5-Morpholino-*N*,*N*-γ-oxapentamethylene-2,4-pentadienylideniminium fluoroborate (4j) had mp 184–186°; ir (KBr) 1560, 1435, 1295, 1240, 1200, 855, and 805 cm^{-1}; nmr (DMSO-d_6) δ 7.85 (d, 2 H, α protons), 7.67 (t, 1 H, γ proton), 6.10 (t, 2 H, β protons), and 3.7 (b, 16 H, ethylene).

Reaction of 2 with Methylamine.—To an ice-cooled solution of 0.82 g (2.0 mmol) of **2** in 10 ml of methanol was added a solution of 0.62 g (20 mmol) of methylamine in 5.0 ml of methanol. After addition of amine the reaction mixture was refluxed for about 1 hr. The hot reaction mixture was rapidly filtered and the filtrate was allowed to stand at room temperature to give 0.08 g of **6** as white needles: mp 215–216°; yield 10%; nmr (DMSO-d_6) δ 8.44 (s, 2 H, β protons), 7.50 (m, 15 H, phenyl), and 3.70 (s, 3 H), methyl protons). The product **6** was determined to be *N*-methyl-2,4,6-triphenylpyridinium fluoroborate by mixture melting point with an authentic sample.[16]

Registry No.—**1** BF$_4$, 41656-11-5; **1** ClO$_4$, 2567-16-0; **2**, 1582-78-1; **4a**, 41656-13-7; **4b**, 41737-40-0; **4c**, 41656-14-8; **4d**, 41724-27-0; **4e**, 41656-15-9; **4f**, 41656-16-0; **4g**, 41656-17-1; **4h**, 41656-18-2; **4i**, 41656-19-3; **4j**, 41656-20-6; **6**, 2355-56-8; aniline, 62-53-3; *p*-toluidine, 106-49-0; *p*-anisidine, 104-94-9; *p*-hydroxyaniline, 123-30-8; *p*-chloroaniline, 106-47-8; *N*-methylaniline, 100-61-8; methylamine, 74-89-5; dimethylamine, 124-40-3; morpholine, 110-91-8.

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Cyanide-Induced Dimerization of (4-Pyridyl)pyridinium Chloride. Synthesis of 4,4'-Bipyridine and (4-Pyridyl)viologen Salts[1a]

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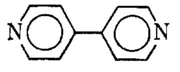
Received February 5, 1973

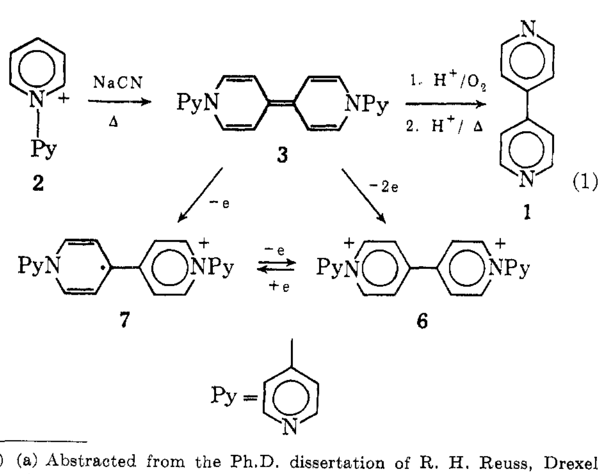
Warming solutions of the title compound (**2**) and sodium cyanide produces 1,1'-di(4-pyridyl)-1,1'-dihydro-4,4'-bipyridine (**3**). After oxidizing **3** in aqueous acid, the resulting solution is heated to afford 4,4'-bipyridine (**1**). This sequence provides a convenient procedure for the synthesis of **1** without simultaneous formation of isomeric side products. The formation of stable (4-pyridyl)viologen cation radicals (**7**) and salts (**6**) from oxidation of **3** is described.

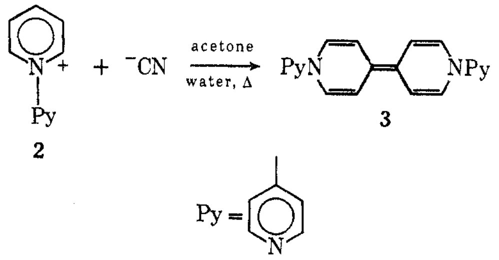
In recent years 4,4'-bipyridine (**1**) has found increasing importance in both organic and organometallic chemistry.[2-4] The synthesis of **1** is usually accomplished by the dimerization of pyridine by metals in inert solvents.[5a] Unfortunately, this procedure suffers from either low yields[5b] or formation of 2,4'- and 2,2'-bipyridine as side products.[5c] In our studies of the cyanide ion induced dimerization of pyridinium salts,[6] we have developed a new, convenient synthesis of **1** which avoids the problem of isomeric side products.

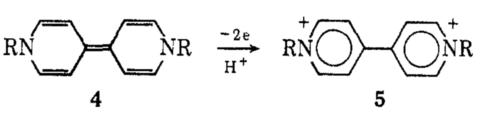


1

When 1-(4-pyridyl)pyridinium chloride (**2**) and sodium cyanide were heated in aqueous acetone (eq 1), a 53% yield of 1,1'-di(4-pyridyl)-1,1'-dihydro-$\Delta^{4,4'}$-bipyridine (**3**) was obtained. Previous work[7] had shown that related dihydrobipyridines (**4**) are readily oxidized to 4,4'-bipyridinium (viologen) salts (**5**) in acidic solution (*vide infra*). Since it is known that acidic solutions of **2** are susceptible to hydrolysis to afford 4-pyridone and pyridine,[8] it was probable that a similar reaction of (4-pyridyl)viologen (**6**) would give **1**.







R = alkyl, Ph

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[1] (a) Abstracted from the Ph.D. dissertation of R. H. Reuss, Drexel University, 1972. (b) NSF Predoctoral Fellow, 1968–1971. (c) Address all correspondence to this author at Department of Chemistry, Virginia Commonwealth University, Academic Center, Richmond, Va. 23220.

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[3] (a) T. R. Musgrove and C. E. Mattson, *Inorg. Chem.*, **7**, 1433 (1968); (b) R. C. Poller and D. L. Toley, *J. Chem. Soc. A*, 1578 (1967); (c) N. I. Lobanov and A. I. Vlasov, *Russ. J. Inorg. Chem.*, **13**, 395 (1968).

[4] (a) *U. S. Govt. Res. Rep.*, **39** (16), 69 (1964); (b) P. E. Wei, A. H. Corwin, and R. Arellano, *J. Org. Chem.*, **27**, 3344 (1962); (c) J. H. Wang and W. S. Brinigar, *Proc. Nat. Acad. Sci. U. S.*, **46**, 958 (1960); (d) J. R. Barber, and E. S. Gould, *J. Amer. Chem. Soc.*, **93**, 4045 (1971).

[5] (a) C. D. Schmulbach, C. C. Hinckley, and D. Wasmund, *J. Amer. Chem. Soc.*, **90**, 6600 (1968). (b) Imperial Chemical Industries Limited, Netherlands Patent 6,603,415; *Chem. Abstr.*, **66**, 28674 (1967). (c) R. Setton and L. Hackspill, *C. R. Acad. Sci.*, **244**, 1205 (1957).

[6] (a) L. J. Winters, N. G. Smith, and M. I. Cohen, *Chem. Commun.*, 642 (1970); (b) L. J. Winters, A. L. Borror, and N. G. Smith, *Tetrahedron Lett.*, 2313 (1967).

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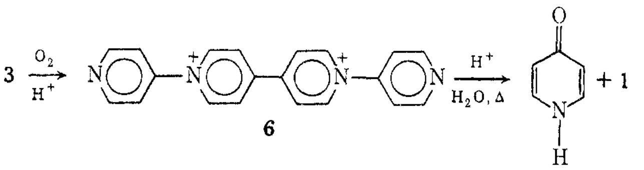
[8] R. F. Evans and H. C. Brown, *J. Org. Chem.*, **27**, 1329 (1962).

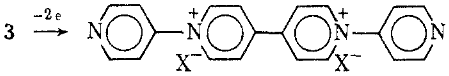
Thus, **3** was oxidized to **6** in acidic media and the resulting solution was heated under reflux to afford **1**.



6

Reaction in aqueous hydrochloric acid afforded a 91% yield of **1**. However, a trace of 4-chloropyridine, which is known to polymerize in the solid state,[9] appeared to contaminate the product, since particles of black solid were noted after standing for several days. While use of the stoichiometric amount of nitric acid afforded **1** in 60% yield, excess nitric acid yielded only 33%. The reaction is carried out most conveniently by the aerobic oxidation of **3** to **6** in excess aqueous sulfuric acid, which afforded a 74% yield of **1**.

If desired, it is possible to isolate viologen **6** by oxidation of **3** with aqueous acid and oxygen (E = 1.23 V).[10] Aqueous nitric acid afforded a 75% yield of (4-pyridyl)viologen nitrate dihydronitrate (**6a**), while

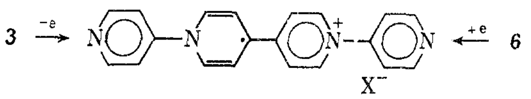


6a, $X = NO_3 \cdot 2HNO_3$
b, $X = Cl$
c, $X = ClO_4 \cdot HClO_4$
d, $X = BPh_4$
e, $X = Br$

hydrochloric acid gave a 52% yield of the chloride salt **6b**. Perchloric acid yielded 75% of a product which contained mostly (4-pyridyl)viologen perchlorate hydroperchlorate (**6c**). The elemental analysis indicated that a small amount of chloride ion was present, which was probably generated by the reduction of perchlorate (1.37 V)[10] by **3**. That the product was predominantly **6c** was demonstrated by the near-quantitative (95%) conversion to the tetraphenylborate salt **6d**.

While the oxidation of **3** could be accomplished readily, certain precautions were necessary. Since base was observed to decompose **6**,[11] it was necessary to either use only the stoichiometric amount of acid, to recover the product from acidic solution, or to cautiously neutralize the excess acid. When iodine or oxygen and hydrochloric (or hydrobromic) acid were used as oxidants, the resulting products tended to decompose in the alcoholic solutions[12] from which they were recrystallized. Metallic oxidizing agents such as Ag^+, Hg^{2+}, and Cu^{2+} could not be used because of the rapid complex formation between **6** and unreacted metal ion, which was demonstrated by both elemental analysis and qualitative tests for the metal ions. However, no further characterization of these complexes was made.

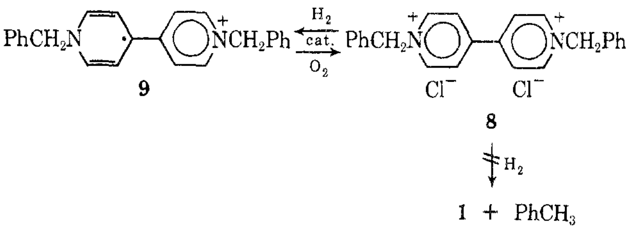
The isolation of the product derived from one-electron oxidation of **3**, (4-pyridyl)viologen cation radical (**7**), was also accomplished. Thus, reaction with bromine afforded bromide **7a** in 99% yield. The structure of **7a** was confirmed by oxidation to the known viologen bromide **6e**.[6b] Alternatively, the viologen salt **6a** was reduced with magnesium to the cation radical nitrate **7b** in 78% yield. While solid samples of **7** were quite



7a, $X = Br$
b, $X = NO_3$

stable, showing no evidence of oxidation even after several weeks, solutions of **7** were rapidly air oxidized.

The successful preparation of **1** from viologen **6** prompted us to attempt the hydrogenolysis of benzylviologen chloride (**8**) to **1**. When solutions of **8** were



9 **8**

exposed to a hydrogen atmosphere over platinum or palladium catalysts, a blue solution was observed. Exposure to oxygen caused immediate decolorization and the viologen was recovered unchanged. This behavior is characteristic of the benzylviologen cation radical (**9**).[6a]

Experimental Section[13]

1,1'-Di(4-pyridyl)-1,1'-dihydro-$\Delta^{4,4'}$-bipyridine (3).—A solution of 8.92 g (4.6 mmol) of **2** hydrochloride (Aldrich) in 60 ml of water was neutralized (pH 7–8) with concentrated ammonium hydroxide. The solution was transferred with filtration[14] into a 300-ml round-botton flask equipped with a long neck (30 cm × 5 mm). After nitrogen was passed through the solution for 10 min, 3.38 g (6.9 mmol) of sodium cyanide in 20 ml of water, 60 ml of acetone, and a small stirring bar were added. The flask was sealed with a gas–oxygen torch and heated at 90° with stirring. After 42 hr the flask was cooled to room temperature and the red precipitate was collected by suction filtration. The solid was washed with water and acetone and dried under vacuum to afford 3.22 g (53%) of **3**: slow decomposition was observed above 130°; ir (KBr) 1660 cm^{-1} (dihydrobipyridine[7]); mass spectrum (70 eV) m/e (rel intensity) 312 (M$^+$, 74), 234 (100), 157 (17), 156 (16), 78 (28), 51 (51).

Anal. Calcd for $C_{20}H_{16}N_4$: C, 76.92; H, 5.13; N, 17.95. Found: C, 76.61; H, 5.22; N, 17.67.

4,4'-Bipyridine (1).—To a solution of 45 ml of water and 5 ml (excess) of concentrated sulfuric acid was added 1.00 g (3.2 mmol) of **3**. After oxygen was passed through the stirred mixture for 6 hr and the resulting solution was heated under reflux for

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(9) A. A. Berlin and E. F. Razvodovskii, *Proc. Acad. Sci. USSR*, **140**, 925 (1961).

(10) "Handbook of Chemistry and Physics," 48th ed, R. C. Weast, Ed., Chemical Rubber Co., Cleveland, Ohio, 1967, p D-86.

(11) It is well known that bases decompose pyridinium salts; see E. M. Kosower, "Molecular Biochemistry," McGraw-Hill, New York, N. Y., 1962, pp 116–219.

(12) Alcohols have been reported to reduce methylviologen: J. A. Farrington, A. Ledwith, and M. F. Stam, *Chem. Commun.*, 259 (1969).

(13) All melting points were determined using a Büchi capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer. Ultraviolet spectra were determined on a Perkin-Elmer 402 spectrophotometer. Nuclear magnetic resonance spectra were recorded using a Varian A-60A spectrometer. The chemical shifts were recorded relative to TMS or DSS as internal standards. The mass spectra were obtained with a RMU-6 mass spectrometer. Elemental microanalyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, West Germany.

(14) Neutral solutions of **2** precipitated a red-brown sludge of unknown composition.

40 hr, the reaction was cooled and made basic. Extraction with ether afforded 0.37 g (74%) of **1**. The melting point and spectral data were identical with those of commerical samples.

Preparation of (4-Pyridyl)viologen Salts. A. (4-Pyridyl)viologen Nitrate Dihydronitrate (6a).—To 50 ml of water containing 0.7 ml (11 mmol) of concentrated nitric acid was added 0.84 g (2.7 mmol) of **3**. Oxygen was passed through the stirred solution for 5 hr. The solution was concentrated under vacuum to give a brown oil which was recrystallized from water–acetone to yield 0.76 g (52%) of **6a**. The mother solution was concentrated to give a second crop of 0.36 g (24%): mp 178° dec; uv max (H_2O) 286 nm (ϵ 24,300); ir (KBr) 1625 cm^{-1} (viologen salts[7]); nmr (D_2O) τ 1.35 (m, 4), 0.65 (m, 8), 0.15 (m, 4).

Anal. Calcd for $C_{20}H_{18}N_8O_{12}$: C, 42.71; H, 3.23; N, 19.92. Found: C, 42.60; H, 3.41; N, 19.83.

B. (4-Pyridyl)viologen Chloride (6b).—Oxygen was passed through a solution of 0.60 g (6 mmol) of 37% hydrochloric acid and 0.93 g (3 mmol) of **3** in 150 ml of water and 300 ml of acetonitrile. After 24 hr the solution was concentrated under vacuum and the residue was dissolved in 20–30 ml of hot ethanol and 2–3 ml of water. Acetone (10 ml) was added and ether was added to the cloud point. After cooling, 0.60 g (52%) of brown needles of **6b** were obtained: mp 270° dec; ir (KBr) identical with that of **6e** (*vide infra*); uv max (H_2O) 287 nm (ϵ 33,200).

C. (4-Pyridyl)viologen Perchlorate Hydroperchlorate (6c) and Tetraphenylborate (6d)—To 140 ml of 50% aqueous nitromethane containing 10 g (70 mmol) of 70% perchloric acid was added 5.18 g of **3**. Oxygen was passed through the stirred solution for 20 hr. After the solution was concentrated and the resulting water-insoluble precipitate was dried under vacuum, 9.20 g (90%) of crude product was isolated. Recrystallization from water gave 7.65 g (75%) of **6c**, ir (KBr) 1615 cm^{-1} (viologen salts[7]).

Anal. Calcd for $C_{20}H_{17}Cl_3N_4O_{12}$: C, 39.27; H, 2.80; N, 91.7. Calcd for $C_{20}H_{17}Cl_3N_4O_{11}$: C, 40.32; H, 2.88; N, 9.47. Found: C, 40.07; H, 3.28; N, 9.43.

When 1.10 g (2 mmol, assuming a molecular formula of $C_{20}H_{17}Cl_3N_4O_{11}$) of **6c** was dissolved in 60 ml of water at 45°, neutralized with sodium bicarbonate, and treated with 1.50 g (4.37 mmol) of sodium tetraphenylborate in 10 ml of water, 1.80 g (95%) of **6d** was obtained, mp 205–207° dec, ir (KBr) 1630 cm^{-1} (viologen salts[7]).

Anal. Calcd for $C_{68}H_{56}B_2N_4$: C, 85.89; H, 5.94; N, 5.89. Found: C, 85.72; H, 5.96; N, 6.11.

D. (4-Pyridyl)viologen Bromide (6e).—Water (20 ml) containing 0.16 g of 50% aqueous hydrogen bromide (1 mmol) was added to 0.39 g (1 mmol) of (4-pyridyl)viologen cation radical bromide (**7a**) and oxygen was passed through the solution overnight. After concentrating to 5–10 ml under vacuum, a few milliliters of ethanol was added, the solution was warmed, and acetone was added to the cloud point. A small amount of black material was removed by filtration. Additional acetone was added to the warmed solution to yield 0.15 g (32%) of **6e**. Concentration of the filtrate afforded another 0.06 g (13%). The ir spectrum was identical with that of an independently prepared sample.[6b]

When 0.19 g (0.49 mmol) of **7a** and 0.08 g (0.50 mmol) of acid were treated as above and filtered to removed insoluble matter, addition of 0.25 g of sodium tetraphenylborate in 10 ml of water afforded 0.37 g (80%) of **6d**.

Preparation of (4-Pyridyl)viologen Cation Radical Salts. A. (4-Pyridyl)viologen Cation Radical Bromide (7a).—To 50 ml of acetonitrile which had been outgassed with nitrogen for 10 min was added 0.16 g (1 mmol) of bromine and 0.63 g (2 mmol) of **3**. The mixture was stirred under nitrogen for 10 min and chilled in the refrigerator for 15 min, and the blue precipitate was collected by suction filtration. Drying under vacuum gave 0.78 g (99%) of **7a**, mp 200° dec, ir (KBr) 1640, 1580 cm^{-1}.

Anal. Calcd for $C_{20}H_{16}BrN_4$: C, 61.24; H, 4.11; N, 14.28. Found: C, 61.03; H, 4.24; N, 14.28.

B. (4-Pyridyl)viologen Cation Radical Nitrate (7b).—Potassium carbonate (0.12 g, 0.84 mmol) and 0.47 g (0.84 mmol) of viologen nitrate **6a** were dissolved in 20 ml of water. The solution was outgassed with nitrogen for 20 min and 0.10 g (0.41 mmol) of magnesium was added. After stirring under nitrogen for 2 hr, the resulting blue solid was collected by suction filtration and dried under vacuum to afford 0.24 g (78%) of **7b**, mp 220° dec, ir (KBr) 1640, 1580 cm^{-1}.

Anal. Calcd for $C_{20}H_{16}N_5O_3$: C, 64.16; H, 4.31; N, 18.71. Found: C, 63.93; H, 4.51; N, 18.47.

Registry No.—**1**, 553-26-4; **2**, 22752-98-3; **3**, 41764-90-3; **6a**, 41764-91-4; **6b**, 41764-92-5; **6c**, 41764-93-6; **6d**, 41766-78-3; **7a**, 41764-94-7; **7b**, 41764-95-8.

Carbon–Nitrogen *vs.* Nitrogen–Nitrogen Bond Formation in Nitrenoid Cyclization Reactions. Pyrolysis of 3-Azido-4-(2-pyridyl)carbostyrils

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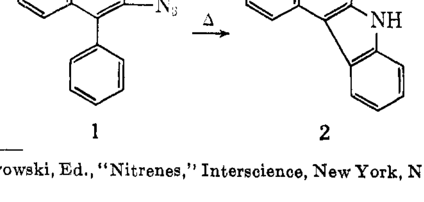
Received July 20, 1973

Pyrolysis of 3-azido-4-(2-pyridyl)carbostyrils **7** and **10** afforded mixtures of isomeric tetracyclic products resulting from nitrenoid cyclization reactions. Pyrido[2′,3′:3,2]pyrolo[5,4-*c*]quinolones **9** and **11**, in which the cyclization involved nitrogen–carbon bond formation, were isolated in amounts comparable to those of the pyrido[1′,2′:2,3]pyrazolo[5,4-*c*]quinolones **8** and **12a**, in which the cyclization involved nitrogen–nitrogen bond formation.

Nitrenoid cyclization reactions constitute an important class of reactions for the synthesis of novel heterocyclic compounds.[1] The pyrolysis of 3-azido-4-phenylcarbostyril (**1**) affords indolo[2,3-*c*]quinolone **2** in high yield.[2] In the course of this investigation, we studied the pyrolysis of 3-azido-4-(2-pyridyl)carbostyrils **7**. Related nitrenoid cyclizations of 2-(2-azidophenyl)pyridine,[3] 2-(2-nitrosophenyl)pyridine,[4] and 2-(2-nitrophenyl)pyridine,[3,5] compounds of type **3**, were reported to yield almost exclusively the pyrido[1,2-*b*]indazole (**4**) and not the isomeric δ-carboline **5**.



1 **2**

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(2) (a) J. B. Petersen and K. H. Lakowitz, *Acta Chem. Scand.*, **23**, 971 (1969). (b) We have observed this transformation independently.

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