Intramolecular (2 + 2) Cycloadditions of Phenoxyketenes

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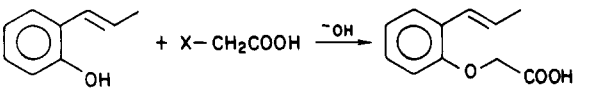
The intramolecular (2 + 2) cycloaddition of phenoxyketenes to alkenyl groups provides an efficient route to polycyclic cyclobutanones. (*o*-Vinylphenoxy)- and (*o*-allylphenoxy)ketenes were prepared from the corresponding acid chlorides by treatment with triethylamine. The ketenes undergo a facile intramolecular (2 + 2) cycloaddition to give polycyclic cyclobutanones. The (*o*-vinylphenoxy)ketenes are clearly more reactive than the (*o*-allylphenoxy)ketenes and provide much better yields of the cycloaddition products because of electronic effects in the transition state in the cycloaddition process.

The intermolecular regiospecific (2 + 2) cycloaddition of ketenes to unsaturated compounds has proved to be a very versatile reaction for the synthesis of a wide variety of cyclic compounds.[1] There are some scattered reports in the literature on intramolecular ketene cycloaddition reactions but most of these reports are on photochemical or pyrolysis reactions and not directed toward synthetic applications.[2] Conversely, interest and publications in the area of intramolecular Diels–Alder reactions, where the diene and the dienophile are constrained in the same molecule, has recently increased exponentially.[3] It is anticipated that intramolecular ketene cycloaddition reactions may be used effectively to synthesize a wide variety of interesting bridged polycyclic compounds. This report describes the intramolecular (2 + 2) cycloaddition of (*o*-alkenylphenoxy)ketenes to give polycyclic cyclobutanones. During the course of this investigation, two excellent communications have appeared in the literature on intramolecular (2 + 2) cycloaddition reactions of ketenes and keteniminium salts.[4]

(*o*-Alkenylphenoxy)acetic acids were used as precursors to the difunctional compounds needed for the intramolecular cycloadditions. These acids were readily prepared from *o*-alkenylphenols and α-halocarboxylic acids as illustrated for (*o*-propenylphenoxy)acetic acid in Scheme I. A solution of sodium α-bromo- or -chlorocarboxylate and sodium phenolate in THF or water were refluxed for 4–16 h. Yields of 50–88% were obtained after recrystallization from hexane or water.

The (*o*-alkenylphenoxy)acetic acids were converted to the corresponding acid chlorides by reaction with an excess of oxalyl chloride in benzene at ambient temperature for 3 h. The excess oxalyl chloride was removed under vacuum and the crude acid chloride diluted with benzene and slowly added to a solution of 2–3 equiv of triethylamine in benzene at gentle reflux. This dehydrochlorination resulted in the phenoxyketene which underwent (2 + 2) cycloaddition with the carbon–carbon double bond in the ortho position as illustrated with (*o*-propenylphenoxy)acetic acid in Scheme II. The cycloaddition products were purified by column chromatography (3–7% ethyl acetate in hexane) or recrystallization from hexane. In the above scheme the intramolecular (2 + 2) cycloaddition reaction

Scheme I



Scheme II

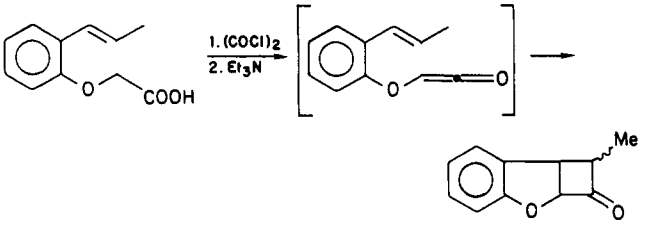
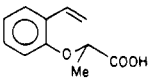
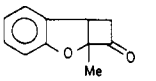
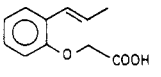
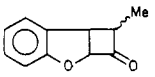
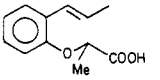
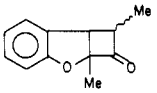
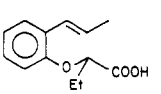
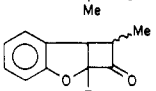
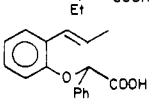
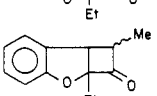
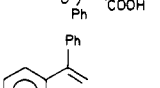
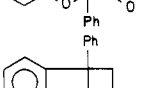
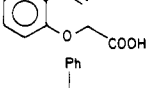
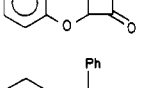
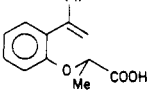
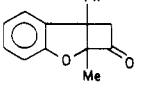
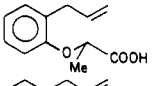
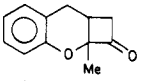


Table I. Intramolecular (2 + 2) Cycloaddition Reactions of Phenoxyketenes Derived from (*o*-Alkenylphenoxy)acetic Acids

entry	acid	cycloadduct	yield (%)
1			60
2			72
3			76
4			71
5			85
6			88
7			84
8			43
9			49

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occurs with the simultaneous formation of a five-membered ring, i.e., the ketene functionality and the double bond are separated by a bridge of three atoms. These cycloadditions occurred in yields of 43–88% and the results are tabulated in Table I. The structures of the cycloaddition products were determined by the presence of the carbonyl band in the infrared spectra at 1777–1789 cm^{-1}, the ^1H and ^{13}C NMR spectra and elemental analysis.

To reduce the probability of dimerization or intermolecular cycloaddition, it is necessary to keep a low concentration of the reacting ketene. This is accomplished by the slow addition of a dilute solution of the acid chloride to a dilute solution of triethylamine.

The (*o*-vinylphenoxy)ketenes clearly give much better yields of the intramolecular (2 + 2) cycloaddition products than the (*o*-allylphenoxy)ketenes as revealed in Table I. This is probably due to the greater reactivity of (*o*-vinylphenoxy)ketenes because in the initial bond formation between the sp-hybridized carbon atom of the ketene and the carbon–carbon double bond any positive charge developed in the transition state is on a benzylic carbon atom. Substitution in the (*o*-vinylphenoxy)acetic acids at the position α to the carboxyl group (acids that would lead to disubstituted ketenes) does not provide any steric problems for the cycloaddition as evidenced by entries 1, 3, 4, 5, and 7. Also, substitution of a methyl or phenyl group on the vinyl substituent as in entries 2–7 provides no diffficulties for the cycloaddition.

This study clearly indicates the usefulness of intramolecular (2 + 2) cycloaddition reactions of ketenes which promises to be a powerful synthetic tool for the synthesis of a wide variety of polycyclic compounds.

Experimental Section

The ^1H NMR spectra were recorded on a Perkin-Elmer R-24B nuclear magnetic resonance spectrometer, employing deuteriochloroform or dimethyl-d_6 sulfoxide as the solvent with tetramethylsilane as the internal standard. The ^{13}C NMR spectra were obtained on a JEOL FX-90Q FT nuclear magnetic resonance spectrometer. The IR spectra were obtained on a Perkin-Elmer 1330 spectrometer and elemental analyses were performed by Midwest Microlab. Melting points are uncorrected.

THF, benzene, and triethylamine were dried and purified by distillation from a sodium–potassium alloy prior to use.

Starting Materials. *o*-Allylphenol, *o*-propenylphenol, and the halo acids were commercially available. *o*-Vinylphenol was prepared by a literature procedure.[5] *o*-(1-Phenylvinyl)phenol was prepared as follows: To a Grignard solution prepared from 17.3 g (0.11 m) of bromobenzene, 2.9 g (0.12 g. atom) of magnesium, and 100 mL of THF was added 6.8 g (0.05 m) of *o*-hydroxyacetophenone in 50 mL of THF with efficient stirring and cooling. The resulting solution was refluxed for 6 h and was then condensed to about 75 mL on a rotatory evaporator, cooled, and treated with 100 mL of 15% aqueous acetic acid at 0 °C. The organic layer was separated, and the aqueous layer extracted with two 75-mL portions of benzene. The combined organic solution was washed with a small amount of aqueous sodium bicarbonate followed by saturated brine and dried over anhydrous magnesium sulfate. Evaporation of the solvent resulted in 9.7 g (91%) of sufficiently pure 1-phenyl-1-(2-hydroxyphenyl)ethanol as white crystals: mp 110–111.5 °C; ^1H NMR ($CDCl_3$) δ 7.82–6.78 (m, 11 H), 2.23 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 155.0 (s), 147.0 (s), 131.4 (s), 128.0 (d), 127.3 (d), 126.4 (d), 126.2 (d), 124.9 (d), 118.6 (d), 116.4 (d), 77.0 (s), 29.8 (q); IR ($CDCl_3$) 3650–2500, 1603, 1583 cm^{-1}.

The alcohol was dissolved in 50 mL of benzene to which 50 mg of iodine was added. This mixture was refluxed overnight and then cooled and washed with aqueous sodium thiosulfate. Upon drying and removal of the solvent a quantitative yield of *o*-(1-phenylvinyl)phenol was obtained as a pale yellow oil: IR (neat) 3570, 1620, 1582 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.34–6.77 (m, 9 H), 5.67 (s, 1 H), 5.44 (s, 1 H), 5.24 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 152.9 (s), 145.0 (s), 139.3 (s), 130.3 (d), 129.2 (d), 128.3 (d), 128.2 (d), 127.5 (s), 126.7 (d), 120.2 (d), 116.3 (t), 115.7 (d).

General Procedure for (*o*-Alkenylphenoxy)acetic Acids. Method A. This method utilizes water as a solvent and was used for the preparation of **2a**, **3a**, and **8a**. To a mixture of equal equivalents (30 mmol) of the *o*-alkenylphenol and α-chloro carboxylic acid in 15 mL of water was slowly added with cooling and stirring 20 mL of a cold aqueous solution containing 65 mmol of NaOH. The mixture was stirred for 20 min and then refluxed for 4–16 h. Upon cooling, the solution was acidified to pH 1 with dilute HCl and extracted with two 30-mL portions of benzene. The combined benzene extracts were washed with water, dried over anhydrous magnesium sulfate, and evaporated under vacuum to yield the crude acid as an oil which was purified by recrystallization from hexane.

Method B. This method utilizes THF as a sovlvent and was used for the preparation of **1a**, **4a**, **5a**, **6a**, **7a**, and **9a**. To a mixture of equal equivalents (30 mmol) of the *o*-alkenylphenol and α-halo carboxylic acid in 30 mL of THF was slowly added with cooling and stirring 65 mmol of sodium hydride as an 80% dispersion in mineral oil. The mixture was stirred for 20 min and then refluxed for 4–16 h. The solution was cooled and acidified to pH 1 with dilute HCl. An 80-mL portion of benzene and 20 mL of saturated brine was added to this solution. The organic layer was washed with four portions of 10 mL of saturated brine, dried over anhydrous magnesium sulfate, and evaporated under vacuum to yield the crude acids. Compounds **1a**, **4a**, **5a**, and **9a** were purified by recrystallization from hexane and the others by column chromatography using silica gel (20% ethyl acetate in hexane).

2-(*o*-Vinylphenoxy)propanoic Acid (a). A 4.3-g (75% yield) portion of this acid was obtained: IR ($CDCl_3$) 3650–2300, 1703, 1625 cm^{-1}; ^1H NMR ($CDCl_3$) δ 11.24 (s, 1 H), 7.19–5.16 (m, 7 H), 4.53 (q, 1 H, J = 5.4 Hz); ^{13}C NMR ($CDCl_3$) δ 178.4 (s), 154.4 (s), 72.5 (d), 18.4 (q).

(*o*-Propenylphenoxy)acetic Acid (2a). A 3.5-g (61% yield) portion of this acid was obtained with mp 101–102 °C; IR (Me_2SO-d_6) 3650–2250, 1710, 1628 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 9.61 (s, 1 H), 7.63–5.69 (m, 6 H), 4.69 (s, 2 H), 1.91 (m, 3 H); ^{13}C NMR (Me_2SO-d_6) δ 169.2 (s), 153.2 (s), 63.9 (t), 17.6 (q).

2-(*o*-Propenylphenoxy)propanoic Acid (3a). A 3.3-g (54% yield) portion of this acid was obtained with mp 95–97 °C: IR ($CDCl_3$) 3680–2200, 1705, 1634 cm^{-1}; ^1H NMR ($CDCl_3$) δ 11.05 (s, 1 H), 7.55–5.65 (m, 6 H), 4.63 (q, 1 H, J = 5.3 Hz), 1.86 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 178.1 (s), 153.9 (s), 72.6 (d), 18.7 (q), 18.2 (q).

2-(*o*-Propenylphenoxy)butanoic Acid (4a). A 5.8-g (88% yield) portion of this acid was obtained with mp 105–106 °C: IR ($CDCl_3$) 3600–2300, 1697, 1632 cm^{-1}; ^1H NMR ($CDCl_3$) δ 11.05 (s, 1 H), 7.55–5.65 (m, 6 H), 4.59 (t, 1 H, J = 6 Hz), 1.91 (m, 2 H), 1.18 (t, 3 H, J = 6 Hz); ^{13}C NMR ($CDCl_3$) δ 177.6 (s), 154.1 (s), 77.5 (d), 26.0 (t), 18.7 (q), 95 (q).

[(*o*-Propenylphenoxy)phenyl]acetic Acid (5a). A 6.4-g (79% yield) portion of this acid was obtained with mp 156–159 °C: IR ($CDCl_3$) 3700–2700, 1720, 1645 cm^{-1}; ^1H NMR (DMSO-d^6) δ 7.62–5.84 (m, 11 H), 5.47 (s, 1 H), 1.72 (d, 3 H, J = 6 Hz); ^{13}C NMR (Me_2SO-d_6) δ 171.0 (s), 153.9 (s), 136.3 (s), 78.4 (d), 18.9 (q).

[*o*-(1-Phenylvinyl)phenoxy]acetic Acid (6a). A 6.2-g (81% yield) portion of this acid was obtained as a pale yellow oil: IR ($CDCl_3$) 3700–2380, 1710, 1623 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.53 (s, 1 H), 7.65–6.63 (m, 9 H), 5.60 (s, 1 146.5 (s), 75.6 (t).

2-[*o*-(1-Phenylvinyl)phenoxy]propanoic Acid (7a). A 5.6-g (70% yield) of this acid was obtained as a pale yellow oil: IR (neat) 3600–2250, 1723, 1612 cm^{-1}; ^1H NMR ($CDCl_3$) δ 10.41 (s, 1 H), 7.45–6.67 (m, 9 H), 5.71 (s, 1 H), 5.42 (d, 1 H, J = 2.8 Hz), 4.62 (q, 1 H, J = 5.4 Hz), 1.31 (d, 3 H, J = 5.4 Hz); ^{13}C NMR ($CDCl_3$) δ 176.8 (s), 154.5 (s), 146.9 (s), 141.3 (s), 72.6 (d), 17.6 (q).

2-(*o*-Allylphenoxy)propanoic Acid (8a). A 3.1-g (50% yield) portion of this acid was obtained with mp 62–64 °C: IR ($CDCl_3$) 3680–2250, 1710, 1629 cm^{-1}; ^1H NMR ($CDCl_3$) δ 10.53 (s, 1 H), 6.96–6.29 (m, 4 H), 6.17–5.52 (m, 1 H), 5.24–4.45 (m, 3 H), 3.23 (d, 2 H, J = 5.6 Hz), 1.44 (d, 3 H, J = 5.5 Hz); ^{13}C NMR ($CDCl_3$)

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δ 177.8 (s), 154.8 (s), 136.6 (d), 129.0 (s), 72.0 (d), 34.1 (t), 18.1 (q).

2-(*o*-Allylphenoxy)butanoic Acid (9a). A 5.3-g (81% yield) portion of this acid was obtained with mp 53–55 °C: IR ($CDCl_3$) 3700–2230, 1715, 1630 cm^{-1}; ^1H NMR ($CDCl_3$) δ 10.56 (s, 1 H), 7.18–6.46 (m, 4 H), 6.31–5.56 (m, 1 H), 5.21–4.95 (m, 1 H), 4.95–4.76 (m, 1 H), 4.52 (t, 1 H, J = 5.9 Hz), 3.48 (d, 2 H, J = 6 Hz), 2.00 (m, 2 H), 1.21 (t, 3 H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 177.6 (s), 155.2 (s), 136.8 (d), 129.1 (s), 76.6 (d), 34.3 (t), 26.0 (t), 9.4 (q).

General Procedure for Acid Chloride Preparation and Subsequent Intramolecular Cycloaddition. The (*o*-alkenylphenoxy)acetic acids were converted to the corresponding acid chlorides by reaction with 5–8 equiv of oxalyl chloride in benzene at ambient temperature for 3 h. The excess oxalyl chloride was removed under vacuum and the crude acid chloride was diluted with benzene and slowly added to a solution of 2 equiv of triethylamine in benzene at gentle reflux. The addition was usually over a period of 2–6 h and the total amount of solvent was 300–450 mL for a 5–10-mmol preparation. (In some instances, such as **8b** and **9b**, where the olefin functionality is not very reactive toward the cycloaddition process, it would be necessary to keep an even lower concentration of the reacting ketene.) After the addition was complete, the mixture was gently refluxed for 4–8 h. Upon cooling, the salt was removed by filtration and the solvent and excess amine were removed under reduced pressure. The crude cycloaddition product was purified by recrystallization from hexane (**5b**, **8b**) or by column chromatography using silica gel (2–7% ethyl acetate in hexane: **1b**, **2b**, **3b**, **4b**, **6b**, **7b**, **9b**).

1-Methyl-2-oxa-3,4-benzobicyclo[3.2.0]heptan-7-one (1b). A 0.54-g (60% yield) portion of **1b** was obtained from 1 g of **1a** with mp 49–50 °C: IR ($CDCl_3$) 1784, 1612, 1593 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.23–6.60 (m, 4 H), 3.70–2.76 (m, 3 H), 1.58 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 207.3 (s), 160.1 (s), 128.8 (s), 128.6 (d), 125.4 (d), 121.5 (d), 109.9 (d), 102.3 (s), 53.7 (t), 39.9 (d), 15.9 (q).

Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 75.56; H, 5.86.

6-Methyl-2-oxa-3,4-benzobicyclo[3.2.0]heptan-7-one (2b). A 0.65-g (72% yield) portion of **2b** was obtained from 1 g of **2a** with mp 65–66 °C : IR ($CDCl_3$) 1781, 1608, 1589 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.15–6.58 (m, 4 H), 5.63–5.36 (m, 1 H), 4.23–3.38 (m, 2 H), 1.21 (d, exo-Me, J = 7.3 Hz), 0.84 (d, endo-Me, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$) δ 2.08.6 (s), 161.1 (s), 128.7 (d), 127.0 (d), 125.2 (s), 121.2 (d), 110.6 (d), 91.9, 59.0 (d), 39.9 (d), 8.6 (q).

Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 75.64; H, 5.70.

1,6-Dimethyl-2-oxa-3,4-benzobicyclo[3.2.0]heptan-7-one (3b). A 0.69-g (76% yield) portion of **3b** was obtained from 1 g of **3a** with mp 69–70 °C: IR ($CDCl_3$) 1778, 1609, 1590 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.08–6.87 (m, 4 H), 3.83–3.81 (m, 2 H), 1.66 (s, 3 H), 0.96 (d, 3 H, J = 6.6 Hz); ^{13}C NMR ($CDCl_3$) δ 210.5 (s), 160.7 (s), 128.6 (d), 126.9 (d), 124.5 (s), 121.0 (d), 110.4 (d), 100.2 (s), 57.3 (d), 45.1 (d), 16.3 (q), 8.4 (q).

Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.51; H, 6.39.

1-Ethyl-6-methyl-2-oxa-3,4-benzobicyclo[3.2.0]heptan-7-one (4b). A 1.31-g (71% yield) portion of a colorless oil was obtained from 2 g of **4a**: IR (Neat) 1781, 1608, 1590 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.10–6.45 (m, 4 H), 3.84–0.79 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 210.4 (s), 160.8 (s), 128.4 (d), 126.7 (d), 124.4 (s), 120.8 (d), 110.1 (d), 104.0 (s), 57.5 (d), 42.9 (d), 23.2 (t), 8.3 (q), 7.4 (q).

Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 76.98; H, 6.78.

6-Methyl-1-phenyl-2-oxa-3,4-benzobicyclo[3.2.0]heptan-7-one (5b). A 1.6-g (85% yield) portion of **5b** was obtained from 2 g of **5a** with mp 95–96 °C: IR (neat) 1783, 1611, 1592 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.65–6.86 (m, 9 H), 4.50–3.76 (m, 2 H), 1.19 (d, 3 H, J = 6 Hz); ^{13}C NMR ($CDCl_3$) δ 208.4 (s), 160.7 (s), 133.5 (s), 129.0 (d), 128.8 (d), 126.9 (s), 126.1 (d), 121.5 (d), 110.8 (s), 59.2 (d), 46.1 (d), 8.7 (q).

Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.40; H, 5.61.

5-Phenyl-2-oxa-3,4-benzobicyclo[3.2.0]heptan-7-one (6b). A 1.31-g (88% yield) portion of **6b** was obtained from 1.6 g of **6a** with mp 162–163 °C: IR ($CDCl_3$) δ 1789, 1608, 1590 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.32–7.41 (m, 9 H), 6.37 (t, 1 H, J = 2.5 Hz), 4.71 (dd, 1 H, J = 16.2, 2.5 Hz), 4.22 (dd, 1 H, J = 16.2, 2.5 Hz); ^{13}C NMR ($CDCl_3$) δ 203.9 (s), 142.0 (s), 131.7 (s), 129.3 (d), 128.8 (d), 127.2 (d), 126.1 (d), 125.5 (d), 122.7 (d), 111.1 (d), 99.5 (d), 59.3 (t), 50.7 (s).

Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.11; H. 4.95.

1-Methyl-5-phenyl-2-oxa-3,4-benzobicyclo[3.2.0]heptan-7-one (7b). A 2.35-g (84% yield) portion of colorless oil was obtained from 3 g of **7a**: IR (neat) 1788, 1718, 1658, 1593 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.16–7.35 (m, 9 H), 4.86 (d, 1 H, J = 16.4 Hz), 4.03 (d, 1 H, J = 16.4 Hz), 2.05 (s, 3 H); ^{13}C NMR ($CDCl_3$) 207.1 (s), 159.9 (s), 138.5 (s), 133.1 (d), 129.0 (d), 128.4 (d), 127.5 (d), 127.0 (d), 125.7 (d), 122.3 (d), 110.5 (d), 104.1 (s), 55.5 (t), 53.2 (s), 13.4 (q).

Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.35; H, 5.65.

1-Methyl-2-oxa-3,4-benzobicyclo[4.2.0]octan-8-one (8b). A 0.39-g (43% yield), of **8b** was obtained from 1 g of **8a** with mp 65–66 °C: IR ($CDCl_3$) 1777, 1610, 1591 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.07–6.84 (m, 4 H), 3.05–2.17 (m, 5 H), 1.48 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 209.9 (s), 154.6 (s), 129.1 (d), 127.5 (s), 123.8 (d), 122.2 (d), 117.3 (d), 92.6 (s), 46.9 (t), 34.4 (d), 28.2 (t), 19.5 (q).

Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.65; H, 6.47.

1-Ethyl-2-oxa-3,4-benzobicyclo[4.2.0]octan-8-one (9b). A 0.45-g (49% yield) portion of a colorless oil was obtained from 1 g of **9a**; IR (neat) 1780, 1605, 1583 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.04–6.89 (m, 4 H), 2.84–2.17 (m, 5 H), 1.72 (q, 2 H, J = 4.8 Hz), 0.92 (t, 3 H, J = 4.8 Hz); ^{13}C NMR ($CDCl_3$) 209.9 (s), 154.8 (s), 129.06 (d), 127.49 (d), 123.86 (s), 122.0 (d), 117.3 (d), 95.8 (s), 47.0 (t), 32.5 (d), 28.5 (t), 26.3 (t), 7.06 (q).

Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.44; H, 7.15.

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Stereocontrolled Synthesis of a Polyether Fragment

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A sequence utilizing selenolactonization of olefinic acid **4**, Ireland–Claisen rearrangement of ketal ester **9**, iodolactonization/epoxidation of olefinic acid **10**, and regioselective hydrolysis of epoxide **15b** is described for the stereocontrolled conversion of *meso*-2,4-dimethylglutaric anhydride to racemic tetrahydropyran lactone **1**.

Continued interest in the synthesis of polyether natural products has given rise of a number of strategic approaches for constructing and concatenating α,α′-disubstituted tetrahydrofuran and -pyran units.[1] For the most part,

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