AN INVESTIGATION INTO THE SYNTHESIS OF CONJUGATED BIPYRIDINIUM-CONTAINING POLYMERS

by

MARTYN ALLEN STILE

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DECLARATION

To the best of my knowledge, this thesis contains no material previously submitted for a degree at any University, nor any written or published by any other person, except where due reference is made in the text.

Martyn Allen Stile

Three passions, simple but overwhelmingly strong, have governed my life: the longing for love, the search for knowledge, and unbearable pity for the suffering of mankind. These passions, like great winds, have blown me hither and thither, in a wayward course, over a deep ocean of anguish, reaching to the very verge of dispair.

Bertrand Russell

ABBREVIATIONS USED

AcA	acetic anhydride
AcOH	acetic acid
Ar	aryl, a general aromatic system
b.p.	boiling point
bipy	4,4'-bipyridyl ($C_{10}H_8N_2$)
c.	circa, approximately
DCM	dichloromethane
DP	degree of polymerization
EA	ethyl acetate
EtOH	ethanol
FAB	fast-atom-bombardment mass-spectrum
GC	gas-liquid chromatography
hr.	hour
IR	infra-red
M	unfragmented species in mass-spectrum
MeOH	methanol
min.	minute
m.p.	melting point
NMR	nuclear magnetic resonance (spectrum)
NCN	(see bipy)
Ph, ϕ	phenyl, C_6H_5
ppm	parts per million
pyr	pyridine (C_5H_5N)
r.t.	room temperature
TFA	trifluoroacetic acid
TLC	thin-layer chromatography
THF	tetrahydrofuran
UV	ultra-violet

ABSTRACT

1,1'-dimethyl-4,4'-bipyridinium dication (methyl viologen) can be reversibly reduced to a blue radical cation, either electrically or photochemically. Other alkyl viologens behave similarly, but aryl viologens are more easily reduced, and this trend increases with the electron-withdrawing capability of the substituents.

Polymers containing viologens have been made and shown to give a permanent blue colouration when irradiated, but the viologen units were always isolated electronically.

The present work describes attempts made to produce polymers containing viologens linked by wholly conjugated chains, either from the 1- (N-) or 2- positions of the bipyridyl. The only polymer produced was made by the condensation of 2,2'-dimethyl-4,4'-bipyridyl with 1,4-diformylbenzene, and contained viologen units linked by "styryl" groups at the 2- positions. By condensation with other aldehydes, several new viologens were made.

In addition, new compounds were made from diamines in which the delocalized system of the viologen was extended over up to six aromatic rings, from the nitrogen atoms.

Model experiments were often performed using pyridinium salts rather than bipyridinium salts, and, because of the chemical differences between the two systems, interesting compounds were made with the former but not with the latter. Amongst these was the novel Wittig reaction of a 1-pyridinium ylid with aromatic aldehydes to give exclusively the unexpected Z-(cis)-olefin products, which are new compounds.

The feasibility of synthesis of the various envisaged polymer types is discussed in general terms.

In order to make certain reaction schemes more readable, it has been necessary to re-number several compounds, which therefore appear in this thesis under two different numbers.

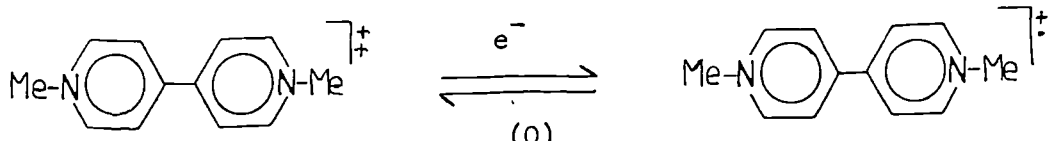
Many of the compounds described in this thesis are salts, but because only the cations were generally of interest, and the anions were unimportant to the reactions occurring, only the cations have been illustrated in the schemes.

INTRODUCTION

GENERAL INTRODUCTION

The 1,1'-dimethyl-4,4'-bipyridyl dication 1 (methyl viologen,"MV") is easily and reversibly reduced by one electron to give a blue radical cation 2 (Scheme 1). This behaviour partially accounts for the general biocidal properties of MV[1], but has also prompted much research into polymeric solids containing the MV (or other viologens) system, as potential optical recording devices[2] similar to the silver (I) ion, (the polymer matrix prevents aerial oxidation of the blue species) and as solar cells[3]. In addition, viologens are used as electron-transfer systems for enzymatic reactions in place of natural co-factors (which are far more costly)[4], and as redox indicators[5].

The published chemistry of the viologens has been reviewed by Bird and Kuhn[6].

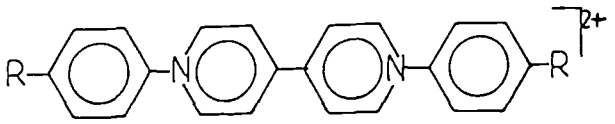


1 (MV^{2+}) 2 (MV^{+})

SCHEME 1

The key property that makes viologens so interesting is the reduction potential of only -440mV. This figure, relative to the Standard Hydrogen Electrode, is found at pH 7 with inert (electrically) anions. Both the pH and the nature of the anions present can alter the redox potential considerably[6]. The nature of the alkyl substituents on the nitrogen atoms does not make any great difference to the reduction potential, unless the substituents can act as electron acceptors or donors (Table 1). N-Arylviologens show these effects most markedly: 4-

cyanophenyl viologen 3 and 4-nitrophenyl viologen 4 are both very easily reduced because of the electron-withdrawing groups, whereas 4-aminophenyl viologen 5 is less so (though still much easier than MV itself), and phenyl viologen 6 shows intermediate properties.



3: R = CN 4: R = NO_2
5: R = NH_2 6: R = H

TABLE 1

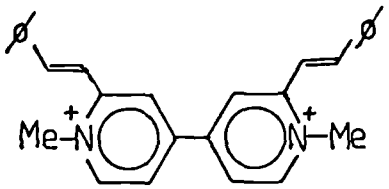
Reduction potentials for viologens

(-mV versus S.H.E. pH 7 in water)

VIOLOGEN		E_1	E_2	Ref.
Methyl	1	440	620	7
Ethyl		450	640	7
i-Propyl		450	630	7
Hexyl		440	685	6
Octyl		465	700	6
Cyanomethyl		130	400	8
Benzyl	7	330	550	6
Phenyl	6	140	-	7
4-MeO-phenyl		140	280	8
4-nitrophenyl	4	+170	70	8
4-cyanophenyl	3	+130	80	2a
4-aminophenyl	5	220	-	9

The effect of substituents at other positions on the reduction potential of a viologen is less clear, mainly because very few such compounds have been made (Table 2), but it appears that alkyl (electron releasing) groups make reduction harder, whilst aromatic groups make reduction easier. The two new "styryl" viologens 8 and 9 have the largest 2- or 6- substituents of any known viologen, and their low

reduction potentials suggest that viologens with even larger conjugated substituents would be even easier to reduce, which in turn suggests that viologens linked by conjugated chains from their 2-positions would be connected electronically.



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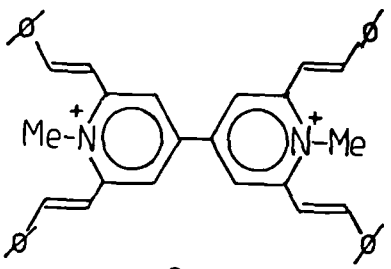

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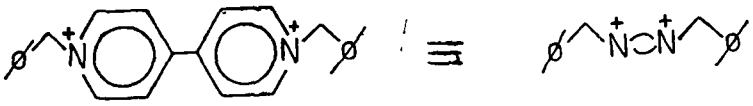

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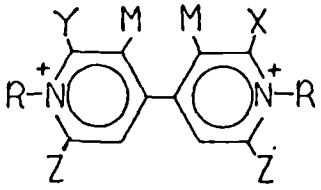

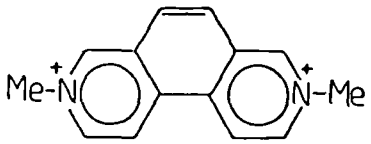

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TABLE 2

Reduction potentials for substituted viologens

(-mV versus S.H.E. pH 7 in water)

VIOLOGEN		E_1	E_2	Ref.
R=Me				
X,Y,Z,M = H	1	440	620	7
X = Me		500	-	3b
X,Y = Me		510	-	3b
"		520	840	8
M = Me		830	-	3b
X,Y,Z = Me		640	-	3b
"		660	260	11
X,Y = Ph		500	-	8
X,Y,Z = Ph		260	40	11
X,Y = styryl	8	270	-	9
X,Y,Z = styryl	9	250	-	9
	10	290	-	10*
X,Y = Cl		250	470	8
R = Et				
X = Me		510	-	3b
R = Bu				
X,Y = Me		480	-	12
X,Y = Et		500	-	12
R = Hexyl				
X = Et		350	570	10*

* Barltrop and Jackson's result[10] with dimethyl-3,8-phenanthroline 10 indicates that unsaturation at the 3-position can play a large part in extending the delocalized system of a viologen. However, their results for other viologens are inconsistent with the results of other workers quoted in Table 2.

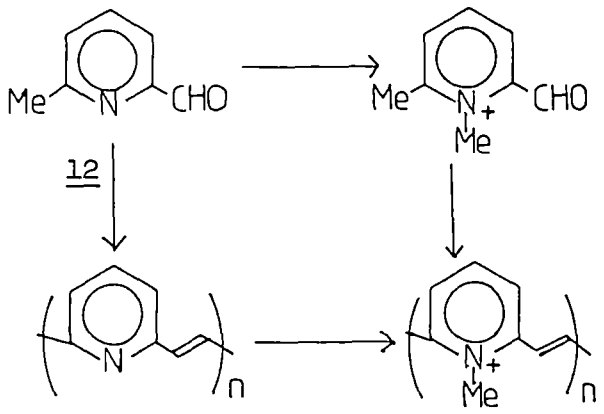
CONJUGATED POLYMERS

The polymers polypyrrole and polyacetylene conduct electricity in one dimension with a degree of polymerisation as low as 19[13] (when doped p- or n-). When crystalline, the iodine-doped polyacetylene will conduct as well as copper[14] (more than 2 x 10^4 S cm^{-1} (Siemens per centimetre)). Poly-(4,4'-bipyridyl), or polypyridine (which have not been investigated, see page 18) could be expected to behave similarly, but a poly-viologen would already be doped (with a positive "hole" on each ring) and should exhibit better conductivity.

For instance, the polymeric "vinylpyridine" salts 11 obtained by Rembaum and Singer[15] by self-condensation of 2-formyl-6-methylpyridine 12 (Scheme 2) have conductivities of 10^{-5} to 10^{-4}S cm^{-1} depending on the anion "comparable to conventional inorganic semi-conductors". The anion that conferred the highest conductivity was tetracyano-quinodimethane (TCNQ)[15b]. The (uncharged) polymer itself has a conductivity of 10^{-8}S cm^{-1} or so. A review of organic conducting salts has been given by Rosseinsky[16].

Conjugated viologen-containing polymers should be even more conducting (because of the redox behaviour, each pyridinium ring contains a positive "hole"). It might also be expected that the counter-anion could be altered to tune the polymer to some desired property, either during the synthesis or by ion-exchange of the polymer. In addition, most viologens are chemically stable (whereas the polyacetylene mentioned above decomposes within days).

The aim of this project was to synthesize such polymers, if possible, with the subsidiary goal of producing new viologens with extended conjugated substituents, for screening as, for instance, herbicides.



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SCHEME 2 - THE SYNTHESIS OF POLY-(VINYLPYRIDINE) SALTS

SCOPE OF THIS WORK

Many different types of structure were envisaged (scheme 3) which would contain bipyridyl or viologen units within conjugated chains, and that would also satisfy the following criteria:

(1) The bipyridyl units should be joined end-to-end

(2) The bipyridyl units should be separated by conjugated units of alternating double (or triple) and single bonds.

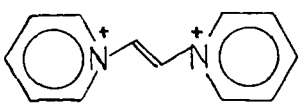
(3) The products should be reasonably air- and water- stable.

The synthetic methods that were selected for study were generally chosen because there were good precedents from pyridine chemistry. No consideration was given at first to the likely degree of polymerization (DP) of the products, for materials with low DP should still have interesting properties.

The 10 structural types illustrated in scheme 3 show one half of two adjacent bipyridyl systems in the anticipated polymer. (The configurations or conformations depicted are purely diagrammatic).

There are only two reports in the literature[17] of bipyridinium compounds with unsaturation on the nitrogen atoms. This is almost certainly explained by the rapidity with which such groups dimerize. 1-Vinylbipyridinium 13 itself is produced[18] (scheme 4) at temperatures below -10° and polymerizes at higher temperatures[14a]. There is no mention in the literature[17] of the interesting compound bis-vinyl viologen 14, although the precursor of it, 2-bromoethyl viologen 15, has been made[8]. This might be a reflection on the (assumed) extreme reactivity of the olefinic bonds in vinyl viologen 14.

Alkyl vinyl viologens (e.g. 16, scheme 4) were produced similarly[18b]. Though no electrochemical results are given, it is clear from UV-visible spectroscopy that the vinyl group does extend the conjugated system of the viologen.



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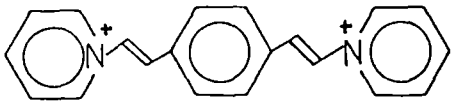

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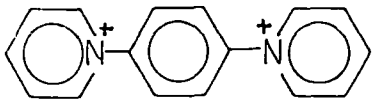

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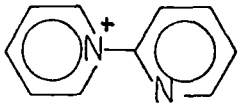

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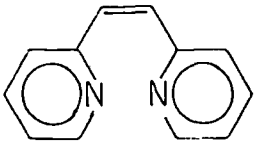

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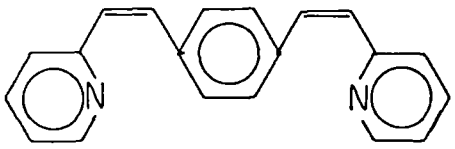

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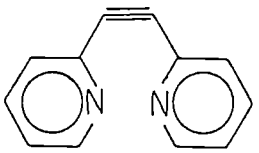
SCHEME 3 - STRUCTURAL TYPES OF TARGET CONJUGATED POLYMERS



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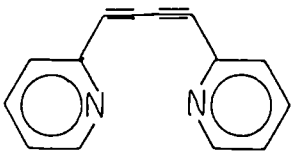

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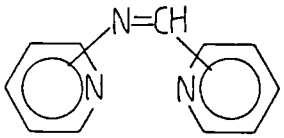

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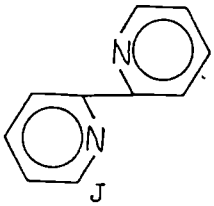

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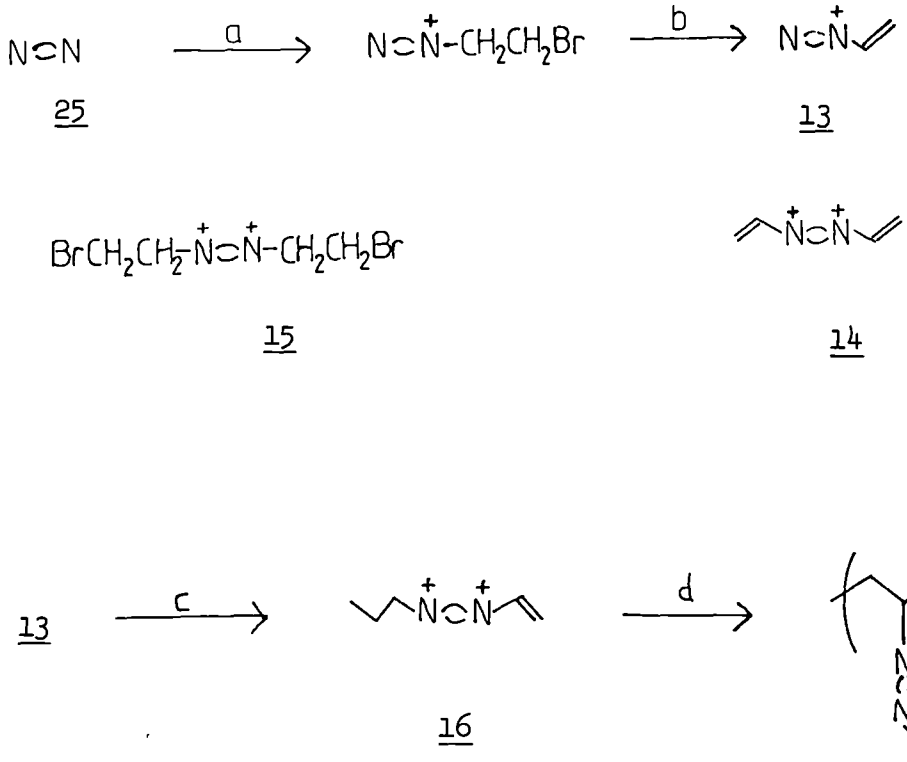
SCHEME 3 - CONTINUED



SCHEME 4 - SYNTHESIS OF 1-VINYL VIOLOGENS

a: Excess $(CH_2Br)_2$ /reflux in DMF

b: NaOH/ toluene/ -10^{o}

c: $CH_3CH_2CH_2Br$

d: "tert-butyl peroxide"

However, there are many references to similar pyridinium compounds, most notably the "styrylpyridinium" salts prepared by the aldol-type condensation of 1-alkylpyridinium salts with aromatic aldehydes. Reaction of a viologen with a dialdehyde might lead to a polymer of structural type (B) (scheme 3). This chemistry is discussed in Chapter 1.

Chapter 2 describes the synthesis of the same compounds, 1-styryl-pyridinium salts, by way of a novel Wittig reaction of a pyridinium-phosphonium ylid. The configuration of these products is, unexpectedly, Z- (cis-), whilst the E- (trans-) isomers were obtained via the route described in chapter 1.

N-phenyl- pyridinium and -bipyridinium salts are well known, being easily prepared by the Zincke reaction[19]. The viologen products are electrochemically interesting, and one, 4-cyanophenylbipyridinium ("CPP", 3, page 2) was the central compound in the I.C.I. P4 project[2a] which was the precursor of this present project. CPP is easily photochemically reduced in polymer matrices to a blue colour, which does not deteriorate. The Zincke reaction with diamines has not been investigated thoroughly (only one mention[17] has been found[20] for this reaction) yet it could be expected to yield polymeric materials of Structural Type (C). Chapter 3 describes this chemistry, and also the formation of imines (Schiff-bases, Structural Type (I)) from amino-phenyl viologens.

Methyl groups at the 2- or 4- positions of a pyridine ring can behave as nucleophiles towards aldehydes (in the same manner as the 1-methyl group, chapter 1). However, the alcohol product is not isolated but is dehydrated in situ to give the olefin. Following the precedent of the

pyridine polymers of Rembaum and Singer[15], the condensation of methyl bipyridinium compounds with a conjugated dialdehyde would be expected to yield a polymer of Structural Type (F) (or E) (scheme 3). There are no literature references to this type of bipyridine. These reactions are discussed in chapter 4.

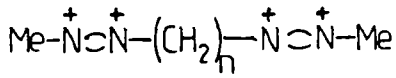
Convenient and high-yielding syntheses of bis-pyridylethyne 17 and 2-ethynyl pyridine 18 (schemes 66 and 67, page 84) have been published[21]. The former is made from a 2-halopyridine and ethyne, suggesting that the same reaction with a 2,2'-dihalobipyridyl would give a polymer of Structural Type (G). The bipyridyl equivalent of ethynylpyridine 18 could be coupled by an Ullmann-type oxidation to produce Structural Type (H). The published literature of alkynyl pyridines is discussed in chapter 5.

Chapter 6 is concerned with miscellaneous other reactions which might have afforded unsaturated viologens. Although this thesis is mostly concerned with the synthesis of new compounds, some preliminary electrochemistry was undertaken, and the results are also presented in chapter 6.

Within each chapter, there is an introduction to the previously known chemistry (generally with reference only to pyridine compounds) followed by a discussion of the chemistry of the bipyridyl case and the possibilities for polymer formation.

POLY VIOLOGENS

The simplest poly-viologens are the "dimeric" polymethylene perchlorate salts produced by Atherton, Tsukahara and Wilkins[21] (scheme 5). The three compounds described therein clearly show that as the chain separating the two viologen systems shortens, the reduction potential falls sharply (Table 3). Unfortunately, the compound with n=1 (20) is not mentioned. Indeed, no mention of this compound is to be found in the literature.



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SCHEME 5

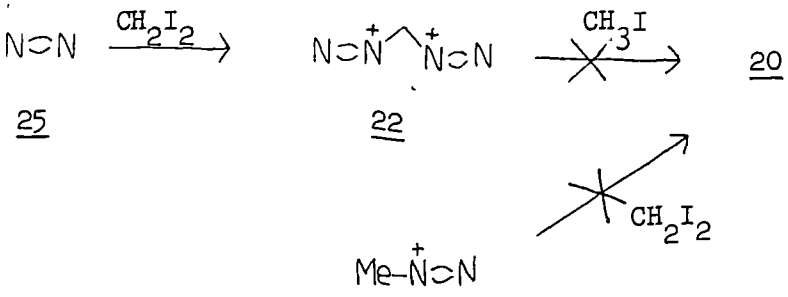
TABLE 3

The reduction potentials of the poly-methylene viologens (20)

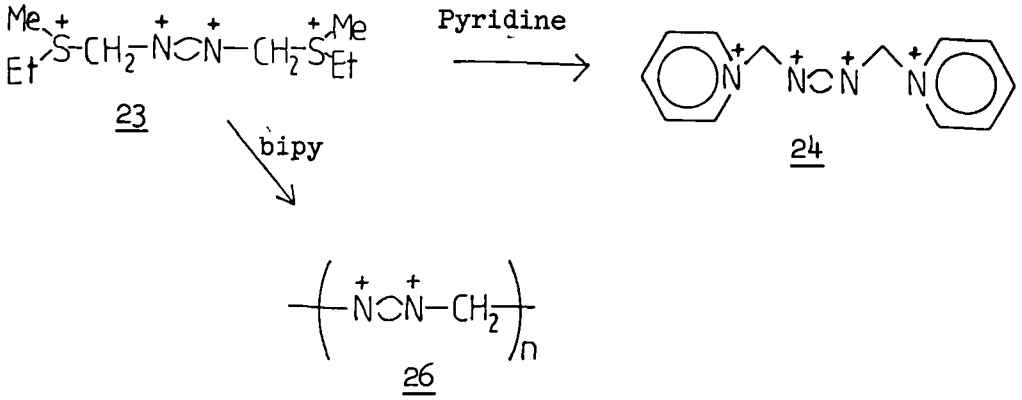
n	E_1 (-mV)
2	280
3	330
4	390
Infinite (1)	440
[1 (22)	220]

The preparation of bis-viologen 20 was attempted, but unsuccessfully: The reaction of excess methyl-bipyridinium iodide 21 with diiodomethane, neat or in propylene carbonate or methanol, yielded a black material containing elemental iodine. Similarly, the methylation of bis-(1-bipyridinium)-methane 22 with iodomethane (scheme 6) gave no isolable product 20. This is presumably because it (the viologen) is being reduced by iodide.

These reactions were not attempted with other anions.



SCHEME 6



SCHEME 7

However, the bis-sulphonium viologen tetrafluoroborate salt 23 reacted both with pyridine, giving 24 (scheme 7), and with bipyridyl 25 to give a white solid, insoluble in TFA, but water-soluble, that gave a proton NMR spectrum (see Spectrum 1, Appendix A) that was consistent with the polymeric structure 26 shown.

The electrochemistry of this polymer and of compound 24 have not yet been investigated.

Many other types of viologen-containing polymer have been synthesized and described:

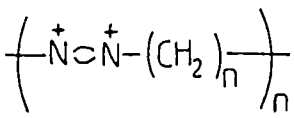
The polymethylene viologens 27 (scheme 8), formed by reaction of bipyridyl 25 with dihaloalkanes are easy to make[3c], but are brittle and have bad film-forming characteristics. Previous I.C.I. workers[2a] have made other polymers from bipyridyl and polyhalo-compounds, such as 28, 29 and 30, but these were also of little use. Polymer 30, made by reaction of bipyridyl with 1,3-dichloro-4,6-dinitrobenzene does not have the viologen units conjugated with each other. The corresponding polymer from a 1,4-dihalobenzene, that would have conjugated viologen units, has not been prepared.

In contrast, the polyamide-polyviologens of Simon and Moore[2b], which were made by interfacial condensation (in the same way as nylon) formed good films.

Most of these polymers contain viologen units that do not differ significantly in electrical properties from MV itself.

Nambu, Yamamoto and Endo[18b] polymerized 1-propyl-1'-vinyl viologen 16 with a free radical initiator and obtained polymer 32 (scheme 4, page 10) which had a "reversible redox peak at -0.47 V" (no reference given).

The methods of polymerization used in the cases above highlight one of the problems of this project-that of having a (very) high-yielding polymerization step. Whereas bond-forming reactions between sp^2- and sp^3-hybridized atoms can approach 100% yield, reactions between two sp^2 centres are seldom high yielding, therefore severely limiting the DP of the product, and, probably more significantly, its purity.



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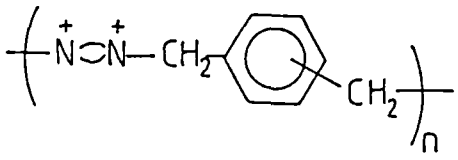

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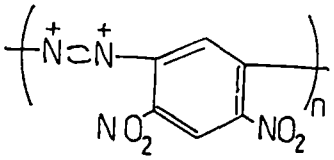

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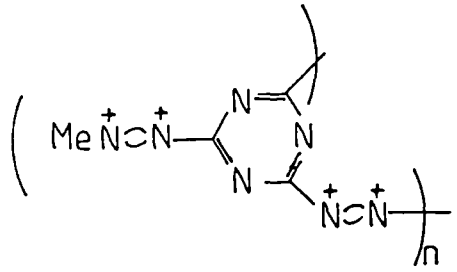

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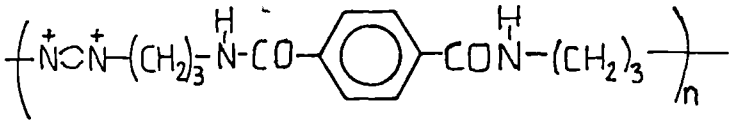

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SCHEME 8 - POLYMERIC VIOLOGENS

POLY-PYRIDINES

Uncharged poly-pyridines are well documented in the literature, being mostly synthesized as chelating ligands for transition metals. They are generally made by the reductive coupling reactions, as described for bipyridyl. (Pyrrole and thiophene are polymerized by electrical oxidation[13], yet pyridine does not seem to have been treated in this way).

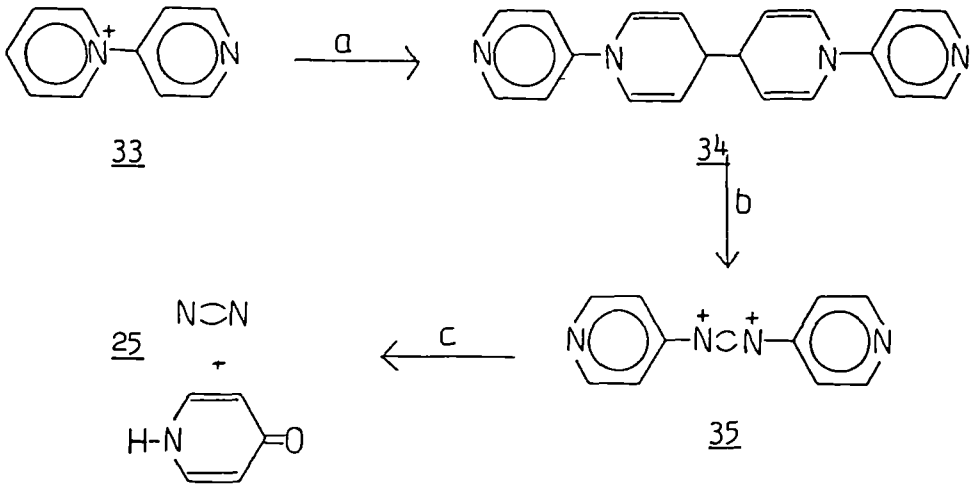
Charged polypyridines, which are less useful as ligands, have not been as well studied:

Reuss and Winters[22] coupled 1-(4-pyridyl)-pyridinium chloride 33 using cyanide (scheme 9) giving the tetrahydro-tetrapyridyl 34, which was oxidized to tetrapyridyl 35 by air. This compound was readily hydrolysed in refluxing aqueous solution, the products being 4,4'-bipyridyl 25 and 4-pyridone.

The isomer of tetrapyridine 35, that is, 36 was prepared by reaction of bipyridyl with excess 2-bromopyridine (scheme 10), in very good yield. Attempted N-methylation of the product with either dimethylsulphate (at 140°), or iodomethane (in ethanol) produced a mixture containing bipyridyl and 2-pyridone, and their methylation products (by NMR analysis). The reaction of 2-iodo-1-methylpyridinium bromide with bipyridyl gave a reaction mixture that could not be analyzed, and which afforded no crystalline products.

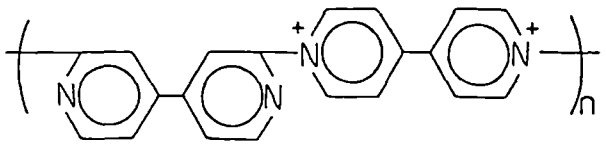
Similarly, pyridine reacted with 2-bromopyridine to give 1,2'-bipyridinium salts 37, but gave a black, intractable, mixture when reacted with 2-iodo-1-methylpyridinium bromide.

It therefore seems highly unlikely that a polymer of type B (scheme 11) would be stable, though the less highly charged polymer A might be. This latter could perhaps be made from 2,2'-diiodobipyridyl and bipyridyl, but 2,2'-dichlorobipyridyl 38, the only such dihalobipyridyl

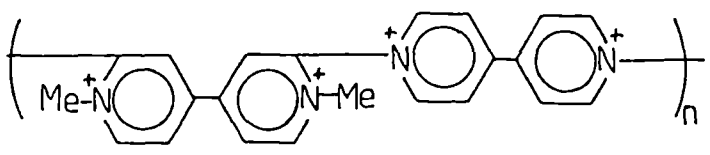


SCHEME 9 - COUPLING BY CYANIDE OF 4-PYRIDYLPYRIDINE (33)

a: NaCN/ acetone b: Air c: Refluxing aqueous acid

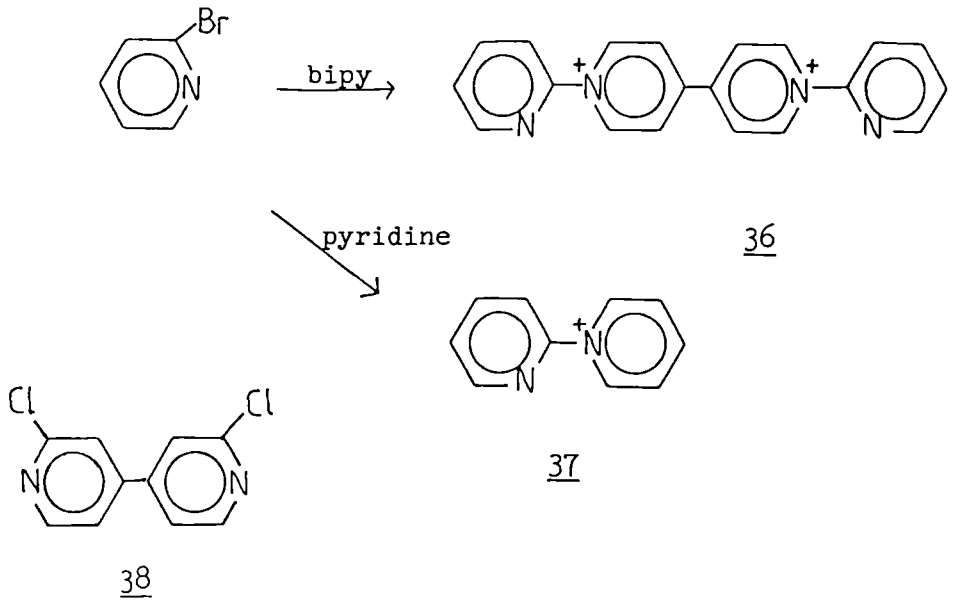


A



B

SCHEME 11 - "POLYPYRIDINES"



SCHEME 10

available, is unreactive towards nucleophiles, reacting with neither iodide nor pyridine under very severe conditions.

SYNTHESIS OF VIOLOGENS

In theory, all bipyridinium salts are synthesizable by four routes:

(1) By coupling a pyridine, then alkylating

(2) By alkylating a pyridine, then coupling.

(3) By elaboration of bipyridyl and N-alkylation

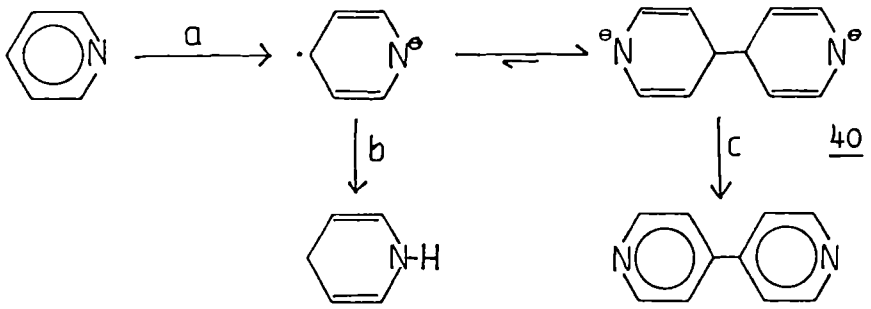
(4) By ring-synthesis

These four routes will now be discussed:

(1) When an electron is added to a pyridine ring, the radical-anion formed will dimerize unless there is a proton source present, in which case the major product is the dihydropyridine 39 (scheme 12). The major product is always reduced at the 1- and 4- carbon atoms, with 1-,2-reduction being a minor side-reaction. 4,4'-Bipyridyl 25 itself is produced commercially by the reductive coupling of pyridine with sodium in liquid ammonia[23], but various other dissolving-metal techniques have also been used successfully[24]. The tetrahydrobipyridyl 40 (from protonation of the dianion shown) is easily oxidized to 25 by air in acidic solution.

In contrast, none of these techniques gives good yields with substituted pyridines. For instance, the product of the conversion of 2-methylpyridine into 2,2'-dimethylbipyridyl 41 (see scheme 16) by sodium in liquid ammonia is only obtained in about 10% yield. Dimethylbipyridyl 41 has also been made by coupling methylpyridine in poor yield in several other ways[25].

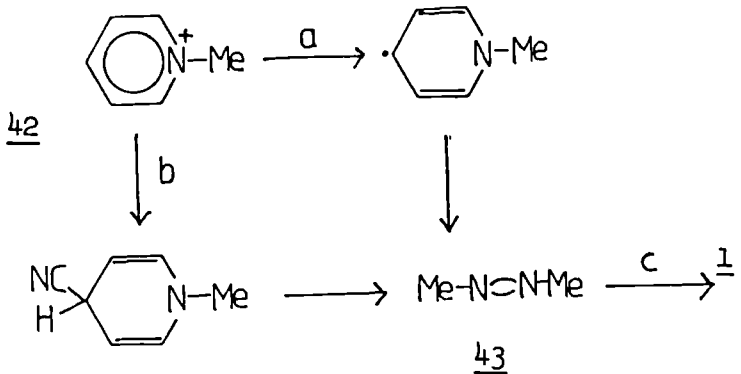
The only methods for producing dimethylbipyridyl 41 in even fair yield are those of Becker and Neumann[26] and of Balanson, Oxsen and Cheng[12] discussed later (pages 64 and 66). With other 2-(non-alkyl) substituted pyridines, however, their yields were poor.



39 25

SCHEME 12 - THE REDUCTIVE COUPLING OF PYRIDINE

a: Sodium/ liquid ammonia b: $H^+/e^-/H^+$ c: H^+/ air



42 43 1

SCHEME 13 - THE COUPLING OF METHYLPYRIDINIUM (42)

a: Electrolysis (cathodic) b: NaCN/ acetone c: Air

(2) Methyl viologen is now commercially produced by the electrolysis of aqueous solutions of 1-methylpyridinium salts[27] 42 (scheme 13). Like the reductive coupling of pyridine, the product is almost exclusively[28] the 4,4'-isomer of the tetrahydrobipyridyl (43), showing that the odd electron resides preferentially at the 4-position, before dimerization occurs. Other alkyl viologens can be coupled in this way, but as the substituent grows in size, the aerial oxidation of the tetrahydro viologen to the viologen itself becomes both slower and poorer yielding.

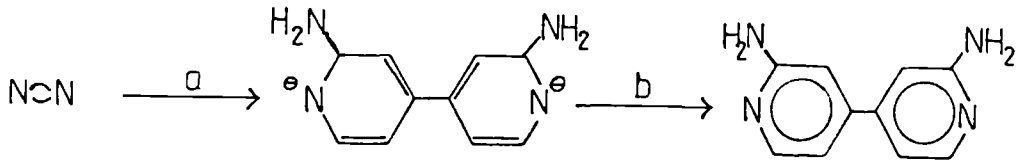
Another method of coupling pyridinium salts to produce bipyridyls is the cyanide-mediated reaction developed by Reuss and Winters[22] (scheme 13). However, although the authors report good yields of simple alkyl viologens[22c], other workers have met with less success[29]. In addition, the reaction does not proceed smoothly when the pyridine ring is further substituted.

(3) Whereas 4,4'-bipyridyl itself is sold commercially, there are no substituted bipyridyls available, and there is also little in the way of literature concerning these compounds.

Thus, a search revealed that only four 2,2'-disubstituted bipyridyls have been synthesized, namely, the diamino-, dichloro-, dihydroxy-, and dimethyl- compounds.

2,2'-Diaminobipyridyl 44 has been made by high temperature reaction of bipyridyl with sodium amide[30] (scheme 14), but experimental details are lacking. The product of this reaction is a brown intractable solid that does not give an NMR spectrum, though the mass-spectrum obtained is consistent with that expected.

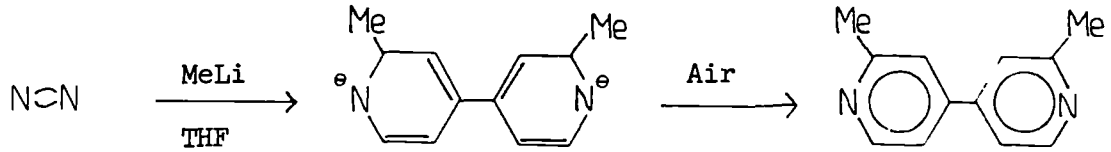
2,2'-Dichlorobipyridyl 38 (scheme 10) has been made, in poor yield, by the gas-phase reaction of bipyridyl with tetrachloromethane[31].



25 44

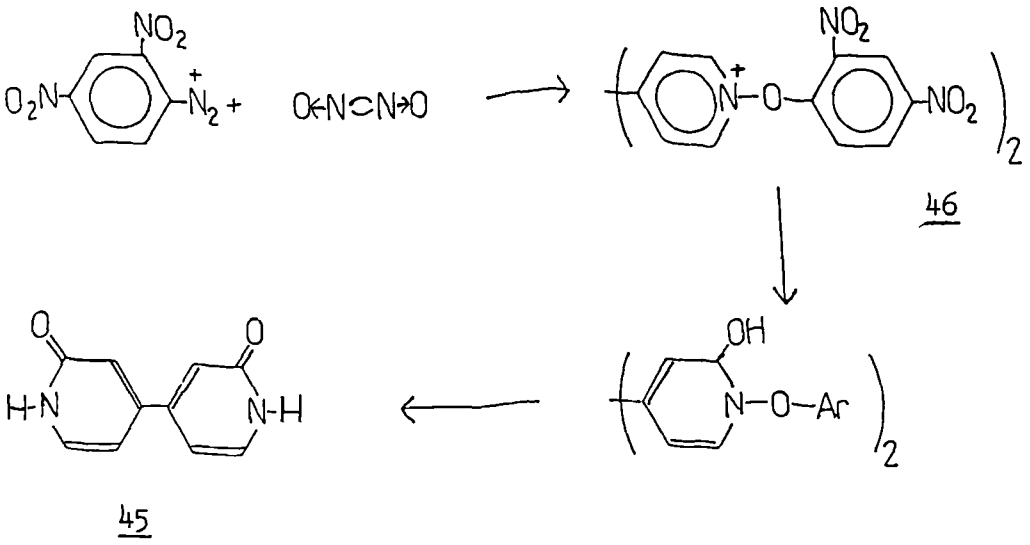
SCHEME 14 - AMIDATION OF BIPYRIDYL (25)

a: $NaNH_2$/ biphenyl at 200° b: Loss of H^-



25 41

SCHEME 16 - C-METHYLATION OF BIPYRIDYL (25)

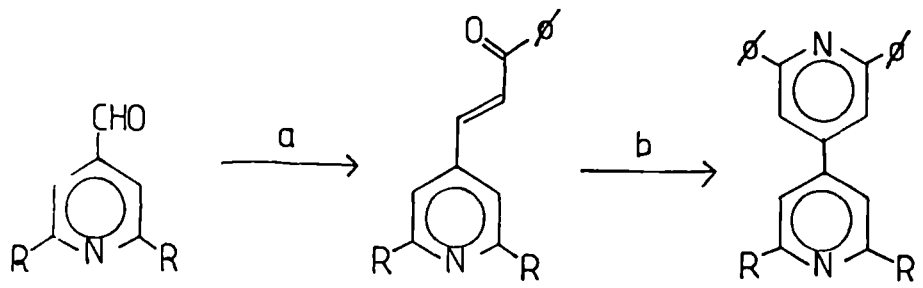


SCHEME 15 - THE SYNTHESIS OF 4,4'-BIPYRIDONE (45)

2,2'-Dihydroxybipyridyl (bipyridone) 45 is available from the rearrangement of N-aryloxy viologen 46 (scheme 15)[32].

2,2'-Dimethylbipyridyl 41 has been made in a variety of ways, the best of which are coupling reactions discussed elsewhere, but it could also be obtained in poor yield by the reaction of methyllithium and bipyridyl[25] (scheme 16). Francis, Davis and Wisener[33] have discussed the reaction of alkyl lithiums with bipyridyl.

(4) In the literature can be found many varied examples of versatile pyridine ring-syntheses, but bipyridine syntheses are much harder to find. Among the few ring-syntheses of viologens published, by far the best is that of Hunig and co-workers[11] (scheme 17). Although this is clearly versatile in respect of the R-group on the original pyridine, the substituents on the ring being formed must include one phenyl group, because of the necessity of having the phenacyl-pyridinium salt



48 R = H

49 R = Ph

SCHEME 17 - THE RING SYNTHESIS OF PHENYLBIPYRIDYLS

a: $PhCOCH_3$ b: $PhCOCH_2pyr^+ Br^-$ (47)/ AcOH

47 involved, (which is a development of the work described earlier by Krohnke[34] for the synthesis of pyridines) and the products are limited to the di- and tetra-phenyl bipyridyls 48 and 49.

J.E.Downes[35] has also demonstrated the synthesis of 2,6-diphenyl-4,4'-bipyridyl 48 by ring-synthesis.

Three general procedures were used for the coupling with aldehydes:

(1) Cold sodium hydroxide solution[36a].

(2) A hot suspension of calcium hydroxide in ethanol[36b].

(3) Potassium acetate in hot acetic anhydride[36c].

There were also several methods for the dehydration of the alcohols to olefins[36b], of which three were tried;

(1) Pyrolysis of the acetate ester.

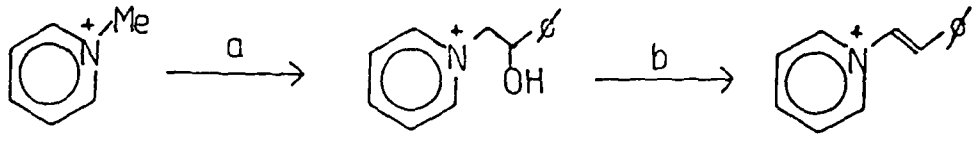
(2) Pyrolysis of the benzoate ester.

(3) Pyrolysis of the oxalate ester.

The isolated yields of alcohol 50 (scheme 20) and olefin 51 were improved upon during the early repetition of these reactions; Krohnke used calcium hydroxide to couple phenacylpyridinium salts, and sodium hydroxide to couple methylpyridinium salts, but not calcium hydroxide, yet using that catalyst, an almost quantitative yield of alcohol 50 has been obtained. Generally, calcium hydroxide in refluxing ethanol gave superior yields of other compounds too, compared with other systems. (Phenacyl salts were not used, for the benzoic acid/ calcium benzoate by-product was often tiresome to remove).

Dehydration of alcohol 50 was only satisfactorily achieved by heating in molten oxalic acid at 140° for three hours, followed by aqueous work-up. The product olefin 51 is the E-isomer (the ^{1}H NMR coupling constant between the two olefinic protons is 15 Hz. Such a large value indicates that the product has the E-configuration[81a]), and was isolated as the hydrated acid oxalate salt, which could be converted, by ion-exchange chromatography, into other salts.

Krohnke also made "pyridinium-ethanols" (i.e. 50) by treating styrene bromohydrin with pyridine[36a], albeit in poor yield (scheme 21).

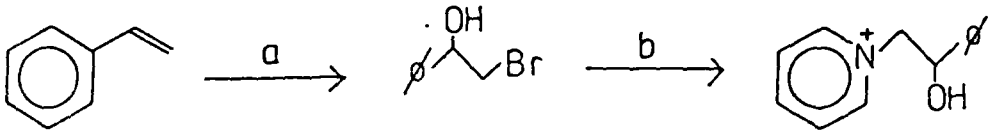


42 50 51

50An ø = $MeOC_6H_4$ 51An ø = $MeOC_6H_4$

SCHEME 20

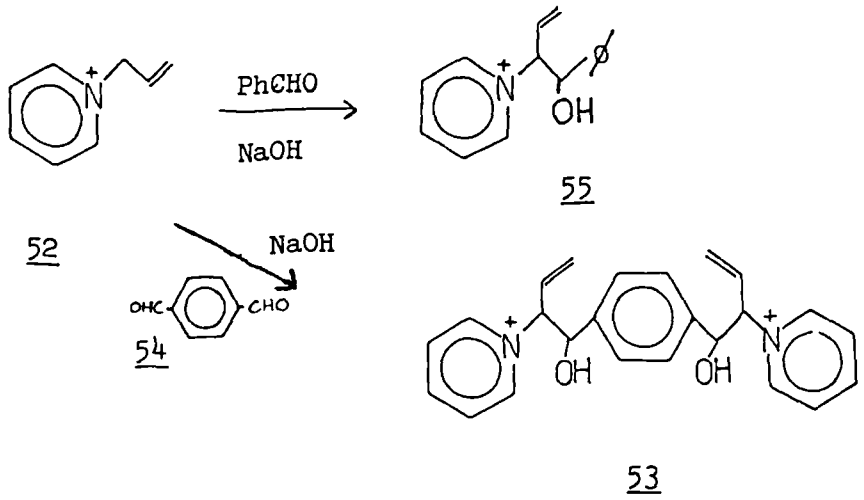
a: PhCHO/ EtOH/ $Ca(OH)_2$ b: Oxalic acid / 150°



50

SCHEME 21

a: Br_2/ H_2O b: Pyridine



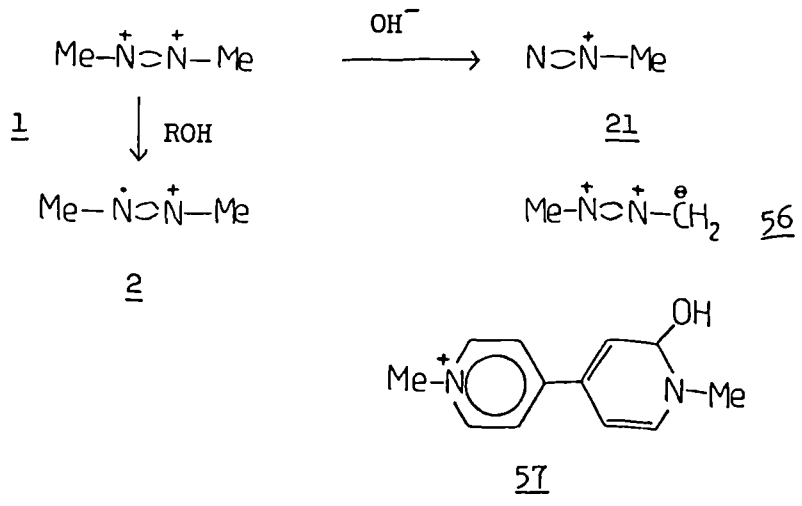
SCHEME 22 - REACTION OF ALLYLPYRIDINIUM (52) WITH ALDEHYDES

Despite a lot of effort, no products were obtained from the reaction of methyl- or phenacyl-pyridinium with either 1,2- or 1,4-diformylbenzene under a variety of conditions. (The ^{1}H NMR spectrum of the crude reaction mixture showed only starting materials). However, 1-allylpyridinium bromide 52 gave a good yield of the diol 53 with 1,4-diformylbenzene 54 (Scheme 22), but 53 could not be dehydrated, by the normal procedure. The "mono" alkyl compound 55 , made from 52 and benzaldehyde likewise failed to undergo dehydration to the olefin, but decomposed back to the starting materials. There was also a white insoluble product, probably a result of the polymerization of the olefinic double bond.

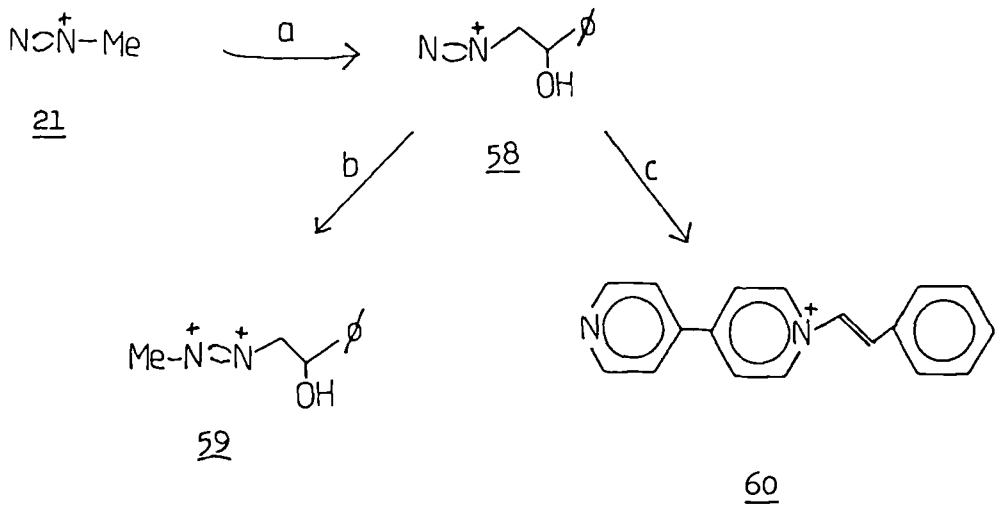
Methyl viologen 1 and bis-phenacylbipyridinium were both reacted with benzaldehyde under all three reaction conditions. The reaction mixtures were deep blue, but no products were ever obtained (NMR spectra of the crude reactions also showed no evidence for product formation), starting materials only were recovered. This is probably due to the electronic behaviour of the bipyridinium structure:

Farrington and co-authors[37] showed that methyl viologen 1 is converted to 1-methylbipyridinium 21 and methanol in alkali (scheme 23), and the methanol then reduces the viologen 1 further to the radical-cation 2 (which is blue). However, the reaction mixture is probably more complicated still, with ylid 56 and hydroxylated species 57 probably also present to a considerable extent.[38]

Ylid 56 (Scheme 23) is stabilized relative to 1, when compared with the pyridinium case, but also less reactive as a nucleophile compared to the corresponding pyridinium salt, so that in the reaction equilibrium, ylid 56 (or alcohol 57) is probably the dominant species and this would revert to starting materials on work-up.



SCHEME 23 - THE REACTION OF MV (1) WITH HYDROXIDE



SCHEME 24

a: PhCHO/ OH^- b: MeI c: Oxalic acid at 150°
(1) Cold EtOH/ NaOH
(2) Hot EtOH/ $Ca(OH)_2$

In contrast to this, 1-methylbipyridinium "monoquat" iodide 21 gave a good yield of the alcohol 58 with both condensation procedures 1 & 2 (Scheme 24). This orange compound was easily methylated to give viologen 59, but the product was readily decomposed to methyl viologen 1 and benzaldehyde, when exposed to air, lending further evidence to the belief that viologen-alcohols or -olefins are unstable with respect to retro-aldol reaction. Alcohol 58 was dehydrated via the oxalate, but this product olefin 60 could not be N-methylated with either dimethyl sulphate at 120° or iodomethane in ethanol.

Pyridinium rings are well-known to cleave on treatment with base to give poly-methine compounds that are highly coloured[39]. This reaction occurs most readily when the nitrogen has an electron-withdrawing substituent, as for instance in the N-phenylpyridinium salts in their reaction with anilines discussed in Chapter 3.

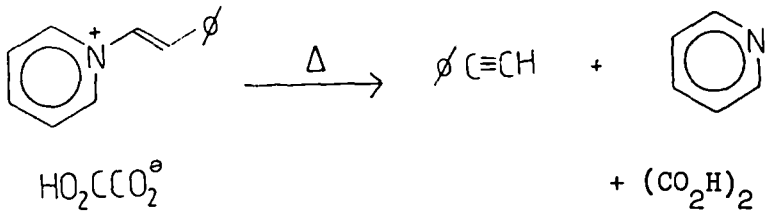
N-styrylpyridinium oxalate 51 was decomposed by dilute aqueous alkali to give a bright red coloured material, due to formation of a poly-methine species such as 61 (Scheme 25).

In addition, a red material was obtained upon reaction of styrylpyridinium 51 with butyllithium, or sodium diethyl malonate, in THF solution; It had been hoped that such nucleophiles might have attacked the olefinic bond, to give interesting products; however, it seems as though nucleophilic attack occurred only at the 2-position of the pyridinium ring.

Olefin 51 was pyrolysed *in vacuo* to pyridine and phenylethyne (Scheme 25). The pyridine was recovered in over 80% yield, but less than 10% yield of alkyne was collected (presumably because it polymerises under reaction conditions).

Olefin 51 was not affected by bromine in refluxing tetrachloromethane, but is reported to react at higher temperatures[36].

Phenylethyne has been reacted with secondary amines to give 3-N-substituted 1,4-diphenylbutynes[40]. Krohnke has stated[36] that it was not known whether this reaction would work with pyridine (to give 1-styrylpyridinium salts). Pyridine and phenylethyne were heated together in the presence of copper (I) chloride. The ether-insoluble residue contained no involatile pyridinium compounds, but was difficult to work with because of the copper salts. The reaction does not seem to proceed.



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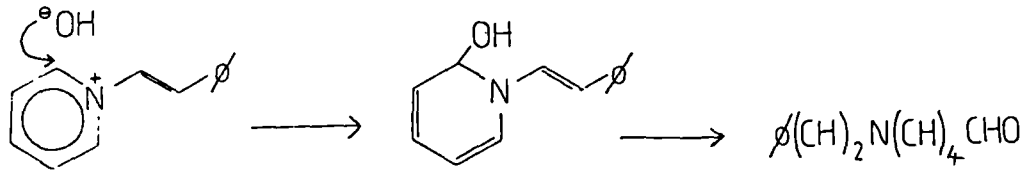
SCHEME 25 - THE DECOMPOSITION OF STYRYLPYRIDINIUM (51)



51 61

CONCLUSION

It seems highly unlikely from the results obtained that N,N'-bis-(styryl)-viologens could be made in the manner described above. They almost certainly would decompose in the presence of moisture. Likewise, the synthesis of any polymeric compounds by this approach is probably not feasible.

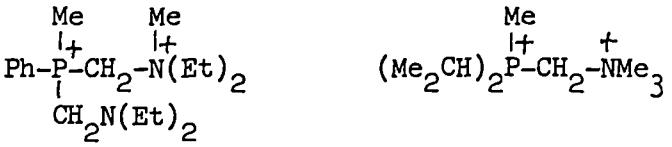
CHAPTER TWO

Wittig chemistry of phosphonium-pyridinium ylids

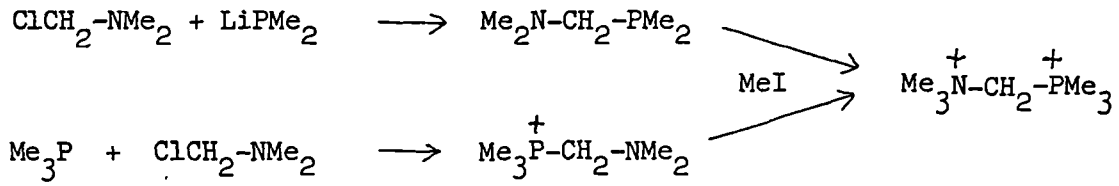
A classical method for generating double bonds in organic chemistry is the Wittig reaction between an aldehyde, and an ylid formed from a phosphonium salt, itself normally formed from an alkyl halide. The reaction is generally high-yielding and often regioselective.
Such ylids have been reported at the 2-position of pyridine[41](see chapter four), and these exhibit normal Wittig behaviour. However the only[27] report[42e] of a 1-alkylphosphonium-pyridinium compound also stated that no Wittig chemistry was accomplished with it.

1-(Phosphoniomethyl)-pyridinium salts

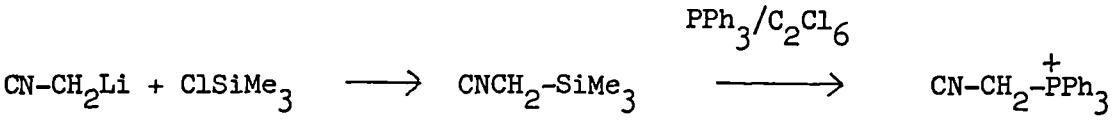
There were very few references[42] in the literature[17] to compounds with positively charged nitrogen and phosphorus both attached to the same carbon atom:
Russian workers's investigation[42b,c] of mixed ammonium-phosphonium salts ended with the synthesis of just a few aliphatic compounds (Scheme 26), and they were mainly interested in the relative nucleophilicities of the amine and phosphine groups.
Lundberg, Rowatt and Miller[42c] made similar compounds in a much more direct and versatile way (Scheme 27).
Zinner and Fehlhammer[42a] made triphenylphosphoniomethyl-isocyanide chloride 62 (Scheme 28) from trimethylsilyl-methylisocyanide and triphenylphosphine in hexachloroethane. Because compound 62 did undergo Wittig reaction with, for instance, fluorenone, it was hoped that pyridine would behave in a similar way to the isocyanide group, but pyridine did not react with chloromethyl-trimethylsilane to yield the expected (trimethylsilylmethyl)-pyridinium salt, so this idea was



SCHEME 26



SCHEME 27



62

SCHEME 28

not pursued.

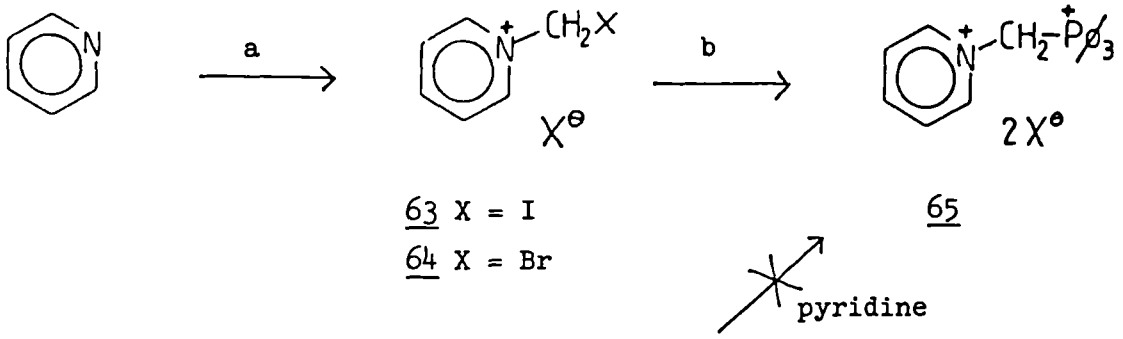
In "normal" Wittig reactions, the phosphonium salt is generally made from the reaction of an alkyl halide with a phosphine. The novel iodomethyl-pyridinium salt 63 (see below) reacted with molten triphenylphosphine to give the phosphonium-pyridinium iodide salt 65 in quantitative yield (Scheme 29).

An alternative route to 65 would be to create the carbon-phosphorus bond first. Thus, triphenylphosphonio-halomethane compounds 63a and 64a were synthesised, firstly using the literature methods[43a] (Scheme 29), then in non-polar solvent, when almost quantitative yields could be obtained.

However, reaction of either of these species with pyridine in several different solvents gave very poor yields of the desired pyridinium salt 65 (From NMR evidence, the CH_2 doublet of phosphonium-pyridinium salt 65 at δ 7.1 ppm in TFA is characteristic) and this compound was not isolated by this route.

The procedure of Sugimoto et al.[42e] (Scheme 30) for the synthesis of the tetrafluoroborate salt of 65 was followed and found to be satisfactory, but not as convenient, due to the cost and nature of the reagents, as the synthesis *via* the iodomethylpyridinium salt 63.

Pyridine reacted easily with chloromethylmethylsulphide (CMMS)(extremely nasty!) in refluxing dichloromethane (DCM) to give the thiapropylpyridinium salt 66, which, again in refluxing DCM, was S-alkylated with excess triethyloxonium tetrafluoroborate to the sulphonium-pyridinium salt 67, which in turn reacted with triphenylphosphine in cold acetonitrile to yield phosphonium-pyridinium salt 65.



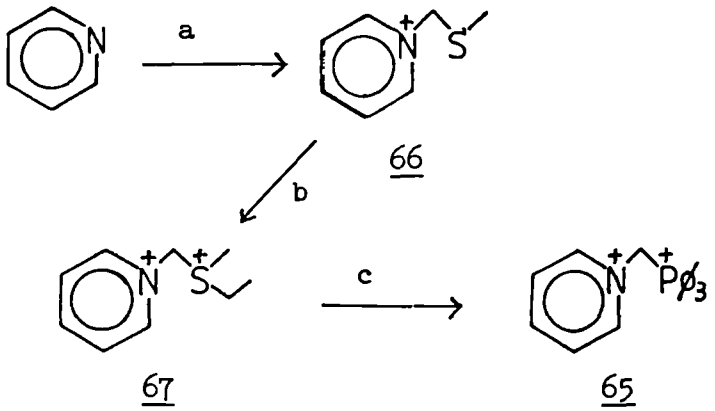
63 X = I
64 X = Br

65

63a X = I
64a X = Br

SCHEME 29

a: Excess CH_2X_2 b: Ph_3P



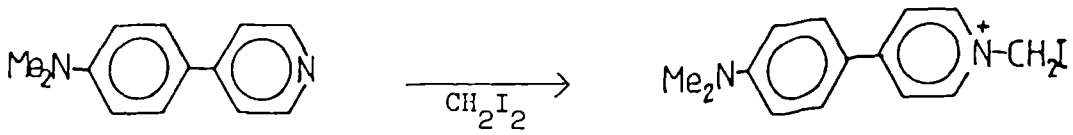
66

67

65

SCHEME 30 - THE PREPARATION OF PHOSPHONIUM-PYRIDINIUM SALT 65BF BY THE METHOD OF SUGIMOTO

a: $MeSCH_2Cl$ b: $Et_3O^+ BF_4^-$ c: Ph_3P



68

SCHEME 31

1-haloalkylpyridinium compounds

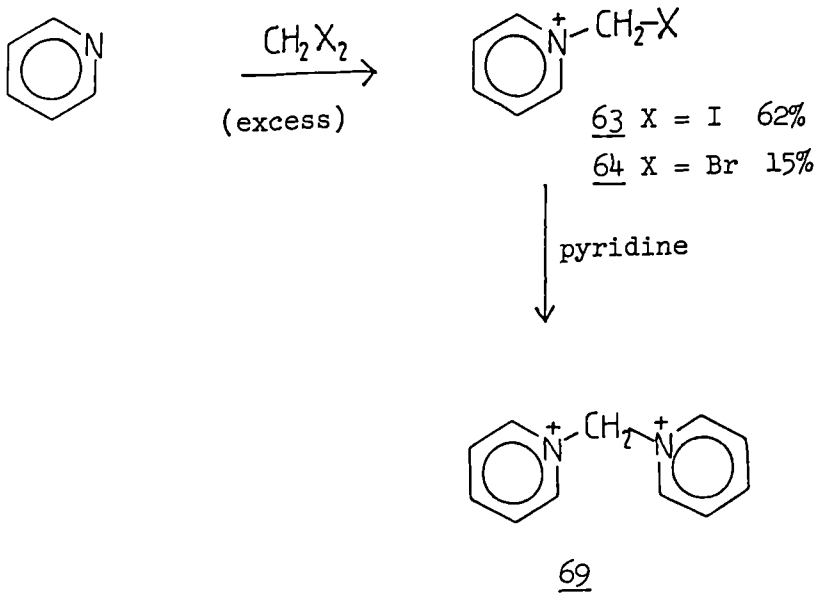
There had only been one[44] report in the literature[17] of the synthesis of a 1-haloalkylpyridinium salt. This was prepared by heating a substituted pyridine with a large excess of diiodomethane to give compound 68 (Scheme 31).

This reaction was repeated with pyridine and excess diiodomethane to give a fair yield of iodomethylpyridinium iodide 63 , and also with dibromomethane to give bromomethylpyridinium bromide 64, but in poor yield (scheme 32). With dichloromethane, reaction was exceedingly slow, and the only product was dipyridylmethane[45](69). (This compound is decomposed in basic solution to hydroxy-methylpyridinium salts, which then decompose further to pyridine and formaldehyde) .

The problem with the synthesis of the halomethyl-pyridinium compounds 63 and 64 is in the increased lability of the second halide after the first has been substituted by pyridine, leading to substantial quantities of di-pyridylmethane 69 being produced (scheme 32). When pyridine was heated in the neat dihalomethane, that was the only product, but in toluene as solvent, greater than 90% of the required halo-methyl compound could be produced, because the first-formed salt precipitated out and was therefore protected from further attack by pyridine.

It was hoped that by using chloroiodomethane, the reaction could be stopped after the substitution of the iodine atom, but in practice, the

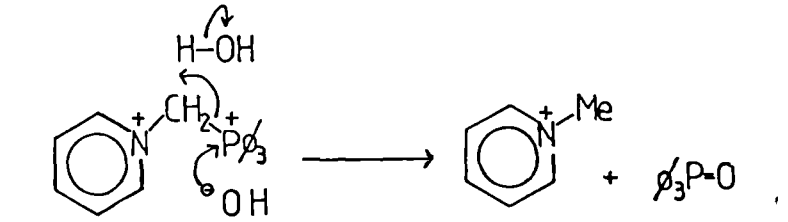
highly nucleophilic iodide (produced by this reaction) reacted with the chloromethylpyridinium product to give iodomethylpyridinium, and the isolated product mixture consisted of three compounds. If an iodide scavenger, such as lead (II) acetate was present in the mixture, though, chloromethylpyridinium could be produced (the NMR spectrum of the reaction mixture contained only the one singlet, due to chloromethylpyridinium), but the product could not be isolated.



SCHEME 32

Reaction of phosphonium-pyridinium salt 65 with aldehydes (Scheme 34)

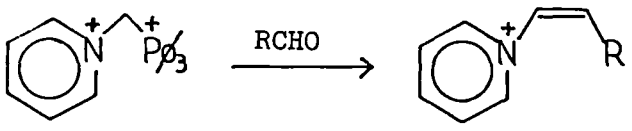
In agreement with the paper of Sugimoto[42e], compound 65 was found to be highly susceptible to base attack, and hydrolysis readily occurred to give methylpyridinium and triphenylphosphine oxide (scheme 33).



65

SCHEME 33 - THE HYDROLYSIS OF PHOSPHONIUM-PYRIDINIUM SALT (65)

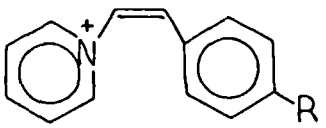
However, compound 65 was found to be indefinitely stable in acidic media, and in acetic anhydride with an amine base, it reacted with benzaldehyde at 120° to give the olefin 70 in fair yield (scheme 34).



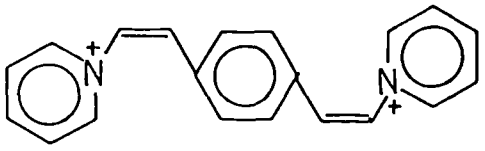
65

70 R = Ph
70c R = 2-Pr

SCHEME 34 - THE WITTIG REACTION OF PHOSPHONIUM-PYRIDINIUM SALT (65)



70a R = OMe
70b R = CHO



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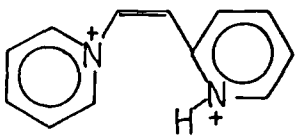

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(The proton NMR of the reaction mixture showed that about 90% of the pyridinium protons were product, with about 10% 1-methylpyridinium. Unfortunately, isolated yields are poor). This novel Wittig reaction was carried out with a variety of aromatic aldehydes. In all cases, the product olefin had the Z-(cis) configuration, as shown by the NMR spectra of the olefinic protons (table 4) (the coupling constant between the two olefinic protons is about 9 Hz, typical of a Z-olefin[81b]). The best yields were obtained when the product was easily crystallized. Thus dicationic diene 72, was obtained in good yield, and the phenyl olefin 70 was obtained in fair yield, but the addition of substituents to the phenyl ring (4-methoxyl or 4-formyl, yielding 70a and 70b respectively) caused the product olefin to become harder to crystallize. This is because the removal of the amine salt by-products was problematical (though with 2-formylpyridine, yielding 71 this problem did not exist), the best method found being a counter-current system between water and an organic solvent. The product olefins were rapidly hydrolysed in basic solution, like the isomeric E-olefins mentioned in chapter 1, and this prevented the conversion of the amine salts into the free amine, and subsequent extraction with an organic solvent.

With analytical high-pressure liquid-chromatography with a C-8 reverse-phase column, and aqueous methanol as solvent, a good separation between the salts was achieved.

With sodium acetate as the base for the Wittig reaction, the major product was 1-methylpyridinium. With aniline or triphenylphosphine, no reaction occurred and unchanged 65 was recovered. The reaction failed for ketones, but proceeded slowly with the aliphatic aldehyde 2-methylpropanal at reflux, but here the product rapidly hydrolysed on work-up.

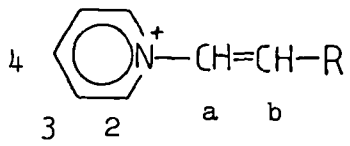
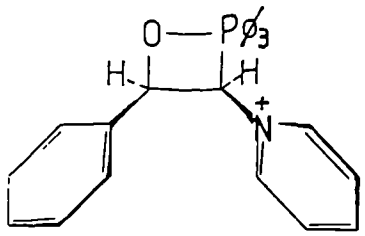


TABLE 4

NMR Data for 1-vinylpyridinium compounds

Compound (anion)	R	Solvent	Proton shift (coupling constant)				
			2	3	4	a	b
51 (ox)	Ph	D_2O	8.86	8.00	8.48	7.81(15Hz)	
51a (ox)	PhOMe	TFA	9.02	8.22	8.67	7.87,7.50(14Hz)	
123 (Br)	CO_2H	D_2O	9.02	8.09	8.62	8.22,6.80(14.2Hz)	
70 (I)	Ph	D_2O	8.72	7.95	8.51	7.32,7.06(9.2Hz)	
72 (BF_4)	-	TFA	8.85	8.22	8.70	7.49,7.17(9.3Hz)	
70a (I)	PhOMe	D_2O	8.57	7.86	8.30	7.09,6.83(9.4Hz)	
70b (I)	PhCHO	D_2O	8.73	7.96	8.53	7.48,7.16(9.3Hz)	
71 (BF_4)	2-pyr	D_2O	8.69	8.15	8.49	7.25,7.07(9.5Hz)	
- (I)	2-Pr	TFA	8.97	8.11	-	6.62,6.17(8.5Hz)	



SCHEME 35

This suggests that the reaction intermediate is of the geometry shown (scheme 35). In all other cases where the ylid is "stabilized", the bulkiest groups (e.g. aromatic rings) would be arranged far apart to lessen steric repulsion between them[47], but in the present case this clearly does not happen (though geometry of intermediate is not always binding on configuration of product olefin[46]). Therefore, either the intermediate ylid is reactive (as opposed to being "stabilized"), or there must be some attractive force between the two aromatic rings, probably of the type postulated for the dimerization of the viologen cation radical 2[6]. (See also Gosney and Rowley[47], p.85 for the difference in isomer ratio between a cyclohexyl group and a phenyl group, the latter giving preferentially the Z-isomer)
It is interesting to note that the 2-pyridine phosphonium ylid 111 discussed in chapter 4 gives only the E-isomer of the product olefins.

The fact that the Wittig reaction proceeded so well between phosphonium-pyridinium salt 65 and terephthaldehyde (to yield compound 72) was encouraging to the idea of making a polymeric species.

Synthesis of bis-(phosphoniomethyl)-bipyridinium salt 73 (Scheme 36)

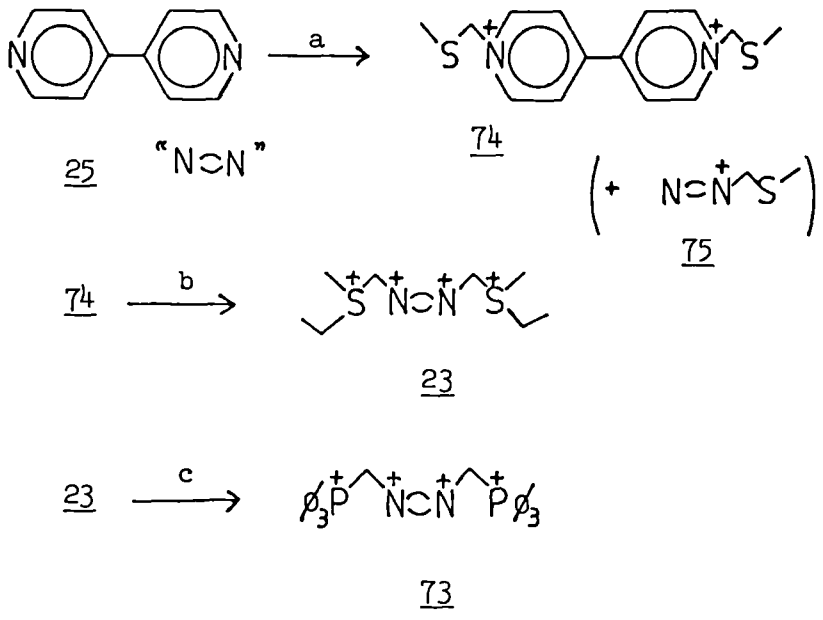
The synthesis of tetracationic species 73 was attempted by the same route as with the corresponding pyridinium compound 65, that is, by reacting bipyridyl 25 with an excess of diiodomethane, but the product was a black semi-solid, and the NMR spectrum of this showed no evidence for the presence of an N-iodomethyl group. However, diiodomethane reacted with excess 25 to give a crystalline bis-(bipyridyl)-methane product 22 (Scheme 6, page 14).

The procedure of Sugimoto[42e] was successfully adapted to use bipyridyl, however (Scheme 36):

When heated in refluxing chloromethylmethylsulphide (CMMS), bipyridyl gave thiapropyl viologen 74 in quantitative yield (in refluxing ethanol as solvent, mono-quaternised compound 75 was the only product with a 5-fold excess of CMMS). The reaction of viologen 74 with triethyloxonium tetrafluoroborate was slow, and satisfactory yields were only obtained by using a 4-fold excess of reagent in refluxing dioxan. The resulting bis-sulphonium viologen salt 23 reacted rapidly with triphenylphosphine in acetonitrile to give the required phosphonium compound 73 in fair yield; Both the sulphonium salt 23 and the phosphonium salt 73 were susceptible to nucleophilic attack, for instance by water, to give N-methyl compounds (as shown by NMR).

As was mentioned in the introduction, on page 15, sulphonium viologen 23 could be used to prepare a variety of other substituted methylene viologens, by reaction with other nucleophiles.

The attempted reaction of phosphonium viologen 73 with benzaldehyde failed with a variety of solvents and bases and temperatures. This may be due to the decomposition of the olefinic product by polymerisation



25 74 75 74 23 23 73

SCHEME 36 - THE SYNTHESIS OF BIS-PHOSPHONIOMETHYL VIOLOGEN (73)

a: Refluxing $ClCH_2SMe$ b: Et_3OBF_4/ dioxan

c: Triphenylphosphine/ acetonitrile

or by hydrolysis and retro-aldol reaction, during the aqueous work-up.

CONCLUSION

As in chapter one, it seems as though no vinyl/ styryl viologens can be formed in the presence of base, but the Wittig reaction, if it could be performed in anhydrous conditions, with a hindered base, could possibly produce such compounds.

CHAPTER THREE

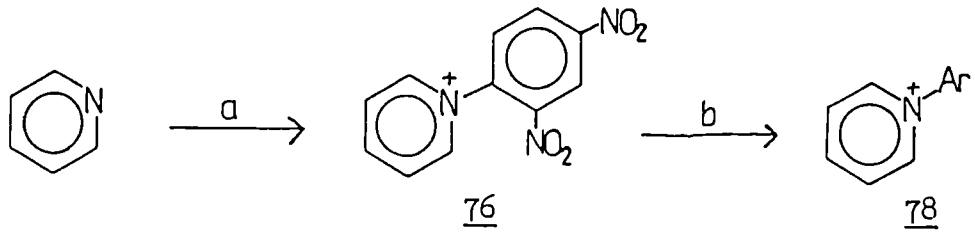
Nucleophilic Aromatic substitution: The Zincke reaction

Halogen atoms on an aromatic nucleus also having electron-withdrawing substituents become labile with respect to nucleophilic substitution. For instance, 2,4,dinitrochlorobenzene reacts readily with pyridine to yield 2,4-dinitrophenylpyridinium chloride 76 (scheme 37) and with bipyridyl to give compound 77 (Scheme 38).

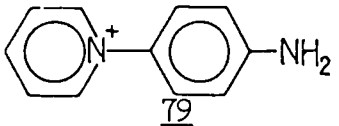
The Zincke Reaction

Dinitrophenylpyridinium salt 76 undergoes reaction with electron-rich aromatic amines to produce dinitroaniline and a new phenylpyridinium salt 78 (Scheme 37a). This reaction, which is known as the Zincke reaction[19a], is a series of equilibria, the position of which depend on the relative electron-richness of the aromatic amines. With aniline itself, reaction is rapid, and the isolated yield of product 78 (Ar = phenyl) is high, but the reaction slows down for p-haloanilines, for example.

Reaction of dinitro compound 76 with 1,4-diaminobenzene gives a high yield of 4-aminophenylpyridinium 79 (scheme 37), but the reaction of this with another mole of dinitro compound 76 is very slow, because of the electron withdrawing nature of the pyridinium substituent. However, this reaction can be made to proceed by the addition of excess pyridine[20a], giving a moderate yield of bispyridinium compound 80. The intermediate in this reaction, the brightly-coloured ring-opened compound 81, and its tautomer 81a, can both ring-close, and whether dinitroaniline, or the starting aniline is produced depends on which of these amines is most electron-poor. The least electron rich aniline will be less nucleophilic and therefore less able to attack the



76 78



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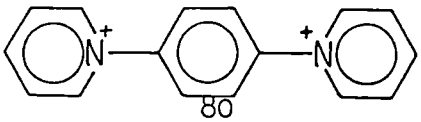

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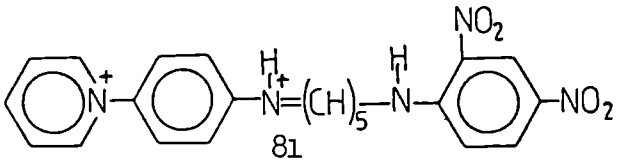

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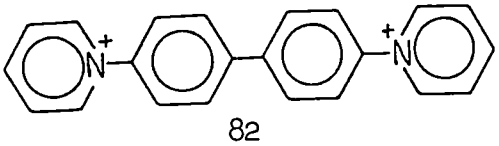

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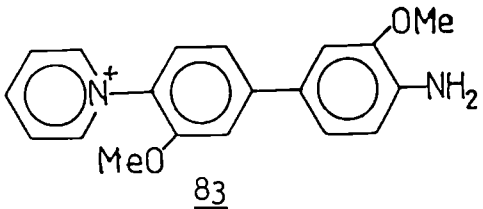

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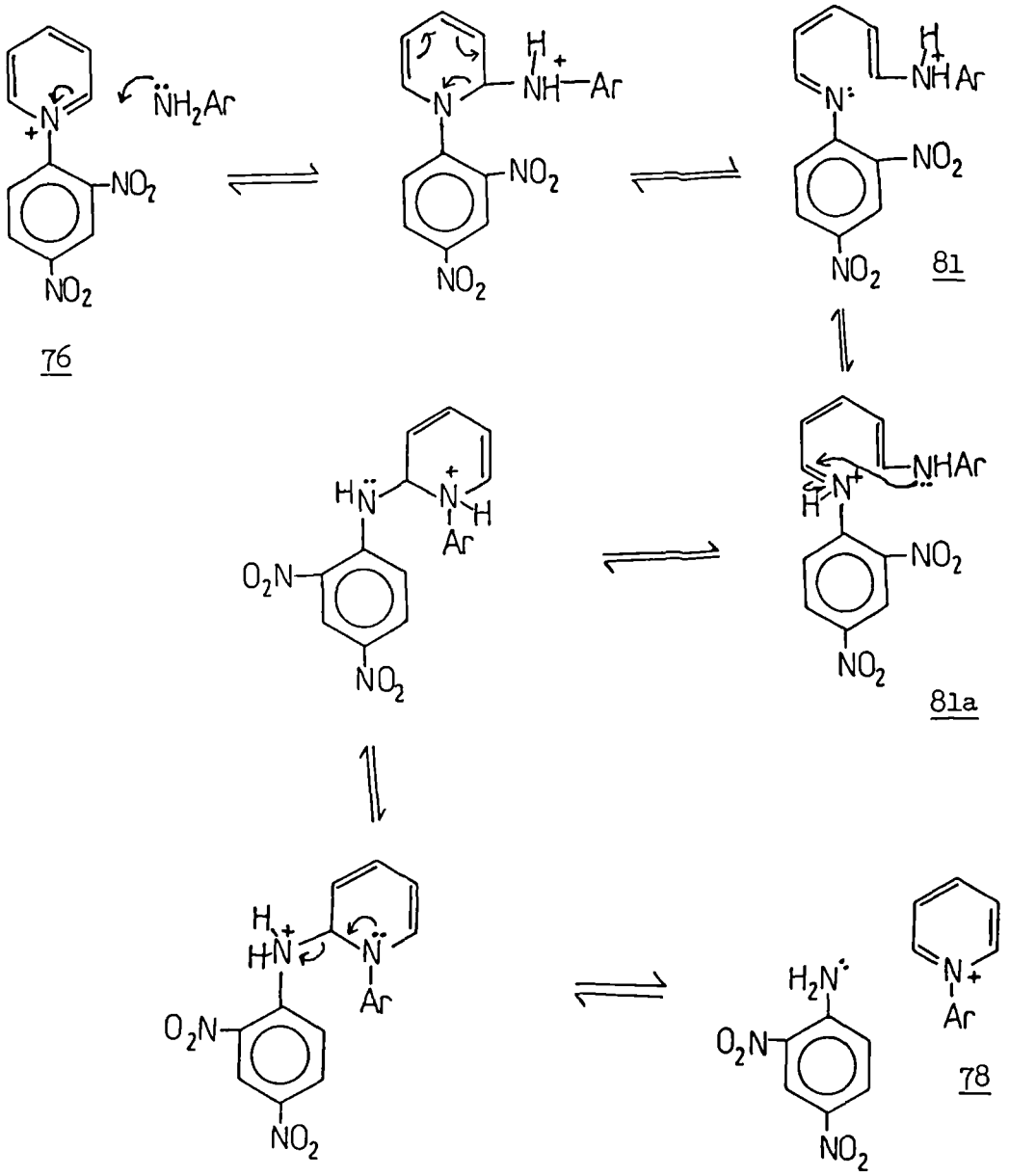
SCHEME 37

a: 2,4-Dinitrochlorobenzene b: $ArNH_2$/ refluxing polar solvent



SCHEME 37a - THE ZINCKE REACTION

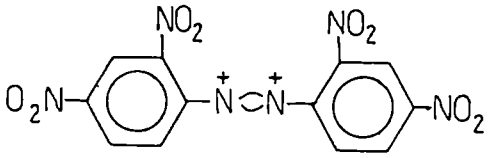
arylpyridinium salt at the 2-position, in the terminal equilibria. 2-aminopyridine was reacted with dinitro- compound 76, but no reaction products could be isolated.

Grigoreva and Gintse[20] investigated the reactions of di-amines with dinitrophenyl pyridinium salts 76. In addition to preparing tricyclic bis-(1-pyridinium)-benzene 80, they also made tetracyclic compound 81 from the reaction of benzidine and dinitro compound 76. The yield of tetra-cycle 82 was low, however, and it was only isolated by vacuum pyrolysis of the intermediate coloured ring-opened compound (corresponding to 81). It is unfortunate that the English translations[48] of their papers are so hard to follow, because many interesting reactions were performed. What can be said, however, is that it is not easy to perform the Zincke reaction with diamines to produce useful yields of pyridinium salts.

The preparation of aminophenylpyridinium compound 79 was not straight forward because of the difficulty in removing excess diaminobenzene from the reaction mixture, and several re-precipitations were necessary to obtain a colourless product. The reaction of 1,5-diaminonaphthalene with dinitro compound 76 was believed to proceed, because dinitroaniline was produced (TLC analysis), but the excess diamine in this reaction prevented the isolation of the product completely. 3,3'-Dimethoxybenzidine (which diamine was believed to be more electron-rich than benzidine itself, and also less carcinogenic.) gave a virtually quantitative yield of tricyclic compound 83 (scheme 37) on reaction with 76.

Disappointingly, no tetracyclic bis-pyridinium salt was obtained (corresponding to compound 82) on reaction of tricycle 83 with more dinitrophenylpyridinium 76. The reaction mixture contained many different compounds, predominantly ring-opened, by NMR analysis.

The yield of tri-cycle 81 achieved by repetition of Grigoreva and Gintse's reaction was lower than they reported, but this preparation was only carried out on the small-scale.



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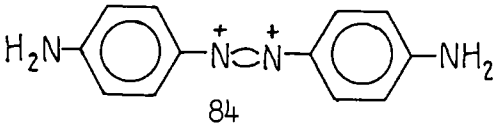

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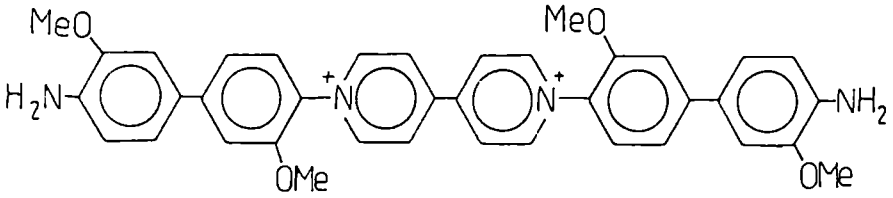

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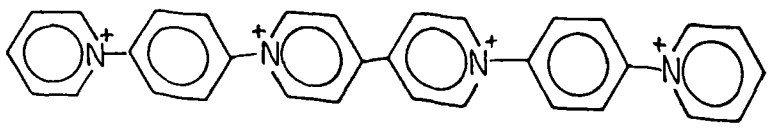
SCHEME 38 - BIPYRIDINIUM ZINCKE PRODUCTS

Bis-(dinitrophenyl)-bipyridinium 77 (scheme 38) has been used as the precursor of many interesting viologens (e.g. 3 - 6, page 2). It presumably has an even lower reduction potential than either p-nitro- 4, or p-cyano- 3, -phenyl viologens, but it is decomposed slowly by water, which is necessary to dissolve it. The Zincke reactions of this compound were not investigated by Grigoreva and Gintse.

Tetranitro viologen 77 reacted easily with diaminobenzene to give the p-aminophenyl viologen 84 (scheme 38), which is red in colour, but in acidic solution is yellow. Again, no product could be obtained from the use of diamino-naphthalene, but dimethoxybenzidine gave rise to the reddish viologen 85 (scheme 38), but as a mixture with unreacted diamine starting material (the ^{1}H NMR spectrum for the solid obtained integrated to five dimethoxybenzidine units per bipyridinium), from which it could not be separated.

Both diamino-viologens 84 and 85 were reacted with dinitro compound 76 in the hope of producing a polycyclic compound such as 86 (scheme 39), but this product could not be isolated. The reaction mixture became very dark, presumably because of the large numbers of ring-opened (coloured) intermediates present, which may be too electron-poor to ring-close.



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SCHEME 39

Schiff Bases

Although the Zincke reaction of diamines with dinitrophenyl viologen 77 seems unlikely to give rise to polymers, the free amino groups of diaminophenyl viologens 84 and 85 open another route to forming conjugated links between the viologen units, by the formation of Schiff -bases.

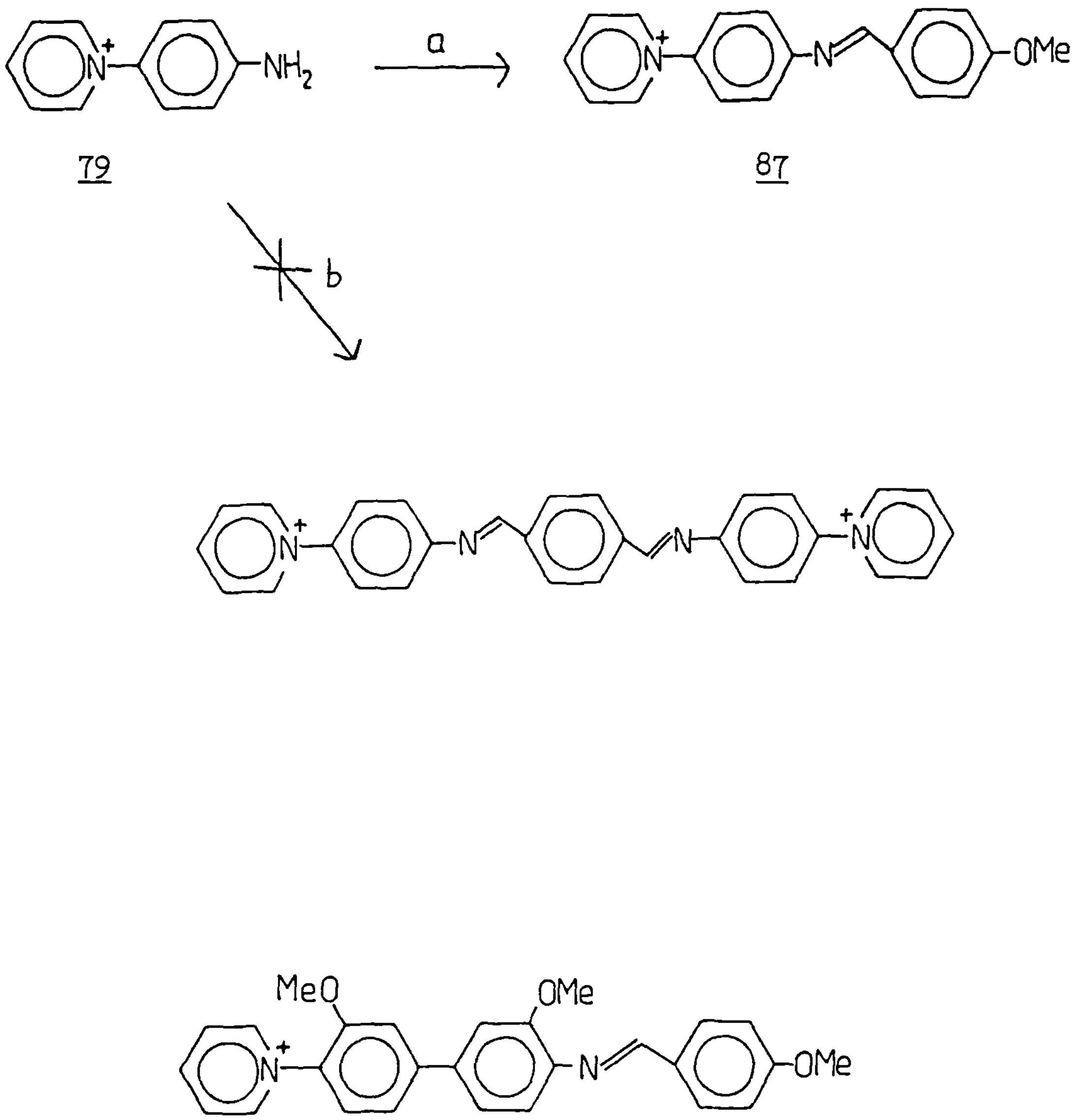
Dinitrophenylpyridinium 78 reacted with 4-methoxybenzaldehyde in refluxing ethanol in dehydrating conditions to give a fair yield of the Schiff-base 87 (scheme 40), as did amine 83 to give Schiff-base 88. However, neither amine reacted with terephthaldehyde 54 in even the most forcing conditions. The reasons for this are probably that 54 is an unreactive aldehyde, and that the amino groups of 78 and 83 are deactivated sufficiently by the positive charge of the pyridinium ring to prevent the reaction occurring.

Aminophenyl viologen 84 also reacted with 4-methoxybenzaldehyde to give the bis-Schiff-base viologen 89 as an insoluble brown solid (scheme 41). The attempted reaction of the mixture of viologen 85 and dimethoxybenzidine with 4-methoxybenzaldehyde in ethanol produced a red gelatinous substance, from which no viologen could be obtained.

2-aminopyridine formed a Schiff base with 4-methoxybenzaldehyde with difficulty, but no product was obtained from the reaction of diaminobipyridyl with that aldehyde.

The alternative way to create the C=N linkage of the intended Schiff-base would be to have the aldehyde on the viologen (activated by the electron-withdrawing pyridinium) and to react that dialdehyde with a diamine (scheme 42). The dialdehyde viologen 90 was unknown, but was synthesized by conventional chemistry from 4-nitrobenzaldehyde (scheme 43).

Unfortunately, in the normal aqueous reaction of the aniline with

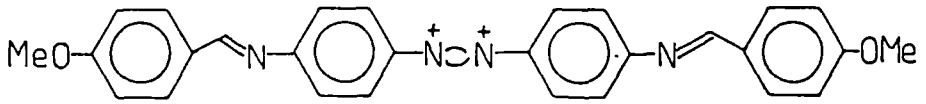


79 87 88

SCHEME 40 - SCHIFF BASES FROM PYRIDINIUM SALTS

a: 4-MeO-benzaldehyde/ H^+/ EtOH

b: 1,4-diformylbenzene/ H^+/ DMF or propylene carbonate



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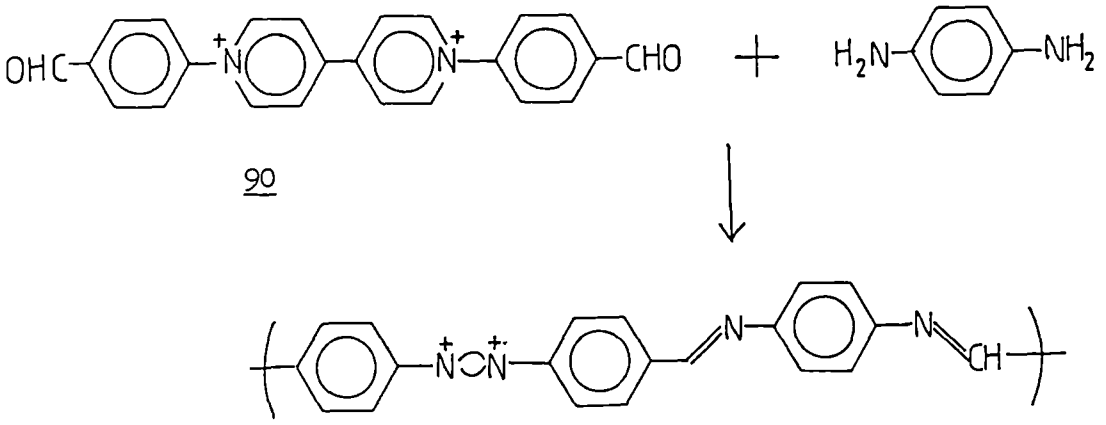
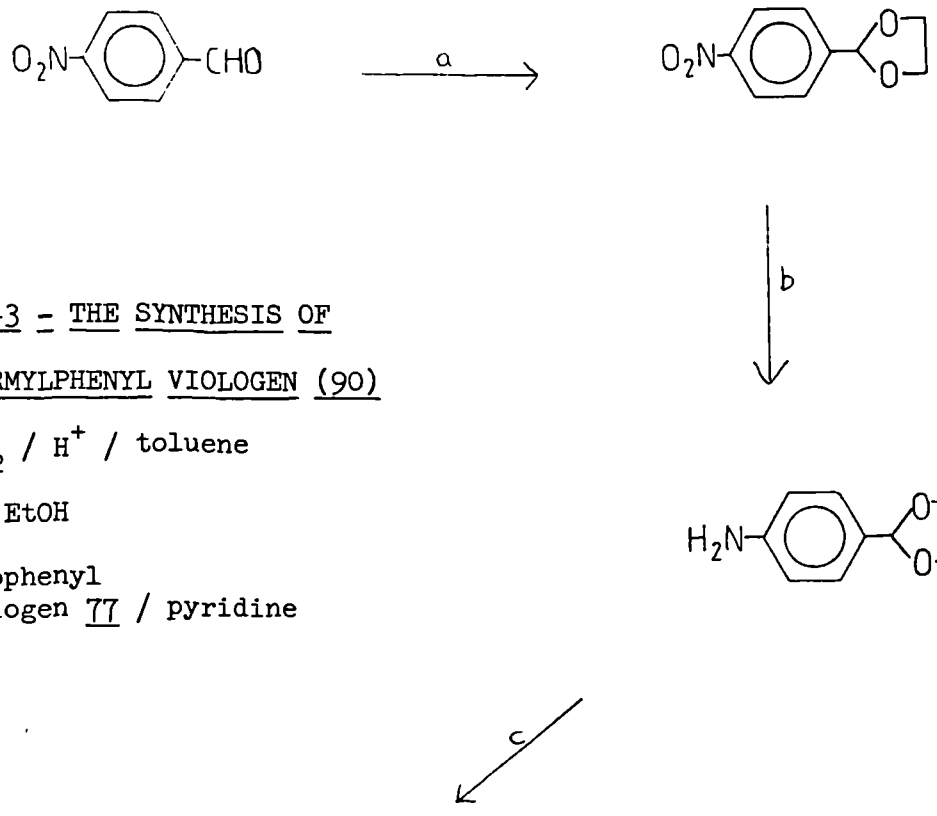
SCHEME 41



STRUCTURAL TYPE (I)

SCHEME 42 - THE POSSIBLE FORMATION OF A POLYMER FROM DIALDEHYDE (90) AND DIAMINOBENZENE



SCHEME 43 - THE SYNTHESIS OF FORMYLPHENYL VIOLOGEN (90)

a: $(CH_2OH)_2$ / H^+ / toluene

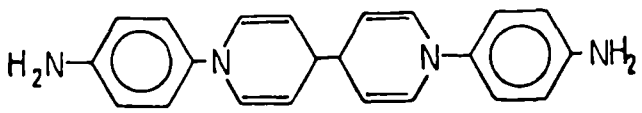
b: Na_2S / EtOH

c: dinitrophenyl viologen 77 / pyridine

90

tetranitro viologen 77, the ketal protecting group was removed from the aminobenzaldehyde, resulting in the production of the polymer from self-condensation of that compound, and none of the expected product was obtained.

In pyridine as reaction solvent, the dialdehyde 90 was the major water-soluble product (not the ketal-protected compound), but this could not be separated from the residue of amines, with which it was probably forming a mixture of Schiff-bases. The presence of dialdehyde 90 was ascertained by the proton NMR spectrum of the reaction residue, which was an orange semi-solid.



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CONCLUSION

Although, it is very likely that new viologens could be made by the reaction of diamines with dinitrophenyl viologen 77, it is highly unlikely that any polymeric material would be made, except for large quantities of black "tar".

Therefore, other methods of linking the phenyl-viologen units must be found. The formation of Schiff's bases using the di-aldehyde 90, when that compound is isolated, is probably a very good contender, but other way of achieving the polymerization can be envisaged.

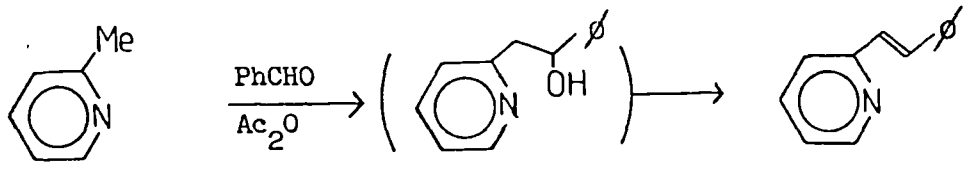
For instance, there are now known high-yielding coupling reactions of halo-arenes[50], which could conceivably work for, say, 4-chlorophenyl viologen, even if the oxidation state of the viologen is altered in the process. This leads on to another point; the chemistry of the viologens is hampered somewhat because they are only soluble in very polar solvents. However, the chemical reduction of all viologens is easily achieved, by the use of a reagent such as dithionite, producing an uncharged "normal organic molecule".

This could then be transformed by standard reactions, polymerized maybe, then oxidized back to the viologen di-cation state (perhaps not fully?, which would not harm the electrical conduction of such a polymer). For instance, aminophenyl viologen 84, if reduced to the dihydrobipyridyl 91 might be more reactive towards aldehydes and give better yields of Schiff bases, and dihydrobipyridyl 91 might also be polymerized by diazo links on treatment with nitrous acid[51].

CHAPTER FOUR

Knoevenagel condensations of methylpyridines with aldehydes

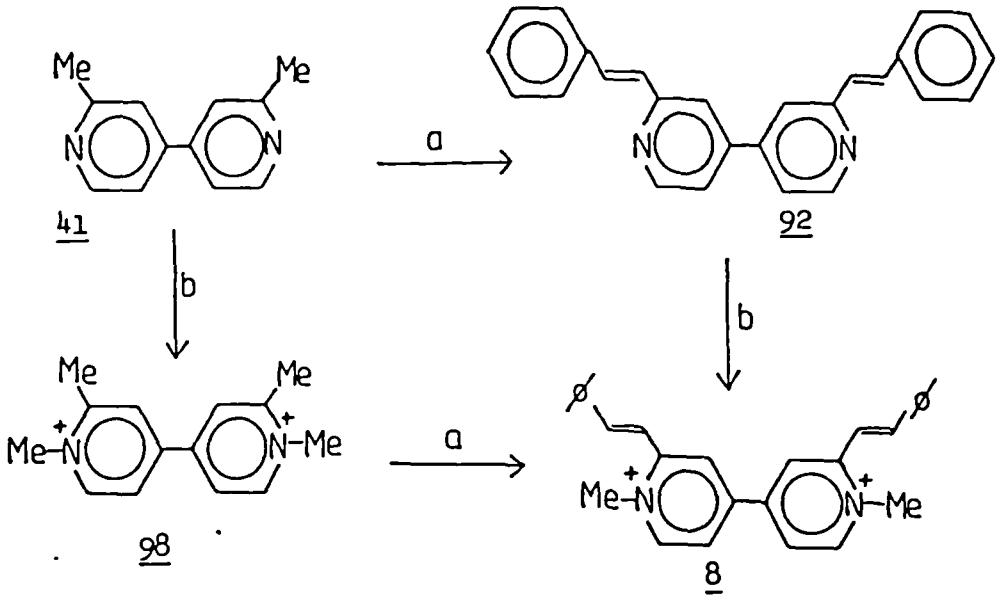
The facile condensation of the picolines with aldehydes, normally in an acid anhydride solvent, has been known for a long time[52]. In contrast to the condensation of 1-methylpyridinium with aldehydes (Chapter 1), the same reactions with 2- or 4-methylpyridine do not stop at the intermediate secondary alcohol, but the isolated product is the olefin, normally[52b] in the E-configuration (Scheme 44). These reactions proceed in high yield (though rather slower for 2- than 4-picoline[53]) and have been extensively used in the preparation of thermally stable polymers[54].



SCHEME 44

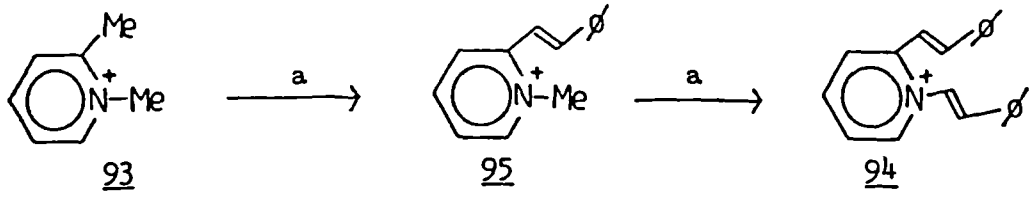
Because of this, it is surprising that 2,2'-distyrylbipyridyl 92, made by condensation of dimethylbipyridyl 41 with benzaldehyde (scheme 45) was unknown[17]. (However dimethylbipyridyl 41 has been condensed with nitroso-compounds to produce cyanine dyes[55]). Distyrylbipyridyl 92 was easily methylated with dimethyl sulphate to give the distyryl viologen 8 (see introduction, page 2).

Upon prolonged reaction with an excess of benzaldehyde in hot propanoic acid, 1,2-dimethylpyridinium 93 is converted into the 1,2-distyryl-pyridine[52c] 94 (scheme 46). However, with a smaller amount of benzaldehyde, the only product is 1-methyl-2-styrylpyridinium 95. 1,2,6-Trimethylpyridinium behaves similarly, reacting with benzaldehyde to give mono-, di- and (more slowly) finally tri-styryl pyridinium salts.



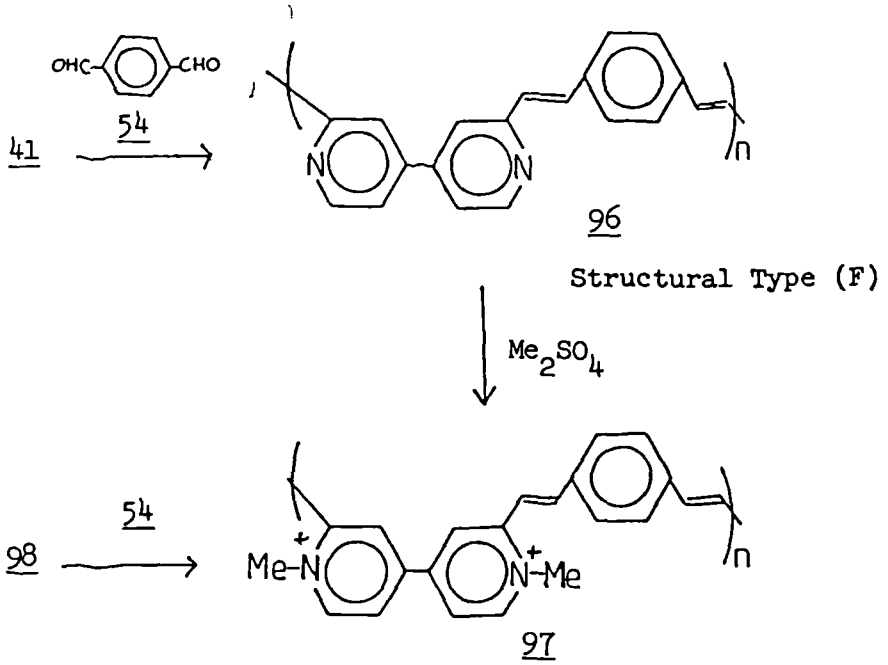
SCHEME 45 - THE REACTION OF DIMETHYLBIPYRIDYL (41) WITH BENZALDEHYDE

a: PhCHO/ Ac_2O b: Me_2SO_4



SCHEME 46 - THE REACTION OF DIMETHYLPYRIDINIUM (93) WITH BENZALDEHYDE

a: PhCHO/ Ac_2O

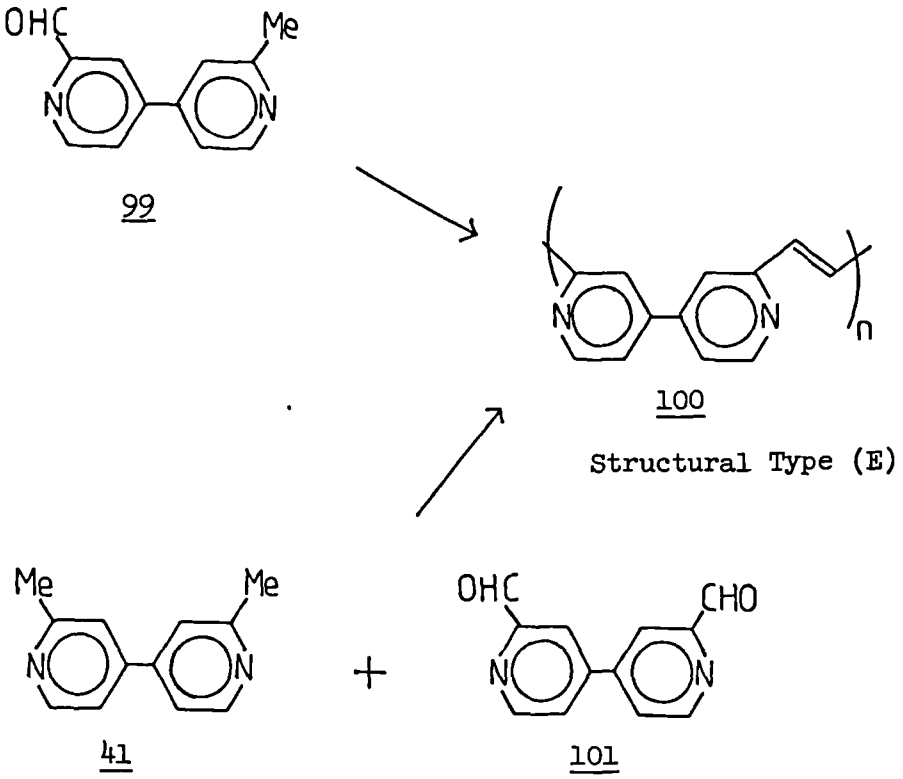


SCHEME 47

POLYMERIC STYRYL VIOLOGENS

The reaction between dimethylbipyridyl 41 and a dialdehyde (for example, 1,4-diformylbenzene 54) was expected to produce a polymer (Structural Type (F)) 96 in which the bipyridyl units were linked by conjugated chains (Scheme 47).

Subsequent N-methylation of this polymer would produce the polyviologen 97, and this polymer could also be produced by the condensation of dimethylviologen 98 with the dialdehyde 54.



SCHEME 48

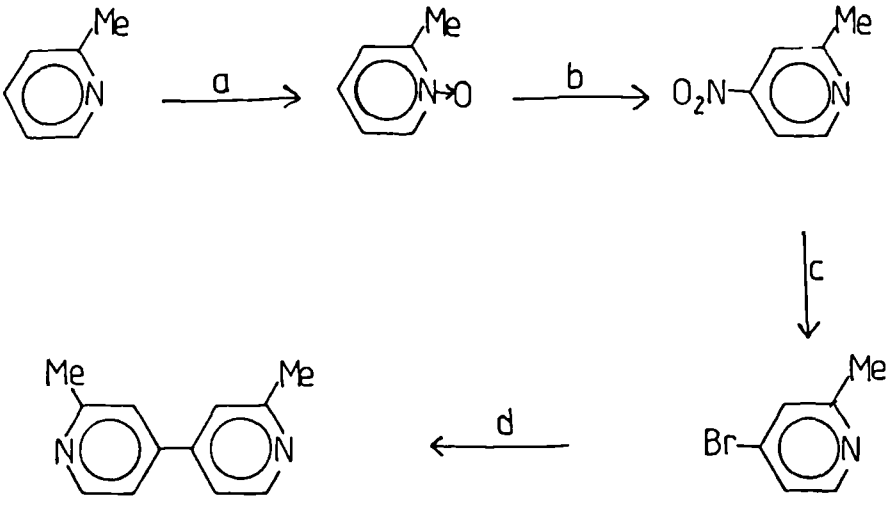
Rembaum and Singer[15] demonstrated that the polymerisation of 2-formyl-6-methylpyridine gave a polymeric product 11 (see Introduction). In analogy to this, the unknown compound 2-formyl-2'-methylbipyridyl 99 would be expected to yield a polymer of type 100 (Scheme 48), or 2,2'-dimethylbipyridyl 41 would condense with the diformylbipyridyl 101 to give the same product, but probably with a smaller DP because the amounts of methyl and formyl groups would not be exactly equal.

Synthesis of 2,2'-dimethyl-4,4'-bipyridyl (41)

Many different syntheses of this compound have been published, some of them rather exotic[25].

Balanson, Oxsen and Cheng[12] coupled 4-bromo-2-methylpyridine with zinc in the presence of a nickel(0) catalyst, and achieved a 42% yield of dimethylbipyridyl 41 (scheme 49). Although this route was flexible, the lengthy series of reactions necessary to provide the bromo-compound, with their often poor yields, makes it unattractive. The authors also comment on the lack of reproducibility of Winter's cyanide-coupling method[22] (discussed on page 23).

(6,6'-Dimethyl-2,2'-bipyridyl has been similarly made by Rode and Breitmayer [50b] by the coupling of 6-bromo-2-methylpyridine using Raney nickel as the reductant).



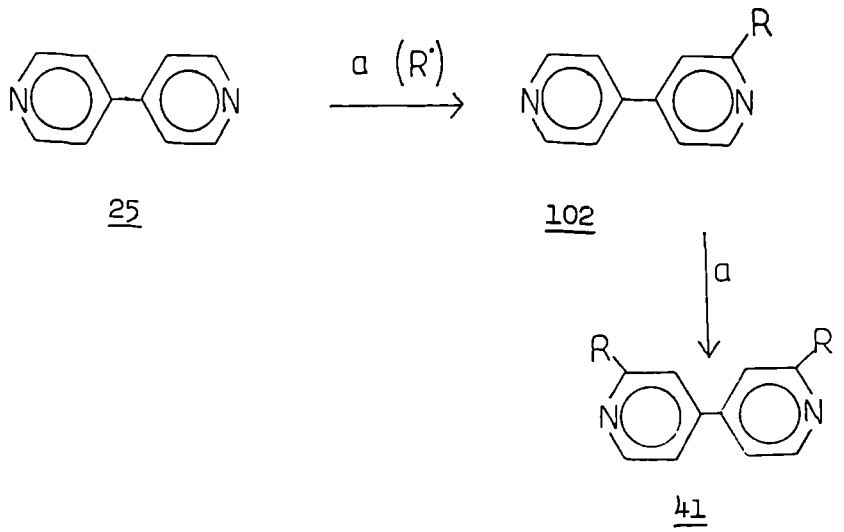
41

SCHEME 49 - SYNTHESIS OF DIMETHYLBIPYRIDYL, BALANSON, OXSEN & CHENG

a: Per-acetic acid b: HNO_3/ H_2SO_4

c: Concentrated HBr (reflux) d: Zn/ $(Ph_3P)_4Ni$/ DMF

The presumed free-radical alkylation method of Minisci et al.[55], as reported by Barltrop and Jackson[10] (Scheme 50) could presumably be improved upon to produce better yields of the di-methyl compound 41 required here (which was obtained as a by-product of the synthesis of monomethylbipyridyl 102).



25 102 41

SCHEME 50 - FREE-RADICAL ALKYLATION OF BIPYRIDYL (25)

a: RCO_2H/ H_2SO_4/ $(NH_4)_2S_2O_8$/ Ag^+

Four methods were actually explored for the synthesis of dimethylbipyridyl 41 in the present work:

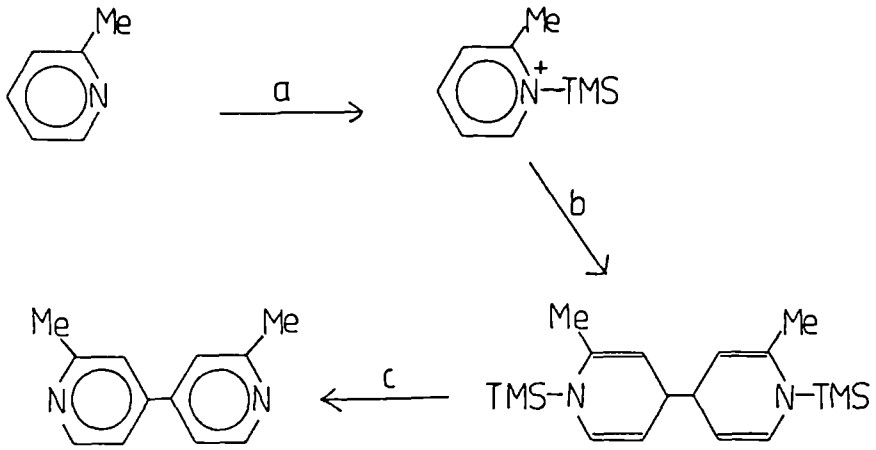
(1) The action of methyl lithium on bipyridyl[33] (Scheme 16, page 24). Three eqivalents of methyllithium at 40° in THF gave a tar, which yielded 10% product dimethylbipyridyl 41 after chromatography.

(2) Coupling of 2-methylpyridine with sodium in THF[24b]. This generated a tar from which no product could be isolated.

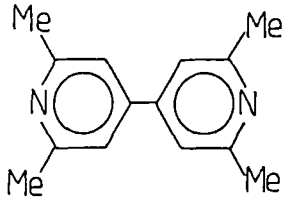
(3) Sodium in liquid ammonia similarly gave a complex mixture from which no product 41 was obtained.

(4) The procedure of Becker and Neumann[26] was used (Scheme 51), giving up to 50% isolated yield from 2-picoline, on the small scale. This is not much inferior to their reported yield using bis-(trimethylsilyl)-mercury (50%), and the problem seems to be in the oxidation of the bis-silyl-compound 103 (55% yield), (with the likelihood of much of the product being absorbed on to the manganese (IV) oxide produced), and not in the actual coupling step. (Attempted synthesis of bis-(trimethylsilyl)-mercury by the procedures of Wiberg[56a] or Fields[56b] failed; after shaking bromotrimethylsilane in the dark with either 9%(solid) or 2%(liquid) sodium amalgam, at room temperature, for a week, no product was obtained by evaporation of an ethereal extract).

This reaction sequence was also used to prepare 2,2',6,6'-tetramethylbipyridyl 104 from 2,6-dimethylpyridine in fair (40%) yield. (However, no bipyridyl products were isolated from the reaction mixtures obtained using this method of coupling with 2-bromopyridine, 2-acetamidopyridine, or the dihydroxyethane ketal of 2-formylpyridine).



41 103



104

SCHEME 51 - SYNTHESIS OF DIMETHYLBIPYRIDYL (41), BECKER & NEUMANN

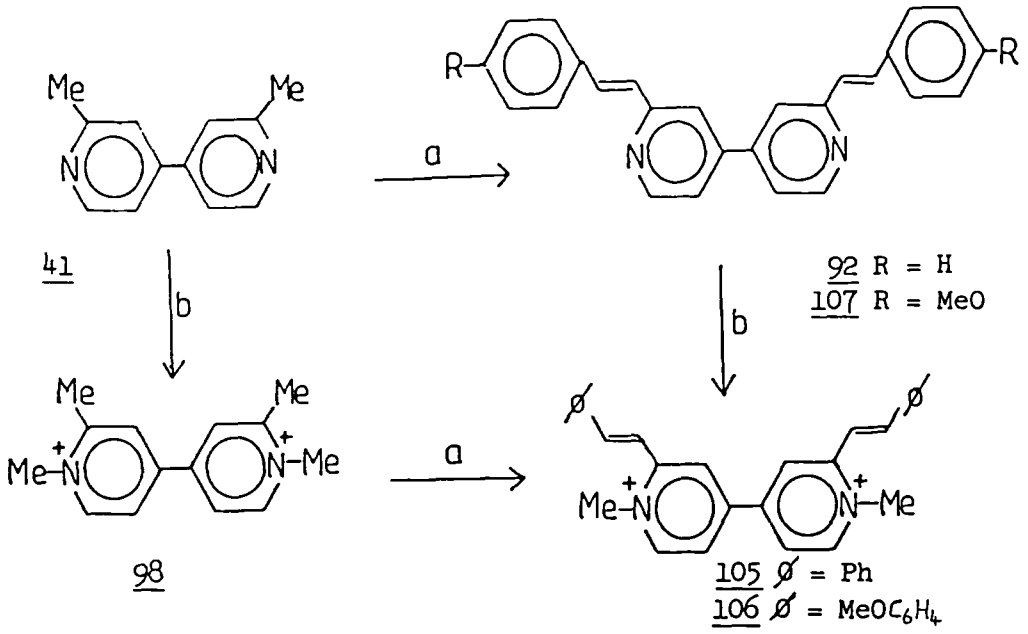
a: Chlorotrimethylsilane/ THF b: Lithium/ THF (reflux)

c: $KMnO_4$/ aqueous acetone/ 0°

Styrylbipyridyls (scheme 52)

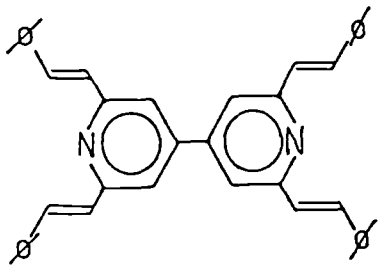
2,2'-Dimethylbipyridyl 41 reacted easily with benzaldehyde in propanoic anhydride at 170° to give the novel compound 2,2'-distyryl-4,4'-bipyridyl 92, as a white powder (scheme 45). Distyrylbipyridyl 92 was methylated to bright-yellow styryl viologen 105, by dimethyl sulphate, (scheme 52) and the corresponding compound prepared using 4-methoxybenzaldehyde (106, via bipyridyl 107) was orange.

2,2',6,6'-Tetramethylbipyridyl 104 reacted with excess benzaldehyde to give tetrastyryl compound 108, which was yellow, and the di-N-methylated salt 109, formed from 108 on methylation, was bright orange. The same products could also be obtained by the methylation of the bipyridyls before reaction with benzaldehyde. Distyryl viologen 105, for example, was obtained in this way, from tetramethybipyridinium 98. However, the yields of product were poorer, and longer reaction times were needed.



SCHEME 52 - STYRYLBIPYRIDYLS AND STYRYL VIOLOGENS

a: Excess RCHO/ $(EtCO)_2O$/ 170° b: Me_2SO_4/ 120°



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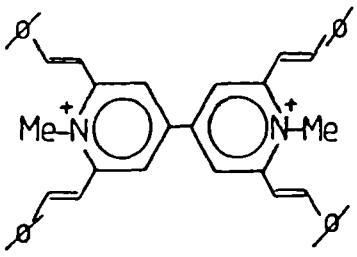
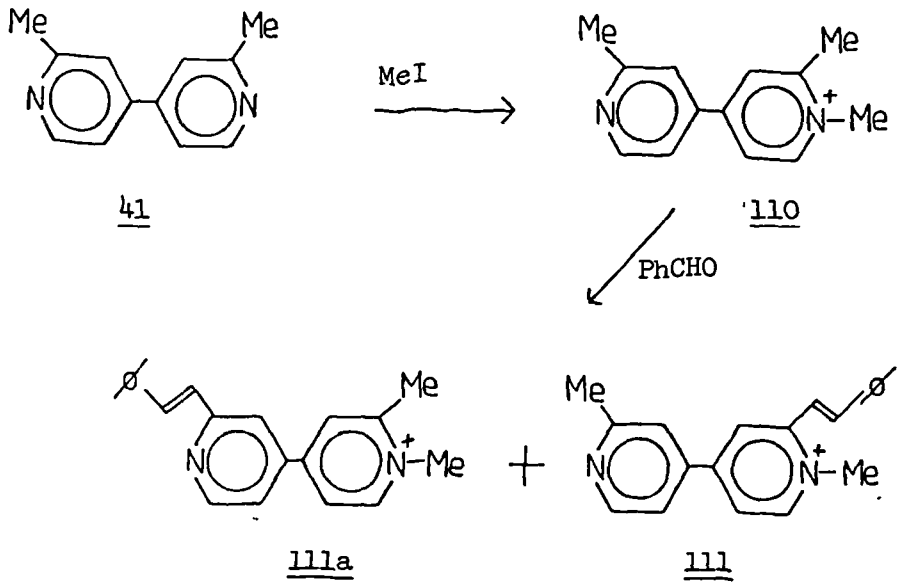


109

On reaction with one equivalent of iodomethane in THF, dimethylbipyridyl 41 was converted into trimethylpyridinium iodide 110 (scheme 53). This compound reacted with one equivalent of benzaldehyde in propanoic anhydride (scheme 53) to give a brown solid that had an NMR spectrum consistent with that expected for monostyrylbipyridyl 111. However, on close examination, the presence of two compounds was revealed, which were presumably 111 and its isomer 111a with the styryl group on the unquaternized ring. these two compounds proved to be inseparable.



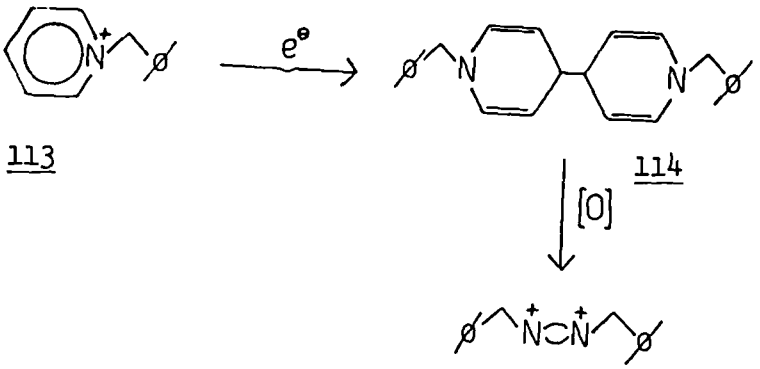
41 110 111a 111

SCHEME 53

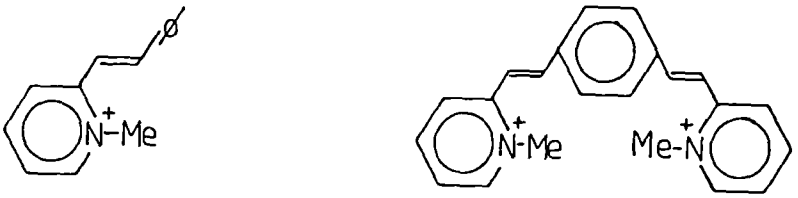
Electrolysis

Simple electrolysis of pyridinium salts at platinum electrodes was investigated as a method for coupling the rings together (see introduction, page 23). For instance, a moderate yield of benzyl viologen 112 was obtained by the electrolysis of an alkaline aqueous solution of 1-benzylpyridinium chloride 113, collection of the precipitate of tetrahydrobipyridyl 114 and oxidation of that substance by air in acidic solution (scheme 54).

1-Methyl-2-styrylpyridinium 95 was electrolysed in the same way, but the precipitate formed very slowly, and when analysed, proved to be a complex mixture (that is to say, the ^{1}H NMR spectrum of the precipitate did not indicate the presence of the expected tetrahydrobipyridyl). The related compound 115 derived from condensation of 2-methylpyridine with 1,4-diformylbenzene 54, followed by methylation, was also electrolysed, because the product was expected to be a polymer. The product probably was a polymer, because the cathode quickly became coated with a thin, insulating, film. Because of this, the electrolysis rapidly ceased.



113 114 112



95 113a

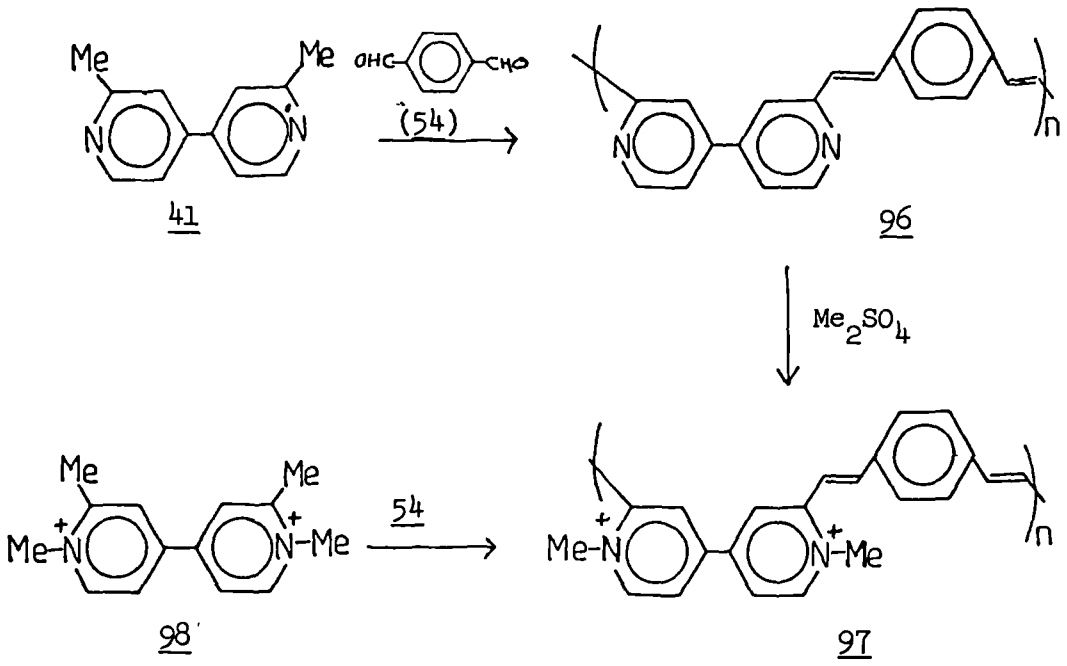
SCHEME 54

Polymeric products (scheme 55)

Equal amounts of dimethylbipyridyl 41 and dialdehyde 54 were reacted together in propanoic anhydride, at 170°, for two days (scheme 47, page 62). The product of the reaction, the polymer 96, was a pale brown solid, resembling "plastic sulphur" in its appearance, that was only partially soluble in TFA. However, the NMR spectrum obtained in TFA showed the absence of any aldehyde protons and near-absence of methyl-protons. The ratio of the integrals of aryl to methyl protons suggested that the degree of polymerization (DP) was about ten, at least for the TFA-soluble part of the product. The broadness of all the signals in the NMR spectrum was seen as evidence for the polymeric nature of the product.

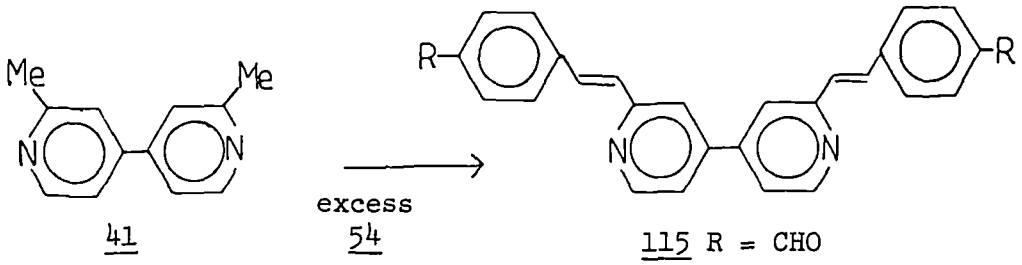
The polymer 96 was methylated by prolonged heating with dimethyl sulphate, giving 80-85% methylation (by NMR; the ratio of N-methyl to aryl protons approached 3:7), but better methylation yields were obtained by methylation of the hot reaction mixture (in propanoic anhydride/ acid). About 90% of the nitrogen atoms could be methylated in this way. This methylated polymer 97 was dark orange-brown, initially rubbery, hardening later to a resin.

A similar solid could be obtained by the reaction of tetramethylbipyridinium 98 with dialdehyde 54 in propanoic anhydride. Although the product appeared (by NMR analysis) to be 100% N-methylated, as might be expected, the ratio of free C-methyl groups to bipyridyl units was larger than that of the un-N-methylated polymer prepared before, indicating a lower degree of polymerization.



SCHEME 55

Upon reaction with a large excess of 1,4-diformylbenzene 54, dimethylbipyridyl 41 was converted largely into formylstyrylbipyridyl 115 (scheme 56). However, small amounts of high molecular mass compounds ("oligomers") were also present, and dialdehyde 115 could not be obtained in a pure state. Attempted methylation of the (impure) dialdehyde 115 with dimethyl sulphate at 120° resulted in the production of a black solid, which was insoluble in water and trifluoroacetic acid.



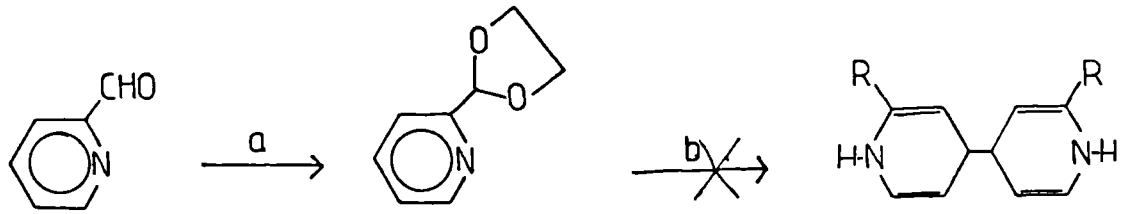
41 115 R = CHO

SCHEME 56

Synthesis of 2,2'-diformylbipyridyl (101)

Three routes to this unknown compound were considered:

(1) The dissolving-metal coupling of 2-formylpyridine (protected) (Scheme 57). The acetal with dihydroxyethane was made, but gave only an intractable reaction mixture with either sodium in THF or in liquid ammonia, or with the chlorotrimethylsilane/ lithium procedure of Neumann and Becker[26]. No evidence was seen in the ^{1}H NMR spectrum of the product mixture for the presence of any tetrahydrobipyridyl.

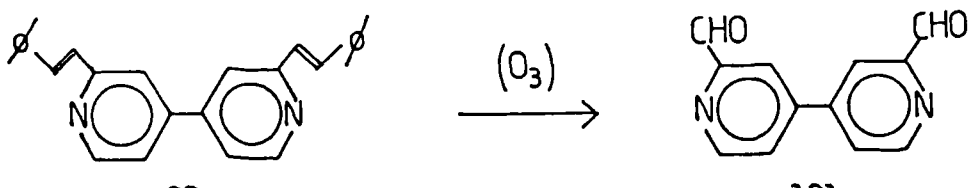


SCHEME 57

a: $(CH_2OH)_2$/ H^+/ toluene b: e^- (dissolving metal)

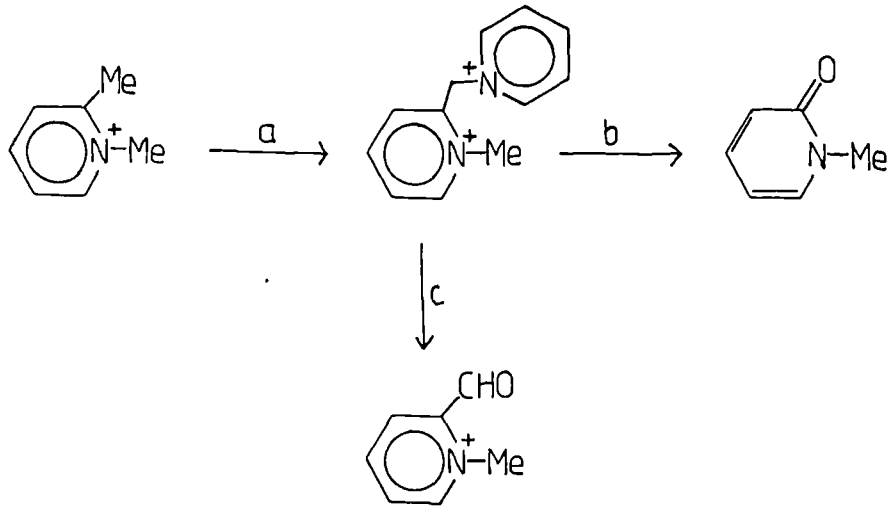
(2) Oxidation of 2,2'-distyrylbipyridyl 92 by "ozonolysis"[57] (scheme 58).

At 70° in aqueous dioxan, osmium tetroxide and sodium periodate[57a] oxidized diolefin 92 to dialdehyde 101 (Scheme 52), in good yield, in one out of four attempts. There was no reaction at 25°. Ozone[57b] at 0° in DCM gave the same product, (by TLC analysis) but it decomposed during work-up. Presumably the N-oxide was formed, decomposing to red (ring-cleaved?) material. The worked-up material displayed no bipyridyl protons in the ^{1}H NMR spectrum.



92 101

SCHEME 58 - OZONOLYSIS OF STYRYLBIPYRIDYL (92)



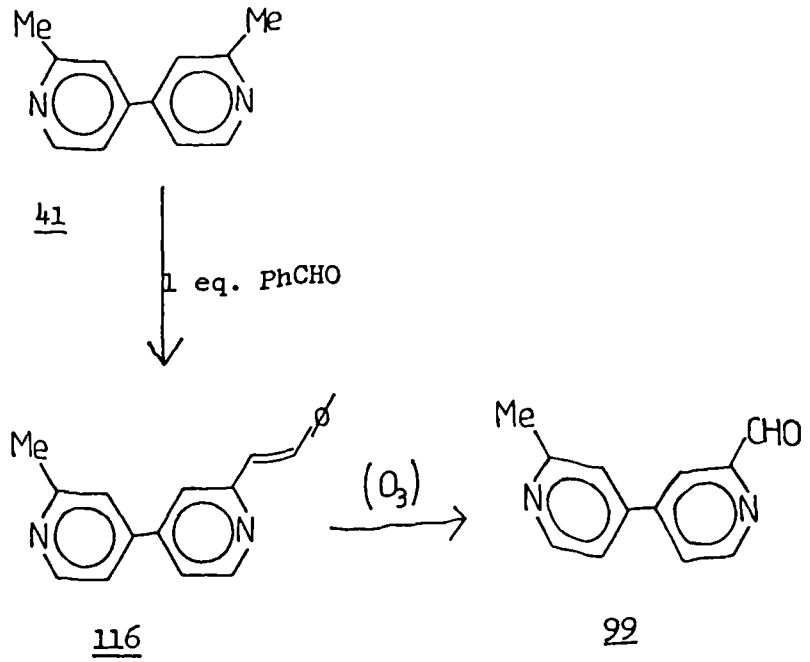
SCHEME 59 - OXIDATION OF PYRIDINIUM SALTS BY IODINE, KROHNKE

a: I_2/ pyridine b: OH^- (aq.) c: (1) OH^-, Ar-NO (2) H^+ (aq.)

(3) Oxidation of dimethylbipyridyl 41 with hydrogen peroxide/ acetic anhydride. 2-Methylpyridine has been oxidised to 2-formylpyridine with hydrogen peroxide and acetic anhydride in fair yield[58]. However, there is a considerable amount of oxidation at the 6-position as well, with the production of pyridones (scheme 72, page 89). Similar side-reactions also weigh against the use of either the iodine/ pyridine method of Krohnke[59a] or that of Markovac and co-workers[59b] (using iodine in dimethylsulphoxide) for the oxidation of the 2-methyl group (which presumably proceed via an iodomethyl compound) (Scheme 59). These reactions were not attempted on either dimethylbipyridyl 41 nor on tetramethyl viologen 98, because of the expected low yield due to the side-reactions.

Synthesis of 2-methyl-2-formylbipyridyl (99)

The reaction of dimethylbipyridyl 41 with one eqivalent of benzaldehyde gave only a trace of the required styrylbipyridyl 116 (scheme 60), (by TLC analysis, a new faintly-fluorescent spot running between dimethylbipyridyl 41 (non-fluorescent) and distyrylbipyridyl 92 (highly fluorescent) was assumed to be methylstyrylbipyridyl 116) leaving half the starting material 41 and an equivalent of distyrylbipyridyl 92 (by TLC and NMR analysis). The use of less benzaldehyde did not raise the proportion of 116 produced, and this compound has not been isolated. Several other syntheses of this bipyridyl have been envisaged, but not investigated. (In a similar manner, tetramethylbipyridyl 104 reacted with an equal quantity of benzaldehyde to give a mixture of tetra-, tri-, two di- and mono- styryl compounds. The predominant products were the tetrastyrylbipyridyl 108, with unchanged tetramethylbipyridyl 104).

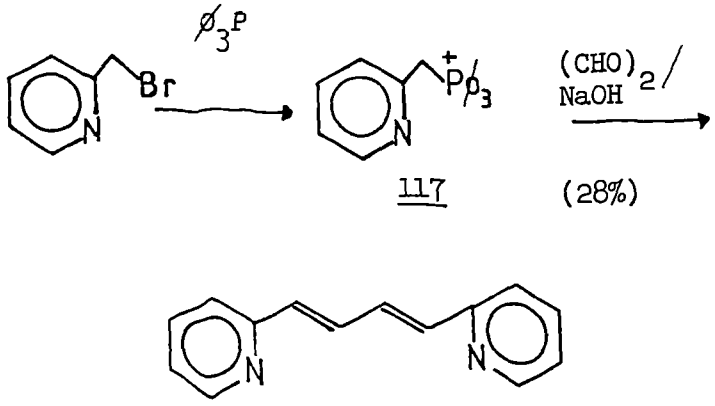


SCHEME 60

Olefin formation from 2-phosphonio-methyl-pyridine ylids

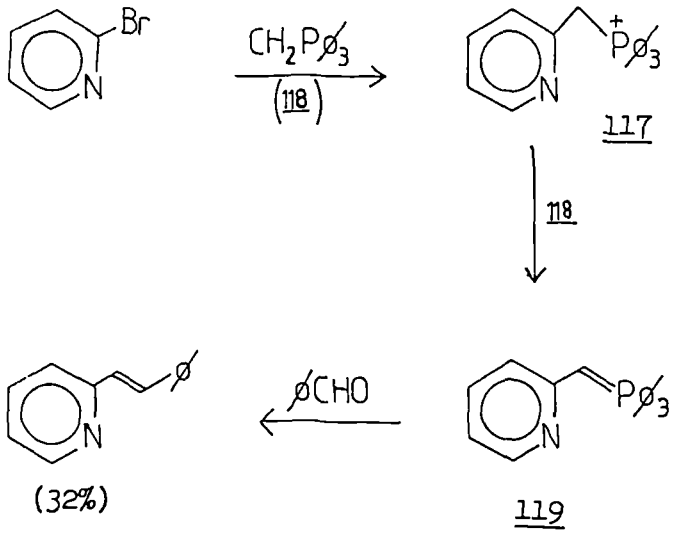
(Structural Type E (or F))

Carsky and co-workers[60] prepared the 2-phosphonio-methyl pyridine 117 from 2-(halo-methyl)-pyridine and triphenylphosphine (Scheme 61), then they reacted phosphonium salt 117 with sodium hydroxide solution and various bis-aldehydes to give low yields of the olefins, exclusively in the E-configuration (in contrast to the present results with the 1-pyridinium ylid. Another obvious difference is that the products are not decomposed by aqueous base). Halomethyl-bipyridyls are not available, and probably would not be obtained from any of the reactions used to prepare the halomethyl-pyridines.



SCHEME 61

Taylor and Martin[61] prepared phosphonium salt 117 from 2-bromopyridine and the methylene ylid 118 (Scheme 62) at -30° in dimethoxyethane, followed by extended reflux. Phosphonium salt 117 was converted to the corresponding ylid 119 by another equivalent of methylene ylid 118. From that ylid 119, a 32% yield of 2-styrylpyridine (E-configuration inferred) was obtained from reaction with benzaldehyde. 2-Chloropyridine could not be used in this reaction, and neither, presumably, 2,2'-dichlorobipyridyl 38.



SCHEME 62

CONCLUSION

The polymeric solids 96 and 97 have not yet been fully investigated. Indeed, it is not certain that the solids have the structures assigned to them. The NMR spectra indicate that a degree of polymerization of about 14 have been achieved, as deduced from the ratio of the integrals of the C-methyl protons to the aryl protons. Similarly, N-methylation of the polymer 96 to give polymer 97 appears to proceed in up to 90% yield.

Polymer 96 is a good insulator (conductivity too low to measure[9]), whereas polymer 97 has a conductivity of $8 \times 10^{-5} Scm^{-1}$.

Polymer 97 has a redox potential of about -280mV[9], which is similar to that of the styryl viologens 8 and 9 (page 2).

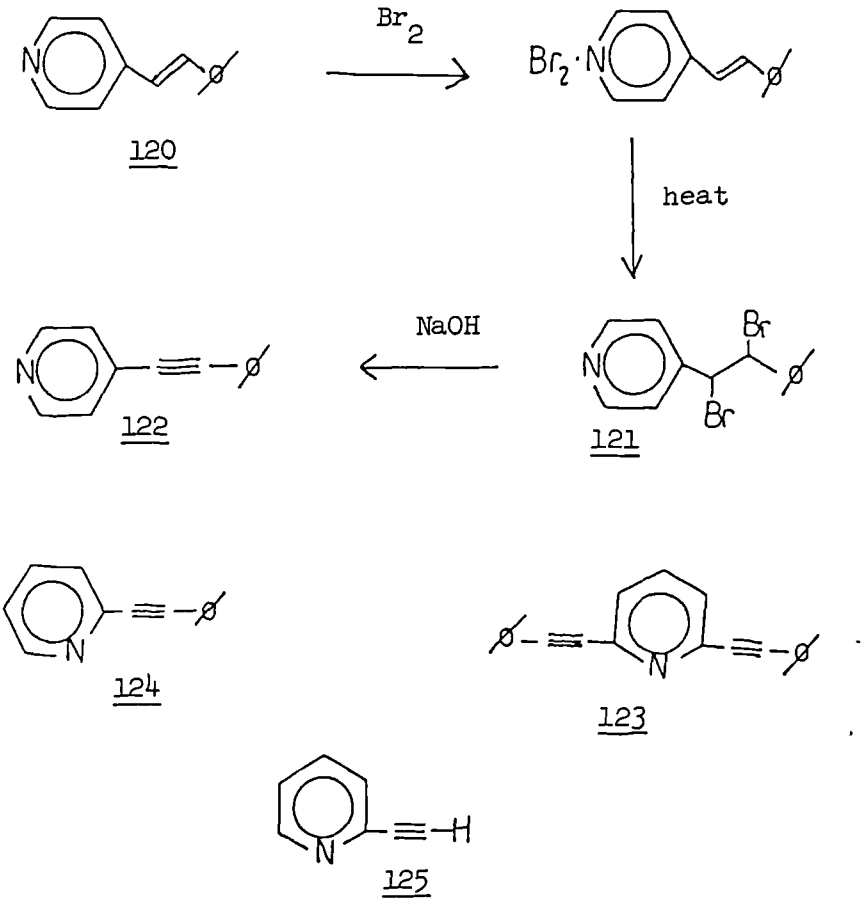
The effect of reaction time and temperature on the condensation process are unknown, apart from the obvious increase in viscosity as the reaction proceeds.

CHAPTER 5

Alkynyl-pyridines and -bipyridyls

There are no literature references[17] to compounds with triple-bonds attached to bipyridyl nuclei. However, there is a wealth of published material concerning alkynyl-pyridines, which have often being used to provide cross-linkages in polymers of vinyl-pyridines[60].

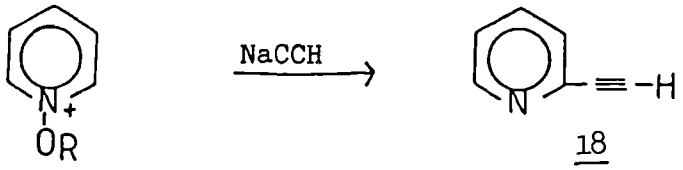
Phenylethynylpyridines have been made in good yield by Smith[61] (scheme 63). 4-Styrylpyridine 120 was treated with bromine at 5°, giving the perbromide, which on heating was converted to the bromocompound 121, which in turn was converted to the alkyne 122 with treatment with base.



SCHEME 63 - ALKYNYLPYRIDINES FROM DIBROMOALKANES

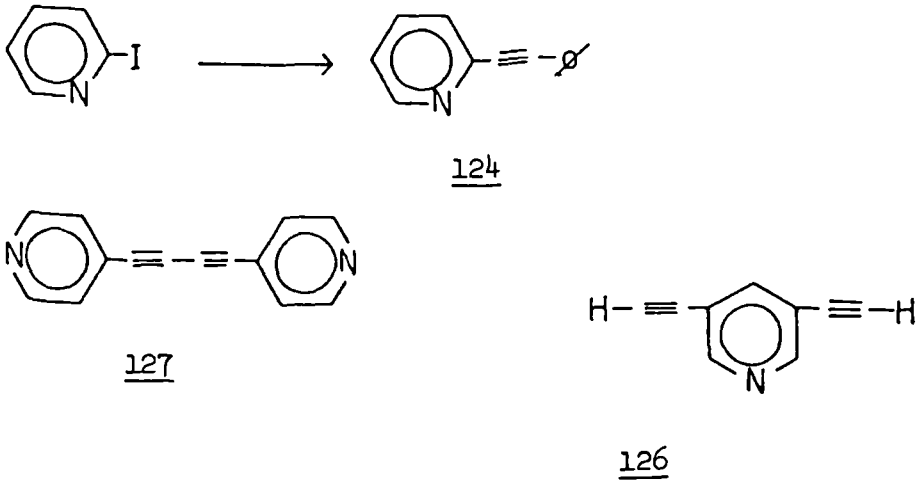
Similarly, Scheuing and Winterhalder[62] made 2,6-bis(2'-phenyl)ethynylpyridine 123, as well as the 2-isomer 124 of phenylethynylpyridine 122, using essentially the same method; In addition, Dykhanov and Ryzhkova[63], and Leaver, Gibson and Vass[64], made 2-ethynylpyridine 18 in moderate yield.

McGill[65] made ethynylpyridines from N-alkoxy-pyridine and sodium acetylide (scheme 64), but no yields were reported for this reaction.



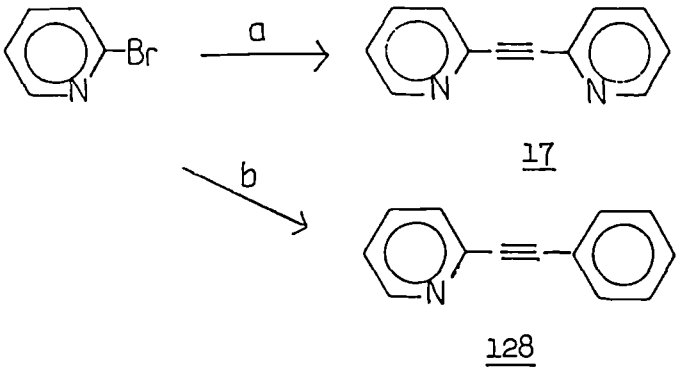
SCHEME 64

Shvartsberg and co-workers[66a] coupled 4-phenylethyne and 2-iodopyridine with copper and potassium carbonate (Scheme 65) to give 2-phenylethynyl pyridine 124 (88% yield), and also 3,5-bis-ethynylpyridine 126. In addition, they made bis-(4-pyridyl)-butadiyne 127 by coupling 4-ethynyl pyridine, using Cu (I) salts as catalysts[66b].



SCHEME 65

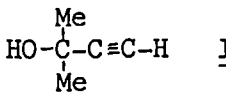
A much more elegant coupling of alkynes with halopyridine was developed using a palladium (II) catalyst in diethylamine as solvent. Thus, Sonogashira[67] reacted 2-bromopyridine with phenylethyne to give 2-phenylethynylpyridine 128 (Scheme 66), and with ethyne itself to give the bis-pyridylethyne 17.



SCHEME 66

a: PhCCH/ $Pd(Ph_3P)_2Cl_2$/ Et_2NH (99%) b: HCCH/ $Pd(Ph_3P)_2Cl_2$/ Et_2NH (60%)

The use of the methylbutynol 129 (which is a synthon for ethyne - on treatment with base it loses acetone to produce ethyne) in this reaction has led to excellent yields of ethynylpyridines; Ames,Bull and Takundwa[68] reacted butynol 129 with 2-bromopyridine to make 2-ethynylpyridine 18 in 70% overall yield (Scheme 67).



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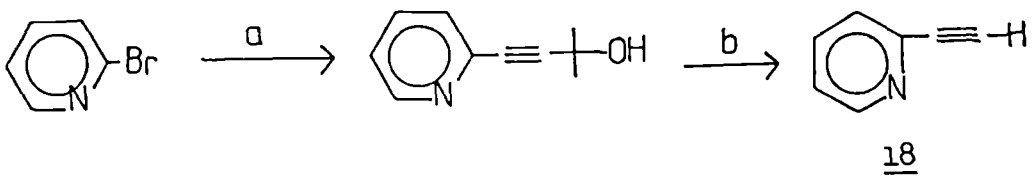
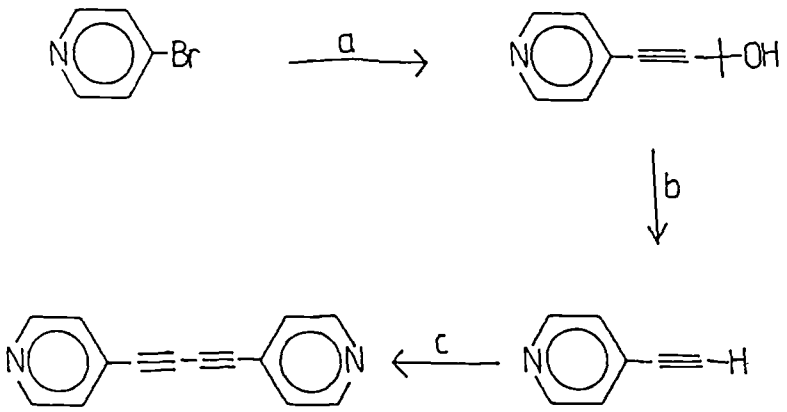


18

SCHEME 67

a: 129/ $Pd(Ph_3P)_2Cl_2$/ Et_2NH b: NaOH/ toluene

Della Ciana and Haim[69] made 4-ethynylpyridine in the same way, and then coupled the product, ethynylpyridine 130, by a Gattermann-type oxidation (Scheme 68) to give bis-(4-pyridyl)-butadiyne 127.

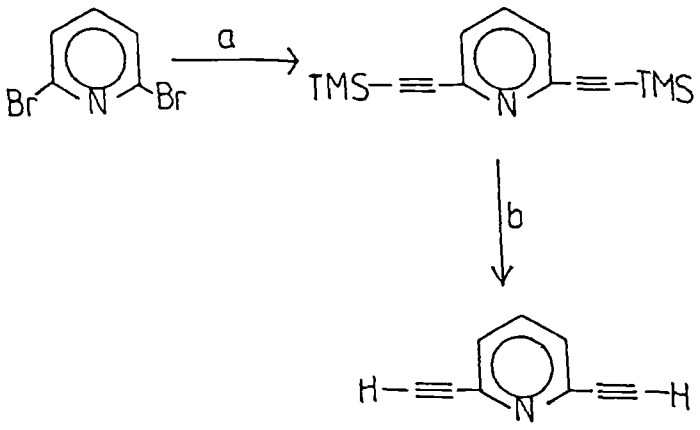


127 130

SCHEME 68

a: 129/ Pd(II)/ Et_2NH (84%) b: NaOH (90%) c: Cu_2Cl_2/ pyridine (92%)

Takahashi et al.[70] have demonstrated the synthesis of 2,6-bis ethynylpyridine 131 by using another half-protected alkyne, trimethylsilylethyne, and reacting that compound with 2,6-dibromopyridine (Scheme 69).



131

SCHEME 69

a: Me_3SiCCH/ Cu_2I_2/ Pd (II)/ Et_2NH (83%) b: OH^- (aq.) (75%)

Only two reactions for preparing alkynyl-bipyridyls were attempted: 2,2'-dichlorobipyridyl 38 did not react at all with phenylethyne or methylbutynol 129 in diethylamine, even at reflux in the presence of a molar equivalent of the palladium (II) catalyst, which was very surprising, but this behaviour does agree with the lack of reactivity found for this chlorine-bipyridyl bond earlier (chapter 3).

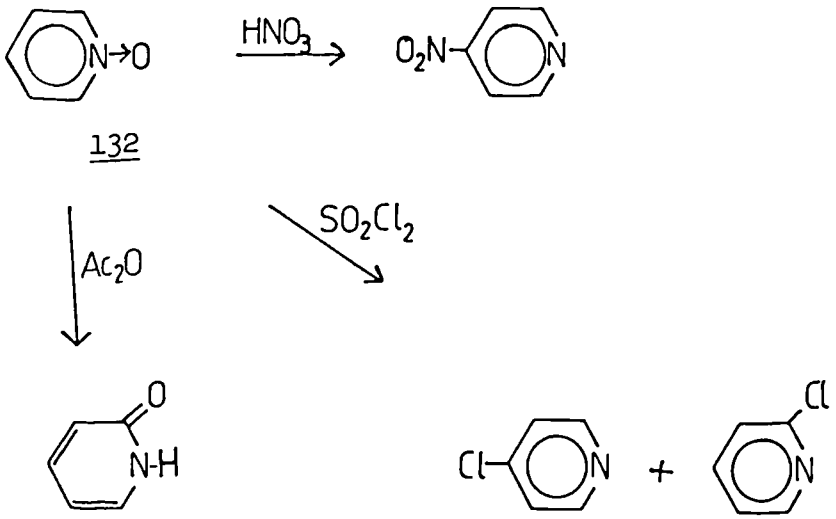
Secondly, 2,2'-distyrylbipyridyl 92 was treated with an excess of bromine in tetrachloromethane, giving a bright red very insoluble complex[24], but this did not decompose at all at reflux in either tetrachloromethane or dimethylformamide, to give an alkyne, but remained unaltered.

The chemistry of bipyridyl bis-N-oxide (133)

Pyridine N-oxide

Pyridine itself is nitrated with difficulty at the 3-position by concentrated nitric/ sulphuric acid[71]. Pyridine N-oxide 132 (scheme 70) is nitrated much faster[72] and the major product is 4-nitropyridine. Therefore the N-oxygen substituent is considered to activate the ring towards electrophilic attack.

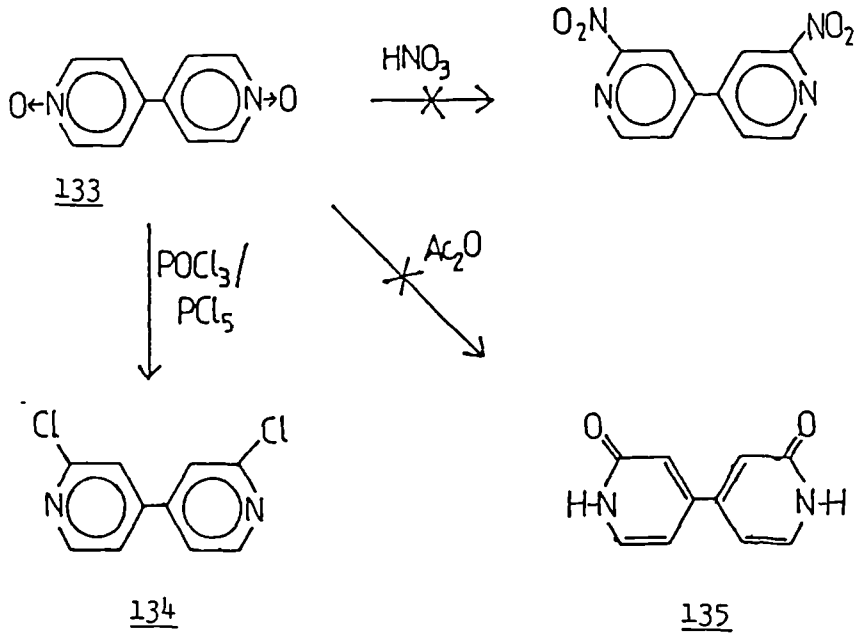
Pyridine-N-oxide 132 also reacts with sulphuryl chloride[73] to give a mixture of 2- and 4-chloropyridines, and with acetic anhydride to give 2-pyridone[32b] (scheme 70).



SCHEME 70 - TRANSFORMATIONS OF PYRIDINE-N-OXIDE

Bipyridyl bis-N-oxide 133, which was easily made by the reaction of bipyridyl with hot peracetic acid, has been little investigated. With the 4-positions blocked to attack, it was hoped that substitution would occur only at the 2-positions;

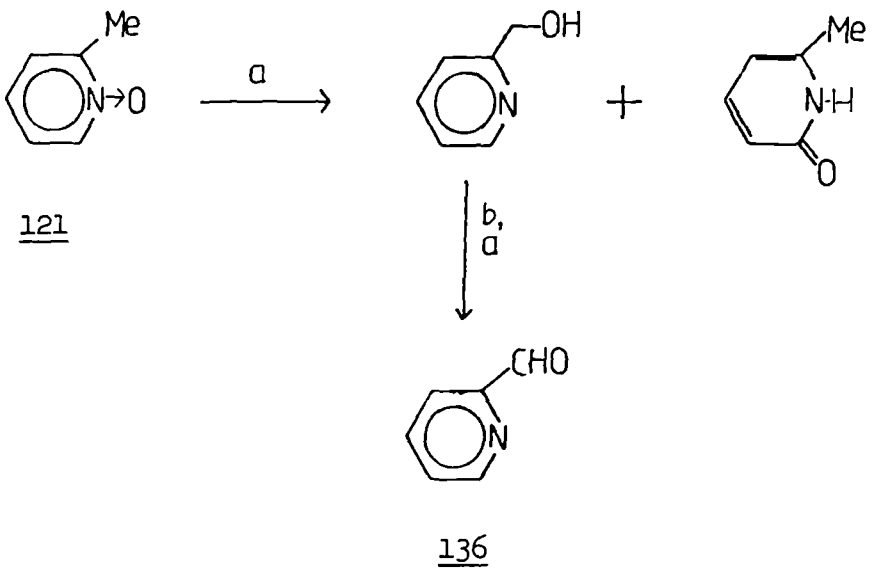
Dioxide 133 was heated under nitration conditions, and with sulphuryl chloride, as above, but no substituted bipyridyls were observed on work-up (TLC and NMR analysis). However, when heated with phosphoryl chloride/ phosphorus pentachloride[73], a poor yield of 2,2'-dichlorobipyridyl 134 was achieved (scheme 71).



SCHEME 71

The reaction of dioxide 133 and acetic anhydride could be expected to yield dione 135, by analogy to the reaction of pyridine N-oxide[32b] (scheme 65). In refluxing acetic, or even propanoic anhydride however, no such ring-oxidation reaction occurred, and bipyridyl 25 itself was the reaction product (scheme 71).

2-Methyl pyridine N-oxide 121 is converted by acetic anhydride into acetoxy-methylpyridine (scheme 72) which can be further transformed[74] into 2-formylpyridine 136, in moderate yield, with pyridones as major side-products. The reaction of 2,2'-dimethyl-1,1'-dioxide (prepared from dimethylbipyridyl 41 and per-acetic acid) with acetic anhydride gave a mixture from which no products were isolated.



121 136

SCHEME 72

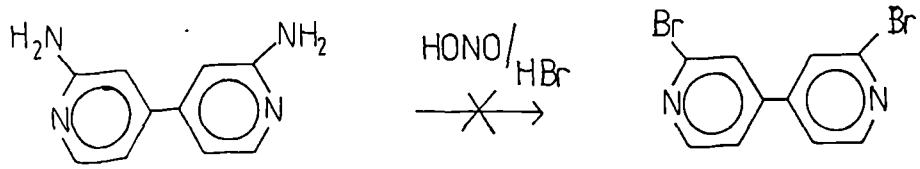
a: (1) Ac_2O (reflux) (2) H^+ (aq.) b: Peracetic acid

The chemistry of 2,2'-dichloro-4,4'-bipyridyl (134)

Whereas 2-chloropyridine has been transformed in a variety of nucleophilic substitution reactions[75], dichlorobipyridyl 134 has been found to be unreactive.

For instance, dichlorobipyridyl 134 was heated at reflux in pyridine, without any obvious reaction (by NMR analysis of the reaction mixture), and with potassium iodide in acetonitrile with no change. The lack of reactivity towards alkynes has been commented on, in stark contrast to the reactivity of 2-bromopyridine (page 84, 2-chloropyridine also reacts under the same conditions).

Other dihalo-bipyridyls are unknown. Although 2-bromopyridine is easily made from 2-aminopyridine[76], the diaminobipyridyl 137 that was available did not afford any halogenated product under the same reaction conditions (scheme 73).

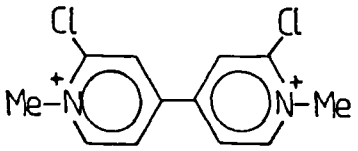


137

SCHEME 73

The synthesis of dichlorobipyridyl 134 as performed in the laboratory (scheme 71) has scope for improvement. The use of a different acid chloride[73] might give better yields, or the isolation of the intermediate dione[77b] 135 (scheme 71, or labelled 45 in scheme 15, page 25) followed by conversion of that dione 135 to chlorocompound 134, might also afford a higher overall yield.

Dichlorobipyridyl 134 was readily methylated with dimethyl sulphate to yield colourless, water-soluble, dichloro- viologen 138, but the product with iodomethane in methanol was a bright red, very insoluble solid. It was not possible to tell whether iodide had displaced the chloro group.



138

CONCLUSION

There seems to be very little scope for the synthesis of alkynyl bipyridyl compounds using existing reactions that produce alkynyl pyridines. The substituted bipyridyls available appear to be too unreactive in these cases.

CHAPTER SIX

MISCELLANEOUS

ELECTROCHEMISTRY

Many of the new viologens synthesized in the course of this project were analyzed by Cyclic Voltammetry (CV), by Paul Monk at Exeter University. The results are displayed in Table 5.

Procedure

A three-electrode system was used to measure the redox potentials: The working (WE) and counter (CE) electrodes were platinum, the reference electrode (RE) was a standard calomel electrode. As the potential difference between RE and WE was swept through a range, usually at 50 mV s^{-1}, the current between WE and CE was recorded. The cell was kept flushed with nitrogen and in the dark. The concentration of the viologen solution was 1 mM, in 100 mM supporting electrolyte (potassium chloride or tetrabutylammonium perchlorate or tetrafluoroborate).

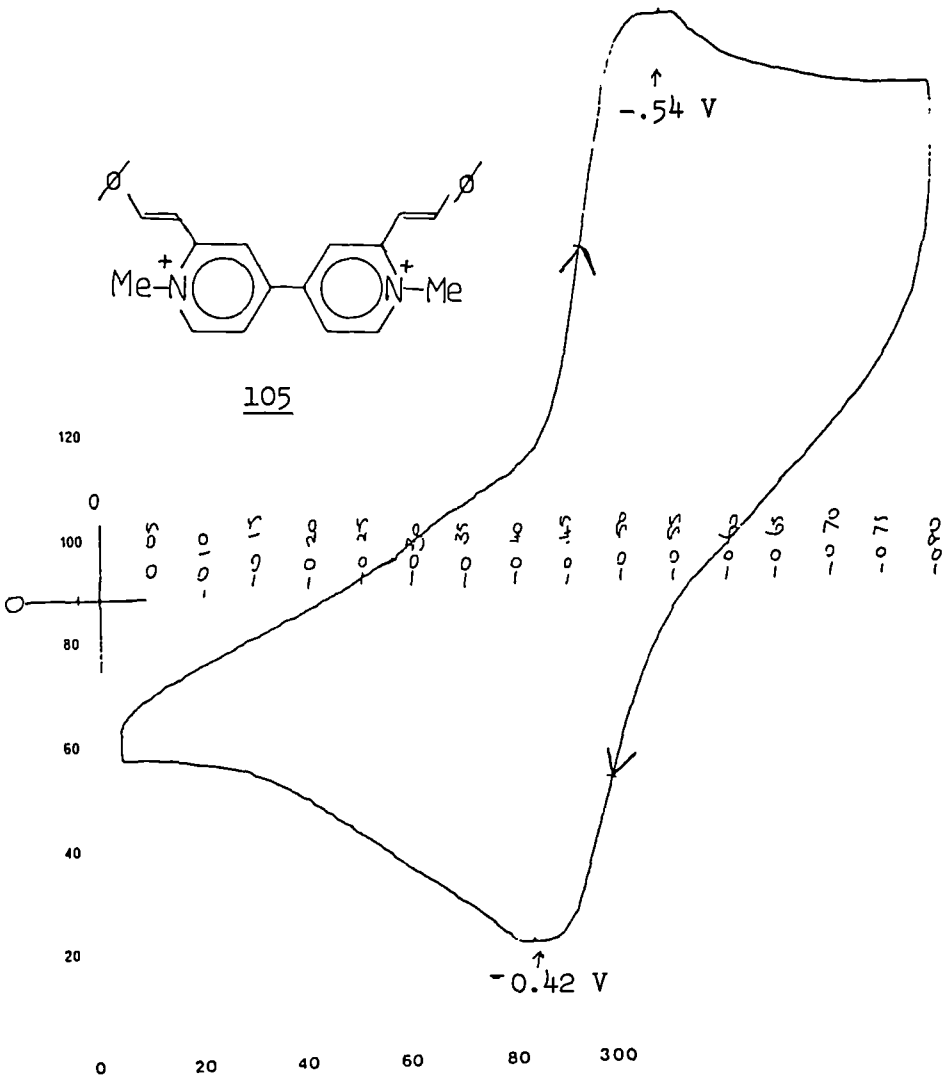
The redox potentials were measured at the mid-point of the two peaks of the cyclic voltammogram (as illustrated in scheme 74 for distyryl viologen 105).

TABLE 5

Redox potentials for new viologens

(-mV versus S.H.E.)

Viologen	E_1	E_2	Solvent	Colour V^{++}	Colour V^{+}
2,2'-distyryl 8, 105	240	-	Water	Yellow	Blue
2,2'-bis-(4-methoxystyryl) 106	230	-	Water	Orange	-
2,2',6,6'-tetra styryl 9, 109	260	-	Water	Orange	Pink
Polymer 97	280	-	(Water)	-	-
Aminophenyl 5, 84	200	-	Water	Red	-
(Schiff base) 89	40	-	Water	Brown	-
Tetramethoxy-aminobiphenyl 85	180	-	Water	Red	Red
2-pyridyl 36	210	-	Water	-	Green
Thiapropyl 74	330	530	Water	-	Blue
Ethylmethyl-sulphonio-methyl 23	150	570	Propylene carbonate	-	Yellow
Triphenyl-phosphonio-methyl 73	160	570	Propylene carbonate	-	Red
1-pyridinium -methyl 24	220	-	Water	-	Green
Poly-methylene viologen 26	220	-	Water	-	Blue
Bis-bipyridyl-methane 22	340	-	Water	(Red)	Yellow
2,2'-dichloro 138	200	-	Water	-	Blue



SCHEME 74 - CYCLIC VOLTAMMOGRAM OF STYRYL VIOLOGEN (105)

HORIZONTAL SCALE: V from standard calomel electrode.

VERTICAL SCALE: mA.

Arrows denote the direction of the sweep at 50 mV s^{-1}

1.0 mM solution in water with 100mM potassium chloride.

The mean of -0.54 V and -0.42 V is -0.48 V (relative to standard calomel electrode) or -0.24 V (relative to standard hydrogen electrode).

Discussion

(1) The pH dependence of E_1 for aminophenyl viologen 5.

The reduction potential of 5 falls (becomes more negative) by about 20 mV for every pH unit increase, and the relationship between E_1 and pH is linear at medium pH values. (see table 6).

Table 6 The pH dependence of the redox potential of aminophenyl viologen (5)

pH	12	9.2	8	7	4	2
E_1 (-mV)	290	240	220	200	150	85

The cause of this behaviour is unknown, for similar pH - E_1 studies have not been performed on other viologens.

(2) The very high (that is, un-negative) redox potential of Schiff-base viologen 89, derived from aminophenyl viologen 5 by reaction with 4-methoxybenzaldehyde, is a very good indication that the extension of the conjugated system of the viologen from the nitrogen atoms will make the reduction of that viologen easier. The hexacyclic viologen 85 (page 53) was expected to be easier to reduce, but the redox potential is similar to that of aminophenyl viologen 5. This can probably be explained by noting that the coupling constant ^3J between the protons of the bipyridinium unit is very small (2.4 Hz), which is indicative of deformation of the planar system. According to the Karplus equation[81b], the coupling constant decreases as the dihedral angle between the adjacent protons increases from zero (which is the angle in a planar aromatic ring). Because ^3J in the other bipyridinium compounds investigated was always at least 5 Hz, it is assumed that the methoxyl groups in viologen 85 are not only hindering rotation of the biphenyl units relative to the bipyridinium unit, but are also deforming the

latter out of planarity, therefore partially destroying pi-electron overlap (conjugation).

(3) The effect of electron-withdrawing substituents on the N-methyl groups.

It has been mentioned in the introduction (page 2) that electron-withdrawing groups on the alkyl substituents on the nitrogen atoms of a viologen will make that viologen easier to reduce. With sulphonium viologen 23 and phosphonium viologen 73, these substituents are cationic, and possess very high (more positive) redox potentials. Pyridinium-methylene viologen 24 has a redox potential of -220 mV, as has the poly-methylene-viologen polymer 26, a figure similar to that given by benzyl viologen 112.

(4) Styryl viologens.

As was expected, the introduction of large conjugated groups onto the viologen nucleus produced a large drop in the redox potential. The reason why the tetra-styryl compound 9 (109)is less easy to reduce than the di-styryl viologen 8 (105)is unclear, but may be due to deformation of the bipyridinium nucleus (and consequent loss of conjugation) by the four bulky substituents. The introduction of methoxyl substituents onto the styryl groups in compound 100 produced a small (10 mV) rise in the redox potential, compared to the unsubstituted styryl viologen 105. The polymeric material (97) was disappointing inasmuch that it had a redox potential not very different from distyryl viologen 105, because it had been hoped that the large conjugated system would alter the redox potential considerably.

Cross-linking of Vinyl and styryl pyridines

The olefinic double bond of vinylpyridines is easily polymerized under polystyrene-producing conditions[80]. Such polymers have been well-studied[80b] and have found various uses. Vinylpyridine is also reported[27] to polymerize on N-methylation.

Styrylpyridines are much more resistant to polymerization, the high temperatures involved in their production bearing witness to this[54c]. No evidence was seen, during the preparation of styrylbipyridyls 92 and 108, to suggest any polymerization was occurring, nor on N-methylation of those compounds with dimethyl sulphate.

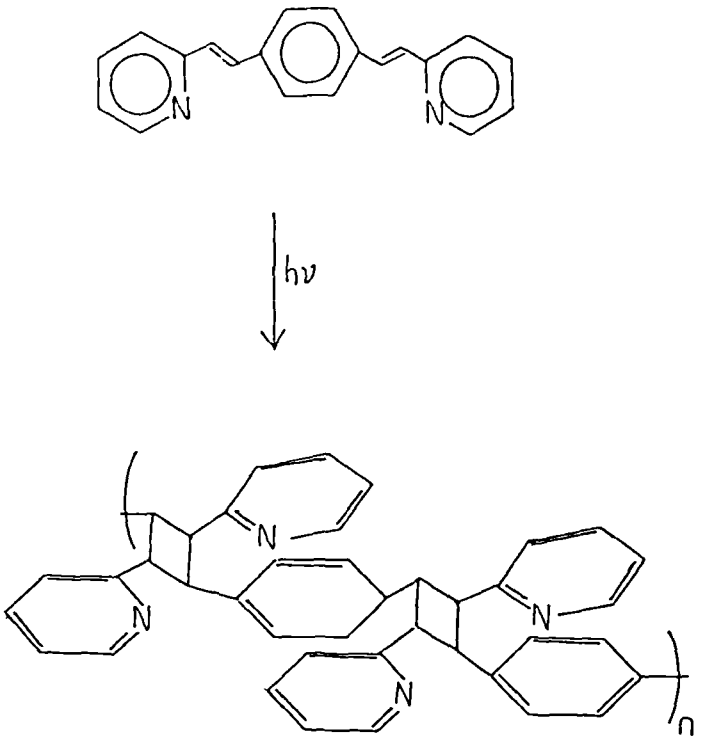
However, styrylpyridines can be polymerized by irradiation with ultra-violet radiation[54a], to give a cyclobutane structure (scheme 75), although the quantum yield for this process is quite low.

FLUORESCENCE

Many of the compounds produced during this study were found to absorb ultra-violet radiation very strongly, and several were highly fluorescent;

2-Styryl viologens 8 and 9 emitted bright yellow light when irradiated at 290 nm, and the 1-Z-methoxyphenylethenylpyridinium salt 70a emitted greenish-yellow light. The 1-Z-styrylpyridinium salt 70 did not seem to fluoresce, but 1-E-styrylpyridinium 51 exhibited blue fluorescence, whilst the 1-styrylbipyridinium 60 glowed with yellow light.

On prolonged irradiation, NMR samples (in TFA) of the Z-olefins 70 and 70a showed some sign of isomerizing to the corresponding Z-olefins 51 and 51An (see p. 29), with the appearance of minute signals attributable (by comparison of the NMR spectra) to the E-olefinic protons with ^{3}J c. 15 Hz. However, like all the compounds mentioned, these olefins also began to show signs of decomposition, with the appearance of many other NMR signals.



SCHEME 75 - THE PHOTOCHEMICAL POLYMERIZATION OF A STYRYLPYRIDINE

The reaction of pyridine with dibromoalkanes

Pyridine is widely used as a reagent for removing the elements of a hydrogen halide from organic compounds, to produce an olefin. With primary alkyl halides, the product of reaction with pyridine is the corresponding pyridinium salt, which can be very thermally stable with respect to pyridine elimination. With secondary and tertiary halides, however, the pyridinium salt is much more prone to elimination, if it is actually formed at all.

With vicinal dihalides, bis-pyridinium salts with two pyridine rings on adjacent carbon atoms are unknown except where both are primary groups, that is, in the compound 1,2-bis-pyridinium ethane 139 (scheme 76).

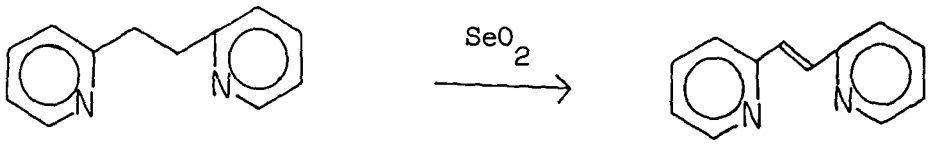
The reaction of pyridine with a variety of 1,2-dibromo- compounds was investigated. In most cases, the only product isolated was pyridinium hydrobromide, with no evidence seen for pyridine-carbon bond formation.

Dibromo-di-acids.

Pfeiffer and Langenburg[78] described the reactions of pyridine with R,S-2,3-dibromo-succinic acid (DBSA), and with dibromoacrylic acid.

With DBSA, their product was the pyridinium propenoic acid 140 (scheme 77), and the intermediate bromodi-acid 141 was not isolated. However, this compound was produced when excess DBSA was heated with pyridine in THF, but on treatment with more pyridine, diacid 141 decarboxylated to give propenoic acid 140. 4,4'-Bipyridyl was similarly reacted with DBSA, but no evidence for bipyridyl-carbon bond formation was seen.

Several similar dibromo-diacids were synthesized and reacted with pyridine, but none of them gave products corresponding to either propenoic acid 140 or to diacid 141. The dimethyl ester of DBSA also did not give any involatile pyridinium compound besides pyridinium hydrobromide.



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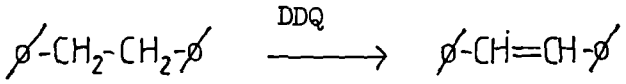
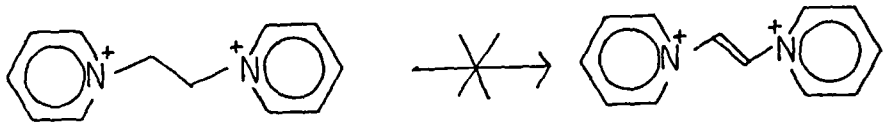


144 145



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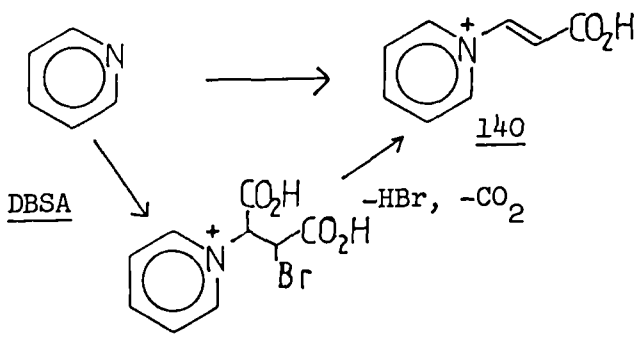
SCHEME 76 - THE OXIDATION OF BIS-ARYLETHANES



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SCHEME 77 - THE REACTION OF PYRIDINE WITH R,S-2,3-DIBROMOSUCCINIC ACID (DBSA)

Oxidation of bis-pyridinium salts

1,2-Di-(2-pyridyl)-ethane 142 has been oxidized to the dipyridyl-ethene 143 with selenium dioxide[79a], and 1,2-diphenylethane 144 was oxidized to stilbene 145 by di-chloro-dicyano-quinone (DDQ)[79b] (scheme 76). Iodine has also been widely used to dehydrogenate ("aromatize") such compounds[79c]. The reaction of 1,2-bis-(1'-pyridinium)-ethane 139 with these reagents in acetonitrile as solvent was attempted, but no reaction was observed to occur.

EXPERIMENTAL SECTION

Unless otherwise stated, all reactions were carried out under an atmosphere of dry nitrogen. When used in reference to solvents, "evaporated" means evaporated under reduced pressure on a rotary evaporator.

The nomenclature of compounds is based on that used in Chemical Abstracts.

Melting-points were determined using a Gallenkamp MFP-595 instrument with samples in open capillaries. Temperatures over 320° were not studied. A melting point of "320+" indicates that the compound did not melt at 320°. "Dec." indicates that visible decomposition accompanied melting.

^{1}H NMR spectra were determined at 220 MHz on a Perkin-Elmer R34 spectrometer. For samples run in deuterochloroform ($CDCl_3$), tetramethylsilane (TMS) was used as internal reference. With trifluoracetic acid (TFA) and deuterium oxide (D_2O), 1,4-dioxan was the reference, at δ 4.10 or 3.60 ppm respectively. These chemical shifts are relative to TMS or to sodium trimethylsilylpropanesulphonate in the same solvents. This pronounced change in chemical shift between solvents often meant that signals unresolved in one solvent were resolved in the other.

Data are presented in this form:

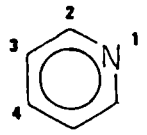
Chemical shift (integration, multiplicity, coupling constant(s) (J) of that multiplet, assignment)

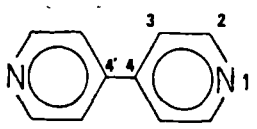
The following abbreviations have been used:

s - singlet d - doublet t - triplet q - quadruplet

m - multiplet br - broad AB - two similar, but different, protons.

For compounds containing 1-substituted pyridine rings, the pattern of 2-proton-triplet (C-3 protons), 1-proton-triplet (C-4), and 2-proton-doublet (C-2) is characteristic, and these assignments have usually been omitted. Similarly, assignments and coupling constants for 2-substituted pyridine compounds, and bipyridinium compounds are generally omitted. The ^{3}J coupling constants for all these rings were fairly invarient at between 5.5 and 7 Hz. Some illustrative spectra are presented in appendix 1.





^{13}C NMR spectra were run on the Bruker WH400 at 100.62 MHz. Dioxan, at 67.4 ppm, was normally used as internal standard. Data are presented as follows:

Chemical shift (multiplicity and coupling constant (J) if any, assignment (q = quaternary carbon, ? = dubious signal))

The assignment of most methine carbons has not been attempted, as this would have involved lengthy heteronuclear decoupling experiments in addition to the fully-proton-decoupled spectra routinely produced.

All mass-spectrometry was performed on a Kratos MS80 instrument. Fast-Atom-Bombardment (FAB) with Xenon was very useful for getting salts into the gas phase, and generally gave good information about both the cation and the anion. Glycerol was the support matrix used (unless otherwise stated) which gave background peaks at masses of 1+n92, of rapidly diminishing magnitude as n increases.

Data are presented as follows:

Relative mass of ion (% intensity, assignment)

The single charge on the ion is assumed. Some illustrative FAB spectra are presented in appendix 2.

Infra-red spectra were obtained using a Perkin-Elmer 580B instrument, with samples supported either in liquid paraffin (Nujol) or hexachlorobutadiene (HCB) and referenced to the polystyrene absorption, nominally at 1601 cm^{-1}.

Most of the spectra do not contain absorption peaks in the range 4000-1600 cm^{-1} apart from C-H stretching at c.3000 cm^{-1} and aromatic breathing at c.1630 cm^{-1}. Only prominent peaks in the "fingerprint" region have been mentioned, in view of the limited information to be obtained from them.

Ultra-violet-visible spectra were run on a Perkin-Elmer 552 UV-Vis spectrometer using ethanol or acetonitrile as solvent. Data are presented thus: Absorption maximum (nm) ($\log_{10}[\epsilon / m^2\ mmol^{-1}]$).

Elemental analyses were carried out by the City University, London or by I.C.I. staff at the Heath, Runcorn. Analytical samples were routinely heated *in vacuo* at 60° for several hours before despatch.

Cyclic voltammetry was done at Exeter University by Paul Monk. (Details are given in chapter 6).

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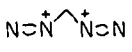

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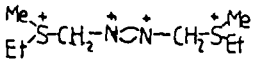
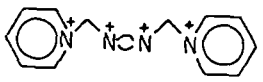


23



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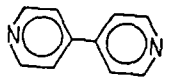

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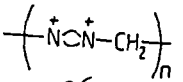

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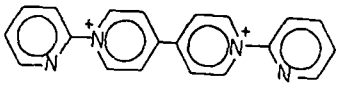

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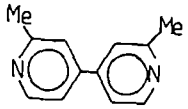

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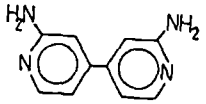

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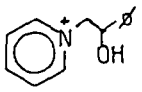

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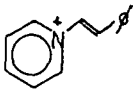

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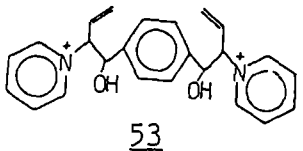

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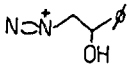

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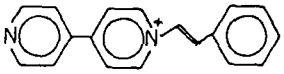

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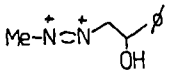
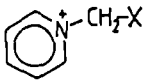


60

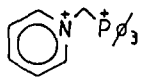
SCHEME 78

ILLUSTRATIONS OF COMPOUNDS MENTIONED IN THE EXPERIMENTAL SECTION



63 X = I

64 X = Br



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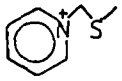

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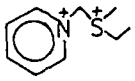

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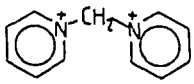

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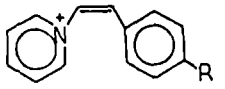
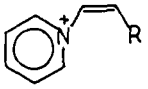


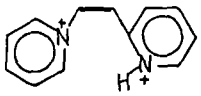
70 R = H

70a R = OMe

70b R = CHO



70c R = 2-Pr



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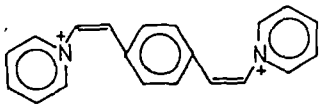

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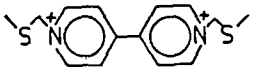

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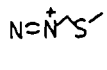

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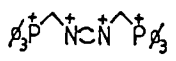

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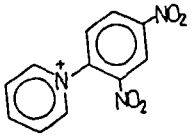

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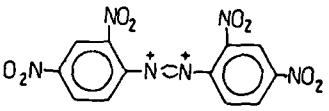

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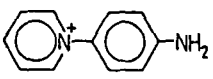

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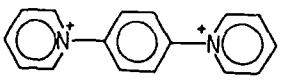

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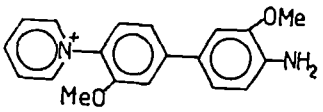

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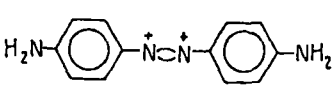

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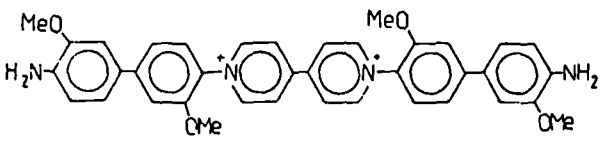

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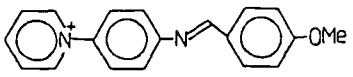

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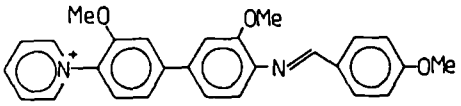

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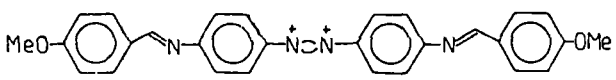

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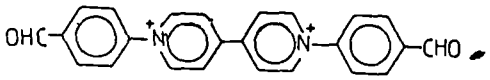

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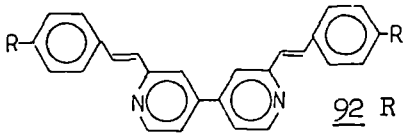
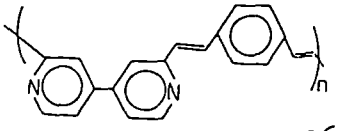


92 R = H



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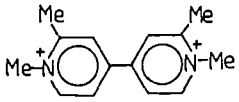

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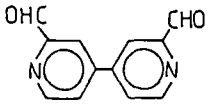

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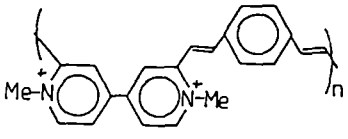

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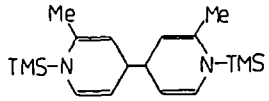

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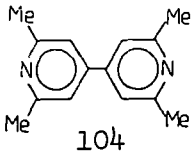

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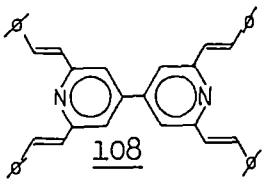

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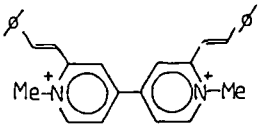

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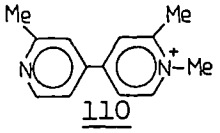

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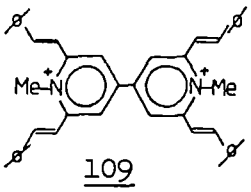

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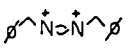

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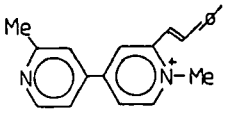

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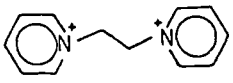

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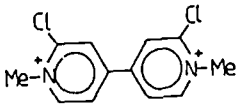

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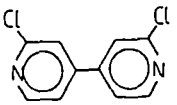

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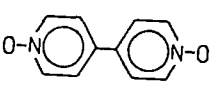

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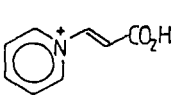

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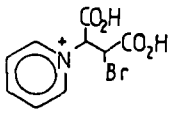


141

EXPERIMENTAL FOR

INTRODUCTION

4,4'-Bipyridyl (25)

Bipyridyl 25 was obtained in a crude state from I.C.I. Organics division. It was twice recrystallized from 5% aqueous acetic acid, which yielded the hydrate. This lost about 10% of its weight on heating in vacuo, and was dehydrated by azeotropic distillation of a toluene solution under a Dean-Stark trap until the condensate was clear, followed by evaporation of the solvent. The product (which lost less than 1% of its weight on heating in vacuo) was stored in a desiccator over potassium hydroxide.

1,1'-Bis-[(1''-pyridinium)-methyl]-4,4'-bipyridinium tetrakis-[tetrafluoroborate] (24)

Bis-sulphonium viologen tetrafluoroborate 23 (see page 134) (110 mg, 0.16 mmol) was dissolved in acetonitrile (2 ml) and pyridine (0.2 ml) was added. After 15 min., the blue solution was evaporated down to 0.3 ml, then diethyl ether (10 ml) was added. After 10 min., the precipitate was filtered off. Yield 105 mg (95%).

24: $C_{22}H_{22}N_4.4BF_4$ = 690 g mol^{-1}. m.p. 170-260° (dec)

^1H(220 MHz, solvent TFA, standard dioxan) δ= 7.57(4 H, s, CH_2), 8.35(4 H, t, J= 7 Hz, pyr-H(3)), 8.8(6 H, m), 9.39(4 H, d, J= 6 Hz, bipy-H), 9.59(4 H, d, J= 6 Hz, bipy-H).

FAB No spectrum was obtained.

Poly-(methylene viologen) tetrafluoroborate (26)

Bis-sulphonium viologen tetrafluoroborate 23 (347 mg, 0.507 mmol) was dissolved in acetonitrile (5 ml) with anhydrous bipyridyl 25 (79 mg, 0.506 mmol). After 5 hr. another 10 mg of bipyridyl was added. After another hour, the white precipitate was filtered off, washed with acetonitrile and diethyl ether, then dried in vacuo. Yield 175 mg (0.508 mmol, 100%) of a white powder.

26: $(C_{11}H_{10}N_2.2BF_4)_n$ = n(344) g mol^{-1} m.p.240-260°(dec).

^1H(220 MHz, solvent D_2O, standard dioxan) δ = 7.52(2 H, s, CH_2), 8.69(4 H, d, J= 6 Hz, bipy-H), 9.52(4 H, d, J= 6 Hz, bipy-H)

Plus four doublets and a singlet at 7.47 ppm of c. 0.2 protons each (probably due to terminal bipyridyl groups).

FAB No spectrum was obtained.

UV λ_{max} (EtOH) 245(6.61), 220(6.45) nm.

1,1'-Bis-(iodomethyl)-4,4'-bipyridinium diiodide

Bis-sulphonium viologen 23 (110 mg, 0.16 mmol) was dissolved in acetonitrile (5 ml) and potassium iodide (0.3 g) was added. The mixture was heated at 50° for 3 hr. then cooled, filtered and poured into diethyl ether (50 ml). The red precipitate was filtered off, then redissolved in acetonitrile and precipitated with diethyl ether. The yield was 105 mg (0.15 mmol, 95%).

$C_{12}H_{12}I_2N_2.I_2$ = 692 g mol^{-1} m.p. 214-6°.

^1H(220 MHz, solvent TFA, standard dioxan) δ = 6.64(4 H, s, CH_2), 8.68(4 H, m, bipy-H), 9.41(4 H, m, bipy-H).

FAB (+) m/z = 438(1%,M), 311(3,M-I).

Bis-[1-(4,4'-bipyridinium)]-methane diiodide (22)

Diiodomethane (2 ml, 26 mmol) and anhydrous bipyridyl 25 (13 g, 80 mmol) were heated together in ethanol (50 ml) overnight at reflux. After cooling, the red crystals were filtered off, washed with ethanol (40 ml) and dried. Yield : 6.7 g (11.6 mmol, 44%). No suitable recrystallization solvent was found. m.p. 239-40° (dec)

Calculated for $C_{21}H_{18}N_4.I_2$: C,43.4%; H,3.1%; N,9.6%; I,43.8%; Found. C,43.3%; H,3.2%; N,9.4%.

^{1}H(220 MHz, solvent TFA, standard dioxan) δ = 8.06(2 H, s, CH_2), 8.73, 8.92, 9.25, 10.02(4 x 4 H, 4 d, J= 6 Hz, bipy-H).

FAB (+) m/z = 453(0.1%,M+I), 325(1,M-H), 297(1), 262,261(1), 219(2), 171(10, bipyCH_3), 157(8, bipyH).

IR (HCB) ν_{max} 3020,2930,2770 (C-H), 1640,1615(Ar) cm^{-1}.

UV No suitable solvent found.

2-Bromopyridine (After Allen and Thirtle[76])

2-Aminopyridine (15.2 g, 161 mmol) was dissolved in 40% hydrobromic acid (80 ml) and cooled to 0°. Bromine (9 ml, 170 mmol) was added, followed by sodium nitrite solution (20 g in 40 ml water), keeping the mixture cooled below 0°, over an hour, and was then stirred for another hour at 0°. Sodium hydroxide solution (40 g in 50 ml water) was added slowly, then the mixture was extracted with diethyl ether (4 x 100 ml). The organic solution was dried and evaporated, then the residue was distilled at the water-pump (b.p. 79°) Yield: 12.3 g, 80 mmol, 48%.

^{1}H ($CDCl_3$) δ = 7.29(1 H, apparent t), 7.5-7.65(2 H, m), 8.39(1 H, d).

Methylation by iodomethane: 2-iodo-1-methylpyridinium bromide

2-Bromopyridine (2.6 g, 16.5 mmol) was dissolved in THF (10 ml) and iodomethane (2 ml). After being allowed to stand overnight, the crystalline precipitate was filtered off and recrystallized from ethanol. Yield 4.9 g, 15 mmol, 90%.

$C_6H_7IN.Br$ = 301 g mol^{-1} m.p. 208-9°.

^{1}H (220 MHz, solvent D_2O, standard dioxan) δ = 4.32(3 H, s, Me), 7.34(1 H, t), 7.42(1 H, t), 8.48(1 H, d), 8.88(1 H, d).

FAB (+) m/z = 220(100%,M-H) 207(20,M-CH_2).

2,1',4',4'',1'',2'''-Tetrapyridinium dibromide (36)

Anhydrous 4,4'-bipyridyl (1.0 g, 4.4 mmol) was heated at 190° in 2-bromopyridine (10 ml) overnight. After cooling, diethyl ether (20 ml) was added and the solid was filtered off. Ethanol (10 ml) was then used to wash the solid, which was recrystallised from ethanol. Yield of yellow 36 2.7 g (90%). m.p. 320+ Calculated for $C_{20}H_{16}N_4.Br_2$: C,50.8%; H,3.3%; N,11.9%; Found: C,50.9%; H,3.4%; N,11.6%;

^{13}C(100.62 MHz, solvent D_2O, standard dioxan) δ = 119.1, 128.1, 128.5, 142.5, 144.6, 150.9, 152.3(br), 152.7.

UV $_{max}$ (EtOH) 325(6.52), 202(6.41) nm.

^1H(220 MHz, solvent D_2O, standard dioxan) δ = 7.76(2 H, td, J= 5.1, 1.6 Hz), 8.05(2 H, d, J= 8.4 Hz), 8.23(2 H, td, J= 8.4, 1.6 Hz), 8.69(2 H, d, J= 5.1 Hz), 8.79(4 H, d, J= 6.7 Hz, bipy-H), 9.68(4 H, d, J= 6.7 Hz, bipy-H).

FAB (+) m/z = 312(100%,M), 234(60,M-pyr).

IR (HCB) ν_{max} 3080,3040, 1635, 1615, 1595 cm^{-1}.

The reactions of 2-iodomethylpyridinium with bipyridyl in propylene carbonate at 120°, and of 36 with dimethylsulphate at temperatures up to 150°, both gave black oily reaction mixtures, from which crystalline products were not obtained (an aqueous extract from a chloroform solution of the residue, when evaporated was only 50 mg, the ^1H NMR spectrum of which displayed no N-Me proton signals).

2,2'-Diamino-4,4'-bipyridyl (44)

Anhydrous bipyridyl (5.0 g, 32 mmol) was dissolved in biphenyl (25 g) at 150°. Sodium amide (5.0 g, 120 mmol) was added slowly over an hour, then the mixture was heated at 200° for 2 days. The mixture was cooled then digested with water (100 ml), toluene (50 ml) and ethanol (20 ml)

at reflux for 6 hr. The brown solid was filtered off and dried *in vacuo*. No solvent suitable for recyrstallization was found.

44: $C_{10}H_{10}N_4$ = 186 g mol^{-1}. m.p. 320+.

^1H(220 MHz, solvent TFA, standard dioxan) No signals were observed (not even the standard dioxan).

MS (EI) m/z = 186(60%,M), 171(35,M-NH), 158(10,M-NCH_2), 28(30), 17(100,NH_3). (CI) m/z = 187(80%,M+H), 172(100,M-N(?)).

2,2'-Dibromo-4,4'-bipyridyl

The brown solid 44 as prepared above was treated with sodium nitrite and concentrated hydrobromic acid in the same manner as for 2-aminopyridine. On work-up, the ethereal extracts were evaporated and no residue remained. The aqueous solution and solid matter were not further investigated.

EXPERIMENTAL FOR

CHAPTER 1

1-[2'-Hydroxy-2'-phenylethyl]-pyridinium iodide (50)

1-Methylpyridinium iodide (24.9 g, 113 mmol) was refluxed for a day in EtOH (250 ml) with calcium hydroxide (12 g) and benzaldehyde (20 ml, 200 mmol). The cooled solution was filtered, and the filtrate evaporated. This residue was washed with diethyl ether (50 ml) and EtOH (100 ml) to give 4.3 g of a white solid, which was combined with the filtered off solid and recrystallised from boiling water (1 l), giving pure 50 (25 g). The mother liquor was evaporated to quarter volume, potassium iodide (5 g) was added, and 8 g more 50 was obtained. Total yield 32.3 g (99 mmol, 88%).

m.p. 250° (subl. dec.) Calculated for $C_{13}H_{14}NO.I$: C,47.7%; H,4.3%; N,4.3%; Found: C,47.6%; H,4.0%; N,4.1%;

^1H(220 MHz, solvent TFA, standard dioxan) δ = 5.10(2 H, ddd, CH_2), 5.63(1 H, dd, CHOH), 7.42(2 H, m, Ph-H), 7.50(3 H, m, Ph-H), 8.10(2 H, t), 8.63(1 H, t), 8.79(2 H, d).

FAB (+) m/z = 200(100%,M).

IR ν_{max} (nujol) 3290(O-H), 1635(Ar), 680 cm^{-1}.

UV No suitable solvent found.

1-[2'-Hydroxy-2'-(4''-methoxyphenyl)-ethyl]-pyridinium iodide (50an)

The reaction was repeated with 4-methoxybenzaldehyde instead of benzaldehyde. The cooled ethanolic solution was evaporated. Crystals of product grew slowly from the residue and an 80% yield was obtained.

50An $C_{14}H_{16}NO_2.I$ = 355 g mol^{-1} m.p. 86-7°.

^1H(220 MHz, solvent TFA, standard dioxan) δ = 4.05(3 H, s, MeO), 5.0-5.25(1 H, m), 5.3-5.45(1 H, m), 5.55-5.65(1 H, m), 7.08(2 H, d, J= 8 Hz, Ar-H), 7.50(2 H, d, J= 8 Hz, Ar-H), 8.13(2 H, t,), 8.65(1 H, t), 8.73(2 H, d). FAB (+) m/z = 230(100%,M).

Hydrogen 1-[(E)-2'-phenylethenyl] pyridinium oxalate (51)

50 (10.7 g, 33 mmol) and oxalic acid dihydrate (30 g) were heated together at 150° for 3 hr. The cooled residue was washed with water (2 x 50 ml) then recrystallised from water (200 ml) to give 51 as fine white needles 9.5 g, 26 mmol, 80%). The aqueous solution of 51 was acidic, and titrated to 3 moles of acid per mole of product. m.p. 141°

Calculated for $[C_{13}H_{12}N]^+.[C_2HO_4]^-.C_2H_2O_4.H_2O$: C,53.8; H,4.5; N,3.7.

Found: C,53.6%; H,4.4; N,3.5%.

^{13}C (220 MHz, solvent D_2O, standard dioxan) δ= 128.6, 129.0, 130.1, 130.3(q), 131.3, 132.1, 142.3, 147.2, 164.1(oxalate).

^1H (220 MHz, solvent D_2O, standard dioxan) δ= 7.31(4 H, m), 7.49(2 H, m), 7.81(1 H, d, J= 15 Hz, =CH-N), 8.00(2 H, t), 8.48(1 H, t), 8.86(2 H, d). FAB (+) m/z = 182(100%,M).

IR ν_{max} (Nujol) 3480(O-H), 3240, 1765(C=O), 1715, 1635,1610(Ar) cm^{-1}.

UV λ_{max} (EtOH) 325(5.70), 232(5.11) nm.

On standing overnight, NMR samples of alcohols 50 and 58, in TFA, were converted into the respective trifluoroacetate esters. Heating of the solid left after solvent evaporation at 170° for 2 hr. gave brown residues that were the respective olefins 51 and 60, apparently in about 60% yield (NMR analysis) but with considerable pyrolysis occurring. The acetate and benzoate esters needed even higher temperatures before decomposition occurred, and was accompanied by considerable pyrolysis to phenylethyne and pyridine (or bipyridyl).

TFA ester of alcohol 50: ^1H(220 MHz, solvent TFA, standard dioxan) δ= 5.05-5.3(2 H, m), 6.4-6.48(1 H, m), 7.28(2 H, m), 7.50(3 H, m), 8.10(2 H, t), 8.63(3 H, m).

TFA ester of alcohol 58: ^1H(220 MHz, solvent TFA, standard dioxan)

δ_H = 5.43(2 H, m), 5.6(1 H, m), 7.45(2 H, m), 7.58(3 H, m), 8.65, 8.66, 9.13, 9.24(4 x 2 H, 4 d, J= 6 Hz, bipy-H).

Hydrogen 1-[(E)-2'-(4''-methoxyphenyl)-ethenyl] pyridinium oxalate 51an:

Alcohol 50an was dehydrated by heating with oxalic acid as described above. The product was recrystallized from ethanol, to give a 75% yield of olefin 51an. m.p. 138-40°.

Calculated for $[C_{14}H_{17}NO]^+.[C_2O_4H]^-.C_2H_2O_4.H_2O$: C,52.7%; H,5.4%; N,3.4%. Found: C,50.6%; H,4.3%; N,3.1%.

^1H(220 MHz, solvent TFA, standard dioxan) δ = 4.12(3 H, s, MeO), 7.13(2 H, d, J= 7.5 Hz, Ar-H), 7.50(1 H, d, J= 14 Hz, =CH-Ar), 7.61(2 H, d, J= 7.5 Hz, Ar-H), 7.87(1 H, d, J= 14 Hz, =CH-pyr), 8.22(2 H, t), 8.67(1 H, t), 9.02(2 H, d).

UV λ_{max} (EtOH) 368(6.15), 245(6.11) nm.

IR ν_{max} (HCB) 3460(O-H), 3120,3100, 1720(br., C=O), 1635,1615 cm^{-1}.

1,4-Bis-1'-(1'-hydroxy-2'-(1''-pyridinium)-3'-butenyl)-benzene dibromide (53)

1-Allylpyridinium bromide 52 (6.2 g, 31 mmol) and terephthaldehyde (2.08 g, 15.5 mmol) were dissolved in EtOH (50 ml). 10M NaOH solution (0.5 ml) was added and the mixture was left at r.t. overnight. The off-white precipitate of 53 was filtered off and washed with EtOH and water (20 ml each), then recrystallised from water. Yield: 4.1 g (7.7 mmol, 50%) m.p. 320°+. Calculated for $C_{24}H_{26}N_2O_2.Br_2$: C,54.0%; H,4.9%; N,5.2%; Br,30.0%: Found: C,53.8%; H,4.9%; N,5.2%; Br,28.3%.

^{13}C(100.62 MHz, solvent TFA, standard dioxan) δ = 75.0(q), 79.5(q), 125.7, 127.4,127.5(q,?), 127.7, 128.3, 129.2, 144.2, 146.6.

^1H(220 MHz, solvent TFA, standard dioxan) δ = 5.5-5.7(8 H, m),

6.2-6.45(2 H, m), 7.50(4 H, s, Ar-H), 8.11(4 H, t), 8.60(2 H, t), 8.93(4 H, d).

FAB (+) m/z = 459,457(9%,M+Br), 375,374(4,M), 328(7), 296,295(10,M-pyr), 278(7,M-pyr-H_2O), 254(38,M-120), 120(80,pyrC_3H_5), 80(100,pyrH).

IR ν_{max} (HCB) 3260(O-H), 3020,2960(C-H), 1630,1610(Ar) cm^{-1}

UV No suitable solvent found.

Pyrolysis of styrylpyridinium oxalate (51)

Styrylpyridinium oxalate 51 (2.1 g,5.8 mmol) was heated at 200° in an evacuated vessel fitted with a trap at liquid nitrogen temperatures, until decomposition had finished. The contents of the trap were washed out with diethyl ether, which was then dried, filtered and evaporated. The liquid residue (402 mg) gave an ^1H NMR spectrum showing a pyridine:phenylethyne ratio of 5:1, plus a trace of diethyl ether, and other compounds (toluene).

(^1H (solvent $CDCl_3$) Phenylethyne 3.90(1 H, s), 8.32(5 H, br.s); Pyridine 7.45(10 H, t), 7.86(5 H, t), 8.12(10 H, d)).

Reaction of pyridine with phenylethyne

Pyridine (5 ml) and phenylethyne (1 ml) were heated together at 100° in the presence of copper (I) chloride (109 mg) for 3 hr. Diethyl ether (50 ml) was added to the cooled mixture, which was then filtered. The solid residue was dried in vacuo for 2 hr. The ^1H NMR spectrum of this residue showed no pyridine compounds. The ethereal filtrate, on evaporation, however, gave about a 90% recovery of pyridine and phenylethyne.

1-Methyl-4,4'-bipyridinium iodide (21)

4,4'-Bipyridyl 25 (10.06 g, 64 mmol) was dissolved in THF (100 ml) with iodomethane (4.5 ml, 64 mmol) and left overnight. The solid was filtered off and recrystallised from MeOH (40 ml). Yield 15.1 g (49 mmol, 79%).

21: $C_{11}H_{11}N_2.I$ = 298 g mol^{-1} m.p. 240-1°

^1H (220 MHz, solvent D_2O, standard dioxan) δ = 4.31(3 H, s, Me), 7.73, 8.23, 8.58, 8.80(8 H,4 d, J= 7 Hz, bipy-H).

FAB (+) m/z = 171(100%,M), 156(10,M-Me).

1-[2''-Hydroxy-2''-phenylethyl]-4,4'-bipyridinium iodide (58)

Methylbipyridinium iodide 21 (4.00 g, 13.7 mmol) was dissolved in EtOH (100 ml) and refluxed overnight with benzaldehyde (5 ml, 50 mmol) and calcium hydroxide (2 g). After cooling, the calcium salt was filtered off, and the filtrate was allowed to stand for several days. Dark orange crystals of 58 appeared, which were removed and washed with EtOH (30 ml). The filtrate was evaporated and the residue was washed with THF (2 x 30 ml) and EtOH (50 ml). Together, the solids weighed 3.1 g (57% yield) and were pure by NMR. An analytical sample was recrystallized from water. m.p. 227-8°.

Calculated for $C_{18}H_{17}N_2O.I$: C,53.5%; H,4.2%; N,6.9%; I,31.4%; Found: C,53.2%; H,4.2%; N,6.9%; I,30.5%.

^1H (220 MHz, solvent TFA, standard dioxan) δ = 5.0-5.3(2 H, m, CH_2), 5.6(1 H, m, CHOH), 7.4,7.5(5 H, m, Ph-H), 8.56, 8.65, 9.06, 9.22(8 H, 4 d, J= 7 Hz, bipy-H).

FAB (+) m/z = 277(100%,M), 157(51,bipy).

IR (HCB) ν_{max} 3230(O-H), 1645,1615,1605(Ar) cm^{-1}.

UV No suitable solvent found. (The propylene carbonate solution of 58 is green).

An identical (^{1}H NMR) orange solid was obtained in 45% yield by the reaction of methylbipyridinium iodide 21 (2.0 g, 6.8 mmol) with benzaldehyde (3 ml) in EtOH (50 ml) and sodium hydroxide solution (10 M, 5 ml) at room temperature overnight.

1-[2''-Hydroxy-2''-phenylethyl]-1'-methyl-bipyridinium diiodide (59)

Alcohol 58 (200 mg, 0.50 mmol) was dissolved in propylene carbonate (10 ml) and iodomethane (1 ml) was added. The red crystals that appeared on standing overnight were filtered off and washed with ethanol. Yield 280 mg (0.42 mmol, 84%). A suitable solvent for recrystallization was not found.

59: $C_{19}H_{20}N_2O.I_2$ = 546 g mol^{-1} No clear m.p.

^{1}H(220 MHz, solvent TFA, standard dioxan) δ = 4.66(3 H, s, Me), 5.05-5.3(2 H, m, CH_2?), 5.64(1 H, m), 7.50(5 H, m, Ph-H), 8.65, 9.13 (2 x 4 H, 2 apparent t, J= 7 Hz, bipy-H).

FAB (+) m/z = 419,420(2%,M+I), 293(100,M), 185,6(40,M-PhCHO), 171(50,M-PhCHO-CH_2).

Hydrogen 1-[(E)-2''-phenylethenyl)-4,4'-bipyridinium oxalate (60)

Alcohol 58 (1 g, 2.5 mmol) was heated with oxalic acid hydrate (10 g) at 150° under a stream of nitrogen for 3 hr. After cooling, the solid was extracted with cold water (20 ml), then the residue was filtered off, recrystallised from water and dried at 50° in vacuo. Yield 1.1 g (2.1 mmol, 80%).

The yellow solid titrated to 5 moles of acid per mole of bipyridyl.

60: $[C_{18}H_{15}N_2]^+.[C_2O_4H]^-.2(C_2O_4H_2)$ = 528 g mol^{-1} m.p. 191-3°(dec.)

^{1}H(220 MHz, solvent TFA, standard dioxan) δ = 7.55-7.86(6 H, m),

8.10(1 H, d, J= 14.0 Hz, CH-pyr), 8.70(4 H, d, J= 7 Hz, bipy-H),

9.26, 9.38(2 x 2 H, 2 d, J= 7 Hz, bipy-H).

^{13}C(100.62 MHz, solvent TFA, standard dioxan) δ = 125.4, 126.3,

127.3, 127.9, 128.5, 130.3, 132.7(q), 141.7, 142.0, 150.0(q),

150.9?(q), 159.8(oxalate).

FAB (+) m/z = 278(35%,M+H_2O?), 260(100,M+H), 259(55), 157(60,bipy).

UV λ_{max} (EtOH) 350(5.88), 260(5.66), 205(5.40) nm.

EXPERIMENTAL FOR

CHAPTER 2

1-(Iodomethyl)-pyridinium iodide (63)

Diiodomethane (DIM) (3 ml, 9.55 g, 36 mmol) was dissolved in toluene (10 ml) and pyridine (1 ml) was added. The mixture was refluxed overnight, then after cooling, the crystals were filtered off, washed with toluene (10 ml) and then pyridine (0.75 ml) was added to the filtrate and this mixture refluxed overnight. This process was iterated until a total of 4 ml of pyridine had been added. The last crop of crystals was less than half 63, being mostly dipyridylmethane diiodide 69i.

The combined crystals (9.1 g) were washed with cold water (20 ml) and THF (20 ml) to leave 63 (7.6 g, 62% (from DIM)) as pale yellow needles. (The washings could be evaporated to give dipyridylmethyl diiodide 69i). m.p. 218°(dec)

Calculated for $C_6H_7NI.I$: C,20.7%; H,2.0%; N,4.0%; I,73.2%. Found: C,21.0%; H,2.0%; N,4.6%; I,71.2%.

^{13}C (100.62 MHz, solvent TFA, standard dioxan) δ_c = 18.3(CH_2), 129.7, 144.7, 147.5.

^{1}H (220 MHz, solvent TFA, standard dioxan) δ_H = 6.56(2 H, s, CH_2), 8.16(2 H, t), 8.73(1 H, t), 9.19(2 H, d).

FAB (+) m/z = 219(100%,M-H). UV No suitable solvent found.

IR ν_{max} (Nujol) 1630, 1490, 1320, 1170, 685 cm^{-1}.

1-(Bromomethyl)-pyridinium bromide (64)

Bis-[1-pyridinium]-methane dibromide (69Br)

Dibromomethane (10 ml, 0.1 mol), toluene (10 ml) and pyridine (1 ml) were heated at reflux overnight. The crystalline precipitate was filtered off, washed with toluene (5 ml) and the combined filtrates with pyridine (1 ml) were refluxed overnight. This process was iterated until 5 ml (0.06 mol) total of pyridine had been added, and 8 g solid

collected. This solid was extracted with EtOH (200 ml) then this solvent was evaporated. The residue was dissolved in MeOH/$CHCl_3$ (1:3) (100 ml) and diethyl ether (200ml) was added to precipitate out pure 64, 2.9 g (8.3 mmol, 15%, based on pyridine). The EtOH-insoluble solid was 69Br, recrystallized from hot water (20 ml). Yield, 5 g (15 mmol, 50%). m.p. 212-4°.

Calculated for $C_6H_7NBr.Br$: C,28.5%; H,2.8%; N,5.5%; Br,63.2%; Found: C,29.0%; H,2.9%; N,5.4%; Br,60.0%.

^1H (220 MHz, solvent D_2O, standard dioxan) δ_H= 6.22(2 H, s, CH_2), 8.02(2 H, t), 8.56(1 H, t), 9.00(2 H, d).

^{13}C (100.62 MHz, solvent D_2O, standard dioxan) δ_C= 50.9(CH_2), 129.7, 145.7, 148.8.

FAB (+) m/z = 424,430(5%),426,428(10%)(2M+Br), 174,172(100,M), (M-Br at m/z = 93, 90% with glycerol).

IR ν_{max} (Nujol) 1630(Ar), 1490, 1280, 1185, 785, 685 cm^{-1}.

UV λ_{max} 264(5.68), 204(5.80) nm.

69Br: $C_{11}H_{12}N.Br_2$ = 332 g mol^{-1} m.p 220° (dec.)

^1H (220 MHz, solvent D_2O, standard dioxan) δ= 7.30(2 H, s, CH_2), 8.16(2 H, t), 8.69(1 H, t), 9.19(2 H, d).

FAB (+) m/z = 251,253(15%,M+Br), 171(60,M-H), 80(100,pyr+H).

Chloroiodomethane

Acetone (200 ml) and DCM (150 ml) were refluxed with sodium iodide (50 g) for 15 hr. in the dark; The mixture was cooled and filtered. The filtrate was evaporated down to c.40 ml and DCM (100 ml) was added. The precipitated sodium iodide was filtered off and added to the collected solvents for another run. The filtrates from 4 such runs gave product (41 g, pure by NMR) on distillation (b.p. 105-110°). (The residue gave

diiodomethane (11 g) on distillation at the water pump (b.p. 125°)).

CH_2ClI = 176.5 g mol^{-1} ^1H(solvent $CDCl_3$) δ = 4.99(s)

Chloromethylpyridinium salts

Pyridine (0.5 ml, 6 mmol) and chloroiodomethane (2 ml, 30 mmol) were heated together in toluene (10 ml) overnight. The yellow precipitate was removed and dried in vacuo. The NMR spectrum of this solid (TFA) showed three singlets, at δ 7.88, 6.53 and 6.36 ppm respectively, integrating in the ratio 1:1:2, as well as three sets of pyridinium signals. The water-soluble part of the mixture only contained the 7.88 ppm singlet, which was assigned to dipyridylmethane 69. The water-insoluble part was a mixture of iodomethylpyridinium 63 (6.56 ppm) and chloromethylpyridinium (6.36 ppm). The iodomethylpyridinium 63 presumably arose from Finkelstein-type substitution of iodide on chloromethylpyridinium; Performing the experiment with an excess of lead (II) acetate present gave a yellow precipitate of lead (II) iodide, from which was extracted with water a product which contained only the 6.36 ppm singlet. This product could not be crystallized. Pyridine reacted with a fifty-fold excess of neat chloroiodomethane to give only dipyridylmethane salts.

Chloromethyl methylsulphide

(After F.G.Bradwell, R.M.Pitt, J.Am.Chem.Soc. 1955, 77, 572.

Benzoyl chloride (50 ml, 0.5 mol) was dissolved in DCM (50 ml) and a solution of DMSO (20 ml, 0.25 mol) in DCM (30 ml) was added dropwise over 30 min. The mixture was refluxed for an hour then distilled. The fraction that boiled at 101-6° was collected (19 g), then redistilled to give GC-pure product (11 g, 45%).

^1H (solvent $CDCl_3$) δ= 2.31(3 H, s), 4.73(2 H, s).

1-[(Methylthio)methyl] pyridinium chloride (66)

Pyridine (2 ml, 25 mmol) and chloromethylmethylsulphide (1 ml, 16 mmol) were refluxed together in DCM (50 ml) for 4 hr. After cooling, the precipitate was filtered off and washed thoroughly with DCM (300 ml), then recrystallized from ethanol. Yield: 2.4 g (14 mmol, 85%).

66: $C_7H_{10}NS.Cl$ = 175.5 g mol^{-1} m.p. 147-9°.

^1H(220 MHz, solvent TFA, standard dioxan) δ = 2.23(3 H, s, Me), 5.73(2 H, s, CH_2), 8.21(2 H, t), 8.68(1 H, t), 9.09(2 H, d).

1-[(Ethylmethylsulphonio)methyl] pyridinium bis-(tetrafluoroborate) (67)

Thiomethylpyridinium chloride 66 (0.70 g, 4.0 mmol) was heated in DCM (50 ml) at reflux for 2 hr. with triethyl oxonium tetrafluoroborate (15 ml of 1M DCM solution, 15 mmol). After cooling, the precipitate was filtered off and recrystallized from acetonitrile/diethyl ether. Yield, 1.12 g (3.2 mmol, 80%).

67: $C_9H_{15}NS.B_2F_8$ = 342 g mol^{-1} m.p. 115-20° (lit.[42e] 128-9°).

^1H(220 MHz, solvent TFA, standard dioxan) δ = 1.70(3 H, t, MeC), 3.32(3 H, s, MeS), 3.85(2 H, m, CH_2C), 6.54(2 H, AB q, J= 18.2 Hz, CH_2N), 8.37(2 H, t, J= 7.0 Hz), 8.86(1 H, t, J= 7.0 Hz), 9.22(2 H, d, J= 7.0 Hz). FAB (+) m/z = 256(3%,M+BF_4), 193(10), 168(6,M-H), 154(4,M-Me), 140(2,M-Et), 75(31,$MeSCH_2CH_2$).

1-[(Triphenylphosphonio)methyl] pyridinium diiodide (65i)

Iodomethylpyridinium iodide 63 (1.48 g, 4.27 mmol) was heated in triphenylphosphine (4 g, 15 mmol) overnight at 130°. Toluene (20 ml) was added and the mixture was refluxed for 30 min. After cooling, the yellow solid was filtered off, washed with toluene and diethyl ether (20 ml each) and recrystallized from acetonitrile/ diethyl ether to give

65i (2.47 g, 95%) as a white hygroscopic powder.

m.p. 233° (dec) Calculated for $C_{24}H_{22}NP.I_2$: C,47.3%; H,3.6%; N,2.3%; Found: C,47.1%; H,3.7%; N,2.2%.

^{13}C (100.62 MHz, solvent TFA, standard $DCCl_3$ = 76.9 ppm.) δ_c= 54.8(d, ^1J= 52.6 Hz, CH_2), 112.3(d, ^1J= 87.2 Hz, C-P), 130.0, 131.9(d, J= 13.2 Hz), 134.7(d, J= 10.4 Hz), 137.9, 146.4, 149.0.

^1H (220 MHz, solvent TFA, standard dioxan) δ_H= 7.13(2 H, d, ^2J= 7.0 Hz, CH_2), 7.90(12 H, m), 8.08(3 H, m), 8.20(2 H, t, J= 7.0 Hz, pyr-H(3)), 8.77(1 H, t, J= 7.0 Hz, pyr-H(4)), 8.96(2 H, d, J= 7.0 Hz, pyr-H(2)).

FAB (+,thioglycerol) m/z = 354(14%,M-H), 279(9,M-Ph), 274(9,M-pyr+H), 216(11), 181(36), 131(30), 126(23), 119(24), 91(45), 69(100).

IR ν_{max} (Nujol) 1633, 1590, 1490, 1440, 1115, 685 cm^{-1}.

1-[(Triphenylphosphonio)methyl] pyridinium bis-(tetrafluoroborate) (65BF)

This salt was prepared according to the method of Sugimoto et al[42e]. Sulphoniomethylpyridinium tetrafluoroborate 67 (355 mg, 1.04 mmol) was dissolved in acetonitrile (10 ml) with triphenylphosphine (0.3 g, 1.1 mmol) and left overnight at r.t. The solvent was evaporated and the residue was redissolved in acetonitrile (3 ml), then diethyl ether (5 ml) was added. The white crystalline 65BF was filtered off. Yield: 480 mg (91%).

65BF: $C_{24}H_{22}NP.B_2F_8$ = 528 g mol^{-1} m.p.239-40° (lit.[42e] 214-5°).

^1H(220 MHz, solvent TFA, standard dioxan) δ= 6.65(2 H, d, J= 7.0 Hz, CH_2), 7.7-7.9(12 H, m), 8.0-8.2(5 H, m), 8.68(2 H, d, pyr-H(2)), 8.75(1 H, t, pyr-H(4)).

UV λ_{max} (acetonitrile) 262(6.03), 227(6.50) nm.

(Iodomethyl)triphenylphosphonium iodide

Triphenylphosphine (5.0 g, 19 mmol) and diiodomethane (4 ml, 13 g, 50 mmol) were dissolved in toluene (100 ml) and refluxed for 3 hr. After cooling, the precipitate was filtered off, washed with toluene (50 ml) and air-dried.

The product was recrystallized from DCM/ toluene to give a yield (pure by NMR) 7.2 g, 14 mmol, 73%.

26: $C_{16}H_{17}IP.I$ = 494 g mol^{-1} m.p. 235-7°.

^1H (220 MHz, solvent TFA, standard dioxan) δ = 4.46(2 H, d, J= 7.5 Hz, CH_2), 7.8(12 H, m), 7.9(3 H, m).

(Bromomethyl)triphenylphosphonium bromide

(After D.W.Grisley[43])

Triphenylphosphine (17.0 g, 65 mmol) was heated in dibromomethane (DBM) (61 g, 0.35 mol) at reflux for 5 hr. The cooled mixture was poured into diethyl ether (100 ml) and stirred until it solidified. The ether was decanted (and carefully evaporated to recover 31 g DBM) and the residue was dissolved in MeOH (40 ml). EA (100 ml) was added, and the white precipitate of bis-triphenylphosphonio-methane dibromide (6 g) was filtered off after an hour. The filtrate was evaporated to a ginger gum, which was triturated under EA (50 ml) until it crystallized. The solvent was decanted and the residue was redissolved in MeOH (15 ml), then treated with EA (60 ml) and allowed to stand overnight. The crystals (9.1 g) were filtered off, washed with EA and air-dried. The remaining filtrate, on partial evaporation gave an off-white solid (4 g), mostly methyltriphenylphosphonium bromide, but containing some product.

Yield: 9.1 g (29 mmol) (44% based on P)

$C_{19}H_{17}BrP.Br$ = 436 g mol^{-1} m.p. 200-6°(dec).

^1H (220 MHz, solvent TFA, standard dioxan) δ = 4.78(2 H, d, J= 6 Hz, CH_2), 7.55-8.00(15 H, m, Ph-H).

Triphenylphosphine (3.4 g, 13 mmol) and DBM (5 g, 20 mmol) were dissolved in toluene (50 ml) and heated at reflux overnight. The white precipitate was filtered off and recrystalized from MeOH/EA as above. Yield of bromomethyltriphenylphosphonium bromide: 4.1 g, 9.4 mmol, 72%, after recrystallization from DCM/ toluene.

1-[(Z)-2'-Phenylethenyl]-pyridinium iodide (70)

Phosphoniomethylpyridinium iodide 65 (1.14 g, 1.9 mmol) was heated in AcA (1 ml) to 90°, and benzaldehyde (0.5 ml, 5 mmol) was added. After 10 min. triethylamine (0.3 ml, 3 mmol) was added, and the mixture was heated at 100° for 3 hr. The mixture was cooled, and diethyl ether and water (20 ml each) were added. The aqueous layer was washed with chloroform (2 x 20 ml) and evaporated to a gum, from which product crystallized on treatment with chloroform and diethyl ether (2 ml of each). Yield of off-white crystals: 410 mg (1.3 mmol, 68%), recrystallized from EtOH. m.p. 161-3°.

Calculated for $C_{13}H_{12}N.I$: C,50.5%; H,3.9%; N,4.5%: Found: C,50.1%; H,3.8%; N,4.6%.

^{13}C (100.62 MHz, solvent TFA, standard dioxan) δ_c= 127.8(2 signals), 128.2(q), 128.7, 129.3, 131.5, 134.5, 141.6, 146.2.

^{1}H (220 MHz, solvent TFA, standard dioxan) δ_H= 6.98(1 H, d, J= 9.2 Hz, CH-Ar), 7.2-7.45(6 H, m), 8.13(2 H, t), 8.67(1 H, t), 8.87(2 H, d) (In D_2O, decomposition occurs within hours).

FAB (+) m/z = 182(100%,M).

UV (tetrafluoroborate salt) λ_{max} 300(sh)(5.43), 233(6.23), 206(6.35) nm.

IR (Nujol) ν_{max} 1635,1610(Ar), 1585 cm^{-1}.

1,4-Bis-[(Z,Z)-2'-(1''-pyridinium)-ethenyl]-benzene diiodide (72)

Phosphoniomethylpyridinium iodide 65 (808 mg, 1.3 mmol) was heated in acetic anhydride (2 ml) to 90° and terephthaldehyde (90 mg, 0.65 mmol) was added. After 10 min., triethylamine (0.2 ml, 2 mmol) was added, and the mixture was stirred at 100° for 3 hr. The mixture was cooled, and diethyl ether and water (50 ml each) were added. After an hour, the layers were separated. The aqueous layer was washed with chloroform (2

x 20 ml), evaporated, and the residue washed again with chloroform. The residue crystallized on standing. Yield: 235 mg, 0.44 mmol, 67%.

m.p. 221-3°.

Calculated for $C_{20}H_{18}N_2.2BF_4$: C,52.2%; H,3.9%; N,6.1%: Found: C,48.3%; H,3.9%; N,6.2%.

^1H (220 MHz, solvent TFA, standard dioxan) δ_H = 7.04(4 H, s, Ar-H), 7.17(2 H, d, J= 9.3 Hz, CH-Ar), 7.49(2 H, d, J= 9.3 Hz, CH-pyr), 8.22(4 H, t, J= 7.0 Hz, pyr-H(3)), 8.70(2 H, t, J= 7.0 Hz, pyr-H(4)). 8.85(d, J= 7.0 Hz, 4 H, pyr-H(2)).

^{13}C (100.62 MHz, solvent TFA, standard dioxan) δ_C = 129.5(3-pyr, and CH-C), 130.0(Ph-H), 132.4(Ph-C), 132.5(CH-N), 144.9(2-pyr), 148.1(4-pyr).

FAB (+) m/z = 413(50%,M+I), 287(100,M+H), 286(50,M), 208(60), 207(70,M-pyr), 206(65).

IR (Nujol) ν_{max} 1630, 1420, 685 cm^{-1}.

UV (EtOH) λ_{max} 325(5.73) 252(6.15) nm.

1-[(Z)-2'-(4''-Methoxyphenyl)-ethenyl]-pyridinium iodide (70a)

Phosphoniomethylpyridinium iodide 65 (1.0 g, 1.64 mmol), 4-methoxybenzaldehyde (1 ml) and 1,4-diaza-bicyclooctane (DABCO) (185 mg, 1.6 mmol) were reacted as before in acetic anhydride (3 ml) at 120°. The reaction mixture was cooled, and the precipitate that formed on standing was filtered off. The filtrate was evaporated and taken up in a few drops of DCM, and the product crystallized out from this was recrystallized from DCM/diethyl ether. Yield 22 mg (0.07 mmol, 4%). The residue was dissolved in DCM and extracted by counter-current technique (in test-tubes) with water. The aqueous end accumulated DABCO salts. The organic end was evaporated and the residue was recrystalized from DCM/diethyl ether. Yield 104 mg, 0.3 mmol, 19%.

$C_{14}H_{14}NO.I$ = 337 g mol^{-1}. m.p. 165-7°

^1H (220 MHz, solvent D_2O, standard dioxan) δ = 3.62(3 H, s, MeO), 6.78(4 H, AB q, Ar-H), 6.96(1 H, d, J= 9.3 Hz, =CH-C), 7.20(1 H, d, J= 9.3 Hz, 1 H, =CH-N), 7.95(2 H, t), 8.50(1 H, t), 8.72(2 H, d). FAB (+) m/z = 210(100%,M). IR(Nujol) ν_{max} 1630,1610(Ar) cm^{-1}. UV (tetrafluoroborate salt) λ_{max} 355(6.82), 245(6.80), 205(6.94) nm.

1-[(Z)-2'-(4''-formylphenyl)-ethenyl]-pyridinium iodide (70b)

With a 5-fold excess of 1,4-diformylbenzene, no crystalline product could be obtained:

70b: ^1H(220 MHz, solvent D_2O, standard dioxan) δ = 7.13(2 H, d, J= 8.0 Hz, Ar-H), 7.16(1 H, d, J= 9.3Hz), 7.47(1 H, d, J= 9.3 Hz), 7.70(2 H, d, 8.0 Hz, Ar-H), 7.96(2 H, t), 8.53(1 H, t), 8.74(2 H, d), 9.75(1 H, s, CHO).

1-[(Z)-2'-(2''-Pyridyl)-ethenyl]-pyridinium hydrogen bis-(tetrafluoroborate) (71)

Phosphoniomethylpyridinium tetrafluoroborate 65BF (342 mg, 0.648 mmol) was heated with 2-formylpyridine (0.1 ml, 1 mmol) in acetic anhydride at 120° overnight. The mixture was cooled, diluted to 50 ml with diethyl ether, then extracted with water (2 x 15 ml). The aqueous solution was freeze-dried to give a black powder (250 mg). This was recrystallised from 0.1M HBF_4 solution to give yellowish non-crystalline 71 (200 mg, 80%).

71 $C_{12}H_{12}N_2.B_2F_8$ = 358 g mol^{-1} m.p. Indeterminate.

^1H (220 MHz, solvent D_2O, standard dioxan) δ = 7.07(1 H, d, J= 9.8 Hz, 7.25(2 H, d, 6.7 Hz), 7.43(1 H, d, J= 9.8 Hz), 7.73(1 H, t, J= 6.7 Hz), 7.92(2 H, t, J= 7.3 Hz), 8.15(1 H, d, J= 6.7 Hz), 8.49(1 H, t, J= 7.3 Hz), 8.69(2 H, d, J= 7.3 Hz).

(220 MHz, solvent TFA, standard dioxan) δ = 7.61(2 H, d), 7.86(1 H, m), 8.13(1 H, d), 8.20(1 H, t), 8.33(2 H, t), 8.61(1 H, t), 8.86(1 H, t), 9.03(2 H, d).

FAB (+) m/z = 279(40%,?), 184(20,M), 183(100,M-H), 104(15,M-pyrH).

1-[3'-Methyl-(Z)-1'-butenyl] pyridinium iodide (70c)

With 2-methylpropanal, after 3 hr. at 70° about 20% of the original phosphonium salt 65 was still left unreacted (by NMR). No crystalline product was produced because the aqueous work-up caused considerable decomposition of the product.

The ^{1}H NMR spectrum of the crude reaction mixture, in TFA, contained, besides 65, (doublet (7 Hz) at 7.15 ppm.) and methylpyridinium: δ = 1.27(6 H, d, J= 6.5 Hz, Me), 6.17(1 H, m, CHMe$_2$), 6.62(1 H, d, J= 8.5 Hz, CH-N), 8.11(2 H, t), 8.97(2 H, d) (These signals are related by their integrals).

1,1'-Bis-[(methylthio)methyl]-4,4'-bipyridinium dichloride (74)

Anhydrous bipyridyl 25 (1.56 g, 10 mmol) was heated with chloromethylmethylsulphide (CMMS) (4 ml) at 110° overnight (at reflux). The residue was washed with DCM (3 x 50 ml) leaving an almost odourless yellow solid, which was recrystallised from EtOH. Yield 3.4 g (9.6 mmol, 95%). m.p. 206-7°(dec) .

Calculated for $C_{14}H_{18}N_2S_2.Cl_2$: C,48.1%; H,5.2%; N,8.0%; Found: C,47.9%; H,5.2%; N,8.0%;

^{13}C(100.62 MHz, solvent D_2O, standard dioxan) δ = 14.8(Me), 66.2(CH_2), 128.0, 145.8, 151.6.

^{1}H(220 MHz, solvent TFA, standard dioxan) δ = 2.32(s, 6 H, Me),

5.88(ABq, ^{2}J= 18.3 Hz, 4 H, CH_2), 8.74(d, 4 H), 9.42(d, 4 H).

FAB (+) m/z = 278(5%,M), 217(10), 61(100,CH_2SMe).

UV (EtOH) λ_{max} = 245(6.18) nm. IR (Nujol) ν_{max} = 1630 cm^{-1}.

1-[(Methylthio)methyl]-4,4'-bipyridinium chloride (75)

Anhydrous bipyridyl(1.56 g, 10 mmol) was heated with CMMS (5 ml) at reflux in acetonitrile overnight. The off-white precipitate was filtered off and found to be entirely 75 (2.4 g, 14 mmol, 95%).

75: $C_{12}H_{13}N_2S.Cl$ = 252.5 g mol^{-1} m.p. 190°.

^{1}H(220 MHz, solvent TFA, standard dioxan) δ = 2.32(s, 3 H, Me), 5.88(s, 2 H, CH_2), 8.68(br.s., 4 H), 9.25, 9.39(2 br.s., 4 H).

1,1'-Bis-[(ethylmethylsulphonio)methyl]-bipyridinium tetrakis-(tetrafluoroborate) (23)

Thiomethyl viologen tetrafluoroborate 74 (198 mg, 0.567 mmol) was heated in dioxan (10 ml) with triethyloxonium tetrafluoroborate (5 mmol) overnight at reflux. The reaction was cooled and the white solid was filtered off, washed with dioxan (10 ml) and DCM (2 x 10 ml) and air-dried. Yield 385 mg (0.564 mmol, 99%). m.p. 200° (dec).

Calculated for $C_{18}H_{28}N_2S_2.B_4F_{16}$: C,31.7%; H,4.1%; N,4.1%; S,9.4%:

Found: C,32.2%; H,4.1%; N,5.1%; S,9.1%.

^{13}C(100.62 MHz, solvent TFA, standard dioxan) δ_c = 7.4($\underline{C}H_3C$), 21.1(MeS), 38.1($\underline{C}H_2Me$) 66.0(CH_2N), 129.4, 147.6, 153.9.

^{1}H (220 MHz, solvent TFA, standard dioxan) δ_H = 1.73(t, 6 H, MeC), 3.34(s, 6 H, MeS), 3.85(AB q, 4 H, $C\underline{H}_2Me$), 6.62(s, 4 H, CH_2N), 8.82(s, 4 H), 9.43(s, 4 H) All signals are broadened and poorly resolved.

FAB (+) m/z = 336(5%,M), 231(4), 207(4), 193(33), 157(13), 115(10).

IR (HCB) ν_{max} = 3150,3090,3050,2990,2960, 1640, 1615 cm^{-1}.

UV (acetonitrile) λ_{max} = 262(6.64), 210(6.45) nm.

1,1'-Bis-[(triphenylphosphonio)methyl]-4,4'-bipyridinium tetrakis -(tetrafluoroborate) (73)

Sulphoniomethyl viologen tetrafluoroborate 23 (430 mg, 0.65 mmol) and triphenylphosphine (0.8 g, 3 mmol) were dissolved in acetonitrile (10 ml) and stirred overnight. The blue solution was poured into diethyl ether (100 ml) and the precipitate was filtered off. This was recrystallised from DCM/toluene to give 73 as a pale brown powder (0.40 g, 50%). m.p. 175° (dec)

Calculated for $C_{48}H_{42}N_2P_2.B_4F_{16}$: C,54.6%; H,4.0%; N,2.7%: Found: C,53.7%; H,4.3%; N,2.6%.

^{13}C (100.62 MHz, solvent d-TFA, standard dioxan) δ_c = 56.05(d, ^1J= 52 Hz, CH_2), 112.1(d, ^1J = 87 Hz), 129.2, 132.0(d, J= 7 Hz), 134.65(d, J= 5 Hz), 138.1, 147.5.

^1H (220 MHz, solvent TFA, standard dioxan) δ_H = 6.72(d, J= 7.1 Hz, 4 H, CH_2), 7.7-7.95(m, 12H), 8.1(m, 3 H), 8.63, 8.90(2 d, J= 5.8 Hz, 8 H, bipy-H).

FAB (+) m/z = 587(3%), 557(1), 464(1), 445(2), 369(2), 325(3), 277(12).

IR (HCB) ν_{max} 3140, 3080, 3010, 2960(C-H), 1630,1610(Ar) cm^{-1}.

UV(acetonitrile) λ_{max} 272(6.66), 230(sh,6.90), 210(7.04) nm.

EXPERIMENTAL FOR

CHAPTER 3

1-(2',4'-Dinitrophenyl)-pyridinium chloride (76)

Pyridine (8 ml, 100 mmol) was heated at reflux in EtOH (100 ml) with 2,4-dinitrochlorobenzene (18 g, 90 mmol) for 3 hr. The mixture was cooled and partially evaporated. The precipitate was filtered off and recrystallised from EtOH to give white needle-like crystals of 76 (16 g, 70%). 76: $C_{11}H_8N_3O_4.Cl$ = 282.5 g mol^{-1} m.p. 199-200°

^1H(220 MHz, solvent TFA, standard dioxan) δ = 8.30(1 H, d), 8.43(2 H, t, J= 7.0 Hz, pyr-H), 8.95(2 H, m), 9.11(2 H, d, J= 7.0 Hz, pyr-H), 9.37(s, 1 H, N=C-H).

UV λ_{max} (EtOH) 235(7.17) nm.

1-(4'-Aminophenyl)-pyridinium chloride (79)

Dinitrophenylpyridinium chloride 76 (4.0 g, 14 mmol) and 1,4-diaminobenzene (8.0 g, 74 mmol) were heated in water (20 ml) for 3 hr. The mixture was diluted to 100 ml and washed with DCM (2 x 50 ml). The aqueous solution was treated with charcoal, filtered and evaporated. The residue was recrystallized thrice from EtOH/ diethyl ether to give bright yellow 79 (2.8 g, 95%). m.p. 197-9° Calculated for $C_{11}H_{11}N_2.Cl$: C,63.9%; H,5.3%; N,13.6%: Found: C,63.1%; H,5.4%; N,13.3%.

→ (In ref. 20, a product containing EtOH was obtained, m.p. 252°

^{13}C (100.62 MHz, solvent D_2O, standard dioxan) δ = 117.1, 118.7(q), 125.7, 128.8, 144.6, 146.2.

^1H (220 MHz, solvent D_2O, standard dioxan) δ= 6.87(2 H, d, J= 7.5 Hz, Ph-H), 7.33(2 H, d, J= 7.5 Hz, Ph-H), 7.99(2 H, t), 8.46(1 H, t), 8.77(2 H,d).

FAB (+) m/z = 171(100%,M). UV λ_{max} (EtOH) 395(5.90), 248(6.40), 206(6.51) nm.

IR (HCB) ν_{max} 3470,3300(N-H), 3160,3060,3030(C-H), 1630,1600(Ar) cm^{-1}.

1,4-Bis-(1'-pyridinium)-benzene dichloride (80)

Aminophenylpyridinium chloride 79 (1.6 g, 7.8 mmol) and dinitrophenylpyridinium chloride 76 (1.0 g, 35 mmol) were heated in EtOH (5 ml) and pyridine (1 ml) for 2 hr. Then the mixture was cooled and filtered. The filtrate was evaporated, then the residue was dissolved in EtOH (20 ml) and poured into acetone (100 ml). The precipitate was filtered off and redissolved in EtOH (20 ml). Precipitation as before from EtOH (20ml) in acetone (100 ml) gave 250 mg of pale pink solid, which was recrystallized from EtOH to yield 80 (210 mg, 0.7 mmol,20%). m.p. 320+

Calculated for $C_{16}H_{14}N_2.Cl_2$: C,63.0%; H,4.6%; N,9.2%: Found: C,62.6%; H,4.7%; N,9.4%.

^1H(220 MHz, solvent TFA, standard dioxan) δ_H = 8.28(4 H, s, Ph-H), 8.44(4 H, t), 8.93(2 H, t), 9.23(4 H, d).

^{13}C (100.62 MHz, solvent D_2O, standard dioxan) δ_c = 126.1(q), 127.6, 129.4, 145.4, 148.5.

FAB (+) m/z = 271,269(9%,M+Cl), 235(35,M+H), 234(30,M), 155(100,M-pyr).

UV λ_{max} (EtOH) 370(5.92), 260(6.93), 205(7.43) nm.

IR (Nujol) ν_{max} 1635,1625(Ar) cm^{-1}.

1-[4'-(4''-Amino-3''-methoxyphenyl)-2'-methoxyphenyl]-pyridinium chloride (83)

Dinitrophenyl pyridinium chloride 76 (1.0 g, 3.5 mmol) and 3,3'-dimethoxybenzidine (2.0 g, 9.0 mmol) were heated together in EtOH (10 ml) at reflux for 3 hr. The residue after solvent evaporation was washed with EA (2 x 50 ml) then recrystallised from EtOH. Yield 1.15 g, (3.3 mmol, 90%). m.p. 219-22° Calculated for $C_{19}H_{19}N_2O_2.Cl$: C,66.4%; H,5.5%; N,8.1%; Found: C,59.3%; H,5.9%; N,7.1%.

^{1}H(220 MHz, solvent TFA, standard dioxan) δ = 4.06, 4.14(2 x 3 H, 2 s, MeO), 7.44, 7.51(2 x 2 H, 2 s, each with peaks of quarter height at 0.04 ppm upfield which merge with them when heated), 7.69(2 H, m), 8.29(2 H, t), 8.8(3 H, m, in d-TFA 1 H, t), 8.91(2 H, d).
(See spectrum, appendix A).
FAB (+) m/z = 307(100%,M), 292(26), 276(16), 75(27).
IR (HCB) υ_{max} 3440,3350(N-H), 1635, 1610 cm^{-1}.
UV λ_{max} (EtOH) 310(6.20), 220(6.72) nm.

Attempted reaction of compound (83) with (76)

Biphenylpyridinium salt 83 (260 mg, 0.756 mmol) and dinitrophenylpyridinium chloride 76 (200 mg, 0.71 mmol) were dissolved in water (5 ml) and pyridine (1 ml) and heated at reflux for 3 hr. The hot reaction mixture was poured into acetone (100 ml). The precipitate was filtered off and air-dried. (The ^{1}H NMR spectrum of this solid was very complex). This solid was recrystallized from EtOH but the product was found to be 83 (80 mg).

1,1'-Bis-(2'',4''-dinitrophenyl)-4,4'-bipyridinium chloride (77)

(Dinitrophenyl viologen)

Bipyridyl hydrate (6.2 g, 36 mmol) and 2,4-dinitrochlorobenzene (17 g, 84 mmol) were refluxed in ethanol (300 ml) for 4 hr. After cooling, the precipitate was filtered off and recrystallized from ethanol. Yield of colourless 77 (17 g, 95%). Stored under nitrogen in the dark.
77: $C_{22}H_{14}N_6O_4.Cl_2$ = 497 g mol^{-1} m.p. 320°+
^{1}H(220 MHz, solvent D_2O, standard dioxan) δ = 8.22(2 H, d, J= 9 Hz,), 8.85(6 H, m), 9.33(2 H, s), 9.39(4 H, d, bipy-H).

1,1'-Bis-(4''-aminophenyl)-4,4'-bipyridinium dichloride (5, 84)

(Aminophenyl viologen)

Dinitrophenyl viologen 77 (5.9 g, 10.5 mmol) was dissolved in water (100 ml) and EtOH (5 ml) with 1,4-diaminobenzene (7.0 g, 65 mmol) and heated at reflux overnight. The mixture was cooled, diluted to 300 ml with water, treated with charcoal (5 g) and filtered through Kieselguhr. Evaporation of solvent left a black solid (7.7 g) which was washed with THF (2 x 50 ml) then recrystallised from water to give 5 as a blue-black solid (3.3 g, 76%). m.p. 320+

Calculated for $C_{22}H_{20}N_4.Cl_2$: C,64.2%; H,4.9%; N,13.6%. Found: C,64.0%; H,5.0%; N,13.5%.

^{13}C (100.62 MHz, solvent D_2O, standard dioxan) δ_c= 108.8(q), 117.3, 125.9, 127.5, 145.4, 134.2(?), 150.0(?).

^1H (220 MHz, solvent TFA, standard dioxan) δ_H= 8.12(8 H, s, Ph-H), 8.92(4 H, br.s), 9.49(4 H, br.s).

FAB (+) m/z = 340(100%,M), 248(40,M-$PhNH_2$).

UV λ_{max} (EtOH) 505(6.26), 265(6.65), 215(6.81) nm.

IR (Nujol) ν_{max} 3300(N-H), 1635,1600(Ar) cm^{-1}.

1,1'-Bis-[4''-(4'''-amino-3'''-methoxyphenyl)-2''-methoxyphenyl]-4,4'-bipyridinium dichloride (85)

Dinitrophenyl viologen 77 (2.0 g, 4.0 mmol) and 3,3'-dimethoxybenzidine (3.0 g, 12.3 mmol) were heated together in water (10 ml) and pyridine (2 ml) at reflux for 13 hr. The mixture was cooled and poured into acetone (100 ml). The precipitate was filtered off, washed with acetone, then reprecipitated from hot EtOH/ acetone. The red residue (2.9 g) gave an NMR spectrum corresponding to a mixture of the expected product 85 and dimethoxybenzidine, in a molar ratio of 2:3.

85: $C_{38}H_{36}N_4O_4.Cl_2$ = 683 g mol^{-1} m.p. 226-8°

^1H(220 MHz, solvent TFA, standard dioxan) δ = 4.1-4.2(36 H, several singlets), 7.32(4 H, d, J= 9.3 Hz), 7.4-7.5(20 H, m), 7.59(4 H, d, J= 8.0 Hz), 7.68(4 H, d, 8.0 Hz), 8.36(4 H, dd, J= 9.3, 2.4 Hz, bipy-H), 8.9(10 H, br.s, NH_2), 9.34(4 H, d, J= 2.4 Hz, bipy-H).

FAB (+) m/z = 613(2%,M+H), 412(6,?), 307(27,M/2), 289(10), 171(16).

1-(2',5'-Dioxolanato)-4-nitrobenzene

4-Aminobenzaldehyde (5.9 g, 39 mmol) was heated with 1,2-dihydroxyethane (8 ml, 130 mmol) and TFA (0.5 ml) in toluene (100 ml) at reflux under a Dean-Stark trap, until the condensate was clear (6 hr.). The residue was cooled and sodium carbonate (2 g) was added and stirred for 5 min. Then saturated sodium carbonate solution (20 ml) was added and stirring was continued for 20 min. The layers were separated, and the toluene part was dried and evaporated to a yellowish solid containing less than 1% aldehyde by NMR. Yield: 7.2 g (95%). m.p. 87-8°.

$C_9H_9NO_4$ = 195 g mol^{-1}

^1H(220 MHz, solvent $CDCl_3$, standard TMS) δ = 4.13(4 H, d, CH_2), 5.95(1 H, s, CHO_2), 7.72(2 H, d, Ph-H), 8.30(2 H, d, Ph-H).

4-(1'-(2',5'-Dioxolanato))-aniline

(After H.K.Porter, Chemical Reactions, 1973, 20, 455.

Sodium hydroxide (5 g, 120 mmol) was dissolved in boiling water (50 ml), then sulphur (3 g, 90mmol) was added and stirred to dissolution. 4-(1-(2,5-dioxolanato))-nitrobenzene (7.0 g, 36 mmol) was dissolved in refluxing ethanol (50 ml) then the solution of sodium polysulphide was added dropwise to this over 3 hr. The solution was cooled and poured into diethyl ether (100 ml) and brine (100 ml). Then the layers were

separated, and the aqueous layer was washed with diethyl ether (50 ml). The organic solutions were combined, dried and evaporated to leave an oily residue. This was dissolved in diethyl ether (10 ml) and petrol was added dropwise to precipitate the product. Yield 3.7 g (65%).

$C_9H_{11}NO_2$ = 165 g mol^{-1} m.p. 76-7°

$^1H(CDCl_3)$ δ = 3.75(2 H, br.s., NH_2), 4.0, 4.1(4 H, 2 m, CH_2) 5.72(1 H, s, CHO_2), 6.69(2 H, d, Ph-H), 7.29(2 H, d, Ph-H).

1,1'-Bis-(4''-formylphenyl)-4,4'-bipyridinium chloride (90)

4-(1-(2,5-Dioxolanato))-aniline (1.8 g, 11 mmol) was reacted with dinitrophenyl viologen 77 (2.0 g, 4.0 mmol) in water (10 ml) and pyridine (1 ml) for 3 hr. at reflux. The reaction mixture was poured into acetone (100 ml), then the precipitate was taken up into water (10 ml), treated with charcoal, filtered and evaporated. The residue contained no aldehyde nor ketal protons by NMR, but the EtOH insoluble part of it was identified as poly-formyl-aniline (NMR given). m.p. 320+

^1H(220 MHz, solvent TFA, standard dioxan) δ = 7.12(d, 2 H, Ph-H), 8.33(d, 2 H, Ph-H), 9.28(s, 1 H, CH=N).

Repetition of this procedure in pyridine (10 ml) only as reaction solvent, gave a residue with no poly-formylaniline present, but from which no product 90 could be recovered. On exposure to light, a blue insoluble substance formed.

NMR analysis of the residue revealed it to consist of about 90% of 90.

^1H(220 MHz, solvent TFA, standard dioxan) δ = 8.05(2 H, d, Ph-H), 8.46(4 H, apparent t), 9.15(2 H, d, bipy-H), 10.26(1 H, s, CHO) as well as small signals at 8.2, 8.9 and 9.5 ppm, perhaps due to a Schiff-base.

1-[4'-(1''-Aza-2''-(4'''-methoxyphenyl)-ethenyl)-phenyl]-pyridinium chloride (87)

Aminophenylpyridinium chloride 79 (1.0 g, 4.8 mmol) was dissolved in ethanol (50 ml) with 4-methoxybenzaldehyde (5 ml). This mixture was refluxed overnight, through 3A molecular sieves in a Soxhlet extractor, then cooled and evaporated down to 10 ml. Diethyl ether (50 ml) was added, and the reddish precipitate was filtered off, then recrystallized from ethanol. The yield was 1.2 g (3.7 mmol, 77%).

87: $C_{19}H_{17}N_2O.Cl$ = 325 g mol^{-1} m.p. 194-5°.

^1H(220 MHz, solvent D_2O, standard dioxan) δ = 3.74(3 H, s, MeO), 6.82(2 H, d, J= 8 Hz), 7.44(2 H, d, J= 8 Hz), 7.60(4 H, d, J= 8 Hz), 7.96(2 H, t), 8.47(1 H, t), 8.84(2 H, d), 9.45(1 H, s, CH=N).

FAB (+) m/z = 289(30%,M), 211(50), 209(20), 171(100,M-(4-MeO-PhCHO)), 169(60), 137(55), 121(45).

UV λ_{max} (EtOH) 380(5.97), 290(5.70), 245(6.24), 205(6.32) nm.

This reaction was repeated with benzaldehyde in place of 4-methoxybenzaldehyde, and the product was obtained in 66% yield from EtOH/ diethyl ether. m.p. 206°.

^1H (220 MHz, solvent D_2O, standard dioxan) δ = 6.85(2 H, d, J= 8 Hz, 7.33(2 H, d, J= 8 Hz), 7.45(2 H, t), 7.60(1 H, t), 7.68(2 H, d), 7.99(2 H, t), 8.46(1 H, t), 8.79(2 H, d), 9.75(1 H, s, CH=N).

1-[4'-(4'')-(1''-[1'''-Aza-2'''-(4''''-methoxyphenyl)-ethenyl]-2''-methoxyphenyl)-2'-methoxyphenyl]-pyridinium chloride (88)

Biphenylpyridinium salt 83 (1 g, 2.9 mmol) and 4-methoxybenzaldehyde (3 ml) were reacted in the same way to give 88, (1.2 g, 2.7 mmol), when recrystallized from EtOH/ diethyl ether. The product loses 9% of its weight on heating to 80° in vacuo (corresponding to one mole of EtOH).

88: $C_{26}H_{25}N_2O_3.Cl$ = 449 g mol^{-1} m.p. 102-3°

^1H(220 MHz, solvent TFA, standard dioxan) δ = 4.05, 4.07, 4.18(3 x 3 H, 3 s, OMe), 7.19(1 H, d), 7.32(2 H, d, J= 8 Hz), 7.5-7.6(6 H, m), 7.68(1 H, d), 7.86(1 H, d), 8.05(1 H, d), 8.28(4 H, apparent t), 8.78(1 H, t, pyr-H(4)), 8.91(2 H, d, pyr-H(2)), 9.76(1 H, s, CH=N).

UV λ_{max} (EtOH) 280(6.25), 210(6.61) nm.

IR (HCB) ν_{max} 3420(O-H), 1640,1615(br) cm^{-1}.

1,1'-Bis-[4''-(1'''-aza-2'''-[4''''-methoxyphenyl]-ethenyl)-phenyl] bipyridinium dichloride (89)

Aminophenyl viologen 5 (0.8 g, 1.9 mmol) was placed in a Soxhlet thimble with 3A molecular sieves and extracted with ethanol (100 ml) and methanol (10 ml) into 4-methoxybenzaldehyde (5 ml). When the extract was no longer coloured (c. 48 hr.) the solution was evaporated down to 10 ml, diluted with diethyl ether (50 ml) and the precipitate was filtered off. The yield of brown solid weighed 1.06 g (1.6 mmol, 87%), for which a suitable recrystallization solvent could not be found.

89: $C_{38}H_{28}N_4O_2.Cl_2$ = 643 g mol^{-1} m.p. 320+

Calculated: C,70.9%; H,4.3%; N,8.7%. Found: C,70.1%; H,4.4%; N,8.5%.

^1H(220 MHz, solvent D_2O, standard dioxan) δ = 3.77(6 H, s, OMe), 6.96(8 H, d, J= 8 Hz), 7.48(4 H, d, J= 8 Hz), 7.74(4 H, d, J= 8 Hz), 8.57(4 H, d, J= 6 Hz, bipy-H), 9.14(4 H, d, J= 6 Hz, bipy-H), 9.58(2 H, s, CH=N).

FAB (+) m/z = 270(25%), 242(100), 150(60), 115(20).

IR (Nujol) ν_{max} 1630,1605(Ar) 1580,1575(both broad) cm^{-1}.

UV No suitable solvent found.

Attempted Schiff-base formation with hexacyclic diamine (85)

The diamine 85 (1.6 g, c. 1.5 mmol viologen) was heated in EtOH (40 ml) with 4-methoxybenzaldehyde (2 ml) at reflux overnight. Upon cooling, the reaction mixture formed a gel. On re-heating and pouring into acetone (150 ml) a thick flocculent precipitate formed that was filtered off with difficulty, dried in vacuo, but it gave a puzzling NMR spectrum that appeared to contain no viologen. This product was assumed, therefore, to be just the Schiff-base of the free dimethoxybenzidine.

Attempted Schiff-base formation with 1,4-diformylbenzene

Aminophenylpyridinium chloride 79 (0.50 g, 2.4 mmol) was dissolved in EtOH (100 ml) with 1,4-diformylbenzene (0.160 g, 1.2 mmol). The mixture was heated at reflux overnight, through a soxhlet thimble containing (a) 3A molecular sieves, or (b) phosphorus pentoxide. The solvent was evaporated, and the residue was found to contain only starting materials by NMR analysis (complete absence of CH=N protons). The residue was recrystallized from EtOH to give a 90% recovery of amine 79.

Repetition of this reaction in propylene carbonate or dimethylformamide as solvent, likewise gave residues containing no Schiff-base (in these cases a little toluene was added to azeotrope off any water that might be formed, with phosphorus pentoxide in the thimble).

Repetition with five times the amount of dialdehyde also gave no Schiff-base in the reaction residue.

EXPERIMENTAL FOR

CHAPTER 4

2,2'-Dimethyl-4,4'-bipyridyl (41)

(After H.P.Becker and W.P.Neumann[26])

2-Methylpyridine (26 ml, 0.27 mol), chlorotrimethylsilane (35 ml, 0.27 mol) and lithium (1.9 g, 0.27 mol) were added to THF (150 ml) and this mixture was heated at reflux until the metal had gone. The mixture was cooled and filtered, the filtrate being evaporated to leave an oil (40 g) plus lithium chloride. This was dissolved in acetone (100 ml) and treated in two halves with a solution of potassium permanganate (16 g, 0.11 mol) in water/acetone (1:1, 500 ml) cooled to remain below 10°. When a purple colour persisted, the mixture was filtered and the solid washed well with acetone (500 ml). The acetone was evaporated from the combined liquids, which were then taken to pH 10 with sodium hydroxide solution and continuously extracted with diethyl ether overnight. Evaporation of the ether gave 41 as a yellow gum, which crystallized in vacuo, and was purified by flash chromatography (10% EtOH in EA). Yield 10.9 g (50%). The isolation of the intermediate tetrahydro compound 103 in 85% distilled yield (c. 170° at 0.1 mmHg) on one occasion showed that it is the permanganate oxidation step that is low-yielding, not the actual coupling reaction. However, a better oxidizing agent was not found.

41: $C_{12}H_{12}N_2$ = 184 g mol^{-1} m.p. 77-80°

^1H (220 MHz, solvent $DCCl_3$, standard TMS) δ = 2.65(6 H, s, Me), 7.34(2 H, d, J= 5.2 Hz, H(5)), 7.41(2 H, s, H(3)), 8.63(2 H, d, J= 5.2 Hz, H(6)). FAB (+) m/z = 185(100%,M+H).

UV λ_{max} (EtOH) 280(sh,6.04), 245(6.34), 215(6.72) nm.

2,2',6,6'-Tetramethyl-4,4'-bipyridyl (104)

2,6-Dimethylpyridine (33.7 g) was coupled using the same procedure as for compound 41. The yield after chromatography was 9.1 g, (28%).

104: $C_{14}H_{16}N_2$ = 212 g mol^{-1} m.p. 136°

^1H(220 MHz, solvent TFA, standard dioxan) δ_H= 2.99(12 H, s, Me), 8.07(4 H, s, Ar-H)

^{13}C(100.62 MHz, solvent $CDCl_3$, standard TMS) δ= 23.4(Me), 117.0(C-H), 156.6, 157.3(C-Me).

FAB (+) m/z = 213(100%, M+H), 199(12), 108(17).

UV λ_{max} (EtOH) 280(sh,5.95), 245(6.20), 215(6.60) nm.

Reaction of bipyridyl with methyllithium

Dry bipyridyl 25 (1.57 g, 10.1 mmol) was dissolved in dry THF (50 ml) and cooled in a dry-ice/ acetone bath. A solution of methyllithium (c. 0.5 M, 60 ml, 30 mmol) was added dropwise over 10 min., then the reaction was left for an hour before being allowed to warm to r.t., then it was kept at reflux for 3 hr. After cooling to r.t., the mixture was slowly quenched with EtOH (5 ml). The solvents were evaporated and the residue was extracted with diethyl ether (2 x 50 ml). These extracts were combined, dried and evaporated, then the residue was dissolved in 2M HCl (20 ml) and air was passed through for 6 hr. The solution was treated with charcoal and filtered, then the filtrate was taken to pH 10 with sodium hydroxide solution, then extracted with diethyl ether (2 x 50 ml). The diethyl ether extracts were dried and evaporated. The residue was flash-chromatographed (5% EA in 60-80° petrol) and a fraction containing dimethylbipyridyl 41 was collected. The yield of dimethylbipyridyl 41 after evaporation of solvents was 96 mg, 0.52 mmol, 10%.

2,2'-Bis-([E]-2''-phenylethenyl)-4,4'-bipyridyl (92)

Dimethylbipyridyl 41 (1.0 g, 5.4 mmol), benzaldehyde (1.6 g, 1.7 ml) and potassium carbonate (50 mg) were heated together in propanoic anhydride (4 ml) for 2 days. After cooling, water (20 ml) and diethyl ether (20 ml) were added and the mixture was stirred for 3 hr. The precipitated solid was filtered off and recrystallised from chloroform/diethyl ether. Yield 1.2 g (80%).

m.p. 171-2°. Calculated for $C_{26}H_{20}N_2$: C,86.6%; H,5.6%; N,7.8%: Found C,84.9%; H,5.6%; N,7.8%

^{1}H(220 MHz, solvent TFA, standard dioxan) δ = 7.53(2 H, d, J= 16 Hz, =CH-Ph), 7.6(6 H, m), 7.78(4 H, m), 8.14(2 H, d, J= 16 Hz, =CH-bipy), 8.26(2 H, d, J= 6 Hz, bipy-H(5)), 8.71(2 H, s, bipy-H(3)), 8.91(2 H, d, J= 6 Hz, bipy-H(6)).

FAB (+) m/z = 361(1%,M+H). IR (Nujol) ν_{max} 1640, 1585, 1530, 1205, 985, 890, 815, 740, 695 cm^{-1}.

2,2'-Bis-[(E)-2''-(4'''-methoxyphenyl)ethenyl]-4,4'-bipyridyl (107)

The reaction was repeated with 4-methoxybenzaldehyde instead of benzaldehyde, and 107 was obtained in 76% yield.

m.p. 203-6°. Calculated for $C_{28}H_{24}N_2O_2$: C,80.0%; H,5.7%; N,6.7%. Found: C,79.7%; H,5.6%; N,6.6%.

^{1}H(220 MHz, solvent $DCCl_3$, standard TMS) δ_H = 3.86(6 H, s, MeO), 6.96(4 H, d, J= 9 Hz, Ar-H), 7.05(2 H, d, J= 17 Hz, =CH-Ph), 7.39(2 H, d, J= 17 Hz, =CH-bipy), 7.55-7.63(6 H, m), 7.71(2 H, d, J= 6 Hz, bipy-H(5)), 8.72(2 H, d, J= 6 Hz, bipy-H(6)).

^{13}C(100.62 MHz, solvent $DCCl_3$, standard TMS) δ_C= 55.4(MeO), 114.3, 119.4, 119.5, 125.3, 128.6, 129.2, 133.3, 139.2, 146.6, 150.3, 157.0. FAB (+) m/z = 421(2%,M+H).

UV λ_{max} (chloroform) 340(6.58), 320(sh,6.32).

IR (Nujol) ν_{max} 1635, 1605, 1585, 1575(sh), 1530, 1515, 1255, 1025, 970.

1,1'-Dimethyl-2,2'-bis-[(E)-2''-phenylethenyl]-4,4'-bipyridinium methosulphate (styryl viologen) (8, 105)

(Standard Methylation Procedure)

Distyrylbipyridyl 92 (1.0 g, 2.8 mmol) was heated in dimethylsulphate (4 ml) at 120° for 3 hr. After cooling, THF (50 ml) was added, then the yellow solid was filtered off, washed with diethyl ether, then recrystallized from propylene carbonate. Yield 1.6 g, 2.6 mmol, 95%.

105: $C_{28}H_{26}N_2.2CH_3SO_4$ = 612 g mol^{-1} m.p. 320+

^1H (220 MHz, solvent TFA, standard dioxan) δ = 4.07(6 H, s, MeO), 4.63(6 H, s, MeN), 7.59(10 H, m), 7.89(4 H, apparent d), 8.14(2 H, d, J= 15 Hz, =CH-bipy), 8.42(2 H, d, J= 7 Hz, bipy-H(5)), 8.94(2 H, s, bipy-H(3)), 9.00(2 H, d, J= 7 Hz, bipy-H(6)).

UV λ_{max} (EtOH) 395(6.31), 305(6.26), 205(6.62) nm.

1,1'-Dimethyl-2,2'-bis-[(E)-2''-(4'''-methoxyphenyl)ethenyl]-4,4'-bipyridinium methosulphate (106)

Bipyridyl 107 was methylated by the standard procedure. The yield of viologen 106 was 90% after recrystallization from propylene carbonate.

106: $C_{30}H_{30}N_2O_2.2CH_3SO_4$ = 672 g mol^{-1} m.p. 320+

^{13}C(100.62 MHz, solvent and standard TFA) δ = 55.3(NMe), 56.3(OMe), 114.0, 115.2, 121.8, 122.7, 127.7, 130.9, 141.4, 145.5, 152.6(q), 153.4(q), 162.3.

^1H(220 MHz, solvent TFA, standard dioxan) δ= 4.01(3 H, s), 4.08(3 H, s), 7.20(4 H, d, J= 8.5 Hz), 7.40(2 H, d, J= 16 Hz, =CH-Ar), 7.80(4 H, d, J= 8.5 Hz), 8.09(2 H, d, J= 16 Hz, =CH-bipy), 8.19(2 H, d, J= 6 Hz), 8.64(2 H, s), 8.90(2 H, s).

UV λ_{max} (EtOH) 405(6.27), 315(6.15), 205(6.55) nm.

IR ν_{max} (Nujol) 1635, 1615, 1600 cm^{-1}.

2,2'-Bis[(E)-2''-(4'''-formylphenyl)-ethenyl]-4,4'-bipyridyl

Dimethylbipyridyl 41 (1.2 g, 6.5 mmol) was heated with 1,4-diformylbenzene (5 g, 37 mmol) in propanoic anhydride (5 ml) at 120° for 5 hr. After cooling, the addition of diethyl ether (50 ml) produced a brown precipitate, which was filtered off and washed with diethyl ether. Yield: 2.2 g (5.3 mmol, 80%). This waxy product gave a reasonable ^1H NMR spectrum, but could not be recrystallized to a pure substance. The NMR indicated the presence of "oligomers" formed from reaction of the aldehyde with more than one molecule of the bipyridyl.

^1H (220 MHz, solvent TFA, standard dioxan) δ = 7.24(8 H, AB q), 7.72(2 H, d, J= 16 Hz), 8.00(2 H, d, J= 7 Hz), 8.23(6 H, m), 8.49(2 H, d, J= 6 Hz), 8.82(2 H, s), 9.03(2 H, d, J= 6 Hz), 10.08(2 H, s, CHO).

2,2',6,6'-Tetrakis-([E]-2''-phenylethenyl)-4,4'-bipyridyl (108)

Tetramethylbipyridyl 104 (0.80 g) was reacted with benzaldehyde using the same procedure as for compound 92, to produce 108 as a pale yellow powder, yield 0.96g, (80%). An analytical sample was recrystallized from chloroform. m.p. 292°.

Calculated for $C_{42}H_{32}N_2$: C,89.4%; H,5.7%; N,5.0%; Found: C,87.7%; H,5.7%; N,4.6%.

^1H(220 MHz, solvent TFA, standard dioxan) δ_H= 7.47(4 H, d, J= 16.2 Hz, =CH-Ar), 7.58(12 H, m,), 7.74(8 H, m), 8.05(4 H, d, J= 16.2 Hz, =CH-bipy), 8.37(4 H, s, bipy-H).

^{13}C(100.62 MHz, solvent and standard TFA) δ_C= 115.7, 118.7, 128.3, 129.1, 132.1, 133.5, 145.2, 152.2(q), 152.7(q).

MS (EI) m/z = 564(2%,M), 355,354(3), 282(35,M/2), 122(17), 105(100). IR ν_{max} (HCB) 3050,3030, 1640, 1615, 1600 cm^{-1}.
UV (Chloroform) λ_{max} 390(sh, 6.31), 292(6.90) nm.

1,1'-Dimethyl-2,2',6,6'-tetrakis-([E]-2''-phenylethenyl)-4,4'-bipyridinium methosulphate (tetrastyryl viologen) (9, 109)

108 (101 mg) was methylated by the standard prodedure giving 9 as a bright orange powder, which was recrystallised from water (120 mg,90%).
9: $C_{44}H_{38}N_2.SO_4$ = 690 g mol^{-1} m.p. 320°+
^1H(220 MHz, solvent TFA, standard dioxan) δ = 3.95(6 H, s, MeN), 7.50(4 H, d, J= 16 Hz, =CH-Ar), 7.55(12 H, m), 7.75(8 H, m), 8.05(4 H, d, J= 16 Hz), 8.38(4 H, s, bipy-H).
UV λ_{max} (EtOH) 370(5.95), 290(6.34), 205(6.73) nm.
IR (Nujol) ν_{max} 1700(br), 1625, 1610(br) cm^{-1}.

The polymer (96)

Pure dimethylbipyridyl 41 (852 mg, 4.63 mmol) and 1,4-diformylbenzene 54 (620 mg, 4.63 mmol) were heated at 160° in propanoic anhydride (5 ml) for 13 hr. More 41 (10 mg) was added, and heating continued for 6 hr. After cooling, water (20 ml) was added and the yellow-brown solid formed was filtered off, and heated in vacuo at 60° overnight. Yield 1.17 g, 415 mmol (90%).
Calculated for $(C_{20}H_{14}N_2)_n$: C,85.1%; H,5.0%; N,9.9%; Found: C,74.8% H,5.5%; N,6.8. m.p. None.
^1H(220 MHz, solvent TFA, standard dioxan) δ = (less than 0.3 residual C-Me protons at 3.05 ppm), 7.66(1 H, s), 7.95(2 H, m), 8.2-8.4(2 H, m), 8.8(1 H, m), 8.96(1 H, m) All the signals are broad and poorly resolved.

Methylation of polymer (96): Polyviologen (97)

To the hot reaction mixture (4.63 mmol) prepared as above, was added dimethylsulphate (2 ml), then heating was continued at 150° for 2 hr. The mixture was cooled and THF (50 ml) was added. The dark precipitate was filtered off, washed with EtOH (20 ml) and THF (20 ml), then dried in vacuo. Yield 2.06 g, 3.9 mmol, 82%. m.p. 320+

^{1}H(220 MHz, solvent TFA, standard dioxan) δ = 3.05(c. 0.3 H, s, residual C-Me), 4.60(3 H, s), 7.6-7.7(1 H, m), 7.9(2 H, m), 8.2-8.5(2 H, m), 8.8-9.0(2 H, m).

A similar solid was obtained by the reaction of viologen 98 with dialdehyde 54 in propanoic anhydride, but the integral of residual C-methyl protons at 3.05 ppm in the ^{1}H NMR spectrum indicated a bipy:Me ratio of only 4 or 5.

2,2'-Diformyl-4,4'-bipyridine (101)

Distyrylbipyridyl 92 (1.0 g, 2.8 mmol) was suspended in water (50 ml), dioxan (50 ml) and 2M sulphuric acid (5 ml), and sodium metaperiodate (5 g, 23 mmol) and one crystal of osmium tetroxide were added. The mixture was stirred at 70° overnight then it was cooled, filtered and the dioxan was stripped off. The solution was made alkaline (saturated sodium bicarbonate solution), diluted to 200 ml, then extracted with chloroform (3 x 50 ml). The chloroform extracts were dried and evaporated, and the residue was washed with diethyl ether (100 ml) then recrystallised from chloroform/diethyl ether to yield 101 (410 mg, 70%). This preparation was only successful on one occasion out of four.

m.p. 169-72° Calculated for $C_{12}H_8N_2O_2$: C,67.9%; H,3.8%; N,13.2%; Found: C,57.3% H,3.3%; N,10.4%.

^{13}C (100.62 MHz, solvent TFA, standard dioxan) δ = 127.8, 130.5,

145.0, 153.8(q), 154.0(q), 200.0(CHO).

^{1}H(220 MHz, solvent $CDCl_3$, standard TMS) δ= 7.87(2 H, d, J= 6 Hz, H(5)), 8.30(2 H, s, H(3)), 9.00(2 H, d, J= 6 Hz, H(6)), 10.22(2 H, s, CHO). UV No suitable solvent found (dec ?).

MS (EI) m/z = 212(11%,M), 184(100,M-CO), 155(27), 69(70), 28(82).

(CI) 213(100%), 185(22), 157(10).

IR ν_{max} (HCB) 2925(C-H), 2855(CO-H), 1703(CO), 1630 cm^{-1}.

Ozonolysis:

Distyrylbipyridyl 92 (1.0 g, 2.8 mmol) was dissolved in dry DCM (150 ml) and ozonized oxygen was passed through the solution until the blue fluorescent spot of the starting material had gone from the TLC (EA). Workup with water and zinc, or addition of triethylphosphite then water both gave reddish gum. Evaporation to dryness gave colourless material that reddened on standing. None of these residues gave reasonable NMR spectra for 101.

1,1',2,2'-Tetramethyl-4,4'-bipyridinium sulphate (98)

Dimethylbipyridyl 41 (1.0 g, 5.4 mmol) was methylated by the normal procedure, yielding 1.7 g (70%) of off-white 98 after recrystallization from methanol/ diethyl ether.

98: $C_{14}H_{18}N_2.2CH_3SO_4$ = 436 g mol^{-1} m.p. 196-8°

^{1}H(220 MHz, solvent TFA, standard dioxan) δ= 2.45(6 H, s, MeC), 4.05(6 H, s, MeO), 4.50(6 H, s, MeN), 8.39(2 H, d), 8.46(2 H, s), 9.02(2 H, d).

FAB (+) m/z = 313(1%,M+HSO_4), 214(6,M), 213(5,M-H), 107(60,M/2).

Cyanide-coupling

1,2-Dimethylpyridinium iodide 93 (3.6 g, 15.3 mmol) and sodium cyanide (2 g, 40 mmol) were dissolved in water (10 ml) and dioxan (10 ml), and

the mixture was heated at reflux overnight. The solvent was evaporated, then the residue was extracted with diethyl ether (3 x 20 ml). The ether extracts were dried and evaporated to give an oil (1.2 g), which was dissolved in 2M HCl solution and air was passed through for 3 hr. The solution was evaporated, and the residue was recrystallized from water to give viologen 98Cl (620 mg, 2.2 mmol, 30%).

The reaction of 98 with excess benzaldehyde in propanoic anhydride at 170° gave a 55% yield of bis-styryl viologen 8, identical to the product made by methylation of bipyridyl 92.

1,2,2'-Trimethyl-4,4'-bipyridinium iodide (110)

Dimethylbipyridyl 41 (0.51 g, 3.3 mmol) was dissolved in THF (50 ml) and left standing overnight with iodomethane (0.4 ml, 7 mmol). The off-white precipitate was filtered off and recrystallized from EtOH. Yield: 650 mg, 2.0 mmol, 60%. 110: $C_{13}H_{15}N_2 \cdot I$ = 326 g mol^{-1} m.p. 320+

^1H(220 MHz, solvent TFA, standard dioxan) δ = 2.43(3 H, s, MeC), 2.73(3 H, s, MeC), 4.14(3 H, s, MeN), 7.46(1 H, d, J= 5 Hz), 7.54(1 H, s), 7.96(1 H, d, J= 6.5 Hz), 8.06(1 H, s), 8.37(1 H, d, J= 5 Hz), 8.67(1 H, d, J= 6.5 Hz).

Reaction of 110 with benzaldehyde.

Trimethylbipyridinium iodide 110 (506 mg, 1.55 mmol) was heated with benzaldehyde (179 mg, 1.69 mmol) in propanoic anhydride at 170° overnight. After cooling, the residue was diluted to 50 ml with diethyl ether, and the precipitate was filtered off, pulverized, then washed with water. A solvent suitable for recrystallization was not found. Yield of brown powder: 460 mg (c. 50%)

The NMR spectrum of this solid appeared at first to be the expected compound with the styryl group on the quaternized ring. However, on

closer inspection, it appears that the isomer with the styryl group on the unquaternized ring is also present (ratio of N-Me proton integrals of the two compounds is 85:15).

^{1}H(220 MHz, solvent TFA, standard dioxan) δ = 3.05(3 H, s), 4.48(0.85 x 3 H, s), 4.55(0.15 x 3 H, s), 7.56(5 H, m), 7.80(2 H, m), 8.39(2 H, d), 8.50(1 H, s), 8.90(1 H, m), 9.00(2 H, d).

EXPERIMENTAL FOR

CHAPTER 5

4,4'-Bipyridyl-N,N'-dioxide (133)

4,4-Bipyridine hydrate (5.02 g, 32 mmol), acetic acid (50 ml) and 34% hydrogen peroxide solution (10 ml) were heated together at 80-90° for added, and the solid was filtered off. The residue was recrystallised from ethanol, yield 4.8 g (90%).

133: $C_{10}H_8N_2O_2$ = 188 g mol^{-1} m.p. 335° (82)

^1H(220 MHz, solvent TFA, standard dioxan) δ = 8.44(4 H, br.s), 9.07(4 H, br.s). FAB (+) m/z = 189(100%,M+H) (-) 188(100%,M).

IR (Nujol) ν_{max} 1630(br), 1240(br), 1190(br), 840(br) cm^{-1}.

2,2'-Dimethyl-4,4'-bipyridyl-N,N'-dioxide

Dimethylbipyridyl 41 (2.6g, 14 mmol) was treated with peracetic acid in the same way, to produce the dioxide (2.3 g, 11 mmol, 77%) as an off-white microcrystalline solid.

$C_{12}H_{12}N_2O_2$ = 216 g mol^{-1} m.p. 200-260° (dec)

^1H (TFA) (220 MHz, solvent D_2O, standard dioxan) δ= 3.0(6 H, br.s), 8.3(4 H, br.m), 9.05(2 H, br.s). FAB (+) m/z = 217(100%,M+H).

UV λ_{max} 270(5.81), 210(6.14) nm.

IR (Nujol) ν_{max} 1650(br), 1240(br), 725(br) cm^{-1}.

2,2'-Dichloro-4,4'-bipyridyl (134)

Dry bipyridyl di-N-oxide 133 (2.0 g, 10 mmol) was heated in phosphoryl chloride (20 ml) at 130° for 7 hr. Excess reagent was then distilled off, then the residue was quenched with water and made alkaline with sodium hydroxide solution (5 M). Extraction with chloroform (4 x 40 ml), drying the extract and evaporation left a white residue (200 mg) which was recrystallized from DCM/ diethyl ether, yielding 110 mg (0.49 mmol, 5%) of 134. 134: $C_{10}H_6Cl_2N_2$ = 225 g mol^{-1} m.p. 234°

^1H(220 MHz, solvent $CDCl_3$, standard TMS) δ = 7.51(2 H, d, J= 6 Hz,

H(5)), 7.62(2 H, s, H(3)), 8.61(2 H, d, J= 6 Hz, H(6)).

MS (EI) m/z = 223,225,227(40%,60%,10%,M), 189(30), 153(20).

UV λ_{max} (EtOH) 255(5.11), 240(5.45), 215(5.83) nm.

IR (HCB) ν_{max} 3050, 1635, 1615 cm^{-1}.

2,2'-Dichloro-1,1'-dimethyl-4,4'-bipyridinium methosulphate (138)

Dichlorobipyridyl 134 was methylated as usual, giving a 82% yield of the viologen. $C_{12}H_{12}Cl_2N_2.2CH_3SO_4$ = 447 g mol^{-1} m.p. 177-9° (dec)

^1H(220 MHz, solvent TFA, standard dioxan) δ = 3.95(6 H, s, MeO), 4.66(6 H, s, MeN), 8.60(2 H, d), 8.64(2 H, s), 9.23(2 H, d).

With iodomethane in propylene carbonate, a red insoluble solid was precipitated, so insoluble that no spectral data were obtained.

Reaction of dichlorobipyridyl (134) with terminal alkynes

Dichlorobipyridyl 134 (0.50 g, 2.2 mmol), 2-methyl-2-hydroxy-but-3-yne 129 (2 ml, 20 mmol), copper (I) iodide (15 mg) and bis-(triphenylphosphonio)-palladium (II) chloride (15 mg) were stirred together in diethylamine (20 ml) at reflux for 24 hr. TLC (EA) showed that considerable amounts of starting material were still present. Evaporation and crystallization from DCM/ diethyl ether gave an 80% recovery of 134, contaminated with copper compounds.

Repetition of this reaction with phenylethyne also gave no evidence for reaction having occurred.

2,2'-Dioxo-1,1',2,2'-tetrahydro-1,1'-dimethyl-4,4'-bipyridyl

Paraquat methosulphate 1 (6.3 g, 15.4 mmol) was dissolved in water (10 ml) and added dropwise to an ice-cold solution of potassium hexacyanoferrate (III) (20 g, 61 mmol) in water (40 ml) concurrently with a solution of potassium hydroxide (5 g) in water (10 ml). The

solution was left for 2 hr at r.t. then extracted with DCM (5 x 40 ml). The organic extracts were dried and evaporated to leave a yellow solid (1.44 g) which was recrystallised from DCM/ diethyl ether to give pure dione (1.1 g, 5.1 mmol, 32%). $C_{12}H_{12}N_2O_2$ = 216 g mol^{-1}

m.p. 250-5° (dec)

^1H (220 MHz, solvent $CDCl_3$, standard TMS) δ= 3.61(6 H, s), 6.38(2 H, d), 6.78(2 H, s), 7.44(2 H, d).

IR (HCB) ν_{max} 3040(C-H), 1665(C=O), 1605 cm^{-1}.

UV λ_{max} (EtOH) 330(6.33), 240(6.85), 215(6.94) nm.

EXPERIMENTAL FOR

CHAPTER 6

Reaction of pyridine with 2,3-dibromosuccinic acid (DBSA)

3-Bromo-2-(1'-pyridinium)-1,4-butandioic acid bromide (141)

3-(1'-Pyridinium)-(E)-2-propenoic acid bromide (140)

Pyridine (1 ml, 12 mmol) was added to a solution of DBSA (5 g, 18 mmol) in THF (50 ml) and refluxed overnight. The solid was filtered off and washed with THF, before being recrystallized from ethanol. Yield of 141: 2.4 g (6.8 mmol, 56%).

Pyridine (5 ml) was added to a solution of DBSA (5 g, 18 mmol) in ethanol (50 ml) and refluxed overnight. After cooling and evaporation, the residue was recrystallized from ethanol: Yield of 140 was 1.26 g (54%).

141: $C_9H_9BrNO_4.Br$ = 355 g mol^{-1} m.p. 197° (dec)

^1H(220 MHz, solvent D_2O, standard dioxan) δ = 3.18-3.45(1 H, m, CHBr), 5.00-5.08(1 H, m, CH-N), 7.95(2 H, t), 8.45(1 H, t), 8.81(2 H, d).

FAB (+) m/z = 196(10%,M-Br), 150(45), 110(20).

140: $C_8H_8NO_2.Br$ = 230 g mol^{-1} m.p. 225°

^1H(220 MHz, solvent D_2O, standard dioxan) δ = 6.80(1 H, d, J= 14.2 Hz, =CH-C), 8.09(2 H, t), 8.22(1 H, d, J= 14.2 Hz, =CH-N), 8.62(1 H, t), 9.02(2 H, d).

FAB (+) m/z = 379,381(1%,1%,2M+Br), 299(10,2M-H), 150(100,M), 106(M-CO_2), 80(14,PyrH).

(-) 308,310,312(15%,27%,15%,M+2Br), 79,81(100,Br).

^{13}C(100.62 MHz, solvent D_2O, standard dioxan) δ = 122.3, 129.2, 133.2, 143.3, 149.7, 200.3(CO_2H).

IR (Nujol) ν_{max} 1720, 1665, 1630 cm^{-1}

UV λ_{max} (EtOH) 262(6.11), 205(6.16) nm.

1,2-Bis-(1-pyridinium)-ethane dibromide (139)

Pyridine (20 ml, 240 mmol) and 1,2-dibromoethane (5 ml, 40 mmol) were heated together in EtOH (100 ml) at reflux for 48 hr. After cooling, the pyridine was evaporated and the residue was recrystallized from EtOH/ THF, giving 12.1 g (35 mmol, 90%) of white crystalline 139.

139: $C_{12}H_{14}N_2.Br_2$ = 346 g mol^{-1} m.p. 294° (dec)

^1H(220 MHz, solvent, D_2O, standard dioxan) δ = 5.23(4 H, s, CH_2) 8.01(4 H, t), 8.55(2 H, t), 8.72(4 H, d).

Reaction of 139 with selenium dioxide[79a], iodine[79c], or dichlorodicyanoquinone[79b] (DDQ)

Bis-pyridinium-ethane dibromide 139 (1.0 g, 2.9 mmol) was heated in acetonitrile (50 ml) at reflux with 10 mmol of the oxidizing agent, overnight. The mixture was cooled and evaporated, then the residue was analysed by NMR. In neither case was any pyridine-containing compound present apart from unchanged 139.

REFERENCES

1. L.M.Sayre, P.K.Arora, S.C.Feke, and F.L.Urbach, J. Am. Chem. Soc., 1985, 108, 2464.
2. (a) I.C.I. "P4" project reports 1969-71.
   (b) M.S.Simon, P.T.Moore, J. Polym. Sci., 1975, 13, 1-16.
3. (a) K. Kalyanasundaram, Coord. Chem. Revs., 1982, 46, 159.
   (b) A.Launikonis, J.W.Loder, A.W-H.Mau, W.H.F.Sasse, L.A.Summers, and D.Wells, Aust. J. Chem., 1982, 35, 1341.
   (c) R.E.Sassoon, S.Gershani, J.Rabani, J.Phys.Chem., 1985, 89, 1937.
4. E.Stecklan, T.Kuwana, Berichte der Bunsen-Gesellschafte, 1974, 78, 253. W.Heinemann, Bioch. Biophys. Res. Commun., 1973, 50, 89.
5. R.E.V.D. Leest, J.Electroanal.Chem., 1973, 43, 251. A.G.Evans, J.C.Rees, M.W.Baker, J. Chem. Soc. Perkin Trans. 2, 1975, 1310.
6. C.L.Bird, A.T.Kuhn, Chem. Soc. Rev., 1981, 10, 46-82.
7. S.Hunig, W.Schenk, Liebigs. Ann. Chem., 1979, 1523.
8. Results from I.C.I. Plant Protection, compound screening.
9. Results from Paul Monk, Chemistry Department, Exeter University.
10. J.A.Barltrop, A.C.Jackson, J. Chem. Soc. Perkin Trans. 1, 1984, 367
11. S.Hunig, B.J.Garner, G.Ruider, and W.Schenck, Liebigs Ann. Chem., 1973, 1036.
12. R.D.Balanson, M.E.Oxsen, Y.Y.Cheng, J. Chem. Soc. Perkin Trans. 2, 1979, 2704.
13. R.J.Waltman, J.Bargon, J. Can. Chem., 1986, 64, 76, and references within.
14. N.Basescu, Z.X.Liu, D.Moses, A.J.Heeger, H.Naaremann, and N.Theophilou, Nature (London), 1987, 327, 403.
15. (a) A.Rembaum, S.Singer, U.S.Patent 538,053(1970); Chemical Abstracts, 1971, 74, 32178.
(b) J.G.Allen, British patent, 1113219, 1968.

16. D.R.Rosseinsky, Royal Society of Chemistry, Annual Reports, 1985, 82(c), 247.

17. Chemical Abstracts On-line searches (various dates).

18. (a) C.M.Elliott, W.S.Martin, J. Electroanal. Chem., 137, 377-85, (1982)

(b) Y.Nambu, K.Yamamoto, T.Endo, J. Chem. Soc. Chem. Commun., 1986 (7), 574-6.

19. (a) T.Zincke, Annalen, 1904, 330, 361, (and later related papers by the same author) (b) J.G.Allen, British Patent 1514466 1974.

20. (a) N.E.Grigoreva, I.K.Gintse, J. Gen. Chem. USSR., 1956, 26, 249-54. (b) ibid., 1954, 24, 171-5.

(c) Chemical Abstracts, 1976, 50, 13917h.

21. S.J.Atherton, K.Tsukahara, R.G.Wilkins, J. Am. Chem. Soc., 1986, 108, 3380-5.

22. (a) R.H.Reuss, L.J.Winters, J. Org. Chem., 1973, 38, 3993.

(b) L.J.Winters, A.L.Borror, N.Smith, Tetrahedron letters, 1967, 2313. (c) L.J.Winters, N.G.Smith, M.I.Cohen, J. Chem. Soc. Chem. Commun., 1970, 642.

23. (a) G.A.Olah, R.J.Hunadi, J. Org. Chem., 1981, 46(1), 715.

(b) I.C.I. Ltd, Chemical Abstracts, 1967, 67, 73530.

24. (a) O.Dimroth, Ber. Dtsch. Chem. Ges., 1921, 54, 2934.

(b) I.C.I.Ltd, Chemical Abstracts, 1964, 603, 11992.

25. K.Junghans, Chemical Abstracts, 1980, 92, 6421.

V.E.Riskovets, V.V.Saraeva, S.V.Zatonskii, Chemical Abstracts, 1977, 86, 63424.

26. H.P.Becker, W.P.Neumann, J. Organometallic. Chem., 1972, 37(1), 57.

27. J.G.Allen, I.C.I. Electronics Group, personal communication.

28. J.Volke, M.Naarova, Coll. Czech. Chem. Commun., 1972, 37, 3361.

29. See refs. 11 and 12.

30. (a) M.T.Leffler, Organic Reactions, 1942, 1, 91, and references within. (b) Beilstein E II 25 p. 334 (Chemische Zentrallblatt 1924 II p. 1409 does not seem to exist).

31. J.I.Darragh (I.C.I.), U.K.Patents 1494336 and 1491254, 1977.

32. (a) R.Abramovitch, M.N.Inbasekaran, S.Kato, and G.M.Singer, J. Org. Chem., 1976, 41(10), 1717.

(b) M.Katada, Chemical Abstracts, 1951, 45, 9536.

33. R.F.Francis, W.Davis, J.T.Wisener, J. Org. Chem., 1974, 39, 59.

34. F.Krohnke, W.Zecher, Angew. Chem. Int. Ed. Engl., 1962, 1, 626.

35. J.E.Downes, J. Chem. Soc. (c), 1967, 1491.

36. (a) F.Krohnke, Ber. Dtsch. Chem. Ges., 1935, 68, 1351-9.

(b) F.Krohnke, J.Wolff, G.Jentsch, Chem. Ber., 1954, 84, 399-411.

(c) F.Krohnke, M.Meyer-Delius, ibid., 411-23.

(d) F.Krohnke, W.Zecher, Berichte, 1967, 100(5), 1756-60.

37. J.A.Farrington, A.Ledwith, M.F.Stam, J. Chem. Soc. Chem. Commun., 1969, 259.

38. A.W-H.Mau, J.M.Overbeek, J.W.Loder, and W.H.F.Sasse, J. Chem. Soc. Faraday. Trans., 1986, 82, 869.

39. (a) O.R.Rodig in Abramovitch, "Heterocyclic Chemistry" (Wiley Interscience), 14, Supplement part 1, p. 370, and references within.

(b) E.M.Kosower, J.W.Patton, Tetrahedron, 1966, 22, 2081.

40. J.D.Rose, R.A.Gale, J. Chem. Soc., 1949, 792.

41. (a) P.Carsky, S.Hunig, I.Stemmler, and D.Scheutzow, Liebigs. Ann. Chem., 1980, 291.

(b) E.C.Taylor, S.F.Martin, J. Am. Chem. Soc., 96, 8095.

H.R.Brahmana, K.Katsuyama, J.Inanaga, T.Katsuki, and M.Yamaguchi, Tetrahedron letters, 1981, 22, 1695.

42. (a) G.Zinner, W.P.Fehlhammer, Angew. Chem. Int. Ed. Engl., 1985,

97(11), 979-80.

(b) O.Erastov, G.N.Nikonov, B.A.Arbuzov, Chemical Abstracts, 1983, 99, 212595s.

(c) R.G.Kostyanovskii, Y.I.Elnatonov, S.M.Shikhaliev, S.M.Ignatov, I.I.Chervin, Chemical Abstracts, 1982, 98, 16770k.

(d) K.L.Lundberg, R.J.Rowatt, N.E.Miller, Inorg. Chem., 1969, 8(6), 1336-40.

(e) T.Sugimoto, T.Imanishi, M.Okano, S.Tanimoto, Bull. Kyoto. Univ. Chem. Res., 1982, 60, 302-8.

43. D.W.Grisley, U.S.Patent 3330868, 1967, (Chem. Abs., 1967, 67, 100246).

44. A.K.Sheinkman, A.N.Prilepskaya, L.R.Kolomoitsev, and A.N.Kost, Vestn. Mosk. Univ. Ser. II. Khim., 1962, 19(6), 745-50, (Chem. Abs., 1962, 62, 10400h)

45. F.Krohnke, Berichte, 1950, 83, 50-9.

46. B.E.Maryanoff, A.B.Reitz, M.S.Mutter, R.R.Inners, and H.R.Almond, J. Am. Chem. Soc., 1985, 107, 1068.

47. I.Gosney, A.G.Rowley, Chemical Reviews (to be published).

48. Translations of ref. 20 (a) and 20 (b) were obtained from the British Lending Library. It is the diagrams that are ambiguous. The Chemical Abstracts account of ref. 20 (c) is not well written.

49. H.K.Porter, Chemical Reactions, 1973, 20, 455.

50. (a) I.Colon, D.R.Kelsey, J. Org. Chem., 1986, 51, 2627.

(b) T.Rode, E.Breitmayer, Synthesis, 1987(6), 574.

51. T.Cohen, R.J.Lewarchik, J.Z.Tarino, J. Am. Chem. Soc., 1974, 96, 7753.

52. (a) See early indices of Chemical Abstracts under "Stilbazole".

(b) T.Katsumoto, Bull. Chem. Soc. Jap., 1960, 33, 242, Chem.Abstr., 1960, 54, 18504b.

53. T.J.Gilchrist, "Heterocyclic Chemistry", (Pergamon) p.249.

(b) T.Katsumoto, Bull. Chem. Soc. Jap., 1959, 32, 1019, Chem. Abstr., 1960, 54, 18504b.

54. (a) T.Tamaki, Y.Suzuki, M.Hasegawa, Bull. Chem. Soc. Jap., 1972, 45, 1988.

(b) C.Belinski, F. Lalau Keraly, Chem. Abstr., 1977, 87, 6768.

(c) M.Ropars, Chem. Abstr., 1975, 82, 58678n.

(d) W.A.Kaffman, K.P.O'Leary, Chem. Abstr., 1977, 87, 192098d.

55. F.Minisci, F.Bertini, R.Galli, and A.Quilico, Ger.Offen., 2153234, 1972.

56. (a) E.Wiberg, Angew. Chem. Int. Ed. Engl., 1963, 2, 507.

(b) R.Fields, R.N.Haszeldine, R.E.Hutton, J. Chem. Soc. (c), 1967, 2559.

57. (a) L.F.Fieser and M.Fieser "Reagents for organic synthesis", (Wiley Interscience), Vol. 1, p. 813.

(b) E.P.Hart, J. Chem. Soc., 1952, 4540.

58. (a) V.Boekelheide, W.J.Linn, Chemical Abstracts, 1955, 49, 10948.

(b) O.H.Bullitt, J.T.Maynard, J. Am. Chem. Soc., 1954, 76, 1286.

(c) G.Kobayashi, S.Furukawa, J. Am. Chem. Soc., 1954, 76, 1370.

59. (a) F.Krohnke, Angew. Chem. Int. Ed. Engl., 1963, 2, 225 and 380.

(b) A.Markovac, C.L.Stevens, A.B.Ash, and B.E.Hackley, J. Org. Chem., 1970, 35, 841.

60. A.B.Pashkov, N.B.Skakalskaya, E.I.Lyustgarten, B.M.Kuinzhi, M.A.Zepalova, A.K.Valkova, and I.V.Zaitseva, Chemical Abstracts, 1968, 68, 115429.

61. J.M.Smith, H.N.Stewart, B.Roth, and E.H.Northey, J. Am. Chem. Soc., 1948, 70, 3997.

62. G.Scheung, L.Winterhalder, Chemical Abstracts, 1934, 28, 4541-8.

63. N.N.Dykhanov, T.S.Ryzhova, Chemical Abstracts, 1964, 60, 11992h.

64. D.Leaver, W.K.Gibson, J.D.R.Vass, J. Chem. Soc., 1963, 6053.

65. C.K.McGill, Chemical Abstracts, 1962, 57, 15077g.

66. (a) M.S.Shvartsberg, I.L.Kotlyarevskii, A.N.Kozhevnikova, V.N.Andrievskii, Chemical Abstracts, 1970, 73, 130851.

(b) M.S.Shvartsberg, A.A.Moroz, A.N.Kozhevnikova, Chemical Abstracts, 1978, 89, 24101.,

67. K.Sonogashira, Y.Tohda, N.Hagihara, Tetrahedron letters, 1975, 50, 4467.

68. D.E.Ames, D.Bull, C.Takundwa, Synthesis, 1981, 364.

69. L.Della Ciana, A.Haim, J. Heterocyclic. Chem., 1984, 21, 607.

70. S.Takahashi, Y.Kuroyama, K.Sonogashira, and N.Hagihara, Synthesis, 1980, 627.

71. G.A.Olah, J.A.Olah, N.A.Overchuk, J. Org. Chem., 1965, 3373, and refs. therein.

72. F.Krohnke, F.Schafer, Berichte, 1962, 95, 1098.

73. Martino Colonna, Chemical Abstracts, 1940, 34, 7290.

74. (a) V.Boekelheide, W.J.Linn, Chemical Abstracts, 1955, 49, 10948.

(b) O.H.Bullitt, J.T.Maynard, J. Am. Chem. Soc., 1954, 76, 1286.

(c) G.Kobayashi, S.Furukawa, J. Am. Chem. Soc., 1954, 76, 1370.

75. N.B.Chapman, D.Q.Russell, J. Chem. Soc., 1956, 1563.

76. C.F.H.Allen, J.R.Thirtle, Organic Syntheses, collective volume 3, 136.

77. (a) M.Katada, Chemical Abstracts, 1951, 45, 9536.

(b) R.G.Fargher, R.Furness, J. Chem. Soc., 1915, 107, 688.

78. P.Pfeiffer, A.Langenburg, Ber., 43, 2935, (1910).

79. (a) P.G.Campbell, P.C.Teague, J.Am.Chem.Soc., 76, 1371, (1954)

(b) E.A.Braude, A.G.Brook, R.P.Lipstead, J.Chem.Soc., (1954), 3569.

(c) L.F.Fieser and M.Fieser, "Reagents for organic synthesis", J.Wiley (London), Volume 1, p.497.

80. (a) I.Lenina, A.V.Chernobai, Chemical Abstracts, 1977, 87, 39916z.

(b) See Chemical Abstracts under C_7H_7N in formula indices.

81. D.H.Williams, I.Fleming, "Spectroscopic methods in organic chemistry", McGraw-Hill, 3rd edition, (a) p.101 (b) p.100.

82. "Dictionary of organic compounds", publ. Eyre and Spottiswoode, (London)

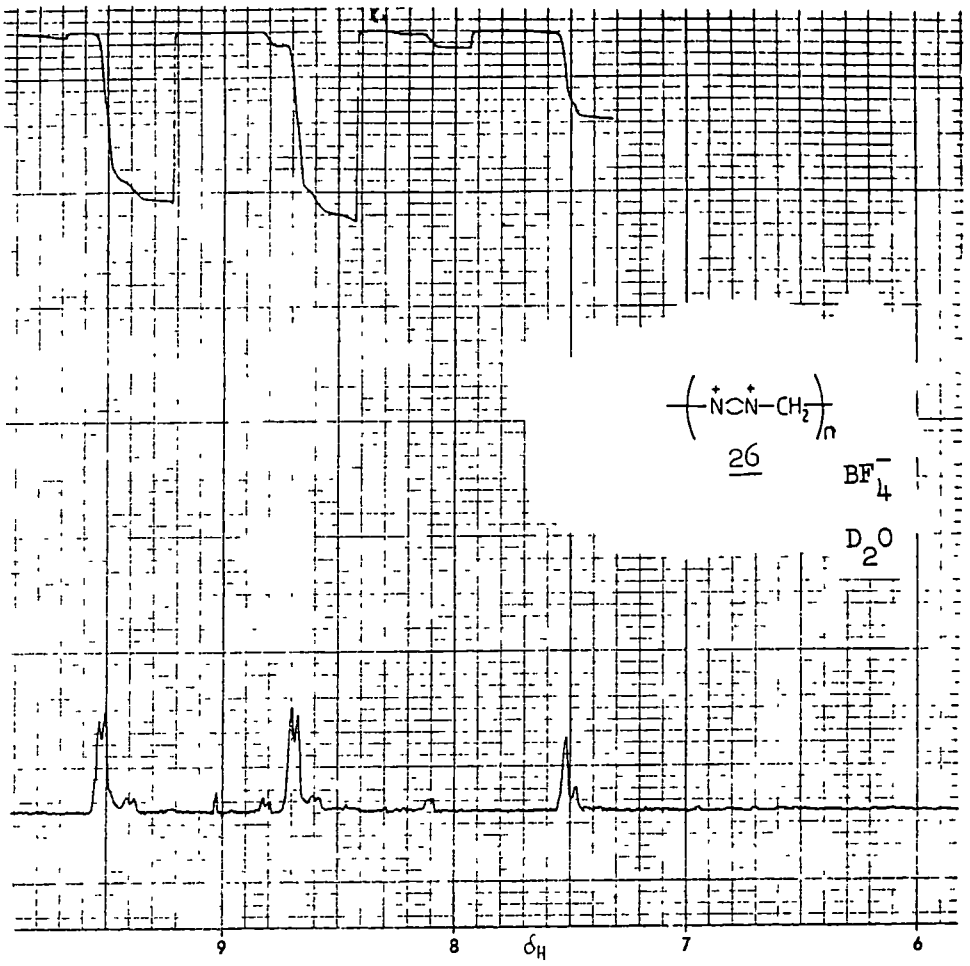
APPENDICES 1 AND 2

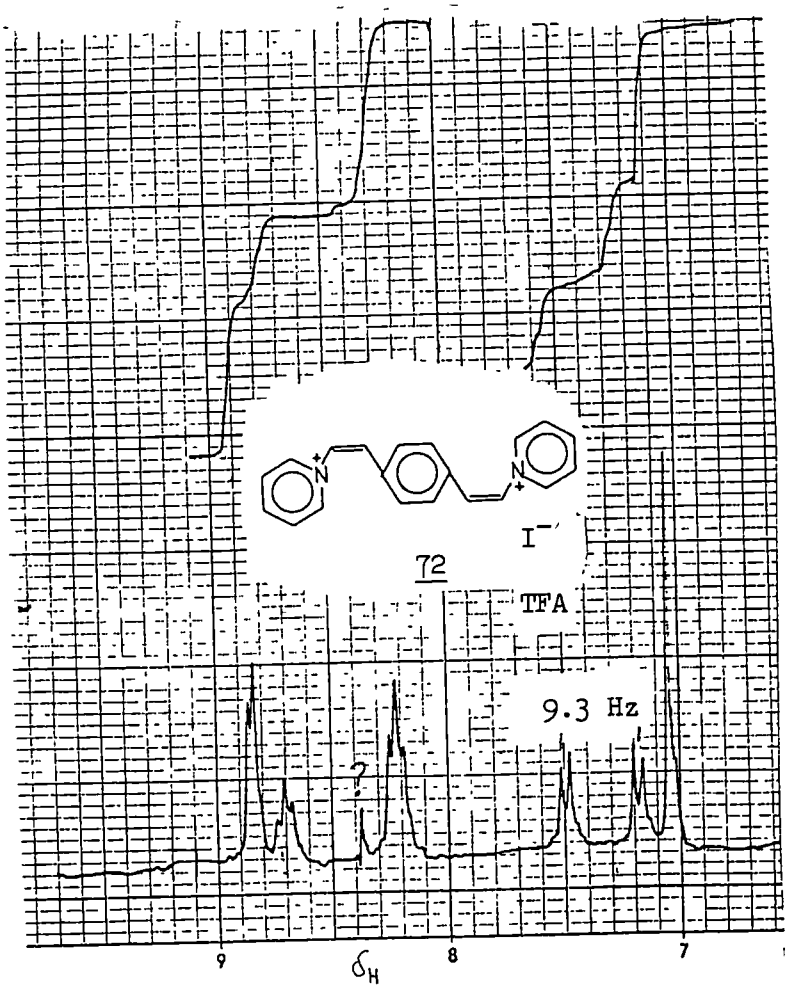
APPENDIX 1:

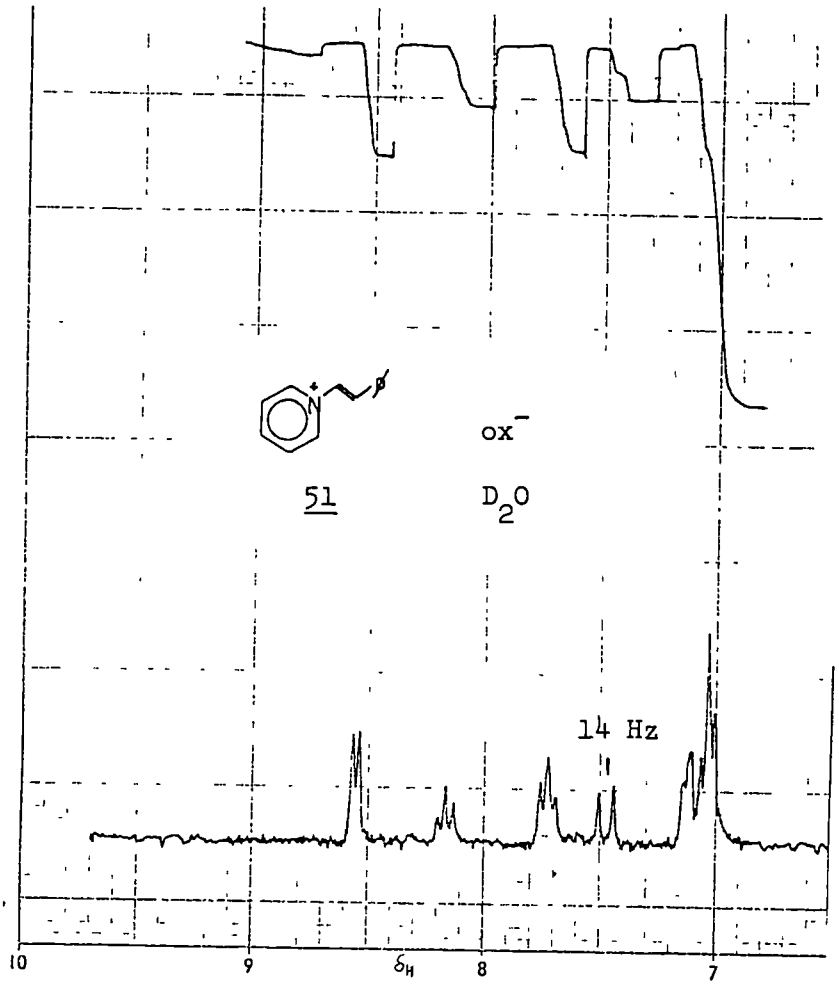
THE UP-FIELD PARTS OF ^{1}H NMR SPECTRA OF COMPOUNDS OF INTEREST

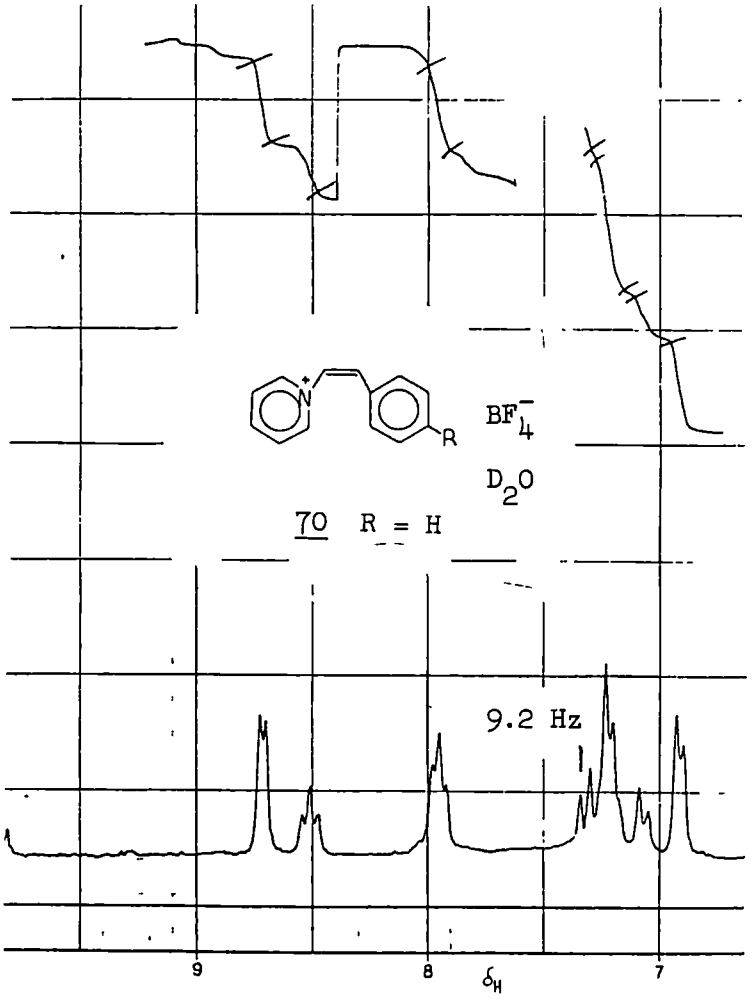
APPENDIX 2:

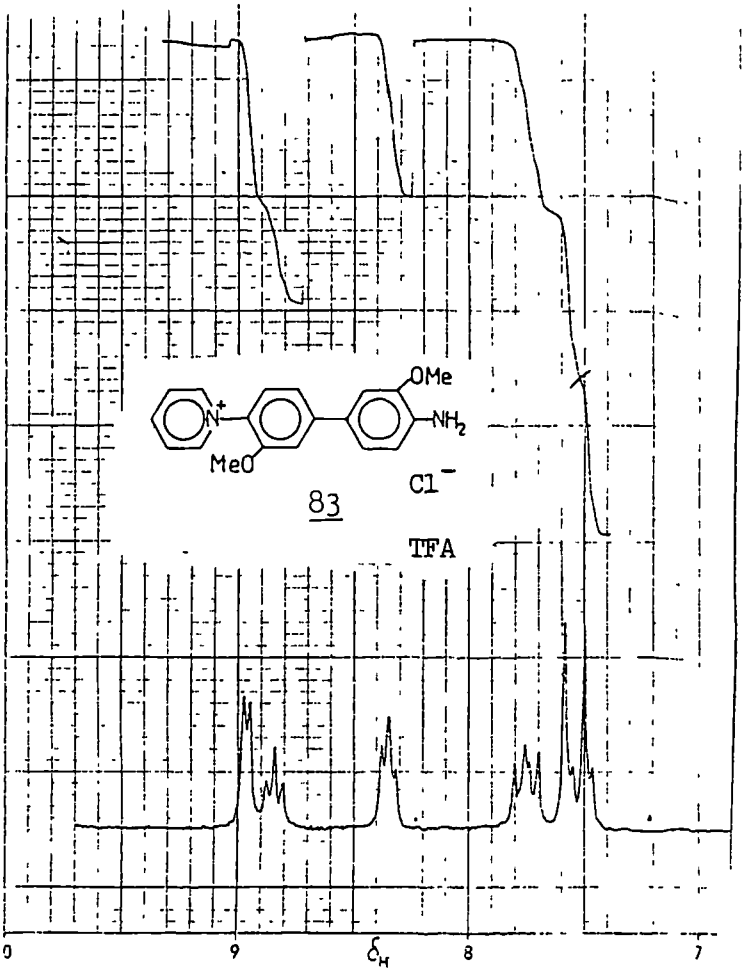
THE MASS-SPECTRA OF FIVE NEW COMPOUNDS

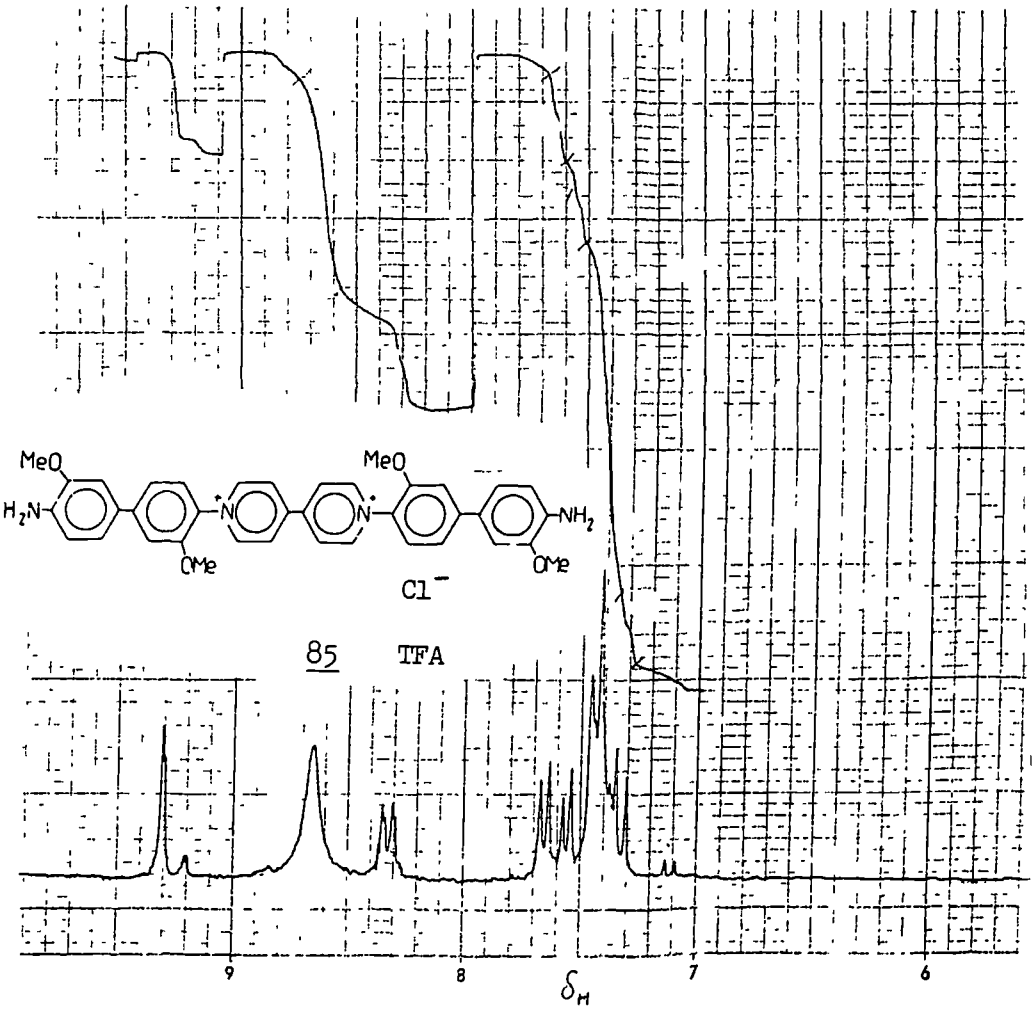

26
BF_4^-
D_2O
9
8
δ_H
7
6

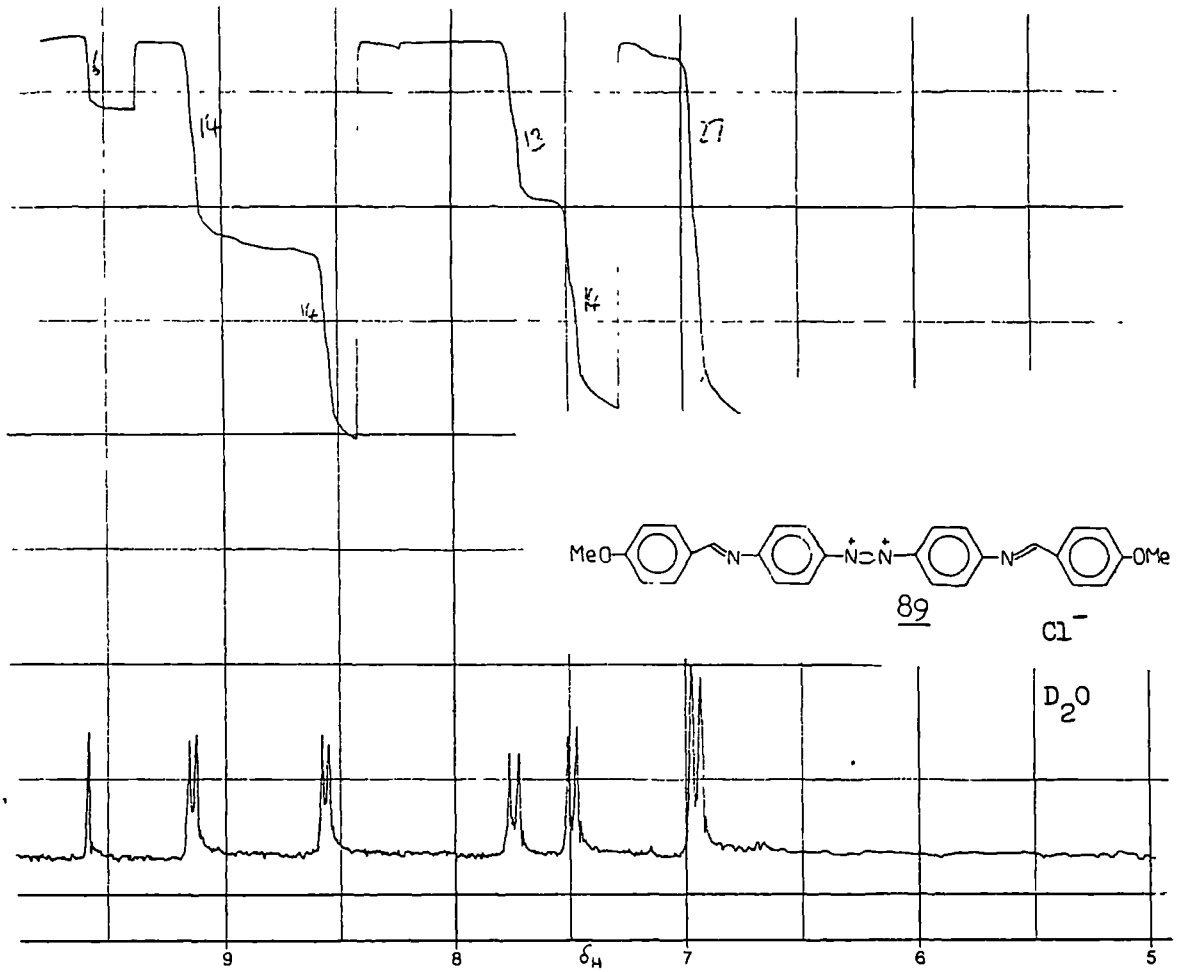

72
I^-
TFA
9.3 Hz
?
9
8
δ_H
7

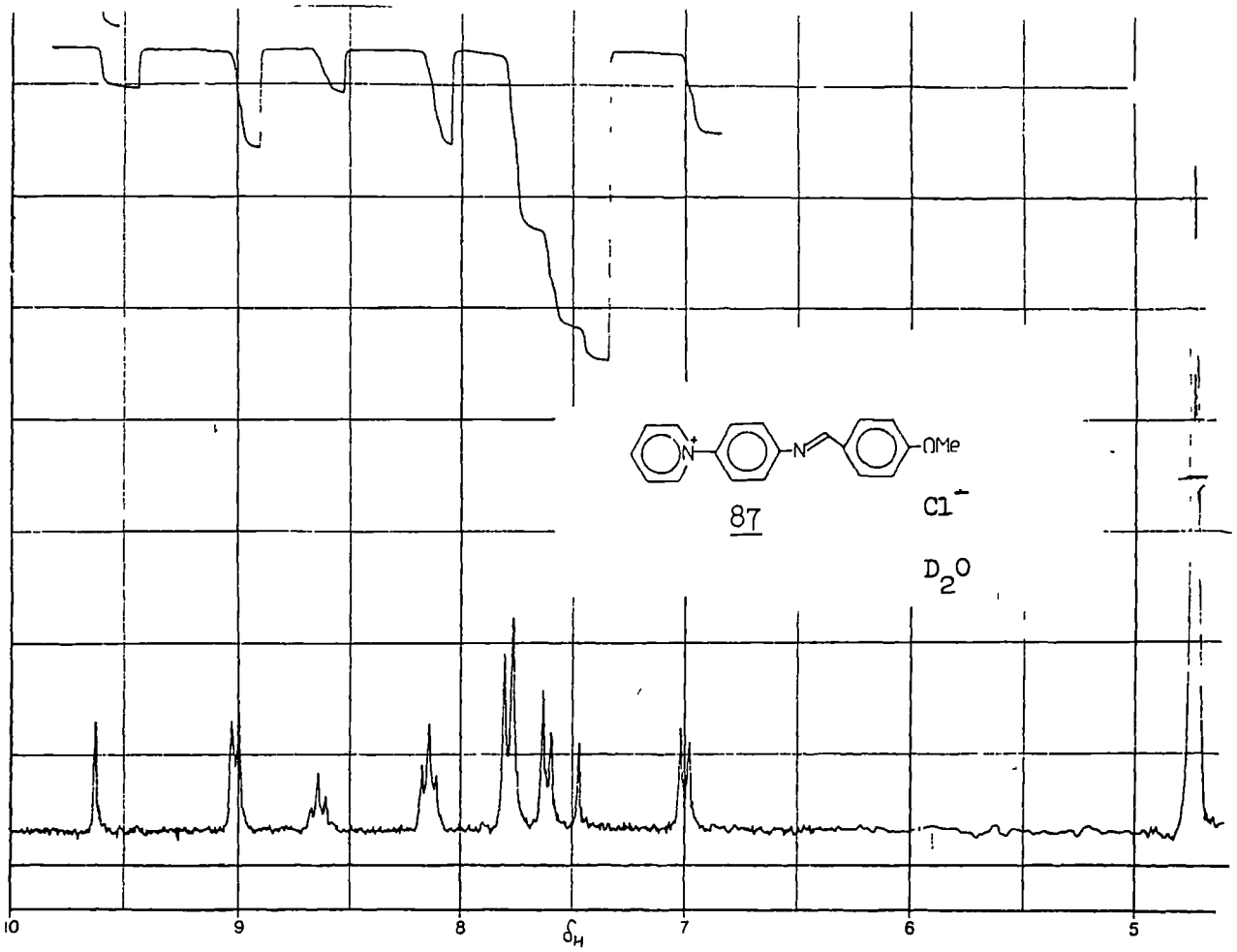

ox⁻
51
D2O
14 Hz
10
9
δH
8
7

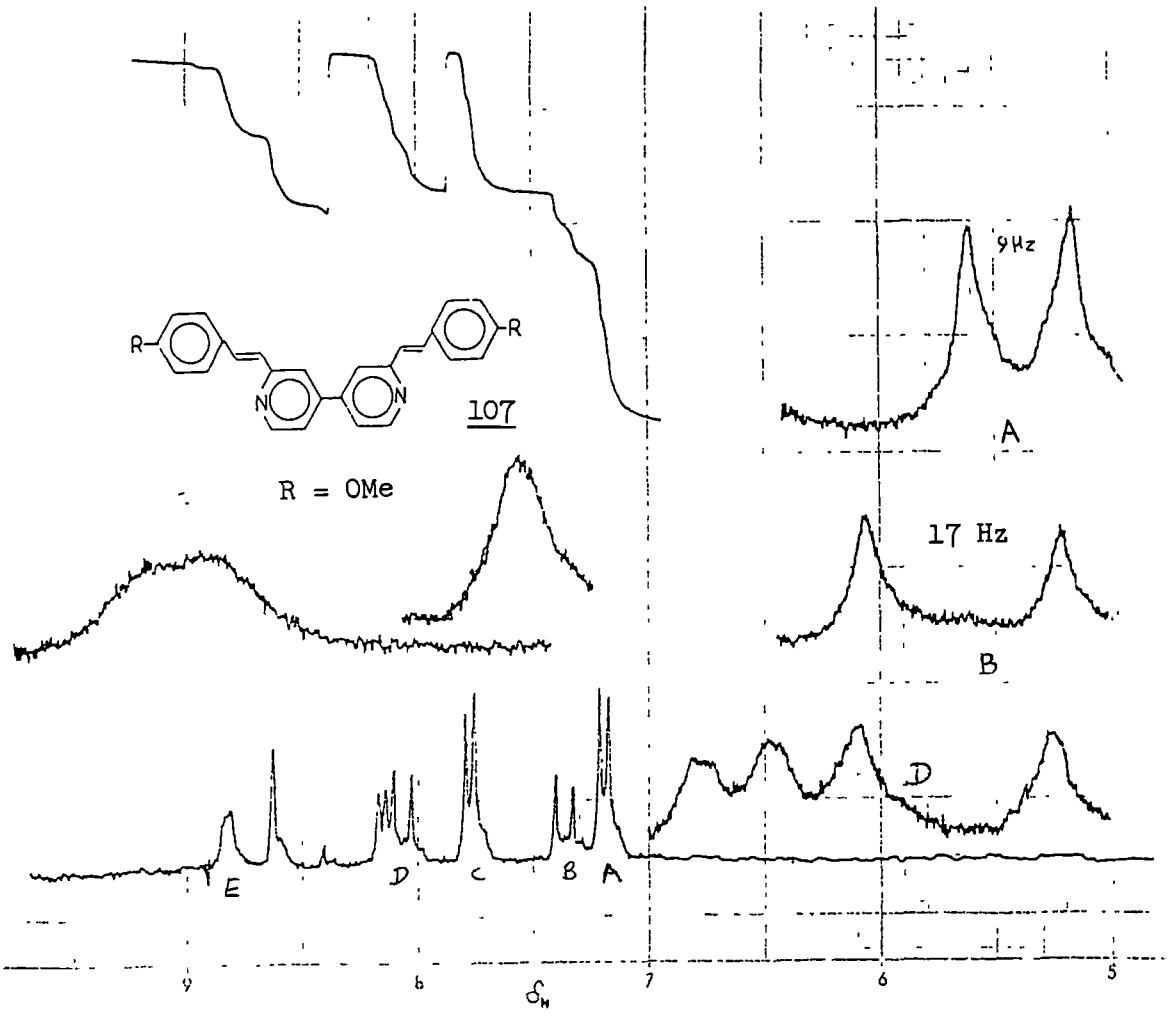

BF4⁻
R
D2O
70 R = H
9.2 Hz
9
8
δH
7

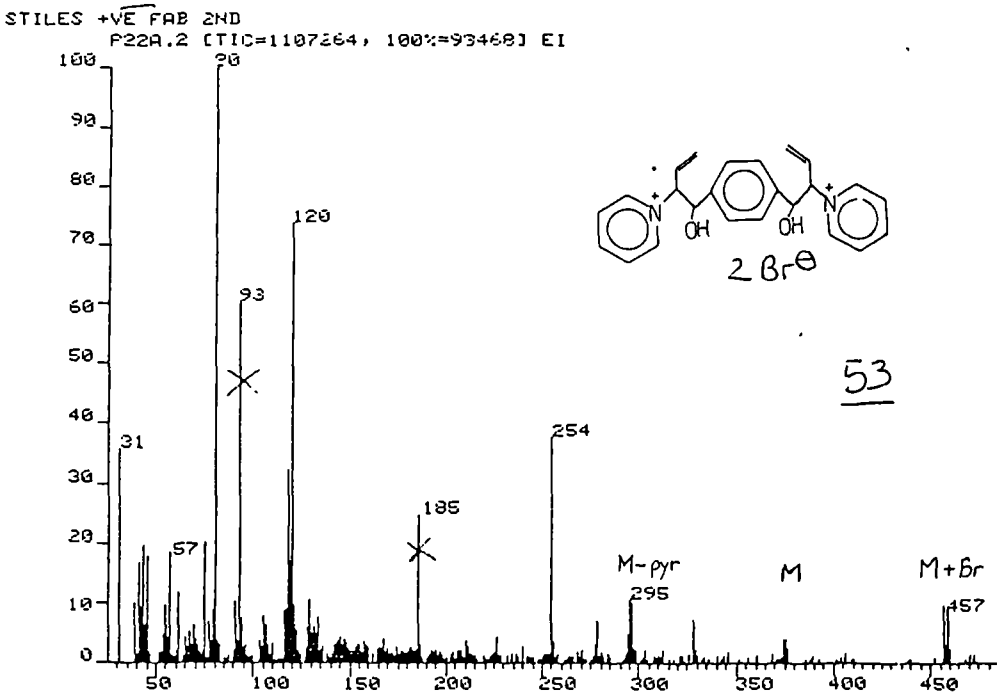

OMe
NH2
MeO
Cl⁻
83
TFA
9
δH
8
7


MeO
MeO
H2N
NH2
OMe
OMe
Cl⁻
85
TFA
9
8
7
6
δH


14
13
17
MeO
OMe
89
Cl⁻
D2O
9
8
δH
7
6
5

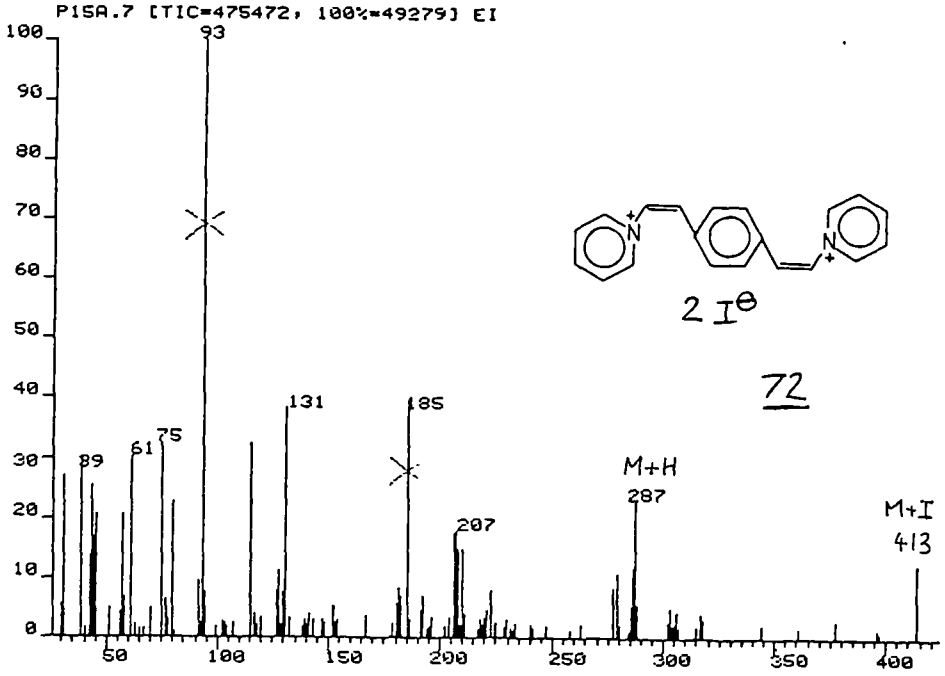

OMe
87
Cl⁻
D2O
10
9
8
δH
7
6
5


R
N
N
R
107
R = OMe
9Hz
A
17 Hz
B
D
E
D
C
B
A
9
8
7
6
5
δH


STILES +VE FAB 2ND
P22A.2 [TIC=1107264, 100%=93468] EI
100
90
80
70
60
50
40
30
20
10
0
50
100
150
200
250
300
350
400
450
90
120
93
31
57
185
254
M-pyr
295
M
M+Br
457
OH
OH
2 Br⊖

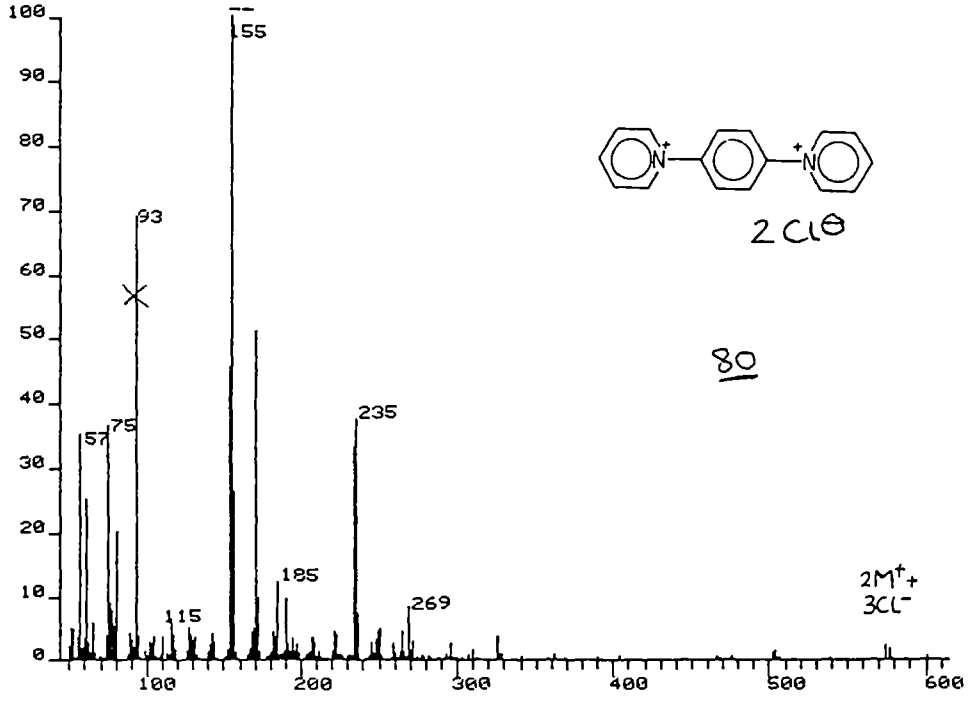
53

STILES +VE FAB
P15A.7 [TIC=475472, 100%=49279] EI

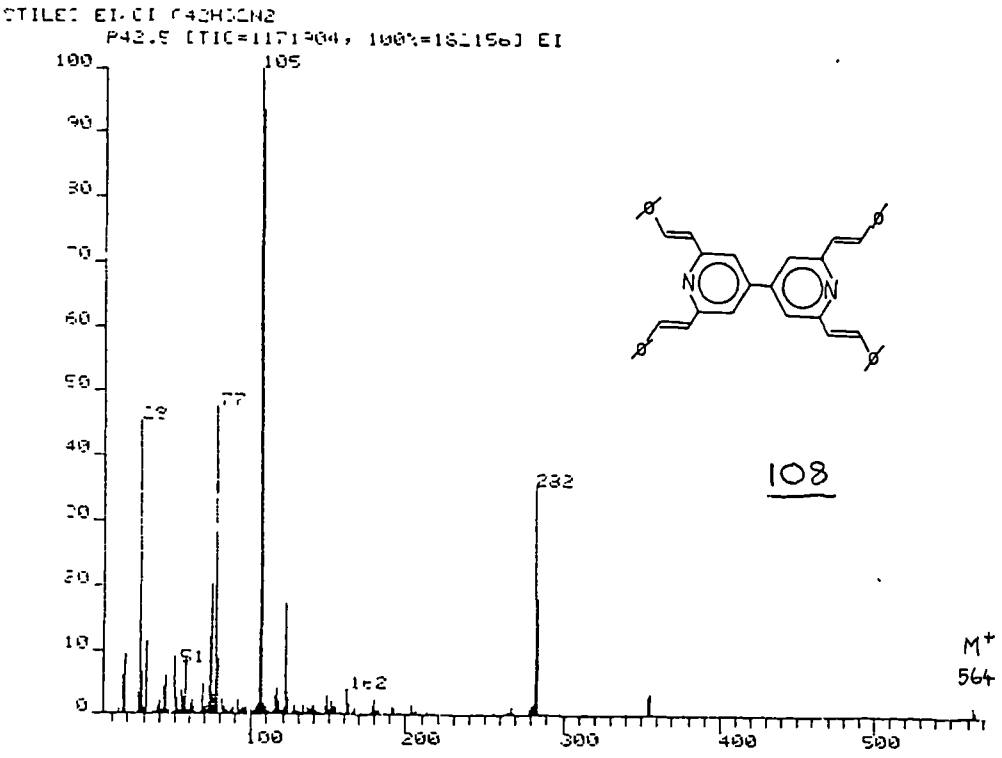


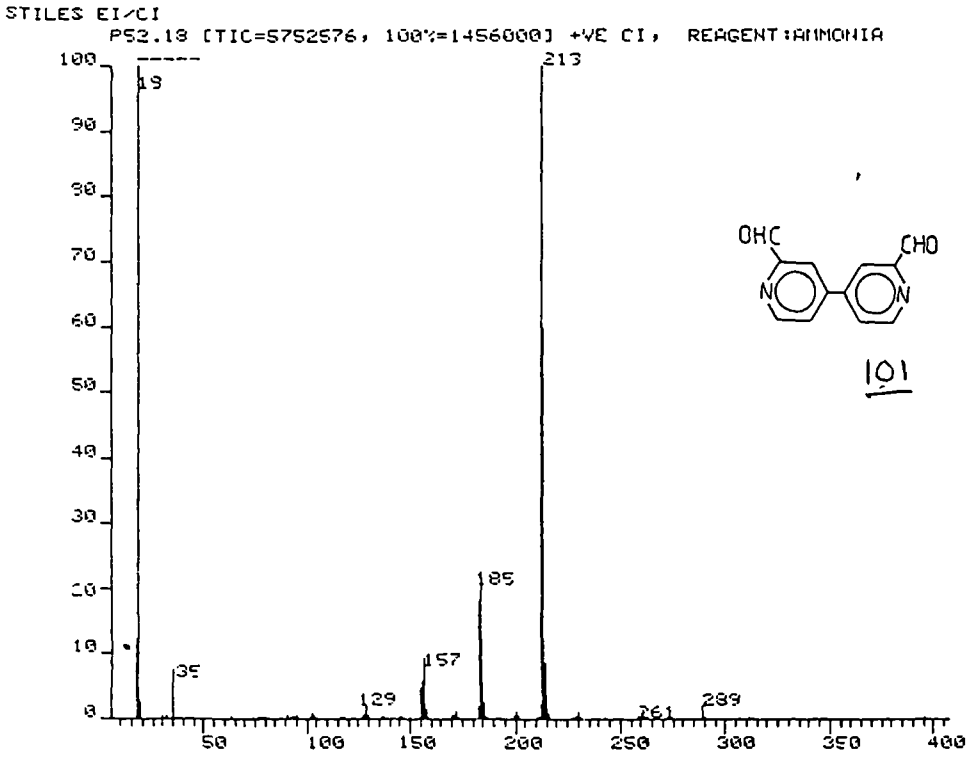
72

STILES +VE FAB GLY H2O
P66.6 [TIC=2609920, 100%=257428] EI



80


STILES EI-CI C42H30N2
P42.5 [TIC=1171904, 100%=182156] EI
105
77
232
M+
564
108


STILES EI/CI
PS2.18 [TIC=5752576, 100%=1456000] +VE CI, REAGENT:AMMONIA
213
185
157
OHC
CHO
101