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LETTERS

A Novel Palladium-Catalyzed Cyclization of β-Iodo-β,γ-enones Toward 2,5-Disubstituted-Furans

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Abstract: The use of palladacycle catalyst to the transformation of various (*Z*)-β-iodo-β,γ-enones into the corresponding 2,5-disubstituted furans in good yields at room temperature was described. The comparison of using other kind of palladium catalysts under the similar reaction conditions was also described. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Palladacycle catalyst, (*Z*)-β-Iodo-β,γ-enones, Furan, Cyclization.

As part of our endeavor in investigating the palladium-catalyzed reaction to the synthesis of 4-substituted-4-decen-2-one and (Z)-α-alkylidene-γ-butyrolactone from (*Z*)-β-iodo-β,γ-enones,[1-3] we found that furanyl derivatives could be obtained from (*Z*)-β-iodo-β,γ-enones by the use of palladacycle catalyst and a tertiary amine as a base at room temperature. Since the preparation of substituted furans is of current interests, various methods have been taken up for this purpose.[4-11] Herein, we present a new route for the preparation of alkyl, aryl, or heteroaryl substituted furans under mild conditions and with good yields. We also present the scope and advantages of using palladacycle catalyst in running this reaction as shown in **Table I**.

As a typical procedure, palladacycle catalyst[12] (0.006 g, 0.0062 mmol), tetrahydrofuran (2 mL), (3*Z*)-3-iodo-1-phenylnon-3-en-1-one (0.042 g, 0.125 mmol), and triethylamine (0.025 g, 0.25 mmol) were sequentially added to a dry flask under nitrogen atmosphere and stirred for 12 h at room temperature. Solvent was evaporated under low pressure, and the residue was passed through a silica gel column with *n*-hexane as the eluant to afford the desired product in 83% yield and with ≥98% GC purity.

The use of palladacycle catalyst is noteworthy. In the case of using other palladium catalyst, such as $Pd_2(dba)_3$, $Pd(OAc)_2$, $Pd(PPh_3)_2Cl_2$, and $Pd(PPh_3)_4$, the formation of the desired 2,5-disubstituted furan derivatives was obtained either in lower yields or only in trace amount. In the use of $Pd(PPh_3)_2Cl_2$ and $Pd(PPh_3)_4$ catalyst, we isolated the corresponding dimers in 70 to 80% yields.[13] In the absence of base, the use of palladacycle catalyst alone could only give 15% yield (Entry 2). While using two equiv of tertiary base alone without adding palladium catalyst could not give detectable amount of the desired product. Use of diisopropylamine instead of tertiary amine in the above reaction, we could also observe the similar results as that of tertiary amine (Entry 4). Huang has reported a novel palladium-catalyzed rearrangement of acetylenic ketone into furan except the simple alkyl acetylenic ketones.[4] However, in our case, there is no problem to realize the cyclization of (*Z*)-β-iodo-β,γ-enones with either alkyl or aryl group adjacent to the carbonyl group in the system. The plausible mechanism of this reaction is that the iodoenones were first undergone dehydroiodination promoted by palladacycle catalyst to form allenyl ketone and then cyclized to form the furan ring as reported in the literature.[4,7,10] It is also interesting to know that neither (*Z*)- nor (*E*)-4-iodo-3-decen-2-one undergoes similar cyclization under the same reaction conditions to form 5-methyl-2-pentylfuran as detected by their GC and crude ^{1}H-NMR spectral analysis. Thus, the use of (*Z*)-β-iodo-β,γ-enones and palladacycle catalyst along with two equiv of base appears to be a simple

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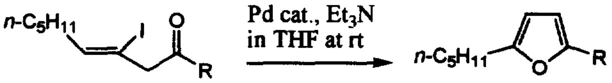
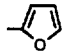
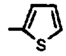
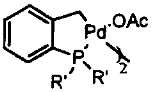
and efficient method to the formation of 2,5-disubstituted furans.

Table I. Transformation of Iodoenones into Furans by the Use of Palladacycle Catalyst[a].



Entry	Catalyst	Furan R =	Iso. Yield (%)
1	Palladacycle	-Ph	83
2	Palladacycle[b]	-Ph	15
3	Palladacycle[c]	-Ph	80
4	Palladacycle[d]	-Ph	72
5	$Pd_2(dba)_3$	-Ph	34
6	$Pd(OAc)_2$	-Ph	37
7	$Pd(PPh_3)_2Cl_2$	-Ph	trace[e,f]
8	$Pd(PPh_3)_4$	-Ph	trace[e,f]
9	Palladacycle		75
10	Palladacycle		81
11	Palladacycle	-Me	68
12	Palladacycle	$-C_5H_{11}$-n	79

[a] Palladacycle catalyst =  (R' = *o*-tolyl).

[b] Run the reaction in the absence of base. [c] Use diisopropylethylamine instead of triethylamine as the base. [d] Use diisopropylamine as the base. [e] Detected by GC analysis. [f] See text.

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