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THE REACTION OF N-ALKYL SUBSTITUTED α-AMINOISOBUTYRONITRILES WITH CARBONYL COMPOUNDS

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Abstract—Saturated and aromatic aldehydes react with $Me_2C(CN)NR_2$ to give the corresponding $R'CH(CN)NR_2$. Saturated aldehydes do not react with $Me_2C(CN)NHR$ but aromatic aldehydes yield Schiff bases (ArCH=NR). α,β-Unsaturated aldehydes react with $Me_2C(CN)NR_2$ or $Me_2C(CN)NMR$ to form $RCH_2CH{=}C(CN)NR_2$ (in both possible geometric forms) or $RCH_2CH_2C(CN){=}NR$.

INTRODUCTION

IN THE reaction of α-aminonitriles with aldehydes and ketones, it was shown that acetone and cyclohexanone react with α-aminonitriles in the presence of MeONa and form iminooxazolidones or ketoglyoxalines.[1,2] Benzaldehyde reacts with α-aminonitriles to yield Schiff bases of the type PhCH=NCH(R')CN.[2]

Some α,β-unsaturated aldehydes and ketones (crotonaldehyde, cinnamic aldehyde, benzalacetone and others) react with unsubstituted and N-monosubstituted α-aminonitriles in the presence of KOH to give pyrroles (Miller–Plöchl synthesis). The ether oxamines of the type RCH=CHCH(OR')(NR''CHR'''CN) are produced as intermediates in the reaction.[3]

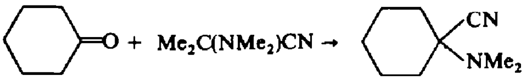
We have studied the reaction of N-alkyl- or N,N-dialkyl-α-aminoisobutyronitriles with different aldehydes and ketones in order to synthesize N-substituted α-aminonitriles by a more simple method than the one at present available.[4] For this purpose the carbonyl compound was mixed with a N-substituted α-aminonitrile[5] (method A) or a primary or secondary amine was added to a mixture of the carbonyl compound with acetone cyanohydrine (method B).

The reaction with saturated or aromatic aldehydes and ketones

It was found that butyric aldehyde or benzaldehyde react with N,N-dialkyl-α-aminoisobutyronitriles according the following scheme:

$$RCHO \xrightarrow[\text{or } Me_2C(OH)CN\,+\,R'_2NH]{Me_2C(NR'_2)CN} RCH(NR'_2)CN$$

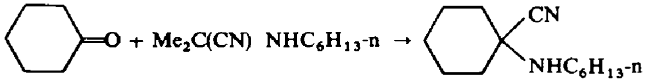
Cyclohexanone reacts similarly with N,N-dimethyl-α-aminoisobutyronitrile to give 1-cyano-1-N,N-dimethylaminocyclohexane:



But di-n-propyl ketone, methyl ethyl ketone, di-isopropyl ketone and acetophenone do not react with N,N-dialkyl-α-aminoisobutyronitriles at room temperature and on prolonged heating at 70–80° small quantities of products were formed which were not studied further.

N-monoalkyl-α-aminoisobutyronitriles react slowly with aliphatic aldehydes. The formation of small quantities of products was observed by GLC only after prolonged standing or heating the reaction mixture under reflux.

Among ketones only cyclohexanone reacts readily with N-n-hexyl-α-aminoisobutyronitrile and forms 1-N-hexylamino-1-cyanocyclohexane in a high yield:



Di-n-propyl ketone reacts similarly with α-N-isobutrylaminoisobutyronitrile and forms 2-N-isobutylamino-2-n-propylvaleronitrile in a very small yield.

Benzaldehyde condenses readily with α-N-n-hexylaminoisobutyronitrile, but N-benzylidenhexylamine is formed instead of aminonitrile:

$$PhCHO \xrightarrow{Me_2C(CN)NHC_6H_{13}\text{-n}} PhCH{=}NC_6H_{13}\text{-n}$$

The Schiff base is obtained in a small yield by the reaction of acetophenone with

Table 1. Yields, constants and analytical data of obtained compounds

Compound	Yield by method A	Yield by method B	B.p.°C/mm	n_D^{20}
n=PrCH(CN)NEt$_2$[a]	57	88	86–88/15	1·4327
i-Pr(CH$_2$)$_2$CH(CN)NEt$_2$[b]		80	101–103/15	1·4308
PhCH(CN)NEt$_2$[c]	62	86	78–80/0·08	1·5014
$\overline{CH_2(CH_2)_4C}(CN)NMe_2$[d]	67	70	93–95/9	1·4675
$\overline{CH_2(CH_2)_4C}(CN)NHC_6H_{13}$-n[e]	75		110/0·08	1·4685
n-Pr$_2$C(CN)NHBu-i[f]	13		93–95/9	1·4368
PhCH=NC$_6$H$_{13}$-n[g]	70		95–97/0·08	1·5150
PhC(Me)=NBu-i[h]	14		112–113/9	1·5190

[a] Found: N, 18·08; Calc: N, 18·06%.

[b] Found: C, 72·03; H, 11·83; Calc: C, 71·98; H, 11·98%.

[c] Found: C, 76·08; H, 8·56; Calc: C, 76·55; H, 8·57%.

[d] B.p. 112°/7 mm;[6] Found: C, 70·81; H, 10·55; Calc: C, 71·00; H, 10·59%.

[e] Found: C, 75·12; H, 11·57; Calc: C, 74·94; H, 11·61%.

[f] Found: C, 72·81; H, 12·14; Calc: C, 73·41; H, 12·32%.

[g] B.p. 133°8 mm;[7] λ_{max}^{EtOH} 246 mμ (ε 13,700); Found: C, 82·65; H, 9·98; Calc: C, 82·48; H, 10·12%.

[h] λ_{max}^{EtOH} 242 mμ (ε 11,300); Found: C, 82·38; H, 9·31; Calc: C, 82·13; H, 9·78%.

N-isobutylaminoisobutyronitrile:

$$\mathrm{PhCOMe} \xrightarrow{\mathrm{Me_2C(CN)ONHBu\text{-}i}} \mathrm{Ph(Me)C{=}NBu\text{-}i}$$

p-Diethylaminobenzaldehyde does not react with N-monoalkyl-α-aminoisobutyronitriles and *p*-nitrobenzaldehyde gives a resin.

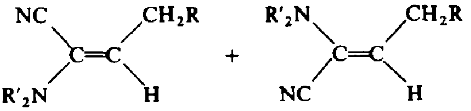
The yields, characteristics and analytical data of compounds obtained by the reaction of saturated and aromatic carbonyl compounds with N-alkylsubstituted α-aminoisobutyronitriles are given in Table 1.

The reaction with α,β-unsaturated aldehydes

α,β-Unsaturated ketones (mesityl oxide, benzalacetone) do not react with N-alkylsubstituted α-aminoisobutyronitriles.

In the case of crotonaldehyde individual products of the reaction were not isolated, but *trans*-4,4-dimethoxybut-2-en-1-al, cinnamic aldehyde and β-furylacrolein reacted vigorously with N,N-dialkyl-α-aminoisobutyronitriles (or with acetone cyanohydrine and secondary amines) to give a mixture of both possible geometric isomers of cyanoenamines (I and II) according the following scheme:

$$\mathrm{RCH{=}CHCHO} \xrightarrow[\text{or } \mathrm{Me_2C(OH)CN\ R'_2NH}]{\mathrm{Me_2C(CH)NR'_2}}$$



I II

TABLE 2. GLC AND TLC OF MIXTURES OBTAINED (I AND II)

Mixture	GLC[a]			TLC[b] R_f	
	t°C	t_R min (the relation of peaks %)			
Ia and IIa	120	11·6[c]		0·65	0·51
Ib and IIb	141	15·2, (43,	20·5 57)	0·78,	0·62
Ic and IIc	155	9·9, (35,	11 65)	0·82,	0·65
Id and IId	138	7·5 (40,	10·3 60)	0·72,	0·52
Ie and IIe	145	11·2, (45,	19·3 55)		

[a] Chromatograph with glass flame-ionization detector constructed in our laboratory;[8] glass column (2 m length, Ø 5 mm) of 0·5 or 1 % silicon elastomer on NaCl, N_2 as carrier gas, 30–34 ml/min.

[b] Plates (13 × 18 cm) with unfixed thin layer (1 mm) of Al_2O_3 (II grade activity), solvent: mixture of ether–n-hexane, 1:1 (by volume); detection by I_2-vapour.

[c] Peak with shoulder.

a: R = CH(OMe)$_2$,R′ = Et; b: R = Ph,R′ = Me; c: R = Ph,R′ = Et; d: R = β-furyl, R′ = Me; e: R = β-furyl, R′ = Et.

The formation of two compounds was proved by GLC and TLC (Table 2) and the structure of the compounds was proved by analytical data (Table 3), UV, IR and PMR spectra (Tables 4 and 5) and by chemical transformation.

GLC and TLC (Table 2) revealed that the reaction products are mixtures of at least two compounds. The amount of each compound was evaluated by GLC. It should be noted that the compound with the lower t_R value (greater R_f value) progressively decreased with time in the mixtures Ib and IIb; Ic and IIc; Id and IId; Ie and IIe.

TABLE 3. YIELDS AND CONSTANTS OF MIXTURES I AND II

N	Mixture	Yield by method A	Yield by method B	B.p.°C/mm	n_D^{20}
1	Ia and IIa		70	81–82/0·2	1·4612
2	Ib and IIb	41	64	106–107/0·4	1·5415
3	Ic and IIc	70	72	95–96/0·2	1·5296
4	Id and IId		85	99–101/0·6	1·5110
5	Ie and IIe		76	89–90/0·29	1·5020

Analytical data

Mixture (Brutto-formula)	C% Found	C% Calc	H% Found	H% Calc
Ia and IIa ($C_{11}H_{20}N_2O_2$)	62·28	62·33	9·84	9·50
Ib and IIb[a] ($C_{12}H_{14}N_2$)	76·65	77·38	7·38	7·58
Ic and IIc[b] ($C_{14}H_{18}N_2$)	77·91	78·46	8·48	8·47
Id and IId[c] ($C_{10}H_{12}N_2O$)				
Ie and IIe ($C_{12}H_{16}N_2O$)	70·24	70·56	7·88	7·90

[a] Found: N, 15·25; Calc. N, 15·04%.
[b] Found: N, 13·11; Calc. N, 13·01%.
[c] Found: N, 15·95; Calc. N, 15·90%.

TABLE 4. UV AND IR SPECTRA OF THE MIXTURE I AND II[a]

Mixture	λ^{EtOH} mμ(ε)	ν_{CN} cm^{-1} (liquid film)
Ia and IIa	273 (3870)	2202, 2214
Ib and IIb	273 (6220)	2210, 2225
Ic and IIc	276 (5980)	2210, 2224
Id and IId	271 (8380), 315 (7540)	2211, 2229

[a] UV spectra were measured with ϕ C-4 spectrometer; IR spectra were measured with UR-10 spectrometer.

As it is seen from the Table 3 the analytical data is in good agreement with the formulae calculated on the assumption that the products are the mixture of isomers.

UV and IR spectra show that the reaction products are mixtures of isomeric cyanoenamines (the presence of α,β-unsaturated CN group and the absence of saturated CN group and CH=CH link conjugated with aromatic nucleus in the mixture Ib and IIb; Ic and IIc; Id and IId).

This conclusion was supported by the analysis of PMR spectra of the mixtures Ia and IIa; Ib and IIb; Ic and IIc (Table 5).

TABLE 5. PMR SPECTRA OF THE MIXTURE I AND II[a]

Mixture	δ ppm					
	Me	OMe	NCH_2	C—CH_2—C	C=CH	CH=
Ia and IIa	0·95 (t) J = 7 c/s 1·02 (t) J = 7 c/s	3·22	3·08 (q)[b]		4·22 (t) J = 5·5 c/s 4·25 (t) J = 5·5 c/s	4·88 (t) J = 7·5 c/s 6·00 (t) J = 7 c/s
	NMe_2	—CH_2—	—CH=	Ph		
Ib and IIb	2·52 (s) 2·38	3·47 (c) J = 7 c/s	4·95 (t) J = 7 c/s 5·72 (t) J = 7 c/s	7·09 (s)		
	Me	NCH_2	C—CH_2—C	—CH=	Ph	
Ic and IIc	0·9 (t) J = 7 c/s	2·6 (q) J = 7 c/s 2·95 (q) J = 7 c/s	3·47 (d) J = 8 c/s	4·98 (t) J = 8 c/s 6·03 (t) J = 8 c/s	7·09	

[a] Measured in CCl_4 at 60 Mc/s using PC–60 spectrometer, hexamethyldisiloxane (HMDS) was used as internal standard (shift against Me_4Si 0·05 ppm).

[b] NCH_2 group quadruplet and CH_2 multiplet of both isomers are overlapped at 2·33–3·20 ppm, therefore the exact identification of these signals is difficult.

s = singlet; d = doublet; t = triplet; q = quadruplet.

PMR spectra of the mixture I and II in CCl_4 (Table 5) show two signals of a vinylic proton in all measured compounds and two signals of a NMe_2 group in Ib and IIb or two signals of the NCH_2 group in Ic and IIc.

The presence of both isomers was confirmed more rigorously in the PMR spectrum without solvent of the mixture Ib and IIb (Table 6). The spectrum reveals two signals

TABLE 6. PMR SPECTRUM WITHOUT SOLVENT OF THE MIXTURE IB AND IIB

δ ppm			
NMe_2	—CH_2—	—CH=	Ph
2·50 (s) 2·36 (s)	3·43 (d) 3·27 (d)	4·92 (t) 5·62 (t)	7·05 (s)

not only of the NMe_2 group and vinylic proton but also of the CH_2 group. The same results were obtained by use of the double proton-proton magnetic resonance.

The ratio of summary integrated intensity of signals at 5·72 and 4·95 ppm (CH_2=) to the integrated intensity of doublet at 3·47 ppm (—CH_2—) in the mixture Ib and IIb (Table 5) is 1:2.

All the data supports the conclusion that the reaction products are mixtures of geometric isomers. The chemical behaviour of the reaction products supports the conclusion which was made on the basis of physico-chemical data. Thus, the acidic hydrolysis of the reaction product yielded β-phenylpropionic acid from mixtures Ia and IIb; Ic and IIc or β-furylpropionic acid from mixture Id and IId; Ie and IIe.

By heating in the presence of Et_3N the mixture of isomers (Ib, c, d and IIb, c, d) was transformed into individual isomers A, B or C characterized (I) by a higher t_R (the second peak on GLC, see Table 2 and Fig. 1); (2) by lower R_f value (Table 2);

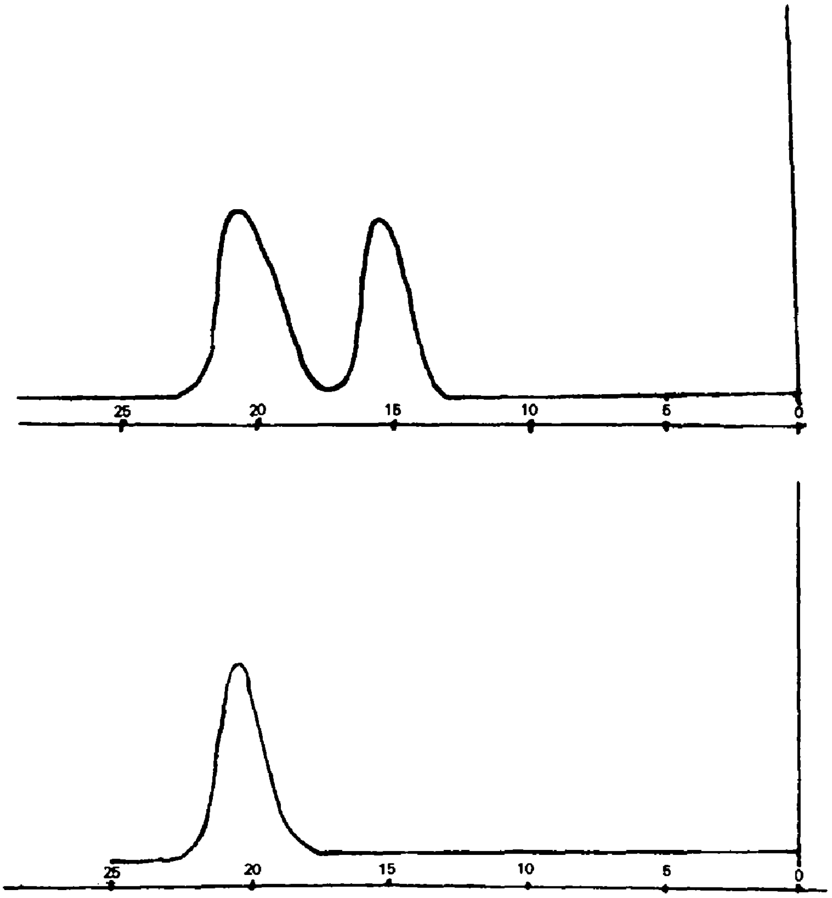


FIG. 1

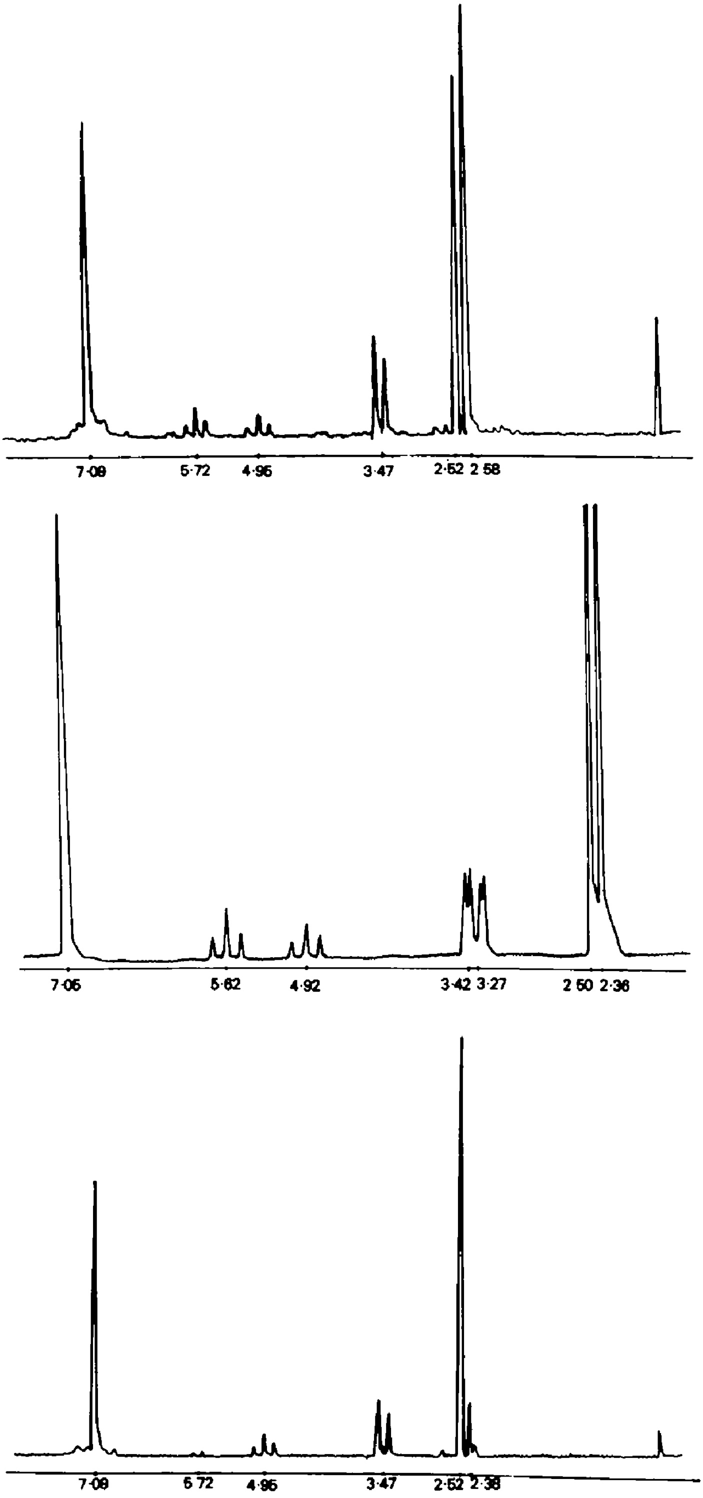

7·09
5·72
4·96
3·47
2·62 2·58
7·06
5·62
4·92
3·42 3·27
2·50 2·36
7·09
5·72
4·96
3·47
2·62 2·38

FIG. 2

(3) by greater ν_{CN} (Table 4) and (4) by PMR spectral signals at high field (Tables 5, 6 and Fig. 2). As is shown in Fig. 1, the isomerization results in the individual products. The mixture of isomers Ia and IIa does not change under these conditions. Characteristics of individual isomers are given in Table 7.

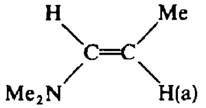
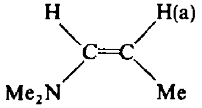
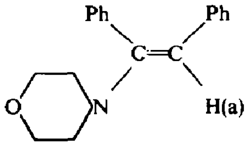
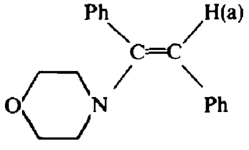
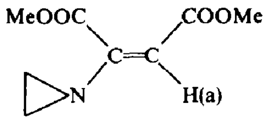
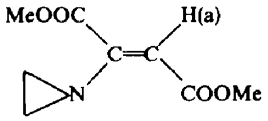
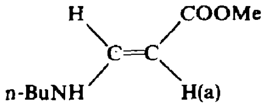
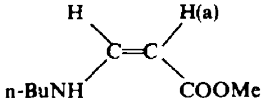
TABLE 7. CHARACTERISTICS OF INDIVIDUAL ISOMERS

Compound (from mixture)	B.p.°C/mm	n^{20}	λ^{EtOH} mμ (ε)	ν_{CN} cm^{-1} (liquid film)
Isomer A[a] (Ib and IIb)	102·2/0·9	1·5440	270 (7670)	2225
Isomer B[b] (Ic and IIc)	128–129/0·55	1·5312	265 (9540)	2228
Isomer C[c] (Id and IId)	95·5–96/0·3	1·5143	267 (9470)	2229

[a] Found: C, 77·06; H, 7·75. $C_{12}H_{14}N_2$ requires: C, 77·38; H, 7·58 %.
[b] Found: C, 78·32; H, 8·41. $C_{14}H_{18}N_2$ requires: C, 78·46; H, 8·47 %.
[c] Found: C, 68·39; H, 6·49. $C_{10}H_{12}N_2O$ requires: C, 68·16; H, 6·68 %.

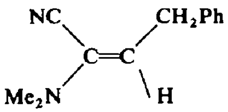
The PMR spectra of pure isomers A and B in CCl_4 (measured at 60 Mc/s, internal standard HMDS) reveal vinylic proton signals at 4·95 ppm (isomer A) and 4·48 ppm (isomer B). To elucidate the configuration of pure isomers A and B and thus the

TABLE 8. CHEMICAL SHIFTS OF VINYLIC PROTON IN ENAMINES
(literature data)

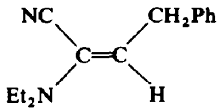
Compound with amino-group in *cis*-position to β-vinylic proton	H(a) δ ppm	Compound with amino-group in *trans*-position to β-vinylic proton	H(a) δ ppm
	4·13[9]		4·35[9]
	5·56[10]		5·71[10]
	5·31[11]		6·15[11]
	4·34[12]		4·56[12]

configuration of the components of the mixture I and II we compared the chemical shifts for vinyl proton in isomers A and B with data obtained for the mixtures Ib and IIb and Ic and IIc (Table 5) and literature data on chemical shifts typical for vinyl proton in *cis*-or *trans*-position to β-amino-group (Table 8).

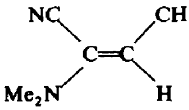
As it is seen from Table 8 the signals of vinylic protons in *cis*-position to the amino group are moved to high field in comparison with those of vinylic protons in *trans*-position to the amino group. Therefore structure Ib may be assigned to the isomer A and structure Ic to the isomer B. By analogy structure Id has been assigned to the isomer C.



Isomer A = Ib



Isomer B = Ic



Isomer C = Id

In the reaction of some α,β-unsaturated aldehydes with N-monoalkyl-α-aminoisobutyronitriles (or acetone cyanohydrine and primary amines) it was found that cinnamic aldehyde and *trans*-4,4-dimethoxybut-2-en-1-al react with N-monoalkylaminoisobutyronitriles to form N-cyanoimines (III).

$$RCH{=}CHCHO + Me_2C(CN)NHR' \text{ (or } Me_2C(OH)CN + R'NH_2) \rightarrow \underset{\text{III}}{RCH_2CH_2C(CN){=}NR'}$$

The constitution of III (R = Ph, R′ = Me) was proved by acidic hydrolisis to β-phenylpropionic acid and by PMR spectra.

The yield of III was low by method A but high by method B. The characteristics of III are given in Table 9.

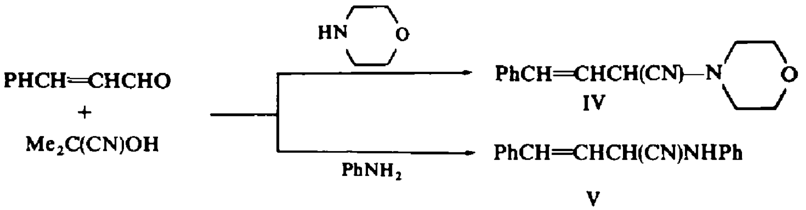
TABLE 9. YIELDS AND CHARACTERISTICS OF III

Compound III R	R′	Yield % (method B)	B.p.°C/mm	n_D^{20}
$(MeO)_2CH$	i-Bu	25	75–77/0·3	1·4470
Ph	Me	83	86–88/0·3	1·5310
Ph	Et	24	105–108/0·7	1·5143
Ph	n-C_6H_{13}	56	115–117/0·6	1·5040

Analytical data

Compound III		C%		H%		N%	
R	R′	Found	Calc	Found	Calc	Found	Calc
$(MeO)_2CH$	i-Bu	62·51	62·23	9·49	9·50		
Ph	Me	76·87	76·71	7·45	7·02	16·06	16·27
Ph	Et	77·03	77·38	7·80	7·58		
Ph	n-C_6H_{13}	79·01	79·29	9·02	9·15	11·59	11·56

In conclusion it should be noted that the isomerization takes place only with N-alkylsubstituted α-isobutyroaminonitriles. Cinnamic aldehyde reacts with acetone cyanohydrine and morpholine or aniline to form unsaturated α-aminonitriles (IV or V).



This type of isomerization has not been described earlier. To a certain degree it resembles the isomerization of α,β-unsaturated aldehydes by action of cyanohydrines in the presence of triethylamine.[13]

DISCUSSION

In order to explain the reactions observed it is reasonable to suppose that the first step of the interaction of aldehydes (or ketones) with N-substituted α-aminoisobutyronitriles (or acetone cyanohydrine and amines) is the formation of ether oxamine VI (method A) or oxyamine VII (method B):

$$RCHO + Me_2C(CN)NR'R'' \rightarrow RCH(NR'R'')OC(CN)Me_2$$

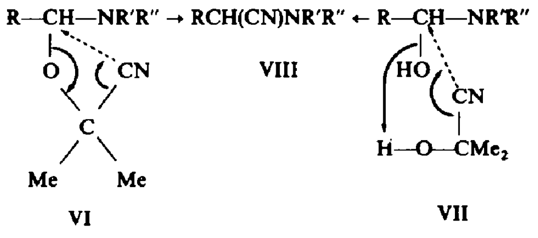
VI

$$RCHO + R'R''NH \rightarrow RCH(OH)NR'R''$$

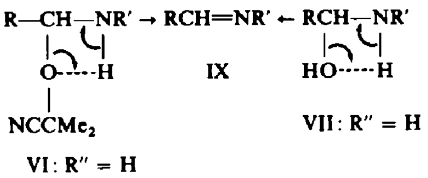
VII

As mentioned, the formation of ether oxamines by the action of α-aminonitriles on α,β-unsaturated aldehydes and ketones in methanol is the first step of the Miller–Plöchl synthesis.[3]

The nucleophilic attack of the aminonitrile or amine should be facilitated by an increased partial positive charge on the C atom of the CO group. This would explain the greater reactivity of aldehydes as compared with the corresponding ketones and the greater reactivity of aldehydes with electron-attracting substituents as compared with unsubstituted aldehydes or aldehydes with electron-donating substituents. Further, the ether oxyamine VI formed would undergo intramolecular nucleophilic substitution at the ether group by the cyano group with elimination of acetone. As a result N-substituted α-aminonitriles VIII are obtained. These aminonitriles VIII are formed by the interaction of oxyamine VII with acetone cyanohydrine. The aminonitriles formed may be stable or could undergo further transformation depending on the nature of R, R′ and R″.



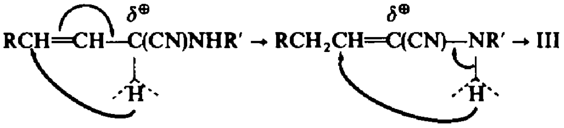
For VI or VII where R′ or R″ = H another path of transformation could yield the Schiff base IX which in turn transforms into the aminonitrile VIII by action of HCN (from acetone cyanohydrine or other source).



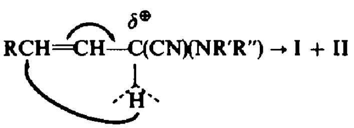
The initial formation of the Schiff base IX (R = Ph, R′ = H, R″ = n-C_6H_{13}) has been proved for the method B. It was found that the reaction of acetone cyanohydrine with hexylamine goes to completion within a few hours (the reaction is second order, at 20° $k = 1{\cdot}33 \times 10^{-5}$ mol l^{-1} sec^{-1}) while the speed of the reaction of hexylamine with cinnamic aldehyde under similar conditions is too fast to be measured.

The formation of aminonitriles by action of acetone cyanohydrine on an aromatic Schiff base was described recently.[14] as well as the formation of N-phenyl-α-aminocinnamonitrile by action of KCN and aniline on Schiff bases of cinnamic aldehyde.[15]

We are convinced that saturated N-monoalkyl- and N,N-dialkyl-α-aminonitriles, aromatic N,N-dialkylaminonitriles, α,β-unsaturated N-phenyl- or morpholylaminonitriles are stable and do not change further, but the α,β-unsaturated N-monoalkyl- or N,N-dialkylaminonitriles (X and XI) formed are capable of transformation according the following scheme:



X



XI

It should be noted that cyanoimine III (R = Ph, R′ = Me) is obtained by the action of acetone cyanohydrine or N-methylamino-α-isobutyronitrile on the N-methylimine of cinnamic aldehyde. There is evidence concerning the formation of iminoethers $RCH_2CH_2C(OR')\!=\!NR''$ from the aromatic Schiff base by the action of KCN in alcohol.[18-18] These facts are in favour of the scheme shown above.

EXPERIMENTAL

Method A. An equimolar quantity of N- or N,N-substituted α-aminoisobutyronitrile was mixed with the aldehyde or ketone. After the reaction ceased, the mixture was distilled without any further treatment.

Method B. An equimolar quantity of amine (or water soln) was added to the mixture of equimolar quantities of carbonyl compound and acetone cyanohydrine at room temperature or cooling with ice water. The reaction product was dried and distilled.

Yields and characteristics of compounds obtained are given in Tables 1, 2, 3, 4, 5, 9.

Compound PhCH=CHCH(CN)NHPh, yield 87%, m.p. 118·5–119° (from benzene), ν_{CN} (KBr) 2225 cm^{-1}; λ_{max}^{EtOH} 226 mμ (ε 12,800), 293 mμ (ε 20,600). (Found: C, 82·22; H, 6·08; N, 11·96. $C_{16}H_{14}N_2$ requires: C, 82·02; H, 6·02; N, 11·96%).

Compound PhCH=CHCH(CN)NHPh (0·28 g; 0·0035 mole), 5N KOH (3 ml) and alcohol (15 mol) were boiled 1 hr, poured into ice water and extracted with ether. After distillation of ether, the anilide of β-phenylpropionic acid, m.p. 95–96·5° was obtained from ether–n-hexane. (Found: N, 6·18. $C_{15}H_{15}NO$ requires: N, 6·22%).

1-*Morpholyl*-1-*cyano*-4-*phenylbut*-2-*ene*, yield 93%, m.p. 93·7–94° was obtained from benzene–ether, (1:10); ν_{CN} (KBr) 2230 cm^{-1}; λ_{max}^{EtOH} 282 mμ (ε 13,100); PMR spectrum (in $CDCl_3$): 4·40 ppm (CH_2), J = 1·75 c/s; 6·66 ppm (—CH=), J = 5 c/s; 6·93 ppm (=CH—), J = 17 c/s; 7·30 ppm (Ph). (Found: C, 73·42; H, 7·12. $C_{14}H_{16}N_2O$ requires: C, 73·65; H, 7·06%).

The isomerization of mixture I *and* II. 9 g mixture I and II were refluxed in the presence of Et_3N. When the isomerization was complete the reaction product was distilled. Characteristics of individual isomers are given in Table 7.

The reaction of N-*methylimine of cinnamic aldehyde with acetone cyanohydrine.* The N-methylimine of cinnamic aldehyde (7 g; 0·048 mole) was mixed with 8·5 g (0·1 mole) acetone cyanohydrine and 10 g Et_3N. The next day the mixture was distilled yielding 5·8 g (70%) of III (R = Ph, R′ = Me), b.p. 71–72°/0·09 mm; λ_{max}^{EtOH} 273 mμ (ε 1870), ν_{CN} (liquid film) 2215 cm^{-1}; PMR spectrum (CCl_4): 2·75 ppm (—CH_2CH_2—), 3·43 ppm (NMe), 7·13 ppm (Ph). (Found: C, 76·87; H, 7·03; N, 16·16. $C_{11}H_{12}N_2$ requires: C, 76·71; H, 7·02; N, 16·27%).

This compound proved to be identical with III (R = Ph, R′ = Me) (GLC and TLC) obtained from cinnamic aldehyde by method B.

In a similar manner the N-phenylimine of cinnamic aldehyde (0·0025 mole) and 0·05 mole acetone cyanohydrine (without addition of Et_3N) yielded 1-cyano-1-phenyl-3-phenylbut-2-en, yield 93%, m.p. 118–119°, which was identical with PhCH=CHCH(CN)NHPh (mixed m.p.) obtained from cinnamic aldehyde by method B.

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