PMe_3 at 20 °C to soluble derivatives which then remain in solution when pure **5** (60% yield) is precipitated with hexanes.

Significantly if $Mo(N_2)_2(PMePh_2)_4$ is used in place of **1** in the reaction then a mixture of **3** (35% based on the starting Mo complex **1**), **5**(20%), and $WOCl_2(PMePh_2)_3$ (30%) is formed. Thus the regiospecificity of the reaction could be attributed to the ability of **1** to coordinate via the η^6-ligand to the tungsten and hence favor heterobimetallic bonding.[12] The complex $W_2Cl_4(PMePh_2)_4$ (**6**)[10] is not produced in any of these reactions. Preliminary work shows that $MoWCl_4(PMe_2Ph)_4$[18] is produced when $Mo(\eta^6\text{-}PhPMe_2)(PMe_2Ph)_3$[19] is used in place of **1** in Scheme I.

Complex **5** is most readily identified by the coupling constants of the inequivalent phosphorus atoms on the ^{183}W–Mo isotopomer in the ^{31}P NMR spectrum. The J values are similar to those observed for the ^{183}W–W isotopomer of complex **6** (Table I). The ^1H NMR spectrum of **5** in C_6D_6 shows two methyl resonances as virtual triplets at 1.90 and 2.07 ppm and two sets of ortho phenyl proton multiplets at 7.56 and 7.73 ppm consistent with two types of phosphines, whereas **3** gives only one methyl peak at 1.98 ppm and one ortho proton multiplet at 7.65 ppm. The λ_{max}(visible) of **5** in benzene at 650 nm falls in the range of $\delta \rightarrow \delta^*$ transitions of homonuclear complexes,[5,8,14,20] including $Mo_2Cl_4(PMe_3)_4$ at 582 nm[5] and $W_2Cl_4(PMe_3)_4$ at 657 nm.[5] It is interesting that the Mo–W complex with bridging carboxylates[2] has a yellow color; perhaps a $\delta \rightarrow \pi^*$ (ligand) transition, recently observed in the 500–600 nm region for $W_2(O_2CR)_4$ complexes,[21] complicates the visible spectrum when these bridging ligands are present. No frequency (IR or Raman) assignable to ν(Mo–W) is observed in the range 250–400 cm^{-1}. Solutions of **5** are sensitive to water and oxygen. Complex **5** decomposes when refluxed in degassed toluene; it does not disproportionate to **3** and **6**.

The substitution reactions of **5** are proving to be fascinating. For example, **5** reacts with excess PMe_3 at 20 °C for 3 h to give $(Me_3P)_2Cl_2Mo$–$WCl_2(PMePh_2)_2$ (**7**)[22] where only the phosphines on the molybdenum have been substituted. Further reaction (45 °C, 19 h) gives $MoWCl_4(PMe_3)_4$.[23] The course of reaction differs from that reported for $Mo_2Me_4(PEt_3)_4$.[24]

The structure of **5** (Scheme I) is proposed on the basis of the D_{2d} geometry of the homonuclear complexes.[5] Work is under way to obtain crystals of **5** or its derivatives suitable for X-ray diffraction in order to verify the structure and obtain further data on this unique heteronuclear bond.

Note Added in Proof. Preliminary X-ray crystallographic analysis of complex **7** confirms the geometry shown in Scheme I. The structure has refined to $R = 3.8\%$ in the space group $I_2/_a$. The molybdenum–tungsten distance is 2.209 (1) Å. (Personal communication from Jeffrey F. Sawyer.)

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Supplementary Material Available: Preparation of **3** and **5** and ^1H and ^{31}P NMR spectra of **5** (4 pages). Ordering information is given on any current masthead page.

(17) Identified by ^{31}P NMR (C_6H_6) δ −16.7 (1 P, J_{PW} = 416, J_{PP} < 5 Hz), 0.0 (2 P, J_{PW} = 339, J_{PP} < 5 Hz).[16]

(18) ^{31}P NMR (C_6H_6) δ −20.1 (2 PMo, J_{PP}^3 = 24.0, J_{PW}^2 = 50 ± 5 Hz), 17.4 (2PW, J_{PP}^3 = 24.0, J_{PW}^1 = 280 Hz).

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(22) ^{31}P NMR (C_6H_6) δ −28.9 (2 PMe_3Mo, J_{PP}^3 = 24.4 Hz), +21.7 (2 $PMePh_2W$, J_{PP}^3 = 24.4, J_{PW}^1 = 273 Hz).

(23) ^{31}P NMR (C_6H_6) δ −28.9 (2 PMe_3Mo, J_{PP}^3 = 25.6 Hz), +9.5 (2 PMe_3W, J_{PP}^3 = 25.6 Hz, $PMe_3{}^{183}W$, J_{PW}^1 = 271, J_{PP}^3 = 24.4 Hz).

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Synthesis of Anatoxin-*a*: Very Fast Death Factor

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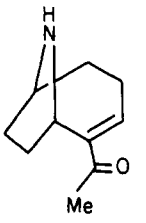
A class of microalgae, the cyanophytes, contains several toxic strains, including *Anabaena flos-aquae*.[1] Graphic descriptions of the death of animals induced by such blue-green algae have been recorded.[2,3] An alkaloidal toxin identified from these sources was shown[4] to be 2-acetyl-9-azabicyclo[4.2.1]non-2-ene (anatoxin-*a*, **1**), also designated "Very Fast Death Factor" (VFDF).[3]



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This structural assignment was confirmed by X-ray crystallography.[5] Anatoxin-*a* has been shown to be a potent muscarinic[1] and nicotinic agonist[6] and has engendered synthetic interest.[7–9]

We report herein an efficient, nitrone-based entry to this interesting natural product. It was anticipated[10,11] that the addition of 1-pyrroline 1-oxide (**2**) to *trans*-3,5-hexadien-2-ol (**3**)[12–14] would exhibit the desired site selectivity and regioselectivity (cf., Scheme I) to afford the isoxazolidine **4a**.[15] The latter, formed in 70% yield, upon oxidation with manganese dioxide (Celite, methylene chloride), produces the ketone **6a**, which exhibits a clean quartet at δ 4.71 (J = 6.71 Hz), assignable to the C-5 proton (isoxazolidine numbering).

Oxidative cleavage[16,17] of the isoxazolidine ring with *m*-chloroperbenzoic acid gives the nitrone **5** as the sole identifiable product in 79% yield. The product is a single regioisomer exhibiting a broad singlet in its ^1H NMR spectrum ($CDCl_3$) 7.0 ppm (1 H) characteristic of the proton at C-2 of the nitrone function. Warming of a solution containing the nitrone to 45 °C leads to the formation of a single cycloadduct, **6a** in 71% overall

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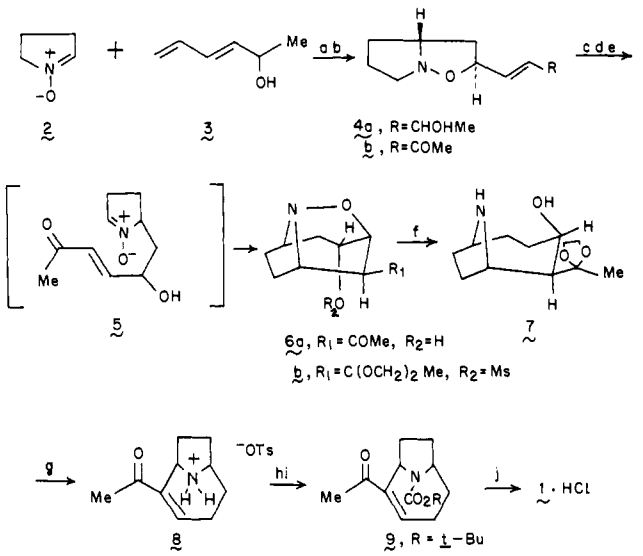
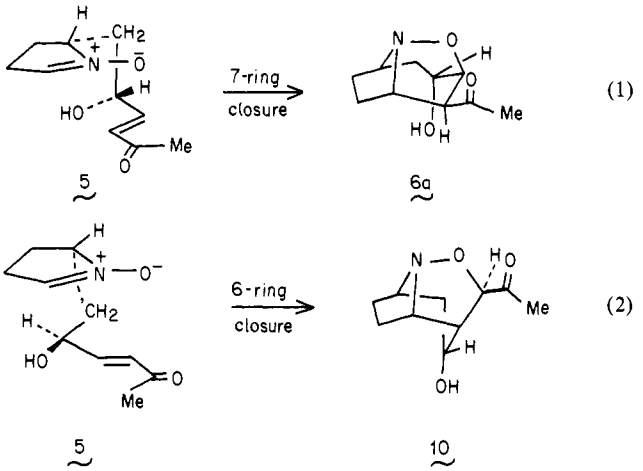
Scheme I



(a) heat, benzene (70%); (b) MnO_2, celite, CH_2Cl_2 (96%); (c) MCPBA, CH_2Cl_2 (71%); (d) $(CH_2OH)_2$, *p*-TsOH, benzene (96%); (e) MsCl, Et_3N (94%); (f) $LiAlH_4$, $NiCl_2$, THF (−40°); (g) *p*-TsOH, acetone; (h) $NaHCO_3$, H_2O; (i) $(t\text{-BuCO})_2O$, $CHCl_3$; (j) 3NHCl, EtOAc.

yield from **4b**. It has already been reported[18] that such *N*-alkenylnitrones can cyclize to produce either the product of 6-ring closure (e.g., **10**) or that of 7-ring closure (e.g., **6a**). A preference was observed in most cases for the transition state resulting in 6-ring closure. This was attributed to diminished strain when compared to its counterpart leading to 7-ring closure.[18] Clearly, nitrone **5** can undergo either 6- or 7-ring closure (cf. eq 1 and 2).



We believed that **5** might overcome the normal predilection for 6-ring closure because of the natural tendency of nitrones, in intermolecular cycloaddition reactions, to afford the adduct with the nitrone oxygen bound to the β-carbon of the dipolarophilic α,β-unsaturated carbonyl system.[17,19-21]

We could only identify a single cycloadduct from **5** (i.e., **6a**).[22] This adduct appears to be of kinetic origin since it is formed conveniently at 45 °C. This fortunate circumstance results in the construction of the ring system of anatoxin-*a*. Subsequent ketalization and mesylation results in the formation of ketal mesylate **6b**. Finally, treatment of **6b** with a 1:1 (molar) mixture of $LiAlH_4/NiCl_2$ in THF (−40 °C) leads to **7**. When direct conversion into anatoxin-*a* by acid hydrolysis proved to be problematic, the hydroxy ketal **7** was treated with a stoichiometric amount of *p*-toluenesulfonic acid in acetone to induce both trans ketalization and dehydration, thereby affording the *p*-toluenesulfonic acid salt (i.e., **18**) of the natural product. For purposes of purification, the crude salt **8** was treated with 2 equiv of sodium bicarbonate and di-*tert*-butyl dicarbonate.[23] The resultant *tert*-butyl carbamate **9** (43% overall yield from mesylate **6b**) was subjected to acid hydrolysis[24] to give anatoxin-*a* hydrochloride. The ^1H NMR, IR, and mass spectral comparisons of the synthetic material with the natural product confirmed the successful outcome of the synthetic effort.

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Registry No. (±)-**1**·HCl, 70470-07-4; **2**, 24423-88-9; (±)-**3**, 3280-51-1; **4a**, 92844-74-1; (±)-**4b**, 92844-75-2; **5**, 92844-79-6; (±)-**6a**, 92844-76-3; (±)-**6b**, 92844-77-4; (±)-**7**, 92844-78-5; (±)-**8**, 92844-80-9; (±)-**9**, 92998-50-0.

Supplementary Material Available: Experimental section for **4a,b**, **6a,b**, **7**, **9**, and **1**·HCl and tables of mass spectral data for **4a**, **6a,b**, **7**, **9**, and **1**·HCl (9 pages). Ordering information is given on any current masthead page.

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1,8-Biphenylenediol Forms Two Strong Hydrogen Bonds to the Same Oxygen Atom

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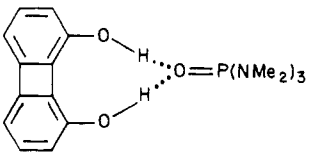
The molecular geometry of 1,8-biphenylenediol is such that the two hydroxyl groups should be capable of forming hydrogen bonds simultaneously to the same basic atom. This expectation is now supported by the isolation and X-ray structure determination of crystalline adducts of the diol[1] with *N,N,N',N',N'',N''*-hexamethylphosphoramide (**1**)[2] and with 1,2,6-trimethyl-4-pyridone[3,4] and 2,6-dimethyl-γ-pyrone.[5]



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(5) Adduct prepared by dissolving equimolar amounts of pyrone (mp 133-137 °C) and diol in chloroform and crystallized by slow evaporation, first from chloroform–cyclohexane and then from ethyl acetate: mp 182-183 °C.

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