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SYNTHESIS OF BIS(ALKYLTHIO)BIPYRIDYLS BY NICKEL MEDIATED HOMO COUPLING OF HALOGENOPYRIDYL ALKYL SULPHIDES

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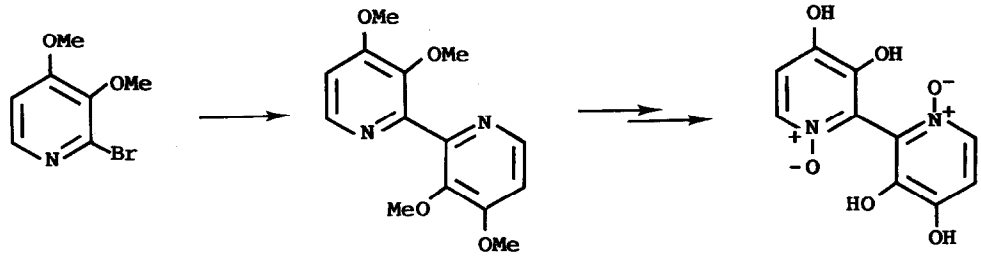
Abstract. The homo coupling of some halogenopyridyl t-butyl sulphides with Ni(0) complex, formed *in situ* from nickel(II) chloride, triphenylphosphine and zinc dust in DMF, afforded bis(t-butylthio)bipyridyls in moderate to good yield. These compounds were dealkylated by electron transfer with sodium in HMPA; the resulting thiolate anions were directly treated with methyl iodide and the bis(methylthio)bipyridyls were obtained. The dealkylation with a solution of sodium in HMPA afforded the mono anions which, after treatment with methyl iodide, gave the t-butylthio(methylthio)bipyridyls.

We have recently reported a simple and efficient method for the synthesis of biaryls by reductive coupling of aryl halides promoted by nickel(0) complexes generated *in situ* from nickel(II) chloride, triphenylphosphine and zinc dust in DMF.[1] 2,2'- and 4,4'-Diquinolyls, 2,2'-, 3,3'-, and 4,4'-bipyridyls, as well as several methoxy substituted bipyridyls, were obtained in good yields. We have also employed this method to effect the crucial step in the total synthesis of the fungal toxine Orellanine, 3, and of its decomposition products, 3,3',4,4'-tetrahydroxy-2,2'-bipyridyl-N-oxide (Orellinine) and 3,3',4,4'-tetrahydroxy-2,2'-bipyridyl (Orelline).[2,3] The key intermediate in these syntheses was the 3,3',4,4'-tetramethoxy-2,2'-bipyridyl, 2, and this was easily obtained from the nickel mediated homo coupling of the 2-bromo-3,4-dimethoxypyridine, 1. In an independent synthesis of Orellanine, Dehmlow and Schulz used our procedure to synthesize 2 from the 2-chloro-3,4-dimethoxypyridine;[4] these Authors also

used the same method for the homo coupling of the 2-bromo-3-fluoro-4-methoxypyridine[4] and for the mixed coupling of 2-iodo-3-methoxypyridine with the 3-bromo-4-methoxypyridine.[5] Very recently our homo coupling method was



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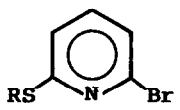
successfully applied to the [2-(trimethylsilyl)ethoxy]methyl ether of the 2-bromo-3-hydroxypyridine to synthesize the key intermediate for a new synthesis of Orelline.[6] 6,6'-Dimethyl-2,2'-bipyridyl was also prepared in a similar way.[7]

Thus, this simple synthesis of bipyridyls seems to be very useful and versatile. However, in order to make this method of more general application, it would be desirable to effect the homo coupling of halogenopyridines holding substituents susceptible of further transformation. In this way, the bipyridyls so formed could be used as starting products for the synthesis of other substituted bipyridyls. One kind of substrates useful for this purpose could be the alkylthiobipyridyls. It has been shown in fact that the alkylthio function linked to a benzene[8,9] or a pyridine[10] ring can be easily replaced by alkyl, vinyl and aryl groups by means of nickel catalyzed cross coupling reactions with Grignard reagents.

We now report that bis(alkylthio)bipyridyls can be obtained by the nickel mediated homo coupling of halogenopyridyl alkyl sulphides. Furthermore, these bipyridyls can be easily dealkylated by electron transfer[11] to afford products in which the two alkyl groups are different. This new type of bis(alkylthio)bipyridyls should result very useful in sequential cross coupling reactions[8,9] to synthesize unsymmetrically substituted bipyridyls.

RESULTS AND DISCUSSION

The starting products employed for the present investigation were the halogenopyridyl alkyl sulphides **4** - **7**. The methyl, **4a** - **7a**, and i-propyl, **4b** - **7b**, derivatives were prepared as previously described.[1,2] The t-butyl, **4c** - **7c**, derivatives were obtained in a similar way from the reactions of the dihalogenopyridines with Me_3CSNa in DMF.



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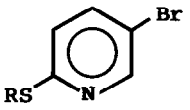

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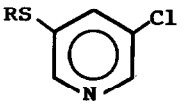

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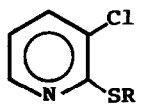

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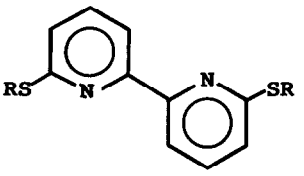
a: R = Me
b: R = Me_2CH
c: R = Me_3C

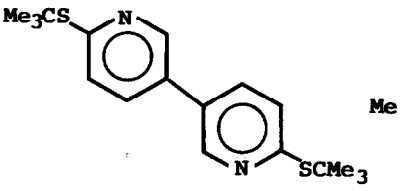
The homo coupling reactions of these substrates were carried out in DMF according to the previously described methodology.[1] Preliminary experiments carried out with some of the methyl and i-propyl derivatives gave rather complex reaction mixtures, indicating that several processes were going on concurrently. Only in the case of **4b** the desired 6,6'-bis(i-propylthio)-2,2'-bipyridyl **8** was formed in reasonable yields (35%); this however was accompanied by other products. Very likely, the complexity of the reaction mixtures can be attributed to the fact that the first step of the reaction, i.e. the oxidative addition of the substrates to the low valent nickel species, is not selective and can involve both the carbon-halogen bond and the carbon-sulphur bond. Moreover, the oxidative addition intermediates can also take other courses different from the homo coupling.

In the previous investigations, concerning the cross coupling reactions of alkylthiobenzenes with Grignard reagents,[9] we observed that the oxidative addition step is strongly influenced by the steric requirements of the alkyl groups. The homo coupling reactions were therefore carried out on the t-butyl derivatives **4c** - **7c**. Substantially better results were obtained with these substrates, compounds **9**, **10** and **11** being produced in 40, 30 and 40% yields, respectively. A further improvement was obtained by effecting the



8: R = Me_2CH

9: R = Me_3C



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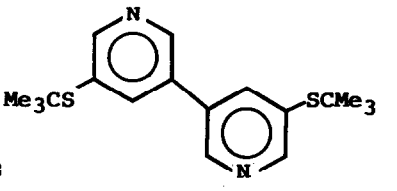

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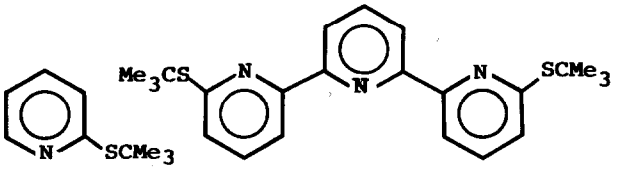
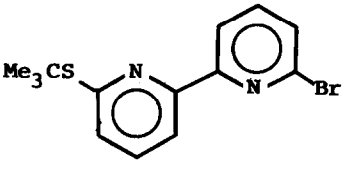
reactions in the presence of potassium iodide. It is known that the addition of iodide ions to the reaction mixture greatly accelerates the coupling reaction,[13] very likely because the aryl halides are first transformed into the more reactive aryl iodides.[13,14] Under these conditions the yields of 8, 9, 10 and 11 increased to 50, 60, 50 and 74%, respectively. Under the same conditions, no homo coupling product could be obtained starting from 7c. The only identified compound was the 2-(t-butyl)pyridine 12. The oxidative addition on the carbon-chlorine bond very likely occurs in this case also, but the nickel complex intermediate does not evolve towards the homo coupling product because of the presence of the t-butyl group in the 2 position. It is known, in fact, that aryl halides, holding bulky substituents in the ortho position, couple with great difficulty and preferentially give the reductive dehalogenation products.[13,14]

The terpyridyl 13 was isolated, in minute amounts, from the reaction of 4c. The structure of this product indicates that, to some extent, the oxidative addition process occurs on the carbon-sulphur bond also. Compound 13, in fact, can be suggested to form through the coupling of the starting



12 13



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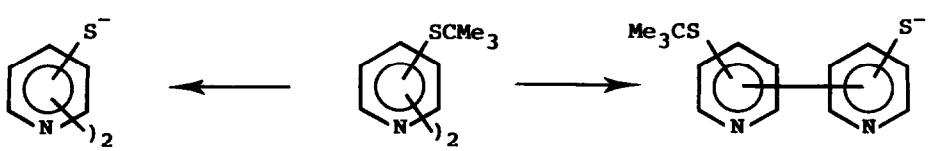
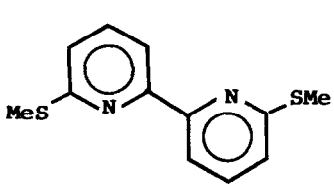
2-bromo-6-(t-butylthio)pyridine **4c** with the bipyridyl **14** or, more likely, with the bipyridyl **9**.

The results reported above indicate that the bis(alkylthio)bipyridyls can be obtained from the homo coupling of the halogenopyridyl alkyl sulphides; this reaction however is limited to the t-butyl derivatives. In order to prepare other types of bis(alkylthio)bipyridyls we have employed our procedures of dealkylation of aryl alkyl sulphides.[11] These reactions, which have been suggested to proceed by electron transfer,[11] can be carried out by adding sodium or a solution of sodium in HMPA to the solution of the sulphide in HMPA. In the first case all the alkylthio groups present in the molecule are dealkylated to afford the corresponding arylthiolate anions; in the second case, on the contrary, the reaction conditions are milder, and the reaction stops after the first dealkylation has occurred. When applied to **8** - **11** these reactions gave the anions **15** and **16**. These can be directly treated with an alkylating agent. In the present case we have employed methyl iodide. Thus, from the anions **15** the bis(methylthio)bipyridyls **17**, **18** and **19** were obtained in 65, 65, and 64% yields, respectively, and from the anions **16** the t-butylthio(methylthio)bipyridyls **20**, **21** and **22** were formed in 55, 65, and 60% yields, respectively. These transalkylation reactions are very useful because they allow to synthesize symmetrical bis(alkylthio)bipyridyls which cannot be obtained by direct homo coupling of the corresponding halogenopyridyl alkyl sulphides. An even more interesting case is the selective monodealkylation process, since in this case bis(alkylthio)bipyridyls containing two different alkyl groups can be prepared.



15 **8-11** **16**



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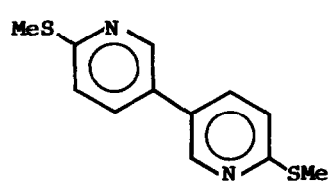

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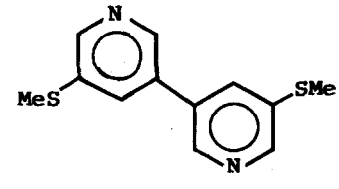

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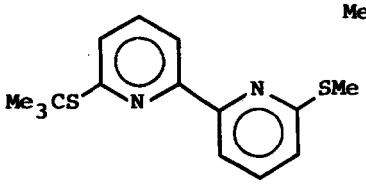

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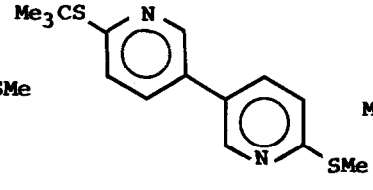

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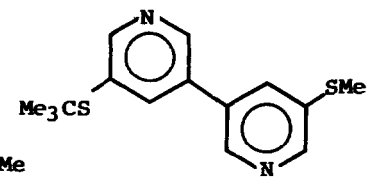

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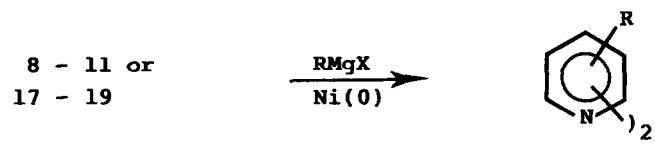
As anticipated in the Introduction all these bis(alkylthio)bipyridyls can be used as starting products to synthesize other bipyridyls. Thus, by means of nickel catalyzed cross coupling reactions with Grignard reagents, compounds 8 - 11 or 17 - 19 can be transformed into the bipyridyls 23, in which R is an alkyl, vinyl or aryl group. Moreover, since these cross coupling reactions are strongly influenced by the steric requirements of the alkyl groups,[9] compounds 20 - 22 can be sequentially transformed into the bipyridyls 24 and 25. These reactions are presently under investigation and will be described in a forthcoming paper.



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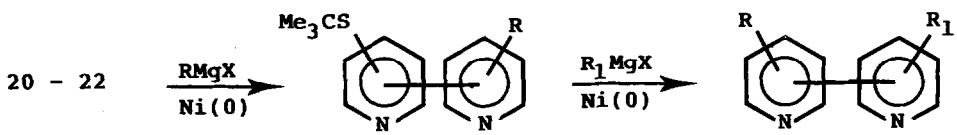

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EXPERIMENTAL

The sulphides **4a** - **7a** and **4b** - **7b** were prepared as previously described.[12] Commercial 2,6- and 2,5-dibromopyridines, 2,3- and 3,5-dichloropyridines were used without further purification. Reaction products were identified by nmr spectroscopy. Proton nmr spectra were recorded on a 90MHz Varian EM390 and carbon-13 nmr spectra were recorded at 20.15 MHz on a Bruker WP80SY instrument operating in the Fourier transform mode with proton decoupling throughout. $CDCl_3$ was used as solvent and TMS as reference. Elemental analyses were carried out on a Carlo Erba 1106 Elemental Analyzer. Glc analyses were performed on a Hewlett-Packard 5830A chromatograph with a 20 in., 10% UCW 982 column. Sulphones were prepared by oxidation with *m*-chloroperbenzoic acid in $CHCl_3$ solution.

Synthesis of Halogenopyridyl t-Butyl Sulphides.

To a stirred solution of *t*-butyl mercaptan (0.01 mol) in DMF (20 ml) sodium hydride (0.01 mol) was added at room temperature. After addition of the bis(halogeno)pyridine (0.01 mol) the mixture was kept at the temperature indicated below and the progress of the reaction was monitored by tlc. After the usual work up the reaction products were purified by column chromatography using a mixture of light petroleum and ether (95:5) as eluant. Reaction temperature, time and yield are given in parentheses below together with the physical and nmr data.

2-Bromo-6-(*t*-butylthio)pyridine (4c). Oil. (25 °C, 2 h, 77%). H-nmr δ 7.4 - 7.0 (m, 1 H), 1.55 (s, 3 H). Sulphone, m.p. 127 - 128 °C. H-mnr δ 8.0 (dd, 1 H, J = 7.2 and 1.8 Hz); 7.8 (t, 1 H, J = 7,2 Hz); 7.65 (dd, 1 H, J = 7.2 and 1.8 Hz); 1.45 (s, 9 H). Anal. Calcd. for $C_9H_{12}BrNO_2S$: C, 38.85; H, 4.35; N, 5.05. Found: C, 39.00; H, 4.15; N, 5.10.

2-t-Butylthio-5-(bromo)pyridine (5c). Oil (25 °C, 5 h, 75%). H-nmr δ 8.5 (dd, 1 H, J = 2.4 and 0.9 Hz); 7.5 (dd, 1 H, J = 8.4 and 2.4 Hz); 7.1 (dd, 1 H, J = 8.4 and 0.9 Hz); 1.55 (s, 9 H). Sulphone, m.p. 116 - 118 °C. H-nmr δ 8.8 (dd, 1 H, J = 2.4 and 0.9 Hz); 8.1 (dd, 1 H, J = 8.4 and 2.4 Hz); 7.95 (dd, 1 H, J = 8.4 and 0.9 Hz); 1.45 (s, 9 H). Anal. Found: C, 38.70; H, 4.20; N, 5.15.

3-Chloro-5-(t-butylthio)pyridine (6c). M.p. 33 - 34 °C. (80 °C, 2 h, 80%). H-nmr δ 8.6 - 8.4 (m, 2 H), 7.8 - 7.7 (m, 1 H); 1.3 (s, 9 H). Sulphone, m.p. 124 - 125 °C. H-mnr δ 8.9 (d, 1 H, J = 2.1 Hz); 8.8 (d, 1 H, J = 2.1 Hz); 8.1 (t, 1 H, J = 2.1 Hz); 1.4 (s, 9 H). Anal. Calcd. for $C_9H_{12}ClNO_2S$: C, 46.25; H, 5.20; N, 6.00. Found: C, 46.15; H, 5.10; N, 6.10.

2-t-Butylthio-3-(chloro)pyridine (7c). Oil. (25 °C, 4 h, 86%). H-nmr δ 8.25 (dd, 1 H, J = 4.8 and 1.8 Hz); 7.45 (dd, 1 H, J = 8.1 and 1.8 Hz); 6.85 (dd, 1 H, J = 8.1 and 4.8 Hz); 1.65 (s, 9 H). Sulphone, m.p. 102 - 105 °C. H-nmr δ 8.6 (dd, 1 H, J = 4.2 and 1.5 Hz); 7.9 (dd, 1 H, J = 8.1 and 1.5 Hz); 7.5 (dd, 1 H, J = 8.1 and 4.2 Hz); 1.5 (s, 9 H). Anal. Found: C, 46.20; H, 5.20; N, 6.10.

Homo Coupling Reactions.

To a stirred, deep blue solution of nickel(II) chloride hexahydrate (5 mmol) and triphenylphosphine (20 mmol) in DMF (25 ml) under nitrogen at 50 °C, zinc powder (5 mmol) was added. After about 1 h the colour of the mixture changed to red brown. Halogenopyridyl alkyl sulphides (5 mmol) and potassium iodide (5 mmol) were added and the mixture was kept at the temperature indicated below. The progress of the reaction was monitored by tlc and glc. When the starting product was completely consumed the mixture was poured into dilute ammonia solution (100 ml) and extracted with chloroform (3 x 50 ml). The organic layer was washed with water (3 x 50 ml), dried over sodium sulphate and evaporated. The residue was chromatographed

through a silica gel column using mixtures of light petroleum and ether (from 99:1 to 90:10) as eluant. Reaction temperature, time, and yield are given in parentheses below together with physical and spectral data.

6,6'-Bis(i-propylthio)-2,2'-bipyridyl (8). M.p. 105 - 107 °C. (50 °C, 16 h, 50%). H-nmr δ 8.05 (dd, 1 H, J = 8.1 and 0.9 Hz); 7.55 (t, 1 H, J = 8.1 Hz); 7.1 (dd, 1 H, J = 8.1 and 0.9 Hz); 4.15 (sept, 1 H, J = 7.0 Hz); 1.5 (d, 6 H, J = 7.0 Hz). ^{13}C-nmr δ 158.7, 155.6, 136.6, 122.6, 116.3, 35.1, 23.1. Anal. Calcd. for $C_{16}H_{20}N_2S_2$: C, 63.10; H, 6.60; N, 9.20. Found: C, 63.30; H, 6.55; N, 9.10.

6,6'-Bis(t-butylthio)-2,2'-bipyridyl (9). M.p. 134 - 136 °C. (50 °C, 10 h, 60%). H-nmr δ 8.15 (dd, 1 H, J = 7.5 and 0.9 Hz); 7.55 (t, 1 H, J = 7.5 Hz); 7.25 (dd, 1 H, J = 7.5 and 0.9 Hz); 1.65 (s, 9 H). ^{13}C-nmr δ 158.8, 155.9, 136.75, 125.8, 117.55, 47.5, 31.0. Anal. Calcd. for $C_{18}H_{24}N_2S_2$: C, 65.00; H, 7.30; N, 8.40: Found: C, 64.00; H, 7.45; N, 8.05

6,6''-Bis(t-butylthio)-2,2':6',2"-terpyridyl (13). M.p. 86 - 88 °C. H-nmr δ 8.4 (d, 2 H, J = 8.4 Hz); 8.3 (dd, 2 H, J = 7.8 and 1.2 Hz); 7.85 (dd, 1 H, J = 8.4 and 7.2 Hz); 7.6 (t, 2 H, J = 7.8 Hz); 7.2 (dd, 2 H, J = 7.8 and 1.2 Hz); 1.6 (s, 18 H). ^{13}C-nmr δ 158.6, 156.0, 155.2, 137.7, 136.7, 125.9, 121.0, 117.6, 47.5, 31.0. Anal. Calcd. for $C_{23}H_{27}N_3S_2$: C, 67.45; H, 6.65; N, 10.25. Found: C, 67.30; H, 6.80; N, 10.15.

6,6'-Bis(t-butylthio)-3,3'-bipyridyl (10). M.p. 107 - 109 °C. (25 °C, 24 h, 50%). H-nmr δ 8.7 (d, 1 H, J = 2.4 Hz); 7.65 (dd, 1 H, J = 8.1 and 2.4 Hz); 7.35 (d, 1 H, J = 8.1 Hz); 1.55 (s, 9 H). ^{13}C-nmr δ 158.8, 147.3, 133.8, 130.0, 126.6, 47.9, 31.0. Anal. Found: C, 65.20; H, 7.20; N, 7.90.

5,5'-Bis(t-butylthio)-3,3'-bipyridyl (11). M.p. 128 - 130 °C. (25 °C, 24 h, 74%). H-nmr δ 8.8 (d, 1 H, J = 2.1 Hz); 8.7 (d, 1 H, J = 2.1 Hz); 8.0 (t, 1

H, J = 2.1 Hz); 1.35 (s, 9 H). ^{13}C-nmr δ 156.3, 147.8, 142.6, 46.75, 31.0. Anal. Found: C, 65.60; H, 7.65; N, 8.00.

2-(t-Butylthio)pyridine (12). Oil.[15] H-nmr δ 8.5 (ddd, 1 H, J = 4.9, 1.9 and 0.9 Hz); 7.45 (ddd, 1 H, J = 7.8, 7.4 and 1.9 Hz); 7.3 (ddd, 1 H, J = 7.8, 1.2 and 0.9 Hz); 7.05 (ddd, 1 H, J = 7.4, 4.9 and 1.2 Hz). ^{13}C-nmr δ 158.9, 149.3, 135.7, 126.7, 120.4, 47.3, 31.0.

Dealkylation Reactions

Method A. To a stirred solution of the bis(t-butylthio)bipyridyl (1 mmol) in HMPA (15 ml), kept under nitrogen at 100 °C, small pieces of sodium (6 eqv) were added. The progress of the reaction was monitored by tlc, treating small aliquots with methyl iodide. After 1 - 3 h the starting product was completely consumed and the mixture was cooled at room temperature. Excess methyl iodide was added and the mixture was stirred for half an hour. After the usual work up and column chromatography the bis(methylthio)bipyridyls reported below were obtained with the yields indicated in parentheses.

6,6'-Bis(methylthio)-2,2'-bipyridyl (17). (65%). M.p. 128 - 130 °C (Litt.[16] 130 - 131 °C). H-nmr δ 8.1 (dd, 1 H, J = 7.5 and 0.9 Hz); 7.55 (t, 1 H, J = 7.5 Hz); 7.1 (dd, 1 H, J = 7.5 and 0.9 Hz); 2.65 (s, 3 H). ^{13}C-nmr δ 158.9, 155.5, 136.5, 121.8, 116.4, 13.2. Anal Calcd. for $C_{12}H_{12}N_2S_2$: C, 58.05; H, 4.85; N, 11.30. Found: C, 57.85; H, 4.65; N, 11.45.

6,6'-Bis(methylthio)-3,3'-bipyridyl (18). (65%). M.p. 114 - 115 °C. H-nmr δ 8.6 (dd, 1 H, J = 2.4 and 0.9 Hz); 7.6 (dd, 1 H, J = 8.1 and 2.4 Hz); 7.2 (dd, 1 H, J = 8.1 and 0.9 Hz); 2.6 (s, 3 H). ^{13}C-nmr δ 159.6, 147.2, 133.7, 128.8, 121.5, 13.27. Anal. Found: C, 58.20; H, 5.00; N, 11.00.

5,5'-Bis(methylthio)-3,3'-bipyridyl (19). (64%). M.p. 151 - 153 °C. H-nmr δ 8.6 - 8.4 (m, 2 H); 7.6 (t, 1 H, J = 2.1 Hz), 2.55 (s, 3 H). ^{13}C-nmr δ

147.1, 144.4, 136.0, 132.9, 132.3, 15.6. Anal. Found: C, 58.15; H, 4.75; N, 11.35.

Method B. Small pieces of sodium (6 eqv) were added to HMPA (15 ml) stirred under nitrogen at 100 °C. When the sodium was completely dissolved, the bis(t-butylthio)bipyridyl (1 mmol) was added. After 3 h the starting product was completely consumed. Excess methyl iodide was added and the reaction mixture was worked up as described in Method A. The following t-butylthio(methylthio)bipyridyls were obtained with the yields indicated in parentheses.

6-t-Butylthio-6'-methylthio-2,2'-bipyridyl (20). (55%). M.p. 91 - 92 °C. H-nmr δ 8.2 (dd, 1 H, J = 7.5 and 0.9 Hz); 8.05 (dd, 1 H, J = 7.5 and 0.9 Hz); 7.55 (t, 2 H, J = 7.5 Hz); 7.25 (dd, 1 H, J = 7.5 and 0.9 Hz); 7.15 (dd, 1 H, J = 7.5 and 0.9 Hz), 2.65 (s, 3 H); 1.65 (s, 9 H). ^{13}C-nmr δ 136.7, 126.0, 121.7, 117.6, 116.4, 47.5, 31.0, 13.2. Anal. Calcd. for $C_{15}H_{18}N_2S_2$: C, 62.00; H, 6.25; N, 9.65. Found: C, 61.25; H, 6.25; N, 9.25.

6-t-Butylthio-6'-methylthio-3,3'-bipyridyl (21). (65%). M.p. 92 - 93 °C. H-nmr δ 8.6 - 8.45 (m, 2 H); 7.6 - 7.45 (m, 2 H); 7.3 - 7.15 (m, 2 H); 2.5 (s, 3 H); 1.5 (s, 9 H). ^{13}C-nmr δ 159.8, 147.3, 147.2, 133.9, 133.7, 126.7, 121.6, 47.9, 31.0, 13.3. Anal. Found: C, 62.20; H, 6.15; N, 9.70.

5-t-Butylthio-5'-methylthio-3,3'bipyridyl (22). (64%). M.p. 107 - 109 °C. H-nmr δ 8.8 - 8.7 (m, 2 H); 8.6 - 8.45 (m, 2 H); 8.0 (t, 1 H, J = 1.8 Hz); 2.6 (s, 3 H); 1.35 (s, 9H). ^{13}C-nmr δ 156.3, 147.8, 147.4, 144.6, 142.6, 132.6, 46.7, 31.0, 15.7. Anal. Found: C, 61.55; H, 6.30; N, 9.45.

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