The first component, a liquid after removal of solvent, was identical with the starting material.

The second component was identified as 2-ethoxy-5-nitrotoluene: mp 65–66 °C; yield 9.87 g (58%); mol wt 181.19; NMR ($CDCl_3$) δ 8.08 (1 H, dd, J_m = 2 Hz, J_o = 9 Hz), 8.0 (1 H, d, J = 2 Hz), 6.79 (1 H, d, J = 9 Hz), 4.12 (2 H, q, J = 6.5 Hz), 2.26 (3 H, s), 1.47 (3 H, t); IR (Nujol) 1612, 1590, 1520, 1498, 1470, 1458, 1390, 1378, 1260, 1142, 1118, 1100, 1040, 940, 902, 812, 780, 750, 718, 658 cm^{-1}. Anal. Calcd for $C_9H_{11}NO_3$: C, 59.66; H, 6.12; N, 7.73. Found: C, 59.12; H, 6.04; N, 7.48.

The third component was identified as 2,3′-dinitro-4,5′-dimethyl-5,4′-diethoxybiphenyl: mp 158–159 °C; yield 1.4 g (4.2%); mol wt 360.37; NMR ($CDCl_3$) δ 7.82 (1 H, brs), 7.54 (1 H, d, J = 2.5 Hz), 7.21 (1 H, d), 6.59 (1 H, brs), 4.10 (4 H, 2 q, J = 7 Hz), 2.35 (3 H, s), 2.28 (3 H, s), 1.48 (6 H, 2 t); IR (Nujol) 1618, 1562, 1540, 1520, 1470, 1380, 1362, 1342, 1300, 1280, 1262, 1242, 1230, 1195, 1180, 1118, 1050, 1035, 1005, 940, 920, 912, 902, 888, 830, 810, 795, 775, 750, 725, 662 cm^{-1}. Anal. Calcd for $C_{18}H_{20}N_2O_6$: C, 59.99; H, 5.59; N, 7.77. Found: C, 60.19; H, 5.27; N, 7.54.

Nitration of 2-Methylanisole. 2-Methylanisole [bp 119 °C (143 mmHg), 12.2 g] was nitrated as described above.

2-Methyl-4-nitroanisole: mp 50–51 °C; yield 4.9 g (29%); mol wt 167.17; NMR ($CDCl_3$) δ 8.10 (1 H, dd, J_m = 2.5 Hz, J_o = 9 Hz), 8.02 (1 H, d, J_m = 2.5 Hz), 6.81 (1 H, d), 3.92 (3 H, s), 2.26 (3 H, s); IR (Nujol) 1610, 1592, 1510, 1498, 1460, 1440, 1380, 1340, 1260, 1186, 1148, 1100, 1042, 1020, 995, 930, 898, 828, 810, 755, 715, 640 cm^{-1}. Anal. Calcd for $C_8H_9NO_3$: C, 57.48; H, 5.43; N, 8.38. Found: C, 57.49; H, 5.60; N, 8.41.

2,3′-Dinitro-4,5′-dimethyl-5,4′-dimethoxybiphenyl: mp 168–169 °C; yield 0.75 g (2.3%); mol wt 332.32; NMR ($CDCl_3$) δ 7.74 (1 H, brs), 7.59 (1 H, d, J = 2 Hz), 7.27 (1 H, d), 6.65 (1 H, brs), 3.94 (3 H, s), 3.92 (3 H, s), 2.38 (3 H, s), 2.28 (3 H, s); IR (Nujol) 1620, 1570, 1530, 1505, 1460, 1380, 1360, 1340, 1298, 1260, 1240, 1180, 1115, 1045, 1002, 902, 890, 870, 820, 780, 760, 740 cm^{-1}. Anal. Calcd for $C_{16}H_{16}N_2O_6$: C, 57.83; H, 4.85; N, 8.43. Found: C, 57.82; H, 4.69; N, 8.46.

Nitration of 2-(Propyloxy)toluene. 2-(Propyloxy)toluene [bp 135–137 °C (130 mmHg), 15 g] was nitrated as described above.

2-(Propyloxy)-5-nitrotoluene: liquid; yield 10.94 g (56%); mol wt 195.22; NMR ($CDCl_3$) δ 8.03 (1 H, dd, J_m = 2.5 Hz, J_o = 9 Hz), 7.86 (1 H, d, J = 2.5 Hz), 6.73 (1 H, d), 3.96 (2 H, t, J = 6 Hz), 2.33 (3 H, s), 1.8 (2 H, m), 1.06 (3 H, t); IR (Nujol) 1610, 1588, 1520, 1498, 1472, 1460, 1392, 1380, 1260, 1145, 1118, 1100, 1050, 940, 900, 812, 782, 755, 718, 660 cm^{-1}. Anal. Calcd for $C_{10}H_{13}NO_3$: C, 61.53, H, 6.71, N, 7.17. Found: C, 61.56; H, 6.44; N, 7.22.

2,3′-Dinitro-4,5′-dimethyl-5,4′-bis(propyloxy)biphenyl: mp 141–142 °C; yield 2.75 g (7%); mol wt 388.42; NMR ($CDCl_3$) δ 7.89 (1 H, brs), 7.57 (1 H, d, J = 2 Hz), 7.27 (1 H, d), 6.64 (1 H, brs), 3.97 (4 H, 2 t, J = 6 Hz), 2.36 (3 H, s), 2.31 (3 H, s), 1.83 (4 H, m), 1.08 (6 H, 2 t); IR (Nujol) 1615, 1560, 1538, 1520, 1500, 1460, 1380, 1318, 1300, 1260, 1230, 1180, 1158, 1110, 1080, 1030, 998, 960, 910, 870, 800, 778, 760, 740, 720, 660 cm^{-1}. Anal. Calcd for $C_{20}H_{24}N_2O_6$: C, 61.85; H, 6.23; N, 7.21. Found: C, 62.17; H, 6.30; N, 7.53.

Crystal data: $C_{18}H_{20}N_2O_6$(I), mol wt 360.37; monoclinic; a = 7.878 (3) Å, b = 8.204 (3) Å, c = 27.843 (11) Å, β = 91.36 (3) Å, U = 1799 Å^3, Z = 4, d_{calcd} = 1.331 g cm^{-3}; absorption coefficient for Cu Kα radiation (λ = 1.5418 Å), μ = 8.6 cm^{-1}. Space group $P2_1/c(C^5_{2h})$ was uniquely established from the systematic absences $0k0$ when $k \neq 2n$ and $h0l$ when $l \neq 2n$.

Acknowledgment. We thank the staff of Analytical Research Services of Schering-Plough Corp. for providing us with microanalytical and spectral data.

Registry No. 1, 82280-90-8; 2-ethoxytoluene, 614-71-1; 2-methylanisole, 578-58-5; 2-propyloxytoluene, 4607-37-8; 2-ethoxy-5-nitrotoluene, 70611-03-9; 2-methyl-4-nitroanisole, 50741-92-9; 2,3′-dinitro-4,5′-dimethyl-5,4′-dimethoxybiphenyl, 82280-91-9; 2-(propyloxy)-5-nitrotoluene, 82280-92-0; 2,3′-dinitro-4,5′-dimethyl-5,4′-bis(propyloxy)biphenyl, 82280-93-1.

Supplementary Material Available: Crystallographic measurements, interatomic distances and angles (Figure 2), monohydrogen atom fractional coordinates (Table II), tables of least-squares plane equation data (Table III), torsion angles (Table IV), anisotropic thermal parameters (Table V), calculated hydrogen atom fractional coordinates (Table VI), and observed and calculated structure amplitudes (Table VII) (16 pages). Ordering information is given on any current masthead page.

Free Radicals in Synthesis. 1. A Two-Step Carbolactonization Procedure

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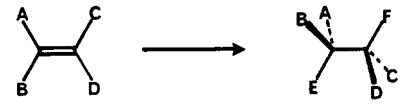
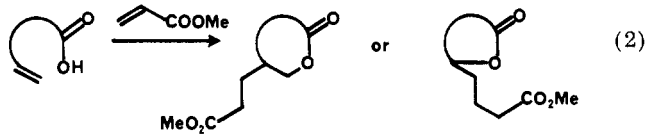
The vicinal functionalization of unactivated olefins with regio- and stereochemical control (generalized in eq 1) is



(1)

an important area of development in organic synthesis.[1] In connection with an ongoing synthetic program, we have made an initial foray into this area, the results of which are described herein.

We required a reliable means of carbolactonization (eq 2) whereby the olefinic linkage became vicinally func-



(2)

tionalized by carboxylate and acrylate residues, respectively. A direct formation of the new carbon–oxygen and carbon–carbon bonds in a single step would be ideal. Unfortunately, the acrylate unit is not a suitable electrophilic trigger for the direct carbolactonization sought. However, the well-established mercurio-,[2] iodo-,[3] and selenolactonization[4] reactions and the demonstrated reductive cleavages of the respective C–Hg,[5] C–I,[6] and C–Se[7] bonds by borohydride salts or hydridostannanes held the promise of an acceptable solution. We therefore executed a systematic study of lactones **1a–c**, **2a–c**, and **3a–c** to compare the acetoxymercurio, iodo, and phenylseleno substituents as functional auxiliaries for the generation of

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0022-3263/82/1947-3348$01.25/0

Table I

lactone substrate	conditions[a]	lactone product	yield,[b] %
1a, X = HgOAc	MA (12.7 equiv), $NaHB(OMe)_3$ (1.14 equiv), CH_2Cl_2 (0.15 M in 1a), 0 → 25 °C	4a	6
1b, X = I	MA (12.0 equiv), Bu_3SnH (3.0 equiv), ABN (catalytic), PhMe (0.21 M in 1b), 110 °C	4a	45
1c, X = SePh	MA (20 equiv), Bu_3SnH (6.0 equiv), ABN (catalytic), PhMe (0.19 M in 1c), 110 °C	4a	69
1a, X = HgOAc	MMA (10.6 equiv), $NaHB(OMe)_3$ (1.14 equiv), CH_2Cl_2 (0.19 M in 1a), 0 → 25 °C	4b	18[c]
1b, X = I	MMA (15 equiv), Bu_3SnH (3.0 equiv), ABN (catalytic), PhMe (0.21 M in 1b), 110 °C	4b	49.5
1c, X = SePh	MMA (9 equiv), Bu_3SnH (3.0 equiv), ABN (catalytic), PhMe (0.15 M in 1c), 110 °C	4b	68
2a, X = HgOAc	MA (14 equiv), $NaHB(OMe)_3$ (1.29 equiv), CH_2Cl_2 (0.12 M in 2a), 0 → 25 °C	5a	20
2b, X = I	MA (10 equiv), Bu_3SnH (2.0 equiv), ABN (catalytic), PhMe (0.07 M in 2b), 110 °C	5a	54
2c, X = SePh	MA (10 equiv), Ph_3SnH (3.0 equiv), PhMe (0.18 M in 2c), 110 °C	5a	70
2a, X = HgOAc	MMA (12 equiv), $NaHB(OMe)_3$ (1.15 equiv), CH_2Cl_2 (0.12 M in 2a), 0 → 25 °C	5b	18[c]
2b, X = I	MMA (11.6 equiv), Bu_3SnH (3.0 equiv), ABN (catalytic), PhMe (0.18 M in 2b), 110 °C	5b	50
2c, X = SePh	MMA (10 equiv), Bu_3SnH (3.0 equiv), ABN (catalytic), PhMe (0.18 M in 2c), 110 °C	5b	73
3a, X = HgOAc	MA, $NaHB(OMe)_3$, CH_2Cl_2 (various attempts)	6a	0
3b, X = I	MA (10 equiv), Bu_3SnH (3.0 equiv), ABN (catalytic), PhMe (0.19 M in 3b), 110 °C	6a	58[c]
3c, X = SePh	MA (10 equiv), Ph_3SnH (3.0 equiv), PhMe (0.17 M in 3c), 110 °C	6a	80
3a, X = HgOAc	MMA, $NaHB(OMe)_3$, CH_2Cl_2 (various attempts)	6b	0
3b, X = I	MMA (15 equiv), Bu_3SnH (3.0 equiv), ABN (catalytic), PhMe (0.19 M in 3b), 110 °C	6b	65[c]
3c, X = SePh	MMA (10 equiv), Ph_3SnH (3.0 equiv), PhMe (0.17 M in 3c), 110 °C	6b	74

[a] These reflect optimal conditions for maximizing isolated yields of the coupling products 4–6 and minimizing the formation of products derived from reduction or the appendage of multiple acrylate residues in a coupling cascade. MA = methyl acrylate; MMA = methyl methacrylate. [b] The yields reported here are for chromatographically and spectroscopically homogeneous materials. Products exhibited IR, mass, ^1H NMR, and ^{13}C NMR spectra and combustion analysis data in accord with the structures assigned. [c] This product was isolated and characterized as a mixture of diastereomers as indicated in Scheme I.

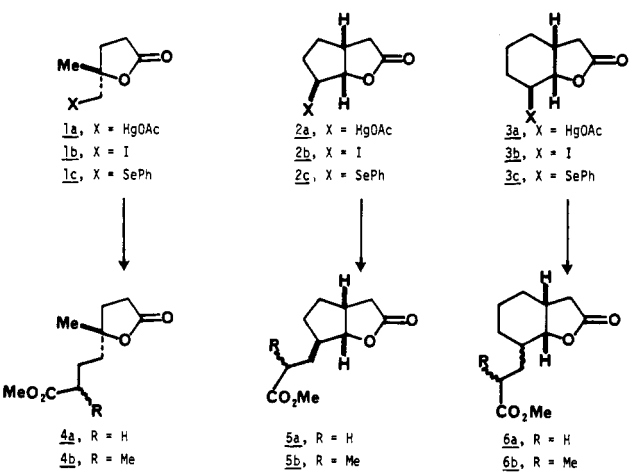
β-carboxy radicals. It was anticipated that production of such radical intermediates in the presence of acrylate trapping agents would give the desired products (4–6) of net carbolactonization (Scheme I).

The results summarized in Table I reflect attempts to optimize the isolated yields of the radical-coupling products **4a,b**, **5a,b**, and **6a,b** from the three respective radical generators for each system. In our experience, a clear trend developed and remained inviolate for the substrates examined. Specifically, the order of effectiveness of the β-carboxy radical precursors (**1a–c**, **2a–c**, **3a–c**) was X = HgOAc < I < SePh. The acetoxymercurio lactones **1a–3a** were uniformly unsatisfying, providing poor yields at best of the carbolactonization products **4–6** when treated with sodium trimethoxyborohydride[5] in methylene chloride containing a large excess of acrylate trapping agent. The major pathway observed for radical precursors **1a–3a** involved hydrogen atom abstraction to give reduction products **1–3**, X = H.

A marked improvement was observed upon investigation of the corresponding iodo lactones **1b–3b** as radical generators. Reproducibly moderate yields (45–65%) of the coupling products **4–6** were obtained when the iodolactones were treated with tri-*n*-butyltin hydride, a catalytic amount of azobis(isobutyronitrile) (ABN), and excess acrylate trapping agent in toluene at 110 °C.[6]

Most effective, however, were the phenylseleno lactones **1c–3c**. These provided the desired carbolactonization products in yields of 68–80% after chromatographic purification. Radical generation from the selenolactones was effected in the presence of excess acrylate in toluene at 110 °C utilizing either *n*-Bu_3SnH/ABN[7] or Ph_3SnH.[7a]

Scheme I



A limitation of this technology is manifest in the rapid loss of stereochemical integrity at developing radical centers. Thus, diastereomeric mixtures will result from systems such as **3**, wherein the radical coupling generates a center of relative asymmetry on a ring system devoid of a controlling steric bias,[8] or from use of a trapping agent such as methyl methacrylate, generating a remote stereo-

(8) As an illustration, the cis-fused bicyclo[3.3.0] system **2** leads to the formation of only the diastereomer **5a**, wherein the radical intermediate has been cleanly trapped from the exo surface. However, the lactone system **3**, wherein the exo–endo differentiation is less pronounced, leads to a 3:1 mixture (determined by ^1H NMR integration at 400 MHz) of exo–endo diastereomers **6a**.

center by hydrogen atom abstraction.

Aside from the caveat cited above, this radical coupling strategy provides a reliable means of carbon–carbon bond formation at a site where conventional electrophile–nucleophile pairing methods are inapplicable. The fact that the phenylseleno lactones serve as the optimal substrates carries the bonus that these are generally stable, readily characterized compounds available in high yield.[4]

The procedures for the conversion of **2a–c** to the product **5a** provide a representative comparison of experimental protocols (see Experimental Section). Refinement and application of this technology will constitute a subsequent report.

Experimental Section

General Procedures. Infrared (IR) spectra were recorded on a Beckman IR 4210 or a Perkin-Elmer 727B spectrometer. Proton magnetic resonance (^{1}H NMR) spectra were recorded at 90 (Varian EM 390) or 400 MHz (Bruker WH-400). Carbon magnetic resonance spectra were recorded on a Varian CFT-20 or an IBM NR-80 spectrometer. Chemical shifts for proton and carbon resonances are reported in ppm (δ) relative to Me_4Si (δ 0.0).

Analytical thin-layer chromatography (TLC) was done on Analtech precoated TLC plates with silica gel GHLF (250-μm layer thickness). Column chromatography was done on Merck silica gel 60 (70–230 mesh ASTM) or Baker silica gel (40–140 mesh).

Methylene chloride was dried by distillation from P_2O_5 and passed through a column of alumina. Toluene was dried by distillation from calcium hydride and storage over sodium. All reactions were run under an atmosphere of dry nitrogen.

Elemental analyses were performed by Robertson Laboratory.

3,3aβ,4,5,6β-Hexahydro-6-(2-(carbomethoxy)ethyl)-2*H*-cyclopenta[*b*]furan-2-one (5a). (A) Production of 5a from the Acetoxymercurio Lactone 2a. To a solution of 0.28 g (2.03 mmol) of sodium trimethoxyborohydride and 1.91 g (22.2 mmol) of methyl acrylate in 7 mL of methylene chloride (CH_2Cl_2) at 0 °C was added 0.608 g (1.58 mmol) of the acetoxymercurio lactone **2a**[2a] in 7 mL of CH_2Cl_2 via syringe pump over a 2-h period. The reaction mixture was allowed to warm to room temperature and was stirred for 12 h. After removal of the solvent in vacuo, the crude product was purified by chromatography on silica gel. Elution with 4:1 hexanes–ethyl acetate gave 66 mg (20%) of the lactone ester **5a** as an oil, homogeneous by TLC and spectroscopic criteria; R_f 0.49 (1:1 hexanes–ethyl acetate); IR ($CDCl_3$) 1770, 1735 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 4.55 (dd, 1 H, J = 2.5, 7.5 Hz), 3.66 (s, 3 H), 3.0–1.1 (m, 12 H); ^{13}C NMR ($CDCl_3$) δ 176.97, 173.17, 89.97, 51.20, 45.59, 37.39, 35.14, 32.07, 31.54, 29.86, 26.90. Distillation [bath temperature 145 °C (0.3 mmHg)] afforded an analytical sample of **5a**.

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.23; H, 7.59. Found: C, 62.43; H, 7.71.

(B) Production of 5a from the Iodo Lactone 2b. To a solution of 100 mg (0.40 mmol) of the iodo lactone **2b**,[9] 0.18 mL (5 equiv) of methyl acrylate and a crystal of ABN in 5 mL of dry toluene at 100 °C was added a solution of 0.105 mL (1 equiv) of tri-*n*-butyltin hydride (Bu_3SnH) in 0.5 mL of toluene via syringe pump over a 5-h period. A second portion (0.18 mL, 5 equiv) of methyl acrylate was then added together with a crystal of ABN. Again, a solution of 0.105 mL (1 equiv) of Bu_3SnH in 0.5 mL of toluene was added dropwise over a 5-h period. The solvent was removed in vacuo and the crude product purified by chromatography on silica gel. Elution with 4:1 hexanes–ethyl acetate gave 46 mg (54%) of the lactone ester **5a**, homogeneous by TLC and spectroscopic criteria.

(C) Production of 5a from the Phenylseleno Lactone 2c. To a solution of 250 mg (0.36 mmol) of the phenylseleno lactone **2c**[4] and 0.80 mL (10 equiv) of methyl acrylate in 2.5 mL of dry toluene at 110 °C was added a solution of 937 mg (3 equiv) of triphenyltin hydride (Ph_3SnH)[7a] in 2.5 mL of toluene over a 12-h period via syringe pump.[10] The solvent was removed in vacuo and the residue chromatographed on 50 g of silica gel. Elution with 4:1 hexanes–ethyl acetate gave 132 mg (70%) of the lactone ester **5a**, homogeneous by TLC and spectroscopic criteria.

Acknowledgment. Grateful acknowledgment is extended to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to Research Corp., and to the National Institutes of Health for their generous support for this research. High-field NMR spectra were obtained through the National Science Foundation Regional NMR Center at the University of South Carolina (Grant CHE 78-18723).

Registry No. **1a**, 82323-00-0; **1b**, 1729-25-5; **1c**, 75826-35-6; **2a**, 82323-01-1; **2b**, 75658-56-9; **2c**, 65234-92-6; **3a**, 82323-02-2; **3b**, 54486-97-4; **3c**, 65291-16-9; **4a**, 82323-03-3; **4b** (isomer 1), 82323-04-4; **4b** (isomer 2), 82323-05-5; **5a**, 82323-06-6; **5b** (isomer 1), 82323-07-7; **5b** (isomer 2), 82372-88-1; **6a** (isomer 1), 82323-08-8; **6a** (isomer 2), 82323-09-9; **6b**, 82337-91-5; methyl acrylate, 96-33-3; methyl methacrylate, 80-62-6.

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(10) More rapid addition of the Ph_3SnH resulted in the formation of increased amounts of the reduction product **2** (X = H) at the expense of **5a**.

Regioselective Aromatic Hydroxylation. An Oxidative Reaction of Arylcopper(I) and Lithium Diarylcopper(I) Ate Complexes

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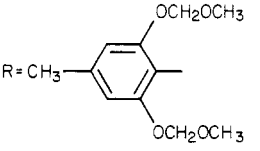
The air oxidation of organocopper compounds (RCu) is a well-documented reaction which leads to dimer as the major product.[1] Preparation of dimers in high yield from aryl-, alkyl-, alkenyl-, alkynyl-, heteroaryl-, and functional alkylcopper compounds have been reported.[2] Whitesides et al.[3] have further shown that high yields of dimer are obtained from air oxidation of copper(I) ate complexes (R_2CuLi) such as primary and secondary alkyl, vinyl, ethynyl, and aryl derivatives. Thus, octane was obtained in 84% yield and biphenyl in 75% yield from air oxidation of lithium di-*n*-butylcuprate and lithium diphenylcuprate, respectively.

We have found that when bis[2,6-bis(methoxymethoxy)-4-methylphenyl]cuprate is prepared and oxidized as shown in eq 1 in the manner described by Whitesides et

$$\mathrm{RH} \rightarrow 2\ \mathrm{RLi} + [\mathrm{ICuP(C_4H_9)_3}]_4 \xrightarrow[-78\ ^\circ\mathrm{C}]{\mathrm{THF}} \mathrm{R_2CuLi} \xrightarrow[-78\ ^\circ\mathrm{C}]{\mathrm{O_2}} \mathrm{ROH + R\text{-}R} \quad (1)$$

$$\mathrm{RLi} + \tfrac{1}{2}\mathrm{CuBr} \xrightarrow[0\ ^\circ\mathrm{C}]{\mathrm{THF}} \mathrm{R_2CuLi}$$

$$\mathrm{RLi} + \mathrm{CuBr} \xrightarrow[0\ ^\circ\mathrm{C}]{\mathrm{THF}} \mathrm{RCu} \xrightarrow[0\ ^\circ\mathrm{C}]{\mathrm{O_2}} \mathrm{ROH + R{-}R} \quad (2)$$



al.[3] for diphenylcuprate, the course of the reaction is changed considerably. The corresponding phenol (ROH

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