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manufacture of nitrile compounds of use in the
synthesis of adiponitrile, an important chemical
intermediate in the manufacture of major chemical
10 compounds, such as hexamethylenediamine and
 ϵ -caprolactam. The invention provides a process for the
manufacture of organic compounds comprising at least
one nitrile functional group by carrying out a
hydrocyanation reaction between hydrogen cyanide and an
15 organic compound comprising at least one ethylenic
unsaturation. This reaction is carried out in the
presence of a catalytic system comprising a metal
element chosen from the group consisting of nickel,
platinum and palladium and an organophosphorus ligand,
20 the reaction medium additionally comprising an ionic
liquid in the liquid state at least at the temperature
at which the hydrocyanation reaction is carried out.



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The present invention relates to the manufacture of nitrile compounds from unsaturated organic compounds by reaction with hydrogen cyanide.

It relates more particularly to the manufacture of nitrile compounds of use in the synthesis of adiponitrile, an important chemical intermediate in the manufacture of major chemical compounds, such as hexamethylenediamine and ϵ -caprolactam. The last two compounds are used in particular in the manufacture of polymers, such as polyamides, and more particularly polyamide-6 and polyamide-6,6, or other polymers, such as polyurethanes.

Several processes for the manufacture of nitrile compounds have been provided. Among these, the direct hydrocyanation of an olefin or polyolefin, such as, for example, 1,3-butadiene, by reaction with hydrogen cyanide is an industrially developed process which forms the subject of numerous patents or publications.

This process consists, basically, in carrying out the addition, in a first stage, of one molecule of HCN to one ethylenic unsaturation, to produce an unsaturated nitrile compound. In fact, this stage leads to the production of numerous isomers of unsaturated

nitriles. The addition of a further molecule of HCN results, in a following stage, in a polynitrile, for example in a dinitrile, such as adiponitrile when the starting olefin is 1,3-butadiene.

5 To avoid and limit the production of byproducts not having significant use properties, the process comprises, after the first hydrocyanation stage, a stage known as the "isomerization stage", which consists in converting most of the branched
10 nitrile isomers to linear nitrile isomers, such as, in the case of the hydrocyanation of butadiene, to 3- and 4-pentenitriles.

 These reactions are generally carried out in the liquid phase in the presence of a catalyst based on
15 a metal, generally nickel, present in the form of a complex with an organic ligand. This reaction can be carried out in a homogeneous medium, the catalyst being soluble in the hydrocyanation medium, in particular in the olefin or the nitriles or in a third solvent. It
20 can also be carried out with a medium exhibiting several liquid phases, the catalyst being soluble in one of the phases, more specifically in the phase formed by a polar third solvent, generally water, which phase is distinct from that formed by the olefin and
25 the nitriles, at least at ambient temperature. The latter embodiment makes it possible to more easily extract and recover the catalyst and thus to obtain

nitrile compounds comprising fewer impurities contributed by the catalyst.

These catalytic systems have been disclosed in numerous patents and several classes of ligands have been studied. The ligands are generally organophosphorus compounds, such as phosphites, phosphinites, phosphonites or phosphines. They can be monodentate or polydentate. In the case of processes in a two-phase medium, these organophosphorus ligands advantageously comprise one or more ionizable groups, such as sulphonate, phosphonate, carboxylate or ammonium groups, for example, to render them soluble in the polar phase.

Mention may be made, as example of the disclosure of these processes, of Patent US 3 496 217, which discloses the synthesis of adiponitrile by reaction of hydrogen cyanide with butadiene in the presence of a catalyst based on nickel complexed with a ligand, such as triaryl phosphite. This reaction is carried out with catalysis in a single-phase medium.

With regard to French Patent No. 2 338 253, it also discloses a process for the synthesis of adiponitrile by hydrocyanation of butadiene. The reaction is carried out in a two-phase liquid medium, the catalyst being present in an aqueous phase. This process makes it possible to recover the adiponitrile, devoid of catalyst and therefore of metal, in the

organic phase. The catalyst disclosed is also a catalyst based on a metal, such as nickel, in combination with a ligand of the phosphine type. However, this ligand comprises sulphonate radicals, making it possible to render the catalyst soluble or dispersible in water.

Furthermore, it is also known to combine the nickel-based catalyst with promoters, such as Lewis acids, such as, for example, zinc chloride or triphenylborane, for the hydrocyanation of an unsaturated nitrile compound.

Research is continually being undertaken to improve the performance of the synthesis of nitriles by hydrocyanation, either by developing novel catalytic systems or by modifying the reaction conditions and compositions of the hydrocyanation medium.

Among the most recent patents published, Patent US 6 169 198 discloses the use of novel ligands of metallocene-phosphorus type. Likewise, Patent US 5 773 637 discloses the use, as Lewis acid, of perfluoroalkylsulphonate compounds.

One of the aims of the present invention is to provide a novel process for the manufacture of nitriles by hydrocyanation of an olefin by reaction with hydrogen cyanide which makes it possible to obtain high yields of and high selectivities for linear nitriles and an improved stability of the catalytic

system.

To this end, the invention provides a process for the manufacture of organic compounds comprising at least one nitrile functional group by carrying out a hydrocyanation reaction between hydrogen cyanide and an organic compound comprising at least one ethylenic unsaturation. The latter compound will be referred to, for greater simplicity, in the present invention as an olefin or polyolefin, when it comprises several ethylenic unsaturations. However, this term "olefin" should not be interpreted as limiting the organic compounds suitable for the invention to hydrocarbons but it also relates to organic compounds comprising at least one ethylenic unsaturation and which can comprise atoms other than carbon and hydrogen or mixtures of hydrocarbons, such as the mixture obtained by distillation of oil known in the hydrocarbons field as the C₄ cut. This cut is advantageously treated to remove or convert impurities, such as compounds comprising an acetylenic unsaturation, for example by hydrogenation, as disclosed in Patent US No. 6 197 992. A compound will be regarded as an "olefin" within the meaning of the present invention which comprises an unsaturation and a nitrile functional group, such as, for example, the unsaturated nitrile compounds obtained by the reaction of HCN with a polyolefin.

According to one characteristic of the

invention, the reaction is carried out in the presence of a catalytic system comprising a metal element chosen from the group consisting of nickel, platinum and palladium and an organophosphorus ligand, the reaction
5 medium additionally comprising an ionic liquid which is in the liquid state at least at the temperature at which the hydrocyanation reaction is carried out.

In a first embodiment, the ionic liquid and the compound to be hydrocyanated are completely
10 miscible, at least at the reaction temperature. The hydrocyanation reaction is carried out in a homogeneous or single-phase medium.

In a second embodiment, the ionic liquid and the compound to be hydrocyanated are immiscible or are
15 only partially miscible at the reaction temperature. The reaction is carried out in a nonhomogeneous or two-phase medium. In this embodiment, the catalytic system is advantageously soluble in the ionic liquid.

In both these embodiments, it is possible to
20 add a solvent of low polarity. This solvent of low polarity can be added from the beginning of the reaction but can also be used only after the end of the reaction, in order thus to promote the separation of the hydrocyanated products and of the ionic liquid, in
25 particular in order to make possible the extraction of the catalytic system. This is because the solvent of low polarity has the role of rendering the ionic liquid

insoluble in the phase composed of the said solvent, the unconverted olefin and the nitrile compounds formed.

Whatever the embodiment, it is preferable for the catalytic system to be at least partially miscible in the ionic liquid. Advantageously, this miscibility can be obtained by the presence of at least one ionizable group in the molecule of the organophosphorus ligand. Mention may be made, as ionizable groups, of groups of anionic type, such as sulphonate, phosphonate, phosphinate, carboxylate or sulphinate, or of cationic type, such as guanidinium, ammonium, pyridinium, imidazolium, phosphonium or sulphonium, for example. The number and the nature of these ionic groups are preferably chosen in order to render the ligand soluble in the ionic liquid. It can be advantageous for the nature of the ionizable group to be identical to that of the anion or of the cation associated with the ionic liquid.

The catalytic systems suitable for the invention are those which preferably comprise the element nickel in the zero oxidation state or a complex with organophosphorus ligands which can comprise several ionizable groups described above or more generally compounds comprising phosphorus capable of giving a coordination compound with transition metals and more particularly the abovementioned catalytic

metals, in particular with nickel. These compounds can be mono-, bi- or polydentate and can exhibit a hydrophobic or hydrophilic nature. These compounds have been disclosed in numerous patents relating to the
5 hydrocyanation of butadiene and belong to several classes, including in particular the organophosphites, organophosponites, organophosphinites and organophosphines.

Such catalytic systems and their preparation
10 processes are disclosed, for example, in French Patents 2 338 253, 2 710 909, 2 711 987, 2 739 378 and 2 778 915.

Mention may be made, as examples of organic phosphorus compounds which are suitable for the
15 invention, of alkylphosphines, arylphosphines, alkylarylphosphines, alkyl phosphites, aryl phosphites, alkylaryl phosphites, alkylphosphinites, arylphosphinites, alkylarylphosphinites, alkylphosponites, arylphosponites or
20 alkylarylphosponites, the organic moiety of which comprises up to 36 carbon atoms and which are preferably substituted by one or more ionic groups described above.

Mention may be made, as examples of
25 compounds, of tributylphosphine, dimethyl(n-octyl)-phosphine, tricyclohexylphosphine, triphenylphosphine, tolylphosphine, tris(p-methoxyphenyl)phosphine,

diphenylethylphosphine, dimethylphenylphosphine, 1,4-bis(diphenylphosphino)butane, triethyl phosphite or diphenyl phosphite, the said compounds preferably comprising at least one ionic group described above.

5 Mention may be made, as examples of such compounds, of triphenylphosphine(mono meta sodium sulphate) (TPPMSNa), (5-sodiocarboxyfur-2-yl)diphenylphosphine or (3-sodiosulphinatophenyl)diphenylphosphine.

10 As is disclosed in the abovementioned patents, the catalyst can be prepared before its introduction into the medium or in situ.

For this, use is preferably made of the compounds of the metals forming the catalytic element, 15 such as nickel, which are added to a medium in which the organophosphorus ligand is also soluble. Such a medium can be the ionic liquid. The catalytic system thus formed is added to the hydrocyanation medium.

The preferred compounds among the 20 abovementioned compounds are those of nickel. Mention may be made, as nonlimiting examples, of:

- the compounds in which the nickel is in the zero oxidation state, such as potassium tetracyanonickelate $K_4[Ni(CN)_4]$, bis(acrylonitrile)nickel(0), 25 bis(1,5-cyclooctadiene)nickel and derivatives comprising ligands from Group Va, such as tetrakis(triphenylphosphine)nickel(0);

- the nickel compounds in which the nickel is in an oxidation state greater than zero, such as the carboxylates (in particular the acetate), carbonate, bicarbonate, borate, bromide, chloride, citrate, thiocyanate, cyanide, formate, hydroxide, hydrophosphite, phosphite, phosphate and derivatives, iodide, nitrate, sulphate, sulphite, aryl- and alkylsulphonates, allyl or acetylacetonate.

It is not necessary for the nickel compound to be itself soluble in the preparation medium, such as the ionic liquid. This is because it is sufficient for the complex to be soluble, that is to say for the dissolution of the nickel to take place during the addition of the ligand to the ionic liquid.

When the nickel compound used corresponds to an oxidation state of the nickel greater than 0, a reducing agent for nickel which preferably reacts with the latter under the reaction conditions is added to the reaction medium. This reducing agent can be organic or inorganic or hydrogen. Mention may be made, as nonlimiting examples, of Zn powder, magnesium, KBH_4 , NaBH_4 and borohydrides preferably soluble in water.

This reducing agent is added in an amount such that the number of oxidation/reduction 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 can also be added but this addition is not essential.

The same reducing agents are suitable when an
5 iron compound is used.

In the case of palladium, the reducing agents can, in addition, be components of the reaction medium (phosphine, solvent, olefin).

According to the invention, the reaction medium comprises an ionic liquid. This ionic liquid is an ionic compound, the cation of which is of onium type having at least one heteroatom, such as N, P or S, carrying the positive charge in conjunction with a 5- or 6-membered aromatic ring, and an anion.

15 Such compounds are described, for example, in
the article by Yves Chauvin and
Hélène Olivier-Bourbigou, entitled "Nonaqueous ionic
liquids as reaction solvents", published in Chemtech,
12, 1995, p. 66, the paper by T. Welton published in
20 Chem. Rev., 1999, p. 2071, or patents, such as Patent
EP 971 854.

According to a preferred characteristic of the invention, the ionic liquid comprises at least one cation chosen from the group consisting of the

25 structures tetraalkylammonium, N-alkylimidazolium, N-alkylpyridinium, N-alkylpicolinium, N-alkyltriazolium, N-alkylfluoropyrazolium,

N-pyrrolidinium, alkylsulphonium, tetraalkylphosphonium and alkyloxonium.

Mention may be made, as examples of preferred cations of the invention, of alkylimidazoliums, such as
 5 1,3-dimethylimidazolium, 1-butyl-2,3-dimethylimidazolium, 1-butyl-3-methylimidazolium or 1,2,3-trimethylimidazolium.

Mention may be made, as preferred anions of the invention, of an anion chosen from halides,
 10 nitrate, phosphate, hydrosulphate, perfluoroalkylsulphonates, bis(perfluoroalkylsulphonyl)amides, bis(fluorosulphonyl)amide, bis(fluorophosphoryl)amide, tris(perfluoroalkylsulphonyl)methides, boron, aluminium, gallium or iron tetrahalides, phosphorus,
 15 arsenic and antimony hexahalides, zinc and tin trihalides, or copper dihalides.

The preferred anions of the invention are Br^- , I^- , BF_4^- , PF_6^- , SbF_6^- , AlCl_4^- , ZnCl_3^- , SnCl_3^- and $(\text{CF}_3\text{SO}_2)_2\text{N}^-$.

20 The ionic liquid, to be suitable for the process of the invention, must be in the liquid state at least at the temperature at which the hydrocyanation reaction is carried out. However, ionic liquids which are found in the liquid state at a temperature of less
 25 than 100°C are preferred as they make possible better separation and extraction of the catalyst from the reaction medium in the case of a two-phase system.

In addition, depending on the embodiment of the invention (single- or two-phase system), the ionic liquid which becomes miscible or at least partially miscible in the reaction medium only at the temperature
5 at which the hydrocyanation reaction is carried out, or in the vicinity of the latter, is entirely compatible for the implementation of the invention.

In the embodiment in a two-phase medium, the immiscibility of the ionic liquid, at least at low
10 temperature, is preferably obtained by addition to the reaction medium of a solvent of low polarity. This solvent dissolves the olefins to be hydrocyanated and the nitriles produced and renders the ionic liquid insoluble in the olefins and nitriles produced. Mention
15 may be made, as solvent of low polarity, of saturated hydrocarbons, such as hexane, heptane, octane or toluene, or ethers, such as diethyl ether, diisopropyl ether or methyl isobutyl ether.

The conditions for carrying out the
20 hydrocyanation reaction are described below, by way of example.

Thus, the amount of nickel compound or compound of another transition metal used is chosen in order to obtain a concentration as moles of transition
25 metal per mole of organic compounds to be hydrocyanated or isomerized of between 10^{-4} and 1 and preferably between 0.005 and 0.5 mol of nickel or of the other

transition metal employed.

The amount of ligand used to form the catalyst is chosen so that the number of moles of this compound with respect to 1 mol of transition metal is
5 between 0.5 and 50 and preferably between 2 and 10.

The hydrocyanation reaction is generally carried out at a temperature of between 10°C and 200°C and preferably between 30°C and 120°C.

The process of the invention can be carried
10 out continuously or batchwise.

The hydrogen cyanide employed can be prepared from metal cyanides, in particular sodium cyanide, or cyanohydrins, such as acetone cyanohydrin, or by any other known synthetic process.

15 The hydrogen cyanide is introduced into the reactor in the gaseous form or in the liquid form. It can also be dissolved beforehand in an organic solvent.

In the context of a batchwise implementation, it is in practice possible to charge to a reactor,
20 purged beforehand using an inert gas (such as nitrogen or argon), either a solution comprising all or a portion of the various constituents, the transition metal compound, the possible reducing agents and solvents, or the said constituents separately.

25 Generally, the reactor is then brought to the chosen temperature and then the compound to be hydrocyanated is introduced. The hydrogen cyanide is then itself

introduced, preferably continuously and unvaryingly.

When the reaction is complete, the reaction mixture is withdrawn after cooling and the reaction products are isolated, for example by separation of the phase comprising the catalytic system and of the phase formed by the solvent of low or no polarity, the hydrocyanated products and those which have not been converted, in the case of a two-phase system. The products from the latter phase can be separated, for example by distillation. In the case of a single-phase system, other separation means can be employed, such as, for example, distillation or liquid/liquid extraction.

In the case where the product to be hydrocyanated is an unsaturated compound comprising a nitrile functional group, it is advantageous to use, with the catalytic system, a cocatalyst comprising at least one Lewis acid.

This reaction consists in particular in converting aliphatic nitriles comprising ethylenic unsaturation, in particular linear pentenenitriles, such as 3-pentenenitrile, 4-pentenenitrile and their mixtures, obtained by hydrocyanation of butadiene, to dinitriles, more specifically to adiponitrile.

These pentenenitriles can comprise amounts, generally minor amounts, of other compounds, such as 2-methyl-3-butenitrile, 2-methyl-2-butenitrile,

2-pentenitrile, valeronitrile, adiponitrile,
2-methylglutaronitrile, 2-ethylsuccinonitrile or
butadiene, originating from the prior reaction for the
hydrocyanation of butadiene and/or from the
5 isomerization of 2-methyl-3-butenitrile to
pentenenitriles.

The Lewis acid used as cocatalyst makes it
possible in particular, in the case of the
hydrocyanation of aliphatic nitriles comprising
10 ethylenic unsaturation, to improve the linearity of the
dinitriles obtained, that is to say the percentage of
linear dinitriles with respect to all the dinitriles
formed, and/or to increase the activity and the
lifetime of the catalyst.

15 The term "Lewis acid" is understood to mean,
in the present text, according to the usual definition,
compounds which accept electron pairs.

It is possible in particular to employ the
Lewis acids cited in the work edited by G.A. Olah,
20 "Friedel-Crafts and Related Reactions", Volume I,
pages 191 to 197 (1963).

The Lewis acids which can be employed as
cocatalysts in the present process are chosen from the
compounds of the elements from Groups Ib, IIb, IIIa,
25 IIIb, IVa, IVb, Va, Vb, VIb, VIIb and VIII of the
Periodic Table. These compounds are generally salts, in
particular halides, such as chlorides or bromides,

sulphates, sulphonates, halosulphonates, perhaloalkylsulphonates, in particular fluoroalkylsulphonates or perfluoroalkylsulphonates, carboxylates, phosphates, bis(perfluoroalkylsulphonyl)-
5 amides and tris(perfluoroalkylsulphonyl)methides.

Mention may be made, as nonlimiting examples of such Lewis acids, of zinc chloride, zinc bromide, zinc iodide, manganese chloride, manganese bromide, cadmium chloride, cadmium bromide, stannous chloride,
10 stannous bromide, stannous sulphate, stannous tartrate, indium trifluoromethylsulphonate, the chlorides or bromides of rare-earth metal elements, such as lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, hafnium,
15 erbium, thallium, ytterbium and lutetium, cobalt chloride, ferrous chloride or yttrium chloride.

Use may also be made, as Lewis acid, of organometallic compounds, such as triphenylborane or titanium diisopropoxide. It is, of course, possible to
20 employ mixtures of several Lewis acids.

Preference is very particularly given, among Lewis acids, to zinc chloride, zinc bromide, stannous chloride, stannous bromide, triphenylborane and zinc chloride/stannous chloride mixtures.

25 The choice will preferably be made of a Lewis acid having an anion identical to or of the same nature as the anion of the ionic liquid, such as, for example,

zinc chloride when the ionic liquid comprises ZnCl_3^- as anion, aluminium chloride when the anion of the ionic liquid is the anion AlCl_4^- , lanthanum tris(bistrifluoromethylsulphonylamide) when the ionic medium is composed of the bistrifluoromethylsulphonyl-
 5 amide anion, or neodymium tris(trifluoromethylsulphonate) when the anion of the ionic medium is the trifluoromethylsulphonate anion. It is also possible to employ an ionic liquid composed of a mixture of
 10 polynuclear anions, such as the anion Zn_2Cl_5^- and of ZnCl_3^- , or Al_2Cl_7^- and of AlCl_4^- .

In a preferred embodiment of the invention, the Lewis acid will be contributed by the anion of the ionic liquid. This ionic liquid itself contributes the
 15 effect of cocatalyst to the medium.

The Lewis acid cocatalyst employed generally represents from 0.01 to 50 mol per mole of transition metal compound, more particularly of nickel compound, and preferably from 1 to 10 mol per mole.

20 It is also possible, under the conditions of the hydrocyanation process of the present invention and more particularly in the presence of an ionic liquid, to carry out, in the absence of hydrogen cyanide, isomerization of 2-methyl-3-butenitrile to
 25 pentenenitriles and more generally of branched unsaturated nitriles to linear unsaturated nitriles.

The 2-methyl-3-butenitrile subjected to

isomerization according to the invention can be employed alone or, as a mixture with other compounds.

Thus, 2-methyl-3-butenitrile can be used as a mixture with 2-methyl-2-butenitrile,
5 4-pentenitrile, 3-pentenitrile, 2-pentenitrile, butadiene, adiponitrile, 2-methylglutaronitrile, 2-ethylsuccinonitrile or valeronitrile.

It is particularly advantageous to treat the reaction mixture originating from the hydrocyanation of
10 butadiene by HCN according to the conditions of the invention, that is to say in the presence of an ionic liquid.

In the context of this preferred alternative form, the catalytic system being already present for
15 the reaction for the hydrocyanation of butadiene, it is sufficient to halt any introduction of hydrogen cyanide to allow the isomerization reaction to take place.

In this alternative form, it is possible, if appropriate, to carry out a slight flushing of the
20 reactor using an inert gas, such as nitrogen or argon, for example, in order to drive off the hydrocyanic acid which might still be present.

The isomerization reaction is generally carried out at a temperature of 10°C to 200°C and
25 preferably of 60°C to 120°C.

In the preferred case of an isomerization immediately following the reaction for the

hydrocyanation of butadiene, it will be advantageous to carry out the isomerization at the temperature at which the hydrocyanation was carried out.

As for the process for the hydrocyanation of
5 compounds comprising ethylenic unsaturation, the catalytic system used for the isomerization can be prepared before its introduction into the reaction region. It is also possible to prepare the catalytic system "in situ" by simple mixing of these various
10 constituents. The amount of transition metal compound and more particularly of nickel compound used and the amount of ligand are the same as for the hydrocyanation reaction.

However, the preparation of dinitrile
15 compounds by hydrocyanation of an olefin such as butadiene can be carried out using a reaction system in accordance with the invention for the stages of formation of the unsaturated nitriles and the stage of isomerization above, it being possible for the reaction
20 for the hydrocyanation of the unsaturated nitriles to dinitriles to be carried out with a reaction system in accordance with the invention or any other catalytic system already known for this reaction.

Likewise, the reaction for the hydrocyanation
25 of the olefin to unsaturated nitriles and the isomerization of the latter can be carried out with a reaction system different from that of the invention,

the stage of hydrocyanation of the unsaturated nitriles to dinitriles being carried out with a reaction system in accordance with the invention.

The examples given below, solely by way of indication, will illustrate the invention and its advantages.

PREPARATION OF IONIC LIQUIDS

Synthesis of 1-butyl-2,3-dimethylimidazolium

10 bis(trifluoromethylsulphonyl)amide (BMMI⁺TF₂N⁻)

40.50 g (0.215 mol) of 1-butyl-2,3-dimethylimidazolium chloride are dissolved in 300 ml of distilled water. 61.62 g (0.215 mol) of lithium bis(trifluoromethylsulphonyl)amide are added and the mixture is stirred under argon for 72 hours at ambient temperature. A two-phase system is formed. After extraction with 250 ml of dichloromethane, the organic phase is washed with 800 ml of water and then concentrated. The compound exists in the form of a slightly pinkish liquid which is purified by chromatography on a neutral alumina column (eluent: dichloromethane). It is then concentrated, taken up in acetonitrile in the presence of active carbon and filtered. After drying for several hours at 60°C, the compound is obtained in the form of a colourless liquid (83.78 g, 90%). The structure of this product: C₁₁H₁₇N₃S₂O₄F₆, is confirmed by NMR spectral analysis.

Synthesis of 1-butyl-3-methylimidazolium

bis(trifluoromethylsulphonyl)amide ($\text{BMI}^+\text{TF}_2\text{N}^-$)

41.92 g (0.240 mol) of 1-butyl-3-methyl-
imidazolium chloride are dissolved in 300 ml of
5 distilled water. 69.46 g (0.242 mol) of lithium
bis(trifluoromethylsulphonyl)amide are added and the
mixture is stirred under argon for 90 hours at ambient
temperature. A two-phase system is formed. After
extraction with 250 ml of dichloromethane, the organic
10 phase is washed with 800 ml of water and then
concentrated. The compound exists in the form of a
slightly pinkish liquid which is purified by
chromatography on a neutral alumina column (eluent:
dichloromethane). It is then concentrated, taken up in
15 acetonitrile in the presence of active carbon and
filtered. After drying for several hours at 60°C, the
compound is obtained in the form of a colourless liquid
(81.47 g). Its structure, $\text{C}_{10}\text{H}_{15}\text{N}_3\text{S}_2\text{O}_4\text{F}_6$, was confirmed by
NMR analysis.

20 Synthesis of 1-butyl-2,3-dimethylimidazolium

hexafluorophosphate ($\text{BMMI}^+\text{PF}_6^-$)

33.37 g (0.200 mol) of sodium
hexafluorophosphate and 37.50 g (0.199 mol) of 1-butyl-
2,3-dimethylimidazolium chloride are dissolved in
25 150 ml of acetone. After vigorous stirring at ambient
temperature under argon for 72 hours, the solution is
filtered through celite and then concentrated. After

chromatography on an alumina column (eluent: dichloromethane), the salt is taken up in acetonitrile in the presence of active carbon and filtered.

Concentrating the solution gives 50.41 g (0.170 mol, 85%) of a white solid. The structure of this product, $C_9H_{17}N_2PF_6$, is confirmed by NMR spectral analysis.

In the examples below, the abbreviations used have the following meanings:

	cod:	1,5-cyclooctadiene
10	eq:	equivalent
	2M3BN:	2-methyl-3-butenenitrile
	2M2BN:	2-methyl-2-butenenitrile
	3PN:	3-pentenenitrile
	4PN:	4-pentenenitrile
15	3+4PN:	3PN + 4PN
	DN:	ADN + MGN + ESN
	MGN:	methylglutaronitrile
	ESN:	ethylsuccinonitrile
20	DC (Y):	degree of conversion of the product Y to be hydrocyanated, corresponding to the ratio of the number of moles of Y converted to the number of starting moles of Y
	TY (X):	true yield of the compound X, corresponding to the ratio of the number of moles of X formed to the maximum number of moles of X
25	YD (X):	selectivity for the compound X, corresponding to the ratio of TY (X) to

DC (Y)

L: linearity: $Y_{D_{AdN}}/Y_{D_{DN}}$

GC: gas chromatography

TPPMSNa: sodium triphenylphosphate

5 $P(Ph)_2PhSO_2Na$: (3-sodiosulphinatophenyl)diphenylphosphine

$P(Ph)_2FuCO_2Na$: (5-sodiocarboxyfur-2-yl)diphenylphosphine

BPh_3 : triphenylborane

$In(CF_3SO_3)_3$

$ZnPh_2$

10 $Zn(CF_3SO_3)_2$

ISOMERIZATION OF 2-METHYL-3-BUTENENITRILE (2M3BN) TO LINEAR PENTENENITRILES

The tests were carried out according to the
15 following procedure and in a "Radleys" parallel reactor
which makes possible simultaneous stirring and
simultaneous reflux of 12 glass tubes known as Schlenk
tubes.

The following are introduced successively and
20 under argon into a glass tube:

- 10 mg (0.036 mmol, 1 equivalent) of $Ni(COD)_2$
- 66 mg (0.18 mmol, 5 equivalents) of TPPMSNa
- 1.5 g of ionic liquid
- 400 mg (4.93 mmol, 137 equivalents) of 2M3BN.

25 The solution is stirred at ambient
temperature for 10 minutes and then 1.2 ml of heptane
are added in order to obtain a two-phase reaction

medium.

The tube is closed, then stirred and heated at 100°C for 3 hours with head cooling. At the end of the reaction, the tubes are cooled in liquid nitrogen.

5 A known amount of butylbenzene (approximately 40 mg, to act as chromatography internal standard) is added to the two-phase reaction medium, which is diluted and homogenized by the addition of 10 ml of THF. The solution obtained is filtered through a short silica

10 column and injected in gas chromatography (GC).

In the tests carried out according to the above procedure, the starting materials comprise 2M3BN and other products. The molar formulation of these products is given in Table I below (the main components

15 are shown).

Table I

Component	Abbreviation	Mol%
2-Methyl-3-butenenitrile	2M3BN	79
2-Methyl-2-butenenitrile	2M2BN	12.70
2-Pentenitrile	2PN	6.30
4-Pentenitrile	4PN	0
3-Pentenitrile	3PN	1.30

The results obtained with various salts are

20 collated in Table II below. By way of comparison, a test was carried out with a catalyst based on nickel

and on a ligand, triphenylphosphine, in a single-phase medium.

Table II

Ex.	Salt	DC (%) 2M3BN	YD (%) 3PN + 4PN	YD (%) 2M2BN	YD (%) 2PN	Mass balance (%)
A	(1)	42	57	-3.1	5.8	86
1	[BMI] [TF ₂ N]	95	90	2.9	-0.4	96
2	[BMMI] [PF ₆]	93	90	0.2	2.3	94
3	[BMMI] [TF ₂ N]	96	94	0.8	1.6	98

(1) comparative test without ionic liquid with triphenylphosphine as ligand

5

Tests were carried out without using a nonpolar solvent, such as heptane, in order to obtain a single-phase system. The procedure used is identical to that described above, with the exception of the absence of nonpolar solvent. The results obtained are listed in Table III below:

Table III

Ex.	Ionic liquid	Dura- tion	DC 2M3BN	YD 3PN + 4PN	YD 2M2BN	YD 2PN	Mass balance
4	[BMMI] [TF ₂ N]	3 h	95	88	-0.1	0.2	92
5	[BMMI] [PF ₆]	3 h	94	90	1.3	1.1	95
6	[BMI] [TF ₂ N]	3 h	94	90	1.1	0.8	97

Hydrocyanation of 3PN to ADN

The following are introduced successively and under argon into a glass tube:

- 40 mg (0.145 mmol, 1 equivalent) of Ni(COD)_2
- 5 - 264 mg (0.72 mmol, 5 equivalents) of TPPMSNa
- 1.5 ml of ionic liquid or 2.1 g, if the salt is solid at ambient temperature
- 400 mg (4.93 mmol, 34 equivalents) of 3PN
- 1 equivalent of Lewis acid.

10 The tube is closed with a stopper fitted with a septum. The reaction mixture is stirred and heated at 70°C for 3 hours, during which period acetone cyanohydrin is slowly added (flow rate 0.12 ml/h, 0.36 ml, 3.95 mmol, 27 equivalents).

15 At the end of the reaction, 15 ml of acetone are added to the tube, which has been cooled to ambient temperature. The solution is stirred for 10 minutes and then poured into a flask containing a known amount of butylbenzene (approximately 250 mg, to act as

20 chromatography internal standard). This solution is filtered and injected in GC.

A first series of examples was carried out using various Lewis acids. The results obtained are shown in Table IV below:

Table IV

Ex.	7	8	9	10	11	12
Ligand	TPPMSNa					
Ionic liquid	BMMI TF ₂ N					
Lewis acid	ZnCl ₂	BPh ₃	In(CF ₃ SO ₃) ₃	CoCl ₂	ZnPh ₂	Zn(CF ₃ SO ₃) ₂
DC (in %)	25.9	11.0	5.1	8.9	3.6	26.8
L (in %)	57.3	45.5	78.5	57.9	50.6	50.9
TY (DN) (in %)	16.0	6.1	0.9	3.9	1.8	13.1
TY (NV) (in %)	2.1	3.6	0.9	1.2	1.5	1.7
Mass balance (in %)	92.1	98.6	96.7	96.2	99.7	87.9

A second series of examples was carried out using various ionic liquids and ligands. The results obtained are shown in Table V below:

Table V

Ex.	13	14	15	16	17
Ligands	TPPMSNa	P(Ph) ₂ PhSO ₂ Na	P(Ph) ₂ FuCO ₂ Na	TPPMSNa	P(Ph) ₂ FuCO ₂ Na
Ionic liquid		BMMI TF ₂ N		BMI TF ₂ N	BMMI PF ₆
Lewis acid			ZnCl ₂		
DC 3PN (in %)	25.9	5.7	12.1	32.5	4.5
L (in %)	57.3	36.6	19.8	60.0	16.9
TY (DN) (in %)	16.0	2.0	7.5	23.3	2.5
TY (NV) (in %)	2.1	1.1	1.3	2.8	1.1
Mass balance (in %)	92.1	97.4	96.7	93.5	99.1

CLAIMS

1. Process for the manufacture of organic compounds comprising at least one nitrile functional group by reaction between hydrogen cyanide and an organic compound comprising at least one ethylenic unsaturation in the presence of a catalyst comprising an element chosen from the group consisting of nickel, platinum and palladium and an organophosphorus ligand, characterized in that the reaction is carried out in the presence of an ionic liquid which comprises at least one cation and at least one anion and which is liquid at least at the temperature at which the reaction is carried out.
2. Process according to Claim 1, characterized in that a solvent of low polarity is added to the reaction medium in order to form a two-phase system.
3. Process according to Claim 1 or 2, characterized in that the organophosphorus ligand comprises at least one ionizable functional group or one ionic group.
4. Process according to Claim 1 or 3, characterized in that the ionic liquid comprises at least one cation chosen from the group consisting of the structures tetraalkylammonium, N-alkylimidazolium, N-alkylpyridinium, N-alkylpicolinium,

N-alkyltriazolium, N-alkylfluoropyrazolium,
N-pyrrolidinium, alkylsulphonium, tetraalkylphosphonium
and alkyloxonium.

5. Process according to one of Claims 1 to
5 4, characterized in that the ionic liquid comprises at
least one anion chosen from the group consisting of
halides, nitrate, phosphate, hydrosulphate,
perfluoroalkylsulphonates, bis(perfluoroalkyl-
sulphonyl)amides, bis(fluorosulphonyl)amide,
10 bis(fluorophosphoryl)amide, tris(perfluoroalkyl-
sulphonyl)methides, boron, aluminium, gallium or iron
tetrahalides, phosphorus, arsenic and antimony
hexahalides, zinc and tin trihalides, and copper
dihalides.

15 6. Process according to Claim 5,
characterized in that the anion is chosen from the
group consisting of Br^- , I^- , BF_4^- , PF_6^- , SbF_6^- , AlCl_4^- ,
 ZnCl_3^- , SnCl_3^- and $(\text{CF}_3\text{SO}_2)_2\text{N}^-$.

7. Process according to one of Claims 4 to
20 6, characterized in that the cation is chosen from the
group consisting of 1,3-dimethylimidazolium, 1-butyl-
2,3-dimethylimidazolium, 1-butyl-3-methylimidazolium
and 1,2,3-trimethylimidazolium.

8. Process according to one of Claims 1 to
25 7, characterized in that the ligand is chosen from the
group consisting of mono- and polydentate
organophosphites, organophosponites,

organophosphinites and organophosphines.

9. Process according to Claim 8, characterized in that the organophosphorus ligand comprises at least one ionic group.

5 10. Process according to Claim 9, characterized in that the ionic group present in the organophosphorus ligands is chosen from the group consisting of groups of anionic type belonging to the group consisting of sulphonate, phosphonate,
10 phosphinite, carboxylate and sulphinate anions or of cationic type belonging to the group consisting of guanidinium, ammonium, pyridinium, imidazolium, phosphonium and sulphonium cations.

11. Process according to one of Claims 1 to
15 8, characterized in that the organophosphorus ligand is chosen from the group consisting of tributylphosphine, dimethyl(n-octyl)phosphine, tricyclohexylphosphine, triphenylphosphine, tolylphosphine, tris(p-methoxyphenyl)phosphine, diphenylethylphosphine,
20 dimethylphenylphosphine, 1,4-bis(diphenylphosphino)butane, triethyl phosphite and diphenyl phosphite.

12. Process according to Claim 9 or 10, characterized in that the organophosphorus ligand is
25 chosen from the group consisting of triphenylphosphine(mono meta sodium sulphate), (5-sodiocarboxyfur-2-yl)diphenylphosphine and

(3-sodiosulphinatophenyl)diphenylphosphine.

13. Process according to one of Claims 2 to 12, characterized in that the solvent of low polarity is chosen from the family consisting of saturated hydrocarbons chosen from the group consisting of hexane, heptane, octane and toluene and/or ethers chosen from the group consisting of diethyl ether, diisopropyl ether and methyl isobutyl ether.

14. Process according to one of the preceding claims, characterized in that the metal element of the catalyst is nickel in the 0 or 1 oxidation state.

15. Process according to one of the preceding claims, characterized in that the organic compound comprising at least one ethylenic unsaturation is an olefin or a diolefin comprising from 3 to 12 carbon atoms.

16. Process according to one of the preceding claims, characterized in that the organic compound comprising at least one ethylenic unsaturation is 1,3-butadiene.

17. Process according to one of Claims 1 to 14, characterized in that the organic compound to be hydrocyanated comprises at least one ethylenic unsaturation and one nitrile functional group.

18. Process according to Claim 17, characterized in that the compound comprising a nitrile

functional group is chosen from the group consisting of 3-pentenitrile and 4-pentenitrile.

19. Process according to one of Claims 1 to 14, characterized in that it consists in isomerizing
5 branched unsaturated nitrile compounds to linear nitrile compounds.

20. Process according to Claim 19, characterized in that the isomerization stage is carried out in the absence of hydrogen cyanide.

10 21. Process according to either of Claims 17 and 18, characterized in that the reaction is carried out in the presence of a Lewis acid.

22. Process according to Claim 21, characterized in that the Lewis acid is chosen from the
15 group consisting of the compounds of the elements from Groups Ib, IIb, IIIa, IIIb, IVa, IVb, Va, Vb, VIb, VIIb and VIII of the Periodic Table.

23. Process according to Claim 22, characterized in that the said compounds are chosen
20 from the group consisting of halides, sulphates, sulphonates, carboxylates, phosphates, halosulphonates, perhaloalkylsulphonates chosen from the group consisting of fluoroalkylsulphonates and perfluoroalkylsulphonates,
25 bis(perfluoroalkylsulphonyl)amides and tris(perfluoroalkylsulphonyl)methides.

24. Process according to Claim 21,

characterized in that the ionic liquid comprises an anion forming the Lewis acid.

25. Process according to one of the preceding claims, characterized in that the reaction is
5 carried out at a temperature of between 10°C and 200°C.