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Synthesis of Fluoren-9-ones by the Palladium-Catalyzed Cyclocarbonylation of *o*-Halobiaryls

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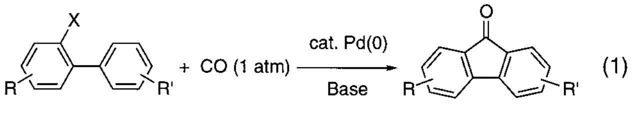
The synthesis of various substituted fluoren-9-ones has been accomplished by the palladium-catalyzed cyclocarbonylation of *o*-halobiaryls. The cyclocarbonylation of 4′-substituted 2-iodobiphenyls produces very high yields of 2-substituted fluoren-9-ones bearing either electron-donating or electron-withdrawing substituents. 3′-Substituted 2-iodobiphenyls afford 3-substituted fluoren-9-ones in excellent yields with good regioselectivity. This chemistry has been successfully extended to polycyclic fluorenones and fluorenones containing fused isoquinoline, indole, pyrrole, thiophene, benzothiophene, and benzofuran rings.

Introduction

Fluoren-9-ones are of considerable interest because of their important biomedical applications[1] and their use as key synthetic intermediates.[2] The most useful syntheses of fluorenones include Friedel−Crafts ring closures of biarylcarboxylic acids and derivatives,[3] intramolecular [4 + 2] cycloaddition reactions of conjugated enynes,[4] oxidation of fluorenes,[5] and remote metalation of 2-biphenylcarboxamides or 2-biphenyloxazolines.[6] Fluorenones have also been synthesized by the palladium-catalyzed cyclization of *o*-iodobenzophenones.[7]

Our interest in fluoren-9-ones has led to the development of a novel palladium-catalyzed cyclocarbonylation of *o*-halobiaryls, which provides a highly efficient and direct route to the fluoren-9-one skeleton, as well as other related cyclic aromatic ketones (eq 1).[8] Herein, we report the full details of this new fluorenone synthesis.



(1)

Results and Discussion

To develop an optimum set of reaction conditions, we first studied the palladium-catalyzed cyclocarbonylation of commercially available 2-iodobiphenyl (**1**) to fluoren-9-one (**2**) as our model system. All of the optimization reactions have been carried out using 0.25 mmol of 2-iodobiphenyl (**1**) in DMF (6 mL) at 110 °C for 7 h under 1 atm of carbon monoxide. It is evident from the results listed in Table 1 that the base added and the ligand present on palladium are critical elements in this reaction. For instance, the use of chelating ligands, such as 1,2-bis(diphenylphosphino)ethane (dppe), 1,1′-bis(diphenylphosphino)ferrocene (dppf), and 1,10-phenanthroline gave poor yields of the desired fluoren-9-one (**2**) (entries 1−3). Monodentate phosphine ligands have a major effect on the yield of the cyclocarbonylation reaction. Use of the electron-deficient ligands tris(*p*-fluorophenyl)phosphine and tris(*p*-chlorophenyl)phosphine gave low yields of fluoren-9-one (33% and 37%, respectively), while the more electron-rich triphenylphosphine produced a 58% yield (entries 4−6). Following this electronic trend, we observed that the bulky, electron-rich ligand tricyclohexylphosphine was by far the most effective ligand, producing a quantitative yield of the desired compound **2** (entry 7). Finally, we explored the effect of different bases on the yield of fluoren-9-one and found that replacing the unusual cesium pivalate (CsPiv) base with NaOAc or Cs_2CO_3 was detrimental to the reaction (entries 8 and 9), the yield dropping from 100% to 92% and 82%, respectively. The use of organic bases, such as pyridine and diisopropylethylamine, gave negligible yields of fluoren-9-one (entries 10 and 11).

The results of this optimization study have led to the development of a standard set of reaction conditions

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[1] (a) Tierney, M. T.; Grinstaff, M. W. *J. Org. Chem*. **2000**, *65*, 5355. (b) Han, Y.; Bisello, A.; Nakamoto, C.; Rosenblatt, M.; Chorev, M. *J. Pept. Res*. **2000**, *55*, 230. (c) Greenlee, M. L.; Laub, J. B.; Rouen, G. P.; DiNinno, F.; Hammond, M. L.; Huber, J. L.; Sundelof, J. G.; Hammond, G. G. *Biorg. Med. Chem. Lett*. **1999**, *9*, 3225. (d) Perry, P. J.; Read, M. A.; Davies, R. T.; Gowan, S. M.; Reszka, A. P.; Wood, A. A.; Kelland, L. R.; Neidle, S. *J. Med. Chem*. **1999**, *42*, 2679. (e) Jones, W. D.; Ciske, F. L.; Dinerstein, R. J.; Diekema, K, A. U.S. Patent No. 6,004, 959, 1999.

[2] (a) Koyama, H.; Kamikawa, T. *Tetrahedron Lett*. **1997**, *38*, 3973. (b) Carney, J. R. *J. Org. Chem*. **1997**, *62*, 320.

[3] (a) Olah, G. A.; Mathew, T.; Farnia, M.; Prakash, S. *Synlett* **1999**, 1067. (b) Yu, Z.; Velasco, D. *Tetrahedron Lett*. **1999**, *40*, 3229.

[4] (a) Danheiser, R. L.; Gould, A. E.; Pradilla, R. F.; Helgason, A. L. *J. Org. Chem*. **1994**, *59*, 5514.

[5] (a) Hashemi, M.; Beni, Y. *J. Chem. Res., Synop*. **1999**, 434. (b) Nikalje, M.; Sudalai, A. *Tetrahedron* **1999**, *55*, 5903.

[6] (a) Ciske, F.; Jones, W. D., Jr. *Synthesis* **1998**, 1195. (b) Wang, W.; Snieckus, V. *J. Org. Chem*. **1992**, *57*, 424.

[7] (a) Qabaja, G.; Jones, G. B. *Tetrahedron Lett*. **2000**, *41*, 5317. (b) Kozikowski, A. P.; Ma, D. *Tetrahedron Lett*. **1991**, *32*, 3317.

[8] For a preliminary communication, see: Campo, M. A.; Larock, R. C. *Org. Lett*. **2000**, *2*, 3675.

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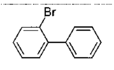
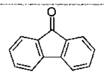
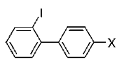
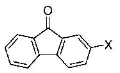
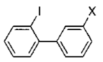
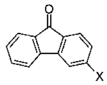
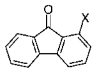
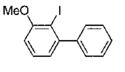
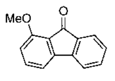
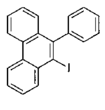
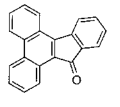
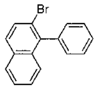
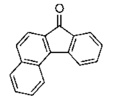
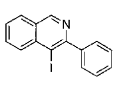
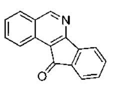
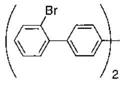
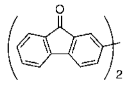
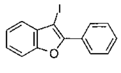
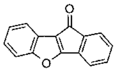
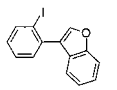
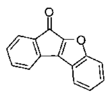
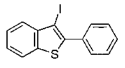
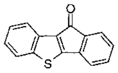
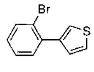
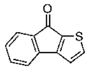
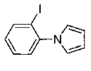
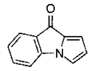
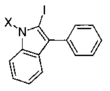
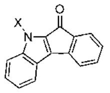
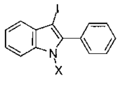
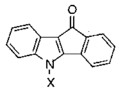
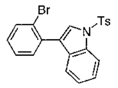
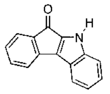
TABLE 1. Palladium-Catalyzed Cyclocarbonylation of 2-Iodobiphenyl (1)[a]

entry	base	Pd catal	ligand (mol %)	time (h)	% isolated yield of **2**
1	CsPiv[b]	$Pd(OAc)_2$	dppe (5)	7	46
2	CsPiv	$Pd(OAc)_2$	dppf (5)	7	25
3	CsPiv	$Pd(OAc)_2$	1,10-phenanthroline (5)	7	<5
4	CsPiv	$Pd(OAc)_2$	$(p\text{-}FC_6H_4)_3P$ (10)	7	33
5	CsPiv	$Pd(OAc)_2$	$(p\text{-}ClC_6H_4)_3P$ (10)	7	37
6	CsPiv	$Pd(OAc)_2$	Ph_3P (10)	7	58 (38[c])
7	CsPiv	$Pd(PCy_3)_2$	*d*	7	100
8	NaOAc	$Pd(PCy_3)_2$	*d*	7	92
9	Cs_2CO_3	$Pd(Pcy_3)_2$	*d*	7	84
10	pyridine	$Pd(PCy_3)_2$	*d*	24	<5
11	$(i\text{-}Pr)_2NEt$	$Pd(PCy_3)_2$	*d*	24	<5

[a] All reactions were run with 0.25 mmol of 2-iodobiphenyl (**1**), 2 equiv of base, 5 mol % of Pd catalyst, and 5 or 10 mol % of an appropriate ligand in 6 mL of DMF at 110 °C for 7 h under 1 atm of CO. [b] CsPiv = cesium pivalate. [c] The amount of DMF solvent was reduced from 6 mL to 1 mL. [d] The palladium catalyst contains 10 mol % of tricyclohexylphosphine, so no further ligand was added to the reaction mixture.

TABLE 2. Synthesis of Fluoren-9-ones by the Pd-Catalyzed Cyclocarbonylation of *o*-Halobiaryls[a]

entry	substrate	product(s)	% isolated yield
1	 3	 2	100
2	 X = H (1)	 2	100
3	X = Me (4)	5	97
4	X = OMe (6)	7	100
5	X = CH_2OMe (8)	9	100
6	X = CHO (10)	11	100
7	 X = Me (12)	 13 +  14	90 + 10
8	X = CHO (15)	16 + 17	94 (9:1)[b]
9	 18	 19	99
10	 20	 21	98
11	 22	 23	96
12	 24	 25	95
13	 26	 27	87[c,d]
14	 28	 29	0
15	 30	 31	81
16	 32	 33	67
17	 34	 35	86[d]
18	 36	 37	96
19	 X = H (38)	 X = H (39)	0
20	X = Me (40)	X = Me (41)	49
21	 X = H (42)	 X = H (43)	0
22	X = Me (44)	X = Me (45)	21
23	X = Ts (46)	X = H (43)	45
24	 47	 39	55[e]

[a] All reactions were carried out under the optimal conditions described in the text. [b] The product ratio was determined by ^1H NMR spectroscopic analysis. [c] To keep the equivalents of aryl halide consistent, we employed 0.125 mmol of aryl dibromide **26**. [d] The reaction period was extended to 14 h. [e] A 42% yield of compound **47** was recovered at the end of the reaction.

employing 1 atm of carbon monoxide, 1 equiv of the aryl halide (0.25 mmol), 5 mol % of commercially available $Pd(PCy_3)_2$, and 2 equiv of anhydrous cesium pivalate in DMF (6 mL) at 110 °C for 7 h. This procedure has been applied to a wide range of aryl halides (Table 2). 2-Iodobiphenyl produced fluoren-9-one in a quantitative yield (entry 2). Under these reaction conditions, 2-bromobiphenyl was also converted to fluoren-9-one (**2**) in a quantitative yield (entry 1). However, (biphenyl-2-yl)trifluoromethanesulfonate failed to afford the desired product.

The utility of this reaction for the synthesis of 2-substituted fluoren-9-ones was assessed by studying the cyclocarbonylation of readily prepared[9] 4′-substituted 2-iodobiphenyls (entries 2−6). As indicated, the reaction works well, tolerating both electron-donating and electron-withdrawing substituents.

We have also addressed the question of regiochemistry in the cyclocarbonylation of 3′-substituted 2-iodobiphenyls[9] (entries 7 and 8). The cyclocarbonylation of the electron-rich 2-iodo-3′-methylbiphenyl (**12**) and the electron-poor 3-(2-iodophenyl)benzaldehyde (**15**) afforded similar 9:1 regiochemical mixtures in excellent yields. In both cases, the predominant isomer arises from ring closure distal to the substituent. These experimental results seem to indicate that there is only a weak electronic effect during the cyclization process, and that a more important steric effect favors the less hindered isomers **13** and **16**.

This cyclocarbonylation does not appear to be significantly affected by the presence of substituents *ortho* to the halo group. For example, the palladium-catalyzed reaction of 2-iodo-3-methoxybiphenyl[10] (**18**) produced 1-methoxyfluoren-9-one (**19**) in 99% yield (entry 9).

Interestingly, this palladium-catalyzed transformation can be readily employed on biaryl systems containing either polycyclic or heterocyclic rings. Thus, treatment of 9-iodo-10-phenylphenanthrene (**20**) with carbon monoxide under our standard reaction conditions produced indene[1,2-*l*]phenanthren-13-one[11] (**21**) in 98% yield. Similarly, 2-bromo-1-phenylnaphthalene[12] (**22**) produced a 96% yield of benzo[*c*]flouren-7-one[13] (**23**) (entry 11). Furthermore, cyclocarbonylation of the nitrogen-containing heterocycle 4-iodo-3-phenylisoquinoline[14] (**24**) produced 11-oxoindeno[1,2-*c*]isoquinoline[15] (**25**) in a 95% yield (entry 12).

This palladium reaction was also effective for the double cyclocarbonylation of 2,2‴-dibromo-*p*-quaterphenyl[16] (**26**) (entry 13). Under the standard reaction conditions, but 14 h reaction time, substrate **26** produced the desired [2,2′]bifluorenyl-9,9′-dione[17] (**27**) in 87% yield.

So far, we have demonstrated the utility of this chemistry by preparing a variety of fluorenones in high yields with good regioselectivity from *o*-halobiaryls containing six-membered ring aromatics, such as benzene, naphthalene, phenanthrene, etc. (Table 2, entries 1−13). We next turned our attention to applying this palladium methodology to *o*-halobiaryls in which one of the aromatic rings is a five-membered ring heterocycle, such as a benzofuran, a benzothiophene, a thiophene, a pyrrole, or an indole (entries 14−24). We began by studying the electronic effects of the carboannulation of *o*-iodobiaryls containing a benzofuran. When 3-iodo-2-phenylbenzofuran[18] (**28**) was subjected to the standard reaction conditions, it failed to give any of the desired benz[*b*]indeno[2,1-*d*]furan-10-one (**29**) (entry 14). On the other hand, the cyclocarbonylation of 3-(2-iodophenyl)benzofuran (**30**), in which ring closure takes place onto the electron-rich benzofuran ring, produced the desired benz[*b*]indeno[1,2-*d*]furan-6-one (**31**) in 81% yield (entry 15). In these benzofuran-containing systems, cyclocarbonylation occurred onto the more reactive benzofuran moiety of the biaryl (entry 15) but failed to do so onto the less electron-rich phenyl ring of the biaryl (entry 14). Similar electronic effects were observed with *o*-halobiaryls containing either benzothiophene or thiophene rings. For instance, 3-iodo-2-phenylbenzothiophene[19] (**32**) produced a 67% yield of 10-oxo-10*H*-benz[*b*]indeno[1,2-*d*]thiophene[20] (**33**) (entry 16), while 3-(2-bromophenyl)thiophene[21] (**34**) produced an 86% yield of indeno[2,1-*d*]thiophen-8-one[22] (**35**) with excellent C-2 regioselectivity (entry 17). It is noteworthy that switching from the oxygen heterocycle of entry 14 to the sulfur analogue of entry 16 resulted in a substantial increase in yield. In like manner, the pyrrole derivative *N*-(2-iodophenyl)pyrrole (**36**) gave a 96% yield of pyrrolo[1,2-*a*]indol-9-one[23] (**37**) (entry 18).

The yield of the palladium-catalyzed cyclocarbonylation of *o*-halobiaryls containing an indole was dependent not only on electronic effects but also on the nature of the protecting group on the indole nitrogen. To illustrate, 2-iodo-3-phenyl-1*H*-indole (**38**) and 3-iodo-2-phenyl-1*H*-indole[24] (**42**), both of which have unprotected nitrogens, failed to give the desired indenoindolones under the standard reaction conditions (entries 19 and 21). However, the *N*-methyl-substituted indole analogues 2-iodo-1-methyl-3-phenylindole (**40**) and 3-iodo-1-methyl-2-phenylindole (**44**) produced the desired 5-methyl-5*H*-indeno[2,1-*b*]indol-6-one[25] (**41**) and 5-methyl-5*H*-indeno[1,2-*b*]indol-10-one[26] (**45**) in 49% and 21% yields, respectively (entries 20 and 22). In an attempt to increase the yield of indeno[1,2-*b*]indol-10-one, 3-iodo-2-phenyl-1-(4-toluenesulfonyl)indole (**46**) was prepared and subsequently cyclocarbonylated under our standard reaction conditions to produce 5*H*-indeno[1,2-*b*]indol-10-one[27] (**43**) in a 45% yield (entry 23). It is worth emphasizing that compound **46** led to the cyclocarbonylated product **43** in which the sulfonamide functionality had been removed under the relatively mild reaction conditions employed. This unusual deprotection was also observed in the cyclocarbonylation of 3-(2-bromophenyl)-1-(4-toluenesulfonyl)indole (**47**), which led to 5*H*-indeno[2,1-*b*]indol-6-one (**39**) in 55% yield (entry 24). Furthermore, 42% of the 3-(2-bromophenyl)-1-(4-toluenesulfonyl)indole (**47**) was recovered at the end of the reaction, which seems to

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[9] These starting materials were prepared using the procedure of the following: Hart, H.; Harada, K.; Du, C. *J. Org. Chem.* **1985**, *50*, 3104.

[10] This starting material was prepared using the procedure of the following: Huisgen, R.; Rist, H. *Liebigs Ann. Chem.* **1955**, *594*, 137.

[11] (a) Sprinzak, Y. *J. Am. Chem. Soc.* **1958**, *80*, 5449. (b) Horspool, W. M. *J. Chem. Soc. C* **1971**, 400. (c) Pandey, B.; Mahajan, M. P.; Tikare, R. K.; Muneer, M.; Rath, N. P.; Kamat, P. V.; George, M. V. *Res. Chem. Intermed.* **1991**, *15*, 271.

[12] Wittig, G.; Hellwinkel, D. *Chem. Ber.* **1964**, *97*, 769.

[13] (a) Fu, J.; Zhao, B.; Sharp, M. J.; Snieckus, V. *J. Org. Chem.* **1991**, *56*, 1683. (b) Harvey, R. G.; Abu-shqara, E.; Yang, C. *J. Org. Chem.* **1992**, *57*, 6313.

[14] This aryl iodide was prepared by the procedure of the following: Huang, Q.; Hunter, J. A.; Larock, R. C. *Org. Lett.* **2001**, *3*, 2973.

[15] (a) Wawzonec, S.; Stowell, J. K.; Karll, R. E. *J. Org. Chem.* **1966**, *31*, 1004. (b) Dusemund, J.; Kroeger, E. *Arch. Pharm.* **1987**, *320*, 617.

[16] Fujioka, Y. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 3494.

[17] Barnett, M. D.; Daub, G. H.; Hayes, N.; Ott, D. G. *J. Am. Chem. Soc.* **1959**, *81*, 4583.

[18] Arcadi, A.; Cacchi, S.; Fabrizi, G.; Marinelli, F.; Moro, L. *Synlett* **1999**, *9*, 1432.

[19] This starting material was prepared using the procedure of the following: Larock, R. C.; Harrison, L. W. *J. Am. Chem. Soc.* **1984**, *106*, 4218.

[20] Sauter, F.; Dzerovicz, A. *Monatsh. Chem.* **1969**, *100*, 913.

[21] Martelli, G.; Spagnolo, P.; Tiecco, M. *J. Chem. Soc. B* **1968**, 901.

[22] MacDowell, D. W. H.; Patrick, T. B. *J. Org. Chem.* **1967**, *32*, 2441.

[23] (a) Mazzola, V. J.; Bernady, K. F.; Franck, R. W. *J. Org. Chem.* **1967**, *32*, 486. (b) Flitsch, W.; Kappenberg, F.; Schmitt, H. *Chem. Ber.* **1978**, 111, 2407.

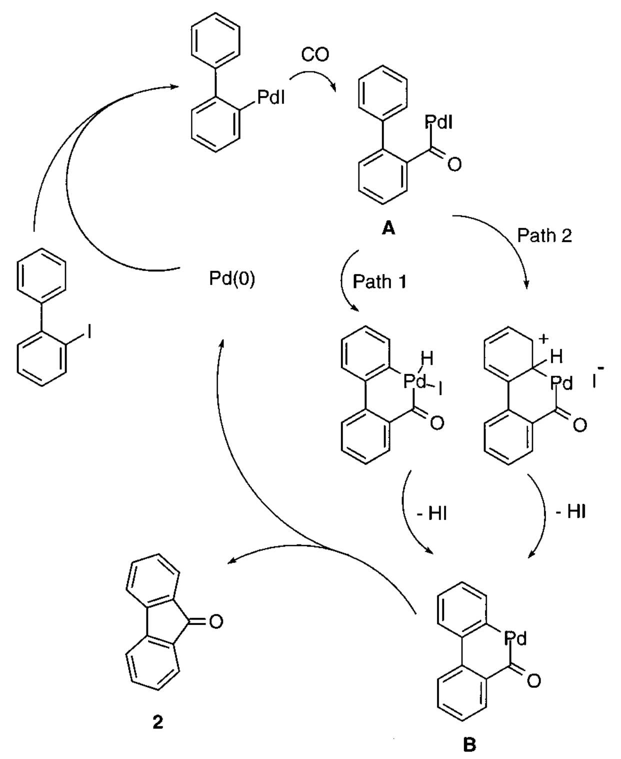
[24] This substrate was prepared by the procedure of the following: Bocchi, V.; Palla, G. *Synthesis* **1982**, 1096.

[25] (a) Kozikowski, A. P.; Ma, D. *Tetrahedron Lett.* **1991**, *32*, 3317. (b) Borsche, W.; Klein, A. *Liebigs Ann. Chem.* **1941**, *548*, 64.

[26] Itahara, T.; Sakakibara, T. *Synthesis* **1978**, 607.

[27] Eisch, J. J.; Abraham, T. *Tetrahedron Lett.* **1976**, 1647.

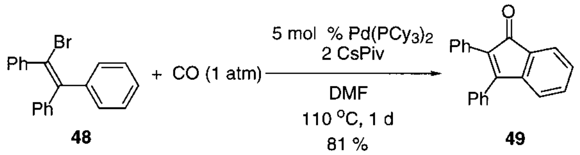
SCHEME 1



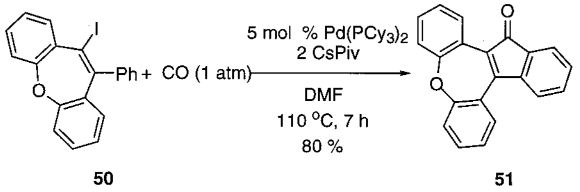
indicate that removal of the sulfonamide functionality occurs during or after the cyclocarbonylation reaction and not before.

In summary, the synthesis of fluorenones have been accomplished in excellent yields with good regioselectivity by the cyclocarbonylation of *o*-halobiaryls containing only six-membered ring aromatics (Table 2, entries 1−13). Similarly, this palladium-catalyzed reaction can also be used to prepare more strained fluorenones containing two fused five-membered rings (Table 2, entries 14−24). In the latter reactions, the yield of fluorenone is strongly dependent on electronic effects. This fact can be rationalized in terms of the ring strain of the palladium intermediates (see Scheme 1) leading to such fluorenones. The transformation is more favorable if cyclization occurs onto an electron-rich system, such as a benzofuran [81% yield (entry 15)], a thiophene [86% yield (entry 17)], a pyrrole [96% yield (entry 18)], or an indole [97% yield based on percent conversion (entry 24)] versus cyclization onto a relatively unreactive phenyl group [0−67% yields (entries 14, 16, and 19−23)].

Finally, this chemistry can also be applied to vinylic halides. For instance, the cyclocarbonylation of commercially available 1,2,2-triphenyl-1-bromoethene (**48**) led to 2,3-diphenyl-1-indenone (**49**) in 81% yield (eq 2). Furthermore, 5-iodo-6-phenyl-dibenz[*b,f*]oxepine[28] (**50**) produced indeno[5,6]dibenz-[*b,f*]oxepin-14-one in 80% yield (eq 3).



(2)



(3)

We propose a possible reaction mechanism for this palladium-catalyzed synthesis of fluorenones involving (1) oxidative addition of the aryl halide to Pd(0), (2) CO insertion to generate the acylpalladium intermediate **A**, (3) either oxidative addition of the neighboring aryl C−H to the acylpalladium to generate a Pd(IV) intermediate (path 1)[29] or electrophilic palladation (path 2)[30] and subsequent elimination of HI to generate intermediate **B**, and (4) reductive elimination of the ketone with simultaneous regeneration of the Pd(0) catalyst (Scheme 1).

Conclusion

The palladium-catalyzed cyclocarbonylation of *o*-halobiaryls provides a short, straightforward route to a variety of substituted fluoren-9-ones under mild reaction conditions and short reaction times. Our success in extending this reaction to other biaryl systems, as well as vinylic halides, indicates its potential for the synthesis of a wide variety of carbocyclic and heterocyclic aromatic ketones.

Experimental Section

General Procedures. All ^{1}H and ^{13}C spectra were recorded at 300 and 75.5 MHz or 400 and 100 MHz, respectively. Thin-layer chromatography was performed using commercially prepared 60-mesh silica gel plates (Whatman K6F), and visualization was effected with short wavelength UV light (254 nm) and a basic $KMnO_4$ solution [3 g of $KMnO_4$ + 20 g of K_2CO_3 + 5 mL of NaOH (5%) + 300 mL of H_2O]. All melting points are uncorrected. High-resolution mass spectra were recorded on a Kratos MS50TC double-focusing magnetic sector mass spectrometer using EI at 70 eV.

Reagents. All reagents were used directly as obtained commercially unless otherwise noted. Anhydrous forms of THF, DMF, diethyl ether, ethyl acetate, and hexanes were purchased from Fisher Scientific Co. 2-Iodobiphenyl (**1**), 2-iodothioanisole, and thiophene-3-boronic acid were obtained from Lancaster Synthesis Ltd. 2-Iodoaniline, 1,2,2-triphenyl-1-bromoethene (**48**), 2-bromobiphenyl (**3**), 1-bromo-2-iodobenzene, 4-bromotoluene, 3-bromotoluene, 2-fluoroanisole, 4-bromoanisole, 2,5-dihydro-2,5-dimethoxyfuran, 2-bromophenylboronic acid, 4,4′-diiodobiphenyl, phenyllithium, phenylacetylene, cesium carbonate, cesium fluoride, pivalic acid, and triethylamine were obtained from Aldrich Chemical Co., Inc. Bis(tricyclohexylphosphine)palladium(0) was purchased from Strem Chemicals, Inc. Cesium pivalate was prepared according to the procedure of Larock and Campo.[8] Compounds **1**−**7**, **10**−**25**, **32**, and **33** have been previously reported.[8]

Synthesis of *o*-Halobiaryls. The following procedures are representative of those used to prepare the *o*-halobiaryls:

3-(2-Bromophenyl)thiophene (34). This aryl bromide was prepared by a selective Suzuki−Miyaura cross-coupling reaction as follows. 1-Bromo-2-iodobenzene (0.2829 g, 1.0 mmol),

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[28] Kitamura, T.; Takachi, H.; Taniguchi, K.; Taniguchi, H. *J. Chem. Soc., Perkin Trans. 1* **1992**, 1969.

[29] Gretz, E.; Oliver, T. F.; Sen, A. *J. Am. Chem. Soc.* **1987**, *109*, 8109.

[30] (a) Catellani, M.; Chiusoli, G. P. *J. Organomet. Chem.* **1992**, *425*, 151. (b) Stock, L. M.; Tse, Kwok-tuen; Vorvick, L. J.; Walstrum, S. A. *J. Org. Chem.* **1981**, *46*, 1757.

thiophene-3-boronic acid (0.140 g, 1.1 mmol), cesium fluoride (0.304 g, 2 mmol), Pd(dba)$_2$ (0.0288 g, 0.05 mmol), and triphenylphosphine (0.026 g, 0.1 mmol) in DME (5 mL) were stirred under Ar at 90 °C for 6 h. The reaction mixture was diluted with diethyl ether (50 mL) and washed with brine (30 mL). The organic layer was dried (MgSO$_4$) and filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography using hexanes to afford 0.210 g (88%) of the desired compound **34** as a clear oil: ^{1}H NMR (CDCl$_3$) δ 7.17 (td, $J = 7.6$, 0.4 Hz, 1H), 7.28–7.40 (m, 5H), 7.65 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 122.6, 124.0, 124.8, 127.4, 128.7, 129.0, 131.3, 133.4, 137.6, 141.1; IR (CH$_2$Cl$_2$) 3112, 3048, 1468 cm^{-1}; HRMS *m*/*z* 237.9455 (calcd for $C_{10}H_7BrS$, *m*/*z* 237.9452).

The characterization of all other *o*-halobiaryls prepared in this study can be found in the Supporting Information.

General Procedure for the Pd-Catalyzed Cyclocarbonylation of *o*-Halobiaryls. DMF (6 mL), Pd(PCy$_3$)$_2$ (8.4 mg, 0.0125 mmol), anhydrous cesium pivalate (0.117 g, 0.5 mmol), and the *o*-halobiaryl (0.25 mmol) were stirred under an Ar atmosphere at room temperature for 5 min. The mixture was flushed with CO and fitted with a CO filled balloon. The reaction mixture was heated to 110 °C with vigorous stirring for 7 or 14 h. The reaction mixture was then cooled to room temperature, diluted with diethyl ether (35 mL), and washed with brine (30 mL). The aqueous layer was reextracted with diethyl ether (15 mL). The organic layers were combined, dried (MgSO$_4$) and filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on a silica gel column.

Fluoren-9-one (2). The reaction mixture was chromatographed using 7:1 hexanes/ethyl acetate to afford 45.1 mg (100%) of the indicated compound as a yellow solid: mp 82–83 °C. This compound was identified by comparing the ^{1}H NMR and ^{13}C NMR spectra and melting point with an authentic sample obtained from Aldrich Chemical Co., Inc.

Characterization of all other fluorenones prepared in this study can be found in the Supporting Information.

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Supporting Information Available: Preparation and characterization data for compounds **8**, **9**, **26**–**28**, **30**, **31**, **35**–**47**, and **49**–**51** and copies of ^{1}H and ^{13}C NMR spectra for compounds **8**, **9**, **26**, **27**, **30**, **31**, **34**, **36**, **38**–**41**, **44**, **46**, **47**, and **51**. This material is available free of charge via the Internet at http://pubs.acs.org.

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