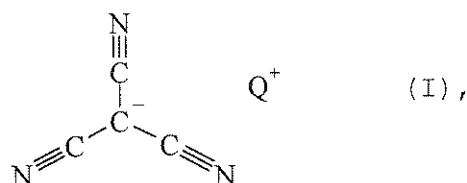


Method For The Production Of Tricyanomethanides Of Organic Cations

The invention relates to a process for preparing ionic liquids of the formula



where Q^+ is an organic cation containing at least one heteroatom selected from the group consisting of nitrogen, phosphorus, sulfur and oxygen.

15 The ionic liquids of the formula I are tricyanomethane salts or tricyanomethanides. Tricyanomethane-metal salts and processes for preparing them are known from Schmidtman, H., *Ber.* 29, **1896**, 1172, and Trofimenko, S. et al., *J. Org. Chem.* 27, **1962**, 433-438. Tricyanomethane-metal salt complexes with organic
20 ligands are also known from Batten, S.R. et al., *Chem. Commun.* **1998**, 439-440. In the synthesis of metal tricyanomethanides, for example potassium tricyanomethanide, by the method of Trofimenko et al. from dibromomalononitrile, potassium cyanide and potassium bromide, 1.5 mol of Br_2 are formally reacted per
25 mole of tricyanomethanide.

Various tricyanomethane salts are also known from, for example, EP-A 0850 921, US 3981 899, Jäger, L. et al., *Z. Anorg. allg. Chem.* 611, **1992**, 62-72, Cioslowski, J. et al., *Chem. Phys. Lett.*
30 170, **1990**, 297-300, Elvidge, L.A. et al., *J. Chem. Soc. Perkin Trans. 1*, 8, **1983**, 1741-1744 and Makhon'kov, D.I. et al., *Zh. Org. Khim.* 15, 1979, 2441-2445. However, these are exclusively solids. EP-A 0010396 discloses various liquid ammonium tricyanomethanides which are used as fungicides and herbicides.

35 Salts of organic cations have a low vapour pressure and often a low melting point. They are referred to as ionic liquids when they are liquid at room temperature. In recent years, ionic

liquids have become known as environmentally friendly solvents for "green chemistry". The melting point of an ionic liquid and thus the temperature range as solvent is influenced by variation of the anions and cations. At present, various ionic liquids for use ranges from about -60 °C to above 300 °C are available.

The organic cations of ionic liquids are usually monovalent quaternary ammonium or phosphonium bases or cations of aromatic, usually nitrogen-containing bases which may be additionally substituted by alkyl groups, halogen atoms or cyano groups and can contain further heteroatoms such as phosphorus, sulfur or oxygen. Examples of customary organic cations are imidazolium, oxazolium, pyrazinium, pyrazolium, pyridazinium, pyrrolidinium, pyrimidinium, thiazolium and triazolium cations. Imidazolium and pyrrolidinium cations are used most frequently. The cations can be represented with a charge localized on at least one heteroatom or delocalized in the middle of a ring or also in complex notation. All types of depiction are used as equivalents to one another.

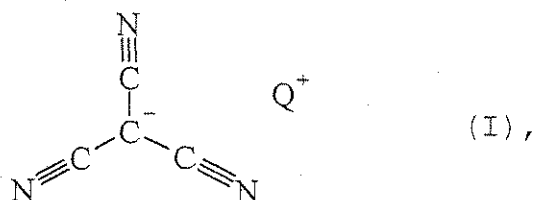
Typical anions in ionic liquids are acetate, AlCl_4^- , AsF_6^- , BF_4^- , bromide, CF_3SO_3^- , $(\text{CF}_3)_2\text{PF}_4^-$, $(\text{CF}_3)_3\text{PF}_3^-$, $(\text{CF}_3)_4\text{PF}_2^-$, $(\text{CF}_3)_5\text{PF}^-$, $(\text{CF}_3)_6\text{P}^-$, chloride, CN^- , FeCl_3^- , NO_3^- , PF_6^- , pyruvate, oxalate or SCN^- . Most frequently used anions are AlCl_4^- , AsF_6^- , BF_4^- and PF_6^- .

Starting materials for the preparation of ionic liquids can be procured, for example, from Merck KGaA, Darmstadt, or IoLiTec, A. Bösmann, Dr T. Schubert G.b.R., Freiburg.

It was an object of the present invention to provide a novel inexpensive process for preparing tricyanomethanides which can be disposed of in an environmentally friendly manner after use.

This object is achieved according to Claim 1.

In one aspect, there is provided a process for preparing ionic liquids of the formula



where Q^+ is an organic cation selected from the group consisting of cations of the formula

a) $[\text{WR}^1\text{R}^2\text{R}^3\text{R}^4]^+$, where W is a nitrogen or phosphorus atom and

i) R^1 to R^3 are each, independently of one another, C_{1-20} -alkyl and R^4 is C_{1-20} -alkyl, C_{3-10} -cycloalkyl or C_{6-10} -aryl, where R^1 to R^4 may each contain, independently of one another, one or more halogen atoms, or

ii) R^1 and R^2 together with W form a 5- to 7-membered ring and R^3 and R^4 are each, independently of one another, C_{1-20} -alkyl, where R^3 and R^4 may each contain, independently of one another, one or more halogen atoms, or

iii) R^1 and R^2 and also R^3 and R^4 in each case together with W form a 5- to 7-membered ring, or

b) $[\text{NR}^5\text{R}^6\text{R}^7]^+$, where N is a nitrogen atom and R^5 and R^6 together with N form a ring in which N formally has one single bond and one double bond to R^5 and R^6 and R^7 is C_{1-20} -alkyl, C_{3-10} -cycloalkyl or C_{6-10} -aryl, where R^7 may contain one or more halogen atoms, or

c) $[\text{SR}^8\text{R}^9\text{R}^{10}]^+$, where S is a sulfur atom and

i) R^8 and R^9 are each, independently of one another, C_{1-20} -alkyl and R^{10} is C_{1-20} -alkyl, C_{3-10} -cycloalkyl or C_{6-10} -aryl, where R^8 to R^{10} may each contain, independently of one another, one or more halogen atoms, or

ii) R^8 and R^9 together with S form a 5- to 7-membered ring and R^{10} is C_{1-20} -alkyl, C_{3-10} -cycloalkyl or C_{6-10} -aryl, where R^{10} may contain one or more halogen atoms, or

d) $[\text{ZR}^{11}\text{R}^{12}]^+$, where Z is a sulfur or oxygen atom and R^{11} and R^{12} together with Z form a ring in which Z formally has a single bond and a double bond to R^{11} and R^{12} , and

one or more substituents from the group consisting of C_{1-20} -alkyl groups, C_{1-20} -alkoxy groups, C_{3-10} -cycloalkyl groups, C_{6-10} -aryl groups, halogen and cyano may be bound to each of the rings formed by the substituents R^1 to R^{12} , where the C_{1-20} -alkyl groups, C_{1-20} -alkoxy groups, C_{3-10} -cycloalkyl groups and C_{6-10} -aryl groups may each contain,

independently of one another, one or more halogen atoms,
and

each of the rings formed by the substituents R^1 to R^{12} may
contain one or two further heteroatoms from the group

consisting of nitrogen, sulfur and oxygen and/or may be fused
to another aromatic or nonaromatic 5- to 7-membered ring,

which comprises mixing malononitrile with a cyano compound of
the formula RCN , where R is selected from the group consisting
of chlorine, bromine, iodine and cyano, in the presence of a
base, if desired in the presence of a solvent, and adding a salt
(Q^+) $_nX^{n-}$, where $n = 1$ or 2 , Q^+ is as defined above and X^{n-} is an
anion selected from the group consisting of halides,
pseudohalides, sulfate and organic acid anions, with the anion
 X^{n-} being replaced in the aqueous phase by a tricyanomethanide
anion formed *in situ* from malononitrile and RCN .

In a preferred process variant, malononitrile, the cyano
compound of the formula RCN and the salt (Q^+) $_nX^{n-}$ are mixed in
the presence of a base, if desired in the presence of a further
solvent, in the aqueous phase, resulting in formation of and
exchange with the tricyanomethanide anion in a one-pot reaction.

A particular order of addition of malononitrile, the cyano
compound of the formula RCN , the base and the salt of the
formula (Q^+) $_nX^{n-}$ is not absolutely necessary. The order of
addition in the examples has been found to be useful from a
process engineering point of view, but in the laboratory any
other order of addition likewise leads to formation of the
compounds according to the invention.

The cyano compound of the formula RCN , the base and/or the salt
of the formula (Q^+) $_nX^{n-}$, where R , Q^+ , X^{n-} and n are as defined
above, can each be used in pure form or in solution, for example
in water and/or methanol. Further suitable solvents and/or
solubilizers can be selected from the group consisting of
acetone, acetonitrile, C_{1-4} -alcohols, chloroform, dichloroethane,
diethyl ether, DMSO, ethyl acetate, hexane, methylene chloride,
propylene carbonate, carbon disulfide, THF, toluene, xylene and

suitable mixtures thereof. Preference is given to using water-miscible solvents.

5 In a preferred embodiment, the cyano compound RCN is selected from the group consisting of cyanogen chloride, cyanogen bromide and dicyanogen, particularly preferably cyanogen chloride or dicyanogen.

10 In a further preferred embodiment, the molar ratio of malononitrile to cyano compound of the formula RCN is in the range from 0.2:1 to 2:1, particularly preferably from 0.9:1 to 1.1:1, very particularly preferably from 0.95:1 to 1.05:1.

15 Suitable bases in the process of the invention can be selected from the group consisting of alkali metal and alkaline earth metal hydroxides, alkali metal and alkaline earth metal carbonates, ammonia, primary, secondary and tertiary amines. The base is particularly preferably an alkali metal or alkaline earth metal hydroxide, very particularly preferably sodium
20 hydroxide and/or potassium hydroxide.

In a preferred process, the pH is maintained at a value above 4, preferably at a value above 7, particularly preferably in the range from 7 to 9, during the reaction.
25

The halide as anion X^{n-} of the salt of the formula $(Q^+)_nX^{n-}$ can be selected from the group consisting of fluoride, chloride, bromide and iodide. Particular preference is given to chloride.

30 As pseudohalide anions X^{n-} in the salt $(Q^+)_nX^{n-}$, it is possible to use anions which consist of at least two electronegative atoms and are chemically similar to halogens. The pseudohalide anions are preferably selected from the group consisting of CN^- , OCN^- , SCN^- and N_3^- . Particular preference is given to CN^- .

35 Suitable organic acid anions are, for example, anions of monobasic and dibasic nonaromatic and aromatic acids, for example acetate, oleate, fumarate, maleate, pyruvate, oxalate

and benzoate. Particular preference is given to acetate and pyruvate.

In a preferred process, the tricyanomethane salts of the formula I formed, where Q^+ is as defined above, are separated off from unreacted starting compounds and purified by extraction methods.

The process of the invention allows the production of ionic liquids having a very low chloride content.

An advantage of the process of the invention is the ability to prepare largely chloride- and sodium-free ionic liquids.

Here and in the following, the expression " C_{1-n} -alkyl" refers to an unbranched or branched alkyl group having from 1 to n carbon atoms. Thus, C_{1-20} -alkyl represents, for example, groups such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, pentyl, 1,4-dimethylpentyl, hexyl, heptyl, octyl, 1,5-dimethylhexyl, nonyl, decyl, 4-ethyl-1,5-dimethylhexyl, undecyl, dodecyl, tridecyl, tetradecyl or eicosyl.

Here and in the following, the expression " C_{3-n} -cycloalkyl" refers to a cycloalkyl group having from 3 to n carbon atoms. Thus, C_{3-10} -cycloalkyl represents, for example, groups such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl or cyclodecyl.

Here and in the following, the expression " C_{6-10} -aryl" refers to an aryl group having from 6 to 10 carbon atoms. Thus, C_{6-10} -aryl represents, for example, groups such as phenyl, benzyl, methylphenyl, dimethylphenyl, ethylmethylphenyl, diethylphenyl or naphthyl.

Here and in the following, the expression " C_{1-n} -alkoxy" refers to an unbranched or branched alkoxy group having from 1 to n carbon atoms. Thus, C_{1-20} -alkoxy represents, for example, groups such as methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, sec-butoxy, tert-butoxy, pentyloxy, 1,4-dimethylpentyloxy, hexyloxy, heptyloxy, octyloxy, 1,5-dimethylhexyloxy, nonyloxy, decyloxy,

4-ethyl-1,5-dimethylhexyloxy, undecyloxy, dodecyloxy, tridecyl-
oxy, tetradecyloxy or eicosyloxy.

Here and in the following, the expression "halogen" refers to
5 fluorine, chlorine, bromine or iodine.

In a preferred embodiment, the cation Q^+ contains at least one
5- to 7-membered aromatic or nonaromatic ring.

10 In a further preferred embodiment, an aromatic or nonaromatic
ring in the organic cation Q^+ contains one or two further
heteroatoms from the group consisting of nitrogen, sulfur and
oxygen. The cation Q^+ particularly preferably contains one
further nitrogen or sulfur atom.

15 Furthermore, one or more substituents from the group consisting
of C_{1-20} -alkyl groups, C_{1-20} -alkoxy groups, C_{3-10} -cycloalkyl groups,
 C_{6-10} -aryl groups, halogen and cyano can preferably be bound to
an aromatic or nonaromatic ring of the cation Q^+ . Here, the
20 C_{1-20} -alkyl groups, C_{1-20} -alkoxy groups, C_{3-10} -cycloalkyl groups,
 C_{6-10} -aryl groups may each contain, independently of one another,
one or more halogen atoms.

In the process of the invention, the cation Q^+ is particularly
25 preferably selected from the group consisting of organic am-
monium, phosphonium and sulfonium cations, pyrrolidinium, pyrro-
linium, pyrazolium, pyrazolium, imidazolium, triazolium,
oxazolium, thiazolium, piperidinium, piperazinium, morpholinium,
pyridinium, pyridazinium, pyrimidinium, pyrazinium, 1,3-dioxo-
30 lium, pyrylium, thiopyrylium, azoniaspiro and phosphoniaspiro
cations.

In a further particularly preferred embodiment, the cation Q^+ is
selected from the group consisting of N,N -di(C_{1-20} -alkyl)- N,N -
35 (dimethyl)ammonium, N -(C_{6-10} -aryl)- N,N,N -tri(C_{1-20} -alkyl)ammonium,
 N,N -di(C_{6-10} -aryl)- N,N -(dimethyl)ammonium, tetramethylphos-
phonium, tetrabutylphosphonium, trimethylsulfonium, tributylsul-
fonium, 1-(C_{1-20} -alkyl)-3-methylpyridinium, 1-(C_{1-20} -alkyl)-3-
cyanopyridinium, 1-(C_{1-20} -alkyl)-1-methylpyrrolidinium, 1-(C_{1-20} -

alkyl)-1,3-dimethylpiperidinium, 1-(C₁₋₂₀-alkyl)-1-methylimidazolium, 1-(C₁₋₂₀-alkyl)-3-ethylpyridinium, 4,5-dimethyl-2-(diphenylmethyl)-1,3-dioxolium, 2-(diphenylmethyl)-4,5-diphenyl-1,3-dioxolium, 6-azoniaspiro[5.5]undecane and 5-phosphonia-spiro[4.4]nonane cations.

Ionic liquids of the formula I, where Q⁺ is as defined above, can, optionally in admixture with one or more other ionic liquids, water or organic solvents, be used as solvents and in particular as constituent of polar solvents. The tricyanomethanides can particularly advantageously be used as conductive solvents in electrochemistry or electrosynthesis, so that the addition of electrolyte salts can be reduced or be dispensed with entirely.

The polarity of ionic liquids based on tricyanomethanides is lower than that of customary ionic liquids but higher than that of customary organic solvents, so that new fields of application are opened here.

Ionic liquids based on tricyanomethanides are relatively nonpolar ionic liquids which have low solubilities in water and low viscosities compared to other ionic liquids.

The use of ionic liquids based on tricyanomethanides has the advantage over many other ionic liquids that no metal-containing residues are formed in thermal disposal. The compounds obtained by the process of the invention also have particularly low halide values.

The following examples illustrate the invention but do not constitute a restriction.

Examples:

Example 1: 1-Butyl-1-methylpyrrolidinium chloride

Methylpyrrolidine (150 g, 1.76 mol) is placed in a reaction vessel and mixed with butyl chloride (163 g, 1.76 mol) at room

temperature. The reaction mixture obtained is then refluxed for 24 hours (reaction temperature about 77 °C), resulting in formation of a slightly yellowish suspension. The reaction mixture is then cooled to room temperature and filtered. The residue is washed with a little MTBE and subsequently dried at 50 °C under reduced pressure to give pure 1-butyl-1-methylpyrrolidinium chloride (27 g, 0.09 mol, 8.6% conversion). The remaining material of the reaction mixture consists exclusively of the unreacted starting materials methylpyrrolidine and butyl chloride, which are recovered completely. The melting point of the 1-butyl-1-methylpyrrolidinium chloride obtained is 199.5 °C. ¹H NMR (d₆-DMSO): δ = 3.50 (m, 4H), 3.36 (m, 2H), 3.02 (s, 3H), 2.08 (s br, 4H), 1.68 (m, 2H), 1.33 (sext, J = 7.3 Hz, 2H), 0.94 ppm (t, J = 7.6 Hz, 3H); ¹³C NMR (d₆-DMSO): δ = 64.0 (CH₂), 63.4 (CH₂), 48.1 (CH₃), 25.6 (CH₂), 21.8 (CH₂), 20.0 (CH₂), 14.2 ppm (CH₃).

Example 2: 1-Butyl-1-methylpyrrolidinium tricyanomethanide
Malononitrile (17.8 g, 264 mmol) and water (300 ml) are placed in a reaction vessel and cyanogen chloride (16.5 g, 0.268 mmol) is passed into the reaction solution at 0-5 °C, with the pH of the reaction solution being maintained at 8.5 by appropriate addition of 30% strength sodium hydroxide solution during introduction of the cyanogen chloride. The reaction temperature of the solution is maintained at 0-5 °C for about 1 hour during the introduction of the cyanogen chloride. A mixture of 1-butyl-1-methylpyrrolidinium chloride (47.5 g, 0.267 mmol) and water (150 ml) is added to the reaction mixture. The organic phase is separated off and the aqueous phase is extracted with dichloromethane (2 × 100 ml). The combined organic phases are extracted with water (4 × 75 ml). The organic phase is admixed with activated carbon (3 g) and stirred at RT for 30 minutes. The organic phase is subsequently filtered off and evaporated at 40-60 °C on a rotary evaporator (from about 500 mbar to about 20 mbar). This gives 1-butyl-1-methylpyrrolidinium tricyanomethanide (46.8 g, 201 mmol, yield: 76%). The chloride content is < 0.1%. The viscosity at 20 °C is 33 mPa·s.

^1H NMR (d_6 -DMSO): δ = 3.44 (m, 4H), 3.28 (m, 2H), 2.98 (s, 3H), 2.08 (s br, 4H), 1.69 (m, 2H), 1.32 (sext, J = 7.3 Hz, 2H), 0.94 ppm (t, J = 7.6 Hz, 3H);

^{13}C NMR (d_6 -DMSO): δ = 120.5 (C_q), 63.5 (CH_2), 63.0 (CH_2), 47.6 (CH₃), 24.9 (CH_2), 21.1 (CH_2), 19.3 (CH_2), 13.4 (CH₃), 4.7 ppm (C_q).

Example 3: 1-Butyl-3-methylimidazolium tricyanomethanide

A solution of 1-butyl-3-methylimidazolium chloride (43.1 g, 178 mmol) in water (100 ml) is added as described in Example 2 to a mixture of malononitrile and cyanogen chloride. This gives 1-butyl-3-methylimidazolium tricyanomethanide (33.6 g, 147 mmol, 82% yield) having a chloride content of < 0.1%. The viscosity at 20 °C is 30 mPa·s.

^1H NMR (d_6 -DMSO): δ = 9.05 (s, 1H), 7.67 (t, J = 1.8 Hz, 1H), 7.61 (t, J = 1.8 Hz, 1H), 4.07 (t, J = 7.2 Hz, 2H), 3.83 (s, 3H), 1.80 (t-sept, 1J = 12.4 Hz, 2J = 1.8 Hz, 2H), 1.26 (t-sext, 1J = 7.5 Hz, 2J = 1.8 Hz, 2H), 0.89 ppm (t, J = 7.4 Hz, 3H);

^{13}C NMR (d_6 -DMSO): δ = 136.5 (CH), 123.5 (CH), 122.2 (CH), 120.5 (C_q), 48.6 (CH_2), 35.7 (CH₃), 31.3 (CH_2), 18.8 (CH_2), 13.1 (CH₃), 4.8 ppm (C_q).

Example 4: 1-Ethyl-3-methylimidazolium tricyanomethanide

A solution of 1-ethyl-3-methylimidazolium chloride (178.4 g, 1.22 mol) in water (180 ml) is added as described in Example 2 to a mixture of malononitrile (84.6 g, 1.28 mol) and cyanogen chloride (79.9 g, 1.30 mol). The reaction mixture obtained in this way does not undergo phase separation and is firstly treated with activated carbon (3%) as in Example 2 and subsequently extracted with dichloromethane (300 ml). The organic phase is then washed with water (2 × 200 ml). Evaporation at 40-60°C on a rotary evaporator (from about 500 mbar to about 20 mbar) gives 169.5 g (69% yield) of 1-ethyl-3-methylimidazolium tricyanomethanide having a chloride content and a sodium content of in each case less than 10 ppm.

^1H NMR (d_6 -DMSO): δ = 9.09 (s, 1H), 7.72 (t, J = 1.7 Hz, 1H), 7.64 (t, J = 1.7 Hz, 1H), 4.21 (t, J = 7.4 Hz, 2H), 3.86 (s, 3H), 1.45 ppm (t, J = 7.4 Hz, 3H);

^{13}C NMR (d_6 -DMSO): δ = 136.4 (CH), 124.4 (CH), 122.8 (CH), 121.7 (C_q), 45.4 (CH_2), 36.7 (CH_3), 15.8 (CH_3), 6.7 ppm (C_q).

Example 5: 1-Butyl-3-methylpyridinium tricyanomethanide

5 A solution of 1-butyl-3-methylpyridinium chloride (939.6 g, 5.06 mol) in water (813 ml) is added as described in Example 2 to a mixture of malononitrile (351.0 g, 5.31 mol) and cyanogen chloride (333.1 g, 5.42 mol). The reaction mixture separates into two phases, and the aqueous phase is separated off and
10 extracted with dichloromethane (1290 ml). The organic phases are combined, treated with activated carbon (3%) and then washed with water (4×900 ml). Evaporation at 40-60 °C on a rotary evaporator (from about 500 mbar to about 20 mbar) gives 1118 g (92% yield) of 1-butyl-3-methylpyridinium tricyanomethanide
15 having a chloride content and a sodium content of in each case less than 10 ppm.

^1H NMR (d_6 -DMSO): δ = 8.95 (s, 1H), 8.87 (d, J = 6.1 Hz, 1H), 8.40 (d, J = 8.0 Hz, 1H), 8.01 (t, J = 7.1 Hz, 1H), 4.53 (t, J = 7.4 Hz, 2H), 2.49 (s, 3H), 1.90 (m, 2H), 1.29 (t-sext, J = 7.5 Hz, 2H), 0.90 ppm (t, J = 7.4 Hz, 3H);
20

^{13}C NMR (d_6 -DMSO): δ = 145.5 (CH), 144.1 (CH), 141.8 (CH), 138.7 (C_q), 127.2 (CH), 120.4 (C_q), 60.4 (CH_2), 32.4 (CH_2), 18.7 (CH_2), 17.7 (CH_3), 13.10 (CH_3), 4.6 ppm (C_q).

25 Example 6: 1-Octyl-3-methylpyridinium tricyanomethanide

A solution of 1-octyl-3-methylpyridinium chloride (125.8 g, 520 mmol) in water (300 ml) is added as described in Example 2 to a mixture of malononitrile (36.0 g, 534 mmol) and cyanogen chloride (31.4 g, 537 mmol). The reaction mixture separates into
30 two phases, and the aqueous phase is separated off and extracted with dichloromethane (300 ml). The organic phases are combined, treated with activated carbon (3%) and then washed with water (4×125 ml). Evaporation at 40-60 °C on a rotary evaporator (from about 500 mbar to about 20 mbar) gives 137.8 g (89% yield)
35 of 1-octyl-3-methylpyridinium tricyanomethanide having a chloride content and a sodium content of in each case less than 100 ppm.

^1H NMR (d_6 -DMSO): δ = 8.96 (s, 1H), 8.88 (d, J = 6.3 Hz, 1H), 8.40 (d, J = 8.0 Hz, 1H), 8.01 (dd, 1J = 8.2 Hz, 2J = 6.2 Hz,

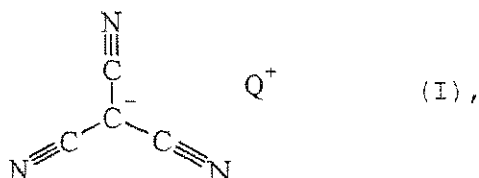
1H), 4.52 (t, $J = 7.4$ Hz, 2H), 2.49 (s, 3H), 1.90 (p, $J = 7.1$ Hz, 2H), 1.26 (m, 10H), 0.83 ppm (m, 3H);

^{13}C NMR ($\text{d}_6\text{-DMSO}$): $\delta = 145.5$ (CH), 144.0 (CH), 141.8 (CH), 138.7 (C_q), 127.2 (CH), 120.3 (C_q), 60.6 (CH₂), 31.0 (CH₂), 30.5 (CH₂),
5 28.3 (CH₂), 28.2 (CH₂), 25.3 (CH₂), 21.9 (CH₂), 17.7 (CH₃), 13.7 (CH₃), 4.6 ppm (C_q).

Claims

1. Process for preparing ionic liquids of the formula

5



10 where Q^+ is an organic cation selected from the group consisting of cations of the formula

- a) $(\text{WR}^1\text{R}^2\text{R}^3\text{R}^4)^+$, where W is a nitrogen or phosphorus atom and

15

- i) R^1 to R^3 are each, independently of one another, C_{1-20} -alkyl and R^4 is C_{1-20} -alkyl, C_{3-10} -cycloalkyl or C_{6-10} -aryl, where R^1 to R^4 may each contain, independently of one another, one or more halogen atoms, or

- ii) R^1 and R^2 together with W form a 5- to 7-membered ring and R^3 and R^4 are each, independently of one another, C_{1-20} -alkyl, where R^3 and R^4 may each contain, independently of one another, one or more halogen atoms, or

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- iii) R^1 and R^2 and also R^3 and R^4 in each case together with W form a 5- to 7-membered ring, or

25

- b) $(\text{NR}^5\text{R}^6\text{R}^7)^+$, where N is a nitrogen atom and R^5 and R^6 together with N form a ring in which N formally has one single bond and one double bond to R^5 and R^6 and R^7 is C_{1-20} -alkyl, C_{3-10} -cycloalkyl or C_{6-10} -aryl, where R^7 may contain one or more halogen atoms, or

30

- c) $(\text{SR}^8\text{R}^9\text{R}^{10})^+$, where S is a sulfur atom and

- i) R^8 and R^9 are each, independently of one another, C_{1-20} -alkyl and R^{10} is C_{1-20} -alkyl, C_{3-10} -cycloalkyl or C_{6-10} -aryl, where R^8 to R^{10} may each contain, independently of one another, one or more halogen atoms, or

35

- ii) R^8 and R^9 together with S form a 5- to 7-membered ring and R^{10} is C_{1-20} -alkyl, C_{3-10} -cycloalkyl or C_{6-10} -aryl, where R^{10} may contain one or more halogen atoms, or

- d) $(\text{ZR}^{11}\text{R}^{12})^+$, where Z is an oxygen or sulfur atom and R^{11} and R^{12} together with Z form a ring in which Z

formally has a single bond and a double bond to R^{11} and R^{12} , and

one or more substituents from the group consisting of C_{1-20} -alkyl groups, C_{1-20} -alkoxy groups, C_{3-10} -cycloalkyl groups, C_{6-10} -aryl groups, halogen and cyano may be bound to each of the rings formed by the substituents R^1 to R^{12} , where the C_{1-20} -alkyl groups, C_{1-20} -alkoxy groups, C_{3-10} -cycloalkyl groups and C_{6-10} -aryl groups may each contain, independently of one another, one or more halogen atoms, and

each of the rings formed by the substituents R^1 to R^{12} may contain one or two further heteroatoms from the group consisting of nitrogen, sulfur and oxygen and/or may be fused to another aromatic or nonaromatic 5- to 7-membered ring,

which comprises mixing malononitrile with a cyano compound of the formula RCN , where R is selected from the group consisting of chlorine, bromine, iodine and cyano, in the presence of a base, if desired in the presence of a solvent, and adding a salt $(Q^+)_nX^{n-}$, where $n = 1$ or 2 , Q^+ is as defined above and X^{n-} is an anion selected from the group consisting of halides, pseudohalides, sulfate and organic acid anions, with the anion X^{n-} being replaced in the aqueous phase by a tricyanomethanide anion formed *in situ* from malononitrile and RCN .

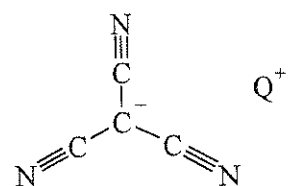
2. Process according to Claim 1, wherein malononitrile, the cyano compound RCN and the salt $(Q^+)_nX^{n-}$ are mixed in the presence of a base, if desired in the presence of a further solvent, in the aqueous phase and the formation of and exchange with the tricyanomethanide anion take place in a one-pot reaction.
3. Process according to Claim 1 or 2, wherein the molar ratio of malononitrile to the cyano compound RCN is in the range from 0.2:1 to 2:1, particularly preferably from 0.9:1 to 1.1:1, very particularly preferably from 0.95:1 to 1.05:1.

4. Process according to any of Claims 1 to 3, wherein the base
is selected from the group consisting of alkali metal and
alkaline earth metal hydroxides, alkali metal and alkaline
earth metal carbonates, ammonia, primary, secondary and
tertiary amines, pyridines and imidazoles.
5. Process according to any of Claims 1 to 4, wherein the pH
is maintained at a value above 4, preferably at a value
above 7, particularly preferably in the range from 7 to 9,
during the reaction.
6. Process according to any of Claims 1 to 5, wherein the
anion X^{n-} is selected from the group consisting of
chloride, bromide, and cyanide.

Method For The Production Of Tricyanomethanides Of Organic Cations

Abstract

The invention relates to a process for preparing ionic liquids based on tricyanomethane salts of the formula



where Q^+ is an organic cation containing at least one heteroatom selected from the group consisting of nitrogen, phosphorus, sulfur and oxygen, and also ionic liquids based on tricyanomethanides.