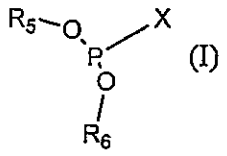
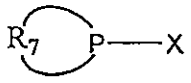
CLAIMS

1. Process for the hydrocyanation of a hydrocarbon-based compound comprising at least one ethylenic unsaturation, by reaction in a liquid medium with hydrogen cyanide in the presence of a catalyst comprising a metal element chosen from transition metals and an organophosphorus ligand, characterized in that the organophosphorus ligand comprises at least one compound corresponding to general formula (I) or (II):



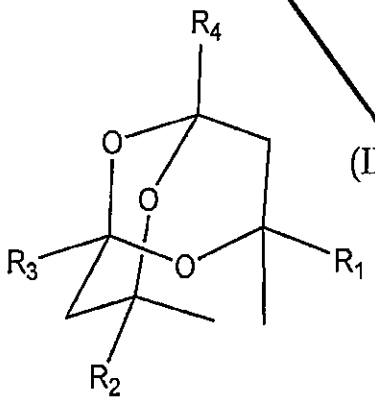
(I)



(II)

in which:

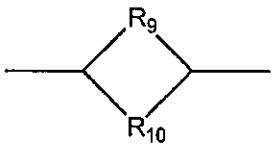
- R_5 and R_6, which may be identical or different, represent a linear or branched, aliphatic monovalent radical, a monovalent radical comprising an aromatic or cycloaliphatic ring, which is substituted or unsubstituted, or several aromatic rings which are condensed or connected to one another by a covalent bond,
- R_7 represents a divalent radical of general formula (III) below:



(III)

or a divalent radical of formula –O-R_8-O-, in which R_8 represents a linear or branched, aliphatic divalent radical, a divalent radical comprising an aromatic or cycloaliphatic ring, which is substituted or unsubstituted, or several aromatic rings which are condensed or connected to one another by a covalent bond,

or a divalent radical of general formula (IV) below:



(IV)

in which R_9 and R_{10}, which may be identical or different, represent a linear or branched, aliphatic divalent radical containing from 1 to 6 carbon atoms,

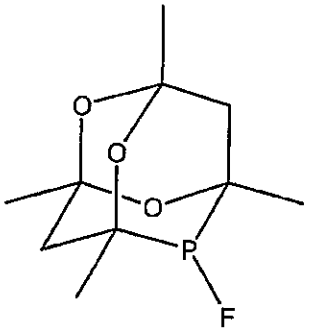
R_1, R_2, R_3 and R_4, which may be identical or different, represent a hydrogen atom, a linear or branched alkyl radical containing from 1 to 12 carbon atoms that may contain heteroatoms, a radical comprising a substituted or unsubstituted aromatic or cycloaliphatic radical which may comprise heteroatoms, a carbonyl, alkoxycarbonyl or alkoxy radical, a halogen atom, a nitrile group or a haloalkyl group containing from 1 to 12 carbon atoms,

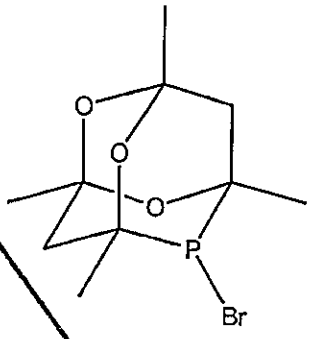
X represents a halogen atom selected from the group consisting of fluorine and bromine.

2. Process according to Claim 1, characterized in that R_1, R_2, R_3 and R_4, which may be identical or different, represent a hydrogen atom, or a linear or branched alkyl radical containing from 1 to 12 carbon atoms that may contain heteroatoms.

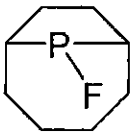
3. Process according to Claim 1 or 2, characterized in that the phosphorus ligand is a compound of general formula (II) in which R_7 represents a divalent radical of general formula (III) or (IV).

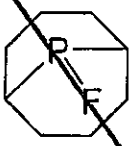
4. Process according to one of the preceding claims, characterized in that the compound of general formula (II) corresponds to either of the following formulae:





5. Process according to one of Claims 1 to 3, characterized in that the compound of general formula (II) corresponds to either of the following formulae:





6. Process according to one of the preceding claims, characterized in that the metal element is selected from the group consisting of nickel, cobalt, iron, ruthenium, rhodium, palladium, osmium, iridium, platinum, copper, silver, gold, zinc, cadmium and mercury.

7. Process according to one of the preceding claims, characterized in that the composition of the catalytic system is expressed by general formula (V):

$$M\,[L_f]_t \qquad (V)$$

in which:

M is a transition metal,

L_f represents the organophosphorus ligand(s), at least one of which corresponds to a compound of formula (I) or (II),
t represents a number between 1 and 10 (limits included).

8. Process according to Claim 7, characterized in that L_f represents a mixture of organophosphorus ligands comprising at least one ligand corresponding to a compound of formula (I) or (II) and at least one monodentate organophosphite ligand.

9. Process according to Claim 8, characterized in that the monodentate organophosphite ligand is selected from the group consisting of tritolyl phosphite and triphenyl phosphite.

10. Process according to one of the preceding claims, characterized in that the organic compounds comprising at least one ethylenic double bond are chosen from diolefins such as butadiene, isoprene, 1,5-hexadiene, 1,5-cyclooctadiene, ethylenically unsaturated aliphatic nitriles, in particular linear pentenenitriles such as 3-pentenenitrile or 4-pentenenitrile, monoolefins such as styrene, methylstyrene, vinylnaphthalene, cyclohexene or methylcyclohexene, and also mixtures of several of these compounds.

11. Process according to one of the preceding claims, characterized in that the amount of compound of nickel or of another transition metal used is chosen such that there is, per mole of organic compound to be hydrocyanated or isomerized, between 10^{-4} and 1 mol of nickel or of the other transition metal used, and in that the amount of organophosphorus compounds used is chosen such that the number of moles of these compounds with respect to 1 mol of transition metal is from 0.5 to 100.

12. Process according to one of the preceding claims, for the hydrocyanation of ethylenically unsaturated nitrile compounds so as to give dinitriles, by reaction with hydrogen cyanide, characterized in that the reaction is carried out in the presence of a catalytic system comprising at least one compound of a transition metal, at least one compound of formula (I) or (II) and a cocatalyst consisting of at least one Lewis acid.

13. Process according to Claim 12, characterized in that the ethylenically unsaturated nitrile compounds are chosen from ethylenically unsaturated aliphatic nitriles comprising linear pentenenitriles, such as 3-pentenenitrile, 4-pentenenitrile, and mixtures thereof.

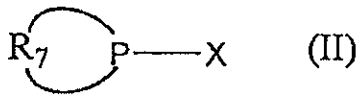
14. Process according to either of Claims 12 and 13, characterized in that the Lewis acid used as cocatalyst is chosen from the compounds of the elements from groups Ib, IIb, IIIa, IIIb, IVa, IVb, Va, Vb, VIb, VIIb and VIII of the Periodic Table of Elements.

15. Process according to one of Claims 12 to 14, characterized in that the Lewis acid is chosen from zinc chloride, zinc bromide, zinc iodide, manganese chloride, manganese bromide, cadmium chloride, cadmium bromide, stannous chloride, stannous bromide, stannous sulphate, stannous tartrate, indium trifluoromethylsulphonate, the chlorides or bromides of rare-earth elements, such as lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, hafnium, erbium, thallium, ytterbium and lutetium, cobalt chloride, ferrous chloride, yttrium chloride and mixtures thereof, and organometallic compounds.

16. Process according to one of Claims 1 to 15, characterized in that the isomerization, so as to give pentenenitriles, of the 2-methyl-3-butenenitrile present in the reaction mixture originating from the hydrocyanation of butadiene is carried out in the absence of hydrogen cyanide, the isomerization being carried out in the presence of a catalyst comprising at least one compound of formula (I) or (II) and at least one compound of a transition metal.

CLAIMS

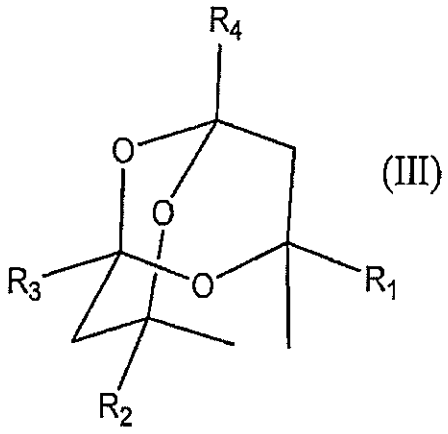
1. Process for the hydrocyanation of a hydrocarbon-based compound comprising at least one ethylenic unsaturation, by reaction in a liquid medium with hydrogen cyanide in the presence of a catalyst comprising a metal element chosen from transition metals and an organophosphorus ligand, characterized in that the organophosphorus ligand comprises at least one compound corresponding to general formula (II):



(II)

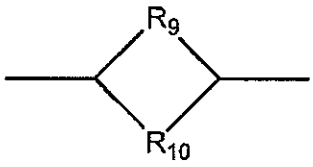
in which:

- R_7 represents a divalent radical of general formula (III) below:



(III)

or a divalent radical of general formula (IV) below:



(IV)

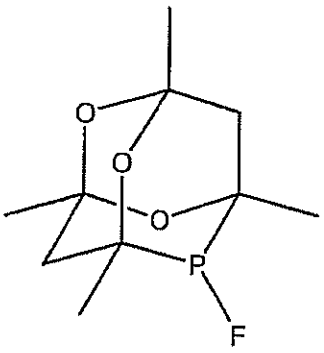
in which R_9 and R_{10}, which may be identical or different, represent a linear or branched, aliphatic divalent radical containing from 1 to 6 carbon atoms,

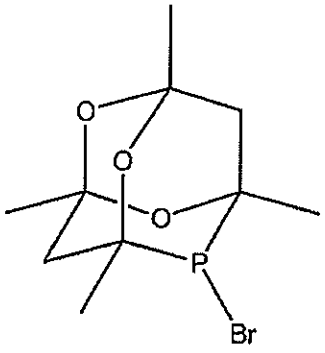
R_1, R_2, R_3 and R_4, which may be identical or different, represent a hydrogen atom, a linear or branched alkyl radical containing from 1 to 12 carbon atoms that may contain heteroatoms, a radical comprising a substituted or unsubstituted aromatic or cycloaliphatic radical which may comprise heteroatoms, a carbonyl, alkoxycarbonyl or alkoxy radical, a halogen atom, a nitrile group or a haloalkyl group containing from 1 to 12 carbon atoms,

X represents a halogen atom selected from the group consisting of fluorine and bromine.

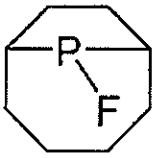
2. Process according to Claim 1, characterized in that R_1, R_2, R_3 and R_4, which may be identical or different, represent a hydrogen atom, or a linear or branched alkyl radical containing from 1 to 12 carbon atoms that may contain heteroatoms.

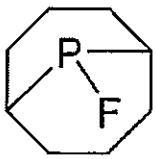
3. Process according to one of the preceding claims, characterized in that the compound of general formula (II) corresponds to either of the following formulae:





4. Process according to one of Claims 1 and 2, characterized in that the compound of general formula (II) corresponds to either of the following formulae:





5. Process according to one of the preceding claims, characterized in that the metal element is selected from the group consisting of nickel, cobalt, iron, ruthenium, rhodium, palladium, osmium, iridium, platinum, copper, silver, gold, zinc, cadmium and mercury.

6. Process according to one of the preceding claims, characterized in that the composition of the catalytic system is expressed by general formula (V):

$$M\,[L_f]_t \qquad (V)$$

in which:
M is a transition metal,
L_f represents the organophosphorus ligand(s), at least one of which corresponds to a compound of formula (II),
t represents a number between 1 and 10 (limits included).

7. Process according to Claim 6, characterized in that L_f represents a mixture of organophosphorus ligands comprising at least one ligand corresponding to a compound of formula (II) and at least one monodentate organophosphite ligand.

8. Process according to Claim 7, characterized in that the monodentate organophosphite ligand is selected from the group consisting of tritolyl phosphite and triphenyl phosphite.

9. Process according to one of the preceding claims, characterized in that the organic compounds comprising at least one ethylenic double bond are chosen from diolefins such as butadiene, isoprene, 1,5-hexadiene, 1,5-cyclooctadiene, ethylenically unsaturated aliphatic nitriles, in particular linear pentenenitriles such as 3-pentenenitrile or 4-pentenenitrile, monoolefins such as styrene, methylstyrene, vinylnaphthalene, cyclohexene or methylcyclohexene, and also mixtures of several of these compounds.

10. Process according to one of the preceding claims, characterized in that the amount of compound of nickel or of another transition metal used is chosen such that there is, per mole of organic compound to be hydrocyanated, between 10^{-4} and 1 mol of nickel or of the other transition metal used, and in that the amount of organophosphorus compounds used is chosen such that the number of moles of these compounds with respect to 1 mole of transition metal is from 0.5 to 100.

11. Process according to one of the preceding claims, for the hydrocyanation of ethylenically unsaturated nitrile compounds so as to give dinitriles, by reaction with hydrogen cyanide, characterized in that the reaction is carried out in the presence of a catalytic system comprising at least one compound of a transition metal, at least one compound of formula (II) and a cocatalyst consisting of at least one Lewis acid.

12. Process according to Claim 11, characterized in that the ethylenically unsaturated nitrile compounds are chosen from ethylenically unsaturated aliphatic nitriles comprising linear pentenenitriles, such as 3-pentenenitrile, 4-pentenenitrile, and mixtures thereof.

13. Process according to either of Claims 11 and 12, characterized in that the Lewis acid used as cocatalyst is chosen from the compounds of the elements from groups Ib, IIb, IIIa, IIIb, IVa, IVb, Va, Vb, VIb, VIIb and VIII of the Periodic Table of Elements.

14. Process according to one of Claims 11 to 13, characterized in that the Lewis acid is chosen from zinc chloride, zinc bromide, zinc iodide, manganese chloride, manganese bromide, cadmium chloride, cadmium bromide, stannous chloride, stannous bromide, stannous sulphate, stannous tartrate, indium trifluoromethylsulphonate, the chlorides or bromides of rare-earth elements, such as lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, hafnium, erbium, thallium, ytterbium and lutetium, cobalt chloride, ferrous chloride, yttrium chloride and mixtures thereof, and organometallic compounds.

15. Process according to one of Claims 1 to 14, characterized in that the isomerization, so as to give pentenenitriles, of the 2-methyl-3-butenenitrile present in the reaction mixture originating from the hydrocyanation of butadiene is carried out in the absence of hydrogen cyanide, the isomerization being carried out in the presence of a catalyst comprising at least one compound of formula (II) and at least one compound of a transition metal.