

ALKYL AND ARYLPROPENONITRILES*

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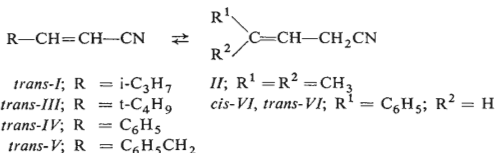
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In an equilibrated mixture of *cis* and *trans* isomers of unsaturated nitriles of the $R-CH=CH-CN$ type $6 \pm 2\%$ of *cis* isomer were found when $R = i-C_3H_7$, when $R = C_6H_5$ the percentage was $15.3 \pm 1\%$ of *cis* isomer, for $R = t-C_4H_9$ it was $1 \pm 0.4\%$ of *cis* isomer, and for $R = C_6H_5-CH_2$ it was 19.9% of *cis* isomer. When the three-carbon isomery of 4-methylpentenenitriles was followed, the equilibrium mixture contained $75 \pm 3\%$ of 4-methyl-3-pentenitriles in addition to 25% of conjugated isomers. From the measurement of the rates and equilibria in base-catalysed isomerization it was inferred that the *cis-trans* isomery takes place simultaneously with the three-carbon isomery by rotation in the delocalised carbanion.

In the preceding paper¹ we found that with increasing volume of the alkyl the amount of the *trans* isomers of conjugated unsaturated nitriles increases in the equilibrium state. For equilibrium of butenenitriles at $30^\circ C$ 99% of α, β -unsaturated isomers was found (of which 58.8% of *cis* isomer), for pentenenitriles the percentage of conjugated unsaturated nitriles was 71% (35.6% of *trans*-2-pentenitrile in addition to 35.4% of the *cis* isomer). Generally the unsaturated nitriles may be classified among compounds with a significant amount of *cis* isomers in equilibrium state, similarly as in the case of 1,2-dichloroethylene², 1-chloro-1-propene³ and unsaturated ethers⁴.

We now extended the study of the three-carbon isomery and *cis-trans* isomery to unsaturated nitriles with branched alkyls. The isomery was followed in the following types of substances:



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In order to enable the study of possible mechanism of isomerization the isomerization of 3-butenitrile with triethylamine was carried out in the presence of tert-butyl alcohol-[1-D].

In three-carbon isomery the splitting off of a proton from the molecule is supposed leading to the formation of carbanions which on protonation give a mixture of isomers. Ingold and coworkers⁵ confirmed this mechanism by studying the isomerization of cyclohexenecarbonitriles under the effect of sodium ethoxide in deuterated ethanol. In view of our finding that the isomerization takes place in the case of 3-butenitrile in tert-butyl alcohol-[1-D] under catalysis with triethylamine without deuterium exchange, it must be supposed that an internal hydrogen shift took place without formation of a free carbanion. This finding is in agreement with the results obtained⁶ for the isomerization under the effect of $\text{ND}(\text{C}_2\text{H}_5)_2$. From the results it follows that the mechanism of the three-carbon isomery may be shifted in dependence on the catalysis and the medium from the mechanism with free carbanion to transition states which have the character of dipoles (Fig. 1).

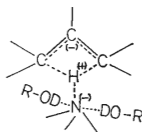
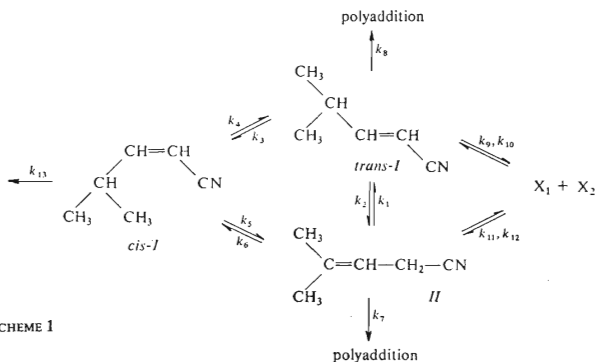


FIG. 1
Three-Carbon Isomery

Another type of mechanism which may occur in media with protic solvents under catalysis with strong bases is the addition-elimination mechanism.

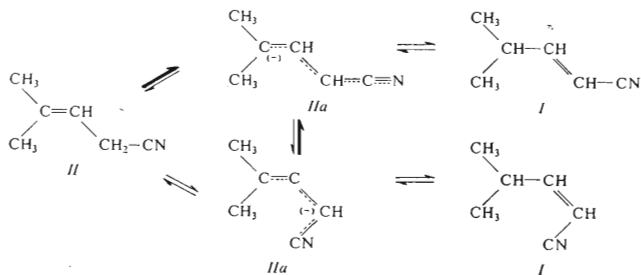
The isomerization of 4-methylpentenenitriles *I* and *II* may be expressed by Scheme 1:



SCHEME 1

The equilibrium mixture contains $6 \pm 2\%$ of isomer *cis-I*, $21 \pm 3\%$ of isomer *trans I*, $75 \pm 3\%$ of isomer *II*. In view of high polymerization rates the equilibrium state cannot be determined starting from isomer *cis-I*. In equilibrium of isomers *cis-I* and *trans-I* the latter isomer prevails ($77 \pm 10\%$) in agreement with the supposition. The isomerization rate of the double bond decreases under identical conditions in the following order: 3-butenitrile > 3-pentenitrile > 4-methyl-3-pentenitrile. This is due to the increasing energies of carbanions which represent intermediary reaction steps (increasing +I and steric effect of alkyls).

According to the ratio of the rate constants $k_1 : k_6 > 20$ the *trans-I* isomer is formed predominantly from the reaction start and we suppose that the carbanion is formed mainly in *trans* configuration *IIa*, as shown in Scheme 2.

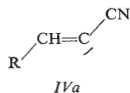
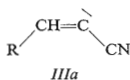


SCHEME 2

In equilibrium of 4-methylpentenenitriles the β,γ -unsaturated nitrile *II* with $\Delta F = -0.7$ kcal/mol prevails significantly (see also Table I). When comparing this value with the difference of heats of formation of analogous hydrocarbons⁷ (ΔH_f^0 of 2-methyl-2-pentene is 15.98 kcal/mol and of *trans*-4-methyl-2-pentene 14.69 kcal/mol), then — because the value $\Delta\Delta S$ is small — the experimental value of the delocalization energy in this series of compounds is close to the value 0.6 kcal/mol. This data agrees with the conclusion, inferred from calorimetric measurements⁸, that the delocalization energy for the system $C=C-CN$ is not constant but depends significantly on the character of substitution not only when the substituents contain hetero atoms, but in the case of alkyls as well. The mentioned value 0.6 kcal/mol may be affected by the difference of non-bonding interaction $H-CN$ and $H-CH_3$.

Neither *cis-III* and *trans-III*, nor *cis-IV* and *trans-3-phenylpropenenitrile* (*trans IV*) could be isomerized under analogous conditions (*i.e.* potassium tert-butoxide in tert-butyl alcohol), but the isomerization could be carried out under the effect of iodine (Table II and III). From this we may deduce that in this case — and probably

in the case of other unsaturated nitriles either — *cis-trans* isomerization does not take place *via* the vinyl carbanions *IIIa* and *IVa*



which are not significantly delocalized and therefore have appreciable energy, but it takes place simultaneously with the three-carbon isomerization by the rotation in the

TABLE I

Equilibrium Constants and Free Energy Changes During Isomerizations of 4-Methylpentenenitriles at 30°C

Isomers	<i>II/trans-I</i>	<i>trans-I/cis-I</i>	<i>II/cis-I</i>
Ratio of equilibrium concentrations	2.8 — 3.5	2.4 — 3.5	12
— ΔF (kcal/mol)	0.62—0.76	0.53—0.76	1.7

TABLE II

Rate Constants of the Isomerization of 4-Methylpentenenitriles at 30°C ($k \cdot 10^{-4} \text{ min}^{-1}$)

k_1	8.2	k_4	2.2	k_7	35.6
k_2	52.7	k_5	4.5	k_8	20
k_3	1.6	k_6	— ^a	k_{9-12}	0.5

^a The constant cannot be determined due to the low equilibrium concentration of isomer *I*.

TABLE III

Equilibrium Concentrations of 4,4-Dimethylpentenenitriles and 3-Phenylpropenenitriles After Isomerization with Iodine

Compound	Temperature, °C	% <i>cis</i>	% <i>trans</i>
$(\text{CH}_3)_3\text{C}-\text{CH}=\text{CH}-\text{CN}$	130	1 ± 0.4	99 ± 0.4
$\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{CN}$	200	19.7	80.3

delocalized carbanion. This phenomenon (*i.e.* the situation when a carbanion cannot be formed and isomerization does not take place) was observed even during the racemization of optically active mandelic acid⁹.

The described isomerization of 3-phenylpropenenitrile¹⁰ (without data on the equilibrium in ethanol-[1-D]) under catalysis with sodium ethoxide therefore takes place by the addition-elimination mechanism. This conclusion was corroborated by the identification of the addition products, *i.e.* $C_6H_5-CH(OC_2H_5) \cdot CH_2COOC_2H_5$, in the case of analogous esters. On distillation of the mixture containing the addition product with sodium ethoxide the addition product disappeared completely which confirms the reversibility of this reaction and its participation in isomerization. Another support for the explanation by addition-elimination mechanism may be found in the fact that simultaneously with isomerization a substitution of the hydrogen atom on the double bond by deuterium¹⁰ takes place in 3-phenylpropenenitrile.

The *cis-IV* and *trans-IV* equilibrium was determined earlier¹¹ by thermal isomerization at 324°C; in equilibrium state 37% of *cis-IV* were found and the equilibrium composition changed only negligibly with temperature. The approximate agreement of the equilibria of *cis* and *trans* isomers of phenylpropenenitrile found in this paper (see Tables III and IV) and of 4-methylpentenenitriles (21% *cis-I*) corresponds to the similar sterical requirements of the phenyl and the isopropyl group. For the determination of equilibrium constants of dimethylpentenenitriles and phenylpropenenitriles isomerization with iodine was carried out, the results of which are given in Table III.

The paper¹² describes the isomerization of dimethylpentene nitriles with approximately the same results.

In the isomerization of 3-phenylpropenenitriles with iodine we observed the formation of another product of molecular weight 131 (3-phenylpropenenitriles have m.w. 129) which may be explained by the reduction of the double bond with hydrogen iodide formed on dehydrogenation of nitrile, which leads simultaneously to polymerization.

Isomerization of 4,4-dimethylpentenenitriles was carried out at a temperature close to their boiling points. The equilibrium is strongly shifted to the advantage of the *trans* isomer (Table III) as was already evident from the large percentual content of the *trans* derivative during the synthesis.

Isomerizations with iodine are carried out at different temperatures than those at which the isomerizations of other substances were done and therefore in the case of 3-phenylpropenenitriles the isomerization with sodium methoxide was also carried out in order to determine the equilibrium constant at low temperature (Table IV).

The formation of the addition product is indicated by the fact that already after 4 hours of isomerization of *cis-IV* at 20°C (when the concentration of *trans-IV* just began to be detectable in the mixture) its content decreased to 85% of the original quantity.

From Table IV it follows that the reactivities of *cis-IV* and *trans-IV* differ appreciably; the difference may be explained by the stereospecificity of the alcoholate addition during which the steric hindrance of the conjugation also may manifest itself. It was found on the basis of NMR spectra that in *cis-IV* the π -electrons of the phenyl nucleus are not in the plane of the π -electrons of the double bond which is then manifested by splitting of the aromatic hydrogens singlet (in *trans* isomer) to a doublet (in *cis* isomer), as shown on Fig. 2.

In attempts at isomerization of *trans*-4-phenyl-3-butenonitrile (*trans-VI*) under the effect of potassium tert-butoxide polymerization took place so rapidly that it was impossible to measure either the rate or the equilibrium constants of isomerization. Only for the confirmation of the equilibrium constant given in the literature¹³ we undertook the isomerization of *trans-VI* with triethylamine in tert-butyl alcohol at 23°C:

Conditions	<i>cis-V</i>	<i>trans-V</i>	<i>cis-VI</i>	<i>trans-VI</i>
23°C, catalyst N(C ₂ H ₅) ₃	20.6	19.8	5.5	54.2
150°C, thermal ¹³	18	18	3.2	60.8

In equilibrium the β,γ -unsaturated isomer prevails which shows that the system with a double bond conjugated with the benzene nucleus is more stable.

Preparation of Compounds

The preparation of 4,4-dimethylpentenenitrile was carried out both by reaction of 2,2-dimethylpropanol with cyanoacetic acid and with cyanomethyltriphenylphosphonium ylide according to literature analogies. The ylide was prepared in

TABLE IV
Isomerization of Phenylpropenenitriles with Sodium Methoxide at 30°C

Starting isomer	Products	Relative content (h)			
		0	9	24	50
<i>cis-IV</i>	<i>cis-IV</i>	100	32.0 ± 0.3	23.3 ± 0.5	15.5 ± 0.9
	<i>trans-IV</i>	0	68.0 ± 0.2	76.7 ± 0.5	84.5 ± 1.0
<i>trans-IV</i>	<i>cis-IV</i>	0	9.2	11.2 ± 0.3	15.2 ± 0.3
	<i>trans-IV</i>	100	90.9	88.8 ± 0.3	84.8 ± 0.8

TABLE V

Composition of the Mixtures (%) of 4-Phenylbutenenitriles Obtained by Various Methods

Method	<i>cis-V</i>	<i>trans-V</i>	<i>cis-VI</i>	<i>trans-VI</i>
<i>A</i>	15.6	20.7	6.8	56.9
<i>B</i>	22.1	41.7	2.7	33.5
<i>C</i>	23.4	16.7	7.3	52.7
<i>D</i> ₁ ^a	3.6	4.4	0.5	91.5
<i>E</i>	25.2	13.4	5.0	56.4
Equilibrium mixture	20.6	19.9	5.5	54.2

^a Product after crystallisation.

non-aqueous medium¹⁴ because when prepared in aqueous medium¹⁵ triphenylphosphine oxide is formed instead of the required ylide. It was observed during the isolation of the ylide from the mixture with the salt that its solubility increased highly in the presence of cyclic trioxans (trimers of aldehydes).

During the preparation of phenylbutenenitriles the nitrile of 4-phenyl-2-hydroxybutanoic acid, necessary as an intermediate, was prepared by reacting 3-phenyl-

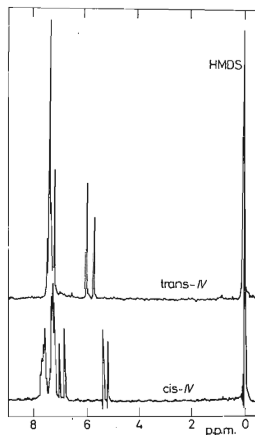


FIG. 2
NMR Spectra of *cis*- and *trans*-Phenyl-propenenitrile (*IV*) at 60 Mc/s

propanal with liquid hydrogen cyanide; however, we were able to isolate from the reaction mixture only a small amount of nitrile. The reaction of the bisulfite compound of phenylpropanal with sodium cyanide is more suitable. Under the effect of thionyl chloride and pyridine on cyanohydrin 4-phenyl-2-chlorobutanenitrile is formed the dehydrohalogenation of which could be carried out only with boiling quinoline under formation of all four unsaturated phenylbutenenitriles. In a similar manner all four isomers are formed from *trans*-cinnamyl chloride under the effect of cuprous cyanide or sodium cyanide and also on reaction of phenylacetaldehyde with cyanoacetic acid or with cyanomethyltriphenylphosphonium ylide (Table V). Fractional distillation on a column gave only *cis*-4-phenyl-2-butenenitrile in pure state. In view of the isomerization taking place the same result was also obtained by preparative gas chromatography. Only when selective bromine addition (in analogy to¹) and subsequent distillation was applied the mixture of α,β -unsaturated isomers was separated, which were identified by NMR spectra; the mixture was then used for the evaluation of gas chromatography.

EXPERIMENTAL

The melting points (Boetius) and boiling points are not corrected. The IR spectra were measured with a UR-10 Zeiss Jena spectrophotometer. Liquid substances were measured as liquids and solid substances in potassium bromide pellets. The NMR spectra of 3-phenylproponitriles were measured on a JNM-3-60 (Jeol, Tokyo) apparatus at 60 Mc/s frequency in tetrachloromethane (0.5M concentration). The spectra of other substances were measured on a Varian apparatus at 100 Mc/s. The *cis*- and *trans*-4-methylpentenenitriles (*I*) and 4-methyl-3-pentenenitrile (*II*) were prepared according to¹⁶.

cis- and *trans*-4,4-Dimethylpentenenitrile (*III*)

A) A mixture of 4.9 g (57 mmol) of 2,2-dimethylpropanal, 4.9 g (57.5 mmol) of cyanoacetic acid, 15 ml of pyridine, and 0.6 ml of piperidine was refluxed for 14 days, then diluted with 50 ml of ether and the ethereal layer extracted with water, 5% hydrochloric acid and again with water. After drying over magnesium sulfate and distillation 1.4 g (22.3%) of a mixture of nitriles was obtained, b.p. 125–134°C. This mixture was further separated by preparative gas chromatography on a 3 m column packed with 15% Reoplex 400 on Chromosorb W. The boiling point of the *cis*-isomer *III* was 146°C/760 Torr, of the *trans*-isomer *III* 128°C/100 Torr. The isomers were isolated in an approximate 1 : 30 ratio.

B) To a solution of 26.8 g (79.3 mmol) of cyanomethyltriphenylphosphonium chloride (prepared according to¹⁴) in 550 ml of water 54 ml of 5% sodium hydroxide in water was added dropwise, giving immediately a precipitate. The mixture was stirred for one hour and the precipitate filtered off, washed three times with 50 ml of water and dried in air; m.p. 130–155°C. After crystallization from 45 ml of benzene and 5 ml of hexane 10 g (45.3%) of crystals were obtained, m.p. 155–158°C (at 130°C the substance begins to sublime). A sample of the substance was sublimated *in vacuo* for analysis, m.p. 156–159°C. For C₁₈H₁₅OP (278.3) calculated: 77.68% C, 5.43% H, 11.13% P; found: 77.02% C, 5.65% H, 10.79% P.

C) To a solution of 1.15 g (50 mmol) of sodium in 20 ml of ethanol a solution of 17.5 g (51.9 mmol) of triphenylcyanomethylphosphonium chloride in 75 ml of ethanol was added under argon with stirring. The precipitate formed was filtered off after 30 min stirring, washed with ether and dried. Extraction with 200 ml of hot benzene gave 1.7 g of ylide of m.p. 194–196°C.

in agreement with literature¹⁷. All work with ylides was carried out in the presence of salt, *i.e.* as isolated during the preparation. In order to secure an excess of aldehyde during the reaction the mixture of ylide and the salt was considered as pure ylide in stoichiometric calculations. To a suspension of 12 g of ylide with salt in 20 ml of benzene 3.44 g (40 mmol) of 2,2-dimethylpropanal was added under argon and exclusion of moisture and the mixture refluxed (under argon) for 12 hours. The precipitate was filtered off and washed with ether. Distillation of the solution gave fraction 1 of m.p. 162°C (mixture of isomeric nitriles with 10% of solvent); fraction 2 of b.p. 127°C/100 Torr (mixture of 5% *cis* isomer *III* and 95% of *trans* isomer *III*). Both fractions were combined and separated to pure substances by preparative gas chromatography. Total yield 2.9 g (86% per ylide present in the mixture with salt). *cis-III*: NMR spectrum: δ 6.35 p.p.m. (d) =CH—CN; 5.22 p.p.m. (d) —CH=C—CN; 1.25 p.p.m. (s) CH₃; $J_{\text{CH}=\text{CH}} = 12.0$ Hz. *trans-III*: For C₇H₁₁N (109.2) calculated: 77.01% C, 10.16% H, 12.83% N; found: 76.65% C, 10.49% H, 12.0% N. NMR spectrum: δ 6.72 p.p.m. (d) =CH—CN; 5.235 p.p.m. (d) —CH=C—CN; 1.075 p.p.m. (s) CH₃; $J_{\text{CH}=\text{CH}} = 16$ Hz.

cis- and *trans*-3-Phenylacrylonitrile (*IV*)

They were prepared by a modified literature procedure¹¹. A mixture of cyanoacetic acid, pyridine with piperidine and benzaldehyde was allowed to react spontaneously and when the exothermic reaction ceased the mixture was heated at 110°C for 5 days under addition of powdered copper and then at 140°C for 10 days. After cooling it was diluted with 500 ml of ether, extracted with water, 5% sulfuric acid and water; after drying over magnesium sulfate the solution was distilled. Yield 96 g of crude product of b.p. 120–150°C/15 Torr. Distillation on a 50 cm long column, internal diameter 18 mm, filling stainless-steel loops (Labora, Prague), gave 23.4 g of *cis* isomer *VI*, b.p. 119°C/12 Torr, $n_D^{20.2} = 1.5827$, and 20.5 g of *trans* derivative, b.p. 135°C/15 Torr, $n_D^{20.2} = 1.6025$.

cis-IV: For C₉H₇N (129.15) calculated: 83.69% C, 5.46% H, 10.85% N; found: 83.36% C, 5.62% H, 11.01% N. IR spectrum: 691, 782 cm⁻¹ γ (CH) in C₆H₅; 800 cm⁻¹ (inflexion) γ (—CH) *cis*; 1619 cm⁻¹ ν (C=C); 2215 cm⁻¹ ν (C=C—CN); 3025, 3060 cm⁻¹ ν (=CH—). NMR spectrum is given on Fig. 2.

trans-IV: For C₉H₇N (129.15) found: 83.55% C, 5.60% N, 10.93% H. IR spectrum: 691, 751 cm⁻¹ γ (CH) in C₆H₅; 971 cm⁻¹ γ (CH) *trans*; 1500 cm⁻¹ ν (C=C—C₆H₅) 1625 cm⁻¹ ν (C=C); 2219 cm⁻¹ ν (C=C—CN); 3025, 3052 cm⁻¹ ν (=CH—). The NMR spectrum is given in Fig. 2.

Diethyl Acetal of 3-Phenylpropanal

A solution of 144 g (0.70 mmol) of diethyl acetal of cinnamaldehyde¹⁸ in 250 ml of methanol was hydrogenated on 20 g of Raney nickel. When the hydrogen absorption ceased the catalyst was filtered off and the filtrate distilled. The distillate was dissolved in 200 ml of methanol and the solution hydrogenated at atmospheric pressure on 10 g of 5% Pd on BaSO₄ to the end of hydrogen absorption (consumption rate 1 litre/10 minutes). Distillation gave 122 g of substance (84%) of b.p. 112–118°C/8 Torr. For C₁₃H₂₀O₂ (208.3) calculated: 74.96% C, 9.68% H; found: 74.92% C, 9.74% H.

3-Phenylpropanal

289 g (1.386 mol) of diethyl acetal of 3-phenylpropanal were refluxed with 300 ml of 10% sulfuric acid for 30 minutes. The mixture was distilled until the temperature of the vapours was 95°C and

oil droplets began to appear in the condenser. The distillation was interrupted and the oil remaining in the flask was cooled and extracted with three 100 ml portions of benzene. After drying with magnesium sulfate and distillation 122 g of substance, b.p. 90–100°C/8 Torr. Literature¹⁹ gives b.p. 115–120°C in a vacuum.

Nitrile of 2-Hydroxy-4-phenylbutanoic Acid

A) A mixture of 133 g (0.995 mol) of 3-phenylpropanal, 60 ml (1.5 mol) of liquid hydrogen cyanide, and 5 g of sodium cyanide was allowed to stand at 0°C (cooling with ice) for 4 hours and one hour at room temperature. After strong acidification with hydrochloric acid it was diluted with 200 ml of benzene. The solution obtained was filtered and benzene distilled off in a vacuum. A small sample of the distillation residue was distilled at initial pressure of 0.1 Torr. As the substance decomposed on distillation, the bulk of the substance was added with 30 ml of conc. hydrochloric acid and after 30 minutes the mixture was diluted with 200 ml of chloroform. After addition of charcoal the solution was filtered and evaporated. The residue was triturated with 300 ml of benzene and the insoluble substance filtered off and washed with benzene. Yield 15.5 g of substance, m.p. 128–133°C. Crystallization from benzene and from water gave 6 g of substance, m.p. 132.8–133.5°C. Literature²⁰ gives for 4-phenyl-2-hydroxybutanoic acid amide m.p. 130°C. The benzene solution after filtration was concentrated, but during an attempt at its distillation it decomposed again; found 13.27% N. The high content of nitrogen proves the presence of polymerized hydrogen cyanide.

B) Sodium salt of 1-hydroxy-3-phenylpropanesulfonic acid. A mixture of 37.8 g (0.282 mol) of 3-phenylpropanal and 70 ml of a saturated sodium pyrosulfite solution in water was shaken for 20 minutes and then allowed to stand overnight. The precipitate formed was filtered off, washed three times with ethanol, dried in air, and triturated again with 200 ml of ethanol, filtered off and dried. Yield 32.7 g (52.5%).

To a suspension of 9.5 g (42.7 mmol) of the bisulphite addition product of phenylpropanal in 20 ml of water a solution of 2.1 g (42.7 mmol) of sodium cyanide in 6 ml of water was added and the mixture shaken. After addition of 3 ml of ether the mixture was shaken for another 5 minutes. The ether layer was separated and the lower phase extracted three times with ether. The combined ethereal extracts were dried over magnesium sulfate and ether distilled off. The residue was stabilised with a drop of 80% phosphoric acid. Yield 5.4 g (78.5%) of an oil. For $C_{10}H_{11}NO$ (161.2) calculated: 8.69% N; found: 8.72% N. After evaporation of the solvents the product was used directly for further reaction²¹.

Nitrile of 4-Phenyl-2-chlorobutanoic Acid

A mixture of 2.6 g (16.1 mmol) of 3-phenylpropanal cyanohydrin, 15 ml (24.8 g; 0.208 mol) of thionyl chloride, and 0.5 ml of pyridine was refluxed for one hour. Excess thionyl chloride was distilled off and the residue added with 30 ml of pyridine, and the mixture refluxed for one hour and allowed to stand overnight. It was poured into water and the aqueous emulsion extracted 5 times with ether. The ethereal solution was extracted twice with water; the insoluble substance was filtered using a fritted filter S3. The ethereal layer was washed twice with hydrochloric acid and water, dried over magnesium sulfate and distilled. Fraction boiling at 108°C/2 Torr was collected, yield 1.25 g (43.2%). Control by gas chromatography (5% of trinitrofluorenone on porovina, 220°C, 0.2 kp/cm² of hydrogen) did not detect any admixtures. For $C_{10}H_{10}ClN$ (179.65) calculated: 66.85% C, 5.61% H, 7.80% N; found: 67.51% C, 5.90% H, 7.40% N. IR spectrum: 705 cm⁻¹ ν (CH) arom., 2245 cm⁻¹ ν (CN) (the band has a three times lower intensity

than the band at 2859 cm^{-1} , $2859\text{ cm}^{-1}\nu(\text{CH}_2)_s$, $2940\text{ cm}^{-1}\nu(\text{CH}_2)_{as}$, 3022 , 3060 , $3080\text{ cm}^{-1}\nu(\text{CH})\text{ arom.}$

Mixtures of 4-Phenylbutenenitriles *Va* and *VI*

A) A mixture of 2.4 g (13.4 mmol) of 4-phenyl-2-chlorobutanoic acid nitrile and 10 ml of quinoline was heated at 200°C for 60 minutes and at 150°C for 20 minutes and then poured into water, acidified with 30 ml of 4M-HCl (pH = 1) and extracted five times with 20 ml of ether. The ethereal extracts were washed with 10 ml of 4M-HCl, 10 ml of water, and 10 ml of saturated sodium hydrogen carbonate, and eventually twice with 10 ml of water. After drying over magnesium sulfate and distillation 1.1 g (57.2%) of a liquid of b.p. $63-71^\circ\text{C}/0.4\text{ Torr}$ was obtained which according to IR spectrophotometry contains compounds with conjugated and non-conjugated nitrile group in a 1 : 1 ratio. The composition of the mixture as determined by gas chromatography is given in Table V.

B) A mixture of 3.5 g (29.1 mmol) of phenylacetaldehyde, 20 ml of benzene, and 8.7 g (28.9 mmol) of cyanomethyltriphenylphosphonium ylide (free of salt) was heated at 60°C under argon for 8 hours. The next day the precipitated material was filtered off, washed three times with benzene, twice with ether, and the solution obtained was distilled. Yield 1.85 g, b.p. $56-83^\circ\text{C}/3\text{ Torr}$. According to gas chromatography the product is a mixture of isomers in the ratio given in Table V.

The used ylide was regenerated in a salt-free form in an experiment where a mixture of ylide with sodium chloride and phenylacetaldehyde was used, which polymerized on standing to 2,4,6-triphenyl-1,3,5-trioxan. The ylide in admixture with salt is less soluble (0.8 g/100 ml of benzene), pure ylide is well soluble (1.4 g of ylide in 25 ml of boiling benzene or 2.6 g of ylide in 10 ml of boiling chloroform). The IR spectrum of the regenerated ylide is identical with the IR spectrum of the ylide obtained by extraction of the mixture with salt with benzene. M.p. 192 to 195°C . After prolonged standing of the preparation in air it is converted to a substance with m.p. $155.5-157^\circ\text{C}$ (triphenylphosphine oxide should have m.p. $156-159^\circ\text{C}$) under simultaneous decrease of the percentual amount of other elements. For $\text{C}_{20}\text{H}_{16}\text{NP}$ (301.3) calculated: 79.72% C, 5.35% H, 4.65% N, 10.28% P; found: 79.18% C, 5.81% H, 5.04% N, 9.84% P.

C) Reaction of phenylacetaldehyde with cyanoacetic acid. The reaction was carried out as the reaction with dimethylpropanal. Yield 49.5% of a mixture of isomers of b.p. $50-80^\circ\text{C}/4\text{ Torr}$. The composition is given in Table V.

trans-4-Phenyl-3-butenitrile (*VI*)

D₁) A mixture of 45 g (295 mmol) of *trans*-cinnamyl chloride²², 30 g of cuprous cyanide, and 50 ml of benzene was refluxed under stirring for 8 hours. After distillation the yield was 7.9 g (19%), b.p. $100^\circ\text{C}/0.1\text{ Torr}$, and m.p. after crystallization from hexane was $59-60.5^\circ\text{C}$. Literature²³ gives m.p. $61-62^\circ\text{C}$. The purity of the product is given in Table V.

D₂) To a solution of 4.9 g (0.1 mol) of sodium cyanide in 25 ml of diethylene glycol 15.3 g (0.1 mol) of *trans*-cinnamyl chloride were added at 95°C . After one hour standing the reaction mixture was cooled and poured into ice. The separated material was filtered off and washed with water. Yield 18 g of a hygroscopic, low-melting, substance which was repeatedly washed and distilled. Yield 8.7 g (61%) of a substance which solidified on cooling. After crystallization from hexane m.p. was $59-60^\circ\text{C}$.

cis-3-Phenyl-2-propen-1-ol

The substance was prepared by catalytic hydrogenation of 3-phenyl-2-propin-1-ol²⁴ on 5% Pd/BaSO₄. Yield 90%, b.p. 129°C/14 Torr, $n_D^{20} = 1.5708$, $n_D^{22} = 1.5705$. Literature²⁴ gives $n_D^{22} = 1.5728$, b.p. 127–128°C/10 Torr. According to gas chromatography the substance does not contain the *trans* isomer.

cis-1-Phenyl-3-chloro-1-propene

It was prepared on reaction of *cis*-1-phenyl-1-propen-3-ol with phosphorus trichloride in pyridine according to literature²⁴. Yield 71%, $n_D^{20.5} = 1.5748$. Literature²⁴ gives $n_D^{25} = 1.5756$. Gas chromatography on a column packed with silicone elastomer SE-30 showed that the product was a mixture of *cis*- and *trans*-cinnamyl chloride. The separation of these isomers by column distillation was unsuccessful.

Reaction of a Mixture of *cis* and *trans*-1-Phenyl-3-chloro-1-propene with Sodium Cyanide

The reaction was carried out analogously as the preparation of *trans*-VI by procedure D₂. Gas chromatography indicated that the product was a mixture of all isomers in a ratio given in Table V. (E). Two experiments were carried out to separate the mixture prepared from the *trans*-isomer, a) preparative gas chromatography (300 cm, 7% Reoplex 400 on porovina, $t = 225^\circ\text{C}$, pressure 1.2 kp/cm²); b) distillation on a column. Both methods gave only *cis*-4-phenyl-2-butenonitrile in pure state. Other isomers were always obtained in mixtures. For the identification of the remaining two peaks (except for *trans*-VI and *cis*-V) in gas chromatogram a mixture of α,β -unsaturated derivatives was prepared by addition of bromine to a mixture of all four isomers (in analogy to¹): To a solution of 3.0 g of a mixture of nitriles in 10 ml of tetrachloromethane a 5% solution of bromine in tetrachloromethane was added until the orange colour persisted for at least five minutes. The mixture was then washed with a sodium sulfite solution, three times with water, dried over magnesium sulfate and distilled (bath temperature 130°C). Yield 0.25 g of a fraction of b.p. 50–58°C/0.4 Torr. The substances in this mixture were identified by NMR spectrometry as a mixture of *cis*-V and *trans*-V. The physical constants of the isomers *cis*-V and *trans*-VI, which were prepared in pure state, and the NMR spectra of all isomers correspond to the data from the literature¹³.

Isomerization

The rate of the three-carbon isomerization was measured by the same method as in the preceding paper¹. The conditions for gas chromatographic control of the isomerization are the following. Carrier gas nitrogen, gas chromatograph Chrom II of Laboratorní přístroje, Prague, FID, support Chromosorb W 80/100 mesh, glass columns of 150 cm length, internal diameter 4 mm.

Isomerization of nitriles with iodine: A mixture of 1 ml of nitrile and 0.01 g of iodine was heated at $200 \pm 1^\circ\text{C}$. At selected time intervals samples were withdrawn from the reaction mixture and analysed by gas chromatography.

Isomerization of 3-phenylpropenenitriles with sodium methoxide: To a 0.5M solution of nitrile (0.5 ml) 12 μl of 4M-CH₃ONa in methanol were added with a micro-doser. The mixture was heated at $30 \pm 0.3^\circ\text{C}$ and the isomerization was stopped at chosen time intervals by addition of 4 μl of acetic acid and the mixture analysed by gas chromatography using an electronic integrator. The calibration curves for *cis* and *trans* cinnamonitrile were identical.

Isomers	Stationary phase	t , °C	p , kp/cm ²
Butenonitriles	10% dinonyl phthalate	95	0.34
4-Methylpentenonitriles	30% polydiethylene glycol succinate ^a	87	0.20
4,4-Dimethylpentenonitriles	15% Reoplex 400	90	0.30
3-Phenylpropenonitriles	15% Reoplex 400	155	0.29
4-Phenylbutenonitriles	5% Reoplex 400 ^{b,c}	210	0.85

^a Carrier Chromosorb W 45/60 mesh; ^b carrier porovina 0.25—0.31 mm; ^c glass column, 300 cm long, i.d. 6 mm.

Reaction of 3-propenenitrile with triethylamine in tert-butyl alcohol-[1-D]. A solution of 4.1 g of 3-propenenitrile in 1.2 g of 2-deuterioxy-2-methylpropane^{25,26} and 0.35 g of triethylamine was refluxed for 135 minutes (20% of *trans*-2-butenonitrile were formed) and the mixture allowed to stand overnight. The mixture obtained (composition 80% of *cis*-2-butenonitrile, 19% of *trans*-2-butenonitrile, and 1% of 3-propenenitrile) was submitted to preparative gas chromatography (product of Development Workshops of the Czechoslovak Academy of Sciences, Prague) on a 3 m column with dinonyl phthalate ($t = 95^\circ\text{C}$, pressure of $\text{N}_2 = 1 \text{ kp/cm}^2$). Control by NMR spectra showed that the isolated substances do not contain deuterium.

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