Palladium-Catalyzed Cross-Carbonylation of Aryl Iodides with Five-Membered Cyclic Olefins

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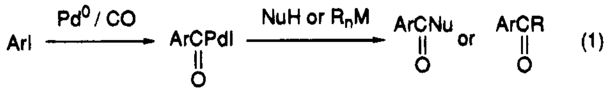
Received July 12, 1995®

Intermolecular cross-carbonylation of aryl iodides with five-membered cyclic olefins such as dihydrofurans and cyclopentene was found to proceed by using a catalyst system of $PdCl_2/PPh_3$ under CO (3–5 atm) in the presence of a tertiary amine. With 2,3- and 2,5-dihydrofurans, 2-aroyl-4,5-dihydro- and 3-aroyl-2,3-dihydrofurans were obtained as the predominant products, respectively, while the reaction of iodobenzene with cyclopentene gave a mixture of three regioisomers of benzoylcyclopentene. The yields of the products were observed to be markedly influenced by the amount of triphenylphosphine added.

Introduction

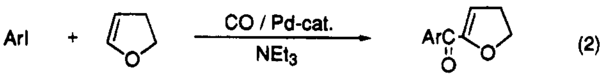
Palladium-catalyzed carbonylation of aryl halides and their synthetic equivalents such as aryl triflates is a highly useful tool for the preparation of various aromatic carbonyl compounds.[1] The reaction involves aroylpalladium species as the common intermediates which react with nucleophiles and organometallic reagents to give the corresponding products (eq 1). Particularly of interest is the Stille type palladium-catalyzed carbonylative coupling reaction of organic halides with organotin compounds ($R_nM = R_4Sn$) which is a valuable synthetic method to unsymmetrical ketones.[1] On the other hand, carbonylation including the addition of the key intermediates to carbon–carbon and carbon–heteroatom multiple bonds, so called acylpalladation, may also be expected to provide effective synthetic routes leading to the carbonyl compounds. For example, intramolecular cyclocarbonylations of 2-alkenoyl-1-iodobenzenes[2] and haloalkenes[3] have been developed. However, intermolecular cross-carbonylation reaction of aryl halides with olefins or cyclic olefins has been less explored.[4] We have recently reported that intermolecular cross-carbonylations of aryl iodides with 1-aryl-2-alkyn-1-ones and *N*-benzylideneamines as the unsaturated species efficiently proceed in the presence of palladium complexes using triethylamine as base to afford 3-aroylfuran[5] and 3-aryl-2,3-dihydro-1*H*-isoindol-1-one derivatives,[6] respectively. Palladium-catalyzed carbonylation reactions of aryl iodides in the presence of γ-hydroxyallenes[7] and 2-alkynyltrifluoroacetanilides[8] to give 1-benzoyl-1-(2-tetrahydrofuryl)ethene and 3-aroylindole derivatives have also been recently described. We report herein our new findings that aryl iodides smoothly undergo cross-carbonylation with three kinds of five-membered cyclic olefins, 2,3- and 2,5-dihydrofurans and cyclopentene, in the presence of palladium catalysts to give the corresponding aryl ketones (eqs 2–4).



$$\mathrm{ArI} \xrightarrow{\mathrm{Pd^0/CO}} \mathrm{Ar\overset{}{\underset{\|}{C}}PdI} \xrightarrow{\mathrm{NuH\ or\ R_nM}} \underset{\mathrm{O}}{\underset{\|}{\mathrm{ArCNu}}} \text{ or } \underset{\mathrm{O}}{\underset{\|}{\mathrm{ArCR}}} \quad (1)$$

Results and Discussion

When iodobenzene (**1a**; 3 mmol) was treated with 2,3-dihydrofuran (**2**; 9 mmol) in the presence of $PdCl_2$ (0.12 mmol) and NEt_3 (3.6 mmol) in benzene under CO (5 atm) at 120 °C for 20 h (eq 2, Ar = Ph), 2-benzoyl-4,5-dihydrofuran (**3a**) was formed in 67% yield based on **1a** used (entry 1 in Table 1). No detectable amounts of 3-benzoylated products and other double-bond regioisomers were formed. While the use of an excess amount of NEt_3 (7.2 mmol) showed no significant influence on the reaction (entry 2), a higher product yield of 76% (entry 3) was obtained by addition of PPh_3 (0.12 mmol; Pd/P = 1.0). Similarly, a combination of $Pd(dba)_2$ (dba = dibenzylideneacetone) with PPh_3 was superior to $Pd(dba)_2$ alone (entry 6 vs 7). However, a further addition of PPh_3 decreased the product yield in both the catalyst systems (entries 4 and 8). In our previous study of the cross-carbonylation with *N*-benzylideneamines,[6] $PdCl_2(dppf)$ (dppf = 1,2-bis(diphenylphosphino)ferrocene) gave favorable results. The use of this catalyst in the present reaction, however, reduced the yield of the ketone (entry 9). While a decrease in the CO pressure to 2 atm showed no significant influence on the reaction, an increase to 10 atm considerably reduced the yield of the ketone (entries 10 and 11). A similar effect was also observed by the use of THF as the solvent (entry 12). These results indicate that the present reaction is very sensitive to the ligands and solvents.



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® Abstract published in *Advance ACS Abstracts*, October 15, 1995.

[1] For example, see: (a) Heck, R. F. *Palladium Reagents in Organic Syntheses*; Academic Press: New York, 1985. (b) Coloquhoun, H. M.; Thompson, D. J.; Twigg, M. V. *Carbonylation*; Plenum Press: New York, 1991.

[2] Negishi, E.; Tour, J. M. *Tetrahedron Lett.* **1986**, *27*, 4869.

[3] Tour, J. M.; Negishi, E. *J. Am. Chem. Soc.* **1985**, *107*, 8289.

[4] A few reactions via intermolecular acylpalladation have been reported. (a) Sen, A.; Lai, T. W. *J. Am. Chem. Soc.* **1982**, *104*, 3520. (b) Pisano, C.; Consiglio, G.; Sironi, A.; Moret, M. *J. Chem. Soc., Chem. Commun.* **1991**, 421. (c) Tanaka, H.; Abdul Hai, A. K. M.; Sadakane, M.; Okumoto, H.; Torii, S. *J. Org. Chem.* **1994**, *59*, 3040.

[5] Okuro, K.; Furuune, M.; Miura, M.; Nomura, M. *J. Org. Chem.* **1992**, *57*, 4754.

[6] Okuro, K.; Inokawa, N.; Miura, M.; Nomura, M. *J. Chem. Res., Synop.* **1994**, 372. *Ibid. J. Chem. Res., Miniprint* **1994**, 2039.

[7] Walkup, R. D.; Gaun, L.; Mosher, M. D.; Kim, S. W.; Kim, Y. S. *Synlett* **1993**, 88.

[8] Arcadi, A.; Cacchi, S.; Carnicell, V.; Marinell, F. *Tetrahedron* **1994**, *50*, 437.

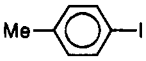
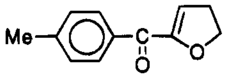
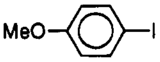
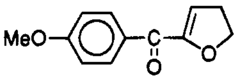
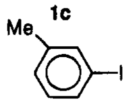
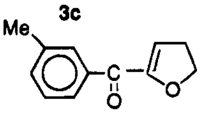
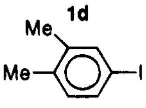
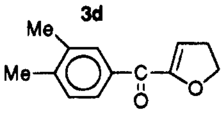
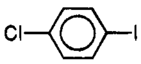
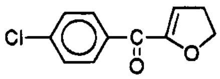
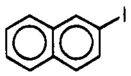
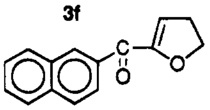
0022-3263/95/1960-7267$09.00/0

Table 1. Cross-Carbonylation of Iodobenzene (1a) with 2,3-Dihydrofuran (2)[a]

entry	Pd-catalyst	yield of **3a** (%)[b]
1	$PdCl_2$	67
2	$PdCl_2$[c]	68
3	$PdCl_2 + 1PPh_3$[c]	76 (73)
4	$PdCl_2 + 2PPh_3$[c]	60
5	$Pd(PPh_3)_4$	10
6	$Pd(dba)_2$[e]	40
7	$Pd(dba)_2 + 1PPh_3$[e]	71
8	$Pd(dba)_2 + 2PPh_3$[e]	64
9	$PdCl_2(dppf)$[f]	43
10	$PdCl_2 + 1PPh_3$[g]	64
11	$PdCl_2 + 1PPh_3$[h]	29
12	$PdCl_2 + 1PPh_3$[i]	49

[a] Reaction conditions: **1a** (3 mmol), **2** (9 mmol), Pd-catalyst (0.12 mmol), and NEt_3 (3.6 mmol) in C_6H_6 (5 mL) under CO (5 atm) at 120 °C for 20 h. [b] Determined by GLC based on amount of **1a** used. [c] NEt_3 (7.2 mmol). [d] Isolated yield. [e] dba = dibenzylideneacetone. [f] dppf = 1,2-bis(diphenylphosphino)ferrocene. [g] Under CO(2 atm). [h] Under CO (10 atm). [i] In THF (5 mL).

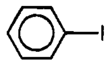
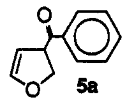
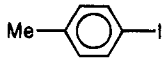
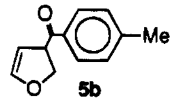
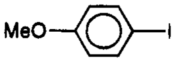
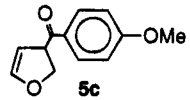
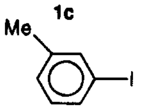
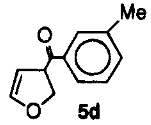
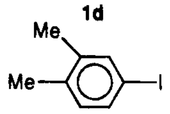
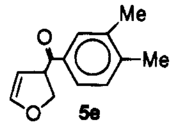
Table 2. Cross-Carbonylation of Aryl Iodides 1 with 2[a]

ArI	product, % yield[b]	
 **1b**	 **3b**	60
 **1c**	 **3c**	66
 **1d**	 **3d**	65
 **1e**	 **3e**	63
 **1f**	 **3f**	38
 **1g**	 **3g**	40

[a] Reaction conditions: **1** (3 mmol), **2** (9 mmol), $PdCl_2$ (0.12 mmol), PPh_3 (0.12 mmol), and NEt_3 (7.2 mmol) in C_6H_6 (5 mL) under CO (5 atm) at 120 °C for 15–20 h. [b] Isolated yield.

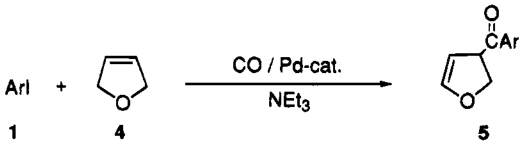
The results of the cross-carbonylations of aryl iodides **1b–g** with **2** using $PdCl_2/PPh_3$ (1:1) are summarized in Table 2. From the reactions the corresponding 2-aroyl-4,5-dihydrofurans **3b–g** were isolated in 38–66% yields.

Table 3. Cross-Carbonylation of Aryl Iodides 1 with 2,5-Dihydrofuran (4)[a]

ArI	product, % yield[b,c]	
 **1a**	 **5a**	64 (5)
		51 (6)[d]
		22 (2)[e]
 **1b**	 **5b**	74 (7)
 **1c**	 **5c**	67 (5)
 **1d**	 **5d**	73 (5)
 **1e**	 **5e**	81 (5)

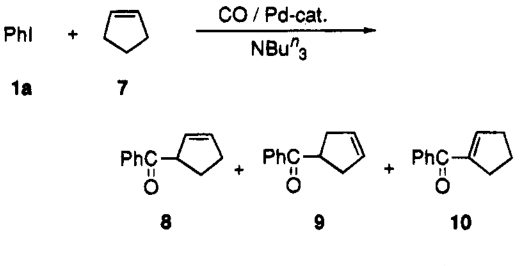
[a] Reaction conditions: **1** (3 mmol), **4** (9 mmol), $PdCl_2$ (0.12 mmol), PPh_3 (0.12 mmol), and NEt_3 (3.6 mmol) in C_6H_6 (5 mL) under CO (5 atm) at 115–120 °C for 20 h. [b] Determined by GLC based on amount of **1** used. [c] Value in parentheses indicates yield of accompanied 3-aroylfurans **6a–e**. [d] Without PPh_3. [e] $Pd(PPh_3)_4$ (0.12 mmol) was used in place of $PdCl_2/PPh_3$.

The reaction of **1a** with 2,5-dihydrofuran (**4**) was also examined under similar conditions employed for the reaction with **2** (eq 3 and Table 3). In this case, 3-benzoyl-2,3-dihydrofuran (**5a**) was formed as the benzoylation product. The catalyst system of $PdCl_2/PPh_3$ (1:1) was also found to be optimal for the reaction to occur as it was for **2** (see entry 3 in Table 1). Other aryl iodides, **1b–e**, also reacted with **4** in the presence of the catalyst to give the corresponding 3-aroyl-2,3-dihydrofurans **5** in 67–81% yields. Note that in each case, a small amount of 3-aroylfuran (**6**; 5–7%), which may have been produced by the dehydrogenation of **5**, was detected.



1 **4** **5** (3)

When cyclopentene (**7**) was allowed to react with **1a** in the presence of palladium catalysts (eq 4 and Table 4), a mixture of double-bond regioisomers (**8–10**) was formed in the reaction. In this reaction, $PdCl_2(PPh_3)_2$ and $Pd(PPh_3)_4$ were more effective than $PdCl_2/PPh_3$ (1:1) (entries 2 and 3 vs 1). This is in contrast to the reactions with dihydrofurans **2** and **4**, where the latter catalyst system was more effective. When the reaction was carried out at 100 °C, the ketones **8** and **9** were formed in a low combined yield (entry 5). At 140 °C, the product ratio of **10** to **8** + **9** increased (entry 6). The effect of CO pressure was similar to that observed in the reaction using **2**; a higher pressure (10 atm) reduced the total ketone yield (entry 8), while a low pressure (3 atm)



1a **7**

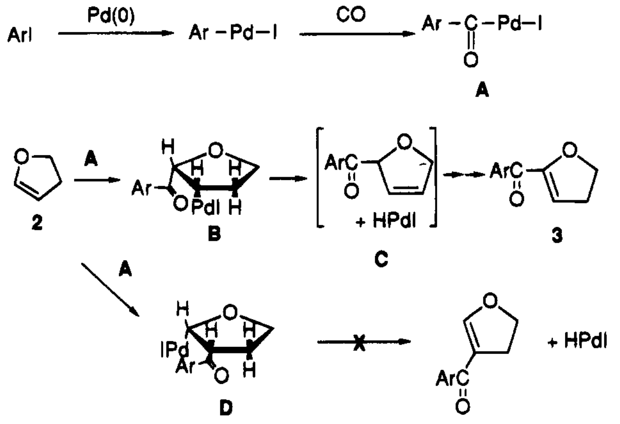
8 **9** **10** (4)

Table 4. Cross-Carbonylation of 1a with Cyclopentene (7)

entry	Pd-catalyst	yield of **8** + **9** + **10** (%)[b]	(**8** + **9**):**10**
1	$PdCl_2$ + 1PPh_3	39	69:31
2	$PdCl_2(PPh_3)_2$	56	71:29
3	$Pd(PPh_3)_4$	57	75:25
4	$Pd(PPh_3)_4$ + 1PPh_3	25	80:20
5	$Pd(PPh_3)_4$[c]	10	100:0
6	$Pd(PPh_3)_4$[d]	56	25:75
7	$Pd(PPh_3)_4$[e]	54	59:41
8	$Pd(PPh_3)_4$[f]	38	84:16
9	$Pd(PPh_3)_4$[e,g]	70	46:54

[a] Reaction conditions: **1a** (1.5 mmol), **7** (4.5 mmol), Pd-catalyst (0.06 mmol), and $NBu^n{}_3$ (2.1 mmol) in C_6H_6 (4 mL) under CO (5 atm) at 120 °C for 20 h. [b] Determined by GLC based on amount of **1a** used. [c] At 100 °C. [d] At 140 °C. [e] Under CO (3 atm). [f] Under CO (10 atm). [g] **7** (7.5 atm).

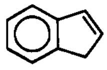
Scheme 1



showed no significant effect (entry 7). An increase in the amount of **7** used from 3 to 5 equiv improved the ketone yield (entry 9).

Additional cyclic olefins (**11**–**14**) were also examined as the substrates. However, none of these olefins were as efficient as **2**, **4**, and **7**: in the cases of **12** and **13**, small amounts of benzoylated products (<5%) were detected by GC–MS and no traces of the desired products were formed using **11** and **14**. The sharp contrast of the result with **7** to that with **11** may provide information concerning the reactivity of intermediary benzoylpalladium species; it is also known that **7** is relatively more strained than **11**.[9]


11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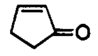
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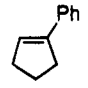
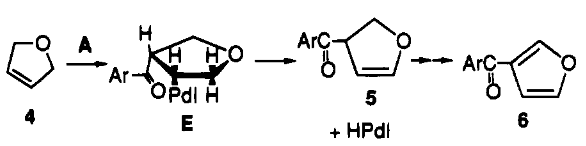

14

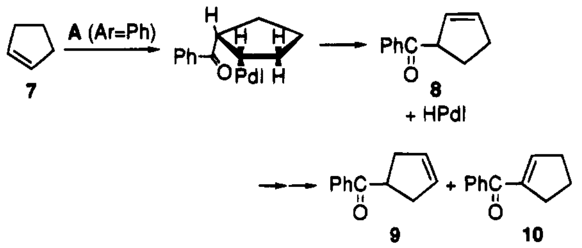
A possible mechanism for the present intermolecular cross-carbonylations of aryl iodides **1** with 2,3-dihydrofuran (**2**) is illustrated in Scheme 1, in which neutral ligands are omitted.

Oxidative addition of **1** to palladium(0) species generated *in situ* followed by CO insertion may give aroylpalladium intermediate (**A**).[1] *Syn*-addition of **A** to **2** gives intermediate **B**, and the subsequent *syn*-elimination of HPdI may afford compound **C**. Under the influence of HPdI[10] and/or the base employed, isomerization of **C** may occur to give **3** which is probably stabilized by conjugation of both the lone pair of the oxygen atom and the carbonyl group with the C–C double bond. It has been reported that *E*-*β*-aroylated vinyl ethers are exclusively produced in the palladium-catalyzed aroylation of acyclic alkyl vinyl ethers with aroyl chlorides.[11] On the other hand, active acyl chlorides are known to react at the *β*-position of vinyl ethers, irrespective of the substrate structures.[12] In the present reaction, however, the corresponding 3-aroylated product was not produced. One of the possible reasons for this is due to the fact that there is no *cis*-hydrogen to the palladium atom when *syn*-addition of **A** to **2** occurs to give 3-aroylated intermediate **D**. However, it is not definitive whether the reaction of **A** with **2** to **D** is reversible or not. If it is irreversible, the formation of **D** would be responsible for uncharacterizable products. It should be noted that while similar α-regioselectivity has been reported in the palladium-catalyzed arylation of 2,3-dihydrofuran,[13] the reaction with acyclic vinyl ethers is known to depend on the electronic nature of the aryl moieties employed.[14]

Scheme 2



Scheme 3



When 2,5-dihydrofuran (**4**) was used in place of **2**, dihydrofuran **5** may be produced as the primary product (Scheme 2). In this case, **5** may be rather stable under the reaction conditions because of the conjugation of the lone pair of the oxygen atom with the C–C double bond, although a small part of **5** was appeared to be dehydrogenated to give 3-aroylfurans **6** (Table 3). It should be noted that **5** could be completely converted to **6** by heating it in the presence of a Pd/C catalyst (see the Experimental Section). Considering the fact that the Friedel–Crafts acylation of furan generally takes place at the 2-position, the present method seems to be useful as a route to 3-aroylfurans.

The reaction with cyclopentene (**7**) may proceed by a mechanism similar to that of dihydrofurans to give **8** as the primary product and a part of this product isomerizing to **9** and **10** (Scheme 3). The fact that the product ratio of **10**/(**8** + **9**) increased at higher temperature indicates that the conjugated isomer **10** is thermodynamically more stable than other isomers. On the other hand, an increase in the ratio of **10**/(**8** + **9**) was also observed when the amount of **7** added was increased. However, the role of the excess olefin is not clear.

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(9) James, D. E.; Stille, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 1810.

(10) Heck, R. F. *J. Am. Chem. Soc.* **1971**, *93*, 6896.

(11) Andersson, C.-M.; Hallberg, A. *J. Org. Chem.* **1988**, *53*, 4257.

(12) Effenberger, F.; Maier, R.; Schönwälder, K.-H.; Ziegler, T. *Chem. Ber.* **1982**, *115*, 2766.

(13) (a) Larock, R. C.; Gong, W. H. *J. Org. Chem.* **1990**, *55*, 407. (b) Ozawa, F.; Kubo, A.; Hayashi, T. *J. Am. Chem. Soc.* **1991**, *113*, 1417.

(14) Daves, G. D.; Hallberg, A. *Chem. Rev.* **1989**, *89*, 1433.

Experimental Section

^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, in $CDCl_3$ as solvent. MS data were obtained by EI. GLC analysis was carried out using a silicon OV-17 column (i.d. 2.6 mm × 1.5 m) or with a CBP-1 capillary column (i.d. 0.5 mm × 25 m).

The complexes $Pd(PPh_3)_4$,[1] $Pd(dba)_2$,[15] $PdCl_2(dppf)$,[16] and $PdCl_2(PPh_3)_2$[1] were prepared by the methods reported previously. Aryl iodides **1c**,[17] **1e**,[18] and **1g**[18] and phenylcyclopentene (**14**)[19] were prepared according to the published procedures. Other starting materials were commercially available. Solvents were purified by standard methods before use.

Cross-Carbonylation of Aryl Iodides 1 with 2,3-Dihydrofuran (2). A mixture of **1** (3 mmol), **2** (0.68 mL, 9 mmol), $PdCl_2$ (21 mg, 0.12 mmol), PPh_3 (31 mg, 0.12 mmol), NEt_3 (1.0 mL, 7.2 mmol), and benzene (5 mL) was placed in a 50 mL stainless steel autoclave with a glass tube. Then, carbon monoxide (5 atm at room temperature) was charged, and the mixture was magnetically stirred at 120 °C for 20 h. After cooling, the reaction mixture was poured into water, extracted with ether, and dried over sodium sulfate. Product **3** was isolated by column chromatography on silica gel using hexane–methylene chloride as eluant.

2-Benzoyl-4,5-dihydrofuran (3a): oil; bp 115–120 °C/3 mmHg; ^{1}H NMR δ 3.06 (dt, 2H, J = 1.5, 9.8 Hz), 4.64 (t, 2H, J = 9.8 Hz), 7.15 (t, 1H, J = 1.5 Hz), 7.41–7.44 (m, 2H), 7.48–7.53 (m, 1H), 7.65–7.67 (m, 2H); ^{13}C NMR δ 28.16, 73.52, 119.42, 127.99, 128.38, 131.39, 140.05, 160.82, 191.12; MS *m/z* 174 (M^+). Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.83; H, 5.80. Found: C, 75.55; H, 5.70.

2-(4-Methylbenzoyl)-4,5-dihydrofuran (3b): mp 92–94 °C; ^{1}H NMR δ 2.40 (s, 3H), 3.04 (dt, 2H, J = 1.5, 9.8 Hz), 4.63 (t, 2H, J = 9.8 Hz), 7.15 (t, 1H, J = 1.5 Hz), 7.22–7.26 (m, 2H), 7.57–7.59 (m, 2H); MS *m/z* 188 (M^+). Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.56; H, 6.44. Found: C, 76.36; H, 6.40.

2-(4-Methoxybenzoyl)-4,5-dihydrofuran (3c): mp 85–86 °C; ^{1}H NMR δ 3.03 (dt, 2H, J = 1.5, 9.8 Hz), 3.85 (s, 3H), 4.62 (t, 2H, J = 9.8 Hz), 6.92 (d, 2H, J = 8.8 Hz), 7.14 (t, 1H, J = 1.5 Hz), 7.68 (d, 2H, J = 8.8 Hz); MS *m/z* 204 (M^+). Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.56; H, 5.93. Found: C, 70.52; H, 5.90.

2-(3-Methylbenzoyl)-4,5-dihydrofuran (3d): oil; bp 125–130 °C/3 mmHg; ^{1}H NMR δ 2.39 (s, 3H), 3.02 (dt, 2H, J = 1.5, 9.8 Hz), 4.62 (t, 2H, J = 9.8 Hz), 7.15 (t, 1H, J = 1.5 Hz), 7.29–7.31 (m, 2H), 7.43–7.47 (m, 2H); MS *m/z* 188 (M^+). Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.56; H, 6.44. Found: C, 76.44; H, 6.33.

2-(3,4-Dimethylbenzoyl)-4,5-dihydrofuran (3e): mp 86–87 °C; ^{1}H NMR δ 2.30 (s, 6H), 3.04 (dt, 2H, J = 1.5, 9.8 Hz), 4.63 (t, 2H, J = 9.8 Hz), 7.15 (t, 1H, J = 1.5 Hz), 7.17 (d, 1H, J = 7.8 Hz), 7.41 (dd, 1H, 1.5, 7.8 Hz), 7.46 (d, 1H, J = 1.5 Hz); MS *m/z* 202 (M^+). Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.19; H, 6.99. Found: C, 77.18; H, 6.99.

2-(4-Chlorobenzoyl)-4,5-dihydrofuran (3f): mp 120–122 °C; ^{1}H NMR δ 3.04 (dt, 2H, J = 2.0, 9.8 Hz), 4.65 (t, 2H, J = 9.8 Hz), 7.14 (t, 1H, J = 1.5 Hz), 7.39–7.43 (m, 2H), 7.60–7.63 (m, 2H); MS *m/z* 208, 210 (M^+). Anal. Calcd for $C_{11}H_9O_2Cl$: C, 63.32; H, 4.36; Cl, 16.99. Found: C, 63.36; H, 4.29; Cl, 17.14.

2-(2-Naphthoyl)-4,5-dihydrofuran (3g): oil; bp 185–200 °C/3 mmHg; ^{1}H NMR δ 2.98 (dt, 2H, J = 1.5, 9.8 Hz), 4.55 (t, 2H, J = 9.8 Hz), 7.12 (t, 1H, J = 1.5 Hz), 7.41–7.49 (m, 2H), 7.66–7.68 (m, 1H), 7.76–7.82 (m, 3H), 8.06 (s, 1H); MS *m/z* 224 (M^+). Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.33; H, 5.40. Found: C, 79.97; H, 5.38.

Cross-Carbonylation of Aryl Iodides 1 with 2,5-Dihydrofuran (4). The reaction conditions were identical with those shown above for **2**. GC and GC–MS analyses of the product mixtures indicated formation of 3-aroyl-2,3-dihydrofurans **5** (64–81%) along with 3-aroylfurans **6** (5–7%). Although products **5** were isolated by column chromatography, they were contaminated by **6**. The structure of **5** was confirmed by NMR analysis of this fraction. Full characterization of the products was made by converting **5** to **6** via dehydrogenation. The dehydrogenation reaction was carried out by heating each product mixture obtained by a separate run in 1-methylnaphthalene (1.0 g) in the presence of a commercial 5% Pd/C catalyst (191 mg) at 200 °C under a slow stream of nitrogen. After complete conversion (monitored by GC; ca. 3 h), compound **6** was isolated by column chromatography on silica gel using hexane–methylene chloride as eluant. The yields of the purified products were 27–35%.

3-Benzoyl-2,3-dihydrofuran (5a): oil; ^{1}H NMR δ 4.49 (dd, 1H, J = 8.8, 9.0 Hz), 4.65–4.70 (m, 1H), 4.98 (dd, 1H, J = 8.8, 9.0 Hz), 5.04 (t, 1H, J = 2.4 Hz), 6.42 (t, 1H, J = 2.4 Hz), 7.48–7.61 (m, 3H), 7.97–7.99 (m, 2H); MS *m/z* 174 (M^+).

3-(4-Methylbenzoyl)-2,3-dihydrofuran (5b): oil; ^{1}H NMR δ 2.43 (s, 3H), 4.48 (dd, 1H, J = 8.8, 9.0 Hz), 4.66 (m, 1H), 4.97 (dd, 1H, J = 8.8, 9.0 Hz), 5.03 (t, 1H, J = 2.4 Hz), 6.41 (t, 1H, J = 2.4 Hz), 7.37–7.40 (m, 2H), 7.76–7.79 (m, 2H); MS *m/z* 188 (M^+).

3-(4-Methoxybenzoyl)-2,3-dihydrofuran (5c): oil; ^{1}H NMR δ 3.88 (s, 3H), 4.48 (dd, 1H, J = 8.8, 9.0 Hz), 4.61–67 (m, 1H), 4.97 (dd, 1H, J = 8.8, 9.0 Hz), 5.02 (t, 1H, J = 2.4 Hz), 6.41 (t, 1H, J = 2.4 Hz), 6.97 (d, 2H, J = 8.9 Hz), 7.97 (d, 2H, J = 8.9 Hz); MS *m/z* 204 (M^+).

3-(3-Methylbenzoyl)-2,3-dihydrofuran (5d): oil; ^{1}H NMR δ 2.43 (s, 3H), 4.48 (dd, 1H, J = 8.8, 9.0 Hz), 4.66 (m, 1H), 4.97 (dd, 1H, J = 8.8, 9.0 Hz), 5.02 (t, 1H, J = 2.4 Hz), 6.41 (t, 1H, J = 2.4 Hz), 7.28–7.30 (m, 2H), 7.87-7.89 (m, 2H); MS *m/z* 188 (M^+).

3-(3,4-Dimethylbenzoyl)-2,3-dihydrofuran (5e): oil; ^{1}H NMR δ 2.33 (s, 6H), 4.48 (dd, 1H, J = 8.8, 9.0 Hz), 4.46 (m, 1H), 4.63–4.68 (m, 1H), 4.97 (dd, 1H, J = 8.8, 9.0 Hz), 4,99 (t, 1H, J = 2.4 Hz), 7.26 (s, 1H), 7,69–7.76 (m, 2H); MS *m/z* 202 (M^+).

3-Benzoylfuran (6a): mp 32–33 °C (lit.[20] mp 39–40 °C); ^{1}H NMR δ 6.92 (d, 1H, J = 2.0 Hz), 7.51 (d, 1H, J = 2.0 Hz), 7.47–7.51 (m, 2H), 7.57–7.61 (m, 1H), 7.85–7.88 (m, 2H), 7.93 (d, 1H, J = 1.5 Hz); MS *m/z* 172 (M^+). Anal. Calcd for $C_{11}H_8O_2$: C, 76.73; H, 4.68. Found: C, 76.68; H, 4.76.

3-(4-Methylbenzoyl)furan (6b): oil; ^{1}H NMR δ 2.44 (s, 3H), 6.90 (d, 1H, J = 2.0 Hz), 7.28 (t, 2H, J = 7.8 Hz), 7.50 (t, 1H, J = 1.7 Hz), 7.76–7.79 (m, 2H), 7.92 (d, 1H, J = 1.5 Hz); MS *m/z* 186 (M^+). Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.02; H, 5.53.

3-(4-Methoxybenzoyl)furan (6c): mp 72–74 °C (lit.[21] mp 75–77 °C); ^{1}H NMR δ 3.89 (s, 3H), 6.89 (t, 1H, J = 1.0 Hz), 6.97–6.99 (m, 2H), 7.50 (t, 1H, J = 1.7 Hz), 7.88–7.90 (m, 2H), 7.92 (t, 1H, J = 1.2 Hz); MS *m/z* 202 (M^+). Anal. Calcd for $C_{12}H_{10}O_3$: C, 71.28; H, 4.99. Found: C, 71.11; H, 5.02.

3-(3-Methylbenzoyl)furan (6d): oil; ^{1}H NMR δ 2.43 (s, 3H), 6.91 (d, 1H, J = 1.9 Hz), 7.37–7.39 (m, 2H), 7.51 (t, 1H, J = 1.5 Hz), 7.63–7.67 (m, 2H), 7.92 (d, 1H, J = 1.0 Hz); MS *m/z* 186 (M^+). Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.01; H, 5.41.

3-(3,4-Dimethylbenzoyl)furan (6e): mp 44–45 °C; ^{1}H NMR δ 2.34 (s, 3H), 2.34 (s, 3H), 6.90 (d, 1H, J = 2.0 Hz), 7.25 (t, 1H, J = 6.5 Hz), 7.50 (t, 1H, J = 1.7 Hz), 7.60 (dd, 1H, J = 2.0, 7.8 Hz), 7.65 (s, 1H), 7.92 (d, 1H, J = 1.5 Hz); MS *m/z* 200 (M^+). Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 78.03; H, 6.09.

Cross-Carbonylation of Iodobenzene (1a) with Cyclopentene (7). The reaction of **1a** (306 mg, 1.5 mmol) with **7** (0.4 mL, 4.5 mmol) was carried out in the presence of $Pd(PPh_3)_4$ (64 mg, 0.06 mmol) and NBu^n_3 (0.5 mL, 2.1 mmol) in benzene (4 mL) under carbon monoxide (5 atm) at 120 °C for 20 h.

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(15) (a) Conard, C. R.; Dolliver, M. A. *Organic Syntheses*; Wiley: New York, 1943; Collect. Vol. II, p 167. (b) Ukai, T.; Kawazura, H.; Ishii, Y. *J. Organomet. Chem.* **1974**, *65*, 253.

(16) Hayashi, T.; Kotani, M.; Kumada, M. *Tetrahedron Lett.* **1979**, 1871.

(17) Takagi, K.; Hayama, N.; Okamoto, T. *Chem. Lett.* **1978**, 191.

(18) Dains, F. B.; Eberly, F. *Organic Syntheses*; Wiley: New York, 1943; Collect. Vol. II, p 355.

(19) Muskat, I. E.; Herrman, M. *J. Am. Chem. Soc.* **1931**, *53*, 252.

(20) Grünanger, P.; Mantegani, A. *Gazz. Chim. Ital.* **1959**, *89*, 913.

(21) Benassi, R.; Folli, U.; Iarossi, D.; Schenetti, L.; Taddei, F.; Musatti, A.; Nardelli, M. *J. Chem. Soc., Perkin Trans. 2* **1987**, 1443.

Column chromatography of the reaction mixture on silica gel using hexane–methylene chloride (8:2, v/v) gave a mixture of benzoylcyclopentenes **8–10** (131 mg, 51%); the product ratio determined by ^{1}H NMR was 43:32:25. Elaborated column chromatography of the reaction mixture afforded each compound having >80% content.

3-Benzoylcyclopentene (8):[22] oil; ^{1}H NMR δ 2.19–2.31 (m, 2H), 2.40–2.57 (m, 2H), 4.48–4.53 (m, 1H), 5.77–5.59 (m, 1H), 5.94–5.96 (m, 1H), 7.48 (t, 2H, J = 7.7 Hz), 7.57 (t, 1H, J = 7.3 Hz), 8.00–8.02 (m, 2H); MS m/z 172 (M$^+$).

4-Benzoylcyclopentene (9): oil; ^{1}H NMR δ 2.67–2.81 (m, 4H), 2.67–2.81 (m, 1H), 5.69 (t, 2H, J = 6.4 Hz), 7.47–58 (m, 3H), 7.96–7.99 (m, 2H); MS m/z 172 (M$^+$).

1-Benzoylcyclopentene (10):[23] oil; ^{1}H NMR δ 1.97–2.05 (m, 2H), 2.59–2.65 (m, 2H), 2.72–2.77 (m, 2H), 6.55 (t, 1H, J = 2.0 Hz), 7.41–52 (m, 3H), 7.72–7.75 (m, 2H); MS m/z 172 (M$^+$).

JO951249F

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(22) Kachinsky, J. L. C.; Salomon, R. G. *J. Org. Chem.* **1986**, *51*, 1393.

(23) Smith, A. B., III; Agosta, W. C. *J. Am. Chem. Soc.* **1973**, *95*, 1961.