *E*-form was transformed into the more stable *Z*-isomer. The reaction of N-1-(2,2-dichloro-3-phenylpropylidene)t-butylamine (**3**, $R_1 = C_6H_5CH_2$, R_2 = t-Bu) under the same circumstances gave a mixture of *E*- and *Z*-2-t-butylamino-3-chloro-4-phenyl-2-butenenitrile **4** and *E*- and *Z*-2-t-butylimino-4-phenyl-3-butenenitrile **6**.

Up to now only few β-chloro-α-cyanoenamines have been prepared by a variety of methods.[8,9,13,14]

However, when R_2 is different from t-Bu, the reaction of **3** with potassium cyanide in methanol seemed to be dependent on the conditions (Table 2). When the reaction was carried out for a short time (2–3 hr) a nearly 50:50 mixture of β-cyanoenamine **4** and imidoyl cyanide **5** was isolated. Prolonged heating of the mixture resulted in a gradual transformation of the β-chloro-α-cyanoenamines **4** ($R_2 \neq$ t-Bu) into α-chloroimidates **7** and small amounts of α-chloro or α-cyanoamides **8**.

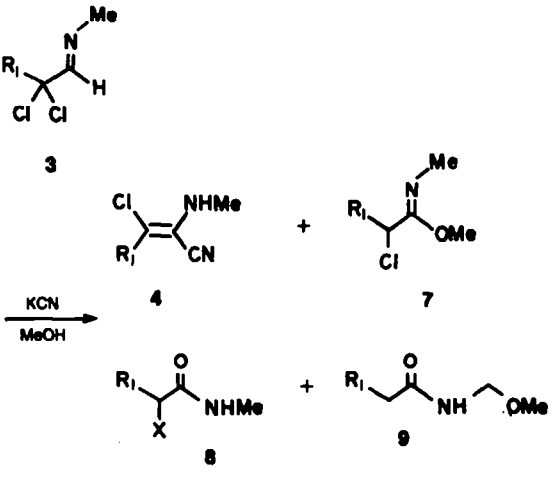
This reaction did not occur with the N-t-Bu derivatives even on heating for 78 hr.



Scheme 3.

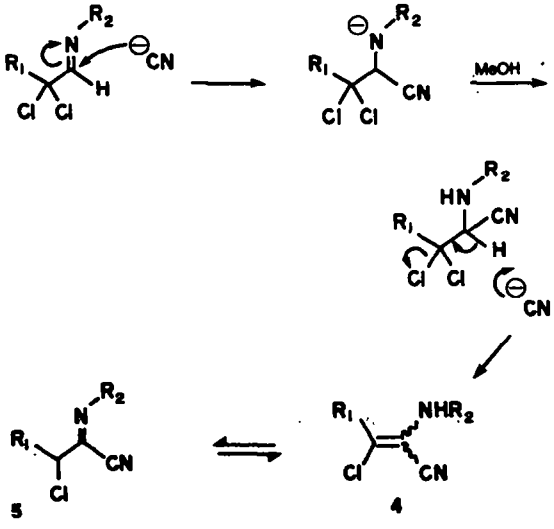
This method represents a new general approach to the preparation of α-chloroimidates. Until now only a limited number of reports were dealing with the synthesis of aliphatic chlorinated imidates.[15]

In the case of the N-Me derivatives the reaction is more complicated. Even at room temperature a mixture of β-chloro-α-cyanoenamine **4** and α-chloroimidate **7** was obtained, the ratio of both depending upon the time.



Scheme 4.

The reaction at reflux temperature produced next to **4** and **7** a mixture of amides **8** and **9** resulting from further transformations of α-chloroimidate **7**.



Scheme 5.

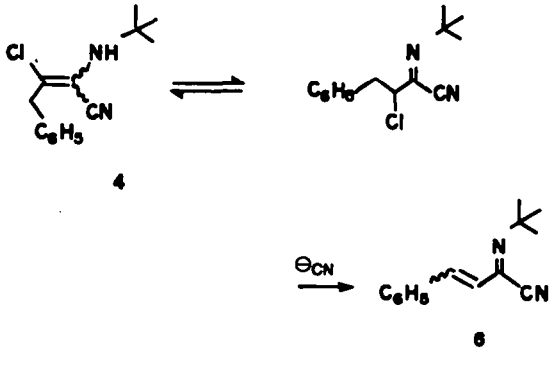
Table 2. Reaction of N-1-(2,2-dichloroalkylidene)amines with KCN in methanol

R_1	R_2	Reaction conditions	Product Distribution (%)[a] α-Cyano enamine 4 (Z)	Imidoyl cyanide 5	α-Chloro-imidate 7	Others
Me	t-Bu	3h/Δ	100 %	-	-	-
Et	Me	10h/r.t°	70 %	-	30 %	-
		3h/Δ	21 %	-	34 %	10 % 8 (X=Cl); 35 % 9
Et	i-Pr	2h/Δ	45 %	45 %	10 %	
		4h/Δ	25 %	25 %	50 %	
		20h/Δ	5 %	5 %	90 %	
Et	s-Bu	2h/Δ	55 %	40 %	5 %	
		24h/Δ	10 %	-	90 %	
Et	t-Bu	12h/Δ	100 %			
Et	cyclohex	3h/Δ	40 %	48 %	12 %	
		20h/Δ	20 %	20 %	50 %	10 % 8 (X=CN)
n-Pr	Me	2h/r.t°	75 %	-	25 %	
		8h/r.t°	55 %	-	30 %	15 % 9
		2h/Δ	25 %	-	30 %	45 % 9
n-Pr	i-Pr	3h/Δ	70 %	-	30 %	
		20h/Δ	10 %	10 %	80 %	
		48h/Δ	-	5 %	50 %	8 % 8 (X=Cl)
						35 % 8 (X=CN)
n-Pr	t-Bu	3h/Δ	100 %	-	-	
i-Pr	t-Bu	3h/Δ	43 % Z	16 %		
			41 % E			
C_6H_5	t-Bu	3h/Δ	100 %			
$C_6H_5CH_2$	t-Bu	3h/Δ	25 % Z			50 % 6
			25 % E			

a) The percentic composition was calculated from the NMR spectra and/or by GLC from the crude reaction mixture.

The spectrometric properties of the β-chloro-α-cyanoenamines 4, α-chloroimidoyl cyanides 5 and α-chloroimidates 7 are compiled respectively in Tables 3–5.

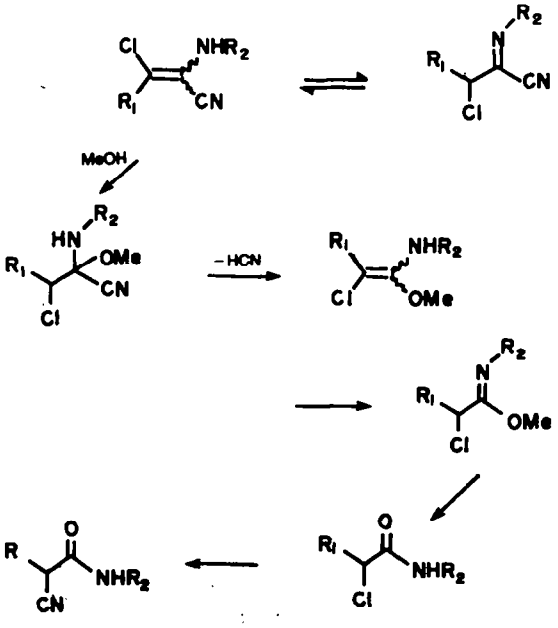
The formation of β-chloro-α-cyanoenamines 4 can be explained by a nucleophilic addition at the C=N double bond followed by protonation by the solvent producing non isolable N-alkylaminonitriles. Dehydrochlorination afforded the enamines 4.



Scheme 6.

As mentioned above the reaction consisted of a mixture of the enaminic and ketiminic form in a few cases. Both isomers could be isolated by preparative glc, so this type of tautomerism should be referred to as desmotropism.

2-t-Butylimino-4-phenyl-3-butenenitrile 6 was produced by elimination of hydrogen chloride from the imino tautomer of enamine 4. This supplementary elimination was possible due to the activating effect of the phenyl group.



Scheme 7.

The formation of α-chloroimidates can be rationalised in terms of an addition of methanol at the double bond followed by elimination of hydrogen cyanide and isomerisation of the enamines into the imidates. A mechanism in which an addition of methanol took place at the C=N double bond of the chlorinated imidoyl cyanides seems less plausible, as we have noted that in the case of the α-chloroimidoyl cyanides no imidate formation was observed in the reaction with potassium cyanide in methanol.[5]

The imidates were transformed into amides by a mechanism discussed earlier during the reaction of 3 with sodium methoxide in methanol.[13]

The formation of the N-methoxymethyl amides 9 when R_2 = Me is initiated by deprotonation of the N-Me group and expulsion of a Cl anion. Addition of methanol at the azabutadiene moiety will be favored at the imino carbon providing an imidate which is transformed into an amide.

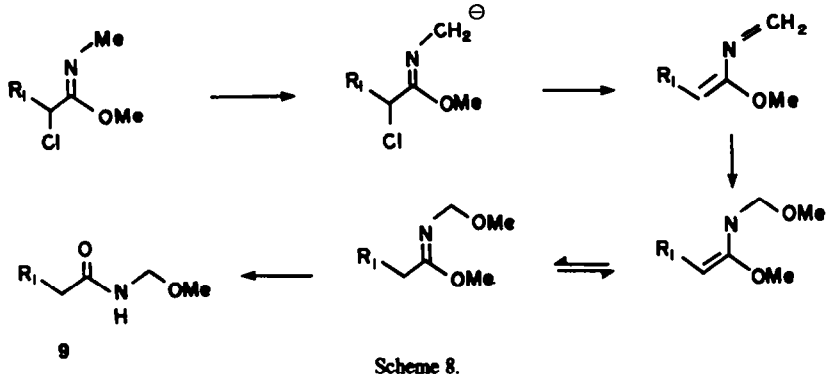
Also the reaction of N-1-(2,2-dichloroalkylidene)amines 3 with an excess of potassium cyanide in dimethylsulfoxide was investivated. At room temperature β-chloro-α-cyanoenamines 4 were formed, however when the reaction was carried out at 60° for 20 hr a mixture of *E*- and *Z*-α,β-dicyanoenamines 10 were isolated. On distillation or preparative glc the *E*-isomers were transformed into the more stable *Z*-compounds. Compounds 10 were formed by addition of cyanide at the double bond of the cyanoenamines 4 followed by elimination of hydrogen chloride (*cf.* nucleophilic vinylic substitution[14]).

The reaction in DMSO at higher temperature (120°) took a completely different course and 2-amino-5-cyanopyrrols 12 (Table 7) were produced via isolable 1,3-dicyano-2-alkylideneamines 11 (mixture of *E*- and *Z*-isomers).

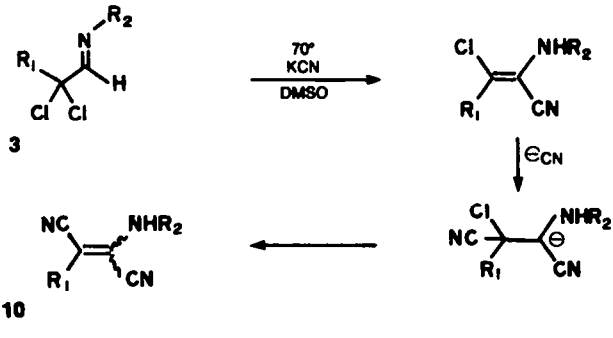
The formation of the pyrrols 12 is visualised to arise from 1,3-dicyano 11 compounds which were formed by dehydrochlorination in a first step. At higher temperature this elimination seems to be favored with respect to the addition reaction as in the previous cases. Michael addition at the C=C double bond and nucleophilic addition of cyanide at the C=N double bond followed by a second elimination reaction provided 11.

Ring closure of the latter compounds by an intramolecular nucleophilic attack of the amino-nitrogen at the cyanide group and prototropy furnished 2-iminopyrroline derivatives 13 which tautomerised into the more stable 2-amino-5-cyanopyrrols 12.

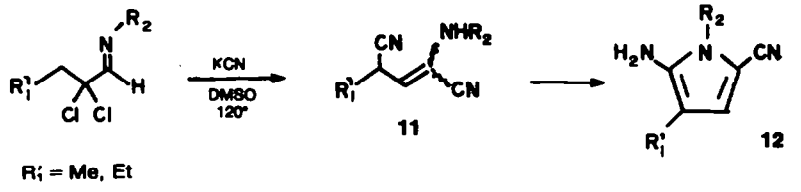
This reaction pathway has been confirmed by the reaction of N-1-(2,2-dichloro-3-methylbutylidene)t-butylamine 3, where next to the 1,3-dicyanoenamine 11 (40%) the intermediate iminopyrrol 13 (45%) could be isolated



Scheme 8.



Scheme 9.



Scheme 10.

Table 3. Synthesis and spectrometric properties of β-chloro-α-cyanoenamines 4

R_1	R_2	B.p. °C/mmHg	Yield (%)	IR (cm^{-1}) ν_{NH}, $\nu_{C\equiv N}$ $\nu_{C=C}$	N.M.R. δ (ppm)	Mass spectrum m/e (%)
Me	t-Bu	87/18	90	3360 2230 1615	1.33(9H,s,t-Bu); 2.37(3H,s, CH_3-C=C); 3.40(1H,s broad,NH)	172/74(M^+, 2); 116/18(15); 81(7); 58(5); 57(100); 42(8); 41(34)
Et	Me	63/15	45	3380 2230 1625	1.20(3H,t,J=6.8Hz,CH_3); 2.62(2H, q,J=6.8Hz,CH_2); 2.90(2H,d,J=6.0 Hz,NH-CH_3); 3.40(1H,m,NH)	144/46(M^+, 30); 129/31(100); 109 (13); 93(6); 82(4); 67(15); 66(9); 58(42); 53(9); 42(6); 41(11); 39(8)
Et	i-Pr	85- 87/15	90	3335 2235 1625	1.19(3H,t,J=7.2Hz,CH_3); 1.20(6H, d,J=5.8Hz,CH_3); 2.61(2H,q,J=7.2 Hz,CH_2); 3.42(1H,sept., J=5.8Hz, CH)	172/74(M^+, 4); 157/59(24); 130/32 (4); 115/17(28); 103(13); 95(13); 88(13); 68(8); 53(11); 44(13); 43 (100); 42(22); 41(56)
Et	s-Bu	98-101/14	82	3370 2230 1620	0.94(3H,t,J=7.0Hz,CH_3); 1.12(3H, d,J=6.5Hz,CH_3); 1.16(3H,t,J=7.1 Hz,CH_3); 1.45(2H,m,CH_2); 2.61 (2H,q,J=7.1Hz,CH_2-C=C); 3.27(2H, m,NH,CH)	186/88(M^+, 19); 171/73(12); 157/59 (100); 151(7); 115(19); 95(10); 57 (41); 56(14); 53(10); 43(25); 42 (12); 41(38)
Et	t-Bu	105/15	94	3370 2230 1620	1.31(9H,s,t-Bu); 1.19(3H,t,J=7.4 Hz,CH_3); 2.65(2H,q,J=7.4Hz,CH_2); 3.38(1H,s broad,NH)	186/88(M^+, 3); 130/32(12); 115(9); 95(6); 58(5); 57(100); 42(9); 41 (38)
Et	cyclohex	100/0.01	78	3400 2240 1625	1.20(3H,t,J=7.2Hz,CH_3); 1.33-2.10 (10H,m); 2.60(2H,q,J=7.2Hz,CH_2); 3.00-3.40(2H,m,NH,N-CH)	212/14(M^+, 37); 197/99(2); 177(4); 169/71(63); 130/32(74); 122(14); 115(31); 95(15); 83(68); 67(23); 55(100); 41(79); 39(30)
n-Pr	Me	74/15	57	3375 2225 1625	0.96(3H,t,J=7.1Hz,CH_3); 1.33-2.10 (2H,m,CH_2); 2.54(2H,t,J=7.1Hz,CH_2) 2.87(3H,d,J=5.5Hz,NH-CH_3); 3.45 (1H,s broad, NH)	158/60(M^+, 17); 129/31(100); 112 (5); 93(5); 67(10); 66(9); 53(9); 42(9); 41(10); 40(7); 39(7)
n-Pr	i-Pr	92- 95/12	83	3350 2225 1620	0.98(3H,t,J=7.6Hz,CH_3); 1.22(6H, d,J=6.0Hz,$(CH_3)_2CH$); 1.45-1.95(2H, m,CH_2); 2.61(2H,t,J=7.2Hz,CH_2-C=C) 3.00-4.55(2H,m,NH,CH)	186/88(M^+, 34); 171/73(75); 157/59 (48); 115/17(95); 87(24); 70(19); 43(100); 42(16); 41(40)
n-Pr	t-Bu	113/18	90	3360 2235 1610	0.95(3H,t,J=7.0Hz,CH_3); 1.32(9H, s,t-Bu); 1.64(2H,m,CH_2); 2.64(2H, t,J=6.8Hz,CH_2); 3.44(1H,s broad,NH)	200/202(M^+, 12); 185/87(9); 144/46 (44); 115/17(59); 57(100); 41(28)
i-Pr	t-Bu	110/15	89	3360 2230 1600	Z:1.15(6H,d,J=6.4Hz,$(CH_3)_2CH$); 1.31(9H,s,t-Bu); 3.28(2H,m,NH,CH) E:1.08(6H,d,J=6.8Hz,$(CH_3)_2CH$); 1.24(9H,s,t-Bu); 2.60(1H,s broad, NH); 3.31(1H,sept.,J=6.8Hz,CH)	200/202(M^+, 9); 185/87(8); 144/46 (45); 129/31(98); 109(24); 57(100); 42(10); 41(43)
C_6H_5	t-Bu	decomposition	15	3360 2235 1600	1.41(9H,s,t-Bu); 7.35(5H,s broad, Ar-H)	234/36(M^+, 15); 177/79(100); 151(5) 143(14); 142(8); 118(13); 106(6); 89(6); 77(4); 57(77); 41(34)
$C_6H_5CH_2$	t-Bu		45[a]	3370 2230 1610	Z:1.36(3H,s,t-Bu); 3.40(1H,s broad,NH); 3.86(2H,s,CH_2-C=C); 7.18(5H,s broad, Ar-H) E:1.23(3H,s,t-Bu); 3.83(2H,s, CH_2-C=C); 7.18(5H, s broad, Ar-H)	248/50(M^+, 8); 233/35(6); 191/93 (42); 156(29); 140(10); 130(8); 91(7); 77(6); 57(100); 55(7); 41 (45)

[a] Yield determined by GLC.

Elemental Analysis of β-Chloro-α-cyanoenamines 4

R_1	R_2	Formula	Required				Founded			
			C	H	Cl	N	C	H	Cl	N
Me	t-Bu	$C_8H_{13}ClN_2$	55.65	7.59	20.53	16.23	55.11	7.41	21.04	15.79
Et	Me	$C_6H_9ClN_2$	49.84	6.27	24.52	19.37	49.14	6.44	25.12	19.44
Et	i-Pr	$C_8H_{13}ClN_2$	55.65	7.59	20.53	16.23	55.12	7.41	20.98	16.47
Et	s-Bu	$C_9H_{15}ClN_2$	57.90	8.10	18.99	15.01	58.14	8.19	19.16	15.08
Et	t-Bu	$C_9H_{15}ClN_2$	57.90	8.10	18.99	15.01	57.64	8.23	18.78	14.98
Et	cyclohex	$C_{11}H_{17}ClN_2$	62.11	8.06	16.67	13.20	62.98	7.94	17.14	13.38
n-Pr	Me	$C_7H_{11}ClN_2$	53.00	6.99	22.35	17.66	53.41	7.21	22.47	17.52
n-Pr	i-Pr	$C_9H_{15}ClN_2$	57.90	8.10	18.99	15.01	58.64	8.34	18.89	15.09
n-Pr	t-Bu	$C_{10}H_{17}ClN_2$	59.84	8.54	17.66	13.96	58.34	8.47	17.22	14.12
i-Pr	t-Bu	$C_{10}H_{17}ClN_2$	59.84	8.54	17.66	13.96	58.97	8.68	17.34	14.02

Table 4. Spectrometric properties of 2-chloroimidoyl cyanides 5[a)]

R_1	R_2	I.R. $\nu_{C\equiv N}$ $\nu_{C=N}$	N.M.R. δ (ppm)	Mass spectrum m/e (%)
Et	Me	2225 1630	1.07(3H,t,J=7.4Hz,CH_3); 2.06(2H,m,CH_2); 3.61(3H,s,N-CH_3); 4.33(1H,t,H=6.1Hz,CHCl)	129/31(1); 116/18(20); 109(29); 93(3); 82(6); 67(100); 53(5); 42(5); 41(6)
Et	i-Pr	2230 1635	1.04(3H,t,J=7.0Hz,CH_3); 1.21(6H,d,J=6.1 Hz,CH_3); 1.98(2H,m,CH_2); 3.96(1H,sept., J=6.1Hz,CH); 4.28(1H,t,J=7.2Hz,CHCl)	157/59(3); 137(6); 95(11); 68(7); 54(5); 43 (100); 42(17); 41(21)
Et	s-Bu	2235 1620	0.85(3H,t,J=6.7Hz,CH_3); 1.05(3H,t,J=6.2 Hz,CH_3); 1.15(3H,d,J=6.0Hz,CH_3); 1.53 (2H,m,CH_2); 2.07(2H,m,CH_2); 3.70(1H,m, CH); 4.36(1H,t,J=7.1Hz,CHCl)	171/73(4); 167/69(46); 151(20); 129(12); 81 (5); 68(9); 57(100); 56(12); 55(9); 54(6); 53(7); 41(33)
Et	t-Bu	2235 1635	1.05(3H,t,J=7.3Hz,CH_3); 1.40(9H,s,t-Bu); 2.05(2H,m,CH_2); 4.26(1H,t,J=7.3Hz,CHCl)	171/73(2); 151(1); 120/22(5); 95(4); 68(3); 67 (2); 57(100); 56(6); 55(4); 43(6); 41(12)
Et	cyclohex	2230 1640	1.03(3H,t,J=7.5Hz,H$_3$CH_3); 1.56(10H,m,CH_2) 1.97(2H,qud,J=7.5,J=7.0Hz,CH_2); 3.60 (1H,m,N-CH); 4.31(1H,t,J=7.0Hz, CHCl)	212/14 (M^+, 1); 197/99(1); 184/86(6); 177(100) 135(10); 95(16); 83(85); 81(30); 67(11); 55 (82); 41(54); 39(38)
n-Pr	i-Pr	2220 1635	0.99(3H,t,J=7.0Hz,CH_3); 1.23(6H,d,J=6.1 Hz,CH_3); 1.69-2.21(4H,m,CH_2); 3.99(1H, sept., J=6.1Hz,CH); 4.40(1H,t,J=7.5Hz, CHCl)	186/88(M^+, 1); 171/73(29); 151(29); 144/46(35) 129/31(41); 109(17); 102(12); 95(7); 82(8); 81 (5); 71(4); 70(4); 55(10); 54(8); 43(100); 42 (17); 41(23)
n-Pr	t-Bu	2225 1630	0.96(3H,t,J=7.1Hz,CH_3); 1.30(9H,s,t-Bu); 1.5-2.0(4H,m,CH_2); 4.36(1H,t,J=6.0Hz, CHCl)	185/87(6); 165(1); 158/60(4); 109(5); 102/04 (3); 82(4); 57(100); 56(6); 55(4); 54(4); 43 (7); 42(4); 41(21)
i-Pr	t-Bu	2230 1640	0.98(6H,d,J=6.4Hz,$(CH_3)_2$); 1.40(9H,s,t-Bu) 2.30(1H,m,CH); 4.03(1H,d,J=9.3Hz,CHCl)	185/87(6); 165(6); 143/45(26); 116/18(11); 109(12); 102/04(11); 58(9); 57(100); 56(5); 43(7); 41(18)

a) All compounds were purified by preparative GLC.

Table 5. Synthesis and spectrometric properties of methyl N-alkyl-2-chloroimidates 7

R_1	R_2	B.p. °C/mmHg	Yield (%)	I.R. $\nu_{C=N}$ (cm^{-1})	N.M.R. δ (ppm)	Mass spectrum m/e (%)
Et	Me	(a)	-	1685	0.97(3H,t,J=7.1Hz,CH_3); 1.70-2.15(2H, m,CH_2); 3.05(3H,s,N-CH_3); 3.56(3H,s, OCH_3); 4.46(1H,t,J=6.8Hz,CHCl)	134/36(0.1); 121/23(22); 116/18(17); 114(32); 109(23); 72(73); 67(100); 42 (33); 41(15)
Et	i-Pr	81-83/13	73	1680	1.05(9H,m,CH_3); 1.85(2H,m,CH_2); 3.60 (3H,s,OCH_3); 3.60(1H,sept., J=6.8Hz, CH); 4.42(1H,t,J=7.7Hz,CHCl)	162/64(11); 149(51(6); 142(10); 114(9) 100(16); 73(5); 68(11); 59(14); 58(100) 43(27); 42(13); 41(33)
Et	s-Bu	85-88/13	68	1675	0.7-1.2(9H,m,CH_3); 1.48(2H,m,CH_2); 1.97(2H,m,CH_2-CHCl); 3.33(1H,m,CH); 4.46(1H,m,CHCl)	191/93(M^+, 0.5); 190/92(1); 176/78(10); 163/65(30); 162/64(100); 156(30); 108 (7); 104(8); 100(11); 70(9); 68(10); 58 (77); 57(16); 56(11); 55(16); 43(8); 42 (10); 41(40); 39(11)
Et	cyclohex	69-73/0.2	50	1680	0.95(3H,t,J=7.2Hz,CH_3); 1.10-1.75 (10H,m,CH_2); 1.85(2H,q x d,J=7.2Hz, J=6.9Hz,CH_2CHCl); 3.30(1H,m,N-CH); 3.59(3H,s,N-OCH_3); 4.43(1H,t,J=6.9 Hz,CHCl)	217/19(M^+, 1); 216/18(3); 202/04(3); 189/91(29); 182(100); 174/76(79); 140 (23); 136(29); 108/10(30); 100(27); 98 (27); 83(35); 81(21); 67(8); 58(24); 55(27); 41(34); 39(8)
n-Pr	Me	(a)	30	1690	0.96(3H,t,J=7.0Hz,CH_3); 1.20-2.20 (4H,m,CH_2); 3.07(3H,s,N-CH_3); 3.60 (3H,s,N-OCH_3); 4.55(1H,t,J=7.2Hz, CHCl)	132/34(1); 127(2); 114/16(7); 107/09 (36); 83(5); 72(8); 58(100); 55(10); 41(5); 39(4)
n-Pr	i-Pr	92-95/12	80	1680	1.06(3H,d,J=6.1Hz,CH_3); 1.07(3H,t, J=7.2Hz,CH_3); 1.13(3H,d,J=6.1Hz,CH_3) 1.15-2.07(4H,m,CH_2); 3.60(3H,s,N-OCH_3) 3.66(1H,sept.,J=6.1Hz,CH); 4.52(1H,t, J=7.3Hz,CHCl)	191/93(M^+, 1); 176/178(7); 156(13); 149/51(12); 114(15); 102(8); 58(20); 43(100); 41(10)

(a) Compound isolated by preparative GLC.

Elemental Analysis of α-Chloroimidates 7

R_1	R_2	Formula	Required				Founded			
			C	H	Cl	N	C	H	Cl	N
Et	i-Pr	$C_6H_{16}ClNO$	54.08	9.08	19.95	7.88	55.14	9.02	19.14	7.84
Et	s-Bu	$C_9H_{18}ClNO$	56.39	9.46	18.49	7.31	57.01	9.14	18.03	7.39
Et	cyclohex	$C_{11}H_{20}ClNO$	60.68	9.26	16.28	6.43	60.53	9.38	16.14	6.53
n-Pr	i-Pr	$C_9H_{18}ClNO$	56.39	9.46	18.49	7.31	56.14	9.22	18.09	7.28

Table 6. Synthesis and spectrometric properties of (Z)-N-alkyl-1,2-dicyano-1-alkenylamines 10

R_1	R_2	B.p. °C/mmHg	Yield (%)	I.R. $\nu_{NH,CN\ C=C}$	N.M.R. δ (ppm)	Mass spectrum m/e (%)
Me	t-Bu		(a)	3335 2235 2215 1605	1.42(9H,s,t-Bu); 2.03(3H,s,CH_3-C=C); 4.50(1H,s broad, NH)	163(M^+, 3); 148(3); 107(7); 58(5); 57(100); 56(9); 55(5); 42(9); 41(37)
		M.p. 97°	82		E (b) : $\delta_{CH_3-C=C}$: 1.82	
Et	Me		(a)	3340 2230 2220 1610	1.19(3H,t,J=7.5Hz,CH_3); 2.60(2H,q, J=7.5Hz,CH_2); 3.09(3H,d,J=5.0Hz, NH-CH_3); 4.90(1H,m,NH)	135(M^+, 4); 120(25); 107(59); 95 (15); 93(25); 92(9); 80(100); 67 (17); 66(9); 53(15); 52(9); 43(13); 41(34); 40(27)
Et	i-Pr	108-110/12	78	3300 2245 1600	1.19(3H,t,J=7.8Hz,CH_3); 1.27(6H,d, J=6.1Hz,$(CH_3)_2$); 2.40(2H,q,J=7.8Hz, CH_2); 3.85(1H,sept.,J=6.1Hz,CH); 4.94(1H,s broad,NH) (E) : $\delta_{CH_2-C=C}$: 2.16	163(M^+, 23); 148(13); 133(5); 121 (20); 120(11); 106(16); 80(12); 67 (4); 66(4); 53(4); 52(4); 43(100); 42(10); 41(24)
Et	t-Bu	110-113/13	73	3340 2240 2210 1590	1.19(3H,t,J=7.6Hz,CH_3); 1.43(9H,s, t-Bu); 2.39(2H,q,J=7.6Hz,CH_2-C=C); 4.50(1H,s broad,NH) (E) : $\delta_{CH_2-C=C}$: 2.16	177(M^+, 5); 162(11); 130(5); 117(6); 100(8); 82(12); 65(5); 57(100); 56 (9); 43(16); 42(6); 41(17)
Et	cyclohex	87- 89/0.01 M.p. : 94°	64	3335 2230 2210 1600	1.17(3H,t,J=7.8Hz,CH_3); 1.3-2.1(10H, m,CH_2); 2.40(2H,q,J=7.8Hz,CH_2-C=C); 3.45(1H,m,N-CH); 4.40(1H,s broad,NH) (E) : $\delta_{CH_2-C=C}$: 2.20	203(M^+, 22); 188(2); 160(27); 132 (3); 122(15); 121(11); 106(7); 83 (100); 82(33); 67(20); 57(65); 41(33)
n-Pr	i-Pr	68- 71/0.05	66	3340 2220 2200 1600	1.00(3H,t,J=7.2Hz,CH_3); 1.28(6H,d, J=6.0Hz,$(CH_3)_2$); 1.4-1.9(2H,m,CH_2); 2.35(2H,t,J=7.2Hz,CH_2-C=C); 3.84(1H, sept.,J=6.0Hz,CH); 4.90(1H,s broad,NH) (E) : $\delta_{CH_2-C=C}$: 2.03	177(M^+, 38); 162(30); 148(96); 135 (21); 121(50); 106(76); 95(25); 81 (93); 79(21); 68(30); 54(29); 43(100) 42(42); 41(82)
n-Pr	t-Bu	74- 76/0.05	71	3335 2235 2210 1595	0.99(3H,t,J=7.6Hz,CH_3); 1.43(9H,s, t-Bu); 1.5-2.0(2H,m,CH_2); 2.34(2H, t,J=7.6Hz,CH_2-C=C); 4.47(1H,s broad, NH)	191(M^+, 6); 176(4); 135(11); 106(10); 79(2); 57(100); 56(6); 42(4); 41(20)
i-Pr	t-Bu		(a)	3335 2215 1600	1.17(6H,d,J=6.1Hz,$(CH_3)_2$); 1.41(9H, s,t-Bu); 2.88(1H,sept.,J=6.1Hz,CH); 4.45(1H,s broad,NH)	191(M^+, 20); 176(12); 135(9); 120 (20); 93(2); 57(100); 43(3); 41(45)

(a) Isolated by preparative GLC.

(b) The NMR of the (E) isomer is identical to the one of the (Z) isomer except for the alkyl group on the double bond.

Elemental Analysis of N-Alkyl-1,2-dicyano-1-alkenylamines 10

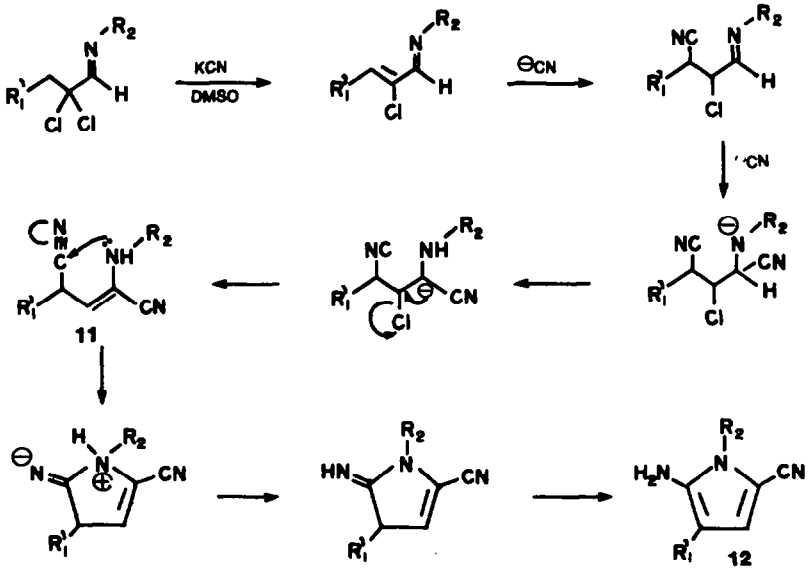
R_1	R_2	Formula	Required			Founded		
			C	H	N	C	H	N
Me	t-Bu	$C_9H_{13}N_3$	66.23	8.03	25.74	65.78	8.14	25.14
Et	i-Pr	$C_9H_{13}N_3$	66.23	8.03	25.74	65.99	8.12	25.43
Et	t-Bu	$C_{10}H_{15}N_3$	67.76	8.53	23.71	67.03	8.14	23.78
Et	cyclohex	$C_{12}H_{17}N_3$	70.90	8.43	20.67	71.34	8.27	20.42
n-Pr	i-Pr	$C_{10}H_{15}N_3$	67.76	8.53	23.71	66.93	8.49	24.04
n-Pr	t-Bu	$C_{11}H_{17}N_3$	69.07	8.96	21.97	69.44	8.78	22.11

Table 7. Synthesis and spectrometric properties of 2-amino-5-cyanopyrrols

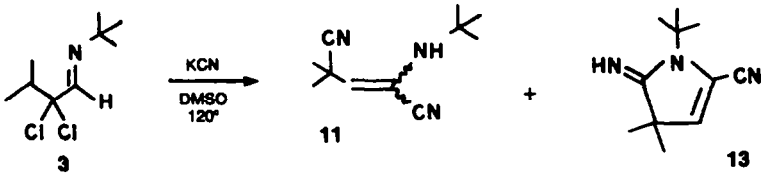
R_1'	R_2	B.p. °C/mmHg	Yield (%)	I.R. $\nu_{NH_2,CN}$ C=C	N.M.R. δ (ppm)	Mass spectrum m/e (%)
Me	i-Pr	131-135/0.05	67	3320 2220 1635	1.32(6H,d,J=6.0Hz,$(CH_3)_2$); 1.97(3H,s,CH_3-C=C); 3.00(2H,s broad,NH_2); 4.43 (1H,sept.,J=6.0Hz,CH); 6.75(1H,s,=CH)	163(M^+, 38); 121(95); 120(100); 119 (8); 93(19); 66(15); 57(7); 43(42); 42(10); 41(30)
Me	t-Bu	140-144/0.05	53	3320 2220 1635	1.16(3H,t,J=7.9Hz,CH_3); 1.61(9H,s,t-Bu) 2.36(2H,q,J=7.9Hz,CH_2-C=C); 2.90(2H,s broad,NH_2); 6.83(1H,s,=CH)	191(M^+, 6); 136(5); 135(67); 134(8); 121(9); 120(100); 93(6); 66(5); 57 (91); 42(5); 41(44)
Et	i-Pr	145-149/0.01	71	3200 2220 1630	1.22(3H,t,J=6.7Hz,CH_3); 1.40(6H,d,J= 6.8Hz,$(CH_3)_2$); 2.51(2H,q,J=6.7Hz,CH_2-C=C); 2.60(2H,s broad,NH_2); 4.50(1H, sept.,J=6.8Hz,CH); 6.90(1H,s,=CH)	177(M^+, 17); 162(5); 150(15); 149(12) 148(60); 135(17); 121(66); 109(9); 107(13); 106(12); 95(12); 81(100); 68 (24); 54(24); 43(26); 42(32); 41(49); 39(20)
Et	t-Bu	151-154/0.01	43	3320 2220 1635	1.16(3H,t,J=7.9Hz,CH_3); 1.61(9H,s,t-Bu) 2.36(2H,q,J=7.9Hz,CH_2-C=C); 2.90(2H,s broad,NH_2); 6.83(1H,s,=CH)	191(M^+, 6); 136(5); 135(67); 134(8); 121(9); 120(100); 93(6); 66(5); 57 (91); 42(5); 41(44)

Elemental Analysis of 2-Amino-5-cyanopyrrols 12

R_1'	R_2	Formula	Required C	Required H	Required N	Founded C	Founded H	Founded N
Me	i-Pr	$C_9H_{13}N_3$	66.23	8.03	25.74	66.78	8.12	25.14
Me	t-Bu	$C_{10}H_{15}N_3$	67.76	8.53	23.71	67.52	8.47	23.27
Et	i-Pr	$C_{10}H_{15}N_3$	67.76	8.53	23.71	67.23	8.43	24.06
Et	t-Bu	$C_{11}H_{17}N_3$	69.07	8.96	21.97	69.74	9.06	22.14



Scheme 11.



Scheme 12.

(no tautomerism is possible due to the geminal dimethyl function).

In conclusion by appropriate choice of the reaction conditions, α,α-dichloroaldimines can be converted into β-chloro-α-cyanoenamines, α-chloroimidates, α,β-dicyanoenamines and 2-amino-5-cyanopyrrols by reaction with potassium cyanide.

EXPERIMENTAL

IR spectra were obtained with a Perkin–Elmer model 257 spectrophotometer (neat NaCl or KBr pellet). NMR spectra were recorded with a Varian T-60 instrument with Me_4Si as internal standard. Low resolution mass spectra were measured with a A.E.I. MS 20 mass spectrometer (70 eV) coupled with a Pye Unicam gas chromatograph (SE 30, 3%, 1.5 m).

Preparative glc was carried out on a Varian 1700 instrument (SE 30, 5%, 3 m).

General procedure for the preparation of N-1-*(2,2-dichloroalkylidene)amines* **3**. To a soln of 0.5 mol aldehyde in 100 ml CCl_4 was added dropwise 0.5 mol of a primary amine. After stirring for 10 min the water layer was separated, followed by drying ($MgSO_4$). After filtration and trituration with 300 ml CCl_4, the soln was treated portionwise with N-chlorosuccinimide (1.1 mol) at 20° and the reaction was stirred overnight. Filtration of the resulting succinimide, evaporation of the solvent and distillation gave **3** (Table 1).

β-Chloro-α-cyanoenamines **4**. A mixture of 0.1 mol **3** and 0.4 mol KCN in 50 ml dry MeOH was refluxed with stirring for a time as indicated in Table 2. Most of the MeOH was evaporated and the mixture was poured into ice-water. Extraction with CH_2Cl_2, drying ($MgSO_4$) and distillation or preparative glc afforded **4**.

(E), (Z)-*2-t-Butylimino-4-phenyl-3-butenenitrile* **6**. IR (NaCl): 2230 (C≡N), 1630 (C=N), 1610 cm^{-1} (C=C). NMR: δ: (*E*): 1.47 (9H, s, t-Bu); 6.83 (1H, d, J = 16.2 Hz, =CH); 7.23 (6H, m, Ar–H, =CH). (*Z*): 1.41 (9H, s, t-Bu); 6.20 (1H, d, J = 12.0 Hz, =CH); 7.25 (6H, m, Ar–H, =CH). MS: *m/e*: 212 (M^+, 6); 197(21); 156(14); 155(13); 140(20); 130(9); 129(12); 103(5); 102(6); 77(6); 57(100); 41(37).

α-Chloroimidates **7** were synthesised following the same procedure as for the preparation of **4**, except for a longer reaction time. The by-products were isolated by preparative glc.

N-*Methyl 2-chlorobutanamide* **8** (R_1 = Et, R_2 = Me, X = Cl). IR (KBr): 3350 (NH); 1665, 1545 cm^{-1} (CONH–). NMR ($CDCl_3$): δ 1.03 (3H, t, J = 6.8 Hz, CH_3); 1.8–2.3 (2H, m, CH_2); 2.89 (3H, d, J = 5.0 Hz, NH–CH_3); 3.15–3.60 (1H, m, NH); 4.20 (1H, t, J = 7.4 Hz, CHCl).

N-*Methoxymethyl butanamide* **9** (R_1 = Et, R_2 = Me). IR (KBr): 3300 (NH); 1665 cm^{-1} (CONH). NMR ($CDCl_3$): δ 0.99 (3H, t, J = 7.0 Hz, CH_3); 1.33–1.95 (2H, m, CH_2); 2.28 (2H, t, J = 7.1 Hz, CH_2CONH); 3.66 (3H, s, OCH_3); 4.08 (2H, s, CH_2OCH_3).

N-*Cyclohexyl butanamide* **8** (R_1 = Et, R_2 = cyclohexyl). IR (KBr): 3420, 3320 (NH); 2260 (C≡N); 1665, 1530 cm^{-1} (CONH). NMR ($CDCl_3$): δ 1.03 (3H, t, J = 7.8 Hz, CH_3); 1.1–2.0 (12H, m, CH_2); 3.72 (1H, m, NH); 4.30 (1H, t, J = 4.8 Hz, CH–CN).

N-*Methoxymethyl pentanamide* **9** (R_1 = Pr, R_2 = Me). IR (KBr): 3350 (NH); 1670 cm^{-1} (CONH). NMR ($CDCl_3$): δ 0.95 (3H, t, J = 7.0 Hz, CH_3); 1.20–1.75 (4H, m, CH_2); 2.27 (2H, t, J = 7.0 Hz, CH_2CONH); 3.63 (3H, s, OCH_3); 4.07 (2H, s, CH_2OCH_3).

N-*Isopropyl 2-chloropentanamide* **8** (R_1 = Pr, R_2 = i-Pr, X = Cl). IR (KBr): 3280 (NH); 1660, 1550 cm^{-1} (CONH). NMR ($CDCl_3$): δ 0.90 (3H, t, J = 7.3 Hz, CH_3); 1.17 (6H, d, J = 6.4 Hz, $(CH_3)_2$); 1.6–2.2 (4H, m, CH_2); 4.02 (1H, sept., J = 6.4 Hz, CH); 4.18 (1H, t, J = 7.0 Hz, CHCl).

N-*Isopropyl 2-cyanopentanamide* **8** (R_1 = Pr, R_2 = i-Pr, X=CN). IR (KBr): 3280 (NH); 2230 (CN); 1655, 1550 cm^{-1} (CONH). NMR ($CDCl_3$): δ 0.97 (3H, t, J = 7.0 Hz, CH_3); 1.19 (6H, d, J = 7.1 Hz, $(CH_3)_2$); 1.3–2.1 (4H, m, CH_2); 4.0 (1H, sept., J = 7.1 Hz, CH); 4.18 (1H, t, J = 5.2 Hz, CHCN).

Reaction of 2,2-dichloroaldimines **3** *with* KCN *in* DMSO. A mixture of 0.1 mol aldimine **3** and 0.4 mole KCN in 100 ml dry DMSO was stirred for 20 hr at different temps as mentioned above. The mixture was poured into a large excess of water and carefully extracted with ether. The ether layer was washed with water and dried ($MgSO_4$). Evaporation and distillation gave **4** (reaction temp. 25°); **10** (reaction temp. 60°) and **11** and **12** (reaction temp. 120°).

(E), (Z)-N-*t-Butyl 1,3-dicyano-1-butenylamine* **11** (R' = Me, R_2 = t-Bu). B.p. 115–120°/0.5 mmHg. Yield: 17%. IR (NaCl): 3340 (NH); 2250, 2200 (CN); 1640 cm^{-1} (C=C). NMR (CCl_4): δ 1.27 (9H, s, t-Bu); 1,52 (3H, dxd, J = 6.9 Hz, CH_3); 3.35 (1H, m, CH–CN); 5.00 (1H, s broad, NH); 6.83–7.06 (1H, m, =CH (E + Z)). MS: *m/e*: 177 (M^+, 9); 162(7); 150(5); 135(7); 121(17); 106(12); 94(15); 93(9); 57(100); 56(12); 42(10); 41(42).

(E), (Z)-N-*Isopropyl-1,3-dicyano-1-pentenylamine* **11** (R_1' = Et, R_2 = i-Pr). B.p. 120–123°/0.1 mmHg. Yield: 23%. IR (NACl): 3330 (NH); 2330, 2195 (C=N), 1640, 1600 cm^{-1} (C=C). NMR (CCl_4): δ 1.00 (3H, t, J = 7.0 Hz, CH_3); 1.25 (6H, d, J = 6.1 Hz, $(CH_3)_2$; 1.60–2.50 (2H, m, CH_2); 3.40 (1H, m, CH–CN); 3.80–4.60 (2H, m, NH, CH); 6.44, 6.63 (1H, d, d, J = 14 Hz, J = 12 Hz, =CH (E + Z)). MS: *m/e*: 177 (M^+, 11): 162(16); 150(13); 148(13); 137(7); 135(16); 123(40); 121(73); 111(12); 105(35); 81(100); 80(11); 79(11); 68(12); 54(57); 44(29); 43(56); 42(33); 41(47).

(E), (Z)-N-*t-Butyl-1,3-dicyano-1-pentenylamine* **11** (R_1' = Et, R_2 = t-Bu). IR (NaCl): 3335 (NH); 2335, 2200 (CN); 1635 cm^{-1} (C=C). NMR (CCl_4): δ 1.10 (3H, t, J = 6.5 Hz, CH_3); 1.34 (9H, s, t-Bu); 1.5–2.1 (2H, m, CH_2); 3.25 (1H, m, CHCN); 5.10 (1H, s broad, NH); 7.00, 7.10 (1H, d, d, J = 14 Hz, J = 12 Hz, =CH (E + Z)). MS: *m/e*: 191 (M^+, 12); 176(8); 162(3); 149(3); 135(14); 106(36); 81(3); 57(100); 56(4); 41(18).

(E), (Z)-N-*t-Butyl-1,3-dicyano-3-methyl-1-butenylamine* **11** (R_1' = $(CH_3)_2$; R_2 = t-Bu). IR (NaCl): 3335 (NH); 2240, 2200 (CN); 1635 cm^{-1} (C=C). NMR ($CDCl_3$): δ 1.26 (9H, s, t-Bu); 1.53 (6H, s, $(CH_3)_2$); 4.90 (1H, s broad, NH); 7.00, 7.26 (1H, s, s, =CH (E + Z)). MS: *m/e*: 191 (M^+, 18); 176(1); 135(100); 134(12); 120(96); 108(4); 107(2); 94(4); 93(6); 66(5); 57(40); 41(22).

1-t-Butyl-5-cyano-2-imino-3,3-dimethyl-4-pyrroline **13**. IR (NaCl): 3300 (NH); 2205 (C=N); 1645, 1610 cm^{-1} (C=C). NMR ($CDCl_3$): δ 1.23 (6H, s, $(CH_3)_2$); 1.54 (9H, s, t-Bu); 7.26 (1H, s, =CH). MS: *m/e*; 191 (M^+, 6); 176(3); 135(13); 120(20); 93(3); 57(100): 56(4); 41(17).

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