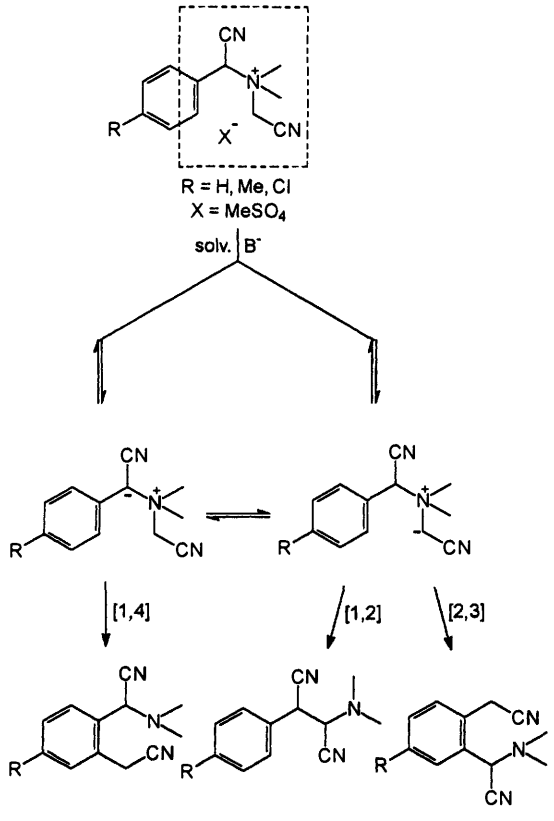
[1,4] and [2,3] Sigmatropic rearrangements of ylides generated from *N*-(α-cyano)allyl-*N*-cyanomethyl-*N*,*N*-dimethylammonium perchlorates

Andrzej Jończyk,* Tadeusz Zdrojewski, Paweł Grzywacz and Paweł Balcerzak

Department of Chemistry, Technical University (Politechnika) Koszykowa 75, 00-662 Warsaw, Poland

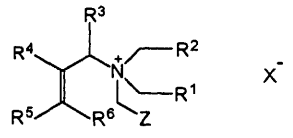
***N*-(α-Cyano)allyl-*N*-cyanomethyl-*N*,*N*-dimethylammonium perchlorates 3a–c when treated with solid K_2CO_3–DMSO (system A) afforded the α-cyano enamines 6a–c by a [1,4] shift of the α-cyano allylides 4a–c^{+-}; when treated with solid $NaHCO_3$–DMF (system C), however, these gave α-amino nitriles 8a–c, by a [2,3] shift of the cyano methylides 5a–c^{+-}. Reaction of the salts 3a,b with aq. NH_3–CH_2Cl_2 (system B) led to the formation of 8a,b, while the salt 3c, under the same conditions, yielded a mixture of 6c and 7c. It is postulated that the high tendency of 3a–c to undergo a [1,4] shift *via* the respective ylides, in contrast to the corresponding benzylammonium salts, is due to a different charge distribution in the anionic parts of the allylides and benzylides.**

Recently we have shown that ylides generated from suitably substituted benzylammonium salts underwent [2,3] (Sommelet–Hauser), [1,2] (Stevens) and hitherto unknown [1,4] ('reverse' Sommelet–Hauser) rearrangements[1-3] (Scheme 1).

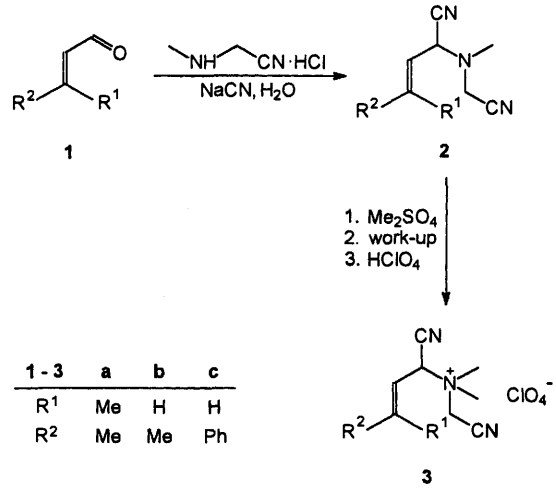


Scheme 1

We have now studied sigmatropic rearrangements of ylides generated from the structurally related allylammonium salts **3a–c** (see the framed skeleton in Scheme 1). Unlike the behaviour of ylides generated from benzylammonium salts,[1-3] [1,4] rearrangement (which accompanied [1,2] rearrangement) has already been observed for allylides generated from allyl(benzyl)dimethyl-[4] or methallyl(trialkyl)-ammonium salts,[5] by means of a strong base. Rearrangements of ylides generated from the salts shown below [R^1 = Ph, R^2 = H, Z = TMS;[6]



$R^1 = R^2 = H$, Z = EWG;[7,8] R^1 = H, R^2 = 2-(alkenyl)ethyl, Z = H, TMS[9] or Z = EWG;[10] $R^1 = R^2$ = Me, R^3 = H, Z = $P(O)(OEt)_2$[11]] by means of a base, or CsF[6,9] and tetrabutylammonium fluoride[9] (TBAF) in the case of silyl substituted salts, usually proceeded in a [2,3] fashion. In rearrangements of ylides generated by desilylation of these salts, both vinylic and aromatic π electrons participated in reorganization of the skeleton.[6] A literature search[6-10] showed that reactions of ylides generated from allylammonium salts substituted with R^3, Z = EWG, have not been earlier investigated.



1-3	a	b	c
R^1	Me	H	H
R^2	Me	Me	Ph

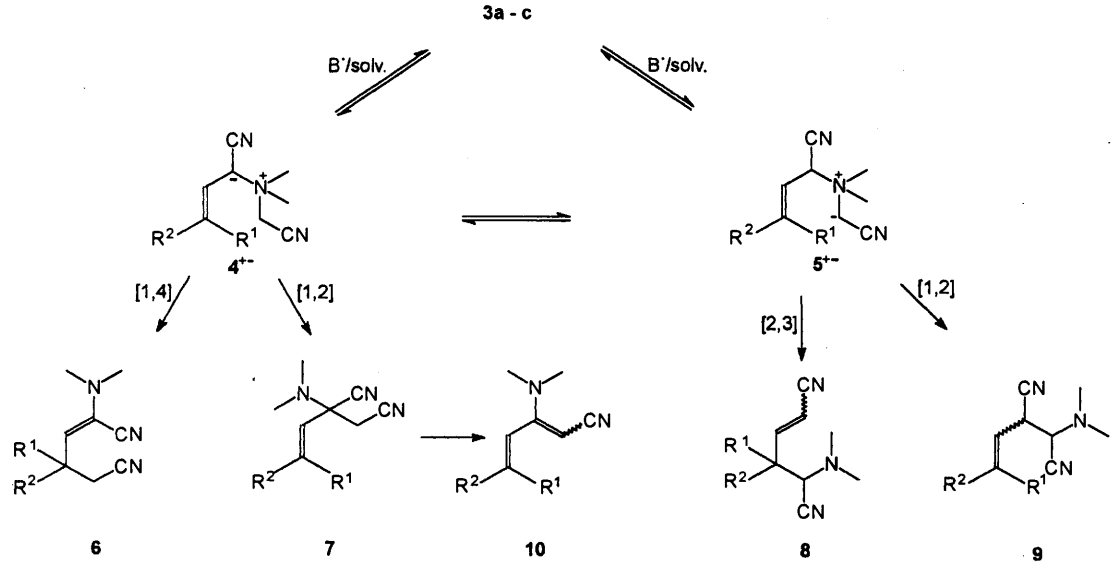
Scheme 2

In planning our work, we assumed that the presence of a vinyl substituent in **3a–c** would shift the equilibrium between ylides toward the more stable α-cyano allylides which would then undergo a [1,4] and/or [1,2] rearrangement.

Table 1 Rearrangements of ylides generated from salts **3a–c**

Entry	Salt	Base–solv. system[a]	Conditions		Products[b] ratio[c]			
			T (°C)	t (h)	**6**	**7(10)**	**8**	**9**
1	**3a**	A	18	1.5	86		8	
2		B	−30	1.5			80	13
3		C	−30	1.0			92	
4	**3b**	A	18	1.5	90			
5		B	−30	1.0	Traces		98[d]	
6		C	−30	1.0	Traces		96[d]	
7	**3c**	A	15	1.0	79	8 (7)		
8		B	−30	1.5	59	31		
9		C	−30	1.5	6		91	

[a] A: solid K_2CO_3–DMSO; B: aq NH_3–CH_2Cl_2; C: solid $NaHCO_3$–DMF. [b] The yields of crude products were ≥90%. [c] Determined in crude mixtures by GC and/or ^1H NMR spectra; unidentified products contributed to bring the product balance to 100%. [d] Product of [2,3] rearrangement decomposed during GC analysis.



Scheme 3

The starting amino nitriles **2a–c**, precursors of the salts **3a–c**, were synthesized from the α,β-unsaturated aldehydes **1a–c**, sodium cyanide and *N*-methylaminoacetonitrile (sarcosine nitrile) hydrochloride (Scheme 2).

Methylation of the amino nitriles **2a–c** with dimethyl sulfate failed to afford methyl sulfates as solids and **3a–c** were, therefore, obtained as crystalline perchlorates by extraction with water and treatment with perchloric acid. They were formed in low to moderate total yields (the highest, 35% in the case of salt **3a**).

The perchlorates **3a–c** thus prepared were deprotonated under a variety of conditions, in the base–solvent systems previously selected for benzylammonium salts:[1–3,12] solid K_2CO_3–DMF (A), aq. NH_3–CH_2Cl_2 (B), and solid $NaHCO_3$–DMF (C). The expected products **6**, **7** and **8**, **9** are formed by [1,4], [1,2] or [2,3], [1,2] rearrangements of the isomeric ylides $\mathbf{4}^{+-}$ and $\mathbf{5}^{+-}$ respectively (Scheme 3).

Fortunately, the reactions often proceeded with high yields and selectivity, to afford products the structures of which depended mainly on the base–solvent system applied (Table 1).

Thus, in all cases system A favoured the formation of products **6** by a [1,4] shift of the ylides $\mathbf{4}^{+-}$; under conditions C, [2,3] rearrangement prevailed and gave the products **8**. These results are in good agreement with our earlier observations on the rearrangements of ylides generated from *N*-(α-cyanobenzyl)-*N*-cyanomethyl-*N*,*N*-dimethylammonium methyl sulfates.[1–3,12]

The main differences were observed in system B. Previously, we had found that this system gave selectively the products of a [1,2] (Stevens) shift of the less stable cyanomethylides (Scheme 1). Now, we found that whilst the ylides generated from salts **3a,b** underwent [2,3] rearrangement in system B, the salt **3c** gave a mixture of **6c** and **7c**, products of [1,4] and [1,2] shifts respectively, both derived from the same, more stable α-cyano allylide $\mathbf{4c}^{+-}$. After distillation of this mixture, a ^1H NMR spectrum of the distillate, indicated that **7c** was converted into **10c**, by elimination of hydrogen cyanide. Reaction of the salt **3c** in the more basic system A resulted, to some extent, in a transformation **7c**→**10c** (Table 1, Entry 7). There are known precedents for base mediated or thermal elimination of hydrogen cyanide from benzylated α-amino nitriles which leads to the formation of the corresponding enamines.[13]

Our data show that the use of a protic solvent (system B in the case of the salts **3a,b**) or a base possessing a hydrogen atom (system C in the case of the salts **3a–c**) favour [2,3] rearrangement of the less stable ylides $\mathbf{5}^{+-}$ which gave **8**. However, under the 'anhydrous' conditions of system A, all the salts **3a–c** produced largely the products of a [1,4] shift **6**, *via* the more stable ylides $\mathbf{4}^{+-}$. Evidently, a protic solvent or base which carries hydrogen (system B or C, respectively), aided a [2,3] shift of the ylides $\mathbf{5a,b}^{+-}$; the ylide $\mathbf{5c}^{+-}$ however in system B underwent mainly [1,4] and [1,2] rearrangements.

Furthermore, we found that the quality of the DMF used in system C influenced the kind of products formed. In freshly purified DMF, products of a [2,3] shift **8b,c** were predominant, while in DMF stored for some time products of a [1,4] rearrangement, the α-cyano enamines **6b,c** appeared. The latter result is possibly due to the presence of minute amounts of dimethylamine which promote the generation of the ylides

4b,c$^{+\cdot}$ which then undergo a [1,4] shift. Indeed, rearrangement of ylides generated from the salt **3c** by means of dimethylamine in DMF, yielded a mixture rich in product **6c** (**6c**:**8c** ≈ 3.5).

These results are at variance with the observation described above for protic solvents and bases possessing a hydrogen atom. Possibly, such factors as hetero- or homo-geneity of the base–solvent system (systems A–C *vs.* Me_2NH–DMF system) also play a role in the generation and rearrangement of particular ylides.

In respect of the stereochemistry of the products, it is noteworthy that the [2,3] rearrangement of **5a**$^{+\cdot}$ gave, stereoselectively, *E*-**8a** ($J_{HC=CH}$ 16.7 Hz), while **8b** and **8c** derived from **5b**$^{+\cdot}$ and **5c**$^{+\cdot}$, respectively, were formed as mixtures of four diastereoisomers, in both cases in comparable amounts. [1,4] Rearrangement of the ylides **4**$^{+\cdot}$ gave, stereoselectively, one isomer each of the trisubstituted cyano enamines **6a–c**. Their stereochemistry was established by ^{13}C NMR spectroscopy on the basis of vicinal coupling constants $^3J_{C,H}$ between the proton and carbon of the cyano group. Values $^3J_{C,H}$ obtained ($^3J_{C,H}$ 13.1, 12.2 and 12.1 Hz for **6a**, **6b** and **6c**, respectively) are typical for *trans*-arrangement of these substituents.[14]

Our study has shown that allylides are much more likely to undergo [1,4] rearrangement than benzylides.[1–3,12] This behaviour may be explained in terms of a different charge distribution in the anionic part of the allyl- and benzyl-ides.[15] Assuming a similarity of allylides and benzylides to allyl and benzyl anions, respectively, it seems likely that a higher electron density at C-3 of allylides relative to the *ortho*-C in benzylides, may facilitate formation of a new C–C bond in the former.

Further work on the synthetic and mechanistic aspects of sigmatropic rearrangements of ammonium ylides is currently being carried out.

Experimental

Mps (measured on a capillary mp apparatus) and bps are uncorrected. ^1H and ^{13}C NMR spectra were measured on a Varian Gemini 200 spectrometer at 200 and 50 MHz, respectively, as solutions in $CDCl_3$ or [$^2H_6$]-DMSO. Gas chromatography (GC) analyses were performed on a Hewlett-Packard 5890 Series II chromatograph, equipped with a HP 50+ capillary column (30 m). EI/HR and GC/MS spectra were determined on the AMD-604 Intectra and a Hewlett-Packard 5791 spectrometers, respectively. Tarry products were removed by filtration through a short column filled with Macherey Nagel MN-Silica Gel 60 (100–200 mesh).

Dimethyl sulfate and DMF were purified according to the literature.[16] Commercial aldehydes **1a–c** were distilled before use.

N-Cyanomethyl-*N*-(1-cyano-3-methylbut-2-enyl)methylamine 2a

The mixture of *N*-methylaminoacetonitrile hydrochloride (5.86 g, 55 mmol), sodium cyanide (2.94 g, 60 mmol), methanol (24 cm^3) and water (12 cm^3) was stirred while the aldehyde **1a** (4.17 g, 49.6 mmol) was added dropwise at room temperature (RT). The stirring was continued at 45 °C for 5 h after which the mixture was diluted with water and extracted with CH_2Cl_2. The organic extracts were washed with saturated aq. $NaHSO_3$ and water, dried ($MgSO_4$) and evaporated. The product was isolated by distillation, bp 100–102 °C/1.2 mmHg (partial decomposition, 6.35 g, 71%), purity (by GC) *ca.* 85%; $\delta_H(CDCl_3)$ 1.76 (3 H, d, $^4J_{trd}$ 1.36, CH_3), 1.81 (3 H, d, $^4J_{csd}$ 1.38, CH_3), 2.49 (3 H, s, CH_3N), 3.48, 3.62 (2 H, q_{AB}, J_{AB} 17.1, CH_2CN), 4.25 (1 H, d, ^3J 8.5, CHCN) and 5.19 (1 H, dm, ^3J 8.5, =CH).

N-Cyanomethyl-*N*-[(*E*)-1-cyanobut-2-enyl]methylamine 2b and *N*-cyanomethyl-*N*-[(*E*)-1-cyano-3-phenylprop-2-enyl)]-methylamine 2c

A mixture of *N*-methylaminoacetonitrile hydrochloride (5.86 g, 55 mmol), the aldehyde **1b** or **1c** (49.6 mmol) and acetonitrile (24 cm^3) was stirred whilst a solution of sodium cyanide (2.94 g, 60 mmol) in water (12 cm^3) was added dropwise at 15–20 °C for **1b** or at 5 °C for **1c**. The mixture was stirred at *ca.* 20 °C for 24 h, and worked up as described above (benzene, instead of CH_2Cl_2 was used for extraction).

Compound **2b**, bp 81–83 °C/0.5 mmHg (partial decomposition, 2.66 g, 36%) (Found: C, 64.2; H, 7.4; N, 28.1. $C_8H_{11}N_3$ requires C, 64.40; H, 7.43; N, 28.16%); $\delta_H(CDCl_3)$ 1.79 (3 H, dm, ^3J 6.6, CH_3), 2.47 (3 H, s, CH_3N), 3.40, 3.54 (2 H, q_{AB}, J_{AB} 16.9, CH_2CN), 4.24 (1 H, dm, ^3J 5.2, CHCN), 5.40 (1 H, ddq, $^3J_{trans}$ 15.5, ^3J 5.2, $^4J_{csd}$ 1.6, =CH) and 6.11 (1 H, dqd, $^3J_{trans}$ 15.5, ^3J 6.6, $^4J_{csd}$ 1.6, =C*H*CH_3).

Compound **2c** (9.5 g), a light tan oil, decomposed during attempted vacuum distillation; $\delta_H(CDCl_3)$ 2.53 (3 H, s, CH_3N), 3.46, 3.60 (2 H, q_{AB}, J_{AB} 16.9, CH_2CN), 4.49 (1 H, dd, ^3J 5.2, $^4J_{csd}$ 1.7, CHCN), 6.07 (1 H, dd, $^3J_{trans}$ 16.1, ^3J 5.2, =CH), 6.95 (1 H, dd, $^3J_{trans}$ 16.1, $^4J_{csd}$ 1.7, =CHPh) and 7.30–7.45 (5 H, m, ArH). For the preparation of the salt **3c**, purity of 100% for **2c** was assumed.

N-Cyanomethyl-*N*-(1-cyano-3-methylbut-2-enyl)-*N*,*N*-dimethylammonium perchlorate 3a

A mixture of **2a** (2.45 g, 15 mmol) and dimethyl sulfate (7.60 g, 6.0 cm^3, 60 mmol) was stored in a stoppered flask protected from the light, at RT for 14 days or at 35 °C for 3 days. The mixture was then diluted with water (*ca.* 20 cm^3) and the phases were separated. The aqueous phase was extracted with CH_2Cl_2, filtered, cooled to *ca.* 0 °C and treated dropwise with 70% aq. $HClO_4$ (4.5 g, 3.0 cm^3, 31.3 mmol); it was then stored in a refrigerator for 0.5 h. The crystals were filtered off, washed with water, dried *in vacuo* (over P_2O_5), and twice crystallized from acetone to give the salt **3a** (2.05 g, 49%), mp 126–127 °C (Found: C, 43.2; H, 5.7; Cl, 12.65; N, 15.1. $C_{10}H_{16}ClN_3O_4$ requires C, 43.25; H, 5.81; Cl, 12.77; N, 15.13%); δ_H([$^2H_6$]-DMSO) 1.88 (3 H, d, $^4J_{trd}$ 1.18, CH_3), 1.90 (3 H, d, $^4J_{csd}$ 1.22, CH_3), 3.34, 3.36 (6 H) (each s, $Me_2\overset{+}{N}$), 4.87, 4.94 (2 H, q_{AB}, J_{AB} 13.0, CH_2CN), 5.62 (1 H, dm, ^3J 10.6, =CH) and 5.99 (1 H, d, ^3J 10.6, CHCN); δ_C([$^2H_6$]-DMSO) 19.17 and 25.97 (CH_3), 49.80 and 51.05 ($Me_2\overset{+}{N}$), 49.87 (*C*H_2CN), 62.44 (*C*HCN), 108.09 (=CH), 111.52 and 112.72 (CN) and 154.57 (=C).

N-Cyanomethyl-*N*-[(*E*)-1-cyanobut-2-enyl]-*N*,*N*-dimethylammonium perchlorate 3b and *N*-cyanomethyl-*N*-[(*E*)-1-cyano-3-phenylprop-2-enyl]-*N*,*N*-dimethylammonium perchlorate 3c

The amino nitrile **2b** or **2c** (26 mmol) and dimethyl sulfate (13.1 g, 9.8 cm^3, 104 mmol) were stored in a stoppered flask protected from light at *ca.* 20 °C for 5 days. The mixture was then diluted with ethyl ether (*ca.* 10 cm^3) and extracted with water (6 × 3.5 cm^3). The aqueous phases were extracted with benzene (2 × 6 cm^3), cooled to temperature of *ca.* 0 °C and then treated dropwise with 70% aq. $HClO_4$ (14.4 g, 8.6 cm^3, 100 mmol); the mixture was then kept in a refrigerator for 12 h. The crystals were filtered off, washed with methanol and purified as described for **3a**. Compound **3b** (1.74 g, 44%), mp 128–132 °C (Found: C, 40.8; H, 5.4; Cl, 13.4; N, 15.9. $C_9H_{14}ClN_3O_4$ requires C, 41.00; H, 5.35; Cl, 13.45; N, 15.94%); δ_H([$^2H_6$]-DMSO) 1.87 (3 H, dd, ^3J 6.7, $^4J_{csd}$ 1.1, CH_3), 3.33 (6 H, s, $Me_2\overset{+}{N}$), 4.92, 4.94 (2 H, q_{AB}, J_{AB} 16.9, CH_2CN), 5.85–6.15 (2 H, m, =CH together with CHCN), 6.40–6.55 (1 H, m, =C*H*CH_3); δ_C([$^2H_6$]-DMSO) 18.21 (CH_3), 50.22 and 51.27 ($Me_2\overset{+}{N}$), 50.27 (*C*H_2CN), 65.64 (*C*HCN), 111.39 and 112.20 (CN), 114.64 (=CH), 146.29 (=*C*HCH_3). Compound **3c** (3.0 g, 35%), mp *ca.* 115 °C (decomp.) (Found: C, 51.6; H, 4.85; Cl, 10.9; N, 13.0. $C_{14}H_{16}ClN_3O_4$ requires C, 51.62; H, 4.95; Cl, 10.88; N, 12.90%); δ_H([$^2H_6$]-DMSO) 3.43 (6 H, s, $Me_2\overset{+}{N}$), 5.02 (2 H, s, CH_2CN), 6.16 (1 H, d, ^3J 8.5, CHCN), 6.70 (1 H, dd, $^3J_{trans}$ 15.4, ^3J 8.5, =CH), 7.25 (1 H, d, $^3J_{trans}$ 15.4, =C*H*Ph) and 7.42–7.45 (3 H) and 7.65–7.70 (2 H) (both m, ArH); δ_C([$^2H_6$]-DMSO) 50.44 and 51.58 ($Me_2\overset{+}{N}$), 50.48 (*C*H_2CN), 66.11 (*C*HCN), 111.46 and 112.06 (CN),

111.89 (=CH), 128.25, 128.88 and 130.49 (all CH_{ar}), 133.69 ($C_{quat\,ar}$) and 145.71 (=CHPh). In the case of the salt **3c**, after addition of aq. $HClO_4$, a gummy product was precipitated which when treated with acetone and then ethyl ether afforded crystals (mp >200 °C, lack of signals of aromatic protons in ^1H NMR spectrum), not investigated further.

Rearrangements of ylides generated from the salts 3a–c

In a solid K_2CO_3–DMSO (system A). The salt **3** (2 mmol), powdered K_2CO_3 (1.4 g, 10 mmol) and DMSO (6 cm^3) were stirred at the temperature and for the time indicated in Table 1. The mixture was then poured into water (100 cm^3) and extracted with benzene (3 × 15 cm^3). The organic extracts were washed with brine and water, dried ($MgSO_4$) and evaporated. The residue was analysed by NMR and/or GC, and purified by distillation.

From salt **3a**: a mixture of **6a** and **8a** (*ca.* 10:1, 0.22 g, 61%), bp 102–108 °C/0.9 mmHg (Found: C, 67.4; H, 8.5; N, 23.6. $C_{10}H_{15}N_3$ requires C, 67.76; H, 8.53; N, 23.71%); **6a**, $\delta_H(CDCl_3)$ 1.30 (6 H, s, 2 × CH_3), 2.50 (2 H, s, CH_2), 2.62 (6 H, s, Me_2N) and 4.88 (1 H, s, =CH); $\delta_C(CDCl_3)$ 28.00 (CH_3), 31.14 (CH_2), 33.29 (>C<), 40.23 (CH_3N), 114.45, 117.58 (both CN), 122.16 (=CH) and 123.94 (=C–N).

From salt **3b**: **6b** (0.20 g, 74%), bp 105–110 °C/1.5 mmHg (Found: C, 66.15; H, 8.05; N, 25.6. $C_9H_{13}N_3$ requires C, 66.23; H, 8.03; N, 25.74%); $\delta_H(CDCl_3)$ 1.10 (3 H, d, *J* 6.76, CH_3), 2.32 (2 H, d, *J* 6.30, CH_2), 2.60 (6 H, s, Me_2N), 2.75–2.97 (1 H, m, CH) and 4.69 (1 H, d, *J* 10.0, =CH); $\delta_C(CDCl_3)$ 20.50 (CH_3), 24.99 (CH_2), 31.45 (>C<), 39.96 (CH_3N), 116.84 (=CH), 113.53, 117.55 (both CN) and 125.01 (=C–N).

From salt **3c**: a mixture of **6c** and **10c** (5:1, 0.20 g, *ca.* 44%), bp 140–142 °C/0.05 mmHg; **6c**, $\delta_H(CDCl_3)$ 2.75 (6 H, s, Me_2N), 2.77 (2 H, d, *J* 6.70, CH_2), 4.12 (1 H, dt, *J* 10.30 and 6.70, CH), 5.09 (1 H, d, *J* 10.30, =CH) and 7.25–7.40 (5 H, m, ArH); $\delta_C(CDCl_3)$ 25.39 (CH_2), 40.24 (CH_3N), 42.15 (>C<), 113.69 (=CH), 113.78, 117.58 (both CN), 125.93 (=C–N), 126.51, 127.41, 128.86 (all CH_{ar}) and 140.69 ($C_{quat\,ar}$); *m/z* (GC/MS) 225 (M^+, 4%), 185(100), 140(12), 115(15) and 91(87).

In aq. NH_3–CH_2Cl_2 (system B). The salt **3** (2 mmol), 26% aq. NH_3 (3.2 cm^3, 44 mmol) and CH_2Cl_2 (3.5 cm^3) were stirred at the temperature and for the time given in Table 1; they were finally worked up as described above.

From salt **3a**: a mixture of **8a** and **9a**. The structure of **9a** was assigned on the basis of its ^1H and ^{13}C NMR spectra, attempts at its isolation failing; **9a** (mixture of two diastereoisomers), $\delta_H(CDCl_3)$ 1.73 (d, *J* 1.36), 1.76 (d, *J* 1.20), 1.79 (d, *J* 1.30) and 1.82 (d, *J* 1.44) (6 H together, 2 × CH_3), 2.34 (s) and 2.40 (s) (6 H together, Me_2N), 3.64–3.83 (2 H, m, HC–CH) and 5.04–5.13 (1 H, m, =CH); $\delta_C(CDCl_3)$ 18.00, 18.16, 25.15 and 25.22 (CH_3), 32.33 and 32.60 (CH), 41.47 and 41.64 (CH_3N), 60.20 and 60.70 (CHN), 113.13 and 113.43 (CN), 113.23 and 114.04 (=CH), 116.89 and 117.17 (CN) and 140.31 and 142.20 (=C); *m/z* (GC/MS) 83(100%), 67(4), 42(9).

From salt **3b**: almost pure **8b** was isolated as described below for system C, and identified by spectral means.

From salt **3c**: the crude mixture was dissolved in benzene and filtered through a short column with silica gel. The filtrate was evaporated under reduced pressure to give a mixture of **6c** and **7c** (*ca.* 2:1) as a pale yellow oil (0.35 g, 78%) (Found: C, 74.4; H, 6.95; N, 18.9. $C_{14}H_{15}N_3$ requires C, 74.64; H, 6.71; N, 18.65%); **7c**, $\delta_H(CDCl_3)$ 2.39 (6 H, s, Me_2N), 2.97 and 3.06 (2 H, q_{AB}, *J* 16.8, CH_2CN), 6.15 (1 H, d, *J* 16.1, =CH), 7.07 (1 H, d, *J* 16.1, =CHPh), signals of ArH overlapped with those of **6c**; $\delta_C(CDCl_3)$ 28.48 (CH_2), 40.57 (CH_3N), 65.53 (C_{quat}), 114.18 and 114.24 (CN), 124.97 (=CH), 126.85, 128.62 and 128.90 (CH_{ar}), 134.15 ($C_{quat\,ar}$) and 134.57 (=CHPh).

Distillation of the crude products (bp *ca.* 140 °C/0.05 mmHg) afforded a mixture of **6c** and **10c** (due to **7c**→**10c** transformation); **10c**, $\delta_H(CDCl_3)$ 2.87 (6 H, s, Me_2N), 3.86 (1 H, s, =CHCN), 6.60 (1 H, d, *J* 16.3, =CH), 7.11 (1 H, d, *J* 16.3, =C*H*Ph), signals of ArH overlapped with those of **6c**; $\delta_C(CDCl_3)$ 40.06 (CH_3N), 62.57 (=*C*HCN), 120.62 (=CH), 122.02 (CN), 126.85, 128.43 and 128.78 (CH_{ar}), 135.08 ($C_{quat\,ar}$), 138.39 (=CHPh) and 162.47 (=C–N); *m/z* (GC/MS) 198 (M^+, 100%), 158(42), 127(40), 121(78) and 81(77).

In a solid $NaHCO_3$–DMF (system C). The salt **3** (2 mmol), powdered $NaHCO_3$ (0.84 g, 10 mmol) and DMF (6 cm^3) were stirred at the temperature and for the time shown in Table 1; the mixture was then worked up as described above.

From salt **3a**: the product **8a** (0.29 g, 81%, purity *ca.* 92%, by GC), bp 106–110 °C/0.6 mmHg [Found: (HRMS; EI), M^+, 177.126 65. $C_{10}H_{15}N_3$ requires *M*, 177.126 60]; $\delta_H(CDCl_3)$ 1.20 (6 H, s, 2 × CH_3), 2.27 (6 H, s, Me_2N), 3.33 (1 H, s, CHCN), 5.37 (1 H, d, *J* 16.70, =CHCN) and 6.84 (1 H, d, *J* 16.70, =CH); $\delta_C(CDCl_3)$ 23.19, 25.13 (both CH_3), 41.74 (>C<), 44.09 (CH_3N), 67.98 (*C*HCN), 99.16 (=*C*HCN), 114.13, 116.94 (both CN) and 158.92 (=CH); *m/z* (EI) 177 (M^+, 0.2%), 105(3), 94(1), 83(100), 56(5) and 42(10).

From salt **3b**: **8b** (mixture of four diastereoisomers, 0.27 g, 83%), bp 80 °C/0.05 mmHg (Found: C, 65.9; H, 7.9; N, 25.5. $C_9H_{13}N_3$ requires C, 66.23; H, 8.03; N, 25.74%); $\delta_H(CDCl_3)$ 1.13, 1.16, 1.22, 1.24 (3 H) (each d, *J* 6.60, CH_3), 2.24, 2.26, 2.29 (6 H) (each s, Me_2N), 2.95–3.15 (1 H, m, CH), 3.20–3.40 (1 H, four d_{AB}, *J* 10.42, 10.72, 11.12 and 11.16, CHCN), 5.36 (dd, *J* 0.55 and 10.90), 5.39 (dd, *J* 1.20 and 16.40), 5.48 (dd, *J* 0.50 and 10.90), 5.51 (dd, *J* 1.10 and 16.30) (1 H together, =CHCN), 6.25 (dd, *J* 10.0 and 10.90), 6.31 (dd, *J* 10.1 and 10.90), 6.59 (dd, *J* 8.20 and 16.30) and 6.61 (dd, *J* 7.90 and 16.40) (1 H together, =CH); $\delta_C(CDCl_3)$ 15.59, 16.57, 16.74, 17.25 (all CH_3), 37.77, 38.14, 38.19, 39.07 (all >C<), 41.47, 41.65, 41.67, 41.93 (all CH_3N), 62.65, 62.82, 63.40, 63.46 (all *C*HCN), 100.09, 100.43, 101.90, 102.41 (all =*C*HCN), 114.70, 114.75, 114.76, 114.78, 114.92, 115.25, 116.41, 116.73 (all CN), 153.16, 153.95, 154.45 and 154.82 (all =CH).

From salt **3c**: the crude mixture partially solidified; the crystals were washed with benzene–hexane to obtain a mixture of two I-*E*/II-*Z* diastereoisomers of **8c** in the ratio of 1:2.4 (0.18 g, 40%), mp 128–136 °C (Found: C, 74.7; H, 6.75; N, 18.6. $C_{14}H_{15}N_3$ requires C, 74.64; H, 6.71; N, 18.65%). Pure I-*E*-**8c** was obtained after two recrystallizations from benzene (0.04 g, 9%), mp 129–130 °C (Found: C, 74.6; H, 6.8; N, 18.75. $C_{14}H_{15}N_3$ requires C, 74.64; H, 6.71; N, 18.65%).

I-*E*-**8c**, $\delta_H(CDCl_3)$ 2.38 (6 H, s, Me_2N), 3.73 (1 H, ddd_{AB}, *J* 1.30, 6.30 and 11.60, CH), 3.80 (1 H, d_{AB}, *J* 11.60, CHCN), 5.32 (1 H, dd, *J* 1.30 and 16.40, =CHCN), 6.98 (1 H, dd, *J* 6.30 and 16.40, =CH) and 7.18–7.45 (5 H, m, ArH); $\delta_C(CDCl_3)$ 41.61 (CH_3N), 49.75 (>C<), 63.58 (*C*HCN), 102.25 (=*C*HCN), 114.14, 116.73 (both CN), 128.27, 128.83, 129.49 (all CH_{ar}) 135.90 ($C_{quat\,ar}$) and 152.61 (=CH).

II-*Z*-**8c**, $\delta_H(CDCl_3)$ 2.40 (6 H, s, Me_2N), 3.88 (1 H, d, *J* 11.70, CHCN), 4.20 (1 H, dd, *J* 10.30 and 11.70, CH), 5.42 (1 H, dd, *J* 0.60 and 10.80, =CHCN), 6.65 (1 H, dd, *J* 10.30 and 10.80, =CH), signals of ArH overlapped with those of I-*E*; $\delta_C(CDCl_3)$ 41.83 (CH_3N), 49.13 (>C<), 63.73 (*C*HCN), 100.81 (=*C*HCN), 114.06, 115.31 (both CN), 127.87, 128.72, 129.48 (all CH_{ar}), 136.28 ($C_{quat\,ar}$) and 151.87 (=CH).

The filtrate after removal of the crystals mainly consisted of the second pair (III-*E* and IV-*Z*) of diastereoisomers of **8c** and a minute amount of **6c**. This mixture was analysed only by spectral means, due to its decomposition during attempted purification.

III-*E*- + IV-*Z*-**8c**, $\delta_H(CDCl_3)$ 2.27, 2.32 (6 H) (each s, Me_2N), 3.79 (ddd_{AB}, *J* 1.20, 7.50 and 11.50), 4.24 (dd, *J* 10.10 and 10.60) (1 H together, CH), 3.90 (d_{AB}, *J* 11.50), 3.97 (d, *J* 10.10) (1 H together, CHCN), 5.43 (dd, *J* 1.20 and 16.20), 5.50 (d, *J* 10.80) (1 H together, =CHCN), 6.88 (dd, *J* 7.50 and 16.20), 6.64 (dd, *J* 10.60 and 10.80) (1 H together, =CH) and 7.15–7.45 (5 H, m, ArH); δ_C ($CDCl_3$) 41.56, 41.81 (both CH_3N), 49.07, 50.24 (both >C<), 62.04, 62.50 (both *C*HCN), 102.21,

103.33 (both =*C*HCN), 114.65, 114.80, 114.91, 116.29 (all CN), 127.21, 127.51, 127.75, 129.03, 129.07, 129.28 (all CH_{ar}), 135.58, 136.53 (both $C_{quat\ ar}$) and 150.68 and 152.00 (both =CH).

Rearrangement of 3c in a Me_2NH–DMF system

The salt **3c** (0.65 g, 2 mmol), DMF (5 cm^3) and anhydrous dimethylamine (*ca.* 0.65 g, 15 mmol) were stirred at −30 °C for 1.5 h and the mixture worked up as described for system A. The crude products (yield *ca.* 100%) were analysed by GC and ^1H NMR to show **6c**, 70%; **7c**, 5%; **8c**, 20% and unidentified products, 5%.

Acknowledgements

Financial support by the State Committee for Scientific Research, Warsaw, Poland (Grant No. 2 2616 92 03) is gratefully acknowledged.

References

1 A. Jończyk, D. Lipiak and K. Sienkiewicz, *Synlett*, 1991, 493.
2 A. Jończyk and D. Lipiak, *J. Org. Chem.*, 1991, **56**, 6933.
3 T. Zdrojewski and A. Jończyk, *Tetrahedron Lett.*, 1995, **36**, 1355.
4 E. F. Jenny and J. Druey, *Angew. Chem.*, 1962, **74**, 152.
5 W. Dietrich, K. Schultze and M. Mühlstädt, *J. Prakt. Chem.*, 1976, **318**, 1008.
6 H. Sugiyama, Y. Sato and N. Shirai, *Synthesis*, 1988, 988.
7 R. W. Jemison, T. Laird, W. D. Ollis and T. O. Sutherland, *J. Chem. Soc., Perkin Trans. 1*, 1980, 1450.
8 J. P. Hagen, K. D. Lewis, S. W. Lovell, P. Rossi and A. Z. Tezcan, *J. Org. Chem.*, 1995, **60**, 7471.
9 K. Honda, S. Inoue and K. Sato, *J. Am. Chem. Soc.*, 1990, **112**, 1999.
10 K. Honda, S. Inoue and K. Sato, *J. Org. Chem.*, 1992, **57**, 428.
11 M. Gulea-Purcarescu, E. About-Jaudet, N. Collignon, M. Saquet and S. Masson, *Tetrahedron*, 1996, **52**, 2075.
12 D. Lipiak, Ph.D. Thesis, Technical University (Politechnika), Warszawa, 1991.
13 C. R. Hauser, H. M. Taylor and T. G. Ledford, *J. Am. Chem. Soc.*, 1960, **82**, 1786.
14 V. Vögeli and W. von Philipsborn, *Org. Magn. Reson.*, 1975, **7**, 617.
15 I. Fleming, *Frontier Orbitals and Organic Chemical Reactions*, John Wiley, New York, 1978, pp. 30 and 55.
16 A. I. Vogel, *Textbook of Practical Organic Chemistry*, 4th edn., Longman, London, 1978; Polish translation, WNT, Warszawa, 1984.

Paper 6/03676G
Received 28*th May* 1996
Accepted 21*st August* 1996