

## Short Communication

---

### Synthesis of 4,4'-bis(tridecyl)- and 4-methyl-4'-tridecyl-2,2'-bipyridine and a 2,2'-bipyridine-substituted polystyrene: an easier method for the preparation of 2,2'-bipyridines with long-chain substituents

CHRISTIAN-HERBERT FISCHER

*Bereich Strahlenchemie, Hahn-Meitner-Institut für Kernforschung Berlin, Glienicker Strasse 100, D-1000 Berlin 39 (F.R.G.)*

(Received October 21, 1983; in revised form December 13, 1983)

#### 1. Introduction

In the photochemistry of metal compounds, the ruthenium(II) bipyridine complex plays an important role [1]. It has often been used as a light-absorbing catalyst in solar photochemical systems, its action consisting of the transfer of an electron to a suitable relay compound such as methylviologen [2]. To avoid the back reaction after the initial charge separation, microheterogeneous systems such as micelles or inorganic colloids have been used, in which the electron is transferred through the interface. In these systems, the reactants have to be kept in fixed positions at the interface. A long hydrocarbon substituent on a metal complex will hold it close to the hydrophobic part of the microheterogeneous system [2].

The preparation of ruthenium bipyridine with one or two hydrocarbon chains has been described by various researchers [3 - 5]. It seems that our method of introduction of the long chain into the ligand is most advantageous. Because of the great interest of many laboratories in working with such substituted metal complexes we wish to describe our method of preparation in detail and to give the exact quantities required for our syntheses.

#### 2. Results

The key product is 4,4'-dimethyl-2,2'-bipyridine 1 which is easily prepared from 4-methylpyridine with palladium on charcoal [6, 7]. Although the methyl groups are very weakly acidic, they form carbanions with strong bases, which can react with the appropriate halides. We apply lithium diisopropylamide [8] as the base, the solvent being tetrahydrofuran (THF). This is more convenient than using sodium in liquid ammonia, and the crude product is so pure that separation by column chromatography is not necessary. Both monoalkylated and dialkylated bipyridines were prepared in this way. To obtain the disubstituted species, the ratio of halide to dimethylbipyridine 1 was 2.2:1. A ratio of 1:1.2 produced the monosubstituted

species, which is in principle more difficult to synthesize. The yields were good in both cases. The degree of conversion as well as the purity of the products were easily checked by  $^1\text{H}$  nuclear magnetic resonance (NMR) and thin layer chromatography (TLC) on RP18 silica gel, where the starting material **1** and the two substituted products could clearly be distinguished and showed only one spot. The preparation and analysis of 4-methyl-4'-tridecyl-2,2'-bipyridine **2** and 4,4'-bis(tridecyl)-2,2'-bipyridine **3** (Fig. 1) are described in Section 3.

The method can also be used to fix the bipyridine complex onto a polymeric chain. For this purpose, **1** was converted with 1 mol of poly(vinylbenzyl chloride) into the polybipyridinylethylstyrene **4** (Fig. 1). The product was purified by reprecipitation. The NMR spectrum showed that about 75% of the chloromethyl groups had reacted. In accordance with this finding, the elemental analysis yielded a chlorine content of 3.2%.

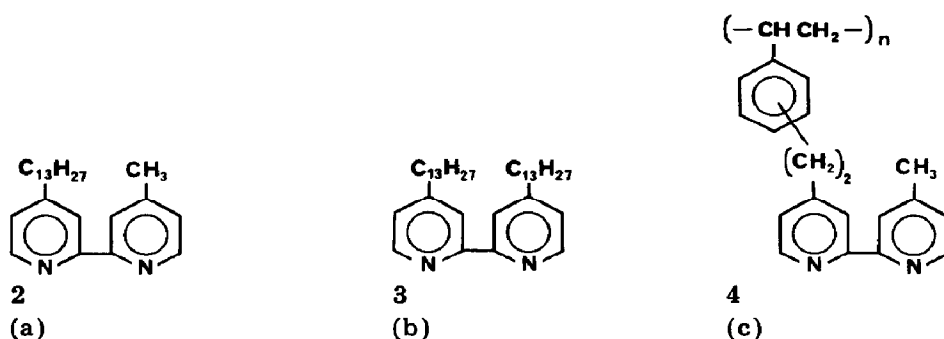


Fig. 1. Structures of (a) 4-methyl-4'-tridecyl-2,2'-bipyridine **2**, (b) 4,4'-bis(tridecyl)-2,2'-bipyridine **3** and (c) polybipyridinylethylstyrene **4**.

### 3. Experimental part

The melting points were determined with a Mettler FP-1. The NMR spectra ( $\delta$  (ppm) values) were measured in  $\text{CDCl}_3$  solution with tetramethylsilane as the internal standard on a Varian EM 390. TLC was carried out on Merck high pressure TLC precoated plates RP18 F254 with 10 ml of  $\text{CHCl}_3$ , 20 ml of methanol and 0.06 ml of concentrated  $\text{H}_3\text{PO}_4$  as eluent. The  $R_f$  values were as follows: **1**, 0.72; **2**, 0.58; **3**, 0.40.

#### 3.1. 4-methyl-4'-tridecyl-2,2'-bipyridine **2**

3.4 ml of 1.6 M butyllithium (5.4 mmol) in hexane were dropped cautiously into 1.34 ml of distilled dry diisopropylamine (5.4 mmol) in 10 ml of absolute THF. The whole reaction was carried out in a nitrogen atmosphere, while the mixture was stirred. After 15 min 1.28 g of **1** (6.9 mmol) in 35 ml of THF were added over a period of 5 min. 1 h later, 1.3 ml of 1-bromododecane (5.4 mmol) in 7 ml of THF were dropped into the dark brownish solution. After 20 h the dark colour had disappeared. The mixture was treated with 200 ml of ice-water and extracted three times with  $\text{CHCl}_3$ .

The combined extracts were dried over  $\text{MgSO}_4$ . After evaporation of the solvent the residue was dissolved in a few millilitres of ethanol. A threefold amount of ether was added and the mixture warmed. A small quantity of 1 was filtered off by suction. After removal of the solvent, recrystallization from ethanol with some drops of water yielded 1.5 g of pure colourless crystals of 2 (melting point, 63 °C).

The NMR data are as follows:  $\delta = 0.9$  ppm (triplet; 3 H;  $J = 6$  Hz);  $\delta = 1.3$  ppm (broad singlet; 20 H);  $\delta = 1.6 - 2.0$  ppm (multiplet; 2 H);  $\delta = 2.5$  ppm (singlet; 3 H);  $\delta = 2.8$  ppm (triplet; 2 H;  $J = 7$  Hz);  $\delta = 7.2$  ppm (doublet of doublets; 2 H;  $J = 6$  Hz and  $J = 1$  Hz);  $\delta = 8.4$  ppm (broad singlet; 2 H);  $\delta = 8.7$  ppm (doublet; 2 H;  $J = 6$  Hz).

$\text{C}_{24}\text{H}_{36}\text{N}_2$  requires 81.76% C, 10.29% H and 7.95% N. The results of analysis were as follows: 81.49% C; 10.29% H; 7.90% N.

### 3.2. 4,4'-bis(tridecyl)-2,2'-bipyridine 3

As described above the following quantities of substances were combined: 26.8 ml of 2.35 M butyllithium (62 mmol) in hexane; 8.8 ml of diisopropylamine (62 mmol) in 50 ml of THF; 5 g of 1 (27 mmol) in 170 ml of THF; 14.3 ml of 1-bromododecane (60 mmol) in 15 ml of THF. After 2 days the dark solution became lighter. The solvent was evaporated and the residue was treated with ice-water and extracted three times with  $\text{CHCl}_3$ . The combined extracts were dried over  $\text{MgSO}_4$  and the solvent was removed. Recrystallization from hot ethanol gave 7.3 g of colourless crystals of 2 (melting point, 72 °C).

The NMR data are as follows:  $\delta = 0.9$  ppm (triplet; 6 H;  $J = 7$  Hz);  $\delta = 1.3 - 2.0$  ppm (multiplet; 44 H);  $\delta = 2.8$  ppm (triplet; 4 H;  $J = 7$  Hz);  $\delta = 7.2$  ppm (doublet of doublets; 2 H;  $J = 6$  Hz and  $J = 1$  Hz);  $\delta = 8.3$  ppm (broad singlet; 2 H);  $\delta = 8.7$  ppm (doublet; 2 H;  $J = 6$  Hz).

$\text{C}_{36}\text{H}_{60}\text{N}_2$  requires 83.01% C, 11.61% H and 5.38% N. The results of analysis were as follows: 82.84% C; 11.79% H; 5.36% N.

### 3.3. Poly-2-[4-(4'-methyl-2,2'-bipyridinyl)]ethylstyrene 4

Under the same conditions as described above 4.0 ml of diisopropylamine (28 mmol) in 25 ml of absolute THF, 12.0 ml of 2.34 M butyllithium (28 mmol) in hexane, 5.0 g of 1 (27 mmol) in 125 ml of THF and 4.1 g of polyvinylbenzylchloride (*ortho:para*, 60:40; EGA; 27 mmol related to benzylchloride units) in 75 ml of THF were combined. After 24 h the dark colour had disappeared and the reaction mixture was dropped slowly into 1.5 l of methanol. The white precipitate was removed by suction, dissolved in THF and reprecipitated in methanol. Then reprecipitation was repeated twice by dropping a  $\text{CHCl}_3$  solution of the product into a large amount of cyclohexane yielding 1.84 g of 4 as colourless crystals.

The NMR data are as follows:  $\delta = 1.2 - 2.0$  ppm (2 H);  $\delta = 2.35$  ppm (3 H);  $\delta = 2.6 - 3.3$  ppm (5 H);  $\delta = 4.3$  (remainder benzylchloride);  $\delta = 6.0 - 6.6$  ppm (2 H);  $\delta = 6.6 - 7.2$  ppm (4 H);  $\delta = 8.2$  ppm (2 H);  $\delta = 8.4$  ppm (2 H).

$(C_{20}H_{20}N_2)_{0.75}(C_9H_9Cl)_{0.25}$  requires 81.42% C, 6.83% H, 8.26% N and 3.48% Cl. The results of analysis were as follows: 81.10% C; 6.66% H; 7.85% N; 3.26% Cl.

The author wishes to express his thanks to Mrs. Sabine Podgurski for assistance in the laboratory work.

- 1 V. Balzani and V. Carassiti, *Photochemistry of Coordination Compounds*, Academic Press, London, 1970, p. 307.
- 2 M. Grätzel, *Acc. Chem. Res.*, **14** (1981) 376.
- 3 O. Johnson, C. Kowala, A. W.-H. Mau and W. H. F. Sasse, *Aust. J. Chem.*, **32** (1979) 1453.
- 4 S. J. Valenty, D. E. Behnken and G. L. Gaines, Jr., *Inorg. Chem.*, **18** (1979) 2160.
- 5 K. D. Bos, J. G. Kraijkamp and J. G. Noltes, *Synth. Commun.*, **9** (1979) 497.
- 6 G. Sprintschnik, H. W. Sprintschnik, P. P. Kirsch and D. G. Whitten, *J. Am. Chem. Soc.*, **99** (1977) 4947.
- 7 P. E. Rosevear and W. H. F. Sasse, *J. Heterocycl. Chem.*, **8** (1971) 483.
- 8 P. K. Ghosh and T. G. Spiro, *J. Am. Chem. Soc.*, **102** (1980) 5543.