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Studies of 2,2′-Bipyridyl *N,N′*-Dioxides[1]

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2,2′-Bipyridyl *N,N′*-dioxide, its derivatives substituted at the 4- and/or 4′-positions by methoxy, nitro, chloro, and bromo groups, and the corresponding N,N′-deoxygenated compounds have been synthesized. The *N,N′*-dioxides were examined in a number of refluxing solvents and under sublimation to investigate a potential liberation of singlet oxygen. All *N,N′*-dioxides were found to be stable under such conditions with no production of the corresponding N,N′-deoxygenated compounds.

Molecular oxygen of the singlet state has proved to be a useful reagent for effecting a number of transformations in organic chemistry.[3] Though principally generated via photosensitization of ground-state molecular oxygen, a number of chemical sources of singlet oxygen[4] are also available. Among the latter, the reaction of sodium hypochlorite with hydrogen peroxide[5] and the decompositions of both triphenyl phosphite ozonide[6] and endoperoxides[7] figure most prominently.

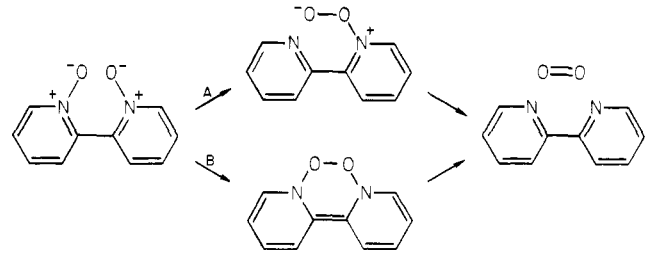
It was felt that 2,2′-bipyridyl *N,N′*-dioxide (1) might

1 2

constitute another potential source of singlet oxygen as pictured. With such a dioxide and the bipyridyl product **2** being of singlet character, the oxygen product by spin conservation would therefore also be in the singlet state.

Examination of the literature revealed that **1** had been previously prepared by heating 2,2′-bipyridyl (**2**) as a solution in glacial acetic acid and 30% hydrogen peroxide and was reported to decompose at 310 °C.[8,9] The dioxide **1**, prepared as such or with *m*-chloroperbenzoic acid in chloroform,[10] was seen here to be a very polar compound that did indeed decompose above 300 °C to a black tar. It was found to be stable to sublimation under vacuum at 240 °C and refluxing for 48 h in chloroform, ethanol, dioxane, and dimethylformamide with no trace of 2,2′-bipyridyl being produced.

For such a fragmentation to occur, two mechanistic pathways can be envisioned as depicted below. Pathway



A might be considered unfavored as it involves a S_N2 attack at a displacement angle of approximately 120°, a process that has been shown not to occur by Eschenmoser and co-workers in their studies of endocyclic vs. exocyclic methyl-transfer reactions.[11]

It was felt that appropriate substitutions at the 4- and 4′-positions of electron-donating and -withdrawing groups might facilitate the formation of the intermediate of pathway B[12] and thus help promote the desired transformation. To this end, all possible 4- and 4′-derivatized

(1) Taken from the Ph.D. Thesis of D. Wenkert, Harvard University, 1979.

(2) (a) Present address: Chemistry Department, University of California—San Diego, La Jolla, CA 92093. (b) Deceased July 8, 1979.

(3) For general reviews on the chemistry of singlet oxygen, see: (a) Kearns, D. R. *Chem. Rev.* **1971**, *71*, 395. (b) Denny, R. W.; Nickon, A. *Org. React.* **1973**, *Volume 20*, 133. (c) Wasserman, H. H., Murray, R. W., Eds. "Singlet Oxygen"; Academic Press: New York, 1979.

(4) For a review, see: Murray, R. W. In "Singlet Oxygen"; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979; p 59.

(5) Foote, C. S.; Wexler, S. *J. Am. Chem. Soc.* **1964**, *86*, 3879.

(6) Murray, R. W.; Kaplan, M. L. *J. Am. Chem. Soc.* **1969**, *91*, 5358.

(7) Wasserman, H. H.; Scheffer, J. R.; Cooper, J. L. *J. Am. Chem. Soc.* **1972**, *94*, 4991.

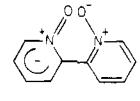
(8) Haginiwa, J. *J. Pharm. Soc. Jpn.* **1955**, *75*, 731.

(9) Murase, I. *Nippon Kagaku Zasshi* **1956**, 77, 682.

(10) Method: Craig, J. C.; Purushothaman, K. K. *J. Org. Chem.* **1970**, *35*, 1721.

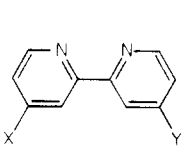
(11) Tenud, L.; Farooq, S.; Seibl, J.; Eschenmoser, A. *Helv. Chim. Acta* **1970**, *53*, 2059.

(12) Its formation can be conceived via consideration of a resonance form of **1**:

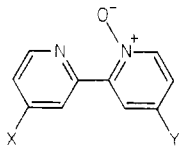


0022-3263/83/1948-0283$01.50/0

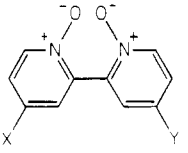
Chart I



7, X = H; Y = NO_2
10, X = H; Y = OCH_3
11, X = NO_2; Y = NO_2
12, X = Cl; Y = Cl
13, X = NO_2; Y = Cl
16, X = Br; Y = Br
18, X = OCH_3; Y = OCH_3



4, X = H; Y = H
5, X = H; Y = NO_2
8, X = H; Y = OCH_3



3, X = NO_2; Y = NO_2
6, X = H; Y = NO_2
9, X = H; Y = OCH_3
14, X = Cl; Y = Cl
15, X = Br; Y = Br
17, X = OCH_3; Y = OCH_3
19, X = NO_2; Y = OCH_3

bipyridyl dioxides of methoxy and nitro substituents as well as the dichloro and dibromo derivatives were prepared. All corresponding bipyridyls were also synthesized for the sake of reference as these would be expected to be produced if singlet oxygen was liberated from any of the dioxides.

Three of the substituted dioxides could be readily made from 2,2′-bipyridyl (**2**). 2,2′-Bipyridyl *N,N′*-dioxide (**1**) could be nitrated on both rings, as reported by Haginiwa[8] and by Murase,[9] to give 4,4′-dinitro-2,2′-bipyridyl *N,N′*-dioxide (**3**, Chart I). 2,2′-Bipyridyl *N*-oxide (**4**), which had been previously synthesized by oxidation of **2** with 30% hydrogen peroxide in glacial acetic acid,[9] could be obtained in higher yield by oxidation with *m*-chloroperbenzoic acid. This could then be nitrated to 4-nitro-2,2′-bipyridyl *N*-oxide **5**, which in turn could be oxidized with *m*-chloroperbenzoic acid to the corresponding dioxide **6** or reduced with phosphorus trichloride[13] to 4-nitro-2,2′-bipyridyl **7**. Compounds **3**, **5**, and **6** had been reported to have been previously synthesized in low yield by 30% hydrogen peroxide–acetic acid oxidation of 2,2′-bipyridyl (**2**) and then nitration of the reaction mixture.[14] 4-Nitro-2,2′-bipyridyl *N*-oxide **5** could also have its nitro group displaced by methoxide anion to give the methoxy derivative **8**, which could then be oxidized with *m*-chloroperbenzoic acid to the dioxide **9** or deoxygenated with phosphorus trichloride to **10**.

4,4′-Dinitro-2,2′-bipyridyl dioxide (**3**) could be used for a number of transformations. It had been reported that **3** could be deoxygenated to 4,4′-dinitro-2,2′-bipyridyl (**11**) in 9% yield by refluxing the dioxide **3** as a suspension in chloroform with phosphorus trichloride.[15] Attempts to repeat this procedure gave a mixture of at least three compounds in low yield. In acetonitrile the same mixture was obtained in greater yield, with the predominant products proving to be 4,4′-dichloro-2,2′-bipyridyl (**12**) and 4-nitro-4′-chloro-2,2′-bipyridyl (**13**). It was found later that 4,4′-dinitro-2,2′-bipyridyl (**11**) could be obtained directly from the parent dioxide **3** when on attempting to repeat a literature procedure,[8] which specified refluxing **3** solely in phosphorus trichloride, 4,4′-dichloro-2,2′-bipyridyl (**12**) was not produced as reported but **11** was obtained instead.

Interestingly, it had been reported that 4,4′-dichloro-2,2′-bipyridyl *N,N′*-dioxide (**14**) and 4,4′-dibromo-2,2′-bipyridyl *N,N′*-dioxide (**15**), prepared by heating **3** with concentrated hydrochloric acid and with acetyl bromide and acetic acid, respectively, were unstable during recrystallization from boiling dimethylformamide.[15] The dibromo dioxide **15** reportedly gave back some of the deoxygenated compound **16** under such conditions. However, the dichloro and dibromo dioxides were found here to be stable in refluxing DMF for 48 h, without any of the corresponding deoxygenated compounds being produced.

Finally, **3** could be transformed, as reported in the literature, on treatment with sodium methoxide, into the dimethoxy dioxide **17**, which could then be reduced with phosphorus trichloride to **18**.[15]

All of the dioxides mentioned were found to be stable to refluxing in chloroform, dioxane, ethanol, and dimethylformamide as well as to sublimation under vacuum at temperatures not lower than 170 °C without any detection of deoxygenated compounds being produced.

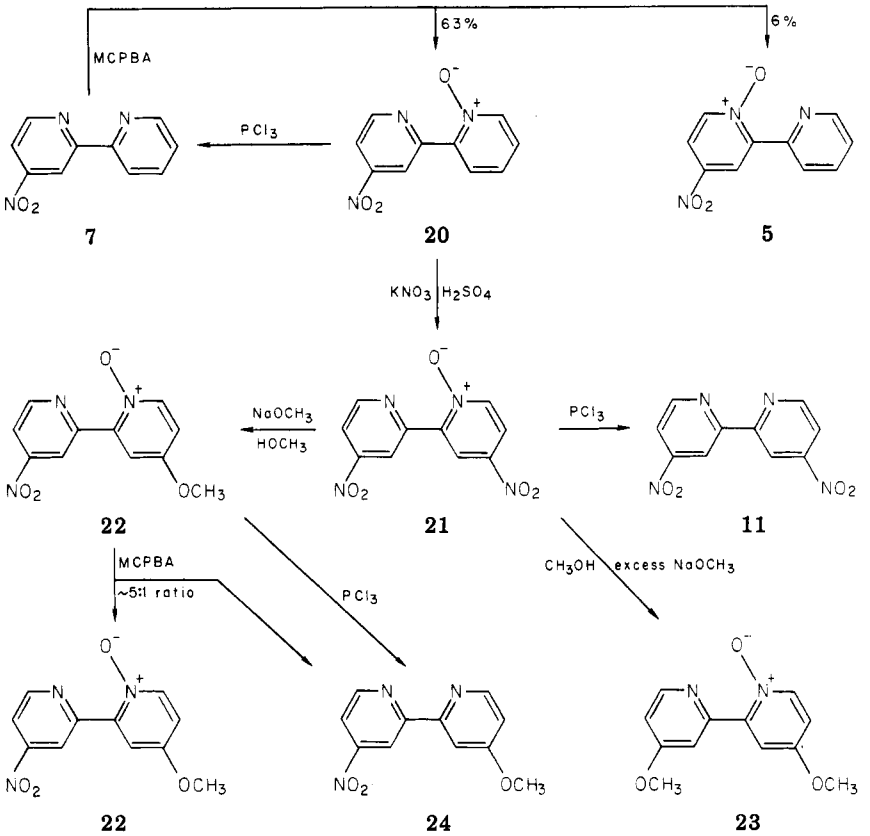
It was decided to synthesize the remaining dioxide, 4-methoxy-4′-nitro-2,2′-bipyridyl *N,N′*-dioxide (**19**), via a route in which a dioxide was only encountered in the last step of the synthesis. All of the previously made dioxides, in contrast to the monoxides, were only sparingly soluble in organic solvents, and though they moved only slightly on silica gel, they could be purified by filtration through basic alumina with chloroform–methanol mixtures, when the last step of their synthesis involved an oxidation of a monoxide with *m*-chloroperbenzoic acid. Also, as the previously mentioned synthesis of 4,4′-dinitro-2,2′-bipyridyl (**11**) had not yet been uncovered, a satisfactory synthesis of this compound was also needed.

For these reasons, the following reactions were performed (Scheme I). 4-Nitro-2,2′-bipyridyl (**7**), on treatment with *m*-chloroperbenzoic acid at 0 °C for 3 days, was oxidized predominantly at the more nucleophilic pyridine ring, giving a 63% yield of the desired 4′-nitro-2,2′-bipyridyl *N*-oxide (**20**) as well as a 6% yield of the previously made 4-nitro-2,2′-bipyridyl *N*-oxide (**5**). Oxidation at room temperature resulted in the additional formation of 4-nitro-2,2′-bipyridyl *N,N′*-dioxide (**6**). The nitro monooxide **20**, which could be converted back to **7** with phosphorus trichloride, was nitrated in moderate yield to **21**. The latter compound could be reduced with phosphorus trichloride to the desired 4,4′-dinitro-2,2′-bipyridyl (**11**). The dinitro monooxide **21** showed only slight solubility in methanol, and when stirred partially as a suspension in the solvent with 1–2 equiv of sodium methoxide at room temperature for several days, selective displacement of the 4-nitro group was effected, providing up to a 30% yield of the desired 4-methoxy-4′-nitro-2,2′-bipyridyl *N*-oxide (**22**), with ca. 45% of starting material being recovered. Longer reaction times did not increase the yield, and use of excess sodium methoxide resulted in substantial formation of 4,4′-dimethoxy-2,2′-bipyridyl *N*-oxide (**23**). Stirring **21** as a solution in dioxane with potassium methoxide and 18-crown-6 substantially decreased the yield of the methoxynitro monooxide **22**.

The oxidation of **22** proved to be interesting. Its treatment with 1.5 equiv of *m*-chloroperbenzoic acid did not give the expected 4-methoxy-4′-nitro-2,2′-bipyridyl *N,N′*-dioxide (**19**) but led to recovered **22** and 4-methoxy-4′-nitro-2,2′-bipyridyl (**24**) in a ca. 5:1 ratio. This

(13) Ochiai, E. *J. Org. Chem.* **1953**, *18*, 534.
(14) Jones, R. A.; Roney, B. D.; Sasse, W. H. F.; Wade, K. O. *J. Chem. Soc. B* **1967**, 106.
(15) Maerker, G.; Case, F. H. *J. Am. Chem. Soc.* **1958**, *80*, 2745.

Scheme I

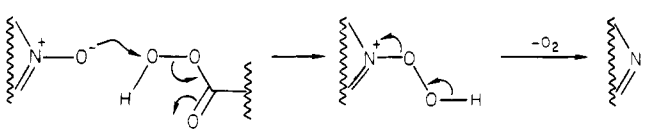


suggested the possibility of a reaction cycle wherein the monooxide **22** was oxidized to the dioxide **19**, which fragmented to singlet oxygen and deoxygenated **24**, the latter of which could then be oxidized back to **22**.

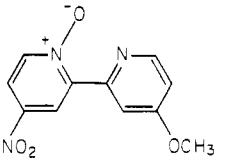
A synthesis of **19** was then attempted directly from 4,4′-dinitro-2,2′-bipyridyl *N,N*-dioxide **3** by treatment of the latter with a slight excess of sodium methoxide in methanol. The desired product **19** could be obtained in 42% yield and, surprisingly, in contrast to the other dioxides, be easily purified by chromatography on silica gel.

The dioxide **19** was found to be stable to refluxing for 48 h in chloroform, dioxane, ethanol, and dimethylformamide as well as to sublimation. It could be reduced directly to 4-methoxy-4′-nitro-2,2′-bipyridyl (**24**) with phosphorus trichloride but was quite stable to the reaction conditions used in the treatment of monooxide **22** with *m*-chloroperbenzoic acid.

It would appear, in light of these results, that a direct deoxygenation of 4-methoxy-4′-nitro-2,2′-bipyridyl *N*-oxide (**22**) is occurring via attack of the oxygen of the *N*-oxide on the peracid. Such deoxygenations of pyridine *N*-oxides are known, though under harsher conditions.[16] The reason for this deoxygenation, especially in light of the ease with which 4-nitro-2,2′-bipyridyl (**7**) and 4-methoxy-2,2′-bipyridyl *N*-oxide (**8**) are oxidized, is unclear.



Oxidation of 4-methoxy-4′-nitro-2,2′-bipyridyl (**24**), which could also be obtained directly from the monooxide **22** by reduction with phosphorus trichloride, with excess *m*-chloroperbenzoic acid led to a similar mixture of starting material and the monooxide, as well as a trace amount of dioxide **19**. The latter might have arisen from a small amount of **25** having been formed, which, rather than being deoxygenated (the amine oxide oxygen of *p*-nitropyridine *N*-oxide being less nucleophilic than that of a *p*-methoxypyridine *N*-oxide), was oxidized to **19**.



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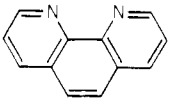
The N-oxidation of the sterically constrained 1,10-phenanthroline **26** was also investigated. The monooxide



26

of this compound had previously been prepared by oxidation with glacial acetic acid and 30% hydrogen peroxide, though no dioxide could be isolated.[15,18] Repetition of this procedure, here, indeed gave only the monooxide, and use of more drastic conditions (refluxing for 2 days in 90% hydrogen peroxide, glacial acetic acid, and concentrated sulfuric acid[19] or heating for 12 h with *m*-chloroperbenzoic

(16) Roberts, S. M.; Suschitzky, H. *J. Chem. Soc. C* **1968**, 1537.

(17) One sidelight to the chemistry of **22** that was examined was the possibility that the oxygen of the *N*-oxide might be able to migrate from one pyridine ring to the other. However, no change in the thin-layer chromatographic properties or infrared spectra for the amine oxide was seen when it was sublimed, refluxed in dioxane for 36 h, or heated to its melting point of 178 °C for a few minutes.

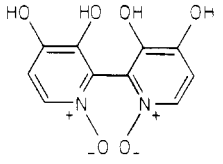
(18) Corey, E. J.; Borror, A. L.; Foglia, T. *J. Org. Chem.* **1965**, *30*, 288.

(19) Method of preparing *N*-oxides of otherwise difficult to oxidize N-heteroaromatic compounds; cf.: Chivers, G. E.; Suschitzky, H. *J. Chem. Soc.* **1971**, 2867.

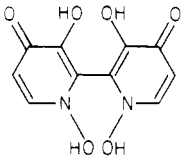
acid with a radical inhibitor, 4,4′-thiobis(6-*tert*-butyl-3-methylphenol),[20] in ethylene dichloride) also did not lead to the isolation of the dioxide.

The conceivable reverse process, 2,2′-bipyridyl or 1,10-phenanthroline reacting with singlet oxygen giving the corresponding dioxide, was also examined. No reaction was observed, however, on attempting the photooxygenation of either compound over prolonged periods (greater than 6 h) in methanol with rose bengal as sensitizer or in methylene chloride with *meso*-tetraphenylporphyrin as sensitizer. In contrast, both α-pinene and 1,1′-bicyclohexenyl were readily oxygenated (less than 40 min) under such reaction conditions, providing the products *trans*-3-hydroperoxypin-2(10)-ene[21] (via an ene reaction) and 3,6-dihydro-3,4,5,6-bis(tetramethylene)-1,2-dioxin[22] (via a 4 + 2 cycloaddition reaction), respectively. Also, both 2,2′-bipyridyl and 1,10-phenanthroline were quantitatively recovered unchanged after refluxing for a week in benzene with a large excess of 9,10-diphenylanthracene peroxide,[7] a chemical source of singlet oxygen.

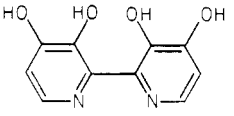
Since the completion of the present work there has appeared a report on the structure analysis of the mushroom constituent orellanine.[23] Its constitution was proposed to be that depicted in formula **27**. On pyrolysis above 150



27



28



29

°C the substance was shown to liberate oxygen gas and be converted into a minor mushroom constituent, orelline **29**. Whereas this observation, in principle, is an example of the transformation of a 2,2′-bipyridyl *N,N′*-dioxide into a 2,2′-bipyridyl and oxygen, it is too early to speculate on the reason for the discrepancy between this result and the thermal stability of the above *N,N′*-dioxides. Confirmation of the proposed structure by X-ray analysis or total synthesis of orellanine is desirable, knowledge of the spin state of the liberated oxygen is needed, and most importantly, the effect of the equilibrium between structure **27** and tautomer **28** on the ease of oxygen extrusion requires investigation.[24]

Experimental Section

Melting points below 250 °C were taken in evacuated, sealed capillary tubes on a Thomas-Hoover capillary melting point apparatus, and those above 250 °C were taken on a Kofler hot-stage instrument. In both cases melting points are uncorrected. ^{1}H NMR spectra were measured at 100 MHz on Varian HA-100 or XL-100 instruments. Chemical shifts and coupling constants are reported in parts per million downfield from internal Me_4Si and Hz, respectively. UV spectra were measured on a Cary Model 14 spectrometer and IR spectra on a Perkin-Elmer 137 instrument, using polystyrene as external reference. Only selected IR absorptions are given. All spectra (including mass spectra) are reproduced in ref 1. Analytical thin-layer chromatography (TLC) was performed on Analtech 0.25 mm silica gel plates or Eastman 0.10 mm silica gel sheets, both containing a 254 nm indicator. For preparative separations Analtech 20 × 20 cm silica gel plates of indicated thickness containing PF 254 indicator were used. Column chromatography was performed on activity I Woelm basic alumina. Elemental analyses were performed by Scandinavian Microanalytical Laboratories, Herlev, Denmark. Prior to analysis, samples were dried at room temperature at 0.3–0.05 mmHg for 12–24 h.

2,2′-Bipyridyl *N,N′*-dioxide (1):[9] ^{1}H NMR (Me_2SO-d_6) δ 7.30–7.72 (m, 6 H), 8.28–8.41 (m, 2 H); UV (95% EtOH) λ_{max} (ε) 221 nm (20 600), 238 (15 200), 267 (15 300); IR (KBr) 7.97 μm.

4,4-Dinitro-2,2′-bipyridyl *N,N′*-dioxide (3):[9] ^{1}H NMR (Me_2SO-d_6) δ 8.38 (dd, H_5 and $H_{5'}$), 8.62 (dd, H_6 and $H_{6'}$), 8.71 (dd, H_3 and $H_{3'}$) [$J_{3,5} = J_{3',5'} = 3.2$, $J_{3,6} = J_{3',6'} = 0.5$, $J_{5,6} = J_{5',6'} = 7.2$ Hz]; UV (95% EtOH) λ_{max} (ε) 232 nm (sh, 14 900), 328 (20 000); IR (KBr) 6.56, 7.43, 7.72 μm.

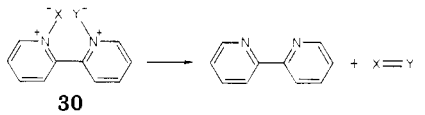
2,2′-Bipyridyl *N*-Oxide (4). A solution of 2,2′-bipyridyl **2** (70.00 g, 448.2 mmol) in 250 mL of $CHCl_3$ was stirred at 0 °C, for 35 min. A solution of *m*-chloroperbenzoic acid (84.5%, 91.56 g, 448 mmol) in 870 mL of $CHCl_3$ was then added dropwise over 80 min and the mixture allowed to stir at room temperature for 13.5 h. The solution was washed three times with 500-mL portions of 5% Na_2CO_3, dried ($MgSO_4$), and evaporated. For the removal of unreacted 2,2′-bipyridyl, the residual oil, 48.68 g, was extracted with boiling hexane. The extract was evaporated and the residue placed under vacuum, leading to 41.21 g of hygroscopic solid 2,2′-bipyridyl *N*-oxide (**4**), mp 59 °C (lit.[9] mp 58.5–59.5 °C).

The Na_2CO_3 washings were extracted four times with 450-mL $CHCl_3$ portions. The extract was dried ($MgSO_4$) and evaporated. Dissolution of the residual oil, 29.06 g, in ether left undissolved 2,2′-dioxide **1** (223 mg, 0.3%). Filtration of the mixture, evaporation of the filtrate, and placement of the residue under vacuum provided 20.12 g more of the grey-brown 2,2′-bipyridyl *N*-oxide (**4**), mp 59 °C, corresponding to 61.33 g (79.47%) of the monooxide **4**: ^{1}H NMR ($CDCl_3$)[25] δ 7.18–7.50 (m, H_4 and H_5 and $H_{5'}$), 7.85 (ddd, $H_{4'}$) 8.12–8.42 (m, H_3 and H_6), 8.75 (ddd, $H_{6'}$), 8.93 (ddd, $H_{3'}$) [$J_{3',4'} = 8.0$, $J_{3',5'} = 1.2$, $J_{3',6'} = 1.0$, $J_{4',5'} = 7.6$, $J_{4',6'} = 1.9$, $J_{5',6'} = 4.7$ Hz]; UV (95% EtOH) λ_{max} (ε) 238 nm (22 400), 267 (11 500), 284 (sh, 9360); IR (KBr) 7.98 μm.

As an aid in the NMR analysis of **4**, a monodeuterated sample, **4-6-*d***, was prepared in a manner similar to that of Kawazoe et al.[26] A 2-mL portion of 1.6 M *n*-butyllithium was added to a solution of 50 mg of **4** in 5 mL of D_2O and the solution refluxed for 14 h. It was extracted exhaustively with CH_2Cl_2. The extract was dried ($MgSO_4$) and evaporated, yielding 42 mg of **4-6-*d*** (NMR integration was compatible with the exchange of one proton): ^{1}H NMR (CDl_3) δ 8.14 (dd, H_3) [$J_{3,4} = 7.0$, $J_{3,5} = 3.0$ Hz].

4-Nitro-2,2′-bipyridyl *N*-Oxide (5). A stirred solution of 2,2′-bipyridyl *N*-oxide **4** (57.77 g, 335.5 mmol) and potassium nitrate (180 g) in concentrated sulfuric acid (450 mL) was refluxed for 23 h. The reaction was poured onto 950 g of ice and neutralized, with cooling, to pH 8.5 with 38.5% NaOH. The light yellow precipitate was filtered and washed with cold water. The filtered precipitate was taken up in $CHCl_3$ and shaken with water, and the aqueous layer exhaustively extracted with $CHCl_3$. The $CHCl_3$ layers were dried ($MgSO_4$) and evaporated to 47.99 g of solid, mp 167–181 °C. Recrystallization from CH_2Cl_2:hexanes provided 30.23 g of 4-nitro-2,2′-bipyridyl *N*-oxide (**5**), mp 181 °C (lit.[14] mp 183–185 °C). The mother liquor was evaporated and

(20) Kishi, Y.; Aratani, M.; Tanino, H.; Fukuyama, T.; Goto, T.; Inoue, S.; Sugiura, S.; Kakoi, H. *J. Chem. Soc. Chem. Commun.* **1972**, 64.
(21) Jefford, C. W.; Boschung, A. F.; Moriarty, R. M.; Rimbault, C. G.; Laffer, M. H. *Helv. Chim. Acta* **1973**, *56*, 2649.
(22) Foote, C. S.; Wuesthoff, M. T.; Wexler, S.; Burstain, I. G.; Benny, R.; Schenck, G. O.; Schulte-Elte, K.-H. *Tetrahedron* **1967**, *23*, 2583.
(23) Antkowiak, W. Z.; Gessner, W. P. *Tetrahedron Lett.* **1979**, 1931.
(24) It is worthy of note that liberation of singlet oxygen from a 2,2′-bipyridyl *N,N′*-dioxide would be an example of a potential general ylide coupling scheme. Other such ylides **30** (e.g., X = CHR, Y = CHR′, giving olefins) could merit study.



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(25) For an analysis of the NMR spectrum, of 2,2′-bipyridyl, see: Kramer, F. A., Jr.; West, R. *J. Phys. Chem.* **1965**, *69*, 673. Gil, V. M. S. *Mol. Phys.* **1965**, *9*, 97.
(26) Kawazoe, Y.; Ohnishi, M.; Yoshioka, Y. *Chem. Pharm. Bull.* **1964**, *12*, 1384.

used for a similar recrystallization to give 8.30 g more of **5**, mp 170–179 °C. The mother liquor from the latter recrystallization was similarly used for a third recrystallization to give an additional 2.54 g of **5**, mp 165–169 °C; corresponding to a total of 41.07 g (56.37%) of **5**: ^{1}H NMR ($CDCl_3$) δ 7.46 (ddd, $H_{5'}$), 7.91 (ddd, $H_{4'}$), 8.09 (dd, H_5), 8.39 (dd, H_6), 8.82 (ddd, $H_{6'}$), 8.92 (ddd, $H_{3'}$), 9.29 (dd, H_3) [$J_{3,5}$ = 3.4, $J_{3,6}$ = 0.5, $J_{5,6}$ = 7.2, $J_{3',4'}$ = 8.0, $J_{3',5'}$ = 1.2, $J_{3',6'}$ = 1.0, $J_{4',5'}$ = 7.5, $J_{4',6'}$ = 2.0, $J_{5',6'}$ = 4.7 Hz]; UV (95% EtOH) λ_{max} (ε) 227 nm (12 400), 285 (14 800), 330 (10 100); IR (KBr) 6.62, 7.44, 7.84 μm.

4-Nitro-2,2′-bipyridyl N,N′-Dioxide (6). A solution of *m*-chloroperbenzoic acid (719 mg, 3.46 mmol) in 15 mL of $CHCl_3$ was added dropwise over 10 min to a stirred solution of 4-nitro-2,2′-bipyridyl *N*-oxide (**5**) (0.500 g, 2.30 mmol) in 30 mL of $CHCl_3$ at 0 °C. The reaction was stirred for 40 h at room temperature, concentrated at room temperature, put on a 30-g basic alumina column, and eluted with 800 mL of $CHCl_3$. The $CHCl_3$ filtrate was evaporated and washed with two cold 10-mL $CHCl_3$ portions, providing 466 mg of 4-nitro-2,2′-bipyridyl *N,N′*-dioxide (**6**; 86.8%), mp 234–238 °C dec (lit.[14] mp 243 °C): ^{1}H NMR (Me_2SO-d_6) δ 7.36–7.80 (m, 3 H) and 8.36–8.46 (m, 1 H) ($H_{3'}$ $H_{4'}$ $H_{5'}$ $H_{6'}$), 8.33 (dd, H_5), 8.57 (dd, H_6), 8.62 (br d, H_3) [$J_{3,5}$ = 3.2, $J_{3,6}$ = 0.5, $J_{5,6}$ = 7.2 Hz]; UV (95% EtOH) λ_{max} (ε) 216 nm (16 100), 256 (6850), 331 (11 200); IR (KBr) 6.53, 7.42, 7.70, 8.00 μm.

4-Nitro-2,2′-bipyridyl (7):[14] ^{1}H NMR ($CDCl_3$) δ 7.32 (dd, $H_{5'}$), 7.78 (ddd, $H_{4'}$), 7.91 (dd, H_5), 8.38 (ddd, $H_{3'}$), 8.65 (ddd, $H_{6'}$), 8.84 (dd, H_6), 9.06 (dd, H_3) [$J_{3,5}$ = 2.2, $J_{3,6}$ = 0.6, $J_{5,6}$ = 5.2, $J_{3',4'}$ = 7.8, $J_{3',5'}$ = 1.2, $J_{3',6'}$ = 1.0, $J_{4',5'}$ = 7.5, $J_{4',6'}$ = 1.8, $J_{5',6'}$ = 4.7 Hz]; UV (95% EtOH) λ_{max} (ε) 236 nm (13 600), 277 (7280), 314 (2830); IR (KBr) 6.53, 7.33 μm.

4-Methoxy-2,2′-bipyridyl N-Oxide (8). Sodium wire (270 mg, 12 mmol) was added to 40 mL of dry methanol, and to this 4-nitro-2,2′-bipyridyl *N*-oxide **5** (1.20 g, 5.53 mmol) was added. After stirring at 50–60 °C for 5 h, the reaction was neutralized with concentrated H_2SO_4 and evaporated. The solid was then taken up in $CHCl_3$ and washed with water. The aqueous layer was exhaustively back-extracted with $CHCl_3$. The combined $CHCl_3$ layers were dried ($MgSO_4$) and evaporated. The resulting solid was recrystallized from CH_2Cl_2:hexanes to provide 936 mg of 4-methoxy-2,2′-bipyridyl *N*-oxide (**8**), mp 117.5–118 °C (lit.[14] mp 117 °C). The mother liquor was evaporated and used for a similar recrystallization to provide 50 mg more of product, mp 117 °C (total yield 941 mg, 88.2%): ^{1}H NMR ($CDCl_3$) δ 3.94 (s, OCH_3), 6.87 (dd, H_5), 7.38 (ddd, $H_{5'}$), 7.77 (d, H_3), 7.87 (ddd, $H_{4'}$), 8.24 (d, H_6), 8.75 (ddd, $H_{6'}$), 9.07 (ddd, $H_{3'}$) [$J_{3,5}$ = 3.6, $J_{5,6}$ = 7.2, $J_{3',4'}$ = 8.0, $J_{3',5'}$ = 1.3, $J_{3',6'}$ = 1.0, $J_{4',5'}$ = 7.7, $J_{4',6'}$ = 1.9, $J_{5',6'}$ = 4.7 Hz]; UV (95% EtOH) λ_{max} (ε) 237 nm (10 600), 272 (7880), 320 (1100); IR (KBr) 8.37 μm.

4-Methoxy-2,2′-bipyridyl N,N′-Dioxide (9). A solution of *m*-chloroperbenzoic acid (85%, 1.19 mg, 5.9 mmol) in 15 mL of $CHCl_3$ was added dropwise over 15 min to a stirred solution of 4-methoxy-2,2′-bipyridyl *N*-oxide 8 (950 mg, 4.70 mmole) in 10 mL of $CHCl_3$ at 0 °C. Stirring was continued at 0 °C for 45 min and at room temperature for 3.75 h more. The reaction was then partially evaporated, put on a 45-g basic alumina column and eluted with 100 mL of $CHCl_3$ and then 350 mL of 15% MeOH in $CHCl_3$. The combined filtrate was evaporated, and the resulting solid was washed with a small portion of CH_2Cl_2. The washing was evaporated and in turn washed with a smaller portion of CH_2Cl_2. This process was repeated four more times. All the washings were collected, evaporated, and recrystallized from CH_2Cl_2:hexanes. The mother liquor of the recrystallization was used for a similar recrystallization and its mother liquor used for another one. The combined three recrystallizations provided 201 mg of starting 4-methoxy-2,2′-bipyridyl *N*-oxide (**8**), mp 105–109 °C. The combined undissolved solids from the original $CHCl_3$ washings provided 317 mg of 4-methoxy-2,2′-bipyridyl *N,N′*-dioxide (**9**), mp 242–246 °C dec (39.2% yield based on recovered **8**): ^{1}H NMR (Me_2SO-d_6) δ 3.85 (s, OCH_3), 7.16 (dd, H_5), 7.32 (d, H_3), 7.39–7.72 (m, 3 H) and 8.30–8.40 (m, 1 H) ($H_{3'}$, $H_{4'}$, $H_{5'}$, $H_{6'}$), 8.24 (d, H_6) [$J_{3,5}$ = 3.5, $J_{5,6}$ = 7.2 Hz]; UV (95% EtOH) λ_{max} (ε) 217 nm (22 100), 237 (14 100), 269 (17 700), 319 (sh, 2100); IR (KBr) 8.03, 8.18 μm. Anal. (sample recrystallized from ethanol:hexanes followed by sublimation (180 °C (0.03 mmHg)), decomposing at 247 °C). Calcd for $C_{11}H_{10}N_2O_3$: C, 60.54; H, 4.62; H, 12.84. Found: C, 60.18; H, 4.55; N, 12.74.

4-Methoxy-2,2′-bipyridyl (10). A solution of 4-methoxy-2,2′-bipyridyl *N*-oxide (**8**) (181 mg, 0.895 mmol) and PCl_3 (0.21 mL, 2.41 mmol) in 3 mL of $CHCl_3$ was refluxed for 2.75 h. The reaction was thrown on 15 mL of ice and neutralized with concentrated NaOH. The aqueous phase was exhaustively extracted with $CHCl_3$. The combined $CHCl_3$ layers were dried ($MgSO_4$) and evaporated to 153 mg of 4-methoxy-2,2′-bipyridyl (**10**), mp 63–65 °C (91.8%). The product could be recrystallized twice from $CHCl_3$:hexanes to afford 90 mg of white crystalline **10**, mp 65.5–66.5 °C (lit.[14] mp 61 °C): ^{1}H NMR ($CDCl_3$) δ 3.88 (s, OCH_3), 6.77 (dd, H_5), 7.22 (ddd, $H_{5'}$), 7.72 (ddd, $H_{4'}$), 7.95 (d, H_3), 8.37 (ddd, $H_{3'}$), 8.43 (d, H_6), 8.61 (ddd, $H_{6'}$) [$J_{3,5}$ = 2.6, $J_{5,6}$ = 5.6, $J_{3',4'}$ = 7.9, $J_{3',5'}$ = 1.2, $J_{3',6'}$ = 1.0, $J_{4',5'}$ = 7.4, $J_{4',6'}$ = 1.9, $J_{5',6'}$ = 4.7 Hz]; UV (95% EtOH) λ_{max} (ε) 218 nm (25 600), 242 (10 400), 277 (13 400).

4,4′-Dinitro-2,2′-bipyridyl (11). 4,4′-Dinitro-2,2′-bipyridyl *N,N′*-dioxide (**3**, 3.00 g, 10.8 mmol) was refluxed in PCl_3 (25 mL, 290 mmol) for 21 h. The reaction was thrown into 200 mL of ice water. This was then basified to pH 13 with concentrated NaOH and extracted exhaustively with $CHCl_3$. The combined $CHCl_3$ layers were dried (Na_2CO_3) and evaporated to 1.82 g of 4,4′-dinitro-2,2′-bipyridyl (**11**), mp 185–186 °C (68.7%). Two recrystallizations from CH_2Cl_2:hexanes provided 1.56 g of **11**, mp 190–192 °C (58.7%): ^{1}H NMR ($CDCl_3$) δ 8.14 (dd, H_5, $H_{5'}$), 9.05 (dd, H_6, $H_{6'}$), 9.22 (dd, H_3, $H_{3'}$) [$J_{3,5}$ = $J_{3',5'}$ = 2.2, $J_{3,6}$ = $J_{3',6'}$ = 0.7, $J_{5,6}$ = $J_{5',6'}$ = 5.3 Hz]; UV (95% EtOH) λ_{max} (ε) 214 nm (sh, 17 400), 228 (19 300), 304 (4980); IR (KBr) 6.49, 7.38 μm.

4-Chloro-4′-nitro-2,2′-bipyridyl (13) and 4,4′-Dichloro-2,2′-bipyridyl (12). 4,4′-Dinitro-2,2′-bipyridyl *N,N′*-dioxide (**3**, 109 mg, 0.393 mmol) and PCl_3 (0.40 mL, 4.6 mmol) were refluxed in 10 mL of dry acetonitrile for 1.75 h. (After 10 min of refluxing, the suspension of the dioxide became a homogeneous solution). The solution then sat at room temperature overnight. The reaction was thrown into 5 mL of ice water. This was evaporated to only the aqueous phase, basified with concentrated KOH to pH 11, and exhaustively extracted with $CHCl_3$. The combined $CHCl_3$ layers were dried (K_2CO_3) and evaporated to 80.2 mg. This was put on two 500-μm silica gel prep plates with $CHCl_3$ and multideveloped five times with 1:40 ethyl acetate:hexanes. Two major UV-active bands were seen and removed with $CHCl_3$. The top band provided 28.8 mg of 4,4′-dichloro-2,2′-bipyridyl (**12**, 32.6%), mp 128 °C, and the middle band 38.6 mg of 4-chloro-4′-nitro-2,2′-bipyridyl (**13**, 41.7%), mp 159 °C. A bottom and weaker UV-active band was also removed and provided only 3.0 mg. This was seen by careful TLC to consist of two spots, one of which was identical in TLC properties to 4,4′-dinitro-2,2′-bipyridyl (**11**, 3.1% yield if it consisted of all 3.0 mg): ^{1}H NMR ($CDCl_3$) of **13**: δ 7.41 (dd, H_5), 8.05 (dd, $H_{5'}$), 8.50 (dd, H_3), 8.63 (dd, H_6), 8.96 (dd, $H_{6'}$), 9.13 (dd, $H_{3'}$) [$J_{3,5}$ = 2.0, $J_{3,6}$ = 0.4, $J_{5,6}$ = 5.2, $J_{3',5'}$ = 2.2, $J_{3',6'}$ = 0.7, $J_{5',6'}$ = 5.3 Hz]; UV (95% EtOH) λ_{max} (ε) 239 nm (15 100), 274 (sh, 6400), 280 (6940), 308 (sh, 3100); IR (KBr) 6.52, 7.36 μm. Anal. (sample recrystallized from CH_2Cl_2:hexanes, mp 159 °C). Calcd for $C_{10}H_6ClN_3O_2$: C, 50.97; H, 2.57; N, 17.83; Cl, 15.05. Found: C, 50.94; H, 2.54; N, 17.80; Cl, 15.08.

4,4′-Dichloro-2,2′-bipyridyl N,N′-dioxide (14):[8] ^{1}H NMR (Me_2SO-d_6) δ 7.64 (dd, H_5, $H_{5'}$), 7.90 (d, H_3, $H_{3'}$), 8.34 (d, H_6, $H_{6'}$) [$J_{3,5}$ = $J_{3',5'}$ = 3.1, $J_{5,6}$ = $J_{5',6'}$ = 7.0 Hz]; UV (95% EtOH) λ_{max} (ε) 223 nm (23 800), 250 (14 800), 277 (20 700); IR (KBr) 8.01 μm.

4,4′-Dichloro-2,2′-bipyridyl (12). 4,4′-Dichloro-2,2′-bipyridyl *N,N′*-dioxide (**14**, 57.7 mg, 0.224 mmol) and PCl_3 (0.40 mL, 4.6 mmol) was refluxed in 10 mL of dry acetonitrile. This was thrown onto 20 mL of ice, evaporated to only an aqueous phase, basified with concentrated KOH to pH 11, and extracted exhaustively with $CHCl_3$. The combined $CHCl_3$ layers were dried (Na_2CO_3) and evaporated to 48.5 mg of 4,4′-dichloro-2,2′-bipyridyl (**12**, 96.0%): mp 128.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.30 (dd, H_5, $H_{5'}$), 8.41 (d, H_3, $H_{3'}$), 8.52 (d, H_6, $H_{6'}$) [$J_{3,5}$ = $J_{3',5'}$ = 2.0, $J_{5,6}$ = $J_{5',6'}$ = 5.2 Hz]; UV (95% EtOH) λ_{max} (ε) 243 nm (12 100), 251 (sh, 11 000), 273 (sh, 12 900), 280 (13 800), 291 (sh, 9300). Anal. (sample recrystallized from CH_2Cl_2:hexanes and sublimed (120 °C (0.03 mmHg)), mp 129 °C). Calcd for $C_{10}H_6N_2Cl_2$: C, 53.36; H, 2.69; N, 12.45. Found: C, 53.51; H, 2.79; N, 12.48.

4,4′-Dibromo-2,2′-bipyridyl N,N′-dioxide (15):[15] ^{1}H NMR (Me_2SO-d_6) δ 7.74 (dd, H_5, $H_{5'}$), 7.99 (d, H_3, $H_{3'}$), 8.25 (d, H_6, $H_{6'}$) [$J_{3,5}$ = $J_{3',5'}$ = 2.8, $J_{5,6}$ = $J_{5',6'}$ = 7.0 Hz]; UV (95% EtOH) λ_{max}

(ε) 223 nm (25 100), 254 (17 400), 277 (24 200); IR (KBr) 8.01 μm. Anal. (sample recrystallized from MeOH:Et_2O, mp 260 °C dec). Calcd for $C_{10}H_6N_2O_2Br_2$: C, 34.72; H, 1.75; N, 8.10; Br, 46.19. Found: C, 34.64; H, 1.71; N, 8.17; Br, 46.00.

4,4-Dibromo-2,2′-bipyridyl (16):[15] ^{1}H NMR ($CDCl_3$) δ 7.53 (dd, H_5, $H_{5'}$), 8.51 (dd, H_6, $H_{6'}$), 8.63 (dd, H_3, $H_{3'}$) [$J_{3,5} = J_{3',5'} = 2.0$, $J_{3,6} = J_{3',6'} = 0.5$, $J_{5,6} = J_{5',6'} = 5.3$ Hz]; UV (95% EtOH) λ_{max} (ε) 214 nm (43 600), 238 (sh, 10 300), 246 (11 500), 253 (sh, 11 000), 275 (sh, 13 100), 282 (14 100), 290 (sh, 10 300).

4,4′-Dimethoxy-2,2′-bipyridyl *N,N′*-dioxide (17):[15] ^{1}H NMR (Me_2SO-d_6) δ 3.85 (s, OCH_3, $OCH_{3'}$), 7.16 (dd, H_5, $H_{5'}$), 7.33 (d, H_3, $H_{3'}$), 8.26 (d, H_6, $H_{6'}$) [$J_{3,5} = J_{3',5'} = 3.5$, $J_{5,6} = J_{5',6'} = 7.2$ Hz]; UV (95% EtOH) λ_{max} (ε) 213 nm (26 200), 246 (sh, 13 300), 272 (20 800), 320 (sh, 3150); IR (KBr) 8.12 μm.

4,4′-Dimethoxy-2,2′-bipyridyl (18):[15] ^{1}H NMR ($CDCl_3$) δ 3.96 (s, OCH_3, $OCH_{3'}$), 6.87 (dd, H_5, $H_{5'}$), 8.00 (d, H_3, $H_{3'}$), 8.50 (d, H_6, $H_{6'}$) [$J_{3,5} = J_{3',5'} = 2.5$, $J_{5,6} = J_{5',6'} = 5.6$ Hz]; UV (95% EtOH) λ_{max} (ε) 212 nm (38 900), 256 (9640), 269 (sh, 911).

4-Methoxy-4′-nitro-2,2′-bipyridyl *N,N′*-Dioxide (19). 4,4′-Dinitro-2,2′-bipyridyl *N,N′*-dioxide (**3**, 101.9 mg, 0.366 mmol) was added to a solution of NaOMe (40.1 mg, 0.742 mmol) in 200 mL of dry MeOH and stirred for 19 h at room temperature under dry nitrogen. The contents were evaporated at room temperature, taken up with H_2O and exhaustively extracted with $CHCl_3$. The combined $CHCl_3$ layers were dried ($MgSO_4$) and evaporated to 60.2 mg. This was placed on a 2000-μm silica gel prep plate with $CHCl_3$:MeOH and developed with 9:1 $CHCl_3$:MeOH. The strongest band, centered in the middle of the plate, was removed with 93:7 $CHCl_3$:MeOH and evaporated to 40.6 mg of 4-methoxy-4′-nitro-2,2′-bipyridyl *N,N′*-dioxide **19**: mp 236 °C dec (42.1%); ^{1}H NMR (Me_2SO-d_6) δ 3.86 (s, OCH_3), 7.21 (dd, H_5), 7.41 (d, H_3), 8.28 (d, H_6), 8.33 (dd, $H_{5'}$), 8.56 (d, $H_{6'}$), 8.61 (d, $H_{3'}$) [$J_{3,5} = 3.5$, $J_{5,6} = 7.2$, $J_{3',5'} = 3.2$, $J_{5',6'} = 7.2$ Hz]; UV (95% EtOH) λ_{max} (ε) 267 nm (14 000), 329 (13 100); IR (KBr) 6.54, 7.40, 7.70, 8.19 μm. Anal. (sample recrystallized from CH_2Cl_2:hexanes, mp 238 °C dec). Calcd for $C_{11}H_9N_3O_5$: C, 50.19; H, 3.45; N, 15.97. Found: C, 49.96; H, 3.55; N, 16.10.

4′-Nitro-2,2′-bipyridyl *N*-Oxide (20) and 4-Nitro-2,2′-bipyridyl *N*-Oxide (5). To a stirred solution of 4-nitro-2,2′-bipyridyl (**7**, 250 mg, 1.24 mmol) in 12.5 mL of $CHCl_3$ at 0 °C was added a solution of *m*-chloroperbenzoic acid (328 mg, 84.7%, 1.61 mmol) in 12.5 mL of $CHCl_3$ dropwise over 1 h. Stirring was continued for 68 h at 0 °C. The reaction solution was evaporated almost to dryness at room temperature, redissolved in a minimum amount of $CHCl_3$, put on a 10-g basic alumina column, and slowly eluted with $CHCl_3$ until no more material came off the column. The combined filtrate was concentrated, providing 232.7 mg of solid. The solid was then swirled with 10 mL of ether, and the ether was withdrawn and filtered. This was repeated seven more times with 7-mL portions of ether. The undissolved solid, 170.2 mg, was recrystallized from $CHCl_2$:hexanes to give 129 mg of pale yellow crystals of 4′-nitro-2,2′-bipyridyl *N*-oxide (**20**), mp 175.5–176.5 °C. The mother liquor was used for another recrystallization to provide 28.6 mg more of crystals, mp 172.5–174 °C. The mother liquor of the last recrystallization was combined with the ether washings, evaporated and placed on a 500-μm silica gel prep plate with $CHCl_3$ and developed with ethyl acetate. Three UV-active bands were then taken off with $CHCl_3$. The middle band gave 26.4 g of recovered 4-nitro-2,2′-bipyridyl (**7**), mp 112 °C (mp of starting material 111 °C, mixed mp 113–115 °C). The top band yielded 15.8 mg of 4-nitro-2,2′-bipyridyl *N*-oxide (**5**), mp 179.5 °C (5.8% conversion of **7** or 6.6% based on recovered **7**). The lower band yielded 11.0 mg more of 4′-nitro-2,2′-bipyridyl *N*-oxide (**20**): mp 170.5–171.5 °C (total yield 169 mg, 62.6% conversion of **7** or 70.0% based on recovered **7**): ^{1}H NMR ($CDCl_3$) δ 7.30–7.54 (m, 2 H) and 8.26–8.42 (m, 2 H) (H_3, H_4, H_5, H_6), 8.10 (dd, $H_{5'}$), 9.03 (dd, $H_{6'}$), 9.81 (dd, $H_{3'}$) [$J_{3',5'} = 2.2$, $J_{3',6'} = 0.6$, $J_{5',6'} = 5.3$ Hz]; UV (95% EtOH) λ_{max} (ε) 238 nm (33 100), 281 (8740), 320 (3800); IR (KBr) 6.54, 7.37, 8.03 μm. Anal. (sample recrystallized from CH_2Cl_2:hexanes, mp 176 °C). Calcd for $C_{10}H_7N_3O_3$: C, 55.30; H, 3.25; N, 19.35. Found: C, 55.26; H, 3.31; N, 19.37.

4,4′-Dinitro-2,2′-bipyridyl *N*-Oxide (21). A stirred solution of 4′-nitro-2,2′-bipyridyl *N*-oxide (**20**, 3.00 g, 13.81 mmol) and potassium nitrate (19.0 g) in concentrated sulfuric acid (47 mL) was refluxed for 24.5 h. The contents were poured into a stirred 600-mL ice–water slurry and allowed to stir at 0 °C for 15 min. The contents were then suction-filtered, and the collected yellow solid was washed with cold water and ether. The combined aqueous phases were neutralized with 16% NaOH to pH 7 with ice cooling and exhaustively extracted with $CHCl_3$. The combined $CHCl_3$ layers were dried ($MgSO_4$) and evaporated to yield 867 mg of recovered **20**, mp 159–169 °C. The collected solid from the original filtration provided 1.203 g of 4,4′-dinitro-2,2′-bipyridyl *N*-oxide (**21**): mp 209 °C (40% based on recovered **20**); ^{1}H NMR ($CDCl_3$) δ 8.17 (dd, H_5), 8.18 (dd, $H_{5'}$), 8.44 (dd, H_6), 9.09 (dd, $H_{6'}$), 9.27 (dd, H_3), 9.76 (dd, $H_{3'}$) [$J_{3,5} = 3.0$, $J_{3,6} = 0.4$, $J_{5,6} = 7.4$, $J_{3',5'} = 2.3$, $J_{3',6'} = 0.7$, $J_{5',6'} = 5.3$ Hz]; UV (95% EtOH) λ_{max} (ε) 217 nm (25 100), 267 (14 300), 323 (11 800); IR (KBr) 6.52, 7.43, 7.75 μm. Anal. (sample recrystallized from CH_2Cl_2 and sublimed (180 °C (0.03 mmHg)), mp 215–216.5 °C). Calcd for $C_{10}H_6N_4O_5$: C, 45.81; H, 2.31; N, 21.37. Found: C, 45.94; H, 2.38; N, 21.29.

4,4′-Dinitro-2,2′-bipyridyl (11). 4,4′-Dinitro-2,2′-bipyridyl *N*-oxide (**21**, 117 mg, 0.446 mmol) and PCl_3 (3.0 mL, 34 mmol) were refluxed together in 150 mL of $CHCl_3$ for 3 h. The reaction was thrown on 50 g of ice and worked-up as described in the previous preparation of **11**. A total of 102 mg of 4,4′-dinitro-2,2′-bipyridyl (**11**, 93.2%), mp 188.5–192 °C, was thus obtained. Anal. (sample sublimed (150 °C (0.04 mmHg)), mp 192.5 °C). Calcd for $C_{10}H_6N_4O_4$: C, 48.79; H, 2.46; N, 22.76. Found: C, 48.55; H, 2.45; N, 22.78.

4-Methoxy-4′-nitro-2,2′-bipyridyl *N*-Oxide (22). 4,4′-Dinitro-2,2′-bipyridyl *N*-oxide **21** (132 mg, 0.503 mmol) was stirred, in most part as a suspension, with sodium methoxide (27.2 mg, 0.503 mmol) in 150 mL of dry methanol under nitrogen for 14 days. The reaction was then suction-filtered and the filtered solid washed with methanol to provide 25.2 mg of recovered **21**. The filtrate was evaporated and taken up with CH_2Cl_2 and washed with water. The aqueous layer was exhaustively extracted with CH_2Cl_2. The combined CH_2Cl_2 layers were then dried ($MgSO_4$) and evaporated to 98.2 mg of solid, which was then shaken with 10 mL of CH_2Cl_2. The insoluble solid present was suction-filtered and washed with 10 mL more of CH_2Cl_2, to provide 22.7 mg more of recovered **21**. The combined CH_2Cl_2 layers were evaporated, placed on a 2000-μm silica gel prep plate with CH_2Cl_2 and developed with 7.5:92.5 MeOH:$CHCl_3$. Two major UV-active bands were seen and were taken off with the same MeOH:$CHCl_3$ mixture. The top band yielded 13.4 mg more of starting **21** (61.3 mg recovered in all), and the bottom band gave 34.4 mg of the desired 4-methoxy-4′-nitro-2,2′-bipyridyl *N*-oxide (**22**): mp 176.5 °C (51.7% based on recovered **21**) (a fainter middle band, the only other band present, was removed and showed on careful TLC three spots, though it weighed only 4.4 mg); ^{1}H NMR ($CDCl_3$) δ 3.96 (s, OCH_3), 6.95 (dd, H_5), 7.85 (d, H_3), 8.09 (dd, $H_{5'}$), 8.28 (d, H_6), 9.00 (d, $H_{6'}$), 9.96 (d, $H_{3'}$) [$J_{3,5} = 3.5$, $J_{5,6} = 7.2$, $J_{3',5'} = 2.2$, $J_{5',6'} = 5.3$ Hz]; UV (95% EtOH) λ_{max} (ε) 237 nm (16 200), 282 (5140), 349 (sh, 760); IR (KBr) 6.56, 7.37, 8.12, 8.38 μm. Anal. (sample recrystallized from CH_2Cl_2:hexanes, mp 178 °C). Calcd for $C_{11}H_9N_3O_4$: C, 53.44; H, 3.67; N, 17.00. Found: C, 53.33; H, 3.77; N, 16.81.

4,4′-Dimethoxy-2,2′-bipyridyl *N*-Oxide (23). 4,4′-Dinitro-2,2′-bipyridyl *N*-oxide (**21**, 114 mg, 0.436 mmol) was stirred with sodium methoxide (471 mg, 8.72 mmol) in 85 mL of dry methanol under nitrogen for 19 days. This was evaporated, taken up with $CHCl_3$ and washed with water. The aqueous layer was exhaustively extracted with $CHCl_3$. The combined $CHCl_3$ layers were dried ($MgSO_4$) and evaporated to 117 mg. This was placed on a 1000-μm silica gel prep plate and developed with 1:9 MeOH:$CHCl_3$. The major UV-active band was removed with 1:19 MeOH:$CHCl_3$. This was evaporated and placed on another 1000-μm silica gel prep plate and multideveloped three times with 1:19 MeOH:$CHCl_3$. The major UV-active band was removed with 1:19 MeOH:$CHCl_3$, dried ($MgSO_4$), and evaporated to 80.5 mg of 4,4′-dimethoxy-2,2′-bipyridyl *N*-oxide (**23**, 79.6%): mp 97.5–98.5 °C; ^{1}H NMR ($CDCl_3$) δ 3.88 (s, 3 H) and 3.89 (s, 3 H) (OCH_3, $OCH_{3'}$), 6.79 (dd, H_5), 6.83 (dd, $H_{5'}$), 7.80 (d, H_3), 8.15 (d, H_6), 8.44 (d, $H_{6'}$), 8.82 (d, $H_{3'}$) [$J_{3,5} = 3.6$, $J_{5,6} = 7.2$, $J_{3',5'} = 2.5$, $J_{5',6'} = 5.6$ Hz]; UV (95% EtOH) λ_{max} (ε) 223 nm (26 200), 246 (15 100), 272 (11 500), 321 (1500); IR (KBr) 8.07 μm. Anal. (sample sublimed (120 °C (0.03 Hg)), mp 98.5–99.5 °C). Calcd for $C_{12}H_{12}N_2O_3$: C, 62.06; H, 5.21; N, 12.06. Found: C, 61.86; H, 5.32; N, 12.00.

4-Methoxy-4′-nitro-2,2′-bipyridyl *N*-Oxide (23) and 4-Methoxy-4′-nitro-2,2′-bipyridyl *N,N′*-Dioxide (19). A solution

of *m*-chloroperbenzoic acid (83.0%, 78.8 mg, 0.379 mmol) in 3 mL of $CHCl_3$ was pipetted into a stirred solution of 4-methoxy-4′-nitro-2,2′-bipyridyl (**24**, 21.9 mg, 0.0947 mmol) in 3 mL of $CHCl_3$ at 0 °C. The reaction was allowed to stir at room temperature for 45 h. The solution was placed on a 5.0-g basic alumina column and eluted with 250 mL of $CHCl_3$, 100 mL of 19:1 $CHCl_3$:MeOH, and 50 mL of 9:1 $CHCl_3$:MeOH. The combined filtrates were evaporated, providing 24.6 mg of solid. This was placed on a 500-μm silica gel prep plate with $CHCl_3$ and developed with 9:1 $CHCl_3$:MeOH. Three UV-active bands were seen and were removed with 19:1 $CHCl_3$:MeOH. The top band yielded 1.6 mg (0.0069 mmol) of 4-methoxy-4′-nitro-2,2′-bipyridyl (**24**), mp 135 °C. The middle band gave 16.0 mg (0.0647 mmol) of 4-methoxy-4′-nitro-2,2′-bipyridyl *N*-oxide (**22**, 68.3% conversion of **24** or 73.3% based on recovered **24**), mp 177–178 °C. The bottom band gave 0.1 mg (0.0004 mmol) of 4-methoxy-4′-nitro-2,2′-bipyridyl *N,N′*-dioxide (**19**, 0.4% conversion of **24** or 0.4% based on recovered **24**), mp 225–230 °C (mp of the dioxide prepared from **3** was 236 °C, mixed mp 225–230 °C; IR and TLC properties also identical).

4-Methoxy-4′-nitro-2,2′-bipyridyl (24). Phosphorus trichloride (0.200 mL, 2.29 mmol) was syringed into a stirred solution of 4-methoxy-4′-nitro-2,2′-bipyridyl *N*-oxide (**22**, 100 mg, 0.405 mmol) in 7 mL of $CHCl_3$. Within a few seconds the yellow color of the solution had disappeared. The reaction was refluxed for 4.25 h and allowed to stand at room temperature overnight. The reaction was worked up with use of the procedure described in the preparation of **10** providing 92.5 mg of 4-methoxy-4′-nitro-2,2′-bipyridyl (**24**): mp 136 °C (98.9% yield); ^1H NMR ($CDCl_3$) δ 3.97 (s, OCH_3), 6.94 (dd, H_5), 8.03 (dd, $H_{5'}$), 8.04 (d, H_3), 8.57 (d, H_6), 8.95 (dd, $H_{6'}$), 9.17 (dd, $H_{3'}$) [$J_{3,5}$ = 2.5, $J_{5,6}$ = 5.7, $J_{3',5'}$ = 2.2, $J_{3',6'}$ = 0.6, $J_{5',6'}$ = 5.3 Hz]; UV (95% EtOH) λ_{max} (ε) 217 nm (36 600), 246 (sh, 15 500), 313 (3700); IR (KBr) 6.53, 7.38 μm. Anal. (sample recrystallized from CH_2Cl_2:hexanes, mp 138 °C). Calcd for $C_{11}H_9N_3O_3$: C, 57.14; H, 3.92; N, 18.18. Found: C, 56.91; H, 3.97; N, 17.94.

4-Methoxy-4′-nitro-2,2′-bipyridyl (24). A solution of *m*-chloroperbenzoic acid (83.0%, 37.9 mg, 0.182 mmol) in 3 mL of $CHCl_3$ was added over 10 min to a stirred solution of 4-methoxy-4′-nitro-2,2′-bipyridyl *N*-oxide (**22**, 30.0 mg, 0.121 mmol) in 3 mL of $CHCl_3$ at 0 °C. The reaction was allowed to stir at room temperature for 38 hours, partially concentrated at room temperature, placed on a 2.0-g basic alumina column, and eluted with 24 mL of $CHCl_3$. This was evaporated to provide 25.8 mg of solid, which was placed on a 500-μm silica gel prep plate with $CHCl_3$ and developed with ethyl acetate. Only two UV-active bands were present. The bottom band was removed with 1:19 MeOH:$CHCl_3$ and provided upon evaporation 18.7 mg of 4-methoxy-4′-nitro-2,2′-bipyridyl *N*-oxide (**22**). Further elution of the original alumina column with 75 mL of $CHCl_3$ gave 3.0 mg more of the monooxide, and thus 21.7 mg (0.0878 mmol) was obtained in all. The top band of the prep plate was removed with $CHCl_3$ and gave 4.2 mg (0.018 mmol) of 4-methoxy-4′-nitro-2,2′-bipyridyl (**24**), mp 136 °C (15% conversion of **22** or 54% based on recovered **22**).

4-Methoxy-4′-nitro-2,2′-bipyridyl (24). A solution of 4-methoxy-4′-nitro-2,2′-bipyridyl *N,N′*-dioxide (**19**, 4.1 mg, 0.016 mmol) and PCl_3 (0.044 mL, 0.50 mmol) in 1.7 mL of $CHCl_3$ was refluxed for 21 h. The reaction was thrown on 7 g of ice and worked up by using the procedure described in the preparation of **10**, providing 3.4 mg of 4-methoxy-4′-nitro-2,2′-bipyridyl (**24**, 94%), mp 112–115 °C (mp of **24** prepared from **22** was 136 °C, mixed mp 129–135 °C; IR and TLC properties of the two samples were identical).

Photooxygenations. Photooxygenations were carried out by using a setup similar to that described on page 179 of ref 3b. A 650-W DWY lamp was used at 90 V. The reaction solution was maintained at approximately room temperature via a continuous flow of tap water in the condenser on the outside of the reaction vessel. Dry oxygen (passed through anhydrous $CaCl_2$) was introduced into the reaction solution via a syringe needle at a flow rate of 25–35 mL/min. Concentration of sensitizer used was between 10^{-3} and 10^{-4} M. Solvent volume was 7–8 mL. Solvent that evaporated during long runs was replaced. Reagent grade MeOH and dry (distilled from CaH_2) CH_2Cl_2 were used as solvents; 50–100 mg of substrate was used.

1,1′-Bicyclohexenyl. 1,1′-Bicyclohexenyl[27] was found to be more conveniently prepared by using the following procedure.[28]

1-Chlorocyclohexene[29] (800 mg, 6.86 mmol) and lithium (150 mg, 21.6 mmol) were stirred together in 25 mL of dry diethyl ether under nitrogen for 18 h at room temperature and then refluxed for 2.5 h. Stirring was stopped, particulate matter allowed to settle, and the ether solution transferred via canula into another flask maintained under a nitrogen atmosphere. The stirred solution was cooled to −65 °C, cuprous iodide (1.31 g, 6.88 mmol) added, and the reaction allowed to warm to 5 °C over 40 min (after 5 min a black solid suspension began to form). An ice bath was placed around the reaction flask, and dry oxygen was then rapidly bubbled into the reaction for 15 min. The reaction contents were then washed with 10% aqueous ammonium hydroxide and the ether layer dried (K_2CO_3) and evaporated to 390 mg. This was placed on an 8-g silica gel column, eluted with 60 mL of hexane, evaporated to 190 mg, and then distilled bulb to bulb (1.0 mmHg, oven temperature 80–110 °C) to provide 167 mg (30%) of 1,1′-bicyclohexenyl.

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(27) Greidinger, D. S.; Ginsburg, D. *J. Org. Chem.* **1957**, *22*, 1406. Isabelle, M. E.; Lake, D. H.; Wightman, R. H. *Can J. Chem.* **1977**, *55*, 3268.

(28) For examples of the oxidative coupling of alkenylcopper(I) reagents, see: Banks, R. B.; Walborsky, H. M. *J. Am. Chem. Soc.* **1976**, *98*, 3732. Posner, G. H. *Org. React.* **1975**, *22*, 253.

(29) Preparation of 1-chlorocyclohexene and cyclohex-1-enyllithium described: Braude, E. A.; Coles, J. A. *J. Chem. Soc.* **1950**, 2014.

Preparation of Primary Amines and 2-Azetidinones via *N*-Trimethylsilyl Imines

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Nonenolizable aldehydes react with lithium bis(trimethylsilyl)amide at ambient temperatures to afford solutions of *N*-trimethylsilyl aldimines. Treatment of these solutions with Grignard reagents or alkyllithiums followed by an aqueous workup gives primary amines in moderate to excellent yields. Treatment of *N*-trimethylsilyl aldimines with ester enolates provides an expedient route to 1-unsubstituted 2-azetidinones.

During the course of executing a total synthesis of the Lythraceae alkaloid vertaline, a need arose to convert benzaldehyde **1** to homoallylic amine **3**. Several conventional procedures for accomplishing this task were ex-

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