

## Terpyridine Derivatives

# Functionalization of Highly Substituted 2,2':6',2"-Terpyridine Derivatives

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Dedicated to Professor Henning Hopf on the occasion of his 75th birthday

**Abstract:** On the basis of an easy access to 2,2':6',2"-terpyridine derivatives bearing 6- and 6"-methyl groups, the functionalization of these substituents was investigated. The direct oxidation or bromination of the methyl groups was not feasible on larger scale; however, a two-step process employing oxidation to the pyridine *N*-oxides followed by acetic anhydride promoted rearrangement (Boekelheide reaction) furnished the corresponding terpyridine derivatives with 6- and 6"-acetoxymethyl groups in reasonable overall yields. These are excellent precursors for the synthesis of tetra- and pentadentate ligands, as demonstrated by several examples. This approach allowed access to a library of new functionalized 2,2':6',2"-terpyridine derivatives.

#### Introduction

On the basis of a simple but highly flexible synthesis of pyridine derivatives from  $\beta$ -ketoenamides,<sup>[1]</sup> we developed a new approach to functionalized 2,2':6',2"-terpyridine derivatives **A** by employing bis( $\beta$ -ketoenamides). These precursors are easily accessible from  $\beta$ -diketones such as acetylacetone, ammonia, and pyridine-2,6-dicarboxylic acids (Scheme 1).<sup>[2]</sup>



Scheme 1. Approach to functionalized 2,2'.6',2''-terpyridine derivatives **A** with highlighted methyl groups (green balls).

This route to terpyridines **A** has the advantage that the 4-, 4'-, and 4"-positions of the three pyridine subunits may selectively be addressed, for example, by nucleophilic substitution or by palladium-catalyzed coupling of the corresponding nonaflates.<sup>[3]</sup> We thus easily prepared 4,4',4"-tris(dimethylamino)terpyridine, a unique Lewis base with unprecedented methyl cation affinity, and novel unsymmetrically substituted terpyridine derivatives.<sup>[2]</sup> A clear limitation of this method is that all com-

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 http://www.bcp.fu-berlin.de/chemie/chemie/forschung/OrgChem/reissig/ index.html pounds bear alkyl groups (in most cases methyl groups) at the 6- and 6"-positions, which may hamper complexation of metal ions with these tridentate ligands. On the other hand, these alkyl substituents offer the opportunity for further functionalization to introduce additional donor moieties, which can finally lead to tetra- and pentadentate ligands that should be of considerable interest for many applications. In this report, we describe our efforts to oxidize the methyl groups of compounds of type **A** to approach novel hydroxy- and amino-substituted terpyridine derivatives.

#### **Results and Discussion**

In our first report on the terpyridine synthesis, we described the conversion of **1** into dialdehyde **3** by using selenium dioxide (1,4-dioxane, 110 °C).<sup>[1a]</sup> This direct oxidation would be an ideal starting point to prepare the envisioned 6- and 6"-substi-



Scheme 2. Reaction of terpyridine derivative **1** with selenium dioxide to aldehyde **2** and dialdehyde **3**.

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tuted compounds. Unfortunately, all attempts to perform this oxidation on a reasonably large scale only led to mixtures of precursor **1**, monoaldehyde **2**, and the desired compound **3** (Scheme 2).<sup>[4]</sup>

Because of this failure, we had a look at less-direct alternatives and first checked bromination reactions. The reaction of terpyridine **1** with bromine in the presence of acetate buffer<sup>[5]</sup> only led to ring bromination, which provided 3,5"-dibromoterpyridine derivative **4** in low yield as the main product in a mixture of various differently brominated species (Scheme 3).



Scheme 3. Ring bromination of 1 leading to dibrominated terpyridine derivative 4.

On the other hand, conditions of a radical reaction with the use of *N*-bromosuccinimide (NBS) and 2,2'-azobisisobutyronitrile (AIBN) as initiator<sup>(6]</sup> caused the expected side-chain halogenation and afforded hexabromo compound **5** in a good yield of 58 % (Scheme 4). Attempts to prepare dibromide **6** by using a smaller amount of NBS or a different brominating agent failed. Target compound **6** was only obtained as one component in a complex mixture still containing starting material **1**. We also attempted to convert the tribromomethyl substituents of **5** into carboxylate groups by treating the compound with strong base; however, no defined products were isolated.<sup>[4]</sup>



Scheme 4. Side-chain bromination of 1 leading to terpyridine derivative 5. DCE = 1,2-dichloroethane.

Given that these methods failed, we finally investigated indirect side-chain functionalization by oxidation of the pyridine nitrogen atoms to *N*-oxides followed by rearrangement (Boekelheide reaction),<sup>[7]</sup> a two-step process successfully employed for many other examples in our group.<sup>[1c,8]</sup> Upon treating terpyridine **1** with an excess amount of *m*-chloroperoxybenzoic acid (*m*CPBA) in dichloromethane and then with acetic anhydride, the desired diester **7** together with monoester **8** was obtained in satisfactory combined yield (Scheme 5). The two com-

pounds were easily separated by column chromatography. The isolation of monoester 8 indicates that the oxidation of terpyridine derivative 1 to the desired bis-N-oxide was incomplete and that considerable amounts of the corresponding mono-Noxide were formed. There was no evidence in these experiments that the central ring of **1** was also oxidized. Apparently, the two more electron-rich methoxy-substituted pyridine subunits are more reactive. The conditions as shown in Scheme 5 could not be improved by using hydrogen peroxide in the presence of acetic acid,<sup>[9]</sup> by employing hydrogen peroxide and methylrhenium trioxide as the catalyst,<sup>[10]</sup> or by using dimethvldioxirane as the oxidizing reagent.<sup>[10b]</sup> To check the electronic effects of the two-step process, we also exposed terpyridine derivative  $\mathbf{9}^{[2,6c,11]}$  to mCPBA followed by acetic anhydride. In this case, the desired diester 10 was isolated in 38 % yield over two steps.



Scheme 5. Two-step syntheses of diesters **7** and **10** by oxidation of **1** or **9** with *m*CPBA followed by Boekelheide rearrangement.

Although the two-step process to convert **1** and **9** into the corresponding diesters **7** and **10**, respectively, was satisfactory, a more convenient and higher yielding process was nevertheless desirable. We therefore also examined the *N*-oxidation of bisnonaflate **11**.<sup>[2]</sup> Again, a very careful optimization was required to obtain reasonably high conversion and selectivity. The best conditions were found by treating **11** repeatedly with fresh *m*CPBA in dichloromethane at room temperature while using washing steps in between to remove the *m*-chlorobenzoic acid byproduct (Scheme 6). This allowed the isolation of mono-*N*-oxide **12** (17 % yield) and bis-*N*-oxide **13** (51 % yield) in satisfac-



Scheme 6. Conversion of bisnonaflate 11 into mono-, bis-, and tris-*N*-oxides 12, 13, and 14.





tory combined yield. More forcing conditions involving the use of a larger excess amount of *m*CBPA at elevated temperatures with prolonged reaction times resulted in the decomposition of **12** and **13**. To increase the yield of **13**, precursor **11** was also treated with the stronger oxidizing mixture of hydrogen peroxide (35 %, as urea complex) and trifluoroacetic anhydride (TFAA),<sup>[12]</sup> as the in situ formed trifluoroperacetic acid is more electrophilic<sup>[13]</sup> and thus more reactive than *m*CPBA. The increased reactivity, however, also led to *N*-oxidation of the central pyridine ring, which thus delivered tris-*N*-oxide **14**.

Unfortunately, none of these terpyridine *N*-oxides could be converted into the corresponding acetoxymethyl-substituted compounds upon heating with acetic acid anhydride.<sup>[4]</sup> Only decomposition of the precursors was observed, very likely as a result of side reactions of the nonafloxy groups, and this led to intractable mixtures of undefined products. We therefore converted mono-*N*-oxide **12** and bis-*N*-oxide **13** into phenyl-substituted terpyridine derivatives **15** and **16** by employing phenyl-boronic acid under standard Suzuki coupling conditions (Scheme 7).<sup>[14]</sup> The two expected products were isolated in excellent yields, which demonstrates again the capacity of this type of palladium-catalyzed reaction and the inertness of the *N*-oxide function to the reaction conditions employed.



Scheme 7. Suzuki couplings of bisnonaflates **12** and **13** to phenyl-substituted terpyridine derivatives **15** and **16**, Boekelheide rearrangement to **17** and **18** and deprotection to terpyridine derivatives **19** and **20**.

With terpyridine derivatives **15** and **16** in hand, we again heated the two compounds with acetic anhydride and then received the desired Boekelheide rearrangement products **17** and **18** in high yields (Scheme 7). Final cleavage of the acetoxy group was efficiently achieved with methanol under mild basic conditions to deliver tetradentate and pentadentate terpyridine derivatives **19** and **20** in very good yields.

Acetoxy-substituted terpyridine derivatives **8** and **7** were similarly deprotected to furnish hydroxymethyl-substituted terpyridine derivatives **21** and **22** almost quantitatively (Scheme 8). Finally, compound **21** was oxidized with 2-iodoxybenzoic acid (IBX, 1.4 equiv.)<sup>[15]</sup> to afford the expected aldehyde **23** in excellent yield. Diol **22** was more resistant to complete oxidation. Even 3 equivalents of IBX only provided a 45:55 mixture of the desired dialdehyde **3**<sup>[1a]</sup> together with hydroxy aldehyde **24**. This transformation certainly requires additional optimization or the use of a different oxidizing reagent.



Scheme 8. Deprotection of  ${\bf 8}$  and  ${\bf 7}$  to terpyridines  ${\bf 21}$  and  ${\bf 22}$  followed by oxidation with IBX.

We previously demonstrated by the conversion of **3** into the corresponding bisoxime<sup>[1a]</sup> that these aldehydes offer the possibility for further functionalization to multidentate ligands. This was confirmed by the conversion of **23** into terpyridine derivative **25** by reductive amination with benzylamine in very good yield (Scheme 9).



Scheme 9. Reductive amination of 23 to tetradentate ligand 25.

#### Conclusions

In this report, we demonstrated that compounds of type A are excellent precursors for the synthesis of a variety of functionalized 2,2':6',2"-terpyridine derivatives. Whereas direct side-chain oxidation and bromination did not provide the desired products, a "detour" via the corresponding pyridine N-oxides followed by Boekelheide rearrangement with acetic anhydride provided the expected 6- and 6"-acetoxymethyl-substituted terpyridines in reasonable overall yields. Depending on the oxidation conditions, bis-nonafloxy-substituted derivative 11 could be converted into mono-, bis-, and tris-N-oxides 12-14. These nonafloxy-substituted compounds were unsuitable substrates Boekelheide rearrangement; for the however, after Suzuki reaction and replacement of the nonafloxy groups by phenyl substituents, resulting N-oxides 15 and 16 also underwent the transformation into the expected acetoxymethyl-substituted terpyridines 17 and 18. Compounds such as 7, 8, 17, and 18 were deprotected to provide the hydroxymethyl-substituted terpyridine derivatives. These constitute an interesting class of tetra- and pentadentate ligands,<sup>[16]</sup> but they also allow



subsequent transformations, as shown by oxidation of compound **21** followed by reductive amination of **23** to furnish the new tetradentate amino-substituted terpyridine derivative **25** in good overall yield.

### **Experimental Section**

Typical Procedure for the Synthesis of 6,6"-Bis(acetoxymethyl)-4,4"-dimethoxy-2,2':6',2"-terpyridine (7) and 6-Acetoxymethyl-4,4"-dimethoxy-6"-methyl-2,2':6',2"-terpyridine (8): A mixture of terpyridine 1 (216 mg, 0.57 mmol) and mCPBA (994 mg, 4.03 mmol, 70 %) in CH<sub>2</sub>Cl<sub>2</sub> (12 mL) was stirred at room temperature for 3 d. TLC analysis indicated incomplete conversion of 1. An additional amount of mCPBA (663 mg, 2.69 mmol, 70 %) and CH<sub>2</sub>Cl<sub>2</sub> (5 mL) were added and stirring was continued at 45 °C under reflux for 2 d. The mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and a solution of satd. aq. Na<sub>2</sub>CO<sub>3</sub> (30 mL). The layers were separated, and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (30 mL). The combined organic layer was dried with Na2SO4, filtered, and concentrated under reduced pressure. The remaining residue was dissolved in Ac<sub>2</sub>O (5 mL) and stirred at 120 °C under reflux for 6 h. The solvent was evaporated under reduced pressure, and the remaining residue was slowly treated with a solution of satd. aq. Na<sub>2</sub>CO<sub>3</sub> (15 mL) and extracted with  $CH_2Cl_2$  (2 × 20 mL). The combined organic layer was dried with Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The obtained crude product was filtered through silica gel (hexanes/EtOAc = 3:2) to provide a mixture of terpyridines 7 and 8 (159 mg). Flash column chromatography on aluminum oxide (activity grade III, hexanes/EtOAc = 6:1->4:1) provided terpyridine 8 (40 mg, 16 %) and 7 (117 mg, 40 %) as colorless solids. For elemental analysis, a sample of 7 was recrystallized from hexanes/EtOAc (1:2). Data for **7**: M.p. 105–108 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta =$ 2.19 (s, 6 H, CH<sub>3</sub>), 3.97 (s, 6 H, OMe), 5.27 (s, 4 H, CH<sub>2</sub>), 6.91 (d, J = 2.4 Hz, 2 H, 5-H), 7.91 (t, J = 7.8 Hz, 1 H, 4'-H), 8.05 (d, J = 2.4 Hz, 2 H, 3-H), 8.44 (d, J = 7.8 Hz, 2 H, 3'-H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 21.0$  (q, CH<sub>3</sub>), 55.3 (q, OMe), 66.9 (t, CH<sub>2</sub>), 105.8 (d, C-3), 107.7 (d, C-5), 121.6 (d, C-3'), 137.8 (d, C-4'), 154.8, 157.0, 157.6 (3 s, C-2, C-2', C-6), 167.3 (s, C-4), 170.7 (s, C=O) ppm. IR (ATR): v = 3100, 3020 (=C-H), 2970, 2940, 2855 (C-H), 1735 (C=O), 1605, 1565 (C=C, C=N), 1455, 1420, 1375, 1255–1160 cm<sup>-1</sup>. HRMS (ESI-TOF): C<sub>23</sub>H<sub>23</sub>N<sub>3</sub>O<sub>6</sub>•H<sup>+</sup>: calcd. 438.1660; found 438.1685. C<sub>23</sub>H<sub>23</sub>N<sub>3</sub>O<sub>6</sub> (437.4): C 63.15, H 5.30, N 9.61; found C 63.20, H 5.24, N 9.56. Data for 8: M.p. 120–122 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 2.20 (s, 3 H, OCOCH<sub>3</sub>), 2.60 (s, 3 H, 6"-CH<sub>3</sub>), 3.94, 3.98 (2 s, 3 H each, OMe), 5.27 (s, 2 H, CH<sub>2</sub>), 6.72 (d, J = 2.4 Hz, 1 H, 5"-H), 6.91 (d, J = 2.4 Hz, 1 H, 5-H), 7.91 (t, J = 7.8 Hz, 1 H, 4'-H), 7.94 (d, J = 2.4 Hz, 1 H, 3"-H), 8.07 (d, J = 2.4 Hz, 1 H, 3-H), 8.43, 8.44 (2 dd, J = 7.8 Hz, J<sub>AB</sub> = 1.0 Hz, 1 H each, 3'-H, 5'-H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ =21.0 (q, COCH<sub>3</sub>), 24.8 (q, 6"-CH<sub>3</sub>), 55.1, 55.3 (2 q, OMe), 66.9 (t, CH<sub>2</sub>), 104.5 (d, C-3"), 105.7 (d, C-3), 107.8 (d, C-5), 108.9 (d, C-5"), 121.3, 121.5 (2 d, C-3', C-5'), 137.7 (d, C-4), 154.8, 155.3, 156.9, 157.3, 157.7, 159.5 (6 s, C-2, C-2', C-2'', C-6, C-6', C-6''), 166.9, 167.3 (2 s, C-4, C-4"), 170.7 (s, C=O) ppm. IR (ATR):  $\tilde{v}$  = 3105, 3015 (=C-H), 2960–2920, 2850 (C-H), 1735 (C=O), 1605, 1570 (C=C, C=N), 1470-1380, 1250-1170 cm<sup>-1</sup>. HRMS (ESI-TOF): C<sub>21</sub>H<sub>21</sub>N<sub>3</sub>O<sub>4</sub>•H<sup>+</sup>: calcd. 380.1605; found 380.1618. C<sub>21</sub>H<sub>21</sub>N<sub>3</sub>O<sub>4</sub> (379.4): C 66.48, H 5.58, N 11.08; found C 66.53, H 5.45, N 10.98.

**6,6**"-**Bis(hydroxymethyl)-4,4**"-**diphenyl-2,2**':**6**',**2**"-**terpyridine (20):** Terpyridine **18** (510 mg, 0.96 mmol) was treated overnight with K<sub>2</sub>CO<sub>3</sub> (1.33 g, 9.64 mmol) in a mixture of CH<sub>2</sub>Cl<sub>2</sub>/MeOH (1:1, 18 mL) to provide terpyridine **20** (396 mg, 92 %) as a yellow solid. Workup was performed with water (100 mL) and CH<sub>2</sub>Cl<sub>2</sub> (6 ×



100 mL), m.p. 222–224 °C. <sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>]DMSO):  $\delta$  = 4.76 (d, *J* = 5.8 Hz, 4 H, CH<sub>2</sub>), 5.60 (t, *J* = 5.8 Hz, 2 H, OH), 7.52–7.61 (m, 6 H, 6 Ph), 7.85 (d, *J* = 1.4 Hz, 2 H, 5-H), 7.91–7.93 (m, 4 H, Ph), 8.12 (t, *J* = 7.8 Hz, 1 H, 4'-H), 8.47 (d, *J* = 7.8 Hz, 2 H, 3'-H), 8.79 (d, *J* = 1.4 Hz, 2 H, 3-H) ppm. <sup>13</sup>C NMR (126 MHz, [D<sub>6</sub>]DMSO):  $\delta$  = 64.4 (t, CH<sub>2</sub>), 116.4 (d, C-3), 118.0 (d, C-5), 120.9 (d, C-3'), 126.8, 129.3, 129.4 (3 d, Ph), 137.8 (d, C-4'), 138.4 (s, Ph), 148.7, 154.8, 155.0, 162.6 (4 s, C-2, C-2', C-4, C-6) ppm. IR (ATR):  $\tilde{v}$  = 3240 (O–H), 3060 (=C–H), 2930, 2870 (C–H), 1605, 1580, 1545, 1500 (C=C, C=N), 1465–1430, 1390, 1320, 1275 cm<sup>-1</sup>. HRMS (ESI-TOF): C<sub>29</sub>H<sub>23</sub>N<sub>3</sub>O<sub>2</sub>-Na<sup>+</sup>: calcd. 468.1682; found 468.1684.

**Supporting Information** (see footnote on the first page of this article): Experimental details, characterization data, and copies of the <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of all key intermediates and final products.

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