

AMENDED SPECIFICATION

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PATENT SPECIFICATION

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NO DRAWINGS

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(54) MANUFACTURE OF BIPYRIDYLIUM SALTS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the manufacture of bipyridylium salts and particularly to a process for the manufacture of 1,1'-disubstituted-4,4'-bipyridylium salts which are useful herbicides.

According to the present invention we provide a process for the manufacture of 1,1'-disubstituted-4,4'-bipyridylium salts wherein each of the substituents is an organic substituent other than phenyl, which is inert under the reaction conditions and contains up to 10 carbon atoms which comprises reacting an N-substituted pyridinium salt with a cyanide under basic conditions and subsequently oxidising the resulting interaction product to produce the bipyridylium salt, provided that when an N-methyl pyridinium salt is reacted the reaction is carried out in a solvent comprising an alcohol or in a solvent (other than aqueous acetone) comprising a polar aprotic solvent. The cyanide is preferably an alkali metal cyanide, notably sodium cyanide.

The reaction can be carried out simply by mixing the reagents and heating the mixture if

necessary, but we prefer to carry out the reaction in a solvent for the N-substituted pyridinium salt. A suitable solvent is water although a wide variety of organic solvents may be employed. Examples of organic solvents which may be used are ethers and thioethers for example tetrahydrofuran, 1,2-dimethoxyethane, bis-(2-methoxyethyl) ether, 1,4-dioxane and thiophene, ketones, for example acetone; hydrocarbons, for example benzene, toluene, xylene and hexane; organic bases, for example pyridine; halogenated hydrocarbons and particularly chlorinated hydrocarbons, for example chlorobenzene, chloroform, carbon tetrachloride and methylene dichloride; amides, particularly tertiary alkylamides, for example dimethylformamide; sulphoxides, for example dimethyl sulphoxide; sulphones, for example sulfolane; nitriles, for example acetonitrile; alcohols, for example ethanol; nitro compounds, for example nitropropane; and alkyl carbonates and sulphates, for example propylene carbonate and dimethyl sulphate. Polar aprotic solvents, especially dimethyl sulphoxide, are particularly suitable solvents since their use leads to high yields of the bipyridylium salts. Mixtures of solvents may be used if desired.

Another particularly suitable solvent is a mixture of water and an alcohol which is miscible with water. The alcohol in such mixtures may be in particular an aliphatic mono-

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hydroxylic alcohol, especially an alkanol, although aromatic or cycloaliphatic alcohols may be used if desired. We prefer to employ alcohols of boiling point less than 100°C at atmospheric pressure, for example ethanol. Mixtures of two or more alcohols with water may be used if desired.

The amounts of water and alcohol in the mixture may vary within wide limits but we have found that for any particular alcohol/water mixture there exists a range of water contents in which particularly good yields of the reaction product, and hence of the bipyridylium salt, are obtained. Although the preferred range of water contents may vary slightly for different alcohols we have found that in general mixtures are preferred which contain from 5% to 50% by volume and especially from 10% to 25% by volume of water. In general the amount of water in the mixture is preferably less than 40% by weight and especially is not more than 25% by weight.

The preferred water contents mentioned above are intended only as a guide and it is to be understood that there is a particularly preferred water content for each alcohol in the mixture. Thus the preferred water content when ethanol or isopropanol is used as the solvent is from 15% to 40% by volume, especially about 20% by volume, but if methanol is used, 20% of water gives results inferior to using methanol alone. It is also to be understood that the preferred water contents mentioned above refer to reaction media which do not contain an added base such as sodium hydroxide and may be different if such a base is present.

The temperature at which the reaction is carried out is not critical although in some cases it is greatly advantageous to heat the reaction mixture. In general the reaction may be carried out at a temperature from 25°C to 120°C, preferably from 40°C to 90°C. Temperatures above 150°C should in general be avoided. Usually the reaction will be carried out under an inert atmosphere.

The reaction is carried out under basic conditions preferably, but not necessarily, in the presence of an added base. A strong base is preferred, for example an alkali metal hydroxide (notably sodium hydroxide), although ammonium hydroxide or an organic amine may be used. In protic solvents, for example aqueous media, the addition of a base is desirable in that higher yields of the desired product and faster rates of reaction are thereby achieved. In alcohols or polar aprotic solvents, for example anhydrous dimethyl sulphoxide the addition of a separate base may not be essential since the cyanide may itself be sufficiently basic under the reaction conditions. A separate base may, however, be added in such cases if desired. The product of the reaction in the presence or absence of an added

base is a 1,1' - disubstituted - 1,1' - dihydro - 4,4' - bipyridyl.

The amount of the cyanide is not critical although we prefer to employ an excess of this reagent. Preferably at least 0.25 mole of the cyanide are used per mole of the pyridinium salt; 1 to 4 moles in the presence of an added base and in excess of 4 moles in the absence of an added base. The concentration of the pyridinium salt in cases where it is employed in the form of a solution will depend upon the solvent used, and the optimum concentration in each case can be determined by simple experiment. In general, however, concentrations of from 0.1 to 2.0 moles per litre and especially about 0.5 mole per litre are suitable. By way of example the optimum concentration of methyl pyridinium ion in a water/ethanol (20% v/v water) mixture is about 0.5 mole per litre.

Any N-substituted pyridinium salt may be converted to a bipyridylium salt by the process of our invention which has an inert (i.e. inert under the reaction conditions) organic N-substituent containing up to 10 carbon atoms, and particularly suitable salts are those having an alkyl or a carbamidoalkyl substituent, and especially a methyl or a carbamidomethyl substituent, on the nitrogen atom of the pyridine nucleus. The carbamidoalkyl substituent has the formula $-R_1-CO-NR_2R_3$ wherein R_1 is a hydrocarbon radical (especially the methylene radical) and R_2 and R_3 are hydrocarbon or substituted hydrocarbon radicals and R_2 and R_3 may, together with the attached nitrogen atom make up a heterocyclic ring. The salt is conveniently a halide and especially a chloride salt, though the anionic species is not critical and other salts may be used, if desired. The pyridine nucleus may be substituted, by an organic substituent, for example by one or more alkyl groups in the 2-, 3-, 5- and 6-positions, but the 4-position preferably should be unoccupied. In the case of an N-alkyl pyridinium salt the alkyl group preferably contains from 1 to 4 carbon atoms.

The interaction product derived from the pyridinium salt and the cyanide is readily oxidised to the corresponding 1,1'-disubstituted-4,4'-bipyridylium salt by treatment with air or with an oxidising agent which is an electron acceptor and has a redox potential in water more positive than -0.50 volts as compared with the saturated calomel electrode. Examples of suitable oxidising agents are ceric sulphate (in dilute sulphuric acid); metal salts, especially the halides; inorganic oxyacid anhydrides, especially sulphur dioxide; chlorine; air, preferably in conjunction with water and/or carbon dioxide and/or an acid for example acetic acid or sulphuric acid; and organic oxidising agents for example quinones such as benzoquinone, chloranil and anthraquinone. The oxidation is advantageously carried out under acidic conditions, the apparent pH of

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the reaction mixture being preferably less than 7, especially from 4 to 6. Addition of the oxidising agent in an acidic medium is usually sufficient to achieve this result.

Depending upon the conditions under which it is prepared the interaction product of the pyridinium salt and the cyanide may be in the form of a solution or a slurry. Thus, for example if the reaction is carried out in a protic solvent, notably an aqueous medium, the intermediate reaction product is in the form of a slurry of a brown solid precipitate in a solution which is usually blue in colour. It is believed that the interaction product may be present in the liquid phase in addition to the solid phase. If, in the other hand, the reaction is carried out in a polar aprotic solvent, notably dimethyl sulphoxide, the intermediate reaction product is in the form of a solution, usually coloured brown.

The intermediate reaction product can be oxidised directly without isolation from the mixture in which it has been prepared. However, if this product is oxidised directly the final bipyridylium salt is impure and requires to be purified. In particular the bipyridylium salt so obtained contains free cyanide ions and these anions may react with the bipyridylium cation so reducing the yield of the salt. Methods for separating the bipyridylium cation from free cyanide ions are described hereinafter; these methods are also described in co-pending Patent Application No. 31366/68 Serial No. 1277734 in which there is described and claimed a process for the manufacture of a 1,1'-disubstituted-4,4'-bipyridylium salt which comprises reacting an N-substituted-4-cyano pyridinium salt with ammonia or an alkali metal hydroxide and subsequently oxidising the resulting interaction product.

It is usually more convenient to isolate the intermediate reaction product prior to oxidising it so that oxidation yields a fairly pure bipyridylium salt substantially free from cyanide ions. In the case where the intermediate interaction product is a solid in the form of a slurry as when the reaction is carried out in the presence of water, the solid can be isolated by filtration or preferably by solvent extraction. Suitable solvents for the extraction are hydrocarbons, particularly aromatic hydrocarbons and notably toluene. The temperature can be from 0°C to 100°C. After removal of the solid there may remain a portion of the intermediate reaction product in the liquid phase; any such portion can be recovered either by oxidising it to the bipyridylium salt and isolating this salt as hereinafter described or by reducing it to form a further amount of a solid (a 1,1'-disubstituted dihydrobipyridyl) which can be isolated as described above prior to oxidising it. The reduction can be effected by any conventional reduction technique, for example using an alkali metal

amalgam or a dithionite for example sodium dithionite.

In the case where the intermediate reaction product is a solution, as for example when it is prepared in a polar aprotic solvent, we have found that a useful technique for isolating it is to add water, an organic acid (notably acetic acid) or a base to the reaction mixture. This addition results in a slurry similar to that obtained if the initial reaction is carried out in a protic solvent. The temperature of this treatment can be from 0°C to 100°C, preferably from 20°C to 50°C. The solid and liquid phases of the slurry can be treated as described above to recover the intermediate reaction product. The product obtained as a result of the treatment is easily oxidised with a greater variety of oxidising agents than is the solution prior to the treatment. The solid obtained as a result of adding water or a base to the solution of the intermediate reaction product is a 1,1'-disubstituted-1,1'-dihydro-4,4'-bipyridyl.

As hereinbefore explained it may be necessary to separate the final bipyridylium salt from free cyanide ions in the reaction mixture, for example if the intermediate reaction product is oxidised without first isolating it from the intermediate reaction mixture. The separation can be carried out at a temperature of from 0°C to 100°C. We have found that 1,1'-disubstituted-4,4'-bipyridylium cations can be separated from cyanide ions in the reaction mixture by treating the mixture with 4,4'-diamino-stilbene-2,2'-disulphonic acid which is commonly known as "amsonic acid". The bipyridylium cation is thereby precipitated from the mixture in the form of its amsonate salt whilst the cyanide ions remain in the mixture. The precipitate can then be removed by filtration, washed and dried in conventional manner and the amsonic acid can be regenerated and recovered for re-use by acidification of the amsonate salt, preferably employing an aqueous solution of an acid. The acid used to recover the amsonic acid can be selected so as to provide the desired anion for the resulting bipyridylium salt and can be for example hydrochloric acid, phosphoric acid or acetic acid.

Amsonic acid is only sparingly soluble in water and it is therefore usually employed in the present invention in the form of an aqueous solution of one of its water-soluble salts, conveniently an alkali metal salt or the ammonium salt. The treatment of the reaction mixture with amsonic acid can be carried out conveniently at a pH in the range 7 to 12, and at a temperature of from 0°C to 100°C.

The 1,1'-disubstituted-4,4'-bipyridylium cation can also be separated from cyanide ions in the reaction mixture by contacting this mixture with a suitable cation-exchange resin. In this way the cyanide ions pass the resin and remain in the mixture so that they are separated from the bipyridylium cation. The bi-

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pyridylum cation can subsequently be liberated from the ion exchange resin by treatment of the resin with an acid. In this way a bipyridylum salt is obtained wherein the anion is that supplied by the acid. Examples of the anions which may be introduced into the mixture in this way are chloride, sulphate and acetate ions.

Alternatively, the cyanide ions can be removed from the bipyridylum cations using an anion-exchange resin.

The temperature at which the mixture is contacted with the ion-exchange resin is not critical but can conveniently be from 0°C to 100°C. Examples of suitable cation-exchange resins are the Zeocarb cation exchange resins, for example Zeocarb 225 (SRC-8), the Amberlite cation exchange resins for example Amberlite Resin C6-120, and the Deacidite resins. An example of an anion exchange resin which can be used is Amberlite IRA 400. "Zeocarb", "Amberlite" and "Deacidite" are Registered Trade Marks.

A further method of removing cyanide ions from the reaction mixture containing the 1,1'-disubstituted-4,4'-bipyridylum salt is to acidify and then de-gas the reaction mixture. In this way the cyanide ions are removed from the mixture in the form of hydrogen cyanide and the process is particularly convenient since the hydrogen cyanide so liberated can be reacted directly with a base, for example sodium hydroxide, to form a cyanide which can be used to prepare a further quantity of the bipyridylum cation. Any mineral or organic acid can be used which results in the formation of hydrogen cyanide and examples of suitable acids are hydrochloric, sulphuric, phosphoric and acetic acids. Alternatively the solution can be acidified by means of sulphur dioxide. The acid used can be selected to provide the required anionic species in the final 1,1'-disubstituted-4,4'-bipyridylum salt.

Acidification of the reaction mixture can be effected at any temperature at which the bipyridylum cation is stable, for example from 0°C to 100°C. The mixture can be de-gassed in conventional manner, for instance by bubbling air or an inert gas through it under vacuum or by boiling the mixture. It will be appreciated that this technique of acidification followed by de-gassing of the mixture is simple to carry out and can be employed to remove from the mixture any anion which forms with a proton a volatile product which can be removed from the mixture by de-gassing. In addition to cyanide ions, halide ions, especially fluoride and chloride ions can be removed by the technique.

Cyanide anions can also be in effect removed from mixtures containing 1,1'-disubstituted-4,4'-bipyridylum cations by addition to the mixtures at a temperature of from 0°C to 100°C of a reagent which forms a complex

salt with the cyanide ions. For example the addition of ferric or ferrous ions in the form of a salt for example a sulphate or halide salt results in the formation of a ferrocyanide. In this case the cyanide ions are not actually removed from the reaction mixture but they are effectively prevented from reacting with the bipyridylum salt by virtue of their being in the form of a complex salt with the added cations.

The invention is illustrated but in no way limited by the following examples:—

Example 1.

Methyl pyridinium chloride (2.9 g—0.02 mole) was dissolved in 30 ml dry dimethyl sulphoxide and the solution was added rapidly to a stirred solution of sodium cyanide (4.9 g—0.1 mole) in dry dimethyl sulphoxide (20 ml) at 75°C under an atmosphere of nitrogen. The mixture was heated under reflux for 30 minutes and a deep brown colour developed.

The deep brown mixture was treated with excess ceric sulphate in dilute sulphuric acid as oxidising agent to yield a 1,1'-dimethyl-4,4'-bipyridylum salt in an amount representing an overall reaction efficiency of 73% with respect to methyl pyridinium chloride fed.

Example 2.

The procedure of Example 1 was repeated except that the solution of sodium cyanide was in 30 ml of dimethyl sulphoxide and contained sodium bicarbonate (10 g) and the temperature was 70°C. The product was a 1,1'-dimethyl-4,4'-bipyridylum salt and the reaction efficiency was 88%.

Example 3.

A mixture of methyl pyridinium chloride (3.1 gms), sodium cyanide (4.9 g) and sodium bicarbonate (10 gms) in dimethyl sulphoxide (80 mls) was heated for 20 minutes at 70°C with stirring under an atmosphere of nitrogen. The resulting brown mixture was treated with a solution of ceric sulphate in dilute sulphuric acid to yield a 1,1'-dimethyl-4,4'-bipyridylum salt. The overall reaction efficiency was 89% with respect to methyl pyridinium chloride fed.

The above procedure was repeated except that the sodium bicarbonate was omitted from the reaction mixture. The product was a 1,1'-dimethyl-4,4'-bipyridylum salt and the overall reaction efficiency was 85% with respect to methyl pyridinium chloride fed.

Example 4.

Methyl pyridinium chloride (3.1 gms) in dimethyl sulphoxide (50 mls) was added with stirring to a suspension of sodium cyanide (4.9 gms) in dimethyl sulphoxide (30 mls) at 70°C under an atmosphere of nitrogen. After 30

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minutes a cooled solution of sulphur dioxide
in dimethyl sulphoxide was added to the brown
reaction mixture. The mixture immediately
turned blue and upon standing for 1½ hours
became brown.

5 Excess sulphur dioxide was then removed
from the mixture by bubbling nitrogen gas
through it. The mixture was found by analysis
to contain a 1,1' - dimethyl - 4,4' -
10 bipyridylium salt. The reaction efficiency was
95% based on methyl pyridinium chloride
fed.

Examples 5 to 8.

15 A suspension of methyl pyridinium chloride
(3.1 gms) in dimethyl acetamide (50 mls) was
added to a stirred suspension of sodium cyan-
ide (4.9 gms) in dimethyl acetamide (50 mls)
at 75°C under an atmosphere of nitrogen. A
yellow colouration developed at once and after
20 1 hour the colour had become dark orange.
This mixture was poured into a solution of
ceric sulphate in dilute acetic acid to yield a
1,1'-dimethyl-4,4'-bipyridylium salt. The re-
action efficiency was 66% with respect to
25 methyl pyridinium chloride fed.

The above procedure was repeated three
times (Examples 6, 7 and 8) but using the sol-
vents shown below instead of dimethyl acet-
amide. The product in each case was a 1,1'-
30 dimethyl-4,4'-bipyridylium salt and the reac-
tion efficiencies were:—

Example No.	Solvent	Efficiency (%)
5	dimethyl acetamide	66
6	dimethyl formamide	36
7	acetone	23
8	hexamethylene phosphotriamide	45

Example 9.

40 A mixture containing 1,1'-dimethyl-4,4'-
bipyridylium cations, methyl pyridinium ions
and cyanide ions and other impurities, ob-
tained by reacting methyl pyridinium chloride
with sodium cyanide in dimethyl sulphoxide,
was neutralised (pH 7) by addition of dilute
45 sulphuric acid.

A neutral aqueous solution of the disodium
salt of amsonic acid was added to the above
neutralised mixture with stirring. The result-
ing mixture became dark in colour and a
black precipitate of 1,1'-dimethyl-4,4'-bi-
pyridylium amsonate was formed. The pre-
cipitate was filtered off and washed with water
and then dried in air. Analysis indicated that
50 the black solid so obtained had a purity of
greater than 98%, and cyanide ions could not
be detected in it.

The black solid was then treated with a
dilute aqueous solution of sulphuric acid,
yielding a yellow solid and a clear solution.
60 The yellow solid, identified as amsonic acid,
was filtered off and the remaining solution
was analysed. The solution contained a 1,1'-

dimethyl-4,4'-bipyridylium salt in an amount
representing a near quantitative recovery of
the 1,1'-dimethyl-4,4'-bipyridylium cation
65 from the initial mixture. The solution was free
from cyanide ions and methyl pyridinium ions.

Example 10.

A mixture containing 1,1'-dimethyl-4,4'-
bipyridylium cations and cyanide ions as in
Example 10 was neutralised by adding dilute
hydrochloric acid solution. A steady stream of
nitrogen gas was bubbled through the mixture
which was heated to about 100°C for 30
75 minutes during which time hydrogen cyanide
was detected in the stream of nitrogen leaving
the reaction vessel. The mixture was then
allowed to cool and analysis of the cooled mix-
ture indicated that a 1,1'-dimethyl-4,4'-bi-
pyridylium salt was present and that the
80 amount of 1,1'-dimethyl-4,4'-bipyridylium
cation was the same as in the original impure
mixture. Cyanide ions could not be detected
in the final mixture.

Example 11.

A mixture containing 1,1'-dimethyl-4,4'-
bipyridylium cations and cyanide ions as de-
scribed in Example 9 was neutralised by add-
ing dilute aqueous hydrochloric acid
solution. The mixture was then added
to an aqueous solution of sodium
hypochlorite at a pH below 9.
Analysis of the resulting mixture failed to
detect the presence of cyanide ions and showed
that the product was a 1,1'-dimethyl-4,4'-bi-
pyridylium salt in which the amount of 1,1'-
95 dimethyl-4,4'-bipyridylium cations was the
same as in the original mixture.

Example 12.

A mixture containing 1,1'-dimethyl-4,4'-
bipyridylium cations and cyanide ions as de-
scribed in Example 9 was neutralised by add-
ing a dilute aqueous solution of hydrochloric
acid. The mixture was then mixed with an
aqueous solution of ferrous sulphate hepta-
hydrate containing a slight molar excess of the
heptahydrate with respect to cyanide ions in
the mixture being treated. Free cyanide ions
could not be detected in the mixture which
contained a 1,1'-dimethyl-4,4'-bipyridylium
salt and from which a small quantity of ferro-
cyanide was removed by filtration.
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Example 13.

A mixture containing 1,1'-dimethyl-4,4'-
bipyridylium cations and cyanide ions as de-
scribed in Example 9 was passed down an
anion exchange column comprising Deacidite
FF resin. The solution recovered from the
base of the column contained no detectable
amounts of cyanide ions. The product was a
1,1'-dimethyl-4,4'-bipyridylium salt and the
amount of 1,1'-dimethyl-4,4'-bipyridylium
cation in the mixture was unchanged.
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Example 14:

5 A mixture containing 1,1'-dimethyl-4,4'-bipyridylium cations and cyanide ions as described in Example 9 was passed down an ion-exchange column comprising Zeocarb 225 (SRC-8) Resin. The solution recovered from the base of the column contained cyanide ions but was free from 1,1'-dimethyl-4,4'-bipyridylium cations.

10 After removal of the cyanide ion-containing solution, N/10 aqueous hydrochloric acid was passed down the column and the solution recovered from the base of the column was found by analysis to contain 1,1'-dimethyl-4,4'-bipyridylium dichloride in an amount representing a quantitative recovery of 1,1'-dimethyl-4,4'-bipyridylium ion from the initial mixture.

Example 15:

20 A de-oxygenated solution of methylpyridinium chloride (3.2 gms, 0.025 mole) in aqueous ethanol (50 ml) containing 20% by volume of water was mixed with sodium cyanide (4.9 g; 0.1 mole) under an atmosphere of nitrogen. The mixture was heated under reflux for 5 hours.

25 The resulting deep-blue reaction mixture was treated with excess ceric sulphate in dilute sulphuric acid as oxidising agent to yield 30 1,1'-dimethyl-4,4'-bipyridylium salt in an amount representing an overall reaction efficiency of 65% with respect to methyl pyridinium chloride fed.

Example 16:

35 An acidic reaction mixture containing 1,1'-dimethyl-4,4'-bipyridylium ion, obtained as in Example 16, was concentrated to one-quarter of its original volume by distillation under atmospheric pressure. The resulting aqueous solution of a 1,1'-dimethyl-4,4'-bipyridylium salt was shown by analysis to be free of alcohol and cyanide ions, and the bipyridylium ion content was the same as in the original mixture.

Example 17:

45 The initial procedure of Example 15 was repeated to produce the deep-blue reaction mixture. This mixture was cooled in an ice/water bath and then liquid sulphur dioxide (15 ml) was added to it. The resulting suspension was mixed with water to yield an aqueous solution containing a 1,1'-dimethyl-4,4'-bipyridylium salt, in an amount corresponding to a reaction efficiency of 65% with respect to methyl pyridinium chloride fed.

Example 18:

50 The procedure of Example 15 was repeated using ethanol containing various proportions of water. The effect of the water content of the ethanol on the reaction is shown in Table 1. In each Example a 1,1'-dimethyl-4,4'-bipyridylium salt was produced.

TABLE 1

Water content (% v/v)	Reaction efficiency (%)
0	54
10	61
20	65
40	38
60	13

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Example 19.

The procedure of Example 15 was repeated but using various molar proportions of sodium

cyanide relative to methyl pyridinium ion. The results are shown in Table 2.

5

TABLE 2

Moles NaCN/mole MPC	Efficiency (%)
12	63
4	65
2	58
1	45

MPC represents methyl pyridinium chloride.

Example 20.

The procedure of Example 15 was repeated but using various volumes of the aqueous

ethanol mixture. The results are summarised in Table 3.

10

TABLE 3

MPC (moles/litre)	Efficiency (%)
0.31	58
0.50	65
1.00	62

Example 21.

The procedure of Example 15 was repeated

using a variety of reaction periods. The results are summarised in Table 4.

15

TABLE 4

Reaction period (hrs)	Efficiency (%)
1	27
2½	44
5	65
9	54

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Example 22.

The procedure of Example 15 was repeated using anhydrous and also aqueous mixture of

n-propanol, *iso*-propanol, *iso*-butanol and *tert*-butanol instead of ethanol. The results are shown in Table 5.

TABLE 5

Alcohol	Water content (% v/v)	Efficiency (%)
<i>n</i> -propanol	0	30
"	20	52
<i>iso</i> -propanol	0	17
"	20	54
<i>iso</i> -butanol	0	20
"	20	37
<i>tert</i> -butanol	0	9
"	20	33

Example 23.

10 A solution of methyl pyridinium chloride (2.80 g) in water (10 ml) was added rapidly to a stirred mixture of sodium cyanide (4.9 g) and sodium hydroxide (3.0 g) in water (10 ml). The mixture was layered with benzene (60 ml) at room temperature under an atmosphere of nitrogen. The mixture was heated to 80°C and the benzene layer (50 ml) which was shown by U.V. spectroscopy to contain 1,1'-dimethyl-dihydro-4,4'-bipyridyl was collected after one half hour and oxidised by addition of an aqueous solution of sulphur dioxide gas. The benzene withdrawn from the mixture was replaced by fresh benzene and further withdrawals and additions were made after periods of 15, 30 and 60 minutes. These were oxidised in the manner described above. The combined aqueous layers were found to contain a 1,1'-dimethyl-4,4'-bipyridylum salt in an amount representing an overall reaction efficiency of 53% based on methyl pyridinium chloride fed.

Example 24.

30 A solution of methyl pyridinium chloride (3.10 g) in water (10 ml) was added rapidly to a stirred mixture of sodium cyanide (2.5 g) and sodium hydroxide (1 g) in ethanol (40 ml) at room temperature under an atmosphere of nitrogen. The mixture was heated under reflux for one half hour and then cooled. Liquid sulphur dioxide (10 ml) was added to the violet coloured mixture and produced an orange coloured solution which was found to contain a 1,1'-dimethyl-4,4'-bipyridylum

salt in an amount representing an overall efficiency of 94% based on methyl pyridinium chloride fed.

Example 25.

45 A solution of methyl pyridinium chloride (3.10 g) in water (10 ml) was added rapidly to a stirred solution of sodium cyanide (4.9 g) and sodium hydroxide (3.0 g) in water (20 ml) at room temperature under an atmosphere of nitrogen. The mixture was heated under reflux for two hours and then cooled. Liquid sulphur dioxide (10 ml) was added to the violet coloured mixture and produced an orange coloured solution which was found to contain a 1,1'-dimethyl-4,4'-bipyridylum salt in an amount representing an overall reaction efficiency of 84% based on methyl pyridinium chloride fed.

Example 26.

60 Methyl pyridinium chloride (3.0 g) and sodium cyanide (4.9 g) were reacted together in dimethyl sulphoxide (80 ml) at 80°C for 30 minutes. The mixture was then cooled to room temperature and poured into a solution of the oxidising agent (see Table 6) in dimethyl formamide (80 ml). After 30 minutes 2N aqueous sulphuric acid was added to adjust the pH to 1 and the solution was then analysed for a 1,1'-dimethyl-4,4'-bipyridylum salt. In some cases (see Table 6) either water (80 ml), solid sodium hydroxide pellets, or acetic acid (10 ml) were added to the reaction mixtures 5 minutes before oxidation was effected.

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TABLE 6

Oxidising Agent	Equivalents of oxidising agent	Additional reagent	Reaction efficiency *
Maleic anhydride	2	None	23
"	2	water	69
"	2	sodium hydroxide	61
"	2	acetic acid	55
"	6	none	65
Chloranil	2	none	0
"	2	water	50
"	4	none	53
Alloxan monohydrate	2	none	3
"	2	water	78
"	4.5	none	63
Indane Trione monohydrate	2	none	65
<i>m</i> -dinitrobenzene	2	none	5
"	2	water	0
"	2	sodium hydroxide followed by acetic acid	59
"	2	acetic acid	14

* based on methyl pyridinium chloride fed.

Example 27.

5 Methyl pyridinium chloride (3.0 g) and sodium cyanide (4.9 g) were reacted together in dimethyl sulphoxide (80 ml) at 80°C for 30 minutes. The mixture was then cooled and toluene (200 ml) was added, followed by water (50 ml). The mixture was separated and the toluene layer was oxidised in a two phase system comprising *m*-dinitrobenzene (10 g) in toluene (100 ml) and acetic acid (10 ml) in water (100 ml) to yield an aqueous phase containing a 1,1'-dimethyl-4,4'-bipyridylium salt (7.7% of the bipyridylium cation) free from cyanide ions and an organic phase containing unchanged *m*-dinitrobenzene.

Example 28.

20 Methyl pyridinium chloride (3.1 gm) in water (10 ml) was added to a mixture of sodium hydroxide (1.0 g) and sodium cyanide (2.5 g) in ethanol (40 ml) at room temperature under an atmosphere of nitrogen. The mixture was stirred at room temperature for 30 minutes, heated under reflux for 30 minutes and then cooled. Chlorine gas was bubbled through the resulting solution until all traces of blue colouration had disappeared and 1,1' - dimethyl - 4,4' - bipyridylium dichloride was produced. An aliquot of this mixture was then reduced in a buffer solution at pH 9.2 by sodium dithionite.

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The solution was analysed and the reaction efficiency as determined by spectrophotometry was 95% in respect of the 1,1'-dimethyl-4,4'-bipyridylium salt, based on pyridinium salt fed.

Example 29.

Methyl pyridinium chloride (3.1 gm) in water (10 ml) was added to a mixture of sodium hydroxide (3.0 g) and sodium cyanide (4.9 g) in water (20 ml) at room temperature under an atmosphere of nitrogen. The mixture was stirred at room temperature for 30 minutes, heated under reflux for two hours and then cooled. Chlorine gas was bubbled through the solution until all trace of blue colouration had disappeared and 1,1'-dimethyl-4,4'-bipyridylium dichloride was produced. An aliquot of this mixture was then reduced in a buffer solution at pH 9.2 by sodium dithionate, and the efficiency was found to be 73% by spectrophotometry.

Example 30.

Methyl pyridinium chloride (6.2 g) in water (20 ml) was added to a mixture of sodium hydroxide (6.0 g) and sodium cyanide (9.8 g) in water (40 ml) at room temperature under an atmosphere of nitrogen. The mixture was stirred at room temperature for 30 minutes, heated under reflux for two hours and then cooled. Toluene (500 ml) was added and the mixture partitioned. The toluene layer was oxidised by sulphur dioxide to yield a 1,1'-dimethyl-4,4'-bipyridylium salt (efficiency

65%). The aqueous layer was treated with 2N sodium hydroxide (25 ml) and sodium dithionate (2 g) and repartitioned with toluene (15 ml). This toluene layer was oxidised by sulphur dioxide to yield a 1,1'-dimethyl-4,4'-bipyridylium salt (efficiency 10%). The residual aqueous layer was found to contain only 2% of the bipyridylium salt after oxidation. The total overall reaction efficiency was 77%.

Example 31.

Methyl pyridinium chloride (3.0 g) in water (10 ml) was added to a solution of sodium hydroxide (3.0 g) and sodium cyanide (4.9 g) in water (30 ml) at room temperature under an atmosphere of nitrogen. The mixture was stirred at room temperature for 30 minutes, heated to reflux temperature over a period of 30 minutes and then heated under reflux for two hours. The reaction mixture was then cooled and treated by one of two procedures A or B.

A. The reaction mixture was diluted to 500 ml with deoxygenated water and the resulting aqueous suspension was filtered. Portions of the solid so produced were oxidised to yield a 1,1'-dimethyl-4,4'-bipyridylium salt by a number of reagents (see Table 7). In each case 0.263 g of solid was reacted with a solution of the oxidising agent (1 g) under nitrogen. After 5 minutes acetic acid (1 ml) was added and the mixture was diluted with water to 100 ml. The filtrate was oxidised with sulphur dioxide and yielded a further quantity of the bipyridylium salt.

TABLE 7

Oxidising Agent	Solvent	Efficiency
<i>m</i> -dinitrobenzene	dimethyl formamide	99
Maleic anhydride/HOAc	dimethyl formamide	87
Potassium ferricyanide	water	96
Ceric sulphate	1N H ₂ SO ₄	85

B. The reaction mixture was extracted by toluene (250 ml). The aqueous layer was removed and oxidised by sulphur dioxide to yield a 1,1'-dimethyl-4,4'-bipyridylium salt (15%). Portions of the organic phase were oxidised using sulphur dioxide or *m*-dinitrobenzene. In the latter case oxidation was carried out in a two-phase system comprising *m*-dinitrobenzene (10 g) in toluene (100 ml) and acetic acid (10 ml) in water (100 ml) to yield an aqueous phase containing 69% of the bipyridylium salt and an organic phase contain-

ing unchanged *m*-dinitrobenzene. In each case A or B free cyanide ions could not be detected in the final solutions.

Example 32.

A reaction mixture comprising methyl pyridinium chloride (3.0 g), sodium hydroxide (1 g) and sodium cyanide (2.5 g) in 80% aqueous ethanol (50 ml) treated in the same manner as in Example 31 but heated under reflux for 30 minutes only, yielded by method A 74% and 20% of a 1,1'-dimethyl-4,4'-

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5 bipyridylium salt from the solid and filtrate respectively, and by method B where water (50 ml) was also added before separation, 45% and 42% from the aqueous and toluene phases respectively.

Example 33.

10 A reaction mixture comprising methyl pyridinium chloride (3.0 g) and sodium cyanide (4.9 g) in dimethyl sulphoxide (80 ml) maintained at 80°C for 30 minutes, yielded by a method A of Example 32, 30% and 62% of a 1,1'-dimethyl-4,4'-bipyridylium salt from the solid and filtrate respectively, and by method B, where water (80 ml) was added before separation, 15% and 77% from the aqueous and toluene phases respectively.

15 We are aware that in Tetrahedron Letters No. 24 pp 2313-2315 (1967) there is described the reaction of ethyl pyridinium bromide with cyanide ion in water solution under forcing conditions (prolonged heating at 100°C) in the absence of an added base to produce a biogen cation radical. We hereby disclaim a process for the manufacture of a 1,1'-disubstituted-4,4'-bipyridylium salt comprising this reaction.

20 Subject to the foregoing disclaimer,
WHAT WE CLAIM IS:—

30 1. A process for the manufacture of 1,1'-disubstituted-4,4'-bipyridylium salts wherein each of the substituents is an organic substituent other than phenyl, which is inert under the reaction conditions and contains up to 10 carbon atoms which comprises reacting an N-substituted pyridinium salt with a cyanide under basic conditions and subsequently oxidising the resulting interaction product to produce the bipyridylium salt, provided that when an N-methyl pyridinium salt is reacted the reaction is carried out in a solvent comprising an alcohol or in a solvent (other than aqueous acetone) comprising a polar aprotic solvent.

45 2. A process as claimed in claim 1 wherein the cyanide is an alkali metal cyanide.

3. A process as claimed in claim 2 wherein the cyanide is sodium cyanide.

50 4. A process as claimed in claim 1, 2 or 3 wherein the pyridinium salt is reacted with the cyanide in the presence of a solvent for the pyridinium salt.

55 5. A process as claimed in claim 4 wherein the solvent is an aqueous medium.

6. A process as claimed in claim 5 wherein the pyridinium salt is a salt other than an N-methyl salt and wherein the solvent is water.

60 7. A process as claimed in claim 5 wherein the solvent is a mixture of water and a water miscible alcohol.

8. A process as claimed in claim 7 wherein the alcohol has a boiling point not greater than 100°C.

65 9. A process as claimed in claim 7 or 8 wherein the alcohol is an aliphatic alcohol.

10. A process as claimed in claim 9 wherein the alcohol is an alkanol.

11. A process as claimed in claim 10 wherein the alcohol is ethanol.

12. A process as claimed in any one of claims 7 to 11 wherein the solvent contains from 5 to 50% by volume of water. 70

13. A process as claimed in claim 12 wherein the solvent contains less than 40% by volume of water. 75

14. A process as claimed in claim 4 wherein the solvent is a polar aprotic solvent.

15. A process as claimed in any one of the preceding claims wherein the reaction is carried out at a temperature of less than 150°C. 80

16. A process as claimed in claim 15 wherein the temperature is from 25°C to 120°C.

17. A process as claimed in claim 16 wherein the temperature is from 40°C to 90°C.

18. A process as claimed in any one of the preceding claims wherein the reaction is carried out under an inert atmosphere. 85

19. A process as claimed in any one of the preceding claims wherein the reaction is carried out in the presence of an added base. 90

20. A process for the manufacture of a 1,1'-dimethyl-4,4'-bipyridylium salt which comprises reacting an N-methyl pyridinium salt with a cyanide under basic conditions in the presence of an added base and subsequently oxidising the resulting interaction product to produce the bipyridylium salt. 95

21. A process as claimed in Claim 20 wherein the N-methyl pyridinium salt is reacted with the cyanide in the presence of a mixture of water and a water-miscible alcohol. 100

22. A process as claimed in Claim 20 or Claim 21 wherein the reaction is carried out under an inert atmosphere.

23. A process as claimed in any one of claims 19 to 22 wherein the added base is an alkali metal hydroxide. 105

24. A process as claimed in claim 23, wherein the alkali metal hydroxide is sodium hydroxide. 110

25. A process as claimed in any one of the preceding claims wherein there is employed at least 0.25 mole of the cyanide per mole of the pyridinium salt.

26. A process as claimed in any one of claims 4 to 25 wherein the reaction is carried out in the presence of a solvent for the pyridinium salt and the concentration of the pyridinium salt is from 0.1 to 2 moles per litre. 120

27. A process as claimed in claim 26 wherein the concentration of the pyridinium salt is about 0.5 mole per litre.

28. A process as claimed in any one of the preceding claims wherein the oxidation of the interaction product is carried out under acidic conditions. 125

29. A process as claimed in claim 28 wherein the oxidation is carried out at a pH of from 4 to 6. 130

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5 bipyridylum salt from the solid and filtrate respectively, and by method B where water (50 ml) was also added before separation, 45% and 42% from the aqueous and toluene phases respectively.

Example 33.

10 A reaction mixture comprising methyl pyridinium chloride (3.0 g) and sodium cyanide (4.9 g) in dimethyl sulphoxide (80 ml) maintained at 80°C for 30 minutes, yielded by a method A of Example 32, 30% and 62% of a 1,1'-dimethyl-4,4'-bipyridylum salt from the solid and filtrate respectively, and by 15 method B, where water (80 ml) was added before separation, 15% and 77% from the aqueous and toluene phases respectively.

20 We are aware that in Tetrahedron Letters No. 24 pp 2313—2315 (1967) there is described the reaction of ethyl pyridinium bromide with cyanide ion in water solution under forcing conditions (prolonged heating at 100°C) in the absence of an added base to produce a biogen cation radical. We hereby 25 disclaim a process for the manufacture of a 1,1'-disubstituted-4,4'-bipyridylum salt comprising this reaction.

Subject to the foregoing disclaimer,

WHAT WE CLAIM IS:—

30 1. A process for the manufacture of 1,1'-disubstituted-4,4'-bipyridylum salts wherein each of the substituents is an organic substituent other than phenyl, which is inert under the reaction conditions and contains up to 10 carbon atoms which comprises reacting an N-substituted pyridinium salt with a cyanide 35 under basic conditions and subsequently oxidising the resulting interaction product to produce the bipyridylum salt, provided that when an N-methyl pyridinium salt is reacted the reaction is carried out in a solvent comprising an alcohol or in a solvent (other than aqueous acetone) comprising a polar aprotic solvent.

45 2. A process as claimed in claim 1 wherein the cyanide is an alkali metal cyanide.

3. A process as claimed in claim 2 wherein the cyanide is sodium cyanide.

50 4. A process as claimed in claim 1, 2 or 3 wherein the pyridinium salt is reacted with the cyanide in the presence of a solvent for the pyridinium salt.

55 5. A process as claimed in claim 4 wherein the solvent is an aqueous medium.

6. A process as claimed in claim 5 wherein the pyridinium salt is a salt other than an N-methyl salt and wherein the solvent is water.

60 7. A process as claimed in claim 5 wherein the solvent is a mixture of water and a water miscible alcohol.

8. A process as claimed in claim 7 wherein the alcohol has a boiling point not greater than 100°C.

65 9. A process as claimed in claim 7 or 8 wherein the alcohol is an aliphatic alcohol.

10. A process as claimed in claim 9 wherein the alcohol is an alkanol.

11. A process as claimed in claim 10 wherein the alcohol is ethanol.

12. A process as claimed in any one of claims 7 to 11 wherein the solvent contains from 5 to 50% by volume of water. 70

13. A process as claimed in claim 12 wherein the solvent contains less than 40% by volume of water. 75

14. A process as claimed in claim 4 wherein the solvent is a polar aprotic solvent.

15. A process as claimed in any one of the preceding claims wherein the reaction is carried out at a temperature of less than 150°C. 80

16. A process as claimed in claim 15 wherein the temperature is from 25°C to 120°C.

17. A process as claimed in claim 16 wherein the temperature is from 40°C to 90°C.

18. A process as claimed in any one of the preceding claims wherein the reaction is carried out under an inert atmosphere. 85

19. A process as claimed in any one of the preceding claims wherein the reaction is carried out in the presence of an added base. 90

20. A process for the manufacture of a 1,1'-dimethyl-4,4'-bipyridylum salt which comprises reacting an N-methyl pyridinium salt with a cyanide under basic conditions in the presence of an added base and subsequently oxidising the resulting interaction product to produce the bipyridylum salt. 95

21. A process as claimed in Claim 20 wherein the N-methyl pyridinium salt is reacted with the cyanide in the presence of a mixture of water and a water-miscible alcohol. 100

22. A process as claimed in Claim 20 or Claim 21 wherein the reaction is carried out under an inert atmosphere.

23. A process as claimed in any one of claims 19 to 22 wherein the added base is an alkali metal hydroxide. 105

24. A process as claimed in claim 23, wherein the alkali metal hydroxide is sodium hydroxide. 110

25. A process as claimed in any one of the preceding claims wherein there is employed at least 0.25 mole of the cyanide per mole of the pyridinium salt.

26. A process as claimed in any one of claims 4 to 25 wherein the reaction is carried out in the presence of a solvent for the pyridinium salt and the concentration of the pyridinium salt is from 0.1 to 2 moles per litre. 120

27. A process as claimed in claim 26 wherein the concentration of the pyridinium salt is about 0.5 mole per litre.

28. A process as claimed in any one of the preceding claims wherein the oxidation of the interaction product is carried out under acidic conditions. 125

29. A process as claimed in claim 28 wherein the oxidation is carried out at a pH of from 4 to 6. 130

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30. A process as claimed in any one of the preceding claims wherein the interaction product is oxidised by means of air.
- 5 31. A process as claimed in any one of claims 1 to 29 wherein the interaction product is oxidised by means of an oxidising agent which is an electron acceptor and which has a redox potential in water more positive than -0.50 volt as compared with the saturated calomel electrode.
- 10 32. A process as claimed in claim 30 wherein air is employed in conjunction with water.
33. A process as claimed in claim 30 or claim 32 wherein air is employed in conjunction with an acid.
- 15 34. A process as claimed in claim 31 wherein an inorganic oxidising agent is employed.
35. A process as claimed in claim 34 wherein the oxidising agent is a metal salt.
- 20 36. A process as claimed in claim 35 wherein the oxidising agent is ceric sulphate.
37. A process as claimed in claim 34 wherein the oxidising agent is an inorganic oxyacid anhydride.
- 25 38. A process as claimed in claim 37 wherein the inorganic oxyacid anhydride is sulphur dioxide.
39. A process as claimed in claim 34 wherein the oxidising agent is chlorine.
- 30 40. A process as claimed in claim 31 wherein an organic oxidising agent is employed.
41. A process as claimed in claim 40 wherein a quinone is employed.
42. A process as claimed in any one of the preceding claims wherein the interaction product is oxidised without first being isolated from the reaction mixture.
- 35 43. A process as claimed in any one of claims 1 to 41 wherein at least a part of the interaction product is separated from the reaction mixture prior to the oxidation.
- 40 44. A process as claimed in claim 43 wherein the reaction is carried out in the presence of water and the resulting solid interaction product is isolated by filtration.
- 45 45. A process as claimed in claim 43 wherein the reaction is carried out in the presence of water and the resulting solid interaction product is isolated by solvent extraction.
- 50 46. A process as claimed in claim 43 wherein the reaction is carried out in the presence of a substantially anhydrous aprotic solvent and water is added to the resulting solution to precipitate at least a part of the interaction product as a solid.
- 55 47. A process as claimed in claim 43 wherein the reaction is carried out in the presence of a substantially anhydrous aprotic solvent and a base is added to the resulting solution to precipitate at least a part of the interaction product as a solid.
- 60 48. A process as claimed in claim 47 wherein the base is sodium hydroxide.
49. A process as claimed in claim 43 wherein the reaction is carried out in the presence of a substantially anhydrous aprotic solvent and an organic acid is added to the resulting solution to precipitate at least a part of the interaction product as a solid.
50. A process as claimed in claim 49 wherein the acid is acetic acid.
51. A process as claimed in any one of claims 46 to 50 wherein the solid is isolated by filtration.
52. A process as claimed in any one of claims 46 to 50 wherein the solid is isolated by solvent extraction.
- 75 53. A process as claimed in claim 45 or claim 52 wherein the solvent used to extract the solid is a hydrocarbon.
- 80 54. A process as claimed in claim 53 wherein the solvent is an aromatic hydrocarbon.
55. A process as claimed in claim 54 wherein the solvent is toluene.
- 85 56. A process as claimed in any one of claims 45 and 52 to 55 wherein the solvent extraction is carried out at a temperature of from 0°C to 100°C.
57. A process as claimed in any one of claims 45 and 52 to 55 wherein the liquid phase remaining after removal of the solid contains a portion of the interaction product and this portion is oxidised directly to the bipyridylium salt.
- 90 58. A process as claimed in any one of claims 45 and 52 to 56 wherein the liquid phase remaining after removal of the solid contains a portion of the interaction product and this portion is reduced to yield a further quantity of a solid.
- 100 59. A process as claimed in claim 58 wherein the reduction is effected by treating the liquid with sodium dithionite.
60. A process as claimed in any one of the preceding claims wherein after oxidation of the interaction product to the bipyridylium salt, the mixture contains free cyanide ions and the bipyridylium cation is separated from the free cyanide ions.
- 105 61. A process as claimed in claim 60 wherein the reaction mixture is treated with amsonic acid to precipitate the bipyridylium cation in the form of the bipyridylium salt of amsonic acid.
- 110 62. A process as claimed in claim 61 wherein the amsonic acid is used in the form of an aqueous solution of one of its water-soluble salts.
- 115 63. A process as claimed in claim 62 wherein the water-soluble salt is an alkali metal salt.
- 120 64. A process as claimed in any one of claims 61 to 63 wherein the treatment with amsonic acid is carried out at a pH in the range 7 to 12.
- 125 65. A process as claimed in claim 60 where-

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- in the bipyridylium cation is separated from free cyanide ions in the reaction mixture by means of an ion-exchange resin.
- 5 66. A process as claimed in claim 65 wherein a cation-exchange resin is employed.
67. A process as claimed in claim 60 wherein free cyanide ions are removed from the reaction mixture by acidifying the reaction mixture and heating the acidified mixture to remove hydrogen cyanide gas.
- 10 68. A process as claimed in claim 67 wherein a mineral acid is employed to acidify the reaction mixture.
69. A process as claimed in claim 67 wherein an organic acid is employed to acidify the reaction mixture.
- 15 70. A process as claimed in claim 69 wherein acetic acid is employed.
71. A process as claimed in claim 67 wherein sulphur dioxide is employed to acidify a reaction mixture.
- 20 72. A process as claimed in claim 60 wherein a reagent is added to the reaction mixture which forms a complex salt with free cyanide ions.
- 25 73. A process as claimed in claim 72 wherein the reagent comprises ferric or ferrous ions.
74. A process as claimed in claim 73 wherein the reagent is a ferric or ferrous salt.
- 30 75. A process as claimed in any one of claims 60 to 74 wherein separation of the bipyridylium cation from free cyanide ions is carried out at a temperature of from 0°C to 100°C.
- 35 76. A process as claimed in any one of claims 1 to 19 or 23 to 75 wherein the N-substituted pyridinium salt is an N-alkyl

pyridinium salt wherein the alkyl group contains up to 10 carbon atoms.

77. A process as claimed in claim 76 wherein the alkyl group contains from 1 to 4 carbon atoms. 40

78. A process as claimed in claim 77 wherein the N-substituted pyridinium salt is an N-methyl pyridinium salt. 45

79. A process as claimed in any one of claims 1 to 19 or 23 to 75 wherein the N-substituted pyridinium salt is an N-carbamido-alkyl pyridinium salt wherein the carbamido-alkyl group contains up to 10 carbon atoms. 50

80. A process as claimed in claim 79 wherein the N-substituted pyridinium salt is an N-carbamidomethyl pyridinium salt.

81. A process as claimed in any one of claims 76 to 80 wherein the pyridine nucleus of the N-substituted pyridinium salt has at least one alkyl group in the 2-, 3-, 5- or 6-position. 55

82. A process as claimed in any one of claims 76 to 81 wherein the N-substituted pyridinium salt is an N-substituted pyridinium chloride. 60

83. A process for the manufacture of a 1,1'-disubstituted-4,4'-bipyridylium salt wherein each of the substituents contains up to 10 carbon atoms substantially as described in any one of the Examples. 65

84. A 1,1'-disubstituted-4,4'-bipyridylium salt wherein each of the substituents contains up to 10 carbon atoms whenever manufactured by the process as claimed in any one of the preceding claims. 70

P. B. TUNNICLIFFE,
 Agent for the Applicants.

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