Scheme I

$$R-OH \xrightarrow[\text{(pyridine)}]{PCl_3} (RO)_2PH + RCl$$

$$H_{13}C_6CH(OH)CH_3 \longrightarrow$$

1 (R,S)
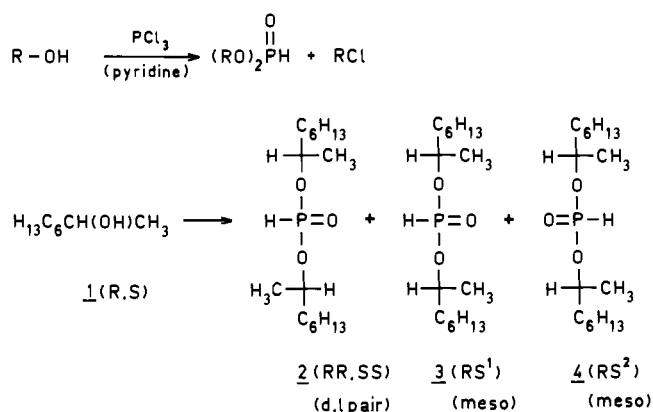
2 (RR,SS)
(d,l pair)

3 (RS¹)
(meso)

4 (RS²)
(meso)

yield a mixture of phosphonates **2** (*RR,SS*), **3** (*RS*¹ meso), and **4** (*RS*² meso) in a 2:1:1 ratio and ³¹P NMR of the reaction mixture shows three well-separated singlets in that ratio.[6,7] Enantiomerically pure (*S*)-(−)-**1** yields exclusively (*SS*)-**2**, as is demonstrated by the absence of the two absorptions due to meso isomers **3** and **4**.

The method described in this paper is especially advantageous for chiral compounds with complicated ¹H or ¹³C NMR spectra, e.g., the phosphonate of enantiomerically pure 3-hydroxy-androst-5-en-17-one shows a single ³¹P NMR absorption at δ 4.30. Byproducts (if present) either gave no ³¹P NMR absorption or singlets well separated from the phosphonate absorptions.

Table I summarizes data on optically pure or partially enriched alcohols and compares ee's determined by weight and by rotation with results obtained by the ³¹P NMR method.[8,9] These results show that during derivatization no racemization of the alcohols occurs and it is also shown that the "loss" of part of the alcohol as the halide does not influence the accuracy of the ee determination. The results of this technique with several racemic alchols are summarized in Table II.[8]

The present method tolerates large variations in alcohol structure, e.g., primary and secondary benzylic and allylic alcohols and α-hydroxy amides and esters. Chiral recognition during the coupling reaction is negligible as is illustrated by the small deviations from 50/50 in the *RR* (*SS*) to meso ratio's in Table II and the accuracy of the calculated and measured ee's (Table I). Chemical shift differences compare favorably with those obtained using chiral derivatizing agents, e.g., for 2-butanol Δδ 0.0056 (C₆D₆)[4c] and 0.20 (CDCl₃)[4b] were reported whereas Δδ 0.35 and 0.46 (CDCl₃) were obtained by the present method. In contrast to prior results with chiral reagents[4b] our method did not give satisfactory results for the enantiomeric excess determination of amines so far. Application of this technique for the determination of enantiomeric purities at submilligram scale is currently under investigation since ³¹P NMR lends itself admirably to this purpose.

A typical procedure to prepare an NMR sample to determine enantiomeric composition follows: The appropriate alcohol (0.75 mmol) was dissolved in 2 mL of CDCl₃ and pyridine (0.75 mmol) was added, if necessary.[6] To the stirred solution was added PCl₃ (0.25 mmol) dissolved in 2 mL of CDCl₃. The mixture was stirred at room temperature for 10 min and subsequently transferred, without the necessity of any workup or further purification, into a 10-mm NMR tube and the ³¹P NMR spectrum recorded.

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(7) The formation of two meso phosphonates **3** and **4** is due to the "pseudoasymmetric" character of the phosphorus center: it is a stereogenic-achirotopic center; for a recent discussion, see: Mislow, K.; Siegel, J. *J. Am. Chem. Soc.* **1984**, *106*, 3319.

(8) All the spectra were obtained in CDCl₃ at 80.988 MHz on a Nicolet 200NT spectrometer using 10-mm tubes; chemical shift values are given in hertz with 85% H₃PO₄ (δ 0.0) as an external standard.

(9) The enantiomeric purity (*p*) was calculated from the integrated peak area's *Q* and *Q'* of the *RR* (*SS*) isomer and the meso isomers, respectively (with *RR* (*SS*)/meso ratio $K = Q/Q'$) using Horeau's formula $p^2 = (K - 1)/(K + 1)$ (see also ref 2).

Excited-State Nitrosyl Bending and Metal Oxidation in K₂[Fe(CN)₅NO] Determined by Excited-State Raman Spectroscopy

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The geometries and the formal oxidation states of metal nitrosyl complexes are proposed to undergo large changes in MLCT excited states.[1–3] A linear $M^nN\equiv O^+$ unit can bend to form bent $M^{n+2}N\!=\!O^-$ when the metal to nitrosyl charge-transfer state is populated. The driving force for the geometry change is the population of the totally π antibonding orbital of the MNO group in the linear geometry and the stabilization upon bending of a σ nonbonded orbital on the nitrogen.[3] A *formal* two-electron oxidation of the metal accompanies the bending. (This valence bond description represents a formal upper limit for the highly covalent system.)[3] The excited-state geometry and oxidation-state changes are indirectly supported by the photochemical reactivity of metal nitrosyls.[1,2,4] Ground-state changes caused by putting in or taking out electrons from the π antibonding orbital have been well documented, e.g., the change from linear to bent MNO when a pair of electrons is added to Co(das)₂NO²⁺ by addition of a ligand and the bent to linear change with a formal one-electron reduction of the metal when Fe(das)₂NOX⁺ is oxidized by one electron.[3,5] We report here direct vibrational spectroscopic evidence for both the excited-state linear to bent geometry change and for the oxidation state increase in Fe(CN)₅NO²⁻ by using excited-state resonance Raman spectroscopy.

Raman spectra of metal complexes in excited electronic states have been obtained by using either pulsed or CW lasers to produce a near-saturation yield of excited states and to simultaneously provide the probe beam for Raman scattering from the excited molecule.[6–11] The pioneering studies of Woodruff et al. showed that the method could probe electronic changes in the MLCT excited state of Ru(bp)₃²⁺.[6] In the experiments reported here, excited-state Raman spectra were obtained by exciting and probing with 406-nm, 9-ns pulses at a 40-Hz repetition rate from an excimer pumped dye laser (Lambda Physik EMG 102E and FL2001). The absorption band at 400 nm has been assigned by Gray et al. to the 6e (d$_{xz,yz}$) to 7e (Π*$_{NO}$) MLCT transition.[12] The Raman scattered light was passed through a Spex double monochrometer, detected by using a C31034 photomultiplier and recorded with an electrometer and strip chart recorder. An aqueous solution (∼1 M) of K₂[Fe(CN)₅NO] was pumped through a needle to produce a roughly 200-μm-diameter jet stream at the laser focus. Each laser pulse irradiated a fresh 10⁻¹¹-L volume of solution.

The Raman spectra taken at three different pulse energies are shown in Figure 1. The lowest trace (Figure 1) was taken at the lowest pulse energy and is the spectrum of the ground-state molecule. The upper two traces (Figure 1b,c) show both the ground- and excited-state Raman peaks. Four new peaks are observed which grow in intensity as the laser pulse energy increases. The intensities of all of the new peaks show a nonlinear dependence on the laser pulse energy. Plots of the log of the

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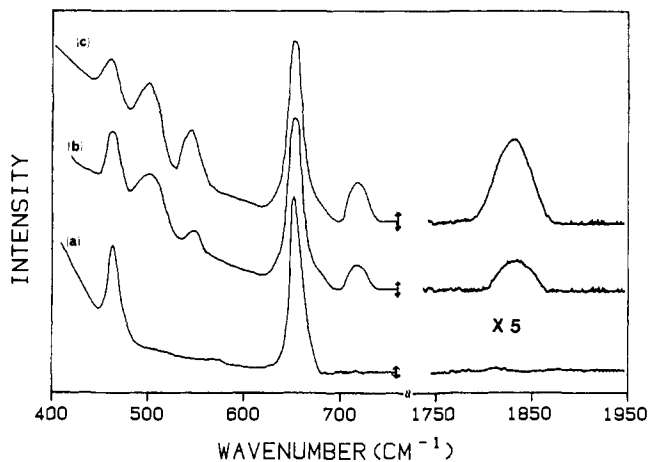(8) Bradley, P. G.; Kress, N.; Hornberger, B. A.; Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 7441–7446.
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Figure 1. Raman spectra of aqueous solutions of K$_2$[Fe(CN)$_5$NO]. All spectra are normalized with respect to the 652-cm^{-1} peak. The 1850-cm^{-1} region is shown magnified 5 times. The magnitude of the background noise, smoothed during digitization, is shown by the arrows. The broad band widths are caused by the large slit widths that were required. The weak ground-state NO stretch at 1940 cm^{-1} is observed at a scale larger than that shown. The laser pulse energies were (a) 1.1 mJ/pulse, (b) 3.0 mJ/pulse, and (c) 4.3 mJ/pulse.

Table I. Excited-State Raman Frequencies in [Fe(CN)$_5$NO]$^{2+}$ and Correlations with Ground-State Normal Modes[a]

obsd excited-state freq, cm^{-1} [b]	correlation with ground-state stretches, cm^{-1}	correlation with ground-state stretches and bends, cm^{-1}
501	400 FeC(eq)	462 ν(FeC)(ax)
548	462 FeC(ax)	652 ν(FeN)
716	652 FeN	665 δ(FeNO)
1835	1940 NO	1940 ν(NO)

[a] Ground-state assignments are from ref 13. [b] The excited-state Raman spectra were taken by using the 406-nm excitation from an excimer pumped dye laser. All values are accurate to 5 cm^{-1}. [c] The same ground-state Raman frequencies were obtained by using pulsed 406-nm and CW 514-nm excitation with the exception of the 400-cm^{-1} mode which was obscured by the Rayleigh scattering and ASE with 406-nm excitation.

intensities vs. the log of the laser pulse energy are linear with slopes of 1.5 ± 0.2 indicating that the peaks arise from a two-photon process with some relaxation of the excited state within the duration of the laser pulse. The energies of the excited-state bands are given in Table 1.

The new peak which grows in at 1835 cm^{-1} is assigned to the NO stretch in the excited-state molecule. Its energy is reduced by 105 cm^{-1} from that of the NO stretch in the electronic ground state.[13] The lower frequency is expected for the bent nitrosyl where the formal bond order is reduced from 3 to 2. The decrease is similar in magnitude to that observed in RuCl(NO)$_2$(PPh$_3$)$_2$ where both a linear and a bent nitrosyl is observed.[14] It is smaller than the 370-cm^{-1} decrease which occurs when Fe(CN)$_5$NO^{2-} is reduced by one electron,[15] although both the geometry and the total charge have changed in Fe(CN)$_5$NO^{3-}. There are no directly applicable cases for comparison.

Two correlations between the observed excited-state modes and the corresponding ground-state modes are given in Table I.[16] The first is a one-to-one correlation with the totally symmetric metal–ligand stretches. In this interpretation, all of the metal–ligand stretching frequencies increase in the excited state. The magnitudes of the increases are larger than those expected for a one-electron oxidation. For example, in a series of Fe(CN)$_5$X^{n-}

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(14) Pierpont, C. G.; Van Derveer, D. G.; Durland, W.; Eisenberg, R. *J. Am. Chem. Soc.* **1970,** *92,* 4760–4762. Linear, 1845 cm^{-1}; bent, 1687 cm^{-1}.

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(16) Work is in progress to differentiate between these correlations by using ^{15}NO isotopic substitution.

complexes, the changes in the M–C stretching frequencies are less than 30 cm^{-1} when the iron is oxidized from Fe(II) to Fe(III).[17] The large observed excited-state frequencies are consistent with the large increase in metal formal charge expected in the excited state. The second correlation associates the 716-cm^{-1} excited-state band with an Fe–NO bending mode and the 548-cm^{-1} band with the Fe–N stretching mode as given on the right of Table I. This correlation is consistent with the trends observed for these modes in ground-state cobalt complexes containing linear and bent NO geometries.[18] The 501-cm^{-1} mode is correlated with an Fe–C stretch which is increased in frequency by about 40 cm^{-1}. These changes, together with the decrease in the NO stretching frequency, are consistent with a linear to bent FeNO geometry change and a concomitant large increase in the positive charge on the metal.

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Chemical Transformations in the Quassinoid Series: Novel Copper(II)-Mediated Ring Contraction of δ-Lactones to γ-Lactones. A Synthetic Entry into the Samaderins

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In connection with our continuing interest in quassinoids,[1-3] in particular quassimarin (**1**)[4] and related congeners, we wish to
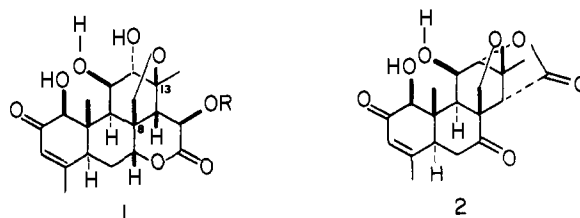
R = COC(OAc)(Me)Et

report a novel, copper(II)-mediated ring contraction reaction which appears to be general within the carbon framework of quassinoids possessing the C(8)–C(13) epoxymethano bridge. The new δ-lactone to γ-lactone conversion (cf. **3** → **4**) provides a unique entry into samaderin B (**2**)[5] and related natural products. For example, bubbling oxygen into a 0.02 M solution of lactone **3** in methanol

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