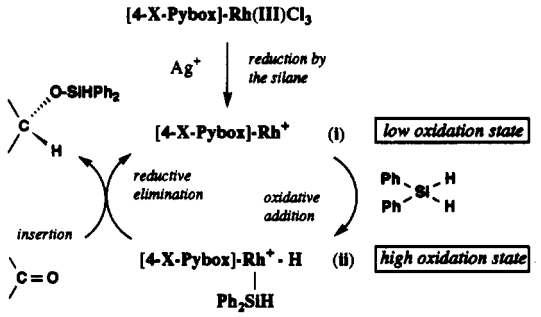
Scheme III



(10 mL) was added an aqueous solution of dimethylamine (50 wt %, 30 mL). The mixture was stirred for 3 days at 40 °C. The workup and purification were similar to those for **5** as described above to give **6** as a white solid in 61% (210 mg, 0.61 mmol) yield: TLC R_f = 0.2 (ethyl acetate); mp 81–82 °C; $[\alpha]^{24}_D$ = −42.5° (CH_2Cl_2, c = 0.52); IR (KBr disk) 1595, 1418, 1350, 1180 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.94 (d, J = 6.6 Hz, 6 H), 1.06 (d, J = 6.6 Hz, 6 H), 1.86 (m, 2 H), 3.11 (s, 6 H), 4.14 (m, 2 H), 4.19 (t, J = 8.3, 8.3 Hz, 2 H), 4.49 (dd, J = 8.3, 9.3 Hz, 2 H), 7.37 (s, 2 H); ^{13}C NMR (67.8 MHz, $CDCl_3$) 18.26, 19.18, 32.85, 39.48, 70.69, 72.79, 108.0, 147.0, 155.0, 163.3. Anal. Calcd for $C_{19}H_{28}N_4O_2(H_2O)$: C, 62.95; H, 8.34; N, 15.46. Found: C, 62.53; H, 8.35; N, 15.79.

(4-Chloro-pybox)$RhCl_3$ (8). A solution of $RhCl_3/(H_2O)_3$ (263 mg, 1.0 mmol) and 4-chloro-pybox (**4**) (336 mg, 1.0 mmol) in ethanol (8.0 mL) was heated at reflux for 2 h. After the solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography with ethyl acetate–methanol as eluents to give **8** as an orange solid in 63% (346 mg, 0.63 mmol) yield: mp 207–208 °C dec; $[\alpha]^{25}_D$ = +551° (CH_2Cl_2, c = 0.54); IR (KBr disk) 1575, 1480, 1375, 1248, 1064, 960, 910 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.99 (d, J = 6.8 Hz, 6 H), 1.00 (d, J = 6.8 Hz, 6 H), 3.05 (m, 2 H), 4.66 (m, 2 H), 4.96 (dd, J = 7.8, 9.3 Hz, 2 H), 5.03 (dd, J = 9.3, 10.3 Hz, 2 H), 7.98 (s, 2 H); ^{13}C NMR (67.8 MHz, $CDCl_3$) 15.09, 19.49, 28.45, 68.87, 73.54, 126.8, 147.7, 148.7, 165.5. Anal. Calcd for $C_{17}H_{22}N_3O_2RhCl_4(0.5H_2O)$: C, 36.85; H, 4.18; N, 7.58. Found: C, 36.41; H, 4.06; N, 7.52.

(4-Methoxy-pybox)$RhCl_3$ (9). $RhCl_3/(H_2O)_3$ (263 mg, 1.0 mmol), 4-methoxy-pybox (**5**) (332 mg, 1.0 mmol), and ethanol (5.0 mL) were refluxed for 3 h. **9** was obtained as an orange solid in 71% yield (383 mg, 0.71 mmol): mp 210–211 °C dec; $[\alpha]^{25}_D$ = +468.7° (CH_2Cl_2, c = 0.53); IR (KBr disk) 1580, 1490, 1465, 1380, 1240, 1120, 1080 cm^{-1}; 1H NMR (270 MHz, $CDCl_3$) δ 0.98 (d, J = 6.8 Hz, 6 H), 1.00 (d, J = 6.8 Hz, 6 H), 3.06 (m, 2 H), 4.10 (s, 3 H), 4.64 (m, 2 H), 4.86–5.05 (m, 4 H), 7.47 (s, 2 H); ^{13}C NMR (67.8 Hz, $CDCl_3$) 15.06, 19.49, 28.36, 57.61, 68.67, 73.13, 113.0, 147.5, 166.0, 169.2. Anal. Calcd for $C_{18}C_{25}N_3O_3RhCl_3(0.5CH_2Cl_2)$: C, 38.10; H, 4.49. Found: C, 38.29; H, 4.55.

(4-(Dimethylamino)-pybox)$RhCl_3$ (10). $RhCl_3/(H_2O)_3$ (263 mg, 1.0 mmol), 4-(dimethylamino)-pybox (**6**) (334 mg, 1.0 mmol), and ethanol (6.0 mL) were refluxed for 1 h. **10** was obtained as an orange solid in 72% yield (396 mg, 0.72 mmol): mp >300 °C; $[\alpha]^{25}_D$ = +447.6° (CH_2Cl_2, c = 0.53); IR (KBr disk) 1580, 1530, 1420, 1380, 1240, 1080 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.96 (d, J = 6.8 Hz, 6 H), 1.00 (d, J = 6.8 Hz, 6 H), 3.05 (m, 2 H), 3.27 (s, 6 H), 4.61 (m, 2 H), 4.87 (dd, J = 8.8, 9.8 Hz, 2 H), 4.90 (dd, J = 8.8, 13.2 Hz, 2 H), 7.06 (s, 2 H); ^{13}C NMR (67.8 MHz, $CDCl_3$) 15.06, 19.49, 28.25, 40.57, 68.44, 72.67, 108.4, 145.2, 156.1, 166.5. Anal. Calcd for $C_{19}H_{28}N_4O_2RhCl_3$: C, 41.21; H, 5.10; N, 10.12. Found: C, 41.18; H, 5.05; N, 10.23.

Typical Procedure for Asymmetric Hydrosilylation: Reduction of Acetophenone with (4-Chloro-pybox)$RhCl_3$ (8) and Diphenylsilane. A suspension of **8** (43.6 mg, 0.08 mmol) and $AgBF_4$ (31 mg, 0.16 mmol) in THF (1.0 mL) was stirred at rt for 1 h. After addition of acetophenone (0.93 mL, 8.0 mmol), diphenylsilane (2.36 g, 12.8 mmol) was added at −5 °C. The mixture was stirred for 3 h and treated with methanol and then hydrochloric acid (1.0 N) at 0 °C. The product yield was determined by GLPC analysis. After Kugelrohr distillation of the product, the enantioselectivity was determined by the optical rotation and by ^1H NMR spectroscopy of the MTPA ester. See ref 2 for the values of optical rotation.

Ring Expansion of *tert*-Butyl 1-Vinylcyclopropane-1-carboxylates to α-Ethylidenebutyrolactones

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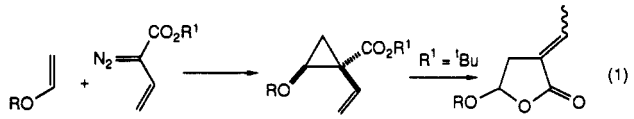
Significant advances have been made recently in the development of synthetic transformations based on cyclopropane ring-expansion reactions.[1,2] Cyclopropanes which contain both donor and acceptor functionalities are particularly effective in this regard because they react under mild conditions.[1,3] Several methods are available for the synthesis of donor–acceptor-substituted cyclopropanes but the most general approach has been cyclopropanation of electron-rich alkenes by metal-stabilized carbenoids.[1,4] Over the last few years we have shown that rhodium(II)-stabilized vinylcarbenoids are useful for the stereoselective synthesis of seven-membered carbocycles.[5] Furthermore, their reaction with electron-rich alkenes leads to an intriguing class of donor–acceptor substituted cyclopropanes **1**.[6] In principle, competing rearrangements are possible for **1** involving either the vinyl or the carbonyl group. In this paper we describe the rearrangements of the *tert*-butyl esters of **1**, which lead to the formation of α-ethylidenebutyrolactones **2** as illustrated in eq 1.[7]



(1)

1 **2**

The thermolysis of the methyl ester **3** at 230 °C resulted in the expected vinylcyclopropane rearrangement to generate the cyclopentene **4** in low yield (20%). Due to the presence of the donor–acceptor functionality in **3**, the reaction occurred under less vigorous conditions than are typically required.[8] The reaction could be carried out

(1) (a) Reissig, H.-U. *Top. Curr. Chem.* **1988**, *144*, 73. (b) Reissig, H.-U. *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: New York, 1987; Part 1, p 375. (c) Vehre, R.; De Kimpe, N. *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley, New York, 1987; Part 1, p 445. (d) Wong, H. N. C.; Hon, M.-Y.; Tse, C. W.; Yip, Y.-C.; Tanko, J.; Hudlicky, T. *Chem. Rev.* **1989**, *89*, 165. (e) Hudlicky, T.; Reed, J. W. *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: Oxford, 1991; Vol. 5, p 899.

(2) Hudlicky, T.; Fleming, A.; Radesca, L. *J. Am. Chem. Soc.* **1989**, *111*, 6691 and references cited therein.

(3) (a) Murray, C. K.; Yang, D. C.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 5660. (b) Wienand, A.; Reissig, H.-U. *Chem. Ber.* **1991**, *124*, 957.

(4) (a) Maas, G. *Top. Curr. Chem.* **1988**, *137*, 75. (b) Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919. (c) Kunz, T.; Reissig, H.-U. *Tetrahedron Lett.* **1989**, *30*, 2079.

(5) (a) Davies, H. M. L.; Clark, T. J.; Smith, H. D. *J. Org. Chem.* **1991**, *56*, 3817. (b) Cantrell, W. R.; Davies, H. M. L. *J. Org. Chem.* **1991**, *56*, 723. (c) Davies, H. M. L.; McAfee, M. J.; Oldenburg, C. E. M. *J. Org. Chem.* **1989**, *54*, 930.

(6) (a) Davies, H. M. L.; Clark, T. J.; Church, L. A. *Tetrahedron Lett.* **1989**, *30*, 5057. (b) Davies, H. M. L.; Hu, B. *Tetrahedron Lett.* **1992**, *33*, 453. (c) Davies, H. M. L.; Hu, B. *J. Org. Chem.* **1992**, *57*, 3186.

(7) For related examples of ring expansion of cyclopropanes to butyrolactones, see: (a) Wenkert, E. *Acc. Chem. Res.* **1980**, *13*, 27. (b) Wenkert, E.; Halls, D. J.; Kwart, L. D.; Magnusson, G.; Showalter, H. D. H. *Tetrahedron* **1981**, *37*, 4017. (c) Wenkert, E.; Alonso, M. E.; Buckwalter, B. L.; Chou, K. J. *J. Am. Chem. Soc.* **1977**, *99*, 4778. (d) Wenkert, E.; Hudlicky, T.; Showalter, H. *J. Am. Chem. Soc.* **1978**, *100*, 4893. (e) Brown, S. P.; Bal, B. S.; Pinnick, H. W. *Tetrahedron Lett.* **1981**, *22*, 4891. (f) Morizawa, Y.; Hiyama, T.; Oshima, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1123.

(8) (a) Goldschmidt, Z.; Cramer, B. *Chem. Soc. Rev.* **1988**, *17*, 229. (b) Hudlicky, T.; Kutchan, T. M.; Naqvi, S. M. *Org. React.* **1985**, *33*, 247.

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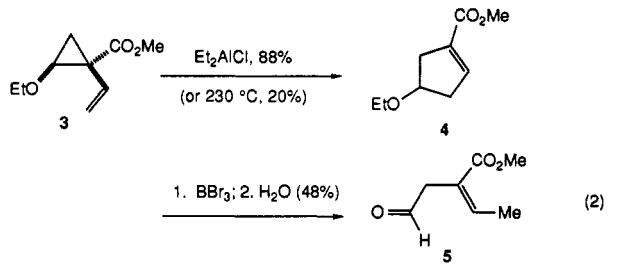
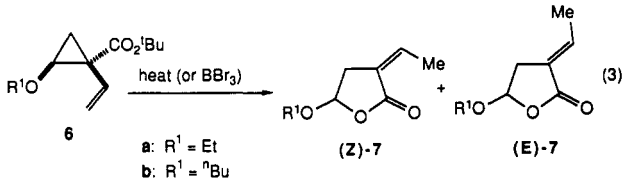
under very mild conditions if diethylaluminum chloride was used as a Lewis acid catalyst (88% yield), and this approach has been used by us as part of a general process for the regioselective construction of cyclopentenes.[6b,c] Alternatively, rearrangement of **3** could be induced by boron tribromide, but in this case, the ring-opened product **5**[9,10] was produced after quenching the reaction mixture with water (48% yield).



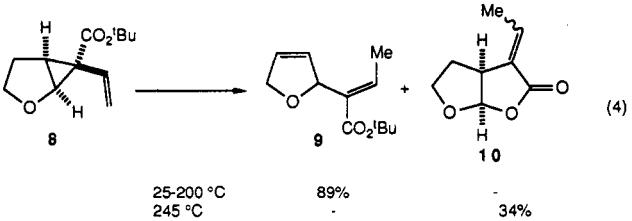
(2)

Decomposition of the corresponding *tert*-butyl ester **6a** proceeded in a different manner. Thermolysis of **6a** at 230 °C resulted in the formation of a mixture of α-ethylidenebutyrolactones (*Z*)-**7a** and (*E*)-**7a** (79% yield).[10] A similar ring-opening reaction was observed for **6b**. The transformations of **6** to (*E*)-**7** could also be carried out with boron tribromide at −78 °C (56–72% yield), and under these conditions the isomeric butyrolactones (*Z*)-**7** were not observed.



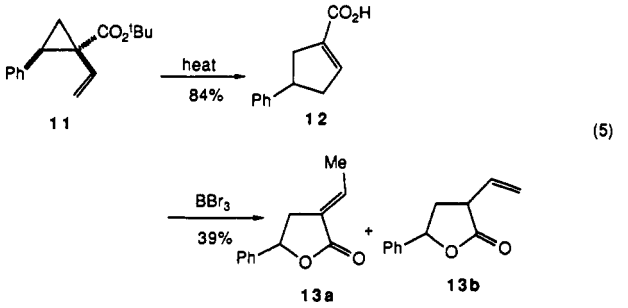
(3)

The thermolysis of the bicyclic system **8** resulted in an additional rearrangement pathway. On gradual heating to 200 °C, **9**, the product of a 1,5-homodienyl rearrangement, was obtained in 89% yield. On rapid heating to 245 °C, however, the product was the fused butyrolactone **10** (36% yield).[10] It is well recognized that 1,5-homodienyl rearrangements can be reversible under high temperatures,[2,8,11] and this may explain why a change in product distribution was observed here. This was confirmed by heating **9** at 245 °C which led to the formation of an *E*/*Z* mixture of **10**. Selective formation of the butyrolactone **10** was also achieved by treatment of **8** with boron tribromide.



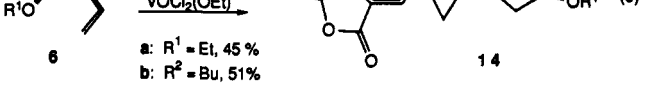
(4)

The requirement of a strong donor for the facile formation of the butyrolactones was readily apparent from the reaction of the phenyl derivative **11**. Thermolysis of **11** at 230 °C generated the cyclopentenecarboxylic acid **12** (84% yield), while boron tribromide catalyzed decomposition of **11** at room temperature resulted in the slow formation of a 1:1 mixture of butyrolactones **13a**[10] and **13b** in low yield (39%).



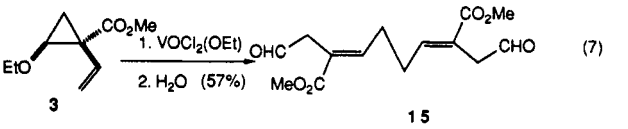
(5)

A number of recent reports have appeared on the use of $VOCl_2(OEt)$ as an oxidant and a Lewis acid which is also capable of inducing ring-opening reactions of cyclobutanones.[12] Treatment of the cyclopropanecarboxylate **6a** with $VOCl_2(OEt)$ at 0 °C resulted in α-ethylidenebutyrolactone formation but in this case the product was the dimer **14a** (45% yield). A similar transformation was observed with **6b**.

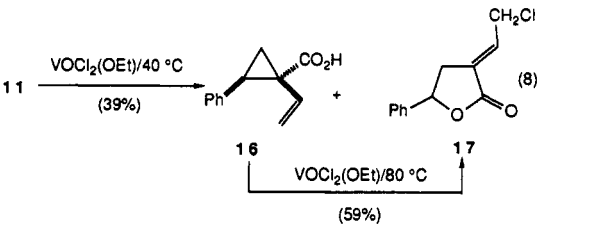


(6)

The reaction of the methyl cyclopropanecarboxylate **3** with $VOCl_2(OEt)$ once again reflected the reluctance of this system to form butyrolactone products (eq 7). The dimeric product **15** was readily formed (57% yield) in which the methyl ester functionality remained intact. As expected, the reaction of the 2-phenyl derivative **11** with $VOCl_2(OEt)$ was much slower than the 2-alkoxy systems. On heating under reflux in CH_2Cl_2 for 30 h, the main product formed was the cyclopropanecarboxylic acid **16** (eq 8). Under forcing conditions, **16** could be made to undergo ring expansion to a butyrolactone but the product in this case was the chlorinated α-ethylidenebutyrolactone **17**[10] rather than a dimeric compound.



(7)



(8)

The rearrangement chemistry of the cyclopropane carboxylates is highly dependent on the ester functionality. With the methyl ester derivative **3**, ring opening or vinylcyclopropane rearrangement was observed in which the methyl ester remained intact. Butyrolactone formation was dominant in the *tert*-butyl series, and as this group is labile under both thermal and Lewis acid conditions, it is reasonable to assume that the reaction proceeded via

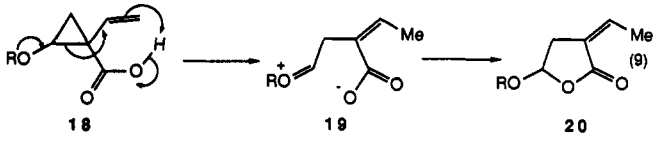
(9) Herrmann, J. L.; Kieczykowski, G. R. *Tetrahedron Lett.* **1973**, *47*, 4711.

(10) The alkene geometry was readily assigned based on distinctive chemical shifts. See: (a) Ohga, K.; Matsuo, T. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2181. (b) Murray, A. W.; Reid, R. G. *Synthesis* **1985**, 35.

(11) Hudlicky, T.; Koszyk, F. J. *Tetrahedron Lett.* **1980**, *21*, 2487.

(12) (a) Hirao, T.; Mori, M.; Ohshiro, Y. *Chem. Lett.* **1991**, 783. (b) Hirao, T.; Mori, M.; Ohshiro, Y. *J. Org. Chem.* **1990**, *55*, 358. (c) Hirao, T.; Ohshiro, Y. *Tetrahedron Lett.* **1990**, *31*, 3917. (d) Hirao, T.; Fujii, T.; Ohshiro, Y. *J. Organomet. Chem.* **1991**, *407*, C1.

the carboxylic acid **18**. Then, the divergence in reactivity between the methyl ester **3** and the carboxylic acid **18** can be rationalized by considering that the rearrangement of **18** proceeded by proton transfer induced ring opening to **19** followed by ring closure to the butyrolactone **20** (eq 9). Equilibration of the initially formed (*Z*)-**20** to the *E* isomer would be expected to occur under both the thermal and Lewis acid catalyzed reaction conditions.



18 **19** **20**

In summary, *tert*-butyl 2-alkoxy-1-vinylcyclopropane-1-carboxylates undergo thermal ring opening to form α-ethylidenebutyrolactones. The reaction may be catalyzed by boron tribromide while the oxidant $VOCl_2(OEt)$ results in the formation of dimeric products. These transformations are further examples of the diverse reactivity that is possible with donor–acceptor substituted cyclopropanes.

Experimental Section

General. ^1H and ^{13}C NMR spectra were recorded at 200 and 50.3 MHz, respectively. Mass spectral determinations were carried out at 70 eV. CH_2Cl_2 was freshly distilled from CaH_2. Column chromatography was carried out on silica gel 60 (230–400 mesh). Dimethylethyl 2-diazobut-3-enoate was prepared by a published procedure.[13]

Rhodium(II) Carboxylate Catalyzed Decomposition of Dimethylethyl 2-Diazobut-3-enoate in the Presence of Vinyl Ethers. General Procedure. A solution of dimethylethyl 2-diazobut-3-enoate (1 equiv) in pentane (0.1–0.5 M) was added dropwise to a stirred mixture of rhodium(II) carboxylate (0.01 equiv) and the vinyl ether (5 equiv, 0.1–0.5 M) in pentane, heated under reflux in an argon atmosphere. After the solution was heated for a further 10–60 min, the solvent was evaporated under reduced pressure. The amounts of dimethylethyl 2-diazobut-3-enoate, vinyl ether, and rhodium(II) catalyst used are presented in that order in abbreviated format. All products were purified by column chromatography on silica using ether–petroleum ether as eluant in the ratio specified in parenthesis.

1,1-Dimethylethyl 2-Ethoxy-1-vinylcyclopropanecarboxylate (6a): (0.62 g, 3.7 mmol), ethyl vinyl ether (1.32 g, 18.3 mmol), pivalate (0.020 g, 0.037 mmol) (1:19); yield 0.67 g (86%); IR (neat) 1710, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.29 (dd, *J* = 17.3, 11.1 Hz, 1 H), 5.08 (d, *J* = 11.1 Hz, 1 H), 5.05 (d, *J* = 17.3 Hz, 1 H), 3.62 (dd, *J* = 6.9, 4.7 Hz, 1 H), 3.49 (dq, *J* = 9.3, 7.1 Hz, 1 H), 3.36 (dq, *J* = 9.3, 7.1 Hz, 1 H), 1.63 (dd, *J* = 6.9, 6.1 Hz, 1 H), 1.43 (s, 9 H), 1.40 (dd, *J* = 6.1, 4.7 Hz, 1 H), 1.13 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 171.5, 130.2, 114.5, 80.7, 66.9, 66.7, 32.7, 28.1, 20.0, 14.8. Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.93; H, 9.52.

1,1-Dimethylethyl 2-Butoxy-1-vinylcyclopropanecarboxylate (6b): (0.67 g, 4.0 mmol), butyl vinyl ether (2.00 g, 20 mmol), pivalate (0.018 g, 0.03 mmol) (1:24); yield 0.95 g (98%); IR (neat) 1705, 1635 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.26 (dd, *J* = 17.6, 10.7 Hz, 1 H), 5.06 (d, *J* = 10.7 Hz, 1 H), 5.04 (d, *J* = 17.6 Hz, 1 H), 3.57 (dd, *J* = 6.8, 4.9 Hz, 1 H), 3.48–3.25 (m, 2 H), 1.61 (dd, *J* = 6.8, 6.1 Hz, 1 H), 1.55–1.20 (m, 5 H), 1.42 (s, 9 H), 0.85 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 171.5, 130.1, 114.6, 80.7, 71.3, 66.9, 32.8, 31.5, 28.1, 20.0, 19.3, 13.8. Anal. Calcd for $C_{14}H_{24}O_3$: C, 69.96; H, 10.06. Found: C, 69.72; H, 10.11.

1,2-Dimethylethyl 6-Vinyl-3-oxabicyclo[3.1.0]hexane-6-carboxylate (8): (0.67 g, 4.0 mmol), dihydrofuran (1.40 g, 20 mmol), pivalate (0.0105 g, 0.018 mmol) (1:9); yield 0.62 g (74%); IR (neat) 1695, 1625 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.70 (dd, *J* = 18.3, 9.8 Hz, 1 H), 5.44 (dd, *J* = 9.8, 2.2 Hz, 1 H), 5.37 (dd, *J* = 18.3, 2.2 Hz, 1 H), 4.22 (d, *J* = 5.6 Hz, 1 H), 4.06 (ddd, *J* = 15.9, 8.7, 5.5 Hz, 1 H), 3.62 (ddd, *J* = 15.9, 6.9, 6.9 Hz, 1 H), 2.35 (dd, *J* = 6.0, 5.6 Hz, 1 H), 2.21 (m, 1 H), 1.91 (ddd, *J* = 13.0, 8.7, 5.3 Hz, 1 H), 1.39 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 167.0, 128.5, 122.3, 80.7, 72.1, 69.7, 36.6, 31.6, 26.0, 25.5. Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.55; H, 8.63. Found: C, 68.45; H, 8.63.

1,1-Dimethylethyl 2-Phenyl-1-vinylcyclopropanecarboxylate (11): (0.51 g, 3.0 mmol), styrene (1.56 g, 15 mmol), pivalate (0.018 g, 0.03 mmol) (1:49); yield 0.58 g (79%); IR (neat) 1705, 1635, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.31–7.09 (m, 5 H), 5.76 (dd, *J* = 17.0, 9.9 Hz, 1 H), 4.97 (d, *J* = 9.9 Hz, 1 H), 4.90 (d, *J* = 17.0, 1 H), 2.90 (dd, *J* = 9.4, 7.0 Hz, 1 H), 1.82 (dd, *J* = 9.4, 5.0 Hz, 1 H), 1.64 (dd, *J* = 7.0, 5.0 Hz, 1 H), 1.49 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 172.4, 135.8, 132.1, 129.3, 127.8, 126.5, 116.6, 80.8, 34.5, 34.2, 28.1, 16.7. Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.79; H, 8.24.

General Procedure for the Thermolysis of Cyclopropanecarboxylates. The cyclopropanecarboxylate was sealed under Ar in a heavy-walled Pyrex tube which had been previously treated with concd NH_4OH. The sealed tube was placed in an oil bath at a specific temperature and time. The amounts of cyclopropanecarboxylate, temperature, and time of heating are presented in that order in abbreviated format. All products were purified by column chromatography on silica using ether–petroleum ether as eluant in the ratio specified in parentheses.

5-Ethoxy-3-ethylidene-2-oxo-4,5-dihydrofuran (7a): **6a** (0.39 g, 1.8 mmol), 230 °C, 35 min (1:1); yield 0.22 g (79%); *Z*/*E* ratio = 1/6; IR (neat) 1755, 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ (*E*)-**7a** 6.85–6.73 (m, 1 H), 5.54 (dd, *J* = 6.3, 2.4 Hz, 1 H), 3.89 (dq, *J* = 9.5, 7.1 Hz, 1 H), 3.61 (dq, *J* = 9.5, 7.1 Hz, 1 H), 2.96 (br d, *J* = 17.2 Hz, 1 H), 2.68 (br d, *J* = 17.2 Hz, 1 H), 1.83 (dt, *J* = 7.1, 2.0 Hz, 3 H), 1.16 (t, *J* = 7.1 Hz, 3 H); (*Z*)-**7a** (6.34–6.22 (m, 1 H), 5.44 (dd, *J* = 6.3, 2.4 Hz, 1 H), 3.87 (dq, *J* = 9.5, 7.1 Hz, 1 H), 3.58 (dq, *J* = 9.5, 7.1 Hz, 1 H), 3.04 (br d, *J* = 16.8 Hz, 1 H), 2.68 (br d, *J* = 16.8 Hz, 1 H), 2.15 (dt, *J* = 7.3, 2.3 Hz, 3 H), 1.20 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ (*E*)-**7a** 169.6, 136.4, 125.8, 101.1, 65.1, 32.6, 15.7, 14.9. Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.74. Found: C, 61.77; H, 7.82.

5-Butoxy-3-ethylidene-2-oxo-4,5-dihydrofuran (7b): **6b** (0.65 g, 2.7 mmol), 245 °C, 30 min (1:1); yield 0.35 g (79%); *Z*/*E* ratio = 1/5; IR (neat) 1762, 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ (*E*)-**7b** 6.87–6.75 (m, 1 H), 5.51 (dd, *J* = 6.4, 2.2 Hz, 1 H), 3.90–3.76 (m, 1 H), 3.56–3.48 (m, 1 H), 2.97 (br d, *J* = 17.4 Hz, 1 H), 2.68 (br d, *J* = 17.4 Hz, 1 H), 1.80 (dt, *J* = 7.1, 1.8 Hz, 3 H), 1.53 (quintet, *J* = 7.2 Hz, 2 H), 1.31 (sextet, *J* = 7.2 Hz, 2 H), 0.86 (t, *J* = 7.2 Hz, 3 H); (*Z*)-**7b** 6.31–6.20 (m, 1 H), 5.40 (dd, *J* = 6.3, 2.3 Hz, 1 H), 3.85–3.73 (m, 1 H), 3.59–3.40 (m, 1 H), 3.01 (br d, *J* = 16.5 Hz, 1 H), 2.66 (br d, *J* = 16.5 Hz, 1 H), 2.12 (dt, *J* = 7.3, 2.3 Hz, 3 H), 1.53 (quintet, *J* = 7.2 Hz, 2 H), 1.31 (sextet, *J* = 7.2 Hz, 2 H), 0.86 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ (*E*)-**7b** 169.6, 136.2, 125.9, 101.3, 69.3, 32.5, 31.4, 19.1, 15.6, 13.7. Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.18; H, 8.76. Found: C, 65.10; H, 8.81.

(*E*)-1-[(1,1-Dimethylethoxycarbonyl)prop-1-en-1-yl]-2,5-dihydrofuran (9): **8** (0.26 g, 1.2 mmol), 200 °C, 15 min (1:9); yield 0.23 g (89%); IR (neat) 1690, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.82 (q, *J* = 7.4 Hz, 1 H), 5.91–5.86 (m, 1 H), 5.84–5.72 (m, 2 H), 4.73–4.66 (m, 2 H), 1.83 (d, *J* = 7.4 Hz, 3 H), 1.43 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 166.2, 139.8, 133.6, 128.2, 126.2, 82.1, 80.4, 75.4, 28.1, 13.6. Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.55; H, 8.63. Found: C, 68.39; H, 8.66.

4-Ethylidene-3-oxobicyclo[3.3.0]-2,8-dioxaoctane (10): **8** (0.34 g, 1.6 mmol), 245 °C, 12 min (9:1–3:7); yield 0.12 g (36%); *Z*/*E* ratio = 1/3.7; IR (neat) 1750, 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ (*E*)-**10a** 6.82 (qd, *J* = 7.2, 2.5 Hz, 1 H), 6.01 (d, *J* = 5.6 Hz, 1 H), 4.03 (dd, *J* = 8.7, 8.7 Hz, 1 H), 3.70 (ddd, *J* = 11.5, 8.7, 5.4 Hz, 1 H), 3.58 (m, 1 H), 2.20 (m, 1 H), 1.90 (dd, *J* = 7.2, 1.6 Hz, 3 H), 1.86 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ (*E*)-**10a** 169.3, 138.0, 130.4, 105.5, 66.8, 41.4, 32.2, 15.5. Anal. Calcd for $C_8H_{10}O_3$: C, 62.33; H, 6.54. Found: C, 62.43; H, 6.57.

4-Phenylcyclopent-1-enecarboxylic acid (12): **11** (0.29 g, 1.2 mmol) in 3 mL of xylene, 230 °C, 4 h, purified by recrystallization from petroleum ether; yield 0.19 g (84%); mp 85–90 °C; IR (neat) 3200–2400, 1710, 1675, 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 11.0–10.5 (br s, 1 H), 7.40–7.21 (m, 5 H), 6.97 (m, 1 H), 3.63 (tt, *J* = 7.9, 7.9 Hz, 1 H), 3.10–2.97 (m, 2 H), 2.80–2.60 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 169.9, 145.6, 145.4, 135.1, 128.6, 126.8, 126.3, 43.3, 41.9, 39.3; MS *m*/*e* (rel intensity) 188 (70), 143 (100), 128 (50), 115 (30); HRMS *m*/*e* calcd for $C_{12}H_{12}O_2$ 188.0837, found 188.0842.

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General Procedure for the BBr_3-Catalyzed Rearrangement of Cyclopropanecarboxylates. A solution of cyclopropanecarboxylate (1 equiv, 0.1–0.4 M) in CH_2Cl_2 was added dropwise to a stirred solution of BBr_3 (1 M in CH_2Cl_2, 0.5 equiv), in CH_2Cl_2 at −78 °C under Ar. The mixture was maintained at −78 °C for 20 min and then warmed to rt for 3 h. After the mixture was quenched with alcohol or water, water was added and the mixture was extracted twice with ether. The combined organic layers were extracted with water and saturated NaCl solution, dried (Na_2SO_4), and concentrated. All proudcts were purified by column chromatography on silica using ether–petroleum ether as eluant in the ratio specified in parenthesis.

Methyl 2-Ethylidene-4-oxobutanoate (5):[9] **3** (0.17 g, 3.0 mmol), H_2O quench (1:4); yield 0.053 g (48%); IR (neat) 2970, 2920, 2910, 1770, 1710, 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.62 (t, J = 1.6 Hz, 1 H), 7.14 (q, J = 7.2 Hz, 1 H), 3.73 (s, 3 H), 3.42 (s, 2 H), 1.79 (d, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 198.2, 167.1, 142.0, 124.7, 52.1, 41.5, 14.8.

3-Ethylidene-2-oxo-5-phenyl-4,5-dihydrofuran (13a) and 2-oxo-5-phenyl-3-vinyl-4,5-dihydrofuran (13b): **11** (0.90 g, 3.7 mmol), stirred at room temperature for 2 h and then quenched with ethanol at −78 °C (3:17) combined yield 0.26 g (37%, 1:1 partially separable mixture). **13a**: IR (neat) 1750, 1675 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.42–7.24 (m, 5 H), 6.91–6.81 (m, 1 H), 5.52 (dd, J = 8.3, 6.4 Hz, 1 H), 3.31 (dddq, J = 17.0, 8.3, 2.6, 1.9 Hz, 1 H), 2.76 (dddq, J = 17.0, 6.4, 2.9, 1.9 Hz, 1 H), 1.84 (dt, J = 7.0, 1.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 170.5, 140.4, 136.1, 128.7, 128.3, 126.8, 125.2, 77.9, 34.0, 15.9. **13b**: ^1H NMR ($CDCl_3$) δ 7.49–7.25 (m, 5 H), 5.99 (ddd, J = 16.9, 10.4, 6.3 Hz, 1 H), 5.41 (dd, J = 10.6, 5.7 Hz, 1 H), 5.29 (d, J = 10.4 Hz, 1 H), 5.24 (d, J = 16.9 Hz, 1 H), 3.50 (ddd, J = 13.3, 8.3, 5.7 Hz, 1 H), 2.83 (m, 1 H), 2.13 (apparent q, J = 11.5 Hz, 1 H). Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.53; H, 6.45.

General Procedure for the $VOCl_2(OEt)$-Induced Reactions of Cyclopropanecarboxylates. A solution of the vinylcyclopropane (1 equiv, 0.05–0.5 M) in CH_2Cl_2 was added dropwise to a stirred solution of $VOCl_2(OEt)$ (2 equiv, 0.1–1 M) in CH_2Cl_2 at 0 °C under stirring. After the solution was stirred for a further 5 min, water was added and the mixture was extracted (2×) with ether. The combined organic layers were washed with water and saturated NaCl solution, dried (Na_2SO_4), and concentrated. The residue was then purified by chromatography on silica with the specified solvent.

5-Ethoxy-3-ethylidene-2-oxo-4,5-dihydrofuran dimer (14a): **6a** (0.21 g, 1 mmol), yield 0.07 g (45%) (ether); IR (CCl_4) 1770, 1590 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.66–6.63 (m, 2 H), 5.54 (dd, J = 6.4, 2.0 Hz, 2 H), 3.49 (dq, J = 9.4, 7.1 Hz, 2 H), 3.36 (dq, J = 9.4, 7.1 Hz, 2 H), 2.98 (br d, J = 17.4 Hz, 2 H), 2.66 (br d, J = 17.4 Hz, 2 H), 2.33 (m, 4 H), 1.20 (t, J = 7.1 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 169.4, 138.5, 126.4, 101.1, 65.2, 32.8, 28.7, 14.9; MS m/e (rel intensity) 311 ($(M + H)^+$, 22), 162 (30), 110 (35), 91 (32), 53 (100). Anal. Calcd for $C_{16}H_{22}O_6$: C, 61.92; H, 7.14. Found: C, 62.00; H, 7.18.

5-Butoxy-3-ethylidene-2-oxo-4,5-dihydrofuran dimer (14b): **6b** (0.24 g, 1 mmol), yield 0.09 g (51%), ether/petroleum ether (3:1); IR (CCl_4) 1750, 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.75–6.51 (m, 2 H), 5.52 (dd, J = 6.4, 2.2 Hz, 2 H), 3.82 (dt, J = 9.5, 6.8 Hz, 2 H), 3.52 (dt, J = 9.5, 6.8 Hz, 2 H), 2.98 (br d, J = 17.4 Hz, 2 H), 2.66 (br d, J = 17.4 Hz, 2 H), 2.33 (m, 4 H), 1.56 (quintet, J = 7.1 Hz, 4 H), 1.35 (sextet, J = 7.1 Hz, 4 H), 0.88 (t, J = 7.2 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 169.4, 138.5, 126.5, 101.4, 69.5, 32.8, 31.4, 28.7, 19.1, 13.8; MS m/e (rel intensity) 366 (M^+, 1), 219 (60), 190 (25), 162 (70), 110 (100); HRMS m/e calcd for $C_{20}H_{30}O_6$ 366.2042, found 366.2031. Anal. Calcd for $C_{20}H_{30}O_6$: C, 65.55; H, 8.25. Found: C, 65.34; H, 8.21.

(*E*,*E*)-3,8-Bis(methoxycarbonyl)deca-3,7-dienedial (15): **3** (0.26 g, 1.5 mmol), yield 0.13 g (57%), ether–petroleum ether (1:1); mp 61–62 °C; IR (CCl_4) 2970, 2920, 2860, 1710, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.61 (s, 2 H), 6.95 (br t, J = 7.3 Hz, 2 H), 3.71 (s, 6 H), 3.41 (s, 4 H), 2.26 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 197.9, 166.9, 144.4, 125.2, 52.2, 41.7, 27.9; MS m/e (relative intensity) 283 ($(M + H)^+$, 65), 162 (65), 110 (100). Anal. Calcd for $C_{14}H_{18}O_6$: C, 59.57; H, 6.43. Found: C, 59.74; H, 6.52.

2-Phenyl-1-vinylcyclopropanecarboxylic Acid (16) and 3-(2-Chloroethylidene)-2-oxo-5-phenyl-4,5-dihydrofuran (17). A solution of cyclopropane **11** (0.37 g, 1.5 mmol) and $VOCl_2(OEt)$ (0.37 g, 7.5 mmol) in 10 mL of CH_2Cl_2 was refluxed for 30 h. Water was then added, and the mixture was extracted with CH_2Cl_2. The organic layer was washed with water and saturated NaCl solution, dried (Na_2SO_4), and concentrated. The residue was purified by chromatography on silica gel with ethyl acetate–hexane (3:7–4:6) as solvent gradient. **16**: yield 0.15 g (24%); mp 84–86 °C; IR (neat) 3500–2550, 1764, 1686, 1604 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.5 (br s, 1 H), 7.45–7.10 (m, 5 H), 5.82 (dd, J = 17.3, 10.2 Hz, 1 H), 5.05 (d, J = 10.2 Hz, 1 H), 4.97 (d, J = 17.3 Hz, 1 H), 3.08 (dd, J = 8.9, 7.5 Hz, 1 H), 1.97 (dd, J = 8.9, 5.3 Hz, 1 H), 1.79 (dd, J = 7.5, 5.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 180.0, 135.0, 130.8, 129.3, 127.9, 126.9, 117.9, 35.7, 33.3, 17.8. Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.41; H, 6.44.

17: 0.10 g (15%); IR (CCl_4) 1755, 1575 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.50–7.28 (m, 5 H), 6.88 (tt, J = 7.6, 2.9 Hz, 1 H), 5.58 (dd, J = 8.1, 6.3 Hz, 1 H), 4.14 (d, J = 7.6 Hz, 2 H), 3.47 (br dd, J = 17.5, 8.1 Hz, 1 H), 2.90 (br d, J = 17.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 169.7, 139.6, 133.4, 130.1, 128.9, 128.7, 125.3, 78.3, 39.7, 33.8; HRMS m/e calcd for $C_{12}H_{11}O_2Cl$: 222.0448, found 222.0444. Heating of **16** with $VOCl_2(OEt)$ in dichloroethane under reflux for 12 h resulted in the formation of **17** in 59% yield.

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Conjugated Macrocycles Related to the Porphyrins. 4.[1] Synthesis of a 23,24-Dioxa-5-oxophlorin[2]

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Oxophlorins **1** are the keto tautomers of *meso*-hydroxyporphyrins **2**. Although the *meso*-hydroxyporphyrin structure can be trapped as, for example, the corresponding acetate by reaction with acetic anhydride–pyridine, the cross-conjugated oxophlorin system is favored in neutral solutions.[3] Oxophlorins **1** are important intermediates in the total synthesis of porphyrins,[4] and an iron complex of the hydroxy tautomer **2** is believed to be an intermediate in heme catabolism.[5] Monoprotonation of the oxophlorin system leads to monocations that also favor the keto form, but the hydroxyporphyrin tautomer is favored by the dications and metal complexes of these compounds.[3-6] Oxophlorins are relatively unstable in

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