

Figure 1. Raman spectra of aqueous solutions of $K_2[Fe(CN)_5NO]$. 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 $[Fe(CN)_5NO]^{2+}$ 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 $\nu(\text{FeC})(\text{ax})$
548	462 FeC(ax)	652 $\nu(\text{FeN})$
716	652 FeN	665 $\delta(\text{FeNO})$
1835	1940 NO	1940 $\nu(\text{NO})$

^aGround-state assignments are from ref 13. ^bThe 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} . 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 $Fe(CN)_5NO^{2-}$ is reduced by one electron,¹⁵ although both the geometry and the total charge have changed in $Fe(CN)_5NO^{3-}$. 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 $Fe(CN)_5X^{n-}$

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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Registry No. $K_2[Fe(CN)_5NO]$, 14709-57-0; $[Fe(CN)_5NO]^{2-}$, 15078-28-1.

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(18) Quinby-Hunt, M.; Feltham, R. D. *Inorg. Chem.* **1978**, *17*, 2515-2520.

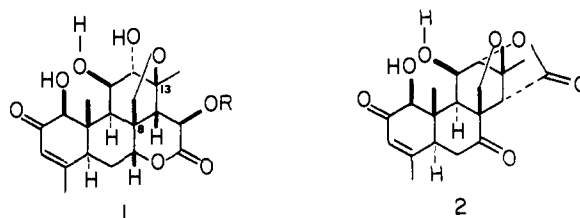
Chemical Transformations in the Quassinoid Series: Novel Copper(II)-Mediated Ring Contraction of δ -Lactones to γ -Lactones. A Synthetic Entry into the Samaderins

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In connection with our continuing interest in quassinoids,¹⁻³ in particular quassinarin (**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** \rightarrow **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

(13) Khanna, R. K.; Brown, C. W.; Jones, L. H. *Inorg. Chem.* **1969**, *8*, 2195-2200.

(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.

(1) For previous work on quassinoids from our laboratory, see: Vidari, G.; Ferrino, S.; Grieco, P. A. *J. Am. Chem. Soc.* **1984**, *106*, 3539. Grieco, P. A.; Lis, R.; Ferrino, S.; Jaw, J.-Y. *J. Org. Chem.* **1984**, *49*, 2342. Grieco, P. A.; Sham, H.-L.; Inanaga, J.; Kim, H.; Tuthill, P. A. *J. Chem. Soc., Chem. Commun.* **1984**, 1345. Kanai, K.-i.; Zelle, R. E.; Sham, H.-L.; Grieco, P. A.; Callant, P. *J. Org. Chem.* **1984**, *49*, 3867 and references cited therein.

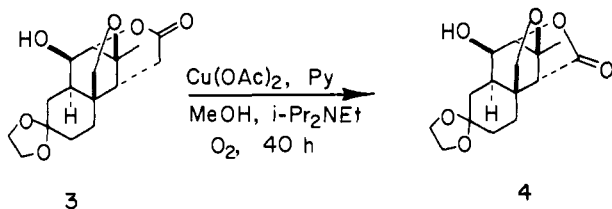
(2) For recent synthetic developments in the quassinoid area, see: Ziegler, F. E.; Kelin, S. I.; Pati, U. K.; Wang, T.-F. *J. Am. Chem. Soc.* **1985**, *107*, 2730 and references cited therein.

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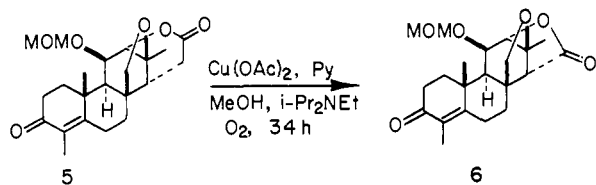
(5) Zybler, J.; Polonsky, J. *Bull. Soc. Chim. Fr.* **1964**, 2016.

containing 1.5 equiv of copper(II) acetate monohydrate, 120 equiv of pyridine, and 28 equiv of Hunig's base [(i-Pr)₂NEt] gave rise after 40 h at ambient temperature to an 85% isolated yield of crystalline γ -lactone **4**,⁶ mp 188–190 °C. In the absence of



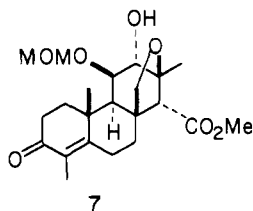
copper(II) acetate the reaction does not proceed. Similarly, if pyridine is not included, there is no reaction. Hunig's base can be replaced by triethylamine; however, the reaction rate is substantially slowed.

Even more surprising is the product obtained from the reaction of pentacyclic δ -lactone **5** with Cu(OAc)₂/O₂ in methanol containing pyridine and Hunig's base. After 34 h at room temperature a 66% yield of γ -lactone **6**,⁶ mp 194–195 °C, was isolated.

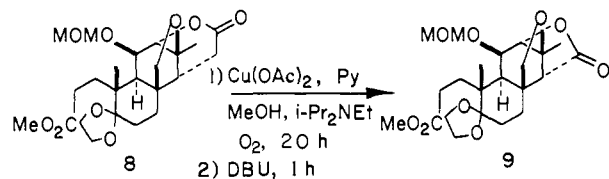


Particularly noteworthy and remarkable is the fact that the enone system in **5** is left intact. It is well-known⁷ that copper(II) salts under similar conditions (Cu(OAc)₂, Py, Et₃N, MeOH, O₂) oxidize cholestenone to Δ^4 -cholestenene-3,6-dione in 75% yield.

During the conversion of **5** into **6**, if the reaction is terminated after a few hours, appreciable amounts of hydroxy ester **7** can



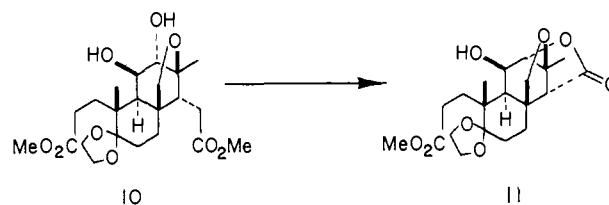
be isolated. For instance, after 21 h a 42% yield of **7**⁶ was obtained along with only 36% of γ -lactone **6**. Under the reaction conditions or on standing, hydroxy ester **7** lactonizes, giving rise to **6**. As illustrated in the case of substrate **8**, the reaction time can be appreciably shortened by addition of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to the reaction mixture which serves to facilitate the relactonization. Workup provided a 71% yield of γ -lactone **9**.⁶ The reaction need not be carried out directly



on a lactone. Exposure of dihydroxy diester **10** to copper(II) acetate under the identical conditions described above for the conversion of **8** into **9** provided, as the sole product, a 90% yield of γ -lactone **11**.⁶ It is indeed noteworthy that the reaction proceeds in excellent yield in view of potential complications due

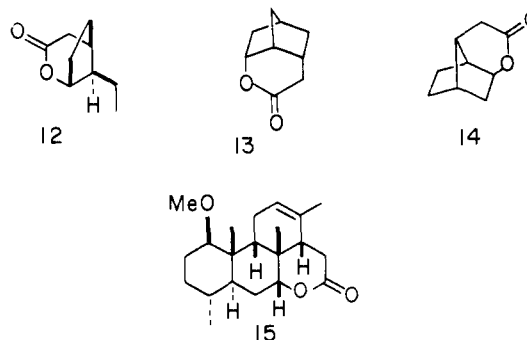
(6) All new compounds have been fully characterized spectrally including elemental composition determined by combustion analysis and/or single-crystal X-ray analysis.

(7) Volger, H. C.; Brackman, W.; Lemmers, J. W. F. M. *Recl. Trav. Chim. Pays-Bas* **1965**, *84*, 1203.

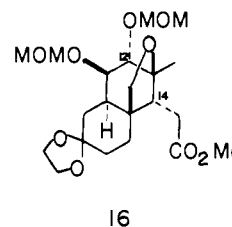


to the additional hydroxyl group and ester moiety.

In an attempt to probe the generality of this novel reaction, several lactones (**12–15**), including δ -valerolactone and capro-

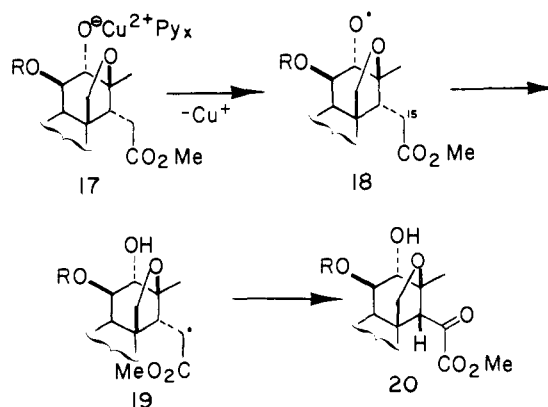


lactone, were subjected to the reaction conditions. No ring contracted products could be detected. In the case of δ -valerolactone, caprolactone, and lactones **12** and **14**, only products derived from methanolysis were isolated. With substrates **13** and **15** there was no reaction. It appears from the above data that a stringent requirement for reaction to occur is a 1,3-axial,axial relationship between an unprotected hydroxyl group at C(12) and a methyl acetate unit at C(14). In those cases examined where the C(12) hydroxyl groups is protected, no reaction takes place. For example, exposure of ester **16** to copper(II) acetate/oxygen



under the identical conditions described above for substrate **10** led to no reaction. The starting material was completely recovered.

The novel ring contraction sequence can be rationalized by initial methanolysis followed by complexation of the C(12)-hydroxyl with copper(II) and pyridine and subsequent electron transfer (**17**) \rightarrow **18**.⁸ Hydrogen atom abstraction from C(15) in intermediate **18** provides access to **19** which undoubtedly gives rise to the α -oxo ester **20**.⁹

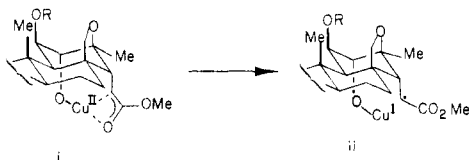


(8) Cf. Finkbeiner, H.; Hay, A. S.; Blanchard, H. S.; Endres, G. F. *J. Org. Chem.* **1966**, *31*, 549.

The formation of ring contracted products such as **6** paves the way for a novel entry into the samaderins. Efforts along these lines are currently in progress.

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(9) A referee has suggested a reasonable alternative mechanism involving formation of a copper(II) enolate via base catalysis followed by electron transfer (cf. i \rightarrow ii).



A Spherand Azophenol Dye: Lithium Ion Specific Coloration with "Perfect" Selectivity

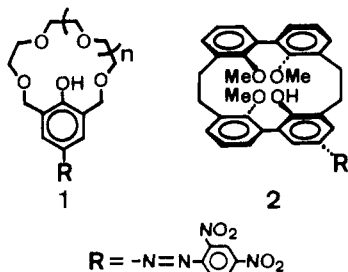
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Designing and synthesizing ligands that can selectively bind a specific metal ion and undergo concomitantly color change are worthwhile subjects in host-guest chemistry. This paper provides such an approach where our attention is focused on lithium.¹ Several macrocyclic ligands have been known as lithium binders, but they also tend to bind other guests.² Recently, we reported ion-selective coloration with crowned (dinitrophenyl)azophenol **1**³ and fluorescent emission with crowned benzothiazolylphenols;⁴



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(2) (a) Lehn, J. M.; Sauvage, J. P. *J. Chem. Soc., Chem. Commun.* **1971**, 440-441. (b) Dale, J.; Krane, J. *J. Chem. Soc., Chem. Commun.* **1972**, 1012-1013. (c) Kobuke, Y.; Hanji, K.; Horiguchi, K.; Asada, M.; Nakayama, Y.; Furukawa, J. *J. Am. Chem. Soc.* **1976**, *98*, 7414-7419. (d) Olsher, U.; Jagur-Grodzinski, J. *J. Chem. Soc., Dalton Trans.* **1981**, 501-505. (e) Nakamura, H.; Sakka, H.; Takagi, M.; Ueno, K. *Chem. Lett.* **1981**, 1305-1306. (f) Cram, D. J.; Lein, G. M.; Kaneda, T.; Helgeson, R. C.; Knobler, C. B.; Maverick, E.; Trueblood, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 6228-6232. (g) Cram, D. J.; Dicker, I. B.; Knobler, C. B.; Trueblood, K. N. *J. Am. Chem. Soc.* **1982**, *104*, 6828-6830.

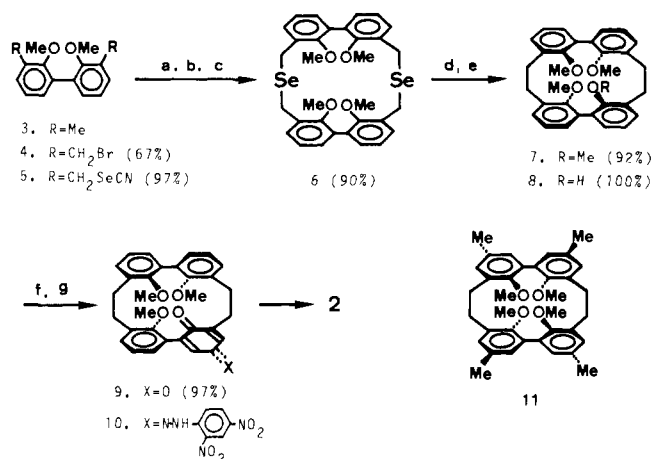


Figure 1. Synthetic scheme. (a) NBS, CCl₄; (b) KSeCN, acetone-benzene; (c) **4**, NaBH₄, THF-EtOH; (d) $h\nu$, (Me₂N)₃P, THF; (e) Li-AlH₄, benzene, reflux; (f) PbO₂, ether-HCOOH; (g) (2,4-dinitrophenyl)hydrazine, EtOH.

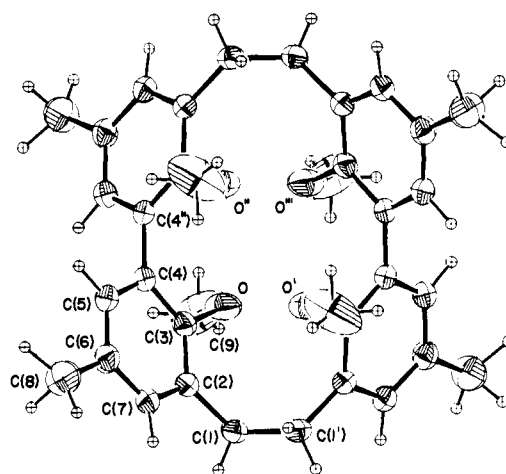


Figure 2. Molecular structure of compound **11** shown by the ORTEP drawing with the thermal ellipsoids at 30% probability level for non-hydrogen atoms and the spheres with radius of 0.1 Å for hydrogen atoms. Compound **11** has a strain-free structure with the dihedral angle of 89.9° between the benzene rings in the biphenyl moiety and the torsional angle of 86.2° around C(1)-C(1') bond.

that is, these crown dyes are active toward lithium and calcium salts.^{3b} In order to achieve a much higher level of lithium selectivity, spherand dye **2** has been designed by considering the fact that Cram's spherand⁵ can reject multivalent metal ions perfectly. We describe here the synthesis of **2**, its lithium ion-specific coloration, and the crystal structure of the relevant spherand **11**.

According to our improved method involving photodeselenation which was useful for preparing cyclophanes,⁶ [2.0.2.0]meta-cyclophane **7**⁷ was obtained via seven steps in 30% overall yield

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(6) Higuchi, H.; Kugimiya, M.; Otsubo, T.; Sakata, Y.; Misumi, S. *Tetrahedron Lett.* **1983**, *24*, 2593-2594.