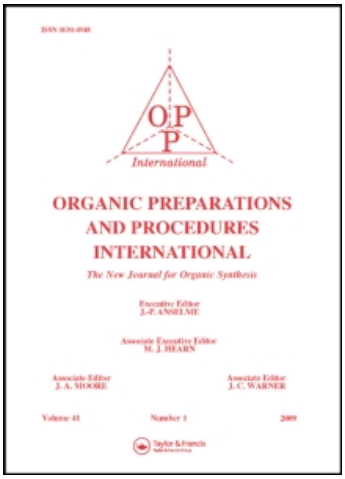


Organic Preparations and Procedures International

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

MONOSUBSTITUTED 2,2'-BIPYRIDINES

Milon Sprecher[a]; Ronald Breslow[b]; Orly Uziel[a]; Todd M. Link[b]
[a] Department of Chemistry, Bar-Ilan University, Ramat Gan, Israel [b] Department of Chemistry, Columbia University, New York, NY, USA

To cite this Article Sprecher, Milon , Breslow, Ronald , Uziel, Orly and Link, Todd M.(1994) 'MONOSUBSTITUTED 2,2'-BIPYRIDINES', Organic Preparations and Procedures International, 26: 6, 696 — 701
To link to this Article: DOI: 10.1080/00304949409458172
URL: http://dx.doi.org/10.1080/00304949409458172

MONOSUBSTITUTED 2,2'-BIPYRIDINES

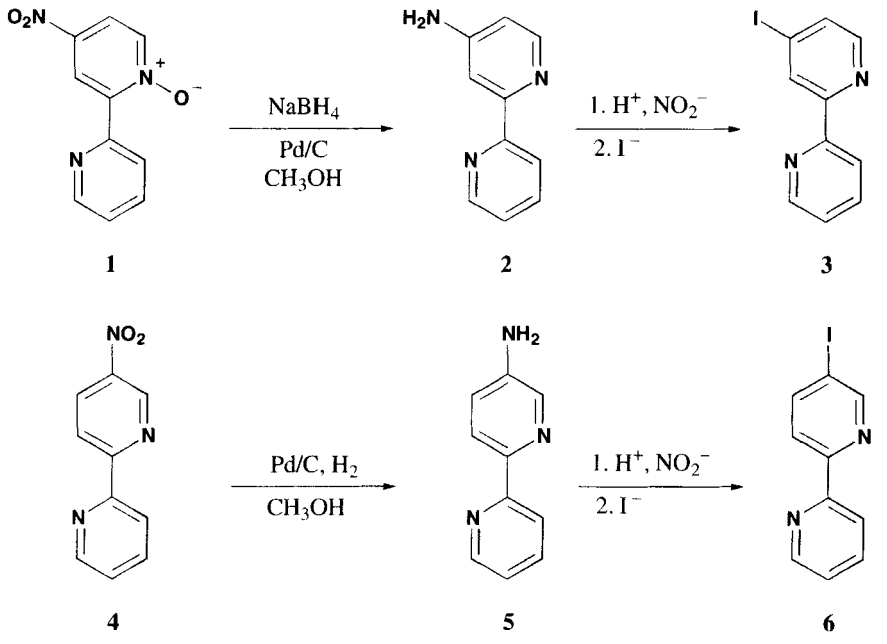
Submitted by (06/13/94) Milon Sprecher*†, Ronald Breslow‡, Orly Uziel† and Todd M. Link‡

† *Department of Chemistry, Bar-Ilan University, Ramat Gan 52900, ISRAEL*
‡ *Department of Chemistry, Columbia University, New York, NY 10027, USA*

The propensity of 2,2'-bipyridine and its derivatives to chelate sundry metal ions has resulted in their now firmly established importance in almost all branches of chemistry both as research tools and in practical applications.[1] Though numerous synthetic pathways have been developed for the preparation of symmetrically substituted 2,2'-bipyridine systems, the established routes available for the preparation of unsymmetrically substituted ones are rare. Specifically, we were interested in 4- and 5-monosubstituted 2,2-bipyridines. The amino and the iodo compounds are clearly the most versatile intermediates for possible conversion to a plethora of other derivatives, including linkage of aliphatic chains and aromatic rings. Gattermann-Sandmeyer chemistry is in principle applicable to the amines, and free radical chemistry, modern organometallic methodology and nucleophilic displacement to the iodides. Procedures for the syntheses and isolation of four compounds are reported herewith.

The reduction of 4-nitro-2,2'-bipyridyl-1-oxide (**1**), prepared by a modification of the method of Jones *et al.*,[2] to 4-amino-2,2'-bipyridyl (**2**), is a feat which has been reported to have been achieved only after many unsuccessful attempts.[2] Unfortunately, the details of the successful experimental procedure for this reduction were incorrectly recorded.[2,3] A protocol by which **2** was obtained in 95% yield is given in the Experimental Section. The further tandem conversion of **2** to a diazonium salt and to 4-iodo-2,2'-bipyridine (**3**), involves a 4-aminopyridine system. The diazotization and further conversion of such and similar systems is frequently problematic and have been the subject of study.[4,5] Two problems have been identified. Diazotization has been found to be reversible, and in some cases, proceeds to only moderate equilibrium concentrations of diazonium cation.[4] Secondly, the nucleophilic displacement of the diazonium group by the solvent (water) is facile and yields 4-pyridones as undesired by-products.[5] In the present work, spectral (UV) monitoring of the reaction of **2** showed that in dilute acid (0.33 N H_2SO_4), both the formation of the diazonium cation and its reaction with the solvent water to give 2-(2'-pyridyl)-4-pyridone are rapid even at 0°. This hydrolysis was the principal culprit for low yields of **3** when extended diazotation periods were used. Reducing the activity of water by increasing the concentration of sulfuric acid, completing nitrite addition in 120 seconds at 0°, then adding KI after a further 60 seconds, made it possible to obtain **3** in satisfactory and reproducible yields (73-80%).

5-Nitro-2,2'-bipyridine (**4**), prepared by the novel method of Tohda *et al.*,[6] was converted, after chromatographic purification, to 5-amino-2,2'-bipyridine (**5**) by catalytic reduction (H_2, Pd/C). Alternatively, **5** may be prepared from 5-carboxy-2,2'-bipyridine[7] by a variation of the Curtius rearrangement using diphenylphosphoryl azide and triethylamine in ethanol solution,[8]



followed by *in situ* hydrolysis of the initially formed ethyl carbamate. Diazotization of **5** with its amino group *meta* to the ring nitrogen, was uneventful and did not require very short reaction periods before addition of iodide to give good yields of 5-iodo-2,2'-bipyridine (**6**).

EXPERIMENTAL SECTION

Melting points were determined in capillaries using a Thomas-Hoover instrument and are uncorrected. NMR spectra were determined on $CDCl_3$ solutions using either a Varian VXR or a Bruker AM spectrometer in the FT mode operating at the frequency stated. Chemical shifts (δ) are reported in ppm downfield from internal tetramethylsilane, and coupling constants (J) in Hz. Mass spectra were determined using a Finnigan-4000 or a VG-7070 EQ mass spectrometer in either the electron impact (EI) or the chemical ionization (CI) mode and are reported as m/z (Relative Intensity). IR spectra were recorded using KBr pellets and FTIR spectrometers, and are reported in cm^{-1} (qualitative relative intensity). UV spectra were recorded on a Varian DMS-100 spectrometer. Elemental analyses were performed by the Analytical Laboratory of the Hebrew University and by the Galbraith Laboratory.

4-Nitro-2,2'-bipyridine-1-oxide (**1**).- As noted by Moran *et al.*,[9] the procedure of Jones[2] is profitably modified by carrying out the oxidation of 2,2'-bipyridine in acetic acid with only a slight excess of H_2O_2, but at 70°. Residual peroxide was destroyed by the dropwise addition of hydrazine hydrate (100%). Acetic acid and water were thoroughly removed under vacuum and the residue[10] was nitrated as described by Jones.[2] The crude product is a mixture of **1** and 4,4'-dinitro-2,2'-bipyridine from which **1** is very effectively isolated in 40% overall yield by extraction with 2 or 3 portions of hot chloroform (rather than ethanol[2]). Filtration and evaporation of the extract after cooling, yielded essentially pure **1**, mp. 184-186°, lit.[2] mp. 183-185°. ^1H NMR (200 MHz, $CDCl_3$): δ 7.44 (ddd, $H_{5'}$, $J_{5',4'}$ = 7.8, $J_{5',6'}$ =

4.8, $J_{5',3'}$ = 1.2), 7.88 (ddd, $H_{4'}$, $J_{4',3'}$ = 7.8, $J_{4',5'}$ = 7.8, $J_{4',6'}$ = 2), 8.07 (dd, H_5, $J_{5,6}$ = 7.2, $J_{5,3}$ = 3.4), 8.36 (dd, H_6, $J_{6,5}$ = 7.2, $J_{6,3}$ = 0.5), 8.80 (ddd, $H_{6'}$, $J_{6',5'}$ = 4.8, $J_{6',4'}$ = 2, $J_{6',3'}$ = 1), 8.89 (ddd, $H_{3'}$, $J_{3',4'}$ = 7.8, $J_{3',5'}$ = 1.2, $J_{3',6'}$ = 1), 9.17 (dd, H_3, $J_{3,5}$ = 3.4, $J_{3,6}$ = 0.5). Mass spectrum: (EI; 62 eV) m/z 218 (21.1%), 217 (M^+, 100%), 201 ([M-O]$^+$, 5.8%), 172 (6.3%), 171 ([M-NO_2]$^+$, 48.9%), 155 ([M-NO_2-O]$^+$, 12.7%), 144 (11.7%), 143 ([M-NO_2-CO]$^+$, 45.4%), 142 (10.8%), 128 ([M-NO_2-HCNO]$^+$, 12.5%), 116 (12.4%), 78 ([C_5H_4N]$^+$, 2%); (CI; CH_4) m/z 219 (29.9%), 218 (MH^+, 100%), 217 (17.7%), 202 (3.9%).

4-Amino-2,2'-bipyridine (2).- A mixture of 1.1 g (5.1 mmol) of **1**, 200 mL methanol and 0.23 g 10% Pd/C was cooled in an ice bath and vigorously stirred under an inert atmosphere. Powdered sodium borohydride (2.5 g, 66 mmol) was added in small portions, and stirring and cooling was continued until gas evolution ceased; the dissolution of suspended **1** was complete during the course of the reaction. The catalyst was removed by gravity filtration and the methanol evaporated under reduced pressure. Water (60 mL) was added and the aqueous solution was thoroughly extracted with five 50 mL portions of methylene chloride. The combined organic extract was dried (Na_2SO_4) and evaporated to yield a white mass which was further dried in vacuum over P_2O_5. The residue was boiled for 45 minutes with 200 mL cyclohexane, filtered hot, and the solid which was collected was boiled again with an additional portion (25 mL) of cyclohexane to essentially complete dissolution . After removal of a very small sticky residue by filtration, the combined cyclohexane extracts were cooled, and slowly deposited a voluminous white precipitate of **2**. A second crop was obtained by concentration of the mother liquor. NMR showed that cyclohexane was occluded in the precipitate. It had to be dried thoroughly in an Abderhalden pistol. The total yield of needle-like colorless crystals was 0.83 g (95%), mp. 127-129.5°, lit.[2] mp. 128-129°. ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.24 (br, $N\underline{H}_2$), 6.55 (dd, H_5, $J_{5,6}$ = 5.4, $J_{5,3}$ = 2.4), 7.28 (ddd, $H_{5'}$, $J_{5',4'}$ = 7.7, $J_{5',6'}$ = 4.8, $J_{5',3'}$ = 1.2), 7.67 (d, H_3, $J_{3,5}$ = 2.4), 7.79 (ddd, $H_{4'}$, $J_{4',3'}$ = 8.0, $J_{4',5'}$ = 7.7, $J_{4',6'}$ = 1.8), 8.31 (d, H_6, $J_{6,5}$ = 5.4), 8.35 (ddd, $H_{3'}$, $J_{3',4'}$ = 8.0, $J_{3',5'}$ =1.2, $J_{3',6'}$ = 0.9), 8.64 (ddd, $H_{6'}$, $J_{6',5'}$ = 4.8, $J_{6',4'}$ = 1.8, $J_{6',3'}$ = 0.9). UV (95% ethanol): λ_{max} 268 nm (24200), 243 nm (25450). Mass spectrum: (EI; 62 eV) m/z 172 (12%), 171 (M^+, 100%), 170 (17%), 155 ([M-NH_2]$^+$, 3%), 145 ([M-CN]$^+$, 12%), 144 ([M-HCN]$^+$, 33%), 143 ([M-H_2CN]$^+$, 39%), 117 (7%), 116 (5%), 93 ([$C_5H_5N_2$]$^+$, 6%), 78 ([C_5H_4N]$^+$, 11%).

4-Iodo-2,2'-bipyridine (3).- A precooled solution (< 0°) of 1.6 g (23.2 mmol) of $NaNO_2$ in 2.5 mL water was added dropwise over a period of 120 seconds to a vigorously stirred solution of 1 g (5.8 mmol) of **2** in 20 mL of 7.5 M aqueous H_2SO_4 at -5 to -10°. After a further 60 seconds, a cold saturated aqueous solution containing 12 g (166 mmol) of KI was added. A brown precipitate appeared. The ice-salt bath was removed and stirring was continued until ambient temperature was reached. The reaction mixture was cautiously neutralized to pH 8 using first NaOH and then Na_2CO_3 solutions, and then vigorously extracted with 6 x 150 mL portions of CH_2Cl_2 until the brown solid had dissolved. The combined CH_2Cl_2 extracts were washed successively with 10 mL each of saturated $NaHSO_3$ solution to remove color and saturated EDTA;2Na^+ solution, and 40 mL of water. After drying (Na_2SO_4) and removal of the solvent, the crude solid product (1.4 g) was found by NMR to contain

–95 mol % **3** and ≤5 % 2-(2'-pyridyl)-4-pyridone. The latter is easily removed by crystallization from a minimum of methanol. Recrystallization from hexane with hot filtration yielded 1.2 g (73 % yield) of **3**, mp. 89-90°. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33 (ddd, $H_{5'}$, $J_{5',4'}$ = 7.5, $J_{5',6'}$ = 4.8, $J_{5',3'}$ = 1.2), 7.68 (dd, H_5, $J_{5,6}$ = 5.1, $J_{5,3}$ = 1.7), 7.82 (ddd, $H_{4'}$, $J_{4',3'}$ = 8.0, $J_{4',5'}$ = 7.5, $J_{4',6'}$ = 1.8), 8.31 (dd, H_6, $J_{6,5}$ = 5.1, $J_{6,3}$ = 0.6), 8.37 (overlapping ddd, $H_{3'}$, $J_{3',4'}$ = 8.0, $J_{3',5'}$ = 1.2, $J_{3',6'}$ = 0.9), 8.68 (ddd, $H_{6'}$, $J_{6',5'}$ = 4.8, $J_{6',4'}$ = 1.8, $J_{6',3'}$ = 0.9), 8.83 (dd, H_3, $J_{3,5}$ = 1.7, $J_{3,6}$ = 0.6). ^{13}C NMR (75.4 MHz; $CDCl_3$): δ 106.50, 121.30, 124.18, 130.43, 132.76, 137.01, 149.19, 149.35, 154.66, 156.64. UV (hexane): $_{max}$ 283 nm (14,600), 238 nm (23,100). IR (KBr): 1585 (m), 1567 (s), 1554 (s), 1532 (s), 1502 (sh), 1472 (w), 1425 (sh), 1378 (s), 1307 (w), 1274 (m), 1264 (w), 1240 (w), 1222 (w), 1156 (w), 1103 (w), 1093 (w), 1082 (w), 1064 (m), 993 (m), 962 (vw), 887 (w), 827 (m), 787 (s), 745 (m), 728 (w), 670 (s), 659 (m), 618 cm^{-1} (m). Mass spectrum: (EI; 62 eV) m/z 282 (M^+, 100%), 155 ([M-I]$^+$, 54.4%), 128 ([M-I-HCN]$^+$, 36%), 78 ([C_5H_4N]$^+$, 12%).

Anal. Calcd. for $C_{10}H_7IN_2$: C, 42.58; H, 2.50; N, 9.93; I, 44.99
Found: C, 42.65; H, 2.42; N, 9.71; I, 45.05

5-Nitro-2,2'-bipyridine (4).- The crude product (reported 72% yield)[6] was purified by flash-chromatography on silica with toluene/chloroform/triethyl amine (82/15/3, v/v; tlc 7/2/1) as eluent, followed by recrystallization from heptane to give a 58% yield of **4**, mp. 169-171°, lit.[6] mp. 173-174°. ^{1}H NMR (200 MHz; $CDCl_3$): δ 7.41 (ddd, $H_{5'}$, $J_{5',4'}$ = 7.6, $J_{5',6'}$ = 4.8, $J_{5',3'}$ = 1.2), 7.89 (overlapping ddd, $H_{4'}$, $J_{4',3'}$ = 8.0, $J_{4',5'}$ = 7.6, $J_{4',6'}$ = 1.7), 8.52 (overlapping ddd, $H_{3'}$, $J_{3',4'}$ = 8.0, $J_{3',5'}$ = 1.2, $J_{3',6'}$ = 0.8), 8.58 (dd, H_4, $J_{4,3}$ = 8.8, $J_{4,6}$ = 2.6), 8.66 (dd, H_3, $J_{3,4}$ = 8.8, $J_{3,6}$ = 0.8), 8.74 (ddd, $H_{6'}$, $J_{6',5'}$ = 4.8, $J_{6',4'}$ = 1.7, $J_{6',3'}$ = 0.8), 9.48 (dd, H_6, $J_{6,4}$ = 2.6, $J_{6,3}$ = 0.8). ^{13}C NMR (75.469 MHz; $CDCl_3$): 121.09 ($C_{3'}$), 122.39 (C_3), 125.07 ($C_{5'}$), 131.89 (C_4), 137.17 ($C_{4'}$), 144.15 (C_5), 144.69 (C_6), 149.55 ($C_{6'}$), 153.91 ($C_{2'}$), 160.92 (C_2). UV (95% ethanol): $_{max}$ 304.6 nm (18,170). IR (KBr): 1597 (m), 1576 (s), 1570 (s), 1506 (s), 1449 (s), 1435 (s), 1344 (vs), 1326 (s), 1304 (m), 1245 (m), 1224 (m), 1195 (sh), 1145 (w), 1126 (w), 1106 (w), 1090 (w), 1052 (w), 1032 (w), 1005 (w), 985 (w), 946 (w), 844 (m), 801 (m), 767 (m), 759 (s), 625 (w), 605 (w), 527 (w), 463 cm^{-1} (w). Mass spectrum: (EI; 62 eV) m/z 202 (30.0%), 201 (M^+, 100%), 185 ([M-O]$^+$, 5.6%), 156 (7.2%), 155 ([M-NO_2]$^+$, 69.8%), 128 ([M-NO_2-HCN]$^+$, 28.3%), 84 (10.1%), 78 (75.5%).

5-Amino-2,2'-bipyridine (5). Method a.- Catalytic reduction of **4** (0.456 g) in methanol solution (250 mL) was carried out at ambient temperature and atmospheric pressure using 0.08 g 10% Pd/C. After filtration, evaporation of solvent, and recrystallization of residue from a minimum of toluene, 0.312 g (80%) of **5** were obtained, mp. 136°. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.63 (b, NH_2), 7.08 (dd, H_4, $J_{4,3}$ = 8.5, $J_{4,6}$ = 2.9), 7.20 (ddd, $H_{5'}$, $J_{5',4'}$ = 7.5, $J_{5',6'}$ = 4.9, $J_{5',3'}$ = 1.2), 7.748 (ddd, $H_{4'}$, $J_{4',3'}$ = 8.0, $J_{4',5'}$ = 7.5, $J_{4',6'}$ = 1.8), 8.14 (dd, H_6, $J_{6,4}$ = 2.9, $J_{6,3}$ = 0.7), 8.18 (dd, H_3, $J_{3,4}$ = 8.5, $J_{3,6}$ = 0.7), 8.23 (overlapping ddd, $H_{3'}$, $J_{3',4'}$ = 8.0, $J_{3',5'}$ = 1.2, $J_{3',6'}$ = 0.9), 8.60 (ddd, $H_{6'}$, $J_{6',5'}$ = 4.9, $J_{6',4'}$ = 1.8, $J_{6',3'}$ = 0.9). ^{13}C NMR (75.469 MHz; $CDCl_3$): 121.01 (C_4), 121.71 ($C_{3'}$), 122.09 (C_3), 122.46 ($C_{5'}$), 136.54 (C_6), 136.76 ($C_{4'}$), 142.88 (C_5), 146.96 (C_2), 148.92 ($C_{6'}$), 156.42 ($C_{2'}$). UV (95% ethanol): $_{max}$ 234 nm (790), 270 nm (sh), 314 nm (18,000). IR (KBr): 1648 (m), 1589 (s), 1570 (s), 1494 (s), 1463 (s),

1436 (m), 1409 (w), 1327 (m), 1283 (m), 1242 (w), 1148 (w), 1135 (w), 1109 (m), 1066 (vw), 1051 (vw), 1013 (w), 990 (w), 960 (w), 886 (w), 837 (m), 789 (m), 751 (m), 736 (m), 649 (w), 588 cm^{-1} (m). Mass spectrum: (EI; 62 eV) m/z 172 (11.9%), 171 (M^+, 100%), 170 (21.6%), 144 (9.9), 143 (14.5%), 117 (12.6%), 116 (5.4%), 89 (8.5%), 78 (12.8%). (CI; isobutane) m/z 173 (10.6%), 174 ($[MH]^+$,100%).

Anal. Calcd. for $C_{10}H_9N_3$: C, 70.16; H, 5.30; N, 24.54. Found: C, 70.00; H, 5.53; N, 24.10

Method b.- A solution of 0.258 g (1.29 mmol) 5-caboxy-2,2'-bipyridine,[7] 0.5 mL (2.32 mmol) diphenylphosphoryl azide and 0.325 mL triethylamine in 15 mL of absolute ethanol was heated at reflux overnight. Potassium hydroxide (1.6 g) was added and reflux was resumed till the following morning. The solvent was removed under vacuum at ambient temperature, and the residue was extracted with brine and CH_2Cl_2. The combined dried CH_2Cl_2 extracts were evaporated and the residue was chromatographed on silica using *i*-PrOH(NH_3)/*t*-butylmethylether/CH_2Cl_2 (3/10/87, v/v) as eluent. A 0.13 g (59 %) yield of **5** was isolated. If desired, the intermediate 5-(ethoxycarbonylamido)-2,2'-bipyridine can be isolated from the reaction mixture before KOH addition and purified by preparative TLC on silica (i-PrOH(NH_3)/t-butylmethylether/CH_2Cl_2, 1/2/7). Its ^1H NMR (300 MHz, $CDCl_3$): δ 1.27 (t, J = 7.2), 4.21 (q, J = 7.2), 7.22 (ddd, J = 7.5, 4.8, 1.2), 7.30 (b), 7.74 (td, J = 7.8, 1.8), 8.02 (bd), 8.26 (dt, J = 8.4, 1.2), 8.30 (d, J = 8.4), 8.56 (d, J = 2.4), 8.61 (dq, J = 0.5, 0.9). ^{13}C NMR (75.469 MHz; $CDCl_3$): 14.4, 61.6, 120.6, 121.3, 123.2, 126.3, 135.1, 136.8, 139.5, 149.0, 151.0, 153.5, 155.8.

5-Iodo-2,2'-bipyridine (6).- A precooled solution of 0.175 g (2.54 mmol) $NaNO_2$ in 4 mL water was added dropwise to a stirred solution of 0.312 g (1.82 mmol) of **5** in 16 mL 0.33 N H_2SO_4 at 0°, and the reaction mixture was stirred for an additional half hour at this temperature. A solution of 1 g (6 mmol) of KI in 1 mL water was added, and a brown precipitate appeared. Stirring was continued for 45 min. at ambient temperature followed by 1 hr at 80°. The reaction mixture was cooled, neutralized with $NaHCO_3$ to pH 7, and extracted with five 30 mL portions of CH_2Cl_2 till the solid had dissolved. The combined CH_2Cl_2 solution was extracted with $Na_2S_2O_3$ solution till colorless, washed in succession with 10 mL H_2O, 4 mL saturated aqueous EDTA;2Na+ solution, and 4 mL H_2O and dried over Na_2SO_4. The residue obtained by evaporation of the CH_2Cl_2 was recrystallized from hexane and from methanol with removal of insoluble impurity to yield 0.377 g (73 % yield) of **6**, mp. 104-105°. ^1H NMR (300 MHz, $CDCl_3$): δ 7.32 (ddd, $H_{5'}$, $J_{5',4'} = 7.5$, $J_{5',6'} = 4.8$, $J_{5',3'} = 1.2$), 7.81 (ddd, $H_{4'}$, $J_{4',3'} = 8.0$, $J_{4',5'} = 7.5$, $J_{4',6'} = 1.8$), 8.12 (dd, H_4, $J_{4,3} = 8.4$, $J_{4,6} = 2.1$), 8.20 (dd, H_3, $J_{3,4} = 8.4$, $J_{3,6} = 0.8$), 8.36 (overlapping ddd, $H_{3'}$, $J_{3',4'} = 8.0$, $J_{3',5'} = 1.2$, $J_{3',6'} = 0.9$), 8.663 (ddd, $H_{6'}$, $J_{6',5'} = 4.8$, $J_{6',4'} = 1.8$, $J_{6',3'} = 0.9$), 8.87 (dd, H_6, $J_{6,4} = 2.1$, $J_{6,3} = 0.8$). ^{13}C NMR (75.469 MHz; $CDCl_3$): 93.79 (C_5), 120.89 ($C_{3'}$), 122.75 (C_3), 124.01 ($C_{5'}$), 136.96 ($C_{4'}$), 145.12 (C_4), 149.15 ($C_{6'}$), 154.89 (C_2), 155.12 (C_6), 155.23 ($C_{2'}$). UV (95% ethanol): $_{max}$ 238 nm (sh), 253 nm (7800), 294 nm (17450), 308 nm (sh). IR (KBr): 1654 (w), 1647 (vw), 1633 (w), 1620 (vw), 1614 (w), 1586 (w), 1573 (w), 1559 (m), 1541 (m), 1522 (w), 1506 (w), 1495 (vw), 1489 (vw), 1472 (vw), 1455 (s), 1495 (s), 1418 (w), 1397 (vw), 1386 (vw), 1342 (s), 1312 (w), 1299 (w), 1267 (w), 1257 (w), 1246 (w), 1215 (vw), 1151 (w), 1119 (w), 1091

(m), 1077 (m), 1071 (m), 1056 (w), 1039 (m), 997 (s), 962 (w), 930 (w), 920 (w), 846 (m), 791 (s), 768 (m), 751 (m), 733 cm^{-1}.(m). Mass spectrum: (EI; 62 eV) m/z 283 (10.4%), 282 (M^+, 100%), 155 ($[M-I]^+$, 32.3%), 128 ($[HI]^+$, 15.2%), 78 (40.4%). (CI; isobutane) m/z 284 (7.0%), 283 ($[MH]^+$,100%), 281 (19.5%).

Anal. Calcd. for $C_{10}H_7IN_2$: C, 42.58; H, 2.50; N, 9.93. Found: C, 42.64; H, 2.55; N, 10.10

Acknowledgment.- We thank Dr. E. Nov for technical assistance.

REFERENCES

1. A perusal of the entries in Chemical Abstracts Indices will convince those in doubt.

2. R. A. Jones, B. D. Roney, W. H. F. Sasse and K. O. Wade, *J. Chem. Soc. (B)*, 106 (**1967**).

3. Other references to the reduction of 4-nitro-2,2'-bipyridine-1-oxide are not easily accessible: X. Huang, F. Qu, J. Yao and A. F. Janzen, *Wuji Huaxue Xuebao,* **6**, 408 (1990); *Chem. Abs.*, **116** 33182e (1992); A. P. Lewis, Ph. D. Thesis, University of East Anglia, 1981; N. S. Bazhenova, Yu. V. Kurbatov, O. S. Otroskchenko and A. S. Sadykov, *Tr. Samarkand Univ.*, **206**, 226 (1972); *Chem. Abs.*, **80**, 95678 (1972).

4. H. Diener, B. Güleç, P. Skrabal and H. Zollinger, *Helv. Chim. Acta* **72**, 800 (1989).

5. E. Kalatzis, *J. Chem. Soc. (B)*, 273, 277 (**1967**); E. Kalatzis and C. Mastrokalos, *J. Chem. Soc. Perkin II*, 498 (**1974**).

6. Y. Tohda, M. Eiraku, T. Nakagawa, Y. Usami, M. Ariga, T. Kawashima, K. Tani, H. Watanabe and Y. Mori, *Bull. Chem. Soc. Jpn.*, **63**, 2820 (1990); M. Sprecher, *Chemtracts - Org. Chem.*, **4**, 391 (1991).

7. The 5-carboxy-2,2'-bipyridine was prepared in 53% yield by permanganate oxidation of 5-methyl-2,2'-bipyridine essentially according to the procedure of F. H. Case, *J. Am. Chem. Soc.*, **68**, 2574 (1946).

8. T. Shioiri, K., Ninoomiya, K. and S. Yamada, *J. Am. Chem. Soc.*, **94**, 6203 (1972).

9. D. B. Moran, G. O. Morton and J. D. Albright, *J. Heterocyclic Chem.*, **23**, 1071 (1986).

10. At this point unoxidized 2,2'-bipyridine may, but need not be, recovered for recycling by extraction of the residue with cold hexane. The hexane extract contains the 2,2'-bipyridine and very little monoxide. The indication in the Experimental Section of the article by D. Wenkert and R. B. Woodward, *J. Org. Chem.*, **48**, 283 (1983) that the monoxide is soluble in hexane while the bipyridine is not, is in error.

****