

CHLORO- AND METHOXYBUTENONITRILES*

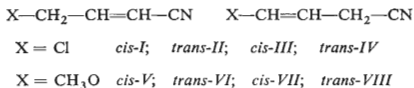
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Prototropic isomerisation of unsaturated nitriles $X-CH=CH-CH_2CN$ and $X-CH_2-CH=CH-CN$ (*cis* and *trans* isomers) for $X = Cl, CH_3O$ has been investigated. At equilibrium the mixture contained 84.6% of 4-chloro-2-butenonitriles (28.9% *cis* and 55.7% *trans* isomer). In the case of methoxybutenonitriles the equilibrium mixture contained *cis*- (51.4%) and *trans*-4-methoxy-3-butenonitrile (48.6%) only.

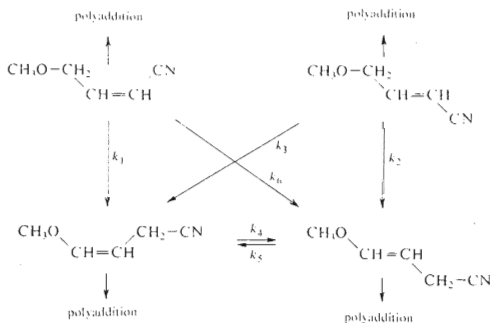
In the preceding paper¹ we investigated prototropic isomerisations in the series of aliphatic unsubstituted unsaturated nitriles and we found that the substituent in the γ -position can considerably affect the position of the equilibrium of the three-carbon atom isomery and the *cis-trans* isomery. Therefore we endeavoured to determine the rate and equilibrium constants for the case of equilibrium under conditions comparable with those of our preceding paper.



During the isomerisation of chlorobutenonitriles *I-IV* it was probable that it would be accompanied by substitution of the allylic halogen. The isomerisation of these nitriles was studied by Mialhe² and Vessière in the presence of triethylamine in acetonitrile, but their results are not comparable with those of our previous paper¹ where the isomerisation was carried out under the effect of potassium tert-butoxide in tert-butyl alcohol. Therefore we followed the relation of the substitution rate and the isomerisation in very dilute solutions (0.05M) by potentiometric titration and gas chromatography. For the *cis*- α, β -isomer *I* the rate constant for substitution was $k = 1.12 \text{ l. mol}^{-1} \text{ s}^{-1}$, while for the *cis*- β, γ -isomer *III* the constant at the beginning of the reaction was $k = 2.48 \text{ l. mol}^{-1} \text{ s}^{-1}$. From the results it follows that under these conditions isomerisation is faster than substitution. By following the composition

* Part III in the series Isomerization of Unsaturated Nitriles; Part II: This Journal 39, 1342 (1974).

of the isomerisation mixture at 0.5M concentration (at this concentration the substitution reaction is much faster than the isomerisation and it causes the latter to stop after a very short time in consequence of catalyst exhaustion) it was found that a larger amount of the isomer of the opposite configuration at the double bond than that of the starting isomer is always formed first during isomerisation (Table I). In view of the great rapidity of the reaction it was impossible to determine the rate constants of the three-carbon atom isomerisation even when the concentration was 0.05M, *i.e.* when the side reaction of the allylic chlorine atom with potassium tert-butoxide is much slower. The shortest time interval during which we were capable of stopping the reaction by neutralizing the catalyst with acetic acid was 4 seconds. During this time the reaction was almost at equilibrium and the ratio of the isomers hardly changed on prolongation of the reaction. Equilibrium concentrations were calculated as an average of 20 experimental values for single time intervals. Equilibrium concentrations of 4-chlorobutenonitriles in tert-butyl alcohol at 25°C were: *cis*-4-Chloro-2-butenonitrile (*I*) $28.9 \pm 2.2\%$; *trans*-4-Chloro-2-butenonitrile (*II*) $55.7 \pm 2.9\%$; *cis*-4-Chloro-3-butenonitrile (*III*) $11.0 \pm 1.6\%$; *trans*-4-Chloro-3-butenonitrile (*IV*) $4.0 \pm 1.1\%$. From the results of the isomerisation it follows that α,β -unsaturated isomers *I* and *II* are much less stable than β,γ -isomers *III* and *IV*, and that *cis*- β,γ -unsaturated isomer *III* is more stable than the *trans*-isomer *IV*. The rate constants of the total loss of 4-chlorobutenonitriles, measured by gas chromatography, were higher than the rates of the decrease in the base concentration, catalysing the reaction, as measured by titration (Table II). This difference is caused by polyaddition reactions of unsaturated nitriles of similar type, as were described in the case of unsaturated esters³. The isomerisation of 4-methoxybutenonitriles *V*–*VIII* may be expressed by Scheme 1. At equilibrium at 30°C 51.4 \pm 3.5% of the *cis*- β,γ -isomer



SCHEME 1

VII and $48.6 \pm 3.9\%$ of the *trans*- β,γ -isomer VIII are present. The concentration of other isomers at equilibrium was below 0.5% , if any. With increasing temperature the ratio of isomers changes negligibly. Equilibrium concentrations of 4-methoxybutenonitriles at various temperatures are:

Temperature, °C	30	55	75
<i>cis</i> -VII, %	51.4 ± 3.5	52.0 ± 2.7	52.3 ± 2.2
<i>trans</i> -VIII, %	48.6 ± 3.9	48.0 ± 3.5	47.7 ± 2.2

In view of the high rates of isomerisation of α,β -unsaturated derivatives (Fig. 1 and 2) their rate constants were calculated from the approximation for a system of first order irreversible reactions for a narrow reaction range, when the validity of Wegscheider's principle^{4,5} was fulfilled. The rate constants $k_1 - k_6$ (min^{-1}) of the isomerisations of 4-methoxybutenonitriles (Scheme 1) at 30°C by potassium tert-butoxide in tert-butyl alcohol (for k_4 and k_5 Wegscheider's principle did not apply in consequence of the slow course of isomerisation, and they were determined graphically) are the following:

k_1	k_2	k_3	k_4	k_5	k_6
21.3	0.32	5.45	0.0097	0.0069	0.79

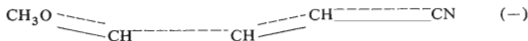
The sum of the rate constants of single reactions is lower than the rate constant of the concentration decrease of the starting nitrile, which is caused by polymerisation.

In the case of 4-methoxybutenonitriles the isomerisation is highly stereospecific as follows from the ratio $k/\sum k_n$ for the conversion of 4-methoxy-3-butenonitriles VII and VIII:

Starting nitrile	<i>cis</i> -V	<i>trans</i> -VI
$k/\sum k_n$ <i>cis</i> -VII	0.96	0.95
$k/\sum k_n$ <i>trans</i> -VIII	0.036	0.055

At the initial stages of the isomerisation the *cis*- β,γ -unsaturated isomer VII is formed from both α,β -unsaturated isomers VI and VI predominantly with a ratio $k/\sum k_n$ approaching one and only later the concentration of this isomer decreases very slowly to the equilibrium concentration (Fig. 1-4) which is attained only after several hours.

Therefore we suppose that in the equilibrium of possible carbanions the anion of *cis*- β,γ -configuration prevails.



Kloosterziel and van Drunen⁶ measured the NMR spectra of methoxyallylic anions and proved their *cis*-structure. Therefore the *cis*- β,γ -isomer *VII* also isomerises very slowly in consequence of a rapid reprotonation of the anion, as was also found during the isotopic exchanges in allyl ethers^{7,8}.

Preparation of Compounds

For the preparation of α,β -unsaturated nitriles the pyrolysis of 3-acetyloxy derivatives seems best. On pyrolysis of 4-chloro-3-acetyloxybutanoic acid nitrile *trans*- β,γ -unsaturated isomer *IV* (in ref.⁹ its formation is not mentioned) was formed in addition to α,β -unsaturated derivatives *I* and *II*. In a similar manner distillation of the nitrile of 4-methoxy-3-acetyloxybutanoic acid in the presence of potassium acetate gave a substance which is given in the literature¹⁰ as 4-methoxy-2-butenitrile; using gas chromatography and NMR spectroscopy we found that it is again a mixture of three isomers, *V*, *VI*, and *VII*.

4-Methoxy-3-butenitriles were prepared on reaction of 4,4-dimethoxybutanenitrile with phosphorus pentoxide in pyridine, because under the effect of *p*-toluene-

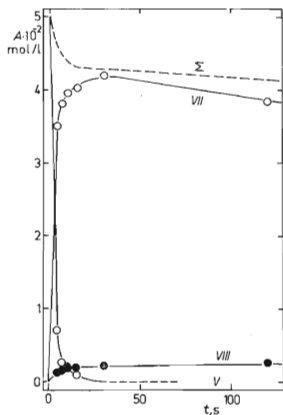


FIG. 1

Course of Isomerisation of Methoxybutenitrile *cis*-*V*

Σ = Sum of concentrations of all isomers.

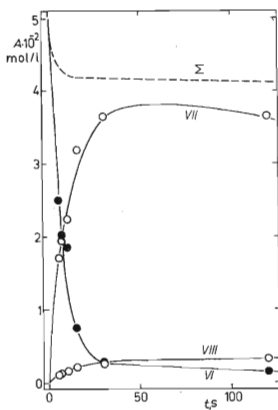


FIG. 2

Isomerisation of *trans*-*VI*

sulfonic acid only polymerisation takes place, while under the effect of boric acid (in analogy to ref.¹¹) or phthalic anhydride¹² oligomers (dimer and trimer) are formed mainly in addition to small amounts of the required isomers VII and VIII.

During the following of the preparation of 4-methoxy-3-butenonitriles from 1-methoxy-3-chloro-1-propene it was found that a direct dehydration of 1-methoxy-3-chloro-2-propanol with phosphoric acid, phosphorus oxychloride, boric acid, or dehydration on $\gamma\text{-Al}_2\text{O}_3$, led in all instances to an extensive polymerisation and the formation of complex mixtures. Therefore pyrolysis of 1-methoxy-3-chloro-2-acetyloxypropane was employed for the preparation of this substance. The starting compound was prepared by acetylation with acetic anhydride in pyridine because when 1-methoxy-3-chloro-2-propanol was refluxed with acetic anhydride under catalysis with sulfuric acid a mixture of 1-methoxy-3-chloro-2-acetyloxypropane and 1-methoxy-2-chloro-3-acetyloxypropane was formed. A similar rearrangement was observed earlier in the case of 1,3-dibromopropanol¹³. In our case only the chloride atom participates in the reaction by compensation of the positive charge on the carbon atom, while the participation of the methoxy group was not observed. However, pyrolysis of 1-methoxy-3-chloro-2-acetyloxypropane gave a mixture of eight substances which could not be separated.

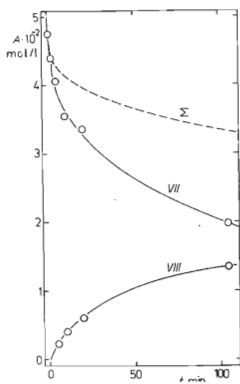


FIG. 3

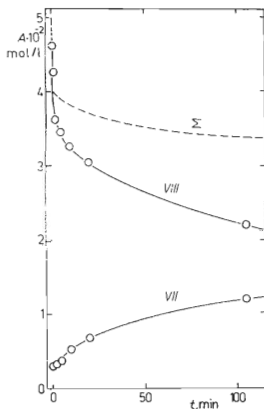
Isomerisation of *cis*-VII

FIG. 4

Isomerisation of *trans*-VIII

EXPERIMENTAL

The infrared spectra were measured on a UR-10 Zeiss, Jena, instrument, and the spectra of methoxy acetates on an apparatus of the Development Workshops of the Czechoslovak Academy of Sciences, Brno. All substances were measured undiluted. The NMR spectra were recorded on a JNM-3-60 (Jeol, Tokyo) instrument of 60 Mc/s frequency, in 0.5*M* solutions in tetrachloromethane.

4-Chlorobutenonitriles

cis-4-Chloro-2-butenonitrile (I) and *trans*-4-chloro-2-butenonitrile (II) were prepared in 41% yield from the nitrile of 4-chloro-3-acetyloxybutanoic acid⁹ by leading the vapours of the acetate through a Sial tube filled with Raschig rings, 50 cm long and 22 mm diameter, at 450°C and 40 Torr. The unreacted acetate was submitted to a new pyrolysis. The mixture obtained of *cis*- and *trans*-4-chloro-2-butenonitriles was distilled on a column (100 cm long, diameter 18 mm, stainless steel helices as filling) under simultaneous control of the distillation by gas chromatography (20% Apiezon L on porovina as stationary phase). In the intermediate fraction the presence of *trans*-4-chloro-3-butenonitrile was established. *cis*-I: b.p. 58°C/12 Torr, n_D^{20} 1.4742 (lit.¹⁴ gives b.p. 57–57.5°C/11 Torr, n_D^{20} 1.4750); *trans*-II: b.p. 73.5°C/10 Torr, n_D^{20} 1.4804 (lit.¹⁴ gives b.p. 73–73.5°C/11 Torr and n_D^{20} 1.4818).

cis-4-Chloro-3-butenonitrile (III) and *trans*-4-chloro-3-butenonitrile (IV) were prepared according to literature¹⁵. *cis*-III: b.p. 65–65.5°C/11 Torr, $n_D^{19.5}$ = 1.4572 (lit.¹⁴ gives b.p. 60–61°C/11 Torr, n_D^{22} = 1.4587); *trans*-IV: b.p. 73.5–74°C/11 Torr and $n_D^{19.5}$ 1.4609 (lit.¹⁶ gives b.p. 67–67.5°C/11 Torr, n_D^{22} 1.461).

4-Methoxy-2-butenonitriles

A mixture of 135.5 g (0.865 mol) of 4-methoxy-3-acetyloxybutanoic acid nitrile and 5.5 g of potassium acetate was distilled according to¹⁰. The fraction boiling at 110–175°C (88.7 g) was collected separately. The fraction boiling above 175°C was distilled under reduced pressure (23 g). Both fractions were combined, extracted with 400 ml of water the phases separated, and the extract neutralised with sodium hydrogen carbonate and reextracted three times with ether. The ethereal layers were combined with the organic phase from the above extraction with water. The combined extracts were washed with sodium hydrogen carbonate, dried over magnesium sulfate and distilled. The fraction boiling at 63–95°C/11 Torr (50.7 g) was collected. According to gas chromatography (100 cm column of 20% Reoplex 400) it consists of two substances. The mixture was distilled on a column of 100 cm length, 18 mm diameter (50 TP) filled with stainless steel helices. The distillation was controlled by gas chromatography (100 cm column with 20% Reoplex 400 on Chromosorb W 80–100 mesh, temperature 145°C, pressure of hydrogen 0.25 kp/cm²). The distillation yielded 5.4 g of pure *cis*-4-methoxy-2-butenonitrile (V) of b.p. 52.5°C/10 Torr and n_D^{20} 1.4374, and 15.1 g of *trans* derivative VI, b.p. 65.5°C/10 Torr, n_D^{20} 1.4410. According to NMR spectrometry the fraction of the *trans* isomer VI contains 30% *cis*-4-methoxy-3-butenonitrile (VII) and it was separated by preparative gas chromatography on poly(ethylene glycol) 20 M as stationary phase.

cis-4-Methoxy-2-butenonitrile (V): For C₅H₇NO (97.1) calculated: 61.9%; 7.06% H, 14.45% N; found: 62.0% C, 7.55% H, 14.55% N. IR spectrum: 735 cm⁻¹ ν (CH) *cis*; 1070 cm⁻¹ ν_s (C—O—C); 1120 cm⁻¹ ν_{as} (C—O—C); 1196 cm⁻¹ ν_{as} (C—O—C); 1402 cm⁻¹ δ (CH); 1460 cm⁻¹ δ (CH₂); 1640 cm⁻¹ ν (C=C conjug.); 2 221 cm⁻¹ ν (C=C—CN); 3063 cm⁻¹ ν (=C—). NMR spectrum: $\text{CH}_3\text{O}-\underset{\text{d}}{\text{CH}_2}-\underset{\text{c}}{\text{CH}}=\underset{\text{b}}{\text{CH}}-\underset{\text{a}}{\text{CN}}$; H_a (6): δ = 5.35 p.p.m., J_{ab} = 10.9, J_{ac} = 1.5 Hz; H_b (5): δ = 6.44 p.p.m., J_{bc} = 11 Hz; H_c (4): δ = 4.01 p.p.m.; H_d (1): δ = 3.28 p.p.m.. *trans*-

-4-Methoxy-2-butenonitrile (VI): Found: 61.94% C, 7.56% H, 14.15% N. IR spectrum: 780 cm^{-1} (CH_2); 960 cm^{-1} $\gamma(\text{CH})$ *trans*; 1042 cm^{-1} $\nu_s(\text{C}-\text{O}-\text{C})$; $1130, 1205\text{ cm}^{-1}$ $\nu_{as}(\text{C}-\text{O}-\text{C})$; 1300 cm^{-1} $\delta(\text{CH})$; 1390 cm^{-1} $\delta(\text{CH}_2)$; 1650 cm^{-1} $\nu(\text{C}=\text{C})$; 1680 cm^{-1} $\nu(\text{C}=\text{C})$ *trans*; 2226 cm^{-1} $\nu(\text{C}=\text{C}-\text{CN})$; 2582 cm^{-1} $\nu(\text{CH}_2)$; 2910 cm^{-1} $\nu_{as}(\text{CH}_2)$; $3020\text{ cm}^{-1}, 3065\text{ cm}^{-1}$ $\nu(\text{CH}-)$. NMR spectrum: H_a (6); $\delta = 5.55$ p.p.m., $J_{ab} = 15.8$ Hz, $J_{ac} = 2.4$ Hz; H_b (6); $\delta = 6.60$ p.p.m., $J_{bc} = 3.6$ Hz; H_c (4); $\delta = 3.96$ p.p.m.;

1-Methoxy-2-acetyloxy-3-chloropropane

a) 1-Methoxy-2-hydroxy-3-chloropropane (261 g; 2.1 mol) was mixed with 20 ml of acetic anhydride and put under reflux. The remaining anhydride (totally 228 g; 2.24 mol) was then added dropwise at such a rate as would keep the reaction mixture boiling (exothermic reaction). After addition of all anhydride the mixture was refluxed for another 20 minutes and distilled. The fraction boiling above 155°C was collected and redistilled on a column with 50 TP, under chromatographic control. The following fractions were collected: 1. $67-83^\circ\text{C}/13$ Torr (7 g), a mixture of substance *A* and the unreacted hydroxy derivative; 2. $82^\circ\text{C}/13$ Torr, 152.7 g of substance *A*; 3. $81-85^\circ\text{C}/11$ Torr, 30.2 g intermediate fraction; 4. $85^\circ\text{C}/11$ Torr, 26.2 g, substance *B*. Substance *A*: b.p. $82^\circ\text{C}/13$ Torr, $n_D^{20} 1.4325$. For $\text{C}_6\text{H}_{11}\text{ClO}_3$ (166.6) calculated: 43.2% C, 6.66% H, 21.3% Cl; found: 43.09% C, 6.7% H, 21.2% Cl.

Substance *A* gives a positive nitrole reaction to primary halogen, it does not react with sodium iodide in acetone, with ethanolic silver nitrate solution in the cold a white opalescence is formed within five minutes, but on heating on a water bath a precipitate of silver chloride is formed rapidly (test for primary halogen).

Substance *B*: b.p. $85^\circ\text{C}/11$ Torr, $192-193^\circ\text{C}/760$ Torr, $n_D^{20} 1.4341$. Found: 43.09% C, 6% H, 21.3% Cl. Substance *B* when submitted to nitrole reaction gave a green-blue coloration which cannot be extracted with chloroform. It does not react with sodium iodide in acetone. It does not react with cold ethanolic silver nitrate. Only after five minutes' boiling a white opalescence is formed. Hence, the structure of 1-acetyloxy-2-chloro-3-methoxypropane may be assigned to substance *B*, and the structure of 1-methoxy-2-acetyloxy-3-chloropropane to substance *A*. Their IR spectra are in agreement with these structural assignments. Lit.¹⁷ gives for 1-acetyloxy-2-chloro-3-methoxypropane b.p. $196-198^\circ\text{C}$, $n_D^{20} 1.436$, and a positive nitrole reaction.

TABLE I

Relative Amounts of the Isomers Formed on Reaction of 1M Potassium Tert-butoxide with 1M Solution of Chlorobutenonitriles I-IV at Various Mutual Ratios, at 30°C Temperature and Neglect of the Starting Isomer Concentration

Starting nitrile	Relative amount of isomers			
	I	II	III	IV
<i>cis-I</i>	—	2	1	1
<i>trans-II</i>	1	—	1	0
<i>cis-III</i>	1	5	—	0
<i>trans-IV</i>	4	2	1	—

b) A mixture of 11.4 g (0.091 mol) of 1-methoxy-2-hydroxy-3-chloropropane, 8.7 ml (9.34 g, 0.091 mol) of acetic anhydride, and 10.3 ml of pyridine was allowed to stand under cooling with ice for 12 hours, then poured into water and the organic layer separated. The aqueous layer was extracted twice with 20 ml of ether and the combined extracts were washed with 20 ml of 10% hydrochloric acid, then twice with water and dried over magnesium sulfate, filtered and distilled. The liquid obtained had b.p. 78–79°C/9 Torr. Gas chromatography (20% Reoplex 400 on Chromosorb W 80/100 mesh as stationary phase) demonstrated that the product is identical with substance A prepared by the first procedure.

Pyrolysis: 56.8 g of 1-methoxy-2-acetyloxy-3-chloropropane were distilled at normal pressure into a pyrolytic tube 100 cm long and 10 mm in diameter, heated at 400–430°C. After condensation the product obtained was distilled through a 20 cm column (glass Raschig rings). Yield 16 g of a fraction of b.p. below 120°C and 34 g of a fraction with b.p. above 120°C which was recycled for a new pyrolysis. The combined lower boiling fractions (a mixture of 8 substances according to gas chromatography) were distilled on a 50 TP column, but the separation was unsuccessful.

Dimethyl Acetal of 3-Cyanopropanal

Dimethyl acetal of 3-chloropropanal¹⁸ (217.8 g; 1.575 mol) was added slowly under stirring at 100°C to a mixture of 78 g (1.575 mol) of sodium cyanide in 240 ml of diethylene glycol. The mixture was stirred for 2 hours at 100°C, then 6 hours at 120°C, and allowed to stand at room temperature for 12 hours. The separated sodium chloride was filtered off, washed with ethanol (25 ml) and the filtrate distilled. The fraction boiling in the 40°C/25–140°C/23 Torr range was collected and the distillate redistilled on a column (8 TP). The following fractions were obtained: 1. up to 50°C/15 Torr, 20 g (unreacted halogen derivative), 2. 50°C/15–82°C/17 Torr, 8 g (intermediate fraction), 3. 82–100°C/17 Torr, 162 g (79.8%) of product. IR spectrum: 1070 and 1090 cm^{-1} (doublet) $\nu(\text{OCH}_3)$; 1132, 1195 cm^{-1} $\nu_{\text{as}}(\text{OCH}_3)$; 1450 cm^{-1} $\rho(\text{CH}_2)$; 2244 cm^{-1} $\nu(\text{CN})$.

¶ *Elimination:* Distillation with boric acid or phthalic anhydride always gave a mixture of compounds, b.p. 70–90°C/10 Torr, in which the required compounds occurred only in low concentrations. Substances with high retention times (gas chromatography; Table III) prevailed. In the mixture 92 g (0.665 mol) of the acetal were added at once to a suspension of 230 g (1.64 mol) of phosphorus pentoxide in 690 ml of dry* pyridine. After about 3/4 of an hour the phosphorus pentoxide started to agglomerate. The mixture was refluxed for 6 hours. Towards the end stirring was no longer possible. The pyridine solution was poured off and the pyridine distilled off on a bubble-cap column (20 TP) at 100 Torr. After concentration to 70 ml the reaction mixture was distilled and the fraction of b.p. 50°C/30–95°C/10 Torr (for composition see Table III) rectified on a 50 cm column (filled with stainless steel helices). Yield 15.1 g of *cis*-4-methoxy-3-butenonitrile (VII), b.p. 63.5°C/10 Torr and 6.3 g of a mixture of *cis*-VII and *trans*-4-methoxy-3-butenonitrile (VIII). The fraction containing least of the *cis* isomer, b.p. 74°C/10 Torr, contained according to gas chromatography 91% of *trans* VIII. Yield: 44% of *cis* VII, 13% of *trans* VIII, and 43% of unreacted acetal.

* Pyridine (1 l) dried for 10 days over solid sodium hydroxide was poured into 15 g of phosphorus pentoxide and shaken, which brought about an increase in temperature to 40°C. The next day pyridine was poured off into another flask containing 15 g of phosphorus pentoxide, shaken and distilled.

cis-4-Methoxy-3-butenonitrile (VII): b.p. 68.5°C/10 Torr. For C₅H₇NO (97.1) calculated: 61.9% C, 7.06% H, 14.45% N; found: 61.88% C, 7.28% H, 14.59% N. IR spectrum: 740 cm⁻¹ γ (CH *cis*); 1059 cm⁻¹ ν_s (C—O—C); 1120, 1232 cm⁻¹ ν_{as} (C—O—C); 1391 cm⁻¹ δ (CH₃); 1697 cm⁻¹ ν (C=C); 2247 cm⁻¹ ν (CN); 2821 cm⁻¹ ν_{as} (CH₃) in OCH₃; 2852 cm⁻¹ ν_s (CH₂); 2910 cm⁻¹ ν_{as} (CH₂). NMR spectrum: CH₃O—CH=CH—CH₂CN; H_a (4): δ = 2.97 p.p.m., J_{ab} = 6.8 Hz, J_{ac} = 1.5 Hz; H_b (4): δ = 4.31 p.p.m., J_{bc} = 5.5 Hz; H_c (6): δ = 6.46 p.p.m.; H_d (1): δ = 3.60 p.p.m..

trans-4-Methoxy-3-butenonitrile (VIII): NMR spectrum: H_a (4): δ = 2.90 p.p.m., J_{ab} = 6.4 Hz, J_{ac} = 1.4 Hz; H_b (4): δ = 4.60 p.p.m., J_{bc} = 12.8 Hz; H_c (6): δ = 6.46 p.p.m.; H_d (1): δ = 3.48 p.p.m..

Isomerisation

a) The rate of three-carbon atom isomerisation at 0.05M concentration was measured as in the preceding paper^{1,19}. 4-Chlorobutenonitriles were chromatographed on 15% Reoplex 400 (temperature 120°C, pressure of H₂ 0.60 kp/cm², column length 300 cm, carrier Chromosorb W 80/100 mesh), or on 30% poly(diethylene glycol succinate) (temp. 110°C, N₂ pressure 0.40 kp/

TABLE II

Comparison of Rate Constants (l mol⁻¹ s⁻¹) of the Total Decrease of Nitriles, Measured by Gas Chromatography (GLC) at 25°C, and of Potassium tert-Butoxide Decrease, Determined Potentiometrically at 30°C

Nitrile	I	II	III	IV
GLC	4.1	7.3	4.6	6.1
Potentiometry	1.12	—	2.48	—

TABLE III

Relative Ratios of the Products of Elimination Reaction of Dimethyl Acetal of 3-Cyanopropanal with Various Reagents as Determined by Gas Chromatography

Reagent	Amount (%) of products of relative retention time ^a				
	0.38(VII)	0.50(VIII)	1.0 ^b	1.96	2.8
H ₃ BO ₃	1.1	1.0	38.6	55.0	4.3
Phthalic anhydride	7.2	3.5	50.0	39.4	—
P ₂ O ₅	29.0	15.0	56.0	—	—

^a 100 cm 20% Reoplex 400 on Chromosorb W, temperature 145°C, pressure H₂ = 0.25 kp/cm²;

^b starting acetal.

/cm², 1.5 m column length, support Chromosorb W 45/60 mesh). 4-Methoxybutenenitriles were chromatographed on 15% Reoplex 400 (temp. 95°C, pressure of N₂ 0.40 kp/cm², column length 150 cm, support Chromosorb W 80/100 mesh).

b) A solution of nitrile in tert-butyl alcohol was mixed with 1M potassium tert-butoxide (ratios chosen between 1 : 1 to 9 : 1). After a chosen period the reaction was stopped by addition of 20 µl of acetic acid and the mixture analysed by gas chromatography. The area of the peaks was determined by multiplying its height by the half-width and the concentration values were calculated from the calibration curve. Error of the measurement was about ±4%.

Measurement of the Drop in Alkali Content During Isomerisation of *cis*-4-Chloro-3-butenonitrile and *cis*-4-Chloro-2-butenonitrile

To 1 ml of 0.05M nitrile solution in tert-butyl alcohol (at 37°C) 1 ml of 0.05M potassium tert-butoxide solution in tert-butanol was added and in selected time intervals the reaction was stopped by addition of 2 ml of 0.05M-HCl, and its excess was determined by retitration with 0.05M-NaOH. For the measurement "dead stop" titration was made use of. The reference electrode was a calomel electrode, the indicating electrode was an antimony electrode. The equivalence potential was determined experimentally in tert-butyl alcohol and water (1 : 1) : 375 mV. For measurements a pH meter PHM 25 was used to which a Titrator T-11 was connected for "dead stop" titrations. The calibrated solution of potassium hydroxide was added from an automatic burette ABU-1. All this equipment was from the firm Radiometer.

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