Demetalation of Dicarbonyl(π-allyl)[hydridotris(pyrazolyl)borato]molybdenum Complexes via Lactonization

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Summary: Demetalation of dicarbonyl(π-allyl)[hydridotris(pyrazolyl)borato]molybdenum complexes can be achieved via lactonization. A carboxylic acid moiety is installed via addition of methyl phenylsulfonylacetate enolate to a diene−Mo(CO)$_2$Tp complex, followed by desulfonylation and hydrolysis, so that the subsequent lactonization can be effected by CO/NO$^+$ exchange or with iodine to give decomplexed products from cyclic and acyclic complexes.

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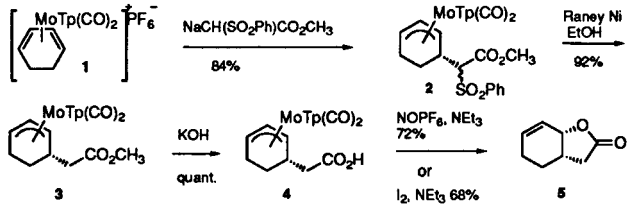
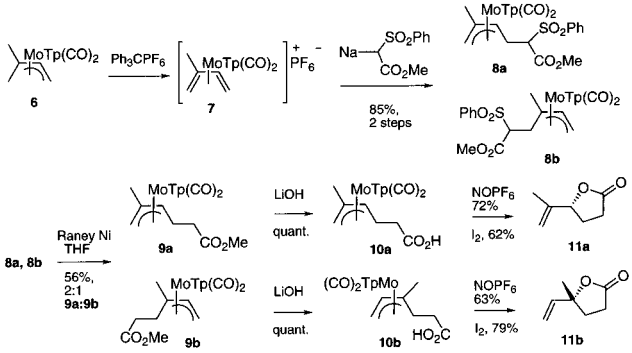
Asymmetric synthesis methods employing π-allylmetal complexes[1] have been developed utilizing organometallic complexes containing molybdenum, iron, cobalt, manganese, and other metal centers. Because the complexed face of the π-system is blocked by the metal, total facial stereocontrol can be achieved in nucleophilic additions and other reactions. Methodologies involving molybdenum complexes have been dominated by the use of the cyclopentadienyl (Cp) spectator ligand. More recently, the bulkier hydridotris(pyrazolyl)borato (Tp) ligand[2] has emerged as an alternative to Cp, exhibiting superior stability, ease of handling, and in some cases greater stereocontrol. Kirchner et al.[3] have reported that attempts to remove the metal from such complexes, by methods commonly employed on the corresponding Cp complexes, failed to work for Tp systems. On the other hand, Liebeskind and coworkers have reported demetalation of π-allyl−Mo(CO)$_2$Tp complexes via hydride reduction of the derived allyl−Mo(CO)(NO)Tp cations,[4] but this external nucleophilic addition process does not generally produce good regiocontrol. We have investigated this problem further, and now we report a convenient protocol for demetalation/lactonization of molybdenum Tp complexes that carry a pendant carboxylic acid group, opening the door to their utilization in synthesis.

A difficulty inherent in π-allyl−molybdenum chemistry is the inability to directly demetalate the complexes to obtain useful organic products. Generally, the decomplexation is accompanied by introduction of a nucleophilic group. An electrophile such as I$^+$ or NO$^+$ is needed first to activate the complex toward nucleophilic attack. In unsymmetrically substituted complexes, nucleophilic attack at the two possible termini of the π system can give mixtures of regioisomers. However, by incorporating an internal nucleophile such as a carboxylate, the regiochemistry of the attack is controlled and a single decomplexed lactone is obtained.

Scheme 1



Scheme 2



The four-step demetalation sequence originally developed in our laboratory for the analogous Mo(CO)$_2$Cp systems[5] has been successfully carried out for Tp complexes with both cyclic and acyclic substrates as shown in Schemes 1 and 2. The requisite carboxylic acid functionality is introduced via a sulfone ester which is then desulfonylated using Raney nickel, followed by hydrolysis of the resulting methyl ester. In the acyclic system, the nucleophilic addition produces two regioisomers due to the asymmetry of the diene substrate, which allows us to test the decomplexation procedure on quite different structures. A regiochemical preference for sulfone **8a** is observed (2:1 selectivity), whereas the Cp analogue gives mixtures of undetermined composition.[6] The sodium/mercury amalgam desulfonylation reported for the analogous Cp complex[5] proved ineffective for Tp complexes. Raney nickel gave a superior result, effecting the transformation from **2** to

(1) Pearson, A. J. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, E. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 12, Chapter 6.3.

(2) Liebeskind, L. S.; Ward, Y. D.; Villanueva, L. A.; Allred, G. D.; Payne, S. C.; Semones, M. A. *Organometallics* **1995**, *14*, 4132−4156.

(3) Kirchner, K.; Slugovc, C.; Mauthner, K.; Mereiter, K.; Schmidt, R. *Organometallics* **1996**, *15*, 2954−2960.

(4) Ward, Y. D.; Villanueva, L. A.; Allred, G. D.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1996**, *118*, 897−898 (see Supporting Information for details).

(5) Pearson, A. J.; Khan, M. N.; Clardy, J. C.; Cun-heng, H. *J. Am. Chem. Soc.* **1985**, *107*, 2748−2757.

(6) Pearson, A. J.; Holden, M. S.; Simpson, R. D. *Tetrahedron Lett.* **1986**, *27*, 4121−4124.

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3 in 92% yield, showing the excellent stability of the $Mo(CO)_2Tp$ moiety to these reaction conditions. It is also noteworthy that the easily separable acyclic complexes **9a** and **9b** exhibit greater stability and ease of handling than their Cp analogues.[7]

The carboxylic acid complexes **4**, **10a,** and **10b** can be demetalated by iodolactonization or alternatively by CO/NO^+ exchange[8] activated lactonization, both methods giving comparable yields. CO/NO^+ exchange is the most convenient method, producing an easily purified product in a 1 h reaction, whereas the product obtained from the 24 h iodine reaction is difficult to purify. However, the iodolactonization reaction is somewhat milder and may be more useful in the presence of sensitive functionality.

The greater stability of the Tp ligand relative to Cp is an asset in the handling of π-allyl$-Mo(CO)_2L$ complexes and requires only a slightly more laborious effort to remove the metal moiety. The introduction of a lactone moiety results in excellent regiocontrol in unsymmetrical complexes, and it can easily be opened and further manipulated. This work should prove useful to workers in this field who seek to apply these methodologies to organic synthesis.

Experimental Section

Solvents and reagents were distilled as follows: Tetrahydrofuran from sodium/benzophenone; dichloromethane, acetonitrile, and triethylamine from calcium hydride. All NMR spectral data were recorded on a 300 MHz spectrometer in $CDCl_3$ unless noted otherwise. Sodium hydride, nickel aluminum alloy, lithium hydroxide monohydrate, and nitrosonium hexafluorophosphate were purchased from Aldrich Chemical Co. Analytical thin-layer chromatography was performed on aluminum foil plates precoated with F254 silica gel 60 (Merck). Chromatography was carried out using flash silica gel 60 (Baker, 200−400 mesh) or alumina where noted (Fisher Scientific, Neutral Brockman Activity I, 60−325 mesh).

Cationic complex **7** was prepared and used immediately without purification due to its lability. It was not fully characterized, and its preparation is described as an intermediate toward the synthesis of complexes **8**. Regioisomeric sulfones **8a** and **8b** form an inseparable mixture and are not fully characterized but rather reduced as a mixture to give separable esters **9a** and **9b**.

Dicarbonyl[hydridotris(1-pyrazolyl)borato](η^4-isoprenyl)molybdenum Hexafluorophosphate (7). Triphenylmethyl hexafluorophosphate (2.543 g, 6.55 mmol) was added to a 0 °C solution of complex **6**[9] (1.788 g, 4.12 mmol) in CH_2Cl_2 (20 mL), and the mixture was stirred in the dark for 1 h or until the reaction was complete according to IR (appearance of peaks at 2035, 1950 cm^{-1}). The solution was concentrated to one-half its volume and injected into degassed ether at −78 °C. The precipitate was filtered off and dried in vacuo to give 3.17 g of brown solid. This crude product was immediately used without purification in the synthesis of **8** as described below. IR (KBr): 2500, 2035 (s), 1950 (s), 1500, 1415, 1310, 1230, 1140, 1062, 840 (s), 560 cm^{-1}.

General Sulfone Addition Procedure. The enolate was generated in dry THF by adding methyl phenylsulfonylacetate (Lancaster Synthesis) (1.00 mmol, 1.3 equiv) to a suspension of 60% sodium hydride (1.22 mmol, 1.6 equiv) in THF (20 mL). The appropriate cationic complex (for $[Mo(CO)_2Tp(\eta^4\text{-}C_6H_8)]^+PF_6^-$ **(1)** see Ipaktschi[10]) (0.774 mmol) was added to the flask with argon backflushing. The orange-brown solution was stirred at room temperature until the reaction was complete by TLC (1−2 h). The product was extracted into CH_2Cl_2, washed with water, and dried over $MgSO_4$. The crude racemic sulfones appeared as a single spot by TLC after purification by flash chromatography.

Dicarbonyl[hydridotris(1-pyrazolyl)borato](methyl (2−4-η-cyclohexenyl)phenylsulfonylacetate)molybdenum (2). The product was isolated as a yellow solid, mp 230−235 °C (dec), 1:3.4 (based on integration of the methyl ester signals) mixture of diastereomers (84%) after purification by flash chromatography (2:1 hexane/ethyl acetate). ^{1}H NMR: Major isomer (includes some minor peaks overlapping) δ 0.64−0.91 (2H, m), 1.91−1.96 (1H, m), 2.12−2.17 (1H, m), 2.98 (1H, bm), 3.52 (3H, s), 3.75 (1H, t, J = 7.0 Hz), 4.32 (1H, d, J = 9.9 Hz), 4.35 (1H, bs), 4.74 (1H, bt), 6.15 (1H, t, J = 2.1 Hz), 6.21 (1H, t, J = 2.1 Hz), 6.29 (1H, t, J = 2.3 Hz), 7.48−7.69 (6H, m), 7.71 (1H, d, J = 1.7 Hz), 7.87 (1H, d, J = 1.9 Hz), 7.98 (2H, dd, J = 1.5, 6.9 Hz), 8.56 (1H, d, J = 2.0 Hz); Distinquishable minor peaks: 1.68 (1H, bd), 2.79 (1H, bm), 3.69 (3H, s), 3.93 (1H, bd), 4.11−4.15 (1H, m), 6.11 (1H, t, J = 2.2 Hz), 7.94 (1H, d, J = 1.5 Hz), 8.55 (1H, d, J = 1.7 Hz). ^{13}C NMR: δ 19.2, 20.1, 22.4, 23.2, 29.6, 33.1, 33.7, 52.7, 67.0, 68.5, 68.7, 71.7, 72.9, 78.8, 100.0, 105.5, 112.8, 129.3, 134.3, 136.1, 137.7, 138.3, 141.7, 147.3, 166.7, 167.2, 191.6, 223.6, 226.0, 226.4. IR (KBr): 1940 (s), 1855 (s), 1742, 1453, 1413, 1308, 1230, 1130 cm^{-1}. HREIMS for calcd $C_{26}H_{27}O_6N_6BSMo$ M^+ 660.0860, found 660.0847.

Dicarbonyl[hydridotris(1-pyrazolyl)borato][4−6-η-(methyl 5-methyl-2-phenylsulfonyl-hex-4-enoate)]molybdenum (8a) and Dicarbonyl[hydridotris(1-pyrazolyl)-borato][4−6-η-(methyl 4-methyl-2-phenylsulfonylhex-4-enoate)]molybdenum (8b). A mixture of four isomers of sulfones **8** was obtained in 85% yield (from **6**, two steps) as an orange-yellow oil after purification by flash chromatography (3:1 hexane: ethyl acetate). The four inseparable isomers (two regioisomers, each having two diastereomers) were later reduced and isolated as two regioisomeric esters. NMR spectra for **8** are omitted here due to their complexity. The regioselectivity of the sulfone addition is determined through isolation and characterization of the subsequent methyl esters. IR (NaCl, neat): 2365, 2325, 1945, 1850, 1750, 1330, 1310, 1285, 1155, 1085, 1055 cm^{-1}. HREIMS calcd for $C_{25}H_{27}O_6N_6BSMo$ M^+ 648.0860, found 648.0887.

General Desulfonylation Procedure. Raney nickel[11] (approximately 4.5 g per mmol) was added to a solution of the sulfone, and the mixture was stirred at reflux for 2−17 h, until the reaction was complete by TLC. The solvent (EtOH or THF; see Schemes 1 and 2) was decanted and filtered through Celite. The nickel was repeatedly rinsed with CH_2Cl_2, and the combined filtrate was evaporated. Ester **3** needed no purification, while regioisomeric esters **9a** and **9b** were separated by flash chromatography (8:1 hexane:ethyl acetate).

Dicarbonyl[hydridotris(1-pyrazolyl)borato][methyl (2−4-η-cyclohexenyl acetate)] molybdenum (3). Yellow powder, mp 185 °C (92%). ^{1}H NMR: δ 0.65−0.71 (1H, m), 0.97 (1H, dd, J = 5.3, 15.0 Hz), 1.94 (1H, bm), 2.26−2.24 (1H, m), 2.48−2.67 (3H, m), 3.67 (1H, t, J = 7.1 Hz), 3.72 (3H, s), 4.23 (1H, d, J = 7.1 Hz), 4.33 (1H, bd, J = 3.6 Hz), 6.16 (2H, quar, J = 2.1 Hz), 6.29 (1H, t, J = 2.1 Hz), 7.50 (1H, d, J = 2.1 Hz), 7.57 (2H, d, J = 2.1 Hz), 7.74 (1H, d, J = 2.1 Hz), 7.76 (1H, d, J = 2.1 Hz), 8.60 (1H, d, J = 2.1 Hz). ^{13}C NMR: δ 20.0, 24.0, 30.7, 42.9, 51.6, 66.9, 71.9, 774.1, 105.3, 105.9, 134.3, 136.0, 141.5, 141.8, 147.3, 173.2, 226.6. IR (NaCl, neat): 1935 (s),

(7) Pearson, A. J.; Babu, M. K. M. *Organometallics* **1994**, *13*, 2539−2541.
(8) Liebeskind, L. S.; Villanueva, L. A.; Ward, Y. D.; Lachicotte, R. *Organometallics* **1996**, *15*, 4190−4200.
(9) Pearson, A. J.; Schoffers, E. *Organometallics* **1997**, *16*, 5365−5367.
(10) Ipaktschi, J.; Hartmann, A. *J. Organomet. Chem.* **1992**, *434*, 303−320.
(11) Pavlic, A. A., Adkins, H. *J. Am. Chem. Soc.* **1946**, *68*, 1471.

1845 (s), 1733, 1415, 1310, 1230, 1135, 1060, 770, 730 cm^{-1}. HREIMS calcd for $C_{20}H_{23}O_4N_6BMo$ M^+ 520.0928, found 520.0928.

Esters 9a and 9b: 56%, 2:1 ratio 9a: 9b. IR (KBr): 3055 (s), 2990 (s), 2305, 1425, 1275 (s), 1265 (s), 1260 (s), 900 cm^{-1}. HREIMS calcd for $C_{19}H_{23}O_4N_6BMo$ M^+ 508.0928, found 508.0935 for both isomers.

Dicarbonyl[hydridotris(1-pyrazolyl)borato][4−6-η-(methyl 5-methylhex-4-enoate)]molybdenum (9a): Yellow foam. ^{1}H NMR: δ 0.64−0.70 (1H, m), 1.50 (3H, s), 1.96 (1H, d, J = 2.1 Hz), 2.40−2.54 (3H, m), 3.47 (1H, t, J = 2.1 Hz), 3.72 (3H, s), 4.05 (1H, d, J = 10.9 Hz), 6.20 (1H, dd, J = 2.1, 5.3 Hz), 6.21 (1H, dd, J = 2.1), 6.23 (1H, t, J = 2.1 Hz), 7.44 (1H, d, J = 2.1 Hz), 7.59 (2H, d, J = 1.7 Hz), 7.88 (1H, d, J = 1.7 Hz), 7.94 (1H, d, J = 1.7 Hz), 8.45 (1H, d, J = 2.1 Hz). ^{13}C NMR: δ 20.4, 28.3, 29.6, 38.5, 51.4, 55.6, 72.5, 82.3, 105.2, 105.7, 134.1, 136.3, 142.5, 147.2, 173.6, 227.0, 228.0.

Dicarbonyl[hydridotris(1-pyrazolyl)borato][4−6-η-(methyl 4-methylhex-4-enoate)]molybdenum (9b): Orange solid. ^{1}H NMR: δ 0.86−1.07 (1H, m), 1.79 (1H, dd, J = 3.8, 9.9 Hz), 1.86 (3H, s), 2.24−2.45 (2H, m), 2.52−2.60 (1H, m), 3.52 (1H, dd, J = 3.8, 7.1 Hz), 3.67 (3H, s), 3.84 (1H, dd, J = 7.1, 9.9 Hz), 6.18 (3H, t, J = 1.9 Hz), 7.52 (3H, bs), 7.75 (3H, b). ^{13}C NMR: δ 14.0, 25.2, 29.6, 33.4, 36.3, 47.2, 51.6, 82.0, 98.8, 105.4, 135.6, 146.6, 173.3, 229.9, 233.5.

Dicarbonyl[hydridotris(1-pyrazolyl)borato](2−4-η-cyclohex-2-enylacetic acid)molybdenum (4). Potassium hydroxide (199 mg, 3.55 mmol, 54 equiv) in water (1 mL) was added to complex **3** (34 mg, 0.066 mmol) in 8:1 MeOH:THF (4.5 mL). The mixture was stirred for 6 h at room temperature, at which time TLC showed completion (1:1 hexane/ethyl acetate, R_f = 0.15). The mixture was acidified with 10% HCl, extracted into ether, dried over sodium sulfate, and evaporated to give a quantitative yield of yellow solid **4**, mp 181−183 °C (dec). ^{1}H NMR: δ 0.71 (1H, m), 1.03 (1H, dd, J = 5.6 Hz, 14.3), 1.26 (1H, s), 1.95 (1H, m), 2.27 (1H, m), 2.53−2.73 (2H, m), 3.69 (1H, t, J = 7.2 Hz), 4.26 (1H, bd, J = 7.2 Hz), 4.35 (1H, bd), 6.17 (2H, t, J = 2.1 Hz), 6.30 (1H, t, J = 2.1 Hz), 7.51 (1H, d, J = 2.1 Hz), 7.57 (2H, d, J = 2.1 Hz), 7.74 (1H, d, J = 1.9), 7.76 (1H, d, J = 1.9), 8.60 (1H, d, J = 1.9 Hz). ^{13}C NMR: δ 19.8, 23.8, 30.3, 42.7, 66.8, 71.9, 73.8, 105.2, 105.9, 134.3, 136.0, 141.5, 141.9, 147.3, 178.2, 226.5, 226.7. IR (KBr): 2950, 2490, 1930 (s), 1840 (s), 1705, 1405, 1310, 1225, 1125, 1050, 765, 725 cm^{-1}. HREIMS calcd for $C_{19}H_{21}O_4N_6BMo$ M^+ 506.0771, found 506.0763.

General Hydrolysis Procedure for Preparation of Acids 10. An aqueous solution of LiOH monohydrate (4 equiv) was added to a solution of ester (0.327 mmol) in methanol (30 mL). The mixture was stirred 18 h at room temperature. The product was neutralized with 10% HCl until heterogeneous, extracted into CH_2Cl_2, dried over sodium sulfate, and evaporated to give quantitaitve yields of the acid in pure form.

Dicarbonyl[hydridotris(1-pyrazolyl)borato](4−6-η-5-methylhex-4-enoic acid)molybdenum (10a): Yellow foam. ^{1}H NMR: δ 0.67−0.61 (1H, m), 1.49 (3H, s), 1.96 (1H, s), 2.55−2.40 (3H, m), 3.46 (1H, s), 4.06 (1H, d, J = 10.9 Hz), 6.17 (2H, q, J = 2.2 Hz), 6.20 (1H, t, J = 2.2 Hz), 7.41 (1H, d, J = 2.1 Hz), 7.56 (2H, d, J = 2.1 Hz), 7.88 (1H, d, J = 2.1 Hz), 7.92 (1H, d, J = 2.1 Hz), 8.42 (1H, d, J = 2.1 Hz). ^{13}C NMR: δ 20.4, 28.0, 38.5, 55.7, 72.3, 82.3, 105.2, 105.7, 124.2, 134.2, 136.3, 142.5, 142.6, 147.2, 179.1, 227.0, 228.0. IR (NaCl, neat): 2360, 2160, 1942 (s), 1854 (s), 1722, 1515, 1415, 1310, 1060 cm^{-1}. HREIMS calcd for $C_{18}H_{21}O_4N_6BMo$ M^+ 494.0771, found 494.0762.

Dicarbonyl[hydridotris(1-pyrazolyl)borato](4−6-η-4-methylhex-4-enoic acid)molybdenum (10b): Orange powder. ^{1}H NMR: δ 1.08 (1H, ddd, J = 6.4, 9.3, 13.4 Hz), 1.85 (1H, dd, J = 3.8, 10.0 Hz), 1.90 (3H, s), 2.29−2.52 (2H, m), 2.59−2.70 (1H, m), 3.57 (1H, dd, J = 3.8, 7.2 Hz), 3.88 (1H, dd, J = 7.2, 10.0 Hz), 6.13 (3H, t, J = 2.1 Hz), 7.48 (3H, bs), 7.80 (3H, bs). ^{13}C NMR: δ 25.2, 33.0, 36.2, 47.4, 82.0, 98.3, 105.4, 135.2, 145.9, 179.4, 229.8, 233.5. IR (KBr): 2490, 1920, 1835, 1415, 1310, 1225, 1125, 1055, 765, 730 cm^{-1}. HREIMS calcd for $C_{18}H_{21}O_4N_6BMo$ M^+ 494.0771, found 494.0767.

General CO−NO Exchange Lactonization Procedure. $NOPF_6$ (0.51 mmol, 1.5 equiv) was added to a solution of acid (0.347 mmol) in dry CH_3CN (10 mL) at 0 °C, and the mixture was stirred under argon at 0 °C for 10 min. A color change from yellow to green to brown was observed. Freshly distilled triethylamine (0.52 mmol, 1.5 equiv) was injected, and the mixture was stirred for 30−60 min. The product was worked up by extraction into CH_2Cl_2, washed with water, 10% HCl, and brine, and dried over sodium sulfate. The crude brown oil was purified by column chromatography through a 4-cm plug of alumina atop a column of silica, 3:1 hexane:ethyl acetate. The lactones are colorless oils that are UV-inactive on TLC but observable by permanganate staining.

***cis*-3a,4,5,7a-Tetrahydro-3-*H*-benzofuran-2-one (5):** 72% yield. ^{1}H NMR: δ 1.44−1.55 (1H, m), 1.76 (1H, dq, J = 4.7, 13.6 Hz), 1.99−2.08 (1H, m), 2.17 (1H, dq, J = 4.7, 20.3 Hz), 2.34 (1H, dd, J = 3.7, 17.0 Hz), 2.54−2.64 (1H, m), 2.72 (1H, dd, J = 8.1, 17.0 Hz), 4.81 (1H, bt), 5.88 (dq, 1H, J = 1.9, 10.1 Hz), 6.13 (1H, m). ^{13}C NMR: δ 22.4, 23.3, 33.3, 34.9, 75.4, 123.1, 134.1, 176.7. IR (NaCl, neat): 1773, 1180, 940 cm^{-1}. HREIMS calcd for $C_8H_{10}O_2$ M^+ 138.0681, found 138.0680. These data are consistent with and more thorough than that previously reported.[4]

1-Propenylbutano-4-lactone (11a): 72% yield. ^{1}H NMR: δ 1.77 (3H, s), 2.04 (1H, dddd, J = 7.4, 9.3, 9.3, 12.1 Hz), 2.37 (1H, dt, J = 7.4, 19.8 Hz), 2.56 (2H, m), 4.89 (1H, t, J = 7.4 Hz), 4.95 (1H, s), 5.06 (1H, s). ^{13}C NMR: δ 17.6, 27.0, 28.5, 82.6, 112.4, 142.1, 171.1. IR (NaCl, neat): 1770, 1480, 1380, 1190, 1100 cm^{-1}. HREIMS calcd for $C_7H_{10}O_2$ M^+ 126.0681, found 126.0683.

1-Methyl-1-ethenylbutano-4-lactone (11b): 63% yield. ^{1}H NMR: δ 1.45 (3H, s), 2.00−2.19 (2H, m), 2.47−2.52 (2H, m), 5.08 (1H, d, J = 10.8 Hz), 5.23 (1H, d, J = 17.2 Hz), 5.84 (1H, dd, J = 10.8, 17.2 Hz). ^{13}C NMR: δ 26.3, 28.7, 33.8, 85.4, 113.7, 140.0, 176.7. IR (NaCl, neat): 2370, 2345, 1785, 1265 cm^{-1}. HREIMS calcd for $C_7H_{10}O_2$ M^+ 126.0681, found 126.0681.

General Iodolactonization Procedure. Iodine (0.395 mmol, 4 equiv) and NEt_3 (359 mmol, 1 equiv) were added to a solution of acid in dry CH_3CN (10 mL) at room temperature, and the mixture was stirred in the dark for 24 h. Slow evolution of gas was observed. The reaction mixture was extracted into CH_2Cl_2, washed with aqueous thiosulfate and 10% HCl, and dried over sodium sulfate. Crude lactone was purified twice on silica, 3:1 hexane:ethyl acetate to give slightly impure lactone. ^{1}H NMR shows only minor impurities, but the oils are colored.

***cis*-3a,4,5,7a-Tetrahydro-3-*H*-benzofuran-2-one (5):** 68% yield.

1-Propenylbutano-4-lactone (11a): 62% yield.

1-Methyl-1-ethenylbutano-4-lactone (11b): 79% yield.

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