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# Syntheses and Spectroelectrochemistry of 2-Cyanobipyridinium Derivatives

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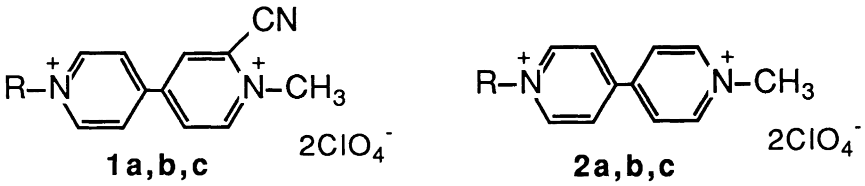
Novel 2-cyanoviologen derivatives having highly anodically shifted reduction potentials were synthesized. The colors of their cation radicals showed a variety of colors as same as those of corresponding viologen derivatives.

Recently, viologens have been investigated towards electrochromic display devices based on their reversible electrochemical behaviors. Their chemical modification shows a wide variety of spectroelectrochemical properties, leading to a multi-color display device.1) The reduction potentials of N-substituted derivatives were located in relatively cathodic region, so that the color disappears immediately by oxidation with oxygen. Both for stabilization of a cation radical and for a save of driving energy in the devices, the viologens with highly anodically shifted redox potential are desirable. For this purpose, the substitution of cyano group on the viologen is considered to be effective. Hüning and Schenk reported that N,N'-dicyano-N,N',4,4'-tetra-hydro-4,4'-bipyridine had the highest anodically shifted reduction potential.2) But N-CN substitution is considered to be chemically unstable. On the other hand, Fielden and Summers reported that 2,2'-dicyano-N,N'-dimethyl-4,4'-bipyridinium salt with chemically stable ring modification had highly anodically shifted reduction potentials.3) However, only methylation is available for N-substitution reaction of the 2,2'-dicyano-4,4'-bipyridine skeleton, because of a steric hindrance and an electron-withdrawing property of cyano substituent. Accordingly, the present idea is that one side of bipyridyl-ring is used to shift the reduction potential to anodic region by cyano substitution and the other ring is used for a variety of colors by the N-substitution. Herein we report syntheses and their spectroelectrochemistry of typical 2-cyanobipyridinium derivatives.

We synthesized three 2-cyanobipyridinium derivatives (N-methyl; N'-methyl, benzyl, phenyl). Figure 1 shows the 2-cyanobipyridinium derivatives(**1a**, **1b**, and **1c**) and their corresponding viologen derivatives(**2a**, **2b**, and **2c**).



**1a,b,c** **2a,b,c**

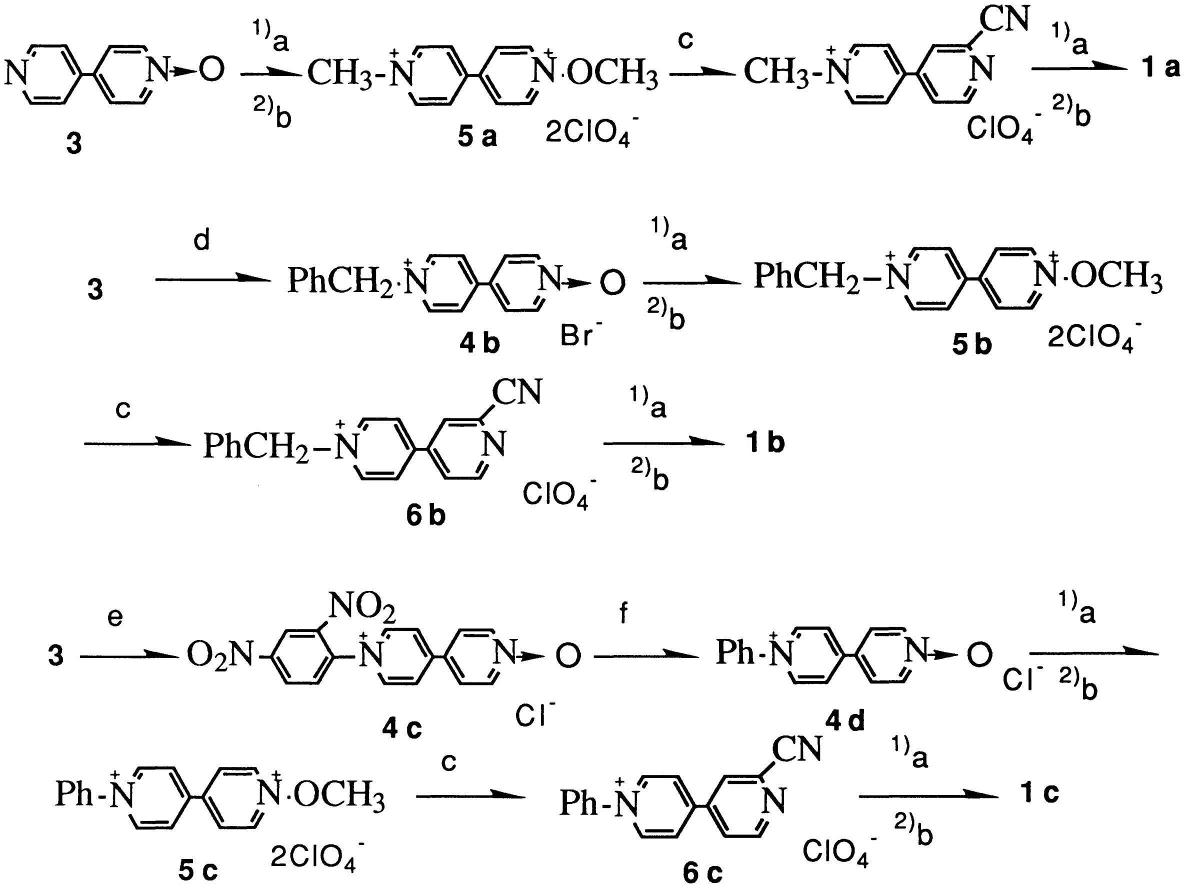
**a**: R=$CH_3$
**b**: R=$PhCH_2$
**c**: R=Ph

Fig. 1. Structures of viologens.

The scheme shows the synthetic pathway. 2-Cyanobipyridine undergoes scarcely N-alkylation except methylation because of steric hindrance and low nucleophilicity at nitrogen. Accordingly prior to cyano-substitution to the pyridine ring, N-substitution to the opposite ring was carried out from 4,4'-bipyridine-N-oxide(**3**). The 2–cyano group was introduced according to the Feely and Beavers procedure.4) The 2-cyanobipyridinium derivatives, **1a**, **1b**, and **1c**, were identified by $^1$H-NMR, IR, and elemental analysis.5) The corresponding viologen derivatives, **2a**, **2b**, and **2c**, were synthesized in the usual way.

Table 1 shows the half wave potentials of these derivatives and the absorption maxima of their cation radicals. Cyclic voltammograms of these derivatives were obtained in DMF containing 0.1 M lithium perchlorate ($LiClO_4$). Three-electrode system, consisting of platinum wire working and counter electrodes, and a saturated calomel electrode(SCE) as reference, was adopted. The first and the second reduction potentials of 2-cyanobipyridinium derivatives differed anodically from those of the corresponding viologens by 230-280 mV, respectively. These highly anodic reduction potentials of 2-cyanobipyridinum derivatives were caused by the strong electron-withdrawing ability of cyano group. Such electron-withdrawing substituents seems effective for preventing disappearance of the colored cation radical with oxygen.

Spectroscopic data of the cation radicals were obtained under the potentiostatic electroreduction by using an indium-tin oxide (ITO) electrode in DMF containing 0.1 M $LiClO_4$. The cation radicals of viologens showed characteristic absorption maxima around 400 nm and at 600 nm. The cation radicals of the present 2-cyanobipyridinium derivatives have almost similar absorption maxima to those of their corresponding viologen derivatives. While the absorption maximum of the cation radical of the N,N'-dicyano-N,N',4,4'-tetrahydro-4,4'-bipyridine is red-shifted in comparison to that of N,N'-dimethyl viologen by 50 nm,2) the cyano substituent on 2-position had small bathochromic effect on the absorption of the cation radicals of the present 2-cyanobipyridinium derivatives. Indeed, the colors of the cation radicals of 2-cyanoviologens were similar to those of the corresponding viologen derivatives: **1a**, blue; **1b**, light blue; and **1c**, green. In conclusion, the present 2-cyano substitution method is a good way for designing the viologens which have highly anodically shifted reduction potentials and show a wide variety of colors of their cation radicals by N-substituents.



a) $(CH_3)_2SO_4$, b) $HClO_4$, c) KCN, d) $PhCH_2Br$, e) 2,4-$(NO_2)_2$-$C_6H_3Cl$, f) $PhNH_2$

Scheme 1. Synthetic scheme.

Table 1. The half-wave potentials and absorption maxima of the cation radicals of 2-cyanobipyridinium derivatives

| R | 1 | | | 2 | | |
|---|---|---|---|---|---|---|
| | $-E^1_{1/2}$ / V | $-E^2_{1/2}$ / V | λ max / nm | $-E^1_{1/2}$ / V | $-E^2_{1/2}$ / V | λ max / nm |
| a $CH_3$ | 0.158 | 0.543 | 400, 612 | 0.423 | 0.804 | 400, 609 |
| b $PhCH_2$- | 0.131 | 0.519 | 403, 622 | 0.394 | 0.801 | 401, 604 |
| c Ph- | 0.086 | 0.407 | 422, 633 | 0.318 | 0.662 | 414, 613 |

## References

1)L. Michaelis and E. S. Hill, *J. Gen. Physiol.*, **16**, 859(1933); A. G. Evans, J. C. Evans, and M. W. Baker, *J. Chem. Soc., Perkin Trans. 2*, **1977**, 1789; J. Brunink, C. G. A. Kregting, and J. J. Ponjee, *J. Electrochem. Soc.*, **124**, 1854(1977); C. L. Bird and A. T. Kuhn, *Chem. Soc. Rev.*, **10**, 49(1981).

2)S. Hünig and W. Schenk, *Liebigs Ann. Chem.*, **1979**, 1523.

3)R. Fielden and L. A. Summers, *Experimentia*, **30**, 843(1974).

4)W. E. Feely and E. M. Beavers, *J. Am. Chem. Soc.*, **81**, 4004(1959).

5)N,N'-Dimethyl-2-cyanobipyridinium bisperchlorate, **1a**; N-Oxide **3** was heated with an excess of dimethylsulfate at 120 °C for 15 min. The cooled mixture was poured into ethanol and then an excess of concd perchloric acid was added. The precipitate of **5a** was collected by filtration. The **5a** was added to potassium cyanide solution at 0 °C and stirred for 1 h. The collected precipitate of **6a** was quaternized and ion-exchanged by a dimethylsulfate and a perchloric acid again. The precipitate was recrystallized from ethanol to afford the desired products **1a** (59% yield) as a white powder: Decomp. 276-288 °C. Anal. Calcd for $C_{13}H_{13}Cl_2N_3O_8$: C, 38.1; H, 3.2; Cl, 17.3; N, 10.3%. Found: C, 38.0; H, 3.1; Cl, 17.2; N, 10.3%. $^1$H-NMR(DMSO-$d_6$) δ ppm 4.45(3H, s), 4.60(3H, s), 8.79(2H, d), 9.07(1H, dd), 9.32(2H, d), 9.53(1H, d), 9.64(1H, d). IR(KBr) 1/λ cm$^{-1}$ 3000, 1633, 1572, 1427, 1356, 1140, 1110, 1090, 853.

N'-Benzyl-N-methyl-2-cyano-4,4'-bipyridinium bisperchlorate, **1b**; A solution of **3** in DMF was heated with an excess benzyl bromide at 60 °C for 12 h. The precipitate of **4b** was collected by filtration. The procedures of cyano substitution and quaternization were the same as those of **1a**. The product **1b** was obtained as a white powder (56% yield): Decomp. 249-251 °C. Anal. Calcd for $C_{19}H_{17}Cl_2N_3O_8$: C, 46.9; H, 3.5; Cl, 14.6; N, 8.6%. Found: C, 46.7; H, 3.3; Cl, 14.5; N, 8.4%. $^1$H-NMR(DMSO-$d_6$) δ ppm 4.60(3H, s), 5.95(2H, s), 7.50(5H, m), 8.81(2H, d), 9.02(1H, dd), 9.49(1H, d), 9.52(2H, d), 9.61(1H, d). IR(KBr) 1/λ cm$^{-1}$ 3000, 1630, 1570, 1421, 1100, 750, 700.

N'-Phenyl-N-methyl-2-cyano-4,4'-bipyridinium bisperchlorate, **1c**; A solution of **3** in DMF was treated with 2,4-dinitrophenylchloride at 60 °C for 12 h. The precipitate of **4c** was collected by filtration and heated with excess of aniline at 100 °C for 10 h to afford **4d**. The procedures of cyano substitution and quaternization were the same as those of **1a**. The desired **1c** was obtained as a slightly brownish powder (23% yield): Decomp. 208-210 °C. Anal. Calcd for $C_{18}H_{15}Cl_2N_3O_8$: C, 45.8; H, 3.2; Cl, 15.0; N, 8.9. %. Found: C, 44.5; H, 3.0; Cl, 15.0; N, 8.3%. $^1$H-NMR(DMSO-$d_6$) δ ppm 4.63(3H), 7.80(3H, m) 7.95(2H, dd), 8.99(2H, d), 9.19(1H, dd), 9.66(1H, d), 9.67(1H, d), 9.72(2H, d). IR(KBr) 1/λ cm$^{-1}$ 3100, 1637, 1588, 1441, 1288, 1090, 773.

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