Pergamon

Tetrahedron Vol. 50, No. 2, pp. 425-436, 1994

0040-4020/94 $6.00+0.00

0040-4020(93)E0106-P

Palladium-Catalyzed Carbonylative Cyclization via Trapping of Acylpalladium Derivatives with Internal Enolates. Its Scope and Factors Affecting the C-to-O Ratio

Ei-ichi Negishi,* Christophe Copéret, Takumichi Sugihara, Izumi Shimoyama, Yantao Zhang, Guangzhong Wu, and James M. Tour

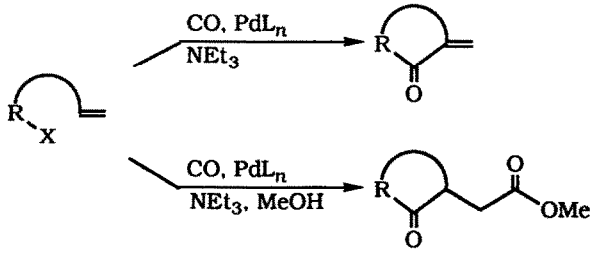
Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, U.S.A.

Abstract: The Pd-catalyzed carbonylative cyclization reaction involving ω-acyl-substituted acylpalladium derivatives can proceed via intramolecular trapping with either C- or O-enolates; the preferential formation of either 5- or 6-membered rings dictates the C-to-O ratio in the trapping with enolates.

INTRODUCTION

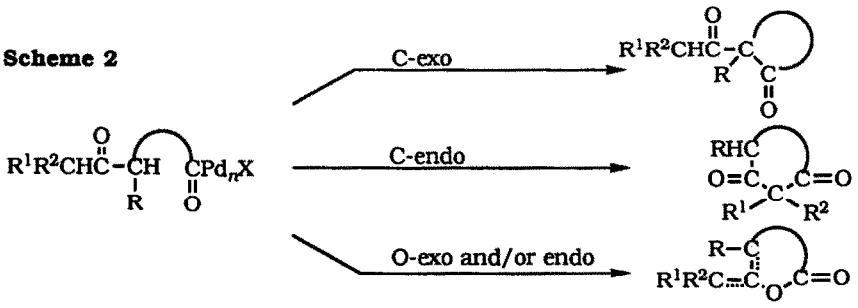
We have previously reported that certain alkenyl,[1] aryl,[1] allyl,[2] and benzyl[3] halides and related derivatives containing an ω-alkenyl group can undergo cyclic acylpalladation with CO in the presence of a palladium-phosphine complex, e.g., $Pd(PPh_3)_4$ or $Cl_2Pd(PPh_3)_2$, and a base, e.g., NEt_3, to give either α-alkylidenecyclanones in the absence of an external proton source or α-methoxycarbonylmethylcyclanones in the presence of MeOH[4] (Scheme 1). In some of these reactions, however, putative acylpalladium intermediates are trapped by internal O-enolates generated *in situ*.[1c, 1e, 3] We have further found that, independent of cyclic acylpalladation of alkenes, certain ω-acyl-substituted acylpalladium derivatives can be trapped by either O-enolates[1f, 5] or C-enolates.[6]

Scheme 1



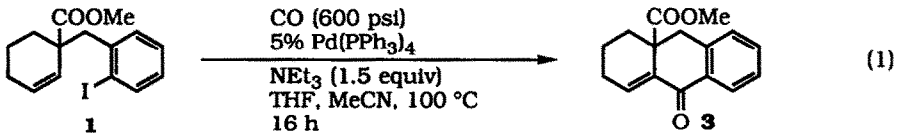
Internal trapping of acylpalladium derivatives by enolates may be classified as (a) C-exo, (b) C-endo, and (c) O (exo and/or endo), as defined in Scheme 2. Each case may be further specified by the size of the ring produced in the reaction. If the C-exo process gives an *n*-membered ring ketone, the competing C-endo and O-exo and/or endo processes would give (*n*+2)-membered rings. In this paper, the scope of these reactions is surveyed with a specific goal of probing the factors affecting the C-to-O ratio in the trapping with enolates.

Scheme 2

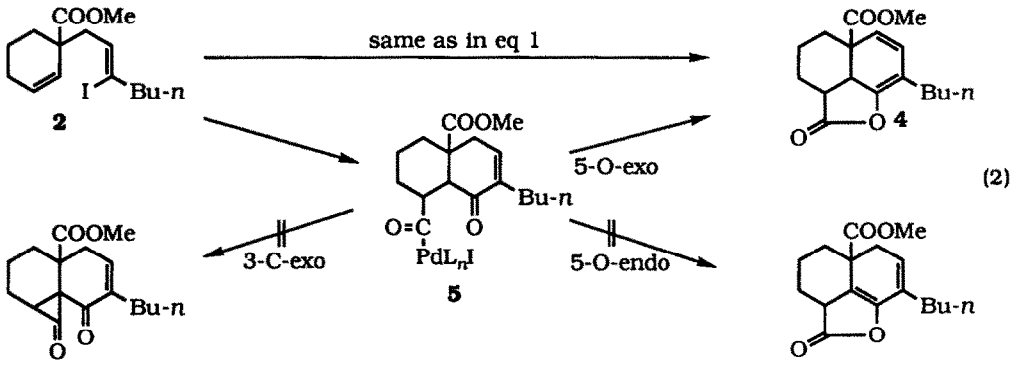


RESULTS AND DISCUSSION

3-C-exo vs. 5-C-endo and/or 5-O. In the cyclic acylpalladation reaction of two closely related iodoalkenes **1** and **2**, prepared via respective allylation and benzylation of methyl 1-cyclohexene-1-carboxylate, using CO (600 psi), 3-5% of $Pd(PPh_3)_4$, NEt_3 (1.5-2 equiv) in THF-MeCN at 100 °C overnight, **1** provided the expected cyclic acylpalladation product **3** (eq 1).[1e] In sharp contrast, **2** gave, under the same conditions, **4** in 67% yield.[1f] The reaction most likely proceeded as shown in eq 2, which may be classified as a 5-O-exo process. Although the structural rigidity of a putative intermediate **5** appears to preclude the 5-C-endo process, the 3-C-exo and 5-O-endo processes may, in principle, take place. However, NMR spectroscopic examination of the crude reaction products did not reveal the presence of compounds corresponding to such processes.

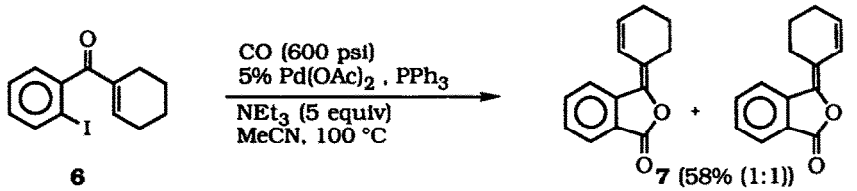


(1)

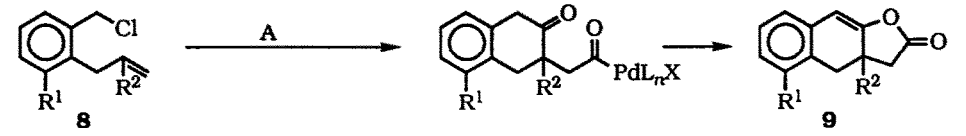


(2)

The 5-O-exo process appears to be facile and widely observable, as indicated by the reactions shown in eqs 2-4. A recent study by Mori, Shibasaki, and their coworkers[7] indicates that **10** gives **11** in high yields (eq 5). The absence of the 5-C-endo products in the reaction of **10** indicates that *the 5-O-exo and/or -endo process overshadows the 5-C-endo process.*



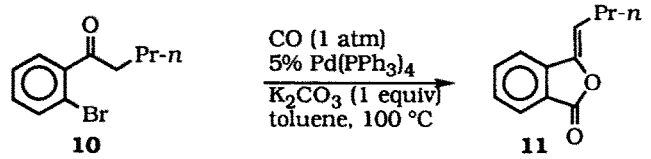
(3)[1c]



(4)[3]

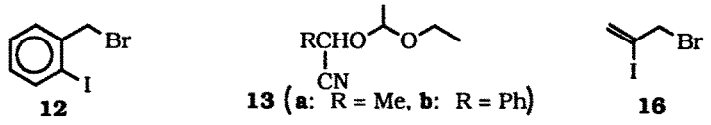
A: CO (600 psi), 5% $Cl_2Pd(PPh_3)_2$ or $Pd(PPh_3)_4$, NEt_3 (1.5-2 equiv), THF-MeCN or DMF, 100 °C, overnight

	R^1	R^2	GLC yield of **9** (%)
a	OMe	H	76
b	H	H	78
c	H	Me	68
d	H	$CH_2CH(COOEt)_2$	47

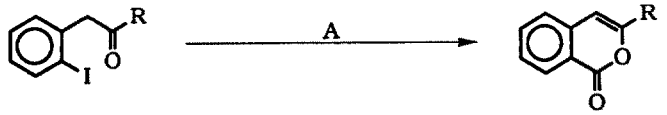


(5)[7]

4-C-exo vs. 6-C-endo and/or 6-O. As test substrates for comparing these cyclization processes, **14**, **15**, **17**, and **18** were prepared as follows. Treatment of **12** with the lithio derivatives of **13a** and **13b** followed by deprotection with H_2SO_4–MeOH and then with aqueous NaOH provided **14** and **15**, while allylation of ethyl acetoacetate and diethyl acetone dicarboxylate with **16**, prepared by successive treatment of propargyl alcohol with Me_3SiI in ether and NBS–Me_2S in CH_2Cl_2,[8] provided **17** and **18**, respectively.



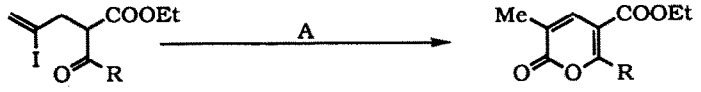
Under the standard reaction conditions (Condition A) using CO (600 psi), NEt_3 (1.5-2 equiv), and 5 mol% of $Cl_2Pd(PPh_3)_2$ or $Pd(PPh_3)_4$ in THF–MeCN or DMF at 100 °C overnight, **14**, **15**, **17**, and **18** were converted to **19-22**, respectively, in the yields shown in eqs 6 and 7. Examination of the reaction mixtures by GLC and NMR spectroscopy failed to detect any of the 4-C-exo and 6-C-endo cyclization products. Here again, *trapping by O-enolates completely overshadows the other potentially competing processes.* All four compounds (**19-22**) are formally the products of the 6-O-endo process in contrast with the 5-O-exo process which predominated in the previous section.



(6)

14: R = Me
15: R = Ph

19: R = Me (77%)
20: R = Ph (89%)

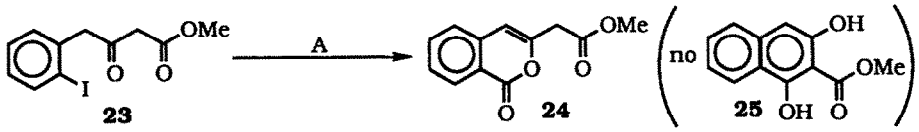


(7)

17: R = Me
18: R = CH_2COOEt

21: R = Me (56%)
22: R = CH_2COOEt (42% GLC)

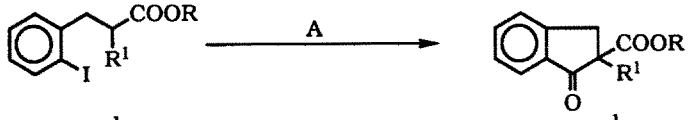
In the reactions of **14** and **17**, the kinetically favored enolates must undergo regioisomerization to induce the 6-O-exo and 6-C-endo processes, the latter of which is not feasible with **15**. In an attempt to observe the 6-C-endo process, we prepared **23** from **12** via cyanation and Reformatsky reaction with $BrZnCH_2COOMe$. The reaction of **23** under the standard conditions (Condition A) gave **24** in 89% yield without producing a detectable amount of **25** (eq 8). The *6-O process, exo or endo, must be strongly favored over the 6-C-endo process.*



(8)

23 **24** **25**

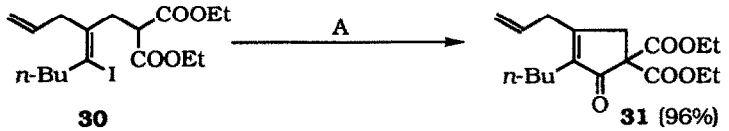
5-C-exo vs. 7-C-endo and/or 7-O. Alkylation of ethyl sodioacetoacetate with **12** provided **26**. Under the standard cyclization conditions (Condition A) using 5 mol % of $Cl_2Pd(PPh_3)_2$ as a catalyst, **26** was converted to **27** in 68% yield. We have failed to obtain any products corresponding to the 7-C-endo and/or 7-O processes. As the results shown in eqs 9-11 indicate, the 5-C-exo process appears to be very favorable and widely observable, irrespective of whether or not the 7-C-endo process is possible.



(9)

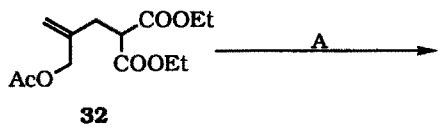
26: R = Et, R^1 = COMe
28: R = Me, R^1 = COOMe
34: R = Et, R^1 = H

27: R = Et, R^1 = COMe (68%)
29: R = Me, R^1 = COOMe (85-90%)



(10)

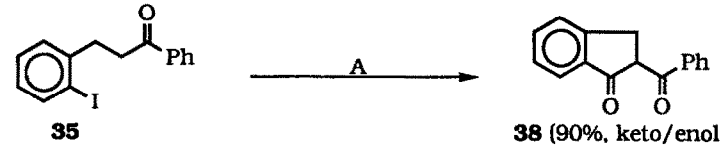
30 **31** (96%)



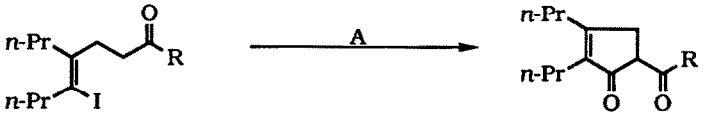
(11)

32 **33** (75%)

The enolates involved in the reactions shown in eqs 9-11 are all extra-stabilized. Attempts to cyclize **34** using NEt_3 or KOBu-*t* as a base have failed. With KOBu-*t* the major product isolated was the corresponding benzoic acid. On the other hand, **35-37** all cyclized to give **38-40**, respectively, under the standard conditions (Condition A) (eqs 12 and 13). The fact that **37** preferentially gives **40** clearly indicates that, regardless of the regiochemistry of enolization, the 5-C-exo process is favored over the other possibilities, i.e., 7-C-endo and 7-O.

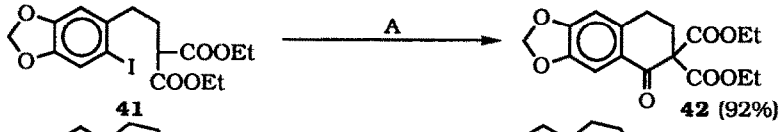


35 **38** (90%, keto/enol = 1/20) (12)

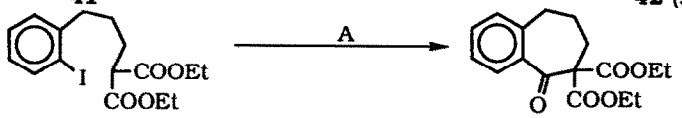


36: R = Ph
37: R = CH_2Ph
39: R = Ph (82%, keto/enol = 2/3)
40: R = CH_2Ph (70%, keto/enol = 2/1) (13)

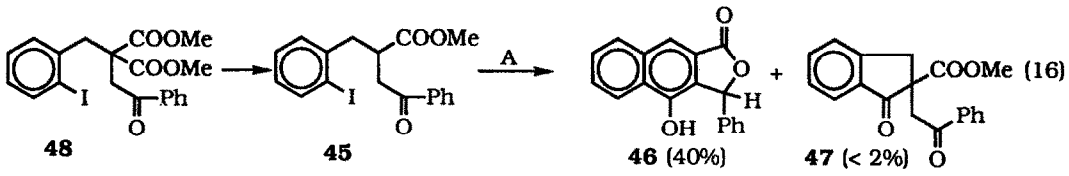
6-C-exo and 7-C-exo Processes. As the results shown in eqs 14-16 indicate, the 6-C-exo and 7-C-exo processes appear to be reasonably facile. In these cases, the 8-O-endo and 9-O-endo processes, respectively, are possible, but they have not been observed. In the reaction of **45** the initial cyclization product must lactonize and aromatize to give **46**. This reaction can, in principle, give the 5-C-exo product **47**, but its yield was < 2%. The corresponding reaction of the diester **48**, which serves as the precursor to **45**, failed to provide a clean reaction product.



41 **42** (92%) (14)



43 **44** (69%) (15)



48 **45** **46** (40%) **47** (< 2%) (16)

The following generalization may be presented on the basis of the results discussed above. Firstly, intramolecular trapping of acylpalladium derivatives by enolates favors the formation of five- and six-membered rings regardless of whether such cyclization reactions involve trapping by C- or O-enolates. Thus, the 5-O-exo, 6-O-endo, 5-C-exo, and 6-C-exo processes are all favorable. The 7-C-exo process is also observable in preference to the potentially competitive 9-O and/or 9-C processes. Secondly, in a competition between O- and C-processes of the same ring size, the O-process is favored over the C-process. All of the examples presented herein obey the above generalization.

EXPERIMENTAL

General Procedures. All reactions were conducted under a dry N_2 atmosphere. Alkyllithiums were titrated with 2-butanol-1,10-phenanthroline. All commercially available reagents were used without further purification unless otherwise noted. THF was distilled from sodium benzophenone ketyl; DMF was distilled from CaH_2. Toluene, pentane and Et_3N were dried over molecular sieves 3A. The preparation of $Pd(PPh_3)_4$[9] and $Cl_2Pd(PPh_3)_2$[10] was performed as reported in the literature. **Carbonylation of Organic Halides.** All Pd-catalyzed carbonylation reactions were carried out in a 22-mL autoclave (Parr Instrument Co.).

Methyl 1-(*Z*-3'-Iodo-2'-hepten-1'-yl)-2-cyclohexene-1-carboxylate (2). To a solution of LDA prepared from *i*-Pr_2NH (1.1 g, 11 mmol) in 20 mL of THF and *n*-BuLi (1.6 M in hexane, 6.25 mL, 10 mmol) at 0 °C were added successively at -78 °C, HMPA (2.15 g, 12 mmol), methyl 1-cyclohexene-1-carboxylate (1.4 g, 10 mmol), and (*Z*)-1-bromo-3-iodo-2-heptene (3.94 g, 13 mmol) in 2 mL of THF. The mixture was stirred at -78 °C for 2 h, quenched with 3 N HCl, extracted with ether, washed with aqueous $NaHCO_3$, and dried over $MgSO_4$. Evaporation and chromatograpy (1/20 ether-pentane) gave 2.65 g (73%) of the title compound: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.89 (t, *J* = 7 Hz, 3 H), 1.4-1.7 (m, 8 H), 1.9-2.5 (m, 6 H), 3.68 (s, 3 H), 5.37 (t, *J* = 7 Hz, 1 H), 5.69 (bd, *J* = 7 Hz, 1 H), 5.83 (dt, *J* = 3, 7 Hz, 1 H); ^{13}C NMR δ 13.89, 19.69, 21.28, 24.90, 30.60, 31.46, 45.24, 46.34, 46.91, 52.03, 112.59, 129.09, 129.42, 129.92, 175.87.

2-Oxo-5a-methoxycarbonyl-8-(*n*-butyl)-2a,3,4,5,5a,8b-hexahydro-2H-naphtho[1,8-bc]furan (4). A mixture of **2** (0.362 g, 1 mmol), $Pd(PPh_3)_4$ (0.034 g, 0.03 mmol), Et_3N (0.202 g, 2 mmol), 1 mL of THF, and 4 mL of MeCN was carbonylated with CO (600 psi) at 100 °C for 24 h. The reaction mixture was quenched with 3 N HCl, extracted with ether, washed with aqueous $NaHCO_3$ and brine. Drying over $MgSO_4$, evaporation, and distillation *in vacuo* gave 0.19 g (67%) of the title compound: bp 110 °C (Kugelrohr, 0.01 mm); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.90 (t, *J* = 7 Hz, 3 H), 1.0-1.5 (m, 7 H), 1.8-2.4 (m, 4 H), 2.95 (dt, *J* = 7, 12 Hz, 1 H), 3.6-3.7 (m, 2 H), 3.78 (s, 3 H), 5.68 (d, *J* = 10 Hz, 1 H), 5.84 (d, *J* = 10 Hz, 1 H); ^{13}C NMR δ 13.87, 20.43, 22.17, 26.14, 27.10, 30.24, 31.28, 37.80, 38.15, 47.18, 52.63, 109.22, 124.44, 126.39, 145.29, 174.82, 176.24; IR (neat) 1814 (s), 1732 (s), 1706 (s), 1648 (w), 1588 (w) cm^{-1}. High resolution MS calcd for $C_{17}H_{22}O_4$: 290.1519; Found: 290.1523.

***o*-Iodophenyl 1-Cyclohexenyl Ketone (6).** This compound was prepared by the reaction of 1-trimethylsilylcyclohexene[11] (2.0 g, 13 mmol), with 2-iodobenzoyl chloride (2.7 g, 10 mmol) in the presence of $AlCl_3$ (1.6 g, 12 mmol) in CH_2Cl_2 (20 mL) at 0 °C for 30 min. The crude material was eluted onto a column of neutral Al_2O_3 with CH_2Cl_2 (10 mL) for 4 h before purifying by column chromatography (silica gel, 5% ethyl acetate in hexane) to afford 1.2 g (39%) of the title compound: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.7 (m, 4 H), 2.1-2.5 (m, 4 H), 6.48 (t, *J* = 4 Hz, 1 H), 7.0-7.5 (m, 3 H), 7.8-7.9 (m, 1 H); IR (neat) 1630 (s), 1420 (s), 1280 (s), 1240 (s) cm^{-1}; MS *m/e* 312.

Carbonylative Cyclization of *o*-Iodophenyl 1-Cyclohexenyl Ketone. A mixture of 0.33 g (1.05 mmol) of *o*-iodophenyl 1-cyclohexenyl ketone, Et_3N (0.51 g, 5 mmol), $Pd(OAc)_2$ (11 mg, 0.05 mmol), and PPh_3 (26 mg, 0.1 mmol) in 5 mL of MeCN was treated with CO (600 psi) at 100 °C, 24 h. The reaction mixture was worked up as described for the preparation of **4**, and distilled (Kugelrohr, 100-105 °C at 0.2 mm) to give 0.13 g (58%) of an essentially 1:1 mixture of the (*E*)- and (*Z*)-isomers of **7**: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.4-2.8 (m, 6 H), 5.95-6.4 (m, 1 H), 6.8-7.0 (m, 1 H), 7.3-8.1 (m, 4 H); IR (neat) 1770 (s), 1660 (s), 1285 (s), 1020 (s) cm^{-1}; High resolution MS calcd for $C_{14}H_{12}O_2$: 212.0838; Found: 212.0835.

***o*-(Chloromethyl)allylbenzenes (8). (a) 3-(Chloromethyl)-2-allylanisole.** 3-Methoxybenzyl alcohol (3.50 g, 25 mmol) was converted in 100% yield to the silyl-protected alcohol (6.3 g) with 4.9 g (32.5 mmol) of *t*-$BuMe_2SiCl$ and and 4.25 g (62 mmol) of imidazole in 50 mL of DMF at 25 °C. To 4.87 g (19.3 mmol) of the protected alcohol in 20 mL of hexane at 25 °C were added successively 9.3 mL (2.3 M, 21 mmol) of *n*-BuLi in hexane (2 h) and 2.0 mL (23 mmol) of allyl bromide (2 days). After the usual workup, the concentrated crude product was dissolved in THF, treated with 21 mL of aqueous Bu_4NF (1.0 M, 21 mmol), and worked up again in the usual manner. Flash chromatography (hexane/Et_2O = 80/20) gave 2.2 g (65%) of 2-allyl-3-methoxybenzyl alcohol. To 0.44 g (3.3 mmol) of NCS in CH_2Cl_2 (0.2 M) at 0 °C were added successively 0.27 mL (3.68 mmol) of Me_2S[8] (10 min, 0 °C) and 412 mg (2.31 mmol) of 2-allyl-3-methoxybenzyl alcohol (-20 °C, 10 min and then 0 °C, 2 h). Usual workup and distillation (Kugelrohr) at 80-85 °C (1.0 mm) gave 0.38 g (90 g) of the title compound: ^1H NMR ($CDCl_3$, Me_4Si) δ 3.56 (dt, *J* = 6, 1.7 Hz, 2 H), 3.82 (s, 3 H), 4.59 (s, 2 H), 4.85-5.05 (m, 2 H), 5.98 (ddt, *J* = 17, 10, 6 Hz, 1 H), 6.87 (bd, *J* = 8 Hz, 1 H), 6.98 (bd, *J* = 8 Hz, 1 H), 7.21 (t, *J* = 8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 29.88, 44.42, 56.07, 111.56, 115.24, 122.94, 127.76, 128.00, 136.97, 137.57, 158.38; IR (neat) 1638 (m), 1586 (s), 1472 (s), 1268 (s), 1066 (s) cm^{-1}. **(b) *o*-(Chloromethyl)allylbenzene. Representative Procedure for the Preparation from *o*-Bromobenzyl Alcohol.** *o*-Bromobenzyl alcohol was protected with dihydropyran and *p*-$TolSO_3H$. After treatment with Mg in refluxing THF using a small amount of MeI as an initiator, allyl bromide was added at 0 °C, and the mixture was stirred at 25 °C for 2 h to give *o*-allylbenzyl alcohol in 82% yield, after deprotection with *p*-$TolSO_3H$. Its treatment with NCS and Me_2S[8] in CH_2Cl_2 for 2 h gave the title compound in 93% yield: ^1H NMR ($CDCl_3$, Me_4Si) δ 3.64 (d, *J* = 6 Hz, 2 H), 4.74 (s, 2 H), 5.0-5.35 (m, 2 H), 6.21 (ddt, *J* = 16, 11, 6 Hz, 1 H), 7.3-7.7 (m, 4 H); IR (neat) 1725 (m), 1640 (m), 1264 (s), 920 (s) cm^{-1}. **(c) *o*-(Chloromethyl)methallylbenzene.** This compound was similarly prepared using methallyl chloride in place of allyl bromide in 81%: ^1H NMR ($CDCl_3$, Me_4Si) δ 1.74 (s, 3 H), 3.46 (s, 2 H), 4.60 (s, 2 H), 7.1-7.4 (m, 4 H); IR (neat) 1718 (m), 1650 (m), 1264 (m), 894 (m) cm^{-1}. **(d) Ethyl 5-(*o*-Chloromethyl)phenyl-2-ethoxycarbonyl-4-methylenepentanoate.** The use of 2-chloromethyl-3-chloro-1-propene provided the title compound: ^1H NMR ($CDCl_3$, Me_4Si) δ 1.25 (t, *J* = 7 Hz, 6 H), 2.67 (d, *J* = 8 Hz, 2 H), 3.50 (s, 2 H), 3.64 (t, *J* = 8 Hz, 1 H), 4.18 (q, *J* = 7 Hz, 4 H), 4.56 (s, 2 H), 4.89 (s, 1 H), 5.27 (s, 1 H), 7.15-7.35 (m, 4 H); IR (neat) 2892 (s), 1732 (s), 1648 (s), 1604 (w) cm^{-1}.

2,3,3a,4-Tetrahydro-2-oxonaphtho[2,3-b]furans (9). (a) 5-Methoxy Derivative (9a).[12] **Representative Procedure.** A mixture of 0.335 g (1.83 mmol) of 3-(chloromethyl)-2-allylanisole (**8a**), 0.38 mL (2.75 mmol) of Et_3N, and 0.07 g (5 mol %) of $Cl_2Pd(PPh_3)_2$ in 4 mL of MeCN was carbonylated (CO, 600 psi) at 100 °C for 36 h. The reaction mixture was poured onto ice-brine, extracted with Et_2O, washed with H_2O, and dried over $MgSO_4$. Evaporation and flash chromatography (hexane/Et_2O = 8/2) afforded 276 mg (70%, 76% by GLC) of the title compound: ^1H NMR ($CDCl_3$, Me_4Si) δ 2.33 (t, *J* = 15.5 Hz, 1 H), 2.46 (dd, *J* = 17.5, 10.5 Hz, 1 H), 2.92 (dd, *J* = 17.5, 9.4 Hz, 1 H), 3.0-3.3 (m, 1 H), 3.60 (dd, *J* = 15.5, 7.1 Hz, 1 H), 3.83 (s, 3 H), 6.08 (d, *J* = 2.5 Hz, 1 H), 6.73 (d, *J* = 8 Hz, 2 H), 7.16 (t, *J* = 8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 27.48, 33.38, 35.03, 55.79, 101.59, 109.46, 119.93, 120.05, 128.29, 135.44, 155.41, 156.83, 174.76; IR (neat) 1802 (s), 1684 (s) cm^{-1}. **(b) 2,3,3a,4-Tetrahydro-2-oxonaphtho[2,3-b]furan (9b).** 78% yield; ^1H NMR ($CDCl_3$, Me_4Si) δ 2.35-3.2 (m, 5 H), 6.08 (s, 1 H), 7.05-7.15 (m, 4 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 33.35, 34.4, 34.8, 101.1, 126.0, 126.4, 127.2, 127.6, 131.7, 133.5, 154.5, 173.8; IR (Nujol) 1805 (s), 1680 (s), 1460 (s), 1380 (s) cm^{-1}; High resolution MS calcd for $C_{12}H_{10}O_2$: 186.0681; Found: 186.0680. **(c) 3b-Methyl Derivative (9c).**

68% yield; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.09 (s, 3 H), 2.63 (s, 2 H), 2.90 (d, *J* = 15 Hz, 1 H), 3.00 (d, *J* = 15 Hz, 1 H), 6.05 (s, 1 H), 7.1-7.2 (m, 4 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 22.11, 37.89, 41.65, 42.88, 100.51, 126.23, 126.39, 127.14, 128.32, 131.31, 132.71, 158.22, 173.55; IR (Nujol) 1806 (s), 1680 (s), 1458 (s), 844 (m), 770 (m) cm^{-1}; High resolution MS calcd for $C_{13}H_{12}O_2$: 200.0837; Found: 200.0835. A byproduct, which has been tentatively identified as 7a-methyl-2,2a,7,7a-tetrahydro-1H-cyclobut[a]inden-2-one, was also obtained in 15% yield. **(d) 3b-Bis(ethoxycarbonyl)ethyl Derivative (9d).** 47% yield; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.1-1.3 (m, 6 H), 2.00 (dd, *J* = 15, 6 Hz, 1 H), 2.19 (dd, *J* = 15, 6 Hz, 1 H), 2.55 (d, *J* = 18 Hz, 1 H), 2.76 (d, *J* = 18 Hz, 1 H), 2.96 (d, *J* = 14 Hz, 1 H), 3.06 (d, *J* = 14 Hz, 1 H), 3.20 (t, *J* = 6 Hz, 1 H), 6.14 (s, 1 H), 7.05-7.25 (m, 4 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.84 (2C), 33.35, 40.07, 40.90, 41.23, 48.33, 61.86 (2C), 102.57, 126.72 (2C), 127.49, 128.36, 130.93, 132.57, 155.73, 168.66, 168.96, 172.83; IR (neat) 1818 (s), 1732 (s), 1678 (s) cm^{-1}; High resoultion MS calcd for $C_{20}H_{22}O_6$: 358.1416; Found: 358.1420. A byproduct identified as 7a-bis(ethoxycarbonyl)ethyl-2,2a,7,7a-tetrahydro-1H-cyclobut[a]inden-2-one was also obtained in 26% yield.

***o*-Iodobenzyl Ketones. (a) *o*-Iodobenzyl Methyl Ketone (14).** Lactonitrile was protected with ethyl vinyl ether.[13] After deprotonation with LDA, it was treated successively with **12** (-78 to 25 °C, 1 h), H_2SO_4-MeOH, and aqueous NaOH[14] to give **14** in 46% yield: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 2.22 (s, 3 H), 3.89 (s, 2 H), 6.9-7.05 (m, 1 H), 7.15-7.4 (m, 2 H), 7.8-7.9 (m, 1 H). **(b) *o*-Iodobenzyl Phenyl Ketone (15).** This compound was prepared as above from α-hydroxyphenylacetonitrile: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 4.46 (s, 2 H), 6.9-7.05 (m, 1 H), 7.2-7.4 (m, 2 H), 7.45-7.65 (m, 3 H), 7.85-7.9 (m, 1 H), 8.0-8.1 (m, 2 H).

3-Methyl-1*H*-2-benzopyran-1-one (19). *o*-Iodobenzyl methyl ketone (0.26 g, 1 mmol), Et_3N (0.15 g, 0.21 mL, 1.5 mmol), MeCN (2 mL), THF (0.5 mL) and $Cl_2Pd(PPh_3)_2$ (0.035 g, 0.05 mmol) were treated with CO (600 psi) at 18 h. After the standard workup, distillation (90-100 °C at 0.1 mm) provided 0.124 g (77%, 84% by GLC) of the title compound[15]: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 2.27 (s, 3 H), 6.25 (s, 1 H), 7.3-8.3 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 19.68, 103.85, 120.30, 125.26, 127.92, 129.85, 135.13, 138.07, 155.02, 163.41; IR (neat) 1724 (s), 1672 (s) cm^{-1}. **3-Phenyl-1*H*-2-benzyopyran-1-one (20).**[15] This compound was prepared in 89% (93% by NMR) from *o*-iodobenzyl phenyl ketone: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 6.92 (s, 1 H), 7.3-7.9 (m, 8 H), 8.2-8.4 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 102.07, 120.83, 125.56, 126.34, 128.48, 129.17, 129.96, 130.31, 132.29, 135.23, 137.87, 154.00, 162.73; IR (Nujol) 1724 (s), 1639 (s), 1069 (s) cm^{-1}. **Ethyl 3,6-Dimethyl-2-oxo-2*H*-pyran-5-carboxylate (21).** Ethyl 2-(2-iodo-2-propenyl)acetoacetate (0.30 g, 1 mmol), prepared from 3-bromo-2-iodopropene and ethyl acetoacetate, Et_3N (0.15 g, 0.21 mL, 1.5 mmol), MeCN (2 mL), THF (0.5 mL) and $Cl_2Pd(PPh_3)_2$ (35 mg, 0.05 mmol) were placed in an autoclave and CO (600 psi) was introduced. The mixture was heated to 100 °C for 18 h. After the standard workup, column chromatography (Et_2O/hexane = 1/1) provided 0.11 g (56%, 76% by GLC) of the title compound: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.37 (t, *J* = 7.1 Hz, 3 H), 2.11 (s, 3 H), 2.63 (s, 3 H), 4.33 (q, *J* = 7.1 Hz, 2 H), 7.63 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.32, 16.29, 20.05, 61.50, 109.54, 122.12, 140.09, 162.77, 164.74, 168.43; IR (neat) 1738 (s), 1709 (s), 1632 (s), 1378 (s), 1261 (s), 1161 (s), 1083 (s), 1025 (s), 778 (s) cm^{-1}; High resolution MS calcd for $C_{10}H_{12}O_4$: 196.0736; Found: 196.0732. **Ethyl 5-Ethoxycarbonyl-3-methyl-2-oxo-2*H*-pyran-6-acetate (22).** This compund was prepared in 40% GLC yield in a manner similar to the preparation of **21** from ethyl 4-ethoxycarbonyl-6-iodo-3-oxo-6-pentenoate: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.27 (t, *J* = 1.3 Hz, 3 H), 4.03 (s, 2 H), 4.20 (q, *J* = 7.2 Hz, 2 H), 4.31 (q, *J* = 7.2 Hz, 2 H), 7.66 (d, *J* = 1.3 Hz, 1 H); ^{13} C NMR ($CDCl_3$) δ 14.19, 16.49, 39.47, 61.83, 111.11, 123.91, 139.53, 162.21, 163.03, 164.16, 168.11; IR (neat) 2990 (s), 1745 (s), 1718 (s), 1084

(s), 1029 (s) cm^{-1}; High resolution MS calcd for $C_{13}H_{16}O_6$: 268.0947; Found: 268.0935.

Methyl 4-(2-Iodophenyl)-3-oxobutanoate (23). 2-Iodophenylacetonitrile was prepared in 84% yield by the reaction of 10.2 g (34.3 mmol) of **12** with NaCN (1.85 g, 37.7 mmol) in 35 mL of DMSO at 70 °C for 2 h. This compound (1.01 g, 4.16 mmol) was refluxed for 10 h in THF with 1.36 g (20.8 mmol) of activated Zn and methyl bromoacetate (1.18 mL, 12.5 mmol) to give, after chromatography (silica gel, hexane/Et_2O = 4/1), 0.99 g (75 %) of methyl 3-amino-4-(2-iodophenyl)-2-butenoate, which was then converted to the title compound in 82% yield by hydrolysis with 3N HCl in THF-H_2O at 50 °C for 30 min, followed by the usual workup and chromatography (silica gel, hexane/Et_2O = 4/1): ^1H NMR ($CDCl_3$, Me_4Si) δ 3.54 (s, 2 H), 3.73 (s, 3 H), 4.01 (s, 2 H), 6.9-7.0 (m, 1 H), 7.2-7.4 (m, 2 H), 7.84 (d, J = 7.8 Hz, 1 H); IR (neat) 1718 cm^{-1}.

1*H*-3-Methoxycarbonylmethyl-2-benzopyran-1-one (24). A mixture of 172 mg (0.54 mmol) of **23**, 19.0 mg (0.03 mmol) of $Cl_2Pd(PPh_3)_2$, and 0.15 mL (1.07 mmol) of Et_3N in 1.0 mL of DMF was stirred at 100 °C under 600 psi of CO for 10 h. After the standard workup, column chromatography (silica gel, hexane/Et_2O = 2/1) gave 105 mg (89%) of the title compound: ^1H NMR ($CDCl_3$, Me_4Si) δ 3.58 (s, 2 H), 3.75 (s, 3 H), 6.47 (s, 1 H), 7.3-7.6 (m, 2 H), 7.6-7.8 (m, 1 H), 8.25 (d, J = 7.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 38.98, 52.45, 106.00, 120.39, 125.42, 128.30, 129.50, 134.79, 136.79, 149.89, 162.14, 168.60; IR (neat) 1734 cm^{-1}; High resolution MS calcd for $C_{12}H_{10}O_4$: 218.0579; Found: 218.0561.

2-Acetyl-2-ethoxycarbonyl-1-indanone (27). This compound was obtained in 68% yield from **26** (prepared in 92% yield from **12** and ethyl acetoacetate) using Et_3N (2 equiv), 5 mol% of $Cl_2Pd(PPh_3)_2$, and MeCN: ^1H NMR ($CDCl_3$, Me_4Si) δ 1.27 (t, J = 7.1 Hz, 3 H), 2.49 (s, 3 H), 3.43 (d, J = 18 Hz, 1 H), 4.07 (d, J = 18 Hz, 1 H), 4.26 (q, J = 7.1 Hz, 2 H), 7.1-7.9 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 13.98, 27.64, 34.12, 62.61, 74.69, 125.50, 126.76, 128.42, 134.60, 136.25, 153.22, 168.71, 196.45, 198.45; IR (neat) 1740 (s), 1718 (s), 1608 (s), 1275 (s), 1250 (s), 1212 (s), 1175 (s) cm^{-1}; High resolution MS calcd for $C_{14}H_{14}O_4$: 246.0892; Found: 246.0897. **2,2-Bis(methoxycarbonyl)-1-indanone (29).** This was prepared in 85-90% yield from **28**: ^1H NMR ($CDCl_3$, Me_4Si) δ 3.81 (s, 6 H), 3.84 (s, 2 H), 7.3-7.9 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 36.39, 53.75, 67.31, 125.74, 126.70, 128.61, 134.55, 136.33, 152.37, 167.86, 195.03; IR (neat) 1725 (s) cm^{-1}; High resolution MS calcd for $C_{13}H_{12}O_5$: 248.0685; Found: 248.0683.

Diethyl 2-[(*Z*)-2'-Allyl-3'-iodo-2'-yl]malonate (30). This compound was prepared from (*Z*)-2-allyl-3-iodo-2-hepten-1-yl bromide (3.17 g, 9.14 mmol), diethyl malonate (2.4 g, 15 mmol) and NaH (0.48 g, 12 mmol) in 96% (3.74 g) yield: ^1H NMR ($CDCl_3$, Me_4Si) δ 0.91 (t, J = 7 Hz, 3 H), 1.27 (t, J = 7 Hz, 6 H), 1.1-1.4 (m, 2 H), 1.49 (quint, J = 7 Hz, 2 H), 2.54 (t, J = 7 Hz, 2 H), 2.86 (d, J = 8 Hz, 2 H), 2.93 (d, J = 6 Hz, 2 H), 3.64 (t, J = 6 Hz, 1 H), 4.19 (q, J = 7 Hz, 4 H), 5.0-5.1 (m, 2 H), 5.6-5.7 (m, 1 H); IR (neat) 1735 (s) cm^{-1}.

2-(*n*-Butyl)-3-(2'-propen-1'-yl)-5,5-bis(ethoxycarbonyl)-2-cyclopenten-1-one (31). This compound was prepared in 96% yield using **30** (0.84 g, 2 mmol), $Cl_2Pd(PPh_3)_2$ (0.041 g, 3 mmol %) and Et_3N (2 equiv): ^1H NMR ($CDCl_3$, Me_4Si) δ 0.89 (t, J = 7 Hz, 3 H), 1.27 (t, J = 7 Hz, 6 H), 1.3-1.5 (m, 4 H), 1.97 (d, J = 7 Hz, 3 H), 2.28 (t, J = 7 Hz, 2 H), 3.27 (q, J = 7 Hz, 2 H), 4.24 (q, J = 7 Hz, 4 H), 6.3-6.5 (dt, J = 16, 7 Hz, 1 H), 6.63 (d, J = 16 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.74, 13.84, 19.22, 22.41, 22.85, 30.55, 35.70, 62.14, 64.57, 125.44, 136.37, 136.88, 162.05, 167.24, 196.72; IR (neat) 1745 (s), 1710 (s), 1640 (s), 1260 (s) cm^{-1}; High resolution MS calcd for $C_{13}H_{26}O_5$: 322.1781; Found: 322.1786

Diethyl 2-(2-Acetoxylmethyl-2-propenyl)malonate (32). This compound was prepared from 2-chloromethylallyl acetate and diethyl malonate in 55 % yield: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.24 (t, J = 7 Hz, 6 H), 2.07 (s, 3 H), 2.66 (d, J = 8 Hz, 2 H), 3.59 (t, J = 8 Hz, 1 H), 4.17 (q, J = 7 Hz, 4 H), 4.52 (s, 2 H), 4.99 (s, 1 H), 5.10 (s, 1 H).

5,5-Bis(ethoxycarbonyl)-3-methyl-2-cyclopenten-1-one (33). ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.29 (t, J = 7 Hz, 6 H), 2.20 (s, 3 H), 3.23 (s, 2 H), 4.25 (q, J = 7 Hz, 4 H), 5.90 (s, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.74, 18.96, 42.12, 62.19, 66.10, 127.55, 166.54, 177.28, 196.59; IR (neat) 1732 (s), 1628 (s) cm^{-1}; High resolution MS calcd for $C_{12}H_{16}O_5$: 240.0997; Found: 240.0991.

3-(*o*-Iodophenyl)-1-phenyl-1-propanone (35). To a suspension of KH (16.6 mmol) in THF (4 mL) were sequentially added at 25 °C a 1 M solution of acetophenone (1.84 mL, 15.8 mmol) in THF (16 mL), a 2 M solution of Et_3B (9.5 mL, 19.75 mmol) in THF, and a solution of *o*-iodobenzyl bromide (23.7 mL, 23.7 mmol) in THF (24 mL).[17] Oxidation with NaOH and 30% H_2O_2 followed by the standard workup and chromatography (pentane/EtOAc = 99/1) yielded 3.0 g (57%) of **35**: mp 49-50 °C; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 3.1-3.4 (m, 4 H), 6.8-7.0 (m, 1 H), 7.2-7.6 (m, 5 H), 7.81 (d, J = 7.4 Hz, 1 H); IR (CCl_4) 1688 (s) cm^{-1}.

(*Z*)-5-Iodo-1-phenyl-4-(*n*-propyl)-4-octen-1-one (36). (*Z*)-5-Iodo-1-phenyl-4-(*n*-propyl)-4-octen-1-ol[18] was prepared in 59% yield by successive treatment of Cp_2ZrCl_2 (3 mmol) in THF with EtMgBr (6 mmol) in THF, 4-octyne (3 mmol), benzaldehyde (3 mmol), and I_2 (6 mmol). The product was then oxidized with PCC to give **36** in 91% yield: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.92 (t, J = 7.4 Hz, 6 H), 1.4-1.6 (m, 4 H), 2.1-2.3 (m, 2 H), 2.4-2.6 (m, 2 H), 2.6-2.7 (m, 2 H), 3.0-3.2 (m, 2 H), 7.4-7.6 (m, 3 H), 7.9-8.1 (m, 2 H).

(*Z*)-6-Iodo-1-phenyl-5-(*n*-propyl)-5-nonen-2-one (37). (*Z*)-6-iodo-1-iodo-5-(*n*-propyl)-5-nonen-2-ol[18] was similarly prepared in 35% yield using phenylacetaldehyde in place of benzaldehyde. Its oxidation with PCC gave **37** in 82% yield: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.8-1.0 (m, 6 H), 1.36 (sex, J = 7.8 Hz, 2 H), 1.52 (sex, J = 7.8 Hz, 2 H), 2.0-2.2 (m, 2 H), 2.3-2.7 (m, 6 H), 3.73 (s, 1 H), 7.1-7.5 (m, 5 H).

2-Benzoyl-1-indanone (38). This compound was prepared in 90% by NMR from 336 mg (1.00 mmol) of **35** using $Cl_2Pd(PPh_3)_2$ (35 mg, 0.05 mmol) in DMF at 125 °C for 20 h under 300 psi of CO. Chromatography on silica gel (pentane/EtOAc = 92/8) yielded 0.19 g (80%) of **38**[19] as a 5:95 mixture of the keto and enol isomeres: mp 94-95 °C; ^{1}H NMR ($CDCl_3$, Me_4Si) δ (enol) 3.81 (s, 2 H), 7.0-8.5 (m, 9 H), 15.1 (bs, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ (enol) 30.50, 110.01, 123.32, 125.91, 127.78, 128.58, 129.05, 131.84, 133.71, 135.02, 138.41, 149.05, 171.41, 196.90; IR (CCl_4) 1638 (s), 1574 (s) cm^{-1}; High resolution MS calcd for $C_{16}H_{12}O_2$: 236.0837; Found: 236.0836. The following signals for the keto isomers were also discernible: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 3.17 (d, J = 7.5 Hz, 1 H), 3.33 (d, J = 7.5 Hz, 1 H), 4.80 (m, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 30.18, 56.87, 105.01.

5-Benzoyl-2,3-di(*n*-propyl)-2-cyclopenten-1-one (39). This compound was similarly prepared in 82% yield (130 mg) from 217 mg (0.59 mmol) of **36** as a 40/60 mixture of the keto and enol isomers of **39**: mp 37-38 °C; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.8-1.1 (m, 6 H), 1.3-1.8 (m, 4 H), 2.16 (t, J = 7.5 Hz, 2 H, enol), 2.32 (t, J = 7.5 Hz, 2 H, enol), 2.4-2.8 (m, 2 H), 2.69 (dd, J = 17.9, 6.5 Hz, 1 Hz, keto), 3.17 (d, J = 17.9 Hz, 1 H, keto), 3.36 (s, 2 H, enol), 4.56 (dd, J = 6.5, 2 Hz, 1 H, keto), 7.3-7.7 (m, 3 H), 7.7-7.9 (m, 2 H, enol), 8.0-8.2 (m, 2 H, keto), 14.45 (bs, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.95, 14.21, 20.75, 21.59, 21.88, 25.21, 25.28, 32.24, 33.05, 35.07, 54.43, 107.73, 127.62, 128.39, 129.71, 130.43, 133.21, 134.81, 140.51, 163.63, 165.25, 174.84, 194.59, 201.01, 202.7; IR (CCl_4) 1770 (s), 1704 (s), 1678 (m),

1642 (w) cm^{-1}; High resolution MS for $C_{18}H_{22}O_2$: 270.1620; Found: 270.1619.

5-(Phenylacetyl)-2,3-di(*n*-propyl)-2-cyclopenten-1-one (40). This compound was similarly prepared in 70% NMR yield (60% isolated) from **37** as a 2/1 mixture of the keto and enol isomers of **40**: ^1H NMR ($CDCl_3$, Me_4Si) δ (keto) 0.7-1.1 (m, 6 H), 1.2-1.6 (m, 4 H), 2.0-2.6 (m, 5 H), 3.03 (d, *J* = 18 Hz, 1 H), 3.7-3.8 (m, 1 H), 4.05 (d, *J* = 15.6 Hz, 1 H), 4.12 (d, *J* = 15.6 Hz, 1 H), 7.1-7.4 (m, 5 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ (keto) 14.03, 14.10, 20.73, 21.71, 25.30, 31.21, 33.09, 49.51, 57.91, 128.65, 128.88, 129.84, 134.02, 137.97, 175.23, 201.73, 202.43; IR (neat) 1722 (s), 1640 (w) cm^{-1}; High resolution MS calcd for $C_{18}H_{22}O_2$: 284.1777; Found: 284.1772. The following signals for the enol isomer are also discernible: ^1H NMR ($CDCl_3$, Me_4Si) δ (enol) 3.02 (s, 2 H), 3.58 (s, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ (enol) 14.15, 14.19, 21.66, 21.90, 32.34, 32.85, 39.95, 108.59, 126.99, 128.81, 128.98, 199.51.

Diethyl 2-(2′-Iodo-4′,5′-methylenedioxyphenylethyl)malonate (41). 2-(2′-Iodo-4′,5′-methylenedioxyphenyl)ethanol was prepared in 56% yield, as described in the literature,[16] and first converted to the corresponding bromide with CBr_4 and PPh_3 in ether in 99% yield and then to **41** in 81% yield: ^1H NMR ($CDCl_3$, Me_4Si) δ 1.29 (t, *J* = 7 Hz, 6 H), 2.15 (dt, *J* = 7, 8 Hz, 2 H), 2.69 (t, *J* = 8 Hz, 2 H), 3.38 (t, *J* = 7 Hz, 1 H), 4.21 (q, *J* = 7 Hz, 4 H), 5.94 (s, 2 H), 6.74 (s, 1 H), 7.20 (s, 1 H); IR (neat) f1732 (s), 1176 (s) cm^{-1}.

2,2-Bis(ethoxycarbonyl)-6,7-methylenedioxy-1-tetralone (42). Under the standard carbonylation conditions (100 °C, 16 h), **41** (0.434 g, 1 mmol) was converted to **42** in 92% (0.307 g) yield: ^1H NMR ($CDCl_3$, Me_4Si) δ 1.18 (t, *J* = 7 Hz, 6 H), 2.61 (t, *J* = 6 Hz, 2 H), 2.79 (t, *J* = 6 Hz, 2 H), 4.17 (q, *J* - 7 Hz, 4 H), 5.90 (s, 2 H), 6.52 (s, 1 H), 7.34 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.75, 25.89, 29.92, 61.96, 66.19, 101.71, 106.49, 107.60, 125.67, 13947, 147.06, 152.48, 167.49, 168.34; IR (neat) 1852 (s), 1728 (s), 1618 (s) cm^{-1}; High resolution MS calcd for $C_{17}H_{18}O_7$; 334.1652; Found: 334.1651.

Diethyl 2-[3-(*o*-Iodophenyl)propyl]malonate (43). This was prepared by alkylation of diethyl malonate with the corresponding alkyl bromide: ^1H NMR ($CDCl_3$, Me_4Si) δ 1.25 (t, *J* = 7 Hz, 6 H), 1.55-1.7 (m, 2 H), 1.9-2.05 (m, 2 H), 2.72 (5, *J* = 8 Hz, 2 H), 3.36 (t, *J* = 7.5 Hz, 1 H), 4.18 (q, *J* = 7 Hz, 4 H), 6.8-6.9 (m, 1 H), 7.15-7.3 (m, 2 H), 7.78 (d, *J* = 7 Hz, 1 H); IR (neat) 1732 (s) cm^{-1}.

7,7-Bis(ethoxycarbonyl)-2,3-benzo-2-cyclohepten-1-one (44). Under the standard carbonylation conditions **43** was converted to **44** in 69% yield: ^1H NMR ($CDCl_3$, Me_4Si) δ 1.21 (t, *J* = 7 Hz, 6 H), 1.95 (quint, *J* = 6 Hz, 2 H), 2.44 (t, *J* = 6 Hz, 2 H), 2.81 (t, *J* = 6 Hz, 2 H), 4.21 (q, *J* = 7 Hz, 4 H), 7.11 (d, *J* = 7 Hz, 1 H), 7.28 (t, *J* = 7 Hz, 1 H), 7.38 (t, *J* = 7 Hz, 1 H), 7.64 (d, *J* = 7 Hz, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.73, 23.11, 29.99, 33.11, 61.98, 70.40, 126.59, 129.22, 130.22, 132.17, 138.32, 138.74, 167.64, 198.69; IR (neat) 1732 (s), 1680 (s) cm^{-1}; High resolution MS calcd for $C_{17}H_{20}O_5$: 304.1310; Found: 304.1309.

4-(*o*-Iodophenyl)-3-(methoxycarbonyl)-1-phenyl-1-butanone (45). Alkylation of **28** with α-bromoacetophenone provided a 78% yield of **48**: ^1H NMR ($CDCl_3$, Me_4Si) δ 3.67 (s, 2 H), 3.74 (s, 2 H), 3.77 (s, 6 H), 6.8-6.9 (m, 1 H), 7.03 (dd, *J* = 7.7, 1.5 Hz, 1 H), 7.1-7.2 (m, 1 H), 7.4-7.5 (m, 2 H), 7.55-7.6 (m, 1 H), 7.80 (dd, *J* = 8.0, 1.0 Hz, 1 H), 7.9-8.0 (m, 2 H). Treatment of **48** (1.40 g, 3 mmol) in DMSO (3 mL) with NaCl (0.16 g, 2.7 mmol) and H_2O (0.16 g, 9.0 mmol) at 155 °C for 10 h followed by the usual workup and chromatography (pentane/EtOAc = 95/5) gave 0.49 g (40% yield) of **45**: ^1H NMR ($CDCl_3$, Me_4Si) δ 3.01 (dd, *J* = 13.5, 8 Hz, 1 H), 3.09 (dd, *J* = 17.0, 3.5 Hz, 1 H), 3.23 (dd, *J* = 13.5, 6.5 Hz, 1 H), 3.4-3.5 (m, 1 H), 3.52 (dd, *J* = 17.0, 9.0 Hz, 1 H), 3.65 (s, 6 H), 6.8-7.0 (m, 1 H), 7.1-7.3 (m, 2 H), 7.4-7.5

(m, 2 H), 7.5-7.6 (m, 1 H), 7.8-7.9 (m, 1 H), 7.9-8.0 (m, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 39.58, 40.98, 42.16, 51.87, 100.84, 127.84, 128.29, 128.50, 130.19, 133.19, 136.36, 139.75, 141.30, 174.90, 197.85; IR (neat) 1736 (s), 1686 (s) cm^{-1}.

4-Hydroxy-3-phenylnaphto[2,3-c]furan-1(3*H*)-one (46). Carbonylation under the standard condition A of **45** (0.44 g, 1.08 mmol) provided a 40% yield of **46**:[20] ^1H NMR (DMSO-d_6, Me_4Si) δ 6.78 (s, 1 H), 7.2-7.5 (m, 5 H), 7.5-7.8 (m, 2 H), 8.0-8.2 (m, 2 H), 8.2-8.4 (m, 1 H); ^{13}C NMR (DMSO-d_6, Me_4Si) δ 81.2, 117.1, 122.2, 124.34, 125.48, 127.10, 127.68, 127.80, 128.02, 128.56, 128.92, 129.82, 134.83, 136.75, 147.69, 170.00; IR (Nujol) 1726, 1638 cm^{-1}.

Acknowledgment. We thank the National Institutes of Health (GM 36792) for support of this research. IS was on leave of absence from NKK Corporation, Japan. TS is a Uehara Memorial Foundation Fellow (1992-93), and CC is a Purdue Research Foundation Fellow (1993-94). We also thank Johnson Matthey for a loan of $PdCl_2$.

REFERENCES AND NOTES

(1) (a) Negishi, E.; Miller, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 6761. (b) Tour, J. M.; Negishi, E. *J. Am. Chem. Soc.* **1985**, *107*, 8289. (c) Negishi, E.; Tour, J. M. *Tetrahedron Lett.* **1986**, *27*, 4869. (d) Negishi, E.; Sawada, H.; Tour, J. M.; Wei, Y. *J. Org. Chem.* **1988**, *53*, 913. (e) Zhang, Y.; O'Connor, B.; Negishi, E. *J. Org. Chem.* **1988**, *53*, 5588. (f) Shimoyama, I.; Zhang, Y.; Wu, G.; Negishi, E. *Tetrahedron Lett.* **1990**, *31*, 2841.

(2) Negishi, E.; Wu, G.; Tour, J. M. *Tetrahedron Lett.* **1988**, *29*, 6745.

(3) Wu, G.; Shimoyama, I.; Negishi, E. *J. Org. Chem.* **1991**, *56*, 6506.

(4) For related non-polymeric acylmetallation reactions of alkenes and alkynes involving CO and Pd or Ni catalysts, see, for example, (a) Chiusoli, G. P.; Merzoni, S.; Mondelli, G. *Tetrahedron Lett.* **1964**, 2777. (b) Brewis, S.; Hughes, P. R. *Chem. Commun.* **1965**, 489. (c) Camps, F.; Coll, J.; Llebaria, A.; Moretó, J. M. *Tetrahedron Lett.* **1988**, *29*, 5811. (d) Oppolzer, W.; Keller, T. H.; Bedoya-Zurita, M.; Stone, C. *Tetrahedron Lett.* **1989**, *30*, 5883.

(5) See also, Roberto, D.; Catellani, M.; Chiusoli, G. P. *Tetrahedron Lett.* **1988**, *29*, 2115.

(6) Negishi, E.; Zhang, Y.; Shimoyama, I.; Wu, G. *J. Am. Chem. Soc.* **1989**, *111*, 8018.

(7) Uozumi, Y.; Mori, E.; Mori, M.; Shibasaki, M. *J. Organomet. Chem.* **1990**, *399*, 93.

(8) Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647.

(9) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.

(10) Jenkins, J. M.; Verkade, J. G. *Inorg. Synth.* **1968**, *11*, 108.

(11) Paquette, L. A.; Fristad, W. E.; Dime, D. S.; Bailey, T. R. *J. Org. Chem.* **1980**, *45*, 3017.

(12) Aristoff, P. A.; Johnson, P.D.; Harrison, A. W. *J. Am. Chem. Soc.* **1985**, *107*, 7967.

(13) Sims, H. J.; Parseghian, H. B.; de Benneville, P. L. *J. Org. Chem.* **1958**, *23*, 724.

(14) Stork, G.; Maldonado, L. *J. Am. Chem. Soc.* **1971**, *93*, 5286.

(15) (a) Hauser, F. M.; Baghdanov, V. M. *J. Org. Chem.* **1988**, *53*, 4676. (b) Duddeck, H.; Kaiser, M. *Spectrochimica Acta* **1985**, *41A*, 913.

(16) Semmelhack, M. F.; Chong, B. P.; Stauffer, R. D.; Rogerson, T. D.; Chong, A.; Jones, L. D. *J. Am. Chem. Soc.* **1975**, *90*, 2507.

(17) Negishi, E.; Idacavage, M. J.; DiPasquale, F.; Silveira, A., Jr. *Tetrahedron Lett.* **1979**, 845.

(18) Copéret, C.; Negishi, E.; Xi, Z.; Takahashi, T. *Tetrahedron Lett.* submitted.

(19) Campbell, R. D.; Gilow, H. M. *J. Am. Chem. Soc.* **1962**, *84*, 1440.

(20) von Sieglitz, A.; Müller, W.; Pomper, K. *Ann. Chem.* **1965**, *682*, 159.

(*Received* 14 *June* 1993)