Palladium-Catalyzed Tandem Dimerization and Cyclization of Acetylenic Ketones: A Convenient Method for 3,3′-Bifurans Using $PdCl_2(PPh_3)_2$

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Alkynones undergo tandem dimerization and cyclization in the presence of $PdCl_2(PPh_3)_2$ and triethylamine in tetrahydrofuran at room temperature to give 3,3′-bifurans predominantly. Other palladium catalysts while under similar conditions, by rearrangement, lead to 2,5-disubstituted furans. This distinguished property of $PdCl_2(PPh_3)_2$ has been attributed to the involvement of hydridopalladium halide. This method provides a simpler route to a variety of furans and a regioselective synthesis of polysubstituted 3,3′-bifurans using easily accessible acetylenic ketones.

Introduction

The furan moiety is frequently found in natural products and in important pharmaceuticals as well as flavoring, aroma, and fragrance compounds. It is often used as a building block in organic synthesis and has always been the driving force for numerous synthetic efforts toward furans.[1−3] Furans can be, in principle, synthesized by either cyclization of acyclic precursors or derivatization of furan rings.[4,5] Introduction of the substituents at the 2- or 5-position of furan is relatively easy, while similar operations at the 3- or 4-position is rather difficult. Thus, much attention has been paid to the synthesis of polysubstituted furans from acyclic precursors.[6−15]

A novel palladium-catalyzed rearrangement of acetylenic ketones into furans has been reported.[16] The reactions were carried out in toluene at reflux and were not applicable to the preparation of simple alkylated furans. In addition, the yields of furan derivatives were low. It has been explained[17] that the same ketones are transformed into dienones by palladium catalysts. Treatment of the alkynones under carbonylation conditions has resulted in the formation of mixture of furans and dienones.[18] Wong et al. have described[5] very interesting furan chemistry starting from 3,4-bis(trimethylsilyl)-furan. The latter has been prepared at 300 °C by a Diels−Alder reaction between phenyloxazole and bis(trimethylsilyl)acetylene. They have performed two successive sequences of reaction on 3,4-bis(trimethylsilyl)furan such as *ipso* substitution to boroxine using BCl_3 and Suzuki coupling to obtain aryl- and heteroaryl-substituted furans. One interesting extension of this sequence was the preparation of bifurans, and it has been achieved by treating boroxine with 2,3-bis(bromomethyl)quinoxaline in the presence of palladium catalyst at 120 °C. The necessity of using 3,4-bis(trimethylsilyl)furan as a starting material to generate boroxine and its further conversion to bifuran limits the potential of this method from a more general pool of substrates. Moreover, synthesis

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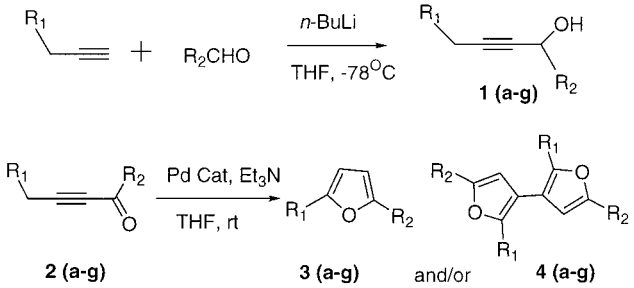
Scheme 1



of substituted 3,3′-bifurans involved five to six steps. (*Z*)-3-Iodo-3-alken-1-ones, acyclic precursors prepared from alkynones, have been converted into furans[9b] and bifurans[9a] using *trans*-di(*μ*-acetato)-bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II)[19] (palladacycle) and $Pd(PPh_3)_4$ or $PdCl_2(PPh_3)_2$, respectively. It was initially conceived to prepare polyaryl furans and bifurans for electroluminescence studies. The preparation[20] of iodoenones by the reported procedure for this purpose from appropriate alkynone (**2g**) resulted in poor yield. In addition, the purity deterioration of iodo compounds and its light sensitivity deter its general application. Neither (*Z*)- nor (*E*)-3-iodo-2-alken-1-ones were reported[9a] to undergo cyclization to furans. During the synthesis of 2,5-disubstituted furans by the reported procedure,[16] we found that in addition to the desired furans, bifurans were formed in trace amounts as detected by MALDI-TOF-MS (Matrix Assisted Laser Desorption Ionization Time-of-Flight Mass Spectrometry) experiments.[21] However, further studies revealed that alkynones themselves could be efficiently converted into alkyl and aryl as well as heteroaryl-substituted furans and bifurans in the presence of palladium catalysts and tertiary amine. Indeed, we could achieve the synthesis of desired compounds in good yields in a single step at room temperature from alkynones.

Results and Discussion

In our effort[21] toward the synthesis of furans and 3,3′-bifurans, we focused our attention to the use of various palladium catalysts and bases in order to study selective formation of mono- and bifurans, the regiochemistry of bifurans, and the mechanism of the reaction. Our studies disclosed (Scheme 1, Table 1) that furans and/or bifurans were formed in various proportions depending on the palladium catalyst that was used in the presence of triethylamine (Table 2). The product distribution in the presence of various amine bases is given in Table 3.

We observed that from alkynones, furans were formed[21] exclusively or predominately in the presence of $Pd(PPh_3)_4$ (Table 2, entries 8−13 and 15). The same alkynones afforded bifurans[21] regioselectively in the presence of $PdCl_2(PPh_3)_2$ (Table 2, entries 21−27). Bifurans formations have been described[9a] in the reaction between (*Z*)-3-iodo-3-alken-1-ones and $Pd(PPh_3)_4$ or $PdCl_2(PPh_3)_2$. We studied the reaction of iodoenone **5** and its corresponding alkynone **2g** with $PdCl_2(PPh_3)_2$, and they make no difference in yielding bifurans (Table 2, entry 26 and Table 5). It has been reported[9b] that palladacycles[19] convert iodoenones more efficiently to furans than $Pd(OAc)_2$. In our present study $Pd(OAc)_2$ was found to work better with alkynones than the palladacycle. It could convert various alkynones to furans (Table 2, entries 1−6) in good yields. The palladacycle transformed alkynones (**2a**, **2b**, **2g**) selectively into furans (Table 2, entries 18, 19, 20), but it yielded a mixture of furans and bifurans (Table 2, entries 16 and 17) from alkynones **2c** and **2d**. The yields of furans from alkynone (**2g**) and iodoenone **5** were compared on treatment with $Pd(OAc)_2$ (Table 2, entry 6) as well as with the palladacycle (Table 2, entry 20) under identical conditions. The yield of furans obtained from alkynone (Table 2, entry 6, 20) were almost the same as from iodoenone (Table 5). Thus, for the synthesis of furans, the palladacycle and iodoenone could be replaced by their starting materials $Pd(OAc)_2$ and acetylenic ketones. The results of the reaction between alkynones and $Pd(OAc)_2$ (Table 2, entries 1−6) were close to that of alkynones and $Pd(PPh_3)_4$ (Table 2, entries 8−15). While extending the same reaction by using 5 mol % $Pd(acac)_2$ or $Pd_2(dba)_3$ under identical condition, we obtained mixture of furans and bifurans in lower yields. Alkynones (R_1 = alkyl) failed to give either of the furan compounds under similar reaction conditions. This could be attributed to the less lability of methylene protons adjacent to the triple bond than to the protons in the corresponding alkynones with R_1 = aryl. To the best of our knowledge, only the two methods discussed in the introduction involving boroxine and iodoenone are available in the literature for the synthesis of 3,3′-bifurans. The third one discussed here is based on simple starting materials, a single step, and mild reaction conditions. Moreover, fine tuning the catalyst could improve selectivity of either furans or bifurans from the same acetylenic ketones.

Thus the use of easily accessible acetylenic ketones and $Pd(PPh_3)_4$ or $Pd(OAc)_2$ catalysts appears to be a simple and more efficient method for the formation of furans, while acetylenic ketones and $PdCl_2(PPh_3)_2$ catalyst leads to the regioselective formation of 3,3′-bifurans.

Our studies of the base (amines) effects on the reactivity of alkynones revealed that tertiary amines are the bases of choice for the reaction. The yields and consistency were very much higher compared to that of secondary (Table 3, entries 4 and 12) or primary amines. The reaction of alkynones (Table 1, **2f** and **2g**) was also studied with morpholine in the presence of $Pd(PPh_3)_4$ and $PdCl_2(PPh_3)_2$. The formation of furans and bifurans were only in trace amounts. Control experiments (Table 3, entry 11) verified the absence of any detectable amount of desired products in the presence of tertiary amine alone. The transformations of alkynones to furans could only be effected along with palladium. *N*,*N*-Diisopropylethylamine and triethylamine provided the same reaction pattern (Table 3, entries 2, 3, 9, 10) when they were used as a base in the reaction medium.

^{1}H NMR, NOE, and HMBC data unambiguously determined the formation of bifuran as a single regioisomer. The structural assignment has also been corroborated by X-ray analysis of crystalline derivative **4f**. X-ray analysis data and the ORTEP diagram of the bifuran compound **4f** (Table 2, entry 25) are given in Table 4.

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Table 1. Substituents of Compounds 1−4

1-4	a	b	c	d	e	f	g
R_1	-Ph	-Ph	-Ph	-Ph	-(3-MeO)-Ph	-Ph	-Ph
R_2	-Ph		n-C_8H_{17}	n-C_5H_{11}		-(3-MeO)-Ph	-(4-Me)Ph

Table 2. Synthesis of Furans and 3,3′-Bifurans

				isol yield: furans (%)	
entry	catalysts	R_1	R_2	**3**	**4**
1	$Pd(OAc)_2$	Ph	*n*-C_5H_{11}	40	07
2	$Pd(OAc)_2$	Ph	Ph	54	06
3	$Pd(OAc)_2$	−Ph	2-thiophene	57	09
4	$Pd(OAc)_2$	(3-MeO)Ph	2-thiophene	51	05
5	$Pd(OAc)_2$	Ph	*n*-C_8H_{17}	44	trace[a]
6	$Pd(OAc)_2$	Ph	(4-Me)Ph	53	04[a]
7	$Pd(OAc)_2$	Ph	(4-Me)Ph	14	26[b]
8	$Pd(PPh_3)_4$	Ph	Ph	55	trace[a]
9	$Pd(PPh_3)_4$	Ph	2-thiophene	70	07
10	$Pd(PPh_3)_4$	Ph	*n*-C_5H_{11}	41	07
11	$Pd(PPh_3)_4$	Ph	*n*-C_8H_{17}	52	trace[a]
12	$Pd(PPh_3)_4$	(3-MeO)Ph	2-thiophene	49	05
13	$Pd(PPh_3)_4$	Ph	(4-Me)Ph	52	02[a]
14	$Pd(PPh_3)_4$	Ph	(4-Me)Ph	13	34[c]
15	$Pd(PPh_3)_4$	Ph	(3-MeO)Ph	53	03[a]
16	palladacycle[d]	Ph	*n*-C_5H_{11}	31	11
17	palladacycle	Ph	*n*-C_8H_{17}	29	09
18	palladacycle	Ph	Ph	52	04
19	palladacycle	Ph	2-thiophene	54	08
20	palladacycle	Ph	(4-Me)Ph	51	02[a]
21	$PdC_2(PPh_3)_2$	Ph	*n*-C_5H_{11}	05	48
22	$PdC_2(PPh_3)_2$	Ph	Ph	08	56
23	$PdC_2(PPh_3)_2$	Ph	2-thiophene	06	53
24	$PdC_2(PPh_3)_2$	(3-MeO)Ph	2-thiophene	05	71
25	$PdC_2(PPh_3)_2$	Ph	*n*-C_8H_{17}	08	42
26	$PdC_2(PPh_3)_2$	Ph	(4-Me)Ph	07	50
27	$PdC_2(PPh_3)_2$	Ph	(3-MeO)Ph	06	46
28	$Pd(acac)_2$	Ph	Ph	30	11
29	$Pd(acac)_2$	Ph	2-thiophene	42	09
30	$Pd(acac)_2$	Ph	*n*-C_5H_{11}	28	08
31	$Pd_2(dba)_3$	Ph	Ph	26	08
32	$Pd_2(dba)_3$	Ph	2-thiophene	28	09
33	$Pd_2(dba)_3$	Ph	*n*-C_5H_{11}	24	06

[a] Detected by GC analysis. [b] Used 1 equiv of Et_3NHI and 4 equiv of PPh_3. [c] Used 1 equiv of Et_3NHI. [d] *trans*-Di(*μ*-acetato)-bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II).[19]

Possible Mechanisms. The formation of simple furans could be justified through allene formation and subsequent cyclization. A plausible mechanism for the formation of bifurans is discussed below.

Synthesis of iodoenone (**5**) was not pursued since the yield was poor. Nevertheless, the reaction with $Pd(PPh_3)_4$ and $PdCl_2(PPh_3)_2$ was studied and compared with the results of corresponding alkynones. $Pd(PPh_3)_4$ as well as $PdCl_2(PPh_3)_2$ reacted with iodoenone **5** to afford bifurans (Table 5) as a major product.

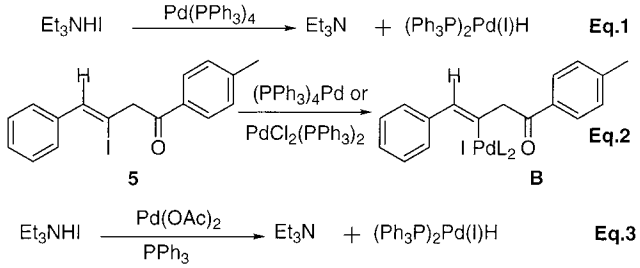
$PdCl_2(PPh_3)_2$ in the reaction with corresponding alkynone (**2g**) also afforded bifuran (Table 2, entry 26), but $Pd(PPh_3)_4$ failed to form the bifuran and yielded only furan (Table 2, entry 13) as a major product. However, $Pd(PPh_3)_4$ in the presence of 1 equiv of Et_3NHI with alkynone (**2g**) gave bifuran in 34% yield (Table 2, entry 14). On the basis of these differences, it may be reasonable to consider the catalytic reaction that involves hydridopalladium halide. In the case of $PdCl_2(PPh_3)_2$, this

Table 3. Influence of the Bases on the Rearrangement of Ketone (2b) in the Presence of $Pd(PPh_3)_4$ or $PdCl_2(PPh_3)_2$

			time	isol yield (%)	
entry	base	catalyst	(h)	furan	3,3′-bifuran
1	n-Bu_3N	$Pd(PPh_3)_4$	12	52	03[a]
2	i-Pr_2Net	$Pd(PPh_3)_4$	10	67	04[a]
3	Et_3N	$Pd(PPh_3)_4$	12	70	07
4	morpholine	$Pd(PPh_3)_4$	24	12	trace[a]
5	1-methylpyrrole	$Pd(PPh_3)_4$	24	trace[a]	trace[a]
6	$PhCH(CH_3)NH_2$	$Pd(PPh_3)_4$	24	trace[a]	trace[a]
7	pyridine	$Pd(PPh_3)_4$	24	04	trace[a]
8	n-Bu_3N	$PdC_2(PPh_3)_2$	12	06	38
9	i-Pr_2Net	$PdC_2(PPh_3)_2$	10	04	52
10	Et_{3N}	$PdC_2(PPh_3)_2$	12	06	53
11	Et_3N	−	24	−	−
12	morpholine	$PdC_2(PPh_3)_2$	24	06	05

[a] Detected by GC analysis.

halide can be formed in the reaction between Et_3NHX and Pd(0) species generated in situ from triethylamine and $PdCl_2(PPh_3)_2$. The hydridopalladium halide can be generated from $Pd(PPh_3)_4$ as given in the eq 1 in the presence of Et_3NHI. Addition of this halide to alkynone may give vinyl palladium intermediate **B** via base-catalyzed isomerization[18] of **A**. The intermediate **B** can be generated from iodoenone **5** (eq 2) directly by both $Pd(PPh_3)_4$ and $PdCl_2(PPh_3)_2$ and lead to bifuran. It may be difficult to rationalize the formation of this intermediate when $Pd(PPh_3)_4$ alone was treated with alkynone.



$Pd(OAc)_2$, palladacycle, and $Pd_2(dba)_3$ with the same iodoenone (**5**) could yield only furan as a major product. $Pd(OAc)_2$ with alkynone (**2g**) even in the presence of Et_3NHI afforded again furan as a major one, and no improvement in the yield of bifuran was observed. $Pd(OAc)_2$ in the reaction with **2g** in the presence of 1 equiv of Et_3NHI and 4 equiv of PPh_3 improved the yield of bifuran to 26% (Table 2, entry 7). All these observations further support the probability for the involvement of HPdX (eq 3). Moreover, the failure of the catalysts $Pd(OAc)_2$, palladacycle, and $Pd_2(dba)_3$ on treatment with iodoenone and the inability of $Pd(OAc)_2$ and Et_3NHI in the absence of PPh_3 to afford bifuran may support the statement that the presence of PPh_3 ligand favors the

Table 4. X-ray Analysis Data and ORTEP Diagram for Compound 4f

Temp (K)	294	abs corr	yes
Chemical formula	$C_{34}H_{26}O_4$	no. of measured	5704
Chemical fw	498.55	reflections	
Cell setting	monoclinic	no. of unobserved	1566
Space group	Pz_1/n	reflns ($F<2\sigma$)	
a (Å)	13.5426(8)	Rint	3.32
b (Å)	16.2218(10)	$R[F^2>4\sigma(F^2)$	0.41
c (Å)	13.6438 (8)	$wR(F^2)$	0.107
β (deg)	119.3860(10)	GoF	1.036
V (A^3)	2611.7(3)		
Z	4		
D_x ($Mg\ m^{-3}$)	1.268		
Radiation type	Mo Kα		
Wave length	0.70932		
Sin θ/λ_{max} (A^{-1})	0.980745		
μ (mm^{-1})	0.082		

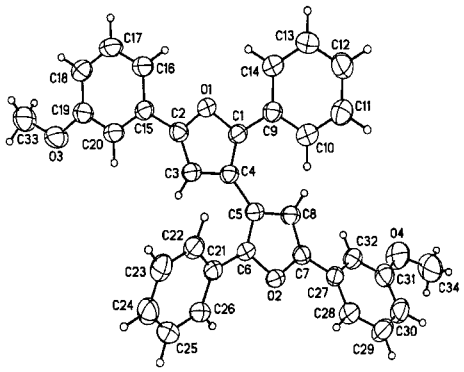
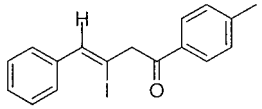


Table 5. Furans from Iodoenone (5)

Table-V. Furans from Iodoeneone (**5**)		
Catalyst	Furan yields(%)	3,3'-Bifurans yields(%)
$Pd(PPh_3)_4$	05	46
$PdCl_2(PPh_3)_2$	02	48
$Pd(OAc)_2$	54	03
Palladacycle	58	03
$Pd_2(dba)_3$	35	02



5

transformation of alkynones to bifurans. The plausible mechanism is depicted in the Scheme 2.

According to the Scheme 2, the complex **A** is generated by the addition of HPdX to alkynone. It subsequently undergoes base-catalyzed isomerization to afford complex **B**. Carbopalladation of allenes are known to favor C−C bond formation at the central carbon of the allene.[22] Accordingly, carbopalladation of allenyl ketone **6** generated in situ with native **B** followed by isomerization lead to **C**. Ring closure of **C** results in the formation of bifuran with regeneration of the key catalytic species. In the case of hydropalladation of allene, instead of carbopalladation, the hydrogen should end up at the central carbon of the allene,[23] which was not observed. Bifurans were formed as a single regioisomer (symmetrical). We have chosen **A** as the sole intermediate in the hydropalladation of **2**. The reverse regiosiomer **D** of **A** may not have potential to contribute to the formation of furan. It could lead to unsymmetrical (Scheme 2) bifuran **7** on carbopalladation to native **2**. Complete absence of other isomers of bifuran in the crude reaction mixture supports the involvement of intermediate **A**. On the basis of these observations and on the similar role of $Pd(PPh_3)_4$ and $PdCl_2(PPh_3)_2$ with iodoenoene **5** and their difference with alkynone **2**, it may be more appropriate to consider the involvement of HPdX rather than PdH.

If intermediate **A** is chosen, it might also be added to either alkynones or allenones to afford bifurans in the same way as explained for **B** except the sequence isomerization and carbopalladation should be reversed. Alkynones **2** could also undergo carbopalladation with intermediate **B** and lead to symmetrical bifurans as given in Scheme 3 through the intermediate **C**. All these possible carbopalladations while involving **A**/**B** could only result in the formation of a single symmetrical regioisomer **4**. This could explain the reason for alkynone **2g** yielding bifuran as efficiently as that obtained from iodoenone **5**, though the latter could undergo direct palladation to intermediate **B**.

One could speculate that Pd(II) is initially reduced to Pd(0) by the organic substrate,[24] and then the analogous Pd(0)/Pd(II)-cycles could be formulated. Pd(0) generated is stabilized by ligands and further favors formation of simple furan under unfavorable conditions, absence of Et_3NHX, for the formation of HPdX.

Mechanistic possibilities for the formation of bifuran in small amounts from catalysts other than $PdCl_2(PPh_3)_2$, based on existing mechanisms that involve steps and

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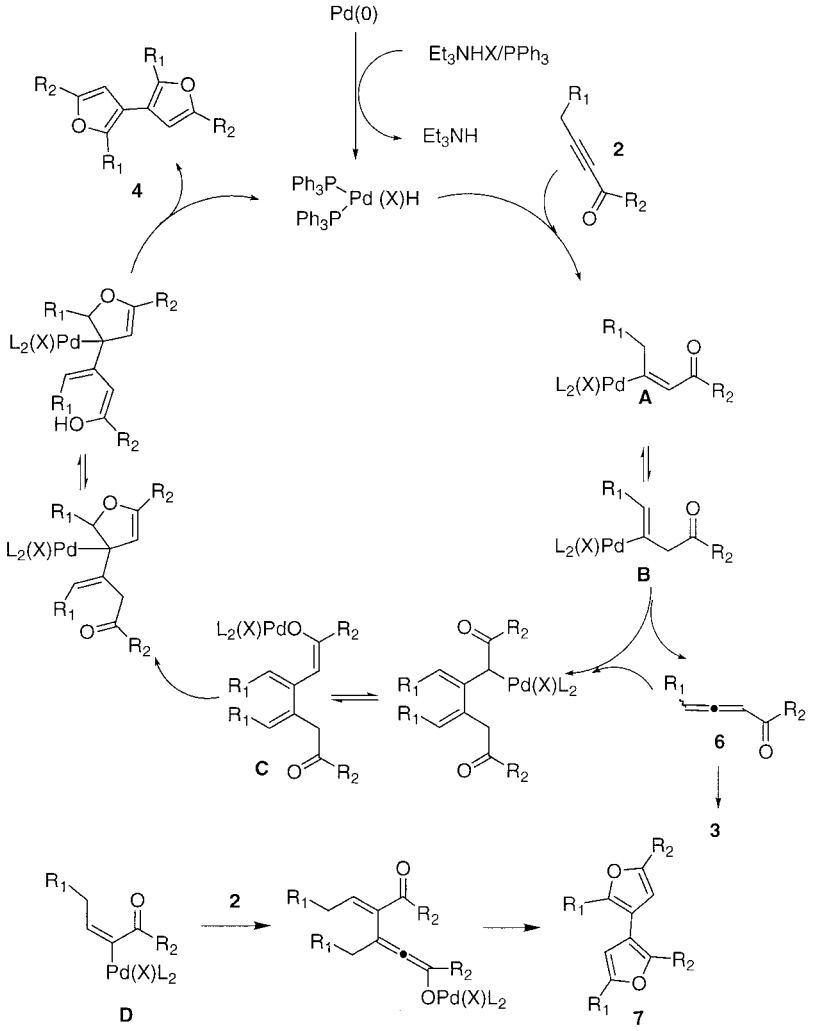
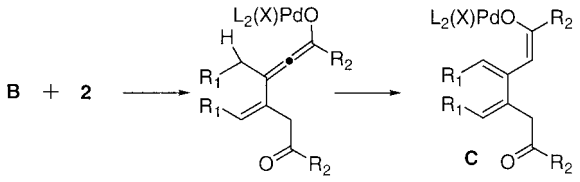
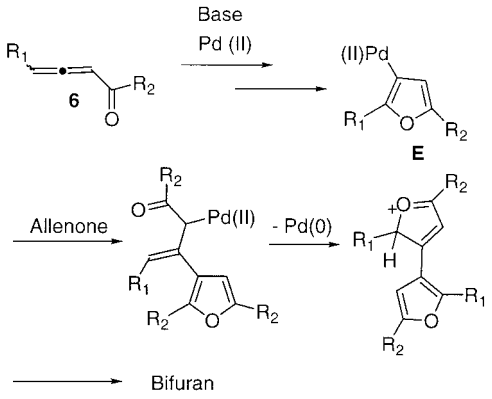
Scheme 2



Scheme 3



Scheme 4



intermediates known from other palladium-catalyzed reactions, are given in Scheme 4. Scheme 4 shows that the interaction of Pd(II) with intermediate allenone **6**, generated from alkynone, leads to furanyl palladium species **E**. Reaction of this species with unreacted allenone **6** results in the formation of bifuran.

In conclusion, a palladium-based method has the advantage of being truly catalytic. It offers the prospect of controlling the nature of the products, shown in Table 2, depending largely upon the nature of the palladium catalyst. This procedure describes an interesting approach, tandem dimerization and cyclization, to bifurans. The reaction proceeds under mild conditions and is highly regioselective. Among the various catalysts, palladium chloride bis(triphenylphosphine) was found to be an ideal candidate for the transformation of alkynones to 3,3′-bifurans. This unique property can be attributed to the involvement of the hydridopalladium halide species.

Experimental Section

General Methods. Melting points were determined in open capillary tube using a Thomas-Hoover apparatus and were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Brucker AC 300 or Brucker AM 400 or Brucker Avance 600 spectrometer. Chemical shifts were recorded relative to $CDCl_3$ or DMSO-d_6. IR spectra were recorded by using Perkin-Elmer 2000 FT-IR spectrometer. High-resolution mass spectra were obtained on a JEOL JMS-HX110 spectrometer. $Pd(OAc)_2$, $Pd_2(dba)_3$, and $Pd(acac)_2$ are commercial products. $Pd(PPh_3)_4$ [25], $PdCl_2(PPh_3)_2$,[26] and palladacycle[19] were prepared by known procedures.

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General Procedure for the Synthesis of Acetylenic Alcohols[27] (1a−g). A solution of 3-aryl-1-propyne[28] (5 mmol) in THF (8 mL) was treated with 1.6 M n-BuLi in hexane (5.2 mmol, −78 °C) followed 30 min later by a solution of corresponding aldehyde (5 mmol) in THF (2 mL). The reaction mixture was warmed to 25 °C, treated with aqueous NH_4Cl, extracted with ethyl acetate, washed with brine, dried over Na_2SO_4, filtered, and evaporated. Chromatography of silica gel (96/4 hexane/ethyl acetate) afforded 1,4-disubstituted-2-butyn-1-ol (**1a−g**) in 58−71% yield.

General Procedure for Acetylenic Ketone (2a−g). A mixture of acetylenic alcohol (500 mg) and activated manganese dioxide (1.5 g, commercial sample) in chloroform (50 mL) was refluxed for 3−4 h. The completion of the reaction was followed by TLC (eluent 1/3 ethyl acetate/hexane). The mixture was filtered through Celite, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography on silica gel to give acetylenic ketones in 72−85% yield.

General Procedure for the Synthesis of Furans (3a−g) and 3,3′-Bifurans (4a−g). To a solution of acetylenic ketone (0.25 mmol) in 2 mL of dry THF, under nitrogen, palladium catalyst (5-mol %) and triethylamine (0.6 mmol) were added sequentially. The reaction mixture was stirred at room temperature until TLC showed complete consumption of starting material (8−12 h). Concentration of the reaction mixture and purification of the crude products on silica gel using hexane afforded the respective furans and bifurans in good yields (Table 1).

2,5-Diphenylfuran (3a). White solid, mp 86−87 °C (from methanol, lit.[6] 87−88); ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.74 (s, 2H), 7.26 (dd, 2H, J = 1.3 Hz, 8.1 Hz), 7.41 (t, 4H, J = 6.7 Hz), 7.74 (dd, 4H, J = 1.3 Hz, 8.2 Hz); ^{13}C NMR (100 MHz): δ 102.22, 123.80, 127.36, 128.71, 130.91, 153.50; IR ($CHCl_3$) cm^{-1}: 3057, 3029, 1602, 1490, 1255, 910, 815, 692; HRMS calcd for $C_{16}H_{12}O$: 220.0888 found 220.0884.

2,2′,5,5′-Tetraphenyl-3,3′-bifuran (4a). Colorless solid, mp 190−192 °C (from hexane−benzene); ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.72 (s, 2H), 7.22 (m, 8H), 7.39 (t, 4H, J = 7.34 Hz), 7.72 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$ and DMSO-d_6): δ 109.89, 116.20, 123.87, 125.19, 127.40, 127.65, 128.54, 128.77, 130.47, 130.88, 148.87, 152.79; IR ($CHCl_3$) cm^{-1}: 3054, 3027, 1603, 1421, 1265, 909, 731, 691. Anal. Calcd for $C_{32}H_{22}O_2$: C, 87.64; H, 5.06. Found: C, 87.59; H, 5.10. HRMS calcd for $C_{32}H_{22}O_2$: 438.1619 found 438.1617.

2-Phenyl-5-(2-thienyl)furan (3b). Colorless solid, mp 82−83 °C (from hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.57 (d, 1H, J = 3.6 Hz), 6.69 (d, 1H, J = 3.5 Hz), 7.04 (dd, 1H, J = 4.6 Hz, 6.4 Hz), 7.23 (m, 2H), 7.20 (d, 1H, J = 4.3 Hz), 7.37 (t, 2H, J = 7.6 Hz), 7.70 (dd, 2H, J = 1.54, 8.60 Hz); ^{13}C NMR (100 MHz): δ 102.12, 102.20, 122.55, 123.71, 124.14, 127.38, 127.67, 128.69, 130.52, 133.91, 149.13, 152.92; IR IR ($CHCl_3$) cm^{-1}: 3058, 3010, 1601, 1480, 1258, 910, 759, 691. Anal. Calcd for $C_{14}H_{10}OS$: C, 74.31; H, 4.45. Found: C, 74.22; H, 4.37. HRMS calcd for $C_{14}H_{10}OS$: 226.0452 found 226.0450.

5,5′-Bis-(2-thienyl)-2,2′-diphenyl-3,3′-bifuran (4b). Colorless syrupy liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.56 (s, 2H), 7.07 (dd, 2H, J = 3.9 Hz, 5.2 Hz), 7.19−7.35 (m, 10H), 7.67 (dd, 4H, J = 1.5 Hz, 8.6 Hz); ^{13}C NMR (100 MHz): δ 109.66, 115.84, 122.98, 124.56, 125.15, 127.48, 127.77, 128.53, 130.49, 133.35, 148.29, 148.52; IR ($CHCl_3$) cm^{-1}: 3057, 2927, 1598, 1495, 1412, 1264, 1223, 919, 766, 691; HRMS calcd for $C_{28}H_{18}O_2S_2$: 450.0748 found 450.0744.

2-Octyl-5-phenylfuran (3c). Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.86 (t, 3H, J = 7.25 Hz), 1.28 (m, 10H), 1.65 (m, 2H), 2.66 (t, 2H, J = 7.5 Hz), 6.03 (d, 1H, J = 3.0 Hz), 6.52 (d, 1H, J = 3.1 Hz), 7.19−7.62 (m, 5H); ^{13}C NMR (100 MHz): δ 14.02, 22.65, 28.15, 28.22, 29.23 (2C), 29.35, 31.88, 105.67, 106.83, 123.42, 127.25, 128.58, 131.44, 152.22, 156.52; IR ($CHCl_3$) cm^{-1}: 3055, 2986, 2960, 1597, 1488, 1420, 1265, 896, 738, 706; HRMS calcd for $C_{18}H_{24}O$: 256.1827 found 256.1823.

5,5′-Dioctyl-2,2′-diphenyl-3,3′-bifuran (4c). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, 6H, J = 6.6 Hz), 1.26 (m, 20H), 1.68 (m, 4H), 2.67 (t, 4H, J = 7.4 Hz), 5.99 (s, 2H,), 7.13 (dd, 2H, J = 1.6 Hz, 7.2 Hz), 7.21 (dd, 4H, J = 7.4 Hz, 8.1 Hz), 7.58 (dd, 4H, J = 1.5 Hz, 8.2 Hz); ^{13}C NMR (100 MHz): δ 14.19, 22.74, 28.15, 28.26, 29.35, 29.43, 31.62, 31.96, 109.90, 115.28, 124.93, 126.67, 128.34, 131.53, 147.31, 155.85; IR ($CHCl_3$) cm^{-1}: 3063, 2955, 2927, 1601, 1448, 1265, 917, 765, 692; HRMS calcd for $C_{36}H_{46}O_2$: 510.3497 found 510.3494.

2-Pentyl-5-phenylfuran (3d). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, 3H, J = 7.2 Hz), 1.35 (m, 4H), 1.67 (m, 2H), 2.65 (t, 2H, J = 7.6 Hz), 6.03 (d, 1H, J = 3.1 Hz), 6.52 (d, 1H, J = 3.1 Hz), 7.17−7.72 (m, 5H); ^{13}C NMR (100 MHz): δ 13.99, 22.42, 27.79, 28.15, 31.40, 105.63, 106.81, 123.32, 126.68, 128.57, 131.29, 152.09, 156.50; IR ($CHCl_3$) cm^{-1}: 3054, 2988, 2960, 1599, 1486, 1421, 1264, 736, 692; HRMS calcd for $C_{15}H_{18}O$: 214.1358 found 214.1354.

5,5′-Dipentyl-2,2′-diphenyl-3,3′-bifuran (4d). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, 6H, J = 7.2 Hz), 1.35 (m, 8H), 1.67 (m, 4H), 2.66 (t, 4H, J = 7.4 Hz), 5.97 (s, 2H,), 7.12−7.60 (m, 10H); ^{13}C NMR (100 MHz): δ 14.02, 22.41, 27.63, 28.02, 31.35, 109.83, 115.20, 124.84, 126.56, 128.25, 131.45, 147.23, 155.75; IR ($CHCl_3$) cm^{-1}: 3054, 2987, 1600, 1265, 896, 738, 705; HRMS calcd for $C_{36}H_{46}O_2$: 510.3497 found 510.3494.

2-(3-Methoxyphenyl-5-(2-thienyl)furan (3e). Colorless syrupy liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.85 (s, 3H), 6.56 (d, 1H, J = 3.7 Hz), 6.67 (d, 1H, J = 3.7 Hz), 6.81 (m, 1H), 7.04 (t, 1H, J = 3.2 Hz), 7.22 (m, 2H), 7.29 (m, 3H) ^{13}C NMR (100 MHz): δ 55.31, 107.21, 107.49, 109.22, 113.00, 116.40, 122.62, 124.20, 127.68, 129.78, 131.70, 133.71, 149.02, 152.22, 159.93; IR ($CHCl_3$) cm^{-1}: 3072, 2950, 2829, 1598, 1484, 1260, 1218, 1044, 775, 737, 698; HRMS calcd for $C_{15}H_{12}O_2S$: 256.0558 found 256.0555.

2,2′-Bis(3-methoxyphenyl)-5,5′-bis(2-thienyl)-3,3′-bifuran (4e). Colorless solid. mp 112−113 °C (from methanol) ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.67 (s, 6H), 6.56 (s, 2H), 6.74 (ddd, 2H, J = 0.9 Hz, J = 1.3 Hz, 10.8 Hz), 7.05 (dd, 2H, J = 3.6 Hz, 5.0 Hz), 7.16 (t, 2H, J = 8.1 Hz), 7.24−7.29 (m, 6H), 7.33 (dd, 2H, J = 1.1 Hz, 3.6 Hz); ^{13}C NMR (100 MHz): δ 55.11, 109.74, 110.22, 113.69, 116.11, 117.75, 123.03, 124.66, 127.28, 129.65, 151.65, 133.24, 148.28, 148.52, 159.61; IR ($CHCl_3$) cm^{-1}: 3041, 2950, 1601, 1541, 1260, 920, 737. Anal. Calcd for $C_{30}H_{22}O_4S_2$: C, 70.57; H, 4.34. Found: C, 70.43; H, 4.29. HRMS calcd for $C_{30}H_{22}O_4S_2$: 510.0959 found 510.0954.

2-(3-Methoxyphenyl)-5-phenylfuran (3f). White solid, mp 88−89 °C (from methanol); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.86 (s, 3H), 6.72 (s, 2H), 6.82 (m, 1H), 7.25−7.32 (m, 4H), 7.39 (t, 2H, J = 7.4 Hz), 7.71 (dd, 2H, J = 1.4 Hz, 8.3 Hz); ^{13}C NMR (100 MHz): δ 55.31, 107.19, 107.55, 109.28, 112.94, 116.40, 123.73, 127.37, 128.89, 129.77, 130.72, 132.06, 153.17, 153.40, 160.00; IR ($CHCl_3$) cm^{-1}: 3057, 2958, 1591, 1488, 1260, 1215, 1021, 737, 688. Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.63. Found: C, 81.69; H, 5.69. HRMS calcd for $C_{17}H_{14}O_2$: 250.0993 found 250.0991.

5,5′-Bis(3-methoxyphenyl)-2,2′-diphenyl-3,3′-bifuran (4f). Colorless solid. mp 124−126 °C (from methanol) ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.86 (s, 6H), 6.71 (s, 2H), 6.83 (m, 2H), 7.16−7.35 (m, 12H), 7.71 (dd, 4H, J = 1.7 Hz, 8.2 Hz); ^{13}C NMR (75 MHz): δ 55.37, 109.39, 110.23, 113.35, 116.16, 116.54, 125.21, 127.45, 128.53, 129.86, 130.83, 131.73, 148.78, 152.60, 160.01; IR ($CHCl_3$) cm^{-1}: 3057, 2996, 2958, 2836, 1598, 1488, 1264, 1218, 1021, 729, 691. Anal. Calcd for $C_{34}H_{26}O_4$: C, 81.90; H, 5.26. Found: C, 81.83; H, 5.32. HRMS calcd for $C_{34}H_{26}O_4$: 498.1831 found 498.1828.

2-(4-Methylphenyl)-5-phenylfuran (3g). Colorless solid, mp 96−98 °C (from hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.38 (s, 3H), 6.68 (d, 1H, J = 3.6 Hz), 6.73 (d, 1H, J = 3.6 Hz), 7.21 (m, 3H), 7.40 (t, 2H, J = 7.2 Hz), 7.64−7.76 (m, 4H); ^{13}C NMR (100 MHz): δ 21.26, 106.45, 107.14, 123.60, 123.66, 127.15, 128.07, 128.65, 129.35, 130.82, 137.19, 152.91, 153.55; IR (KBr) cm^{-1}: 3056, 3030, 2987, 1602, 1263, 1023, 793, 756,

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691. Anal. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 87.10; H, 5.91. HRMS calcd for $C_{17}H_{14}O$: 234.1044 found 234.1042.

5,5′-Bis(4-methylphenyl)-2,2′-diphenyl-3,3′-bifuran (4g). Colorless solid. mp 238−240 °C (from hexane/chloroform 9/1) ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.39 (s, 6H), 6.67 (s, 2H), 7.25 (m, 10H), 7.65−7.76 (m, 8H); ^{13}C NMR (100 MHz): δ 21.33, 109.18, 116.22, 123.79, 125.06, 127.20, 127.73, 128.47, 129.43, 130.89, 137.55, 148.33, 152.93; IR (KBr) cm^{-1}: 3061, 3030, 2990, 1601, 1499, 1262, 1140, 932, 813, 768, 692. Anal. Calcd for $C_{34}H_{26}O_2$: C, 87.52; H, 5.62. Found: C, 87.44; H, 5.53. HRMS calcd for $C_{34}H_{26}O_2$: 466.1932 found 466.1929.

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Supporting Information Available: Copies of both ^{1}H and ^{13}C NMR spectra of furans (**3b**−**g**), bifurans (**4a**−**g**) and X-ray data of the compound **4f**. ^{1}H NMR, IR and HRMS spectral data of compound **1a**−**g**, **2a**−**g**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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