Tetrahedron Letters,Vol.24,No.1,pp 31-32,1983
Printed in Great Britain

0040-4039/83/010031-02$03.00/0

SYNTHESIS OF UNSYMMETRICAL 4,4'-DIALKYL-2,2'-BIPYRIDINES

Dean K. Ellison and Reynold T. Iwamoto*
Department of Chemistry, University of Kansas
Lawrence, Kansas 66045

Summary: Conversion of 4,4'-dimethyl-2,2'-bipyridine to 4-hexadecyl-4'-methyl-2,2'-bipyridine, 4-heptadecyl-4'-methyl-2,2'-bipyridine, and 4,4'-diheptadecyl-2,2'-bipyridine by treatment with lithium diisopropylamine followed by an appropriate alkyl bromide is reported.

Numerous recent studies of ruthenium bipyridine complexes of the type $\mathrm{Rubipy_2L^{2+}}$ where bipy is 2,2'-bipyridine and L is 4-alkyl-4'-methyl-2,2'-bipyridine or 4,4'-dialkyl-2,2'-bipyridine as sensitizers in the photocatalytic cleavage of water[1-6] have called attention to the complexity of the synthesis of unsymmetric 4,4'-dialkyl-2,2'-bipyridine, as well as that of the symmetric analogs.[1-7] This latter situation has led to extensive use in these studies[1-6] of $\mathrm{Rubipy_2L^{2+}}$ complexes with symmetrical 4,4'-dialkyl-2,2'-bipyridines for ligand L in spite of the fact that the complexes with unsymmetrical 4-alkyl-4'-methyl-2,2'-bipyridines for L have been shown to improve drastically the photocatalytic cleavage of water.[1] Reported here is a particularly simple method for the synthesis of unsymmetrical 4-alkyl-4'-methyl-2,2'-bipyridines and symmetrical 4,4'-dialkyl-2,2'-bipyridines in which one or both of the $-CH_3$ groups on 4,4'-dimethyl-2,2'-bipyridine are converted with lithium diisopropylamine to $-CH_2^-$ anionic groups, and the latter subsequently caused to react with alkyl bromides to place long alkyl groups in the 4- or 4,4'- positions.

For the preparation of the unsymmetrical bipyridines, 50 mL of tetrahydrofuran containing 9.2 mmoles (1.69 g) of 4,4'-dimethyl-2,2'-bipyridine (prepared according to Ghosh and Spiro[8]) was added dropwise over a 30 min period to 4.1 mL of a tetrahydrofuran solution containing 9.1 mmoles of lithium diisopropylamine. (The lithium diisopropylamine solution was prepared by the treatment of a mixture of 1.4 mL diisopropylamine and 2.7 mL tetrahydrofuran with 6.4 mL of 1.42 M butyllithium. The resulting mixture was stirred for 15 min under dry argon before the addition of the bipyridine.) After the orange-brown solution was stirred for 1.5 hr, it was cooled to 0° and 9.2 mmoles of n-hexadecyl bromide or n-pentadecyl bromide was added dropwise while stirring was maintained. After 1.5 hr, during which time the solution turned turbid, the reaction was quenched with ice water and the mixture extracted with ether. The residue after removal of ether was recrystallized three times from ethyl acetate to provide the pure product in 60-70% yield.[9]

For the preparation of the symmetrical 4,4'-diheptadecyl-2,2'-bipyridine, the mmoles of lithium diisopropylamine and of n-hexadecylbromide were doubled.

Acknowledgment: We thank Professors R. G. Carlson and R. S. Givens for helpful discussions. We also thank the University of Kansas (General Research Fund) for financial support.

References and Footnotes

1. E. Borgarello, J. Kiwi, E. Pelizzetti, M. Visca, and M. Grätzel, *Nature*, **289**, 158(1981).
2. O. Johansen, C. Kowala, A. W.-H. Mau, and W. H. F. Sasse, *Aust. J. Chem.*, **32**, 1453(1979).
3. N. Alonso, V. M. Beley, and P. Chartier, *Rev. Phys. Appl.*, **16**, 5(1981).
4. R. Memming and F. Schröppel, *Chem. Phys. Lett.*, **62**, 207(1979).
5. A. Mackor and J. Schoonman, *Recl. Trav. Chim. Pays-Bas*, **99**, 71(1980).
6. S. J. Valenty, D. E. Behnken, and G. L. Gaines, Jr., *Inorg. Chem.*, **18**, 2160(1979).
7. K. D. Bos, J. G. Kraaijkamp, and J. G. Noltes, *Synth. Commun.* **9**, 497(1979).
8. P. K. Ghosh and T. G. Spiro, *J. Am. Chem. Soc.*, **102**, 5543(1980).
9. The two unsymmetrical 4,4'-dialkyl-2.2'-bipyridines were characterized by melting point, elemental analysis, and NMR. All the information obtained for 4-hexadecyl-4'-methyl-2,2'-bipyridine agreed excellently with those reported earlier by Johansen et al.[2] for the same compound prepared by a different procedure.

    a. 4-Hexadecyl-4'-methyl-2,2'-bipyridine: M.p. 62-63°; $C_{27}H_{42}N_2$; C, 82.17; H, 10.73; N, 7.10. Found C, 81.94; H, 10.85; N, 6.94. NMR (80 MHz, $CDCl_3$, TMS) δ 0.65-1.95 (multiplet, $C_{15}H_{31}$, 2.41(3H, s, 4'-Me), 2.69 (2H, t, CH_2), 7.10 (2H, d, H5, H5') 8.24(2H, s, H3, H3') 8.53(2H, d, H6, H6').

    b. 4-Heptadecyl-4'-methyl-2,2'-bipyridine: M.p. 73-74°; $C_{28}H_{44}N_2$; C, 82.29; H, 10.85; N, 6.85. Found C, 82.10; H, 10.90; N, 6.80. The NMR spectrum is identical with that of 4a, except for a 33 H multiplet at 0.7-1.95.

    c. 4,4'-Diheptadecyl-2,2'-bipyridine: Although not formally characterized, the NMR spectrum of this compound was similar to that of 4a, except for the absence of the signal at δ 2.39, 4'-Me. The molecular weight of this bipyridine was confirmed by mass spectrometry.

(Received in USA 27 September 1982)