ACTIVATED MANGANESE DIOXIDE AS AN OXIDIZING AGENT FOR THE CONVERSION OF *N*-METHYLPHENANTHROLINIUM SALTS TO *N*-METHYLPHENANTHROLONES

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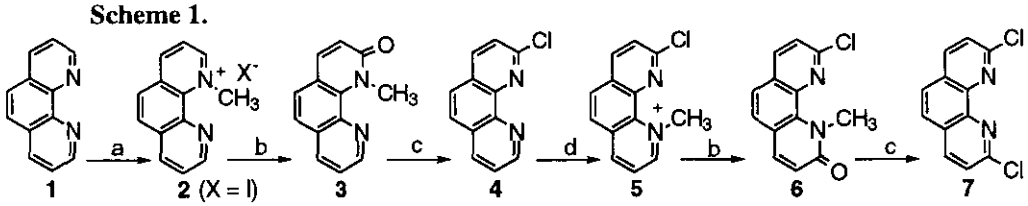
Abstract-Activated manganese dioxide (MnO_2) in dry THF was studied for the transformation of *N*-alkylpyridinium salts to *N*-alkyl-2-pyridones. Only cations of fused ring pyridines (1,10-phenanthroline, quinoline, etc.) were investigated. Nearly quantitative conversion to 1-methyl-1,10-phenanthrol-2-one was achieved under optimum conditions. Oxidative cleavage of ring methyl groups when present also led to pyridones, in some cases producing a 4-pyridone. Different counteranions gave mixed results. Overall, activated MnO_2 is an effective alternative to aqueous ferricyanide for the conversion of fused ring pyridinium salts to the corresponding 2-pyridones.

INTRODUCTION

2,9-Dichloro-1,10-phenanthroline (**7**) is an important intermediate in the synthesis of a number of ligands and macrocycles.[1-11] Its synthesis is a six-step procedure (Scheme 1)[11-13] which involves two troublesome oxidation reactions, where ferricyanide is used to oxidize *N*-alkylphenanthrolinium cations (**2**) and (**5**) to the corresponding phenanthrolones (**3**) and (**6**). Although this sequence is effective, ferricyanide oxidation produces a large volume of toxic waste. We have examined the use of activated manganese dioxide suspended in dry refluxing THF as an alternative oxidization method in the hope of reducing this problem. Activated MnO_2 has been shown to be an effective and mild reagent for a number of oxygen atom transfer reactions,[14] and although it is moderately expensive, its commercial availability in highly activated form makes it a convenient off-the-shelf reagent.

Scheme 1.



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RESULTS AND DISCUSSION

Our initial efforts used the methiodide salt **2** (X = I) as the starting material. Using a 25:1 mole ratio of MnO_2 to substrate under ambient conditions, the reaction was 40% complete after 24 h and 99% complete by GC after 190 h (Figure 1). Refluxing reduced this time to about 24 h . Optimization of the activated MnO_2-to-salt ratio was established in refluxing THF for 24 h. Yields varied from 21% for a 4:1 molar ratio to 79% for a 25:1 ratio (Table 1). Anhydrous conditions were also found to be essential; use of untreated THF greatly reduced yields and addition of 10% v/v water completely inhibited formation of pyridone product. All the substrate salts are sparingly soluble in THF whereas the products are quite soluble. The amount of THF used was usually just sufficient to provide for adequate magnetic stirring of the suspended MnO_2 and variations in amount of THF did not appear to affect the reaction outcome.

We encountered problems with **2** (X = I), as iodide is oxidized by MnO_2, and the resultant I_2 had to be removed with a thiosulfate wash. A test of the inorganic salts KI and NaBr in hot MnO_2/THF was instructive: While the KI/MnO_2 mix rapidly acquired the color of iodine, the NaBr/MnO_2 mix remained colorless even after 3 h reflux. Although we did not have the opportunity to use methyl bromide as an alkylating agent for **1**, we were motivated by this observation. By using other alkylating agents we made different anion salts of **2** and found large differences in product yield. Both triflate and tosylate salts of **2** gave no product whereas mesylate gave a near quantitative yield of **3**. The substrates all seemed to alkylate readily, except for 2,9-dimethylphenanthroline (**14**), from which starting material could be detected in the reaction mixture even after 6 days reflux in benzene. Furthermore, the reaction of **14** with MeOMs had to be protected from light with aluminum foil or else a yellow immiscible liquid formed instead of the product salt.

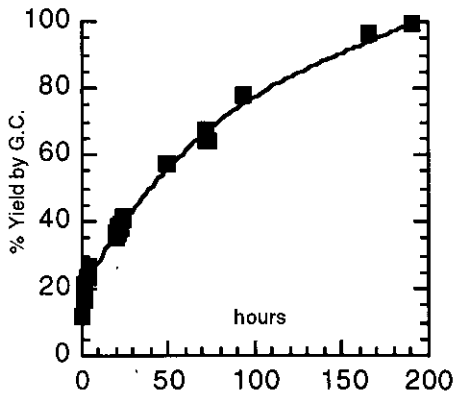
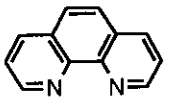
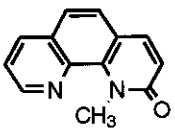
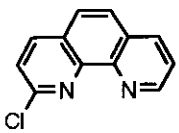
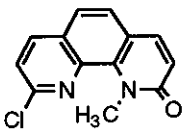
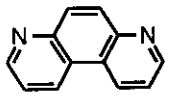
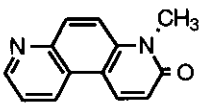
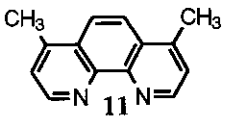
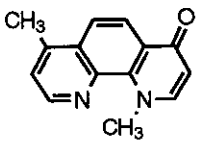
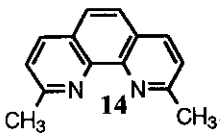
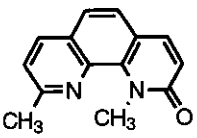
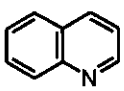
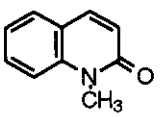
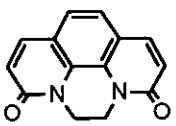
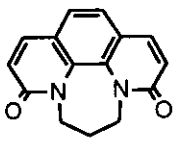
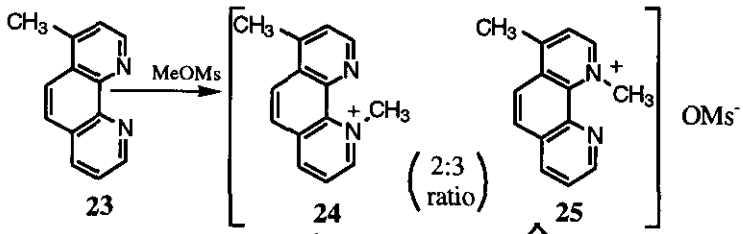


Figure 1. Oxidation of 2^+Ms^- to **3** with MnO_2 in THF at 25 °C.

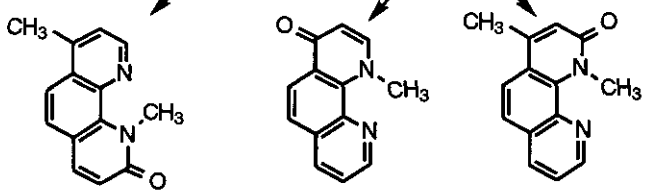
We then turned our attention to the alkylation/oxidation of related compounds as summarized in Table 1. *N*-alkylation promoted the oxidative cleavage of other methyl groups present on the 2- or 4- positions of the alkylated ring. For example, 4,7-dimethyl-1,10-phenanthroline (**11**), upon alkylation and oxidation, gave the 4-pyridone (**13**) instead of a 2-pyridone. Similarly, 2,9-dimethylphenanthroline (**14**), upon alkylation and oxidation with MnO_2, gave the 2-pyridone (**16**). The case of 4-methylphenanthroline (**23**) is most informative (Scheme

Table 1. Oxidation of methylphenanthrolinium salts with MnO_2/THF

Substrate	Alkylating Agent	Mole Ratio MnO_2 / reflux time	Product	Isolated Yield
 **1**	CH_3I (yields **2**I^-)	25:1 / 24 h	 **3**	79%
1	CH_3I	12:1 / 19 h	**3**	44%
1	CH_3I	4:1 / 21 h	**3**	21%
1	$CH_3OSO_2CH_3$	25:1 / 22 h	**3**	95%
1	$CH_3OSO_2CF_3$	29:1 / 48 h	---	0%
1	CH_3OTs	23:1 / 48 h	---	0%
 **4**	CH_3I (**5**, 83%)	32:1 / 22 h	 **6**	42%
 **8**	$CH_3OSO_2CH_3$ (**9**, 76%)	28:1 / 68 h	 **10**	81%
 **11**	$CH_3OSO_2CH_3$ (**12**, 67%)	25:1 / 69 h	 **13**	30%
 **14**	$CH_3OSO_2CH_3$ (**15**, 40%)	25:1 / 24 h	 **16**	19%
 **17**	$CH_3OSO_2CH_3$ (salt not isolated)	25:1 / 96 h	 **18**	14%
1	 (**19**, 65%)	11:1 / 45 h	 **20**	14%
1	 (**21**, 90%)	25:1 / 99 h	 **22**	0%



Scheme 2.



oxidant:	**26**	**27**	**28**
$Fe(CN)_6$	18%	30%	18%
MnO_2	5.2%	28%	--

2). Initial alkylation of **23** with MeOMs gave both 1-methyl and 10-methylphenanthrolinium salts in approximately a 3:2 mixture by NMR. This mixture of salts was not separated, but was oxidized by MnO_2 *in situ* to give predominantly **27**, an oxidatively cleaved 4-pyridone, and a much smaller amount of 2-pyridone (**26**). When this same mixture of salts was treated with aqueous ferricyanide, three apparent products were obtained: **26**, **27**, and a third product which we have tentatively identified as **28**, whose separation from **26** could not be readily achieved with column chromatography.[15] These findings are in accord with earlier work involving **23**.[12]

MnO_2 oxidation of the bridged dications (**19**) and (**21**) were also investigated. Ethylene bridged dication (**19**) gave a 14% yield of dione (**20**) and propylene bridged salt (**21**) gave no product at all. These yields are lower than those previously reported using ferricyanide as oxidant.[13]

Many of the intermediate salts are hygroscopic; some are deliquescent, which undoubtedly accounts for some of the low yields reported, as complete removal of the water from the salt was difficult, and water interferes with the oxidation. The interference of water with the MnO_2 oxidation reaction prompted us to investigate a one-pot synthesis of the amides, where the solvent from the first step was removed under reduced pressure, leaving a crude salt residue which was then treated with MnO_2. Low yields were obtained with the one-pot method (Table 1), presumably due to the interference of unreacted alkylating agent and/or starting material with the oxidant. We believe a more volatile alkylating agent such as MeBr will prove to be much more efficacious in a one-pot procedure.

Most oxidations involving activated MnO_2 are dehydrogenations[14] and are believed to proceed by a free-radical based mechanism. In our case, MnO_2 appears to function as an oxygen atom transfer reagent. Although dialkylanilines are also known to give products of oxygen atom transfer with MnO_2,[16] to our knowledge, this is the first example of a pyridinium cation, or more generally, an ammonium cation which

acts as an oxygen acceptor in reactions with activated MnO_2. Although we were unable to use gaseous CH_3Br as an alkylating agent, our results suggest that a 1-2 combination of alkylation with CH_3Br under pressure followed by MnO_2 oxidation of the bromide salt will provide a convenient entry into the large-scale synthesis of this family of compounds.

EXPERIMENTAL

A Hewlett Packard 5890 series II GC apparatus equipped with either a Hewlett Packard 3396 series II integrator or an HP 5971 mass selective detector were used for yield optimization studies and MS characterization respectively. High resolution mass spectra were obtained from the facility at the University of Maryland, College Park, Maryland, USA. ^1H and ^{13}C NMR spectral data were collected on a Bruker AC-300 NMR spectrometer at 300 and 75 MHz respectively in $CDCl_3$ with TMS reference. Activated manganese dioxide (Aldrich catalog number 21,764-6) was purchased from Aldrich Chemical Co., Milwaukee, WI, USA, and used as recieved. Phenanthroline (**4**) and salts (**2**, **5**, **19**, and **21**) were synthesized by literature procedures.[12,17,18] All other phenanthrolines and quinoline were obtained from commercial sources. Anhydrous THF (Aldrich) was distilled over Na/benzophenone prior to use. Reagent benzene was commercially obtained and used as received. All salts made herein were used directly in the subsequent MnO_2 oxidation without further characterization.

1-Methyl-1,10-phenanthrolinium mesylate (2, X = OMs): 1,10-Phenanthroline monohydrate (**1**·H_2O) (5.1 g, 26 mmol) was placed in a 250 mL round bottom flask, charged with benzene (150 mL), equipped with a Dean Stark trap, and the contents held reflux until all the water was removed. Methyl mesylate (3.9 g, 35 mmol) was added and the flask contents stirred at 60 °C for 36 h. The precipitate so obtained was collected by filtration, washed with dry ether, and dried *in vacuo* to give the product (6.7 g, 23 mmol, 90%) as hygroscopic white crystals.

1-Methyl-1,10-phenanthrolinium tosylate (2, X = OTs): A solution of 1,10-phenanthroline monohydrate (**1**·H_2O) (1.0 g, 5 mmol) and methyl tosylate (2.6 g, 14 mmol) in THF (100 mL) was stirred at 25 °C for 24 h. The precipitate was collected by filtration, washed with ether, and dried to give the product (0.98 g, 2.8 mmol, 55%) as a white powder.

1-Methyl-1,10-phenanthrolinium triflate (2, X = OTf): A solution of 1,10-phenanthroline monohydrate (**1**·H_2O) (1.0 g, 5 mmol) and methyl triflate (1.0 g, 6.1 mmol) in THF (100 mL) was stirred

at 25 °C for 24 h. The precipitate was collected by filtration, washed with ether, and dried to give the product (1.5 g, 4.3 mmol, 86%) as a white powder.

4-Methyl-4,7-phenanthrolinium mesylate (9). 4,7-Phenanthroline **8** (1.12 g, 6.2 mmol) was held at reflux with methyl methanesulfonate (1.13 g, 10.2 mmol) in benzene (150 mL) for 24 h . The resulting precipitate was collected by filtration and dried *in vacuo* to give product **9** (1.44 g, 76%) as a colorless crystalline powder.

1,4-Dimethyl-1,10-phenanthrolinium mesylate (25) and **1,7-Dimethyl-1,10-phenanthrolinium mesylate (24).** 4-methyl-1,10-phenanthroline (0.4 g, 2.1 mmol) was refluxed with methyl mesylate (1.4 g, 13 mmol) in benzene (150 mL) for 48 h. The solid so obtained was collected by filtration and dried *in vacuo* at 50 °C to give a mixture of **25** and **24** (0.60 g, 95%) as a colorless deliquescent powder, in a 3:2 proportion as indicated by ^{1}H NMR.[19]

1,4,7-Trimethyl-1,10-phenanthrolinium mesylate (12). 4,7-Dimethyl-1,10-phenanthroline (0.48 g, 2.3 mmol) was placed in a round bottom flask, charged with benzene (150 mL), equipped with a Dean Stark trap, and the contents held reflux until all the water was removed. Methyl mesylate (2.0 g, 18.3 mmol) was added to the flask and stirred under reflux for six days The precipitate was collected by filtration, washed with cold benzene and dried to give the product **12** (0.49 g, 67%) as a tan powder.

1,2,9-Trimethyl-1,10-phenanthrolinium mesylate (15). 2,9-Dimethyl-1,10-phenanthroline (0.2656 g, 1.28 mmol) was placed in a 250 mL round bottomed flask equipped with a Dean Stark trap and wrapped with aluminum foil. Water was removed by distillation. Methyl mesylate (1.1 g, 10.0 mmol) was then added to the flask and the contents stirred under reflux for six days. The precipitate was collected by filtration, washed with cold benzene and dried to give the product **15** (0.15 g, 40%) as a light purple powder.

Synthesis of Phenanthrolones/diones. General Procedure: The anhydrous phenanthrolinium salt (0.5-0.9 g) in dry THF (150 mL) was refluxed under nitrogen with activated MnO_2 for the specified time period (see Table 1 for reaction times and stoichiometries). The inorganic solid was then removed by filtration, the THF removed by rotary evaporation, and the product recrystallized. For iodide salts, the crude reaction mixture was taken up in CH_2Cl_2, washed with 0.2 N aqueous thiosulfate until colorless, and the solvent again removed prior to recrystallization.

1-Methyl-1,10-phenanthrol-2-one (3). Yield, 79% (C_6H_6); mp 122-124 °C (lit., 123-124 °C).[12] MS m/z 210 (M+). ^{1}H NMR δ 4.46 (s, 3H, -C*H*$_3$), 6.87 (d, 1H, J = 9.3 Hz, aryl H-4), 7.49 (d, 1H, J =

8.2 Hz, aryl H-8), 7.53 (s, 1H, aryl H-6), 7.54 (s, 1H, aryl H-5), 7.75 (d, 1H, J = 9.3 Hz, aryl H-3), 8.15 (d, 1H, J = 8.2 Hz, aryl H-7), 8.92 (d, 1H, J = 8.2 Hz, aryl H-9). ^{13}C NMR δ 37.9, 120.5, 121.85, 122.2, 122.4, 126.7, 130.1, 136.1, 138.0, 139.1, 140.2, 164.3.

9-Chloro-1-methyl-1,10-phenanthrol-2-one (6). Yield, 42% (H_2O); mp 146-148 °C (lit., 153-154 °C).[11] ^{1}H NMR δ 1.60 (s, 3H, -NCH_3), 6.91 (d, 1H, J = 9.3 Hz, aryl H-3), 7.47 (d, 1H, J = 8.5 Hz, aryl H-7), 7.55 (d, 1H, J = 8.3 Hz, aryl H-5), 7.60 (d, 1H, J = 8.4 Hz, aryl H-6), 7.77 (d, 1H, J = 9.3 Hz, aryl H-4), 8.12 (d, 1H, J = 8.5 Hz, aryl H-8). ^{13}C NMR δ 37.0, 121.2, 121.8, 124, 124.1, 127.2, 128.7, 136.9, 138.7, 138.9, 147.2, 163.8, 171.1.

4-Methyl-4,7-phenanthrol-3-one (10). Yield, 81% (H_2O); mp 245-246 °C (lit = 239-240 °C).[20] ^{1}H NMR δ 3.87 (s, 3 H, -NCH_3), 6.93 (d, 1 H, J = 9.7 Hz, aryl H-2), 7.59 (q, 1 H, J = 8.5 Hz, aryl H-9), 7.83 (d, 1 H, J = 9.5 Hz, aryl H-5), 8.28 (d, 1 H, J = 9.5 Hz, aryl H-6), 8.46 (d, 1 H, J = 9.7 Hz, aryl H-1), 8.66 (d, 1 H, J = 8.8 Hz, aryl H-10), 8.95 (d, 1 H, J = 9.7 Hz, aryl H-2) ^{13}C {^{1}H} NMR δ 162.7, 149.9, 144.8, 169.5, 133.5, 133.5, 130.3, 125.5, 123.0, 122.1, 118.7, 117.6, 114.7, 30.7. Anal. Calcd for $C_{13}H_{10}N_2O$: C, 74.3; H, 4.8; N, 13.3. Found: C, 74.05; H, 4.84; N, 13.31.

1,7-Dimethyl-1,10-phenanthrol-4-one (13). Yield, 30% (H_2O); mp 170-171 °C. ^{1}H NMR δ 2.77 (s, 3H, -CCH_3), 4.61 (s, 3H, -NCH_3), 6.53 (d, 1H, J = 7.7 Hz, aryl H-2), 7.40 (d, 1H, J = 4.3 Hz, aryl H-8), 7.64 (d, 1H, J = 7.7 Hz, aryl H-3), 7.89 (d, 1H, J = 9.1 Hz, aryl H-6), 8.57 (d, 1H, J = 8.9 Hz, aryl H-5), 8.79 (d, 1H, J = 4.3 Hz, aryl H-9). ^{13}C NMR δ 19.6, 49.5, 112.5, 119.4, 123.4, 123.6, 127.4, 130.8, 139.1, 141.6, 144.3, 146.4, 146.5, 177.3. Anal. Calcd for $C_{14}H_{12}N_2O \cdot 1.5\ H_2O$: C, 66.9; H, 6.0; N, 11.1. Found: C, 66.89; H, 5.69; N, 11.14.

1,9-Dimethyl-1,10-phenanthrol-2-one (16). Yield, 19% (H_2O); mp 79-80 °C (lit., 72-78 °C)[21]. ^{1}H NMR δ 2.77 (s, 3H, -CCH_3), 4.51 (s, 3H, -NCH_3), 6.90 (d, 1H, J = 9.3 Hz, aryl H-4), 7.38 (d, 1H, J = 8.3 Hz, aryl H-8), 7.52 (s, 2H, aryl H-5, H-6), 7.78 (d, 1H, J = 9.3 Hz, aryl H-3), 8.07 (d, 1H, J = 8.4 Hz, aryl H-7). ^{13}C NMR δ 25.3, 38.0, 120.6, 122, 122.2, 122.5, 125.7, 136.3, 137.6, 138.3, 139.2, 139.6, 156.1, 164.4. MS m/z 224, 195. HRMS m/z = 224.09512. Calcd for $C_{14}H_{12}N_2O$: 224.09497.

3,5,6,8-Tetrahydropyrazino[1,2,3,4-lmn][1,10]phenanthroline-2,9-dione (20). Procedure as above except the reaction was conducted at 25 °C. Yield, 13.6% (MeOH); mp 293-296 °C (lit., 295-297 °C).[5] ^{1}H NMR corresponds to published values.[5]

Oxidation of 4-methyl-1,10-phenanthroline salts (24) and (25). The mixture of salts, 1,7-dimethyl-1,10-phenanthrolinium mesylate (**24**) and 1,4-dimethyl-1,10-phenanthrolinium mesylate (**25**), resulting from the methylation of 4-methyl-1,10-phenanthroline (**23**) were not isolated, but directly oxidized into the subsequent pyridones (**26**) and (**27**) using either a 25:1 mole ratio of MnO_2, or in the case of ferricyanide oxidation, portionwise alternating addition of saturated aqueous $K_3Fe(CN)_6$ and 1N NaOH at 0 °C to an aqueous solution of the phenanthrolinium salts. The products were isolated, then purified via column chromatography (50:1 $CHCl_3$/MeOH), compound (**26**) eluting first. **1,7-Dimethyl-1,10-phenanthrol-2-one (26)**: Yield, 5.2% (H_2O); mp 116-123 °C. MS m/z = 226 (M+). ^{1}H NMR δ 2.72 (s, 3H, -CCH_3), 4.43 (s, 3H, -NCH_3), 6.90 (d, 1H, J = 9.3 Hz, aryl H-3), 7.34 (d, 1H, J = 4.2 Hz, aryl H-8), 7.59 (d, 1H, J = 8.7 Hz, aryl H-6), 7.76 (d, 1H, J = 9.3 Hz, aryl H-4), 7.78 (d, 1H, J = 8.7 Hz, aryl H-5), 8.79 (d, 1H, J = 4.3 Hz, aryl H-9). ^{13}C NMR δ 19.6, 38.4, 120.5, 122.2, 122.9, 126.3, 129.9, 138.5, 139, 140, 143.9, 146.6, 164.4, 118.2. **1-Methyl-1,10-phenanthrol-4-one (27):** Yield, 28% (H_2O); mp 162-164 °C. MS m/z 210 (M+). ^{1}H NMR δ 4.66 (s, 3H, -NCH_3), 6.52 (d, 1H, J = 7.7 Hz, aryl H-3), 7.55 (d, 1H, J = 4.2, 8.2 Hz, aryl H-8), 7.62 (d, 1H, J = 7.7 Hz, aryl H-2), 7.67 (d, 1H, J = 8.7 Hz, aryl H-6), 8.22 (d, 1H, J = 8.3 Hz, aryl H-7), 8.54 (d, 1H, J = 8.7 Hz, aryl H-5), 8.93 (d, H, J = 4.2 Hz, aryl H-9). ^{13}C NMR δ 49.2, 112.6, 122.4, 123.5, 124.1, 127.7, 131, 136.2, 138.6, 138.9, 141.9, 146.2, 147.0, 177.3.

One-pot synthesis of 1-methyl-2-quinolone (18). Quinoline (1.14 g, 8.8 mmol) and benzene (100 mL) were dried with a Dean-Stark trap, then refluxed under nitrogen with methyl mesylate (0.99 g, 9.0 mmol) for 72 h . The benzene was separated from the resultant crude **18** by distillation under N_2. THF and activated MnO_2 were added to the sealed reaction vessel and refluxed 96 h . The inorganic solids were removed by filtration and the THF removed by rotary evaporation. The pyridone (**18**) was isolated by chromatography (silica, acetone eluent) and recrystallized from $CHCl_3$ to give a white solid (0.19 g, 13.5%), mp 73-74 °C (lit., 74 °C),[22] whose ^{1}H NMR corresponds to published values.[23]

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