

PROCESS FOR THE ISOMERIZATION OF 2-METHYL-3-
BUTENENITRILE

The present invention relates to a process for the isomerization of 2-methyl-3-butenenitrile into
5 linear pentenenitrile, in particular into 3-pentenenitrile.

During the hydrocyanation of butadiene, in the presence of a nickel-based catalyst and a catalyst consisting of an aryl phosphite, as described in US
10 Patent 3,496,215, along with 3-pentenenitrile which is the target compound, a large amount of 2-methyl-3-butenenitrile is formed.

The latter compound cannot be used directly for the preparation of adiponitrile, one of the basic
15 compounds for the preparation of nylon 66.

However, the amounts of this by-product are so large, bearing in mind the heavy tonnages of adiponitrile produced, that it is unthinkable to destroy them.

20 Also, it has long been sought to isomerize 2-methyl-3-butenenitrile into 3-pentenenitrile, an adiponitrile intermediate.

Thus, it has been proposed in US Patent 3,536,748 to convert 2-methyl-3-butenenitrile into
25 linear pentenenitrile, by placing it in contact with a nickel-based catalyst of oxidation state 0, such as a tetrakis(alkyl or aryl phosphite)nickel, at a

temperature of 10 to 200°C.

When the results obtained with this isomerization process are studied, it is observed that the percentage of linear pentenenitrile obtained is very low, generally from 0.4% to approximately 14% according to the examples of the patent, even though the reaction lasts for several hours.

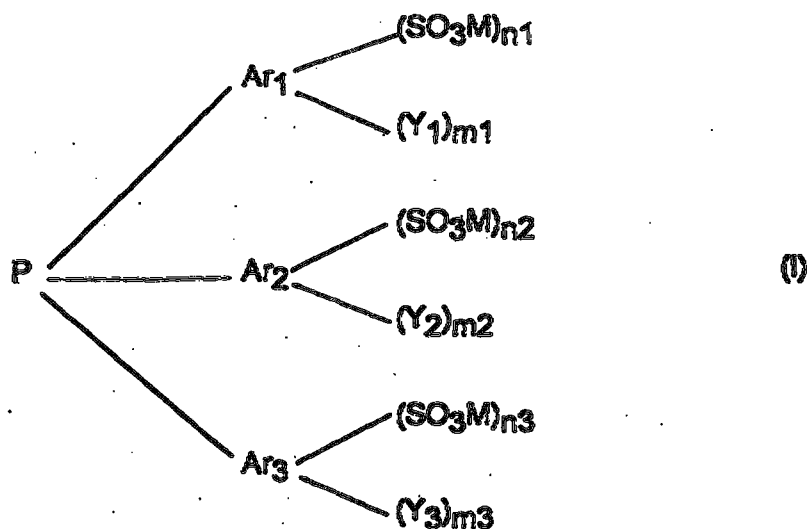
US Patent 3,676,481 describes an improvement of the above isomerization process, by the use of a promoter for the nickel catalyst, consisting either of a boron derivative or of a salt of a metal belonging to groups Ib, IIb, IIIa, IIIb, IVa, IVb, Vb, VIb, VIIb and VIII, in particular the halides of these metals. As above, the reaction takes place in a homogeneous organic phase, which makes the separation of the reaction products and the catalyst difficult, within the context of the - recycling - which is always desirable of the catalyst.

The present invention provides a simple and practical solution to the isomerization of 2-methyl-3-butenitrile into linear pentenenitrile and more particularly into 3-pentenenitrile.

More precisely, it consists of a process for the isomerization of 2-methyl-3-butenitrile into a linear pentenenitrile, characterized in that the reaction is carried out in the presence of an aqueous solution:

- of at least one sulphonated phosphine of

general formula (I)



in which:

- * Ar_1 , Ar_2 and Ar_3 , which may be identical or different, represent aryl groups
- * Y_1 , Y_2 and Y_3 , which may be identical or different, represent

- . an alkyl radical having 1 to 4 carbon atoms,

- . an alkoxy radical having 1 to 4 carbon atoms,

- . a halogen atom,

- . a CN radical,

- . an NO_2 radical

- . an OH radical,

- . a radical NR_1R_2 , in which formula R_1 and R_2 , which may be identical or different, represent an alkyl radical having 1 to 4 carbon atoms,

* M is an inorganic or organic cationic residue chosen, so that the compound of formula (I) is water-soluble, from the group comprising:

5

. H^+ ,

. cations derived from alkali metals or alkaline-earth metals,

. $N(R_3R_4R_5R_6)^+$ with R_3 , R_4 , R_5 and R_6 , which may be identical or different,

10

representing an alkyl radical having 1 to 4 carbon atoms or a hydrogen atom,

. other cations derived from metals for which the benzenesulphonic acid salts are water-soluble,

15

* m_1 , m_2 and m_3 are integers, which may be identical or different, from 0 to 5,

* n_1 , n_2 and n_3 are integers, which may be identical or different, from 0 to 3,

at least one among these being equal to or greater than 1

20

- and of at least one transition metal compound.

As examples of metals for which the benzenesulphonic acid salts are water-soluble, there may be mentioned lead, zinc and tin.

25

The expression water-soluble is understood, in the present text, to refer to a compound which has a solubility of at least 0.01 g per litre of water.

Among the phosphines of formula (I), those are preferred for which:

- Ar_1 , Ar_2 and Ar_3 are phenyl groups,
- X_1 , X_2 and X_3 represent groups chosen from
 - . alkyl radicals having from 1 to 2 carbon atoms,
 - . alkoxy radicals having from 1 to 2 carbon atoms,
- M represents a cation chosen from the group comprising
 - . H^+
 - . cations derived from Na, K, Ca and Ba
 - . NH_4^+
 - . tetramethylammonium, tetraethylammonium, tetrapropylammonium and tetrabutylammonium cations
- n_1 , n_2 and n_3 are integers from 0 to 3
- n_1 , n_2 and n_3 are integers from 0 to 3, at least one also being greater than 1.

Among these phosphines, the sodium, potassium, calcium, barium, ammonium, tetramethylammonium and tetraethylammonium salts of mono(sulphophenyl)diphenylphosphine, di(sulphophenyl)phenylphosphine and tri(sulphophenyl)phosphine, in the formulae in which the SO_3 groups are preferably in the meta-position, are more particularly preferred.

As other examples of phosphines of formula (I) which may be used according to the process of the

invention, there may be mentioned alkali metal or alkaline-earth metal salts, ammonium salts, quaternary ammonium salts of (3-sulpho-4-methylphenyl)di(4-methylphenyl)phosphine; (3-sulpho-4-methoxyphenyl)-
 5 di(4-methoxyphenyl)phosphine; (3-sulpho-4-chlorophenyl)-di(4-chlorophenyl)phosphine; di(3-sulphophenyl)phenylphosphine; di(4-sulphophenyl)-phenylphosphine; di(3-sulpho-4-methylphenyl)(4-methylphenyl)phosphine; di(3-sulpho-4-methoxyphenyl)
 10 (4-methoxyphenyl)phosphine; di(3-sulpho-4-chlorophenyl)(4-chlorophenyl)phosphine; tri(3-sulphophenyl)-phosphine; tri(4-sulphophenyl)phosphine; (tri(3-sulpho-4-methylphenyl)phosphine; tri(3-sulpho-4-methoxyphenyl)phosphine; tri(3-sulpho-4-chlorophenyl)phosphine; (2-sulpho-4-methylphenyl)(3-sulpho-4-methylphenyl)(3,5-disulpho-4-methylphenyl)phosphine; (3-sulphophenyl)(3-sulpho-4-chlorophenyl)(3,5-disulpho-4-chlorophenyl)phosphine.

It is, of course, possible to use a mixture
 20 of these phosphines. In particular, a mixture of mono-, di- and tri-meta-sulphonated phosphines may be used.

Compounds of nickel, of palladium and of iron are preferably used as transition metal compounds. Water-soluble compounds or compounds capable of
 25 dissolving under the reaction conditions are used. The residue bonded to the metal is not critical, as long as it satisfies these conditions.

Among the abovementioned compounds, those of

nickel are the most preferred compounds. There may be mentioned by way of non-limiting examples:

- compounds in which the nickel is in the oxidation state zero, for instance
 5 potassium tetracyanonickelate $K_4(NiCN_4)$,
 bis(acrylonitrile)nickel, bis(1,5-cyclooctadiene)₂nickel and derivatives containing ligands from group Va, for instance tetrakis (triphenylphosphine)-
 10 nickel (in the latter case the compound may be dissolved in a water-immiscible solvent such as toluene, and then an aqueous solution of sulphonated phosphine extracts some of the nickel by
 15 developing a red colour in the aqueous solution which separates out on settling);
- compounds of nickel with an oxidation state greater than 0, for instance
 20 carboxylates (in particular acetate), carbonate, bicarbonate, borate, bromide, chloride, citrate, thiocyanate, cyanide, formate, hydroxide, hydrophosphite, phosphite, phosphate and derivatives,
 25 iodide, nitrate, sulphate, sulphite, arylsulphonates and alkylsulphonates.

It is not necessary for the nickel compound itself to be water-soluble. For example, nickel

cyanide, which is sparingly soluble in water, is very soluble in an aqueous solution of phosphine.

When the nickel compound used corresponds to a nickel oxidation state greater than 0, a nickel-reducing agent which reacts preferentially with nickel under the reaction conditions is added to the reaction medium. This reducing agent may be organic or inorganic. There may be mention by way of non-limiting examples NaBH_4 , Zn powder, magnesium, KBH_4 , and borohydrides which are preferably water-soluble.

This reducing agent is added in an amount such that the number of redox equivalents is between 1 and 10. However, values of less than 1 and greater than 10 are not excluded.

When the nickel compound used corresponds to the 0 oxidation state of nickel, a reducing agent of the type of those mentioned above may also be added, but this addition is not essential.

When an iron compound is used, the same reducing agents are suitable.

In the case of palladium, the reducing agents may additionally be components of the reaction medium (phosphine, solvent or olefin).

The sulphonated phosphines used in the process according to the present invention may be prepared by employing known processes. Thus, in accordance with the teaching of H. Schindlbauer, *Monatsch. Chem.* 96, pages 2051-2057 (1965), the sodium

salt of (p-sulphophenyl)diphenylphosphine may be prepared by reacting sodium p-chlorobenzenesulphonate with diphenylchlorophosphine, in the presence of sodium or potassium. According to the method described in J. Chem. Soc., pages 276-288 (1958) and in English Patent No. 1,066,261, phenylphosphines of formula (I) may be prepared by using the reaction for the sulphonation of aromatic ring-systems using oleum, followed by neutralization of the sulphonic groups formed using a suitable basic derivative of one of the metals represented by M in the formula (I). The crude sulphonated phosphine obtained may contain, as a mixture, the corresponding sulphonated phosphine oxide, the presence of which is not, however, a nuisance for performing the isomerization process according to the present invention.

The 2-methyl-3-butenitrile which undergoes the isomerization according to the process of the invention may be used alone or as a mixture with other compounds.

Thus, 2-methyl-3-butenitrile may be employed as a mixture with 2-methyl-2-butenitrile, 4-pentenitrile, 3-pentenitrile, 2-pentenitrile, butadiene, adiponitrile, 2-methylglutaronitrile, 2-ethylsuccinonitrile or valeronitrile.

Thus, one particularly advantageous variant of the process of the invention consists in treating the reaction mixture obtained from the hydrocyanation

of butadiene with HCN in the presence of an aqueous solution of a sulphonated phosphine of formula (I) and of a transition metal compound, more preferably a compound of nickel of oxidation state 0, as defined
5 above.

In the context of this preferred variant, since the catalytic system is already present for the hydrocyanation reaction of butadiene, it is sufficient to stop any introduction of hydrocyanic acid for the
10 isomerization reaction to occur.

If necessary, it is possible in this variant to flush the reactor gently with an inert gas such as nitrogen or argon for example, in order to expel the hydrocyanic acid which may still be present.

15 The isomerization reaction is generally performed at a temperature of 10°C to 150°C and preferably of 60°C to 120°C.

In the case of an isomerization immediately following the hydrocyanation reaction of butadiene, it
20 will be advantageous to work at the temperature at which the hydrocyanation was carried out.

The catalytic solution used for the isomerization according to the invention may be prepared before its introduction into the reaction
25 zone, for example by addition to the aqueous solution of the phosphine of formula (I), the appropriate amount of the transition metal compound chosen and possibly of the reducing agent. It is also possible to prepare the

catalytic solution "in situ" simply by mixing these various constituents.

The amount of nickel compound used is chosen such that there is between 10^{-4} and 1 and preferably
5 between 0.005 and 0.5 mol of nickel per litre of reaction solution.

The amount of phosphine of formula (I) used in order to prepare the reaction solution is chosen such that the number of moles of this compound relative
10 to 1 mol of elemental metal is from 0.5 to 2000 and preferably from 2 to 300.

Although the reaction is generally carried out without a third solvent, it may be advantageous to add an inert, water-immiscible organic solvent, which
15 may be that of the subsequent extraction.

By way of examples of such solvents, there may be mentioned aromatic, aliphatic or cycloaliphatic hydrocarbons which maintain the reaction medium in the two-phase state.

20 Thus, once the reaction has ended, it is very simple to separate, on the one hand, an aqueous phase containing the sulphonated phosphine of formula (I) and the transition metal compound and, on the other hand, an organic phase consisting of the reactants employed
25 in the reaction, the reaction products and, where appropriate, the water-immiscible organic solvent.

Among the organic solvents which may be used in the isomerization process, there may be mentioned

benzene, toluene, xylenes, hexane and cyclohexane.

The examples which follow illustrate the invention.

EXAMPLE 1

5 1) Preparation of the Ni/TSTPP catalytic solution

500 cm³ of a solution of 350 mmol of the sodium salt of trisulphonated triphenylphosphine (TSTPP) in water are charged into a 1-litre glass
10 round-bottomed flask fitted with a magnetic stirring bar and an ascending condenser; this solution is degassed. Next, 19.20 g (70 mmol) of Ni(cyclooctadiene)₂ are introduced, followed by 350 cm³ of previously degassed orthoxylene, with stirring and
15 under a stream of argon.

The mixture is heated at 45°C for 15 h. After cooling, the two-phase system is allowed to separate by settling and the strongly red-coloured aqueous phase is withdrawn.

20 2) Isomerization of 2-methyl-3-butenitrile

The following are charged into a 150 cm³ glass reactor stirred using a turbine:

- 2-methyl-3-butenitrile (2M3BN):

48.6 g (600 mmol)

25 - aqueous solution containing:

0.14 mol/l of Ni and 0.7 mol/l

of the sodium salt of trisulphonated

triphenylphosphine (TSTPP): 16 cm³

(equivalent to 2.24 mmol of Ni and
11.2 mmol of TSTPP)

The reaction mixture is stirred for 1.5 h at
90°C.

5 After cooling and separation of the phases by
settling, the final organic phase is assayed by gas
chromatography (GC).

The following results are obtained:

Extent of conversion (EC) of 2M3BN: 95%
10 Yield (Yd) of 3-pentenitrile (3PN)
relative to the 2M3BN converted: 91.5%
Yield (Yd) of 2-methyl-2-butenitrile
(2M2BN) relative to the 2M3BN
converted: 8%

15

EXAMPLE 2 - in situ reduction of Ni II

The following are charged into the apparatus
described for Example 1:

20	- NiCl ₂	0.75 mmol
	- TSTPP	3.15 mmol
	- NaBH ₄	0.8 mmol
	- H ₂ O	2.8 g
	- 2M3BN	200 mmol

The mixture is reacted with stirring for 3 h
25 at 110°C.

The organic phase is assayed by GC.

The following results are obtained:

- EC of 2M3BN	64 %
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- Yd of 3PN	97 %
- Yd of 2M2BN	3 %

EXAMPLE 3

Example 2 is repeated with the following

5 charges:

- Ni(Cod) ₂ (Cod = cyclooctadiene)	0.75 mmol
- TSTPP	3.4 mmol
- H ₂ O	3.8 g
- 2M3BN	200 mmol

10 Temperature: 90°C

Time: 2 h

The following results are obtained:

- RC of 2M3BN	87 %
- Yd of 3PN	93 %
15 - Yd of 2M2BN	2 %

EXAMPLE 4

Example 2 is repeated with the following

charges:

- Ni(Cod) ₂	0.75 mmol
20 - TSTPP	3.15 mmol
- H ₂ O	2.8 g
- 2M3BN	200 mmol

Temperature: 110°C

Time: 0.25 h and 0.5 h

The following results are obtained:

	For 0.25 h	For 0.5 h
EC of 2M3BN	75 %	87 %
Yd of 3PN	92 %	94 %
Yd of 2M2BN	5 %	5 %

5

Table 1

EXAMPLE 5

Example 2 is repeated with the following charges:

- 10
- Ni(Cod)₂ 2.5 mmol
 - TSTPP 10.8 mmol
 - H₂O 5.0 g
 - 2M3BN 200 mmol

Temperature: 56°C

Time: 4 h

15

The following results are obtained:

- EC of 2M3BN 87 %
- Yd of 3PN 94 %

EXAMPLES 6 TO 8

20 Example 2 is repeated with the following charges:

- Ni(Cod)₂ 0.7 mmol
- TSTPP see Table 2

- H_2O 5 g
 - 2M3BN 200 mmol (20 cm³)

Temperature: 90°C

Time: see Table 2

5 The results obtained are collated in Table 2 below.

Examples	TSTPP mmol	Time	EC of 2M3BN	Yd of 3PN	Yd of 2M2BN
Example 6	2.15	0.5 h	39 %	80 %	15 %
		1.5 h	81 %	88 %	12 %
Example 7	3.6	0.5 h	45 %	89 %	9 %
		1.5 h	87 %	92 %	7 %
Example 8	5.4	0.5 h	49 %	92 %	6 %
		1.5 h	62 %	92 %	6 %

10

Table 2

EXAMPLES 9 TO 10

Example 2 is repeated with the following charges:

15 - $Ni(Cod)_2$ see Table 3
 - TSTPP 10.5 mmol
 - H_2O 15 g
 - 2M3BN 600 mmol (60 cm³)

Temperature: 90°C

20

Time: see Table 3

The results obtained are collated in Table 3 below.

Examples	Ni(Cod) ₂ mmol	Time	EC of 2M3BN	Yd of 3PN	Yd of 2M2BN
Example 9	0.3	0.5 h	11 %	66 %	33 %
		1.5 h	28 %	66 %	33 %
Example 10	2.85	0.5 h	48 %	93 %	6 %
		1.5 h	94 %	93 %	6 %

Table 3

EXAMPLE 11

Recycling tests

Example 2 is repeated, but after the test the organic phase is separated out and assayed by GC while the organic phase containing the nickel catalyst and the TSTPP is recycled with a new charge of 2M3BN.

The following compounds are charged:

- Ni(Cod)₂ 0.74 mmol
- TSTPP 3.4 mmol
- H₂O 3.8 g
- 2M3BN see Table

Temperature: 90°C

Time: 90 min for each test

The results obtained are collated in Table 4

below.

Recycling	2M3BN charged (mmol)	EC of 2M3BN	Yd of 3PN	Yd of 2M2BN
0	211	93 %	92 %	5 %
1	205	78 %	96 %	4 %
2	225	60 %	90 %	5 %

Table 4

EXAMPLE 12

Recycling tests

Example 11 is repeated with the following

charges:

- Ni(Cod)₂ 2.26 mmol
- TBTTP 10.1 mmol
- H₂O 16 g
- 2M3BN see Table 5

Temperature: 90°C

Time: see Table 5

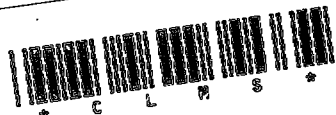
The results obtained are collated in Table 5

below.

Recycling	2M3BN charged (mmol)	Time (min)	KC of 2M3BN	Yd of 3PN	Yd of 2M2BN
0	600	90	95 %	91 %	8 %
1	600	90	73 %	90 %	9 %
2	600	90	47 %	90 %	9 %
		180	72 %	90 %	9 %

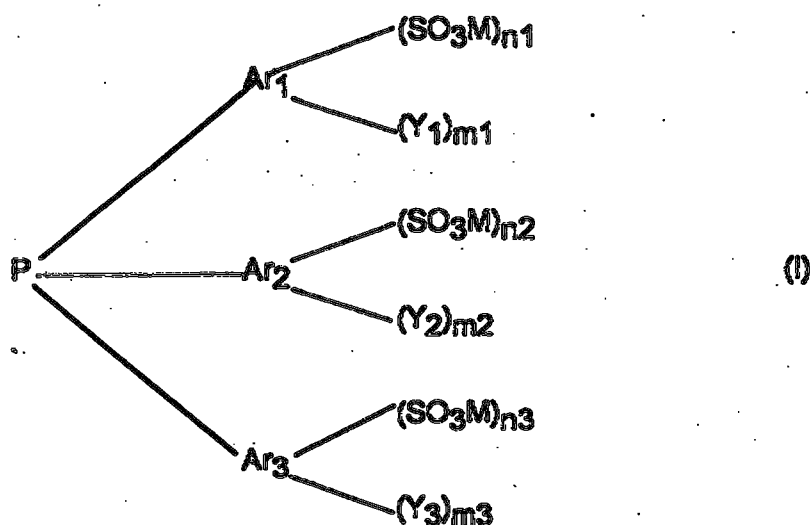
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Table 5

CLAIMS

1. Process for the isomerization of 2-methyl-3-butenitrile into a linear pentenenitrile, characterized in that the reaction is carried out in the presence of an aqueous solution:

- of at least one sulphonated phosphine of general formula (I)



in which:

* Ar_1 , Ar_2 and Ar_3 , which may be identical or different, represent aryl groups

* Y_1 , Y_2 and Y_3 , which may be identical or different, represent

. an alkyl radical having 1 to 4 carbon atoms,

. an alkoxy radical having 1 to 4 carbon atoms,

. a halogen atom,

. a CN radical,

- . an NO_2 radical
- . an OH radical,
- . a radical NR_1R_2 , in which formula R_1 and R_2 , which may be identical or different, represent an alkyl radical having 1 to 4 carbon atoms,

5

* M is an inorganic or organic cationic residue chosen, so that the compound of formula (I) is water-soluble, from the group comprising:

10

- . H^+ ,
- . cations derived from alkali metals or alkaline-earth metals,
- . $\text{N}(\text{R}_3\text{R}_4\text{R}_5\text{R}_6)^+$ with R_3 , R_4 , R_5 and R_6 , which may be identical or different, representing an alkyl radical having 1 to 4 carbon atoms or a hydrogen atom,
- . other cations derived from metals for which the benzenesulphonic acid salts are water-soluble,

15

20

* m_1 , m_2 and m_3 are integers, which may be identical or different, from 0 to 5,

* n_1 , n_2 and n_3 are integers, which may be identical or different, from 0 to 3,

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at least one among these being equal to or greater than 1

- and of at least one transition metal compound.

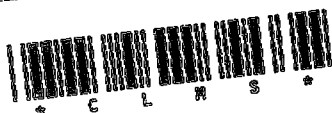




2. Process according to Claim 1, characterized in that the sulphonated phosphine used is chosen from the phosphines of formula (I) in which:

- Ar_1 , Ar_2 and Ar_3 are phenyl groups,
- 5 - Y_1 , Y_2 and Y_3 represent groups chosen from
 - . alkyl radicals having from 1 to 2 carbon atoms,
 - . alkoxy radicals having from 1 to 2 carbon atoms,
- 10 - M represents a cation chosen from the group comprising
 - . H^+
 - . cations derived from Na, K, Ca and Ba
 - . NH_4^+
 - 15 . tetramethylammonium, tetraethylammonium, tetrapropylammonium and tetrabutylammonium cations
- n_1 , n_2 and n_3 are integers from 0 to 3
- n_1 , n_2 and n_3 are integers from 0 to 3, at
20 least one also being greater than 1.

3. Process according to either of Claims 1 and 2, characterized in that the sulphonated phosphine used is chosen from the sodium, potassium, calcium, barium, ammonium, tetramethylammonium and
25 tetraethylammonium salts of mono(sulphophenyl)-diphenylphosphine, di(sulphophenyl)phenylphosphine and tri(sulphophenyl)phosphine, in the formulae in which the SO_3 groups are preferably in the meta-position, are



more particularly preferred.

4. Process according to one of Claims 1 to 3, characterized in that compounds of nickel, of palladium or of iron, which are water-soluble or
5 capable of dissolving under the reaction conditions, and preferably nickel compounds, are used as transition metal compound.

5. Process according to Claim 4, characterized in that the nickel compound used is a
10 nickel zero compound.

6. Process according to Claim 4, characterized in that the nickel compound used is a compound of nickel with an oxidation state greater than zero.

15 7. Process according to Claim 6, characterized in that an organic or inorganic nickel-reducing agent which reacts preferentially with nickel under the reaction conditions is added to the reaction medium.

20 8. Process according to Claim 7, characterized in that the reducing agent is added in an amount such that the number of redox equivalents is between 1 and 10.

25 9. Process according to one of Claims 1 to 8, characterized in that the 2-methyl-3-butenenitrile which undergoes the isomerization is used alone or as a mixture with other compounds, for instance 2-methyl-2-butenenitrile, 4-pentenitrile, 3-pentenitrile,



2-pentenitrile, butadiene, adiponitrile,
2-methylglutaronitrile, 2-ethylsuccinonitrile or
valeronitrile.

10. Process according to one of Claims 1 to
5 9, characterized in that the reaction mixture obtained
from the hydrocyanation of butadiene is treated with
HCN in the presence of an aqueous solution of a
sulphonated phosphine of formula (I) and of a
transition metal compound, more preferably a compound
10 of nickel of oxidation state 0.

11. Process according to one of Claims 1 to
10, characterized in that the isomerization reaction is
performed at a temperature of 10°C to 150°C and
preferably of 60°C to 120°C.

15 12. Process according to one of Claims 4 to
11, characterized in that the amount of nickel compound
used is chosen such that there is between 10^{-4} and 1 and
preferably between 0.005 and 0.5 mol of nickel per
litre of reaction solution.

20 13. Process according to one of Claims 1 to
12, characterized in that the amount of phosphine of
formula (I) used in order to prepare the reaction
solution is chosen such that the number of moles of
this compound relative to 1 mol of elemental metal is
25 from 0.5 to 2000 and preferably from 2 to 300.

· ABSTRACT
PROCESS FOR THE ISOMERIZATION OF 2-METHYL-3-
BUTENENITRILE

The present invention relates to a process for the isomerization of 2-methyl-3-butenenitrile into linear pentenenitrile, in particular into 3-pentenenitrile.

More precisely, it consists of a process for the isomerization of 2-methyl-3-butenenitrile into a linear pentenenitrile, characterized in that the reaction is carried out in the presence of an aqueous solution of at least one sulphonated phosphine and of at least one transition metal compound.

3-Pentenenitrile is an intermediate compound for the preparation of adiponitrile.