conversion process, i.e. rotation around the C(5')-C(4) bond, even down to -90 °C, which is not far from the freezing point of the acetone solvent.[8]

Registry No. 1, 126615-13-2; 3, 126615-14-3.

(7) Filleux-Blanchard, M. L.; Mabon, F.; Martin, G. J. *Tetrahedron Lett.* **1974**, 3907.

(8) The temperature dependence of the chemical shifts (Table I), which is somewhat stronger than usual, may be attributed to a gradual deviation from planarity in the ground states and concomitant change in solvation; see the small but significant decrease of $J_{H(2),H(3)}$ and $J_{H(3),H(5')}$, and the deshielding of the aldehyde and shielding of the NMe protons, as the temperature is increased.

Chemoselective Alcohol Oxidations by the Anionic Molybdenum-Picolinate *N*-Oxidoperoxo Complex MoO_5PICO[1]

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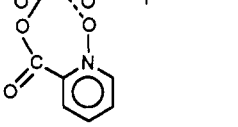
In previous papers[1-3] we reported on the synthesis and chemistry of the anionic peroxomolybdenum complex $[MoO(O_2)_2(C_5H_4N(O)COO)]^-Bu_4N^+$ (MoO_5PICO):



Both peroxogroups of MoO_5PICO react with primary and secondary alcohols in nonpolar solvents under mild conditions to give high yields of aldehydes and ketones, respectively.[2] Although there are several procedures for alcohol oxidations,[4] including recent ones,[6-9] MoO_5PICO may be considered to be of particular synthetic interest because it allows for the oxidation of a primary alcoholic function to aldehyde without overoxidation to the carboxylic acid.[4,7,9] Taking into account its ease of preparation from commercially available reagents as well as its remarkably stability, MoO_5PICO could be proposed as a substitute for classical alcohol oxidation reagents, such as the Cr(VI) derivatives. With a view to enlarging the synthetic scope of this reagent, we have further investigated its chemoselectivity. Previously, we showed that double-bond epoxidation does not compete with alcohol oxidation even in the case of homoallylic and allylic alcohols.[2] In this paper we present results indicating that the oxidation of the alcoholic function by MoO_5PICO also proceeds smoothly in the presence of other functional groups. Table I presents the data obtained in the oxidations of a series of model substrates. As a general comment, it is noteworthy that in all cases the oxidation of a primary alcoholic function leads to the corresponding aldehydic group without further oxidation to the carboxylic acid. In addition, it may be noted that for most of the examples reported, equimolar amounts of active oxygen ($[O]_{act}$ = 2[MoO_5PICO]) and of substrate are used. In the series of the three epoxy alcohols examined, a high yield of the epoxy aldehyde is found for compound **3a**; for **1a** and **2a**, epoxides of homoallylic and allylic alcohols respectively, the yields of the corresponding aldehydes are only moderate, ranging from 60 to 67% (not far, however, from the values obtained for classical oxidation reagents).[4,5] The iodometric and gas chromatographic analyses of the reaction mixtures reveal that appreciable amounts of the oxidant are still present when all the substrate has been consumed. At the same time, higher molecular weight products are detected. Although this behavior has not been investigated in detail, it appears that under the reaction conditions compounds **1a** and **2a** may undergo a parallel condensation reaction, likely Lewis acid catalyzed, for which there is precedent in the literature.[10] At any rate, the yield of epoxy aldehyde may be increased up to 95% for compound **2a** simply by using a 5-fold excess of the substrate thus, presumably, enhancing the rate of oxidation compared with that of the condensation process.

As might have been expected based on previous results concerning double bond vs alcohol oxidations,[2] the pyridine nitrogen (**4a**) and the triple bond (**5a**) do not compete with the oxidation of the OH group. By contrast, the presence of a basic group (**6a**) greatly diminishes the yields of the carbonyl product, probably due to the ability of the substrate to displace the picolinate-*N*-oxido ligand of the reagent.[1] In fact, analysis of the reaction mixture of compound **6a** reveals that ca 80% of the substrate is recovered unreacted. Based on these results, the synthetically significant oxidation of amino alcohols by MoO_5PICO requires the preliminary protection of the amino group. Compounds **7a**, **8a**, **9a** show that the oxidation of the alcoholic function of carbamates or amides is efficiently carried out by this reagent such that, following deprotection by standard methods, amino aldehydes or amino ketones are obtained. Finally, the oxidation of diols has been briefly examined. Both primary alcoholic groups of 1,6-hexanediol are oxidized (**10a**), providing adipaldehyde in good yield. It is interesting to note that the oxidation of meso-hydrobenzoin (**11a**) provides only minor amounts of benzaldehyde, at variance with the behavior of other oxidizing agents[11] and in spite of the ease of carbon-carbon bond cleavage in such model substrates. Instead, a fairly good yield of the more synthetically attractive α-diketone, benzil, is obtained.

Many of the model oxidations examined herein represent a key step in the route to complex molecules containing several functional groups. The scope of MoO_5PICO

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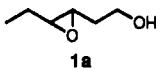
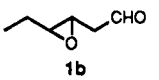
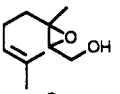
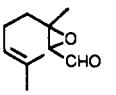
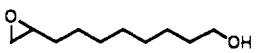
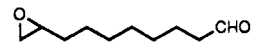
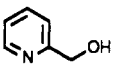
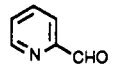
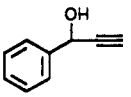
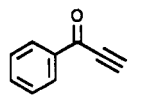
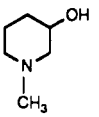
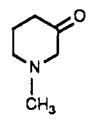
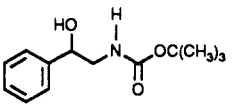
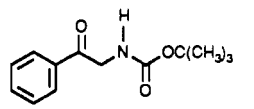
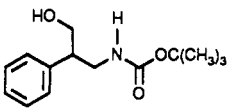
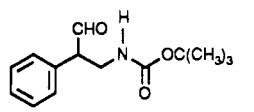
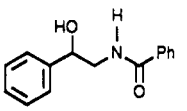
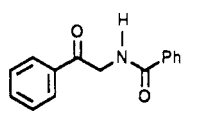
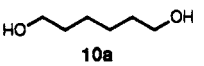
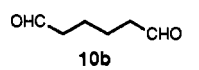
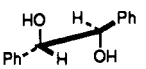
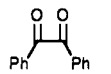
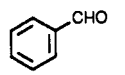
Table I. Oxidation of the Alcoholic Function of Various Substrates by MoO_5PICO, at 50 °C[a]

substrate	[sub]/[O]$_{act}$	time, h	product	yield,[b] %
 1a	1	18	 1b	60
 2a	1	20	 2b	67
2a	5	8	2b	95[c]
 3a	1	10	 3b	95
 4a	1	48	 4b	97
 5a	1	0.5	 5b	80
 6a	1	24	 6b	20
 7a	1	5	 7b	93
 8a	1	15[d]	 8b	81
 9a	1	7	 9b	94
 10a	0.5	15	 10b	72
 11a	0.5	10	 11b	86
			 12b	14

[a] Reaction conditions, unless otherwise noted: [O]$_{act}$ = 2[MoO_5PICO] = 0.02 M, 100 mL of dichloroethane. [b] Isolated yields, see Experimental Section. [c] Yield based on the oxidant after its complete consumption. [d] At 60 °C.

in such transformations is now being investigated.

Experimental Section

Materials. The epoxy alcohols **1a–3a** were synthesized by epoxidation (MCPBA[12] for **1a** and **3a**, VO(acac)$_2$/*t*-BuO_2H[13] for **2a**) of the commercially available olefins *trans*-3-hexen-1-ol, geraniol, and 9-decen-1-ol, respectively. Compounds **7a–9a** were obtained from the parent amino alcohols (FLUKA Chemie AG) by reaction with di-*tert*-butyl dicarbonate, **7a** and **8a**, and with benzoyl chloride, **9a**, following reported procedures.[14] All other substrates were commercially available materials used as received. The preparation and characterization of MoO_5PICO has been described elsewhere.[2] DCE was purified by distillation over P_2O_5. The identity of the products was confirmed after isolation from the reaction mixture (column chromatography) on the basis of spectroscopic (^{1}H NMR) and GS–MS analyses.

Procedures. In a typical run, 50 mL of DCE containing 2.0 mmol of substrate was added to a DCE solution (50 mL) containing the complex (1.0 mmol, 2.0 mmol O_{act}) in a glass reactor maintained at 50 °C. After complete consumption of the reagents,

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(14) Flynn, D. L.; Zelle, R. E.; Grieco, P. A. *J. Org. Chem.* **1983**, *48*, 2424.

the solvent was removed under vacuum and the remaining material was subjected to column chromatography to isolate the products.

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Conformational Effects in Trichothecenes: Structures of 15-Hydroxy C4 and C8 Ketones

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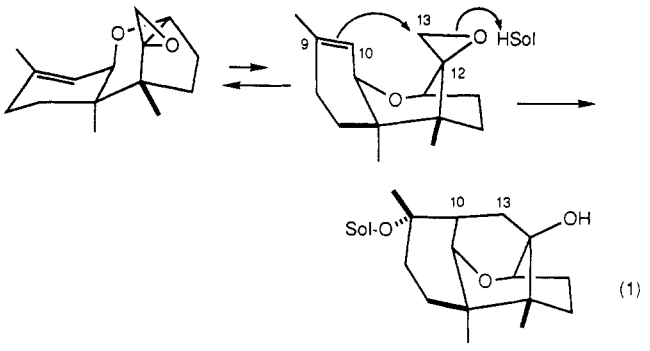
The trichothecene complex of antibiotics constitutes an important group of mycotoxins whose biological activities have attracted a good deal of attention because of their potency and diversity.[1] Interest remains high both in the synthesis[2] and chemical reactivities[3] of the trichothecenes. The chemical reactivity of trichothecenes is particularly rich because of their ability to undergo a variety of intramolecular rearrangements.[1a,3,4]

The course of these rearrangements is strongly influenced by the conformation of this ring system. In particular, the rate of the trichothecene-10,13-cyclotrichothecene rearrangement (eq 1) is increased tremendously when the tetrahydropyranyl B ring assumes the boat form.[5] Although the B ring has a large preference



(1)

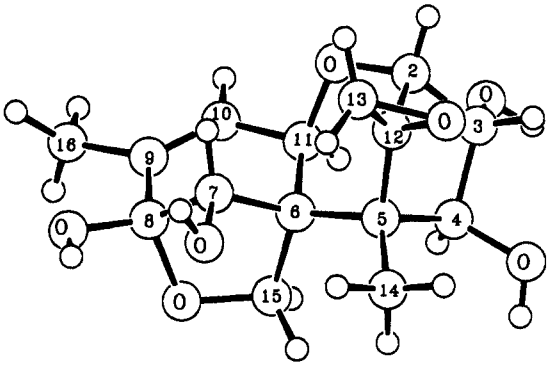


Figure 1. Ball and stick diagram for **1a**. The drawing was labeled and a laser printer file prepared by the PLOTMD[9] program.

for the chair form in typical trichothecenes, this preference can be strongly influenced by bonding and nonbonding interactions in this ring system. Herein, we report the structures of the hemiketals of trichothecenes derived from the intramolecular addition of the C-15 hydroxyl group with the C-8 carbonyl group of nivalenol (**1**, NIV) and with the C-4 carbonyl group of 15-hydroxyscirpene-4,8-dione (**2**). The introduction of the 8,15- and 4,15-hemiketal linkages in these compounds has a marked effect on the conformational mobility of the trichothecene ring system.

Nivalenol (**1**, NIV) is one of the more common naturally occurring trichothecenes and is produced by several species of *Fusarium* associated with grains found worldwide, but especially in Japan.[6] The spectral data[7] for NIV are entirely consistent with the structure illustrated in **1**. It therefore was somewhat unexpected that a single-crystal X-ray diffraction analysis of a single crystal of NIV showed that NIV had crystallized from MeOH–H_2O in the hemiketal form **1a** (Figure 1). The preference for **1a** in the crystalline form may be due either to a kinetic effect of the crystallization of **1a** over that of **1** or to a lower crystal lattice energy for **1a**, compared to that of **1**.

Since none of the published NMR data suggested that NIV in solution exists in any form other than **1**, we have scanned the ^{13}C NMR spectrum of NIV to see if there is any indication of the presence of **1a**, but we found NIV to have limited solubility, and therefore it is not suitable for the detection of minor amounts of **1a**. The only solvent we found in which NIV was sufficiently soluble was DMSO-d_6. In this solvent, NIV exists as a mixture of 82% **1** and 18% **1a** as shown by integrating the ^{13}C signals whose chemical shifts for C-8 and C-10 in **1** are δ 200.0 and 138.0, respectively, and in **1a** are δ 103.8 and 120.7, respectively.

Since NIV is too insoluble to determine this equilibrium in other solvents, we studied the equilibrium for deoxynivalenol (DON, **3**) a mycotoxin which is more commonly encountered than NIV, especially in North America.[1b] In the present study, ^{13}C NMR spectra were recorded in DMSO-d_6, $(CD_3)_2CO$, and CD_3OD, and these data along with the published values obtained in $CDCl_3$[8] are given in Table I. The two signals which are most diagnostic for

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(2) (a) McDougal, P. G.; Schmuff, N. R. *Fortschr. Chem. Org. Naturst.* **1985**, *47*, 153. (b) Tamm, C.; Jeker, N. *Tetrahedron* **1989**, *45*, 2385.

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