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LETTERS

A Novel Palladium-Catalyzed Tandem Dimerization and Cyclization of Acetylenic Ketones. A Convenient Method for 3,3'-Bifurans

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Abstract: Alkynones undergo rearrangement in the presence of $Pd(PPh_3)_4$ and triethylamine in tetrahydrofuran at room temperature to give 2,5-substituted furans, but under similar conditions $PdCl_2(PPh_3)_2$, by a tandem dimerization and cyclization, gives 3,3'-bifurans predominantly.

During the synthesis of furan and thiophene based conjugated polymers for an electroluminescence study, using 2,5-disubstituted furans prepared by a reported procedure,[1] 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. Further studies on this cyclization revealed that alkynones could be selectively transformed either into furans or bifurans in good yields depending upon the catalyst used in the reaction.

The preparation of substituted furans is of current interest and various methods have been used[2-15] for their synthesis. Catalysts including Pd(0), Ag(I) and Rh(I). have been used for this purpose. A novel palladium catalyzed rearrangement of acetylenic ketones into furans has been reported.[1] The reactions were carried out in toluene at reflux, and was not applicable to the preparation of simple alkylated furans. In addition, the yields of furan derivatives were low. Trost has reported furan formation as a minor product during isomerization of alkynones to dienones by palladium catalysts.[16] Herein, we report the preparation of alkyl, aryl or hetero aryl substituted furans in good yields under mild conditions from easily accessible α,β-acetylenic ketones. This procedure demonstrates for the first time that tuning the palladium catalyst could provide bifurans predominantly from the same acetylenic ketone. This improved procedure allows the cyclization of alkynones with an alkyl group adjacent to the carbonyl functionality to the corresponding alkyl furan in moderate yield.

It is interesting to note that when $Pd(PPh_3)_4$ was used, 2,5-disubstituted furans were formed exclusively or predominantly. On the other hand, the use of $PdCl_2(PPh_3)_2$ as a catalyst to bifurans predominantly. Tertiary amines are the bases of choice for the reaction. There is no generalization or consistency, and also poor yields were obtained, when secondary or primary amines were used as base. Using tertiary base alone without adding a palladium catalyst did not yield any detectable amount of desired products. N,N-Diisopropylethylamine and triethylamine provided the same reaction pattern when they were used as a base in the reaction medium.

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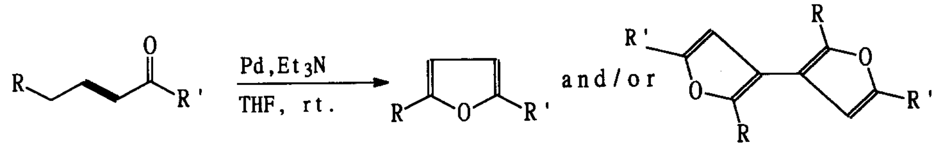
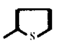
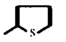
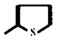
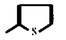
Table I Transformation of alkynones into furans and bifurans by the use of palladium catalysts

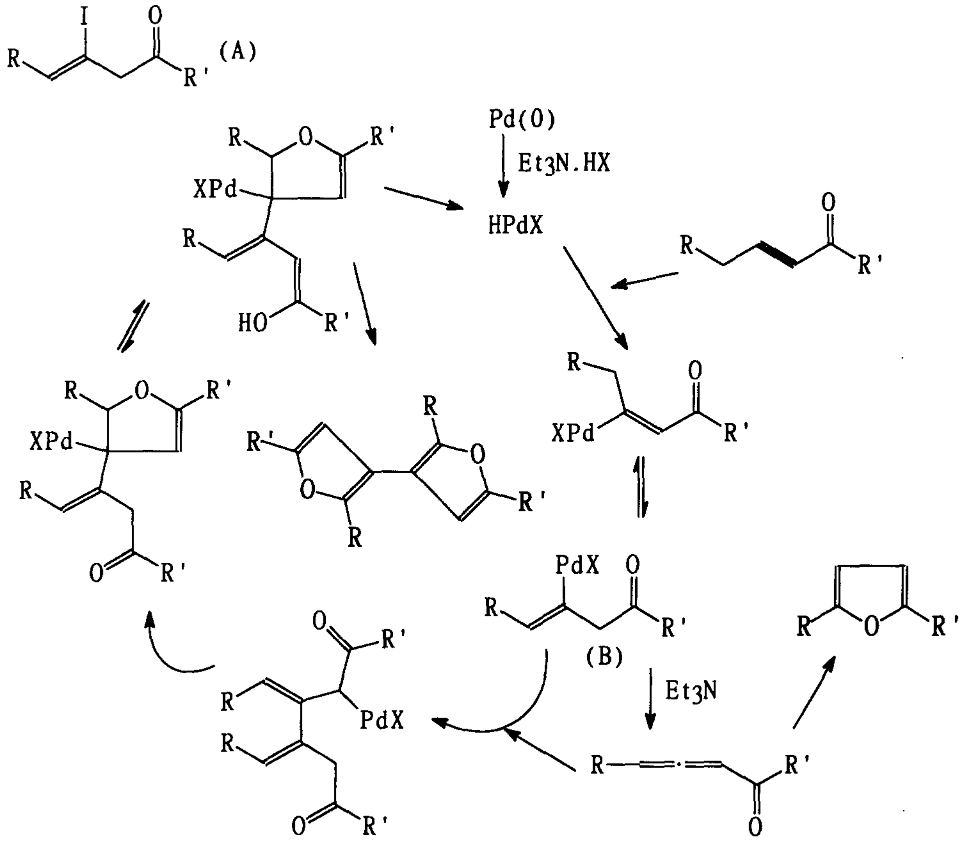


Entry	Catalysts	R	R'	Isolated Yields (%) Furan	Isolated Yields (%) Bifuran
1	$Pd(PPh_3)_4$	-Ph	-Ph	55	trace[b]
2	$Pd(PPh_3)_4$	-Ph		70	07
3[a]	$Pd(PPh_3)_4$	-Ph		67	04
4	$Pd(PPh_3)_4$	-Ph	n-C_8H_{17}	52	trace[b]
5	$Pd(PPh_3)_4$	-Ph	n-C_5H_{11}	41	07
6	$Pd(PPh_3)_4$	-(3-OMe)Ph		49	05
7	$PdCl_2(PPh_3)_2$	-Ph	-Ph	08	56
8	$PdCl_2(PPh_3)_2$	-Ph		06	53
9	$PdCl_2(PPh_3)_2$	-Ph	n-C_8H_{17}	08	42
10	$PdCl_2(PPh_3)_2$	-Ph	n-C_5H_{11}	05	48
11	$PdCl_2(PPh_3)_2$	-(3-OMe)Ph		05	71

[a] Diisopropylethylamine was used as base instead of triethylamine. [b] Detected by GC analysis.

The mechanism for dimerization has not been established, but our qualitative observations suggest a reasonable possibility. Both $Pd(PPh_3)_4$ and $PdCl_2(PPh_3)_2$ yielded bifurans as a major product (with a small amount of furans) when treated with iodoenone (A).[17] Upon the basis of the efficiency of the reaction when either $Pd(PPh_3)_4$ or $PdCl_2(PPh_3)_2$ and iodoenone were employed to form the bifuran, and the inefficiency of $Pd(PPh_3)_4$ to form the same when treated with alkynone, we propose that the active catalyst is a hydridopalladium halide. The halide added to the alkynone could isomerize[13,16] the triple bond to form the same intermediate (B) as that from iodoenone (A). Formation of this intermediate is not possible when $Pd(PPh_3)_4$ was treated with alkynone.

The formation of only simple furans could be justified through allene formation and cyclization. Further detailed mechanistic study is in progress.



The palladium-based catalytic method to cyclize alkynones offers the prospect of controlling the nature of the products as in Table I. The formation of bifurans as a single regioisomer was unambiguously determined by ^{1}H NMR, ^{13}C NMR, NOE and HMBC data.

General Procedure:

To a solution of acetylenic ketone (0.25 mmol) in 2 mL of dry THF, under nitrogen, $Pd(PPh_3)_4$ (5 mol %) and triethylamine (0.63 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 mixtures and purification of the crude products on a silica gel column using hexane afforded the respective products in good yields (Table I).

Representative spectral and analytical data.

Furan (entry-5).

^{1}H NMR (CDCl$_3$, 400 MHz) ∂ 0.89 (t, J = 7.2 Hz, 3H), 1.35 (m, 4H), 1.67 (m, 2H), 2.65 (t, J = 7.6 Hz, 2H), 6.03 (d, J = 3.1 Hz, 1H), 6.52 (d, J = 3.1 Hz, 1H), 7.17-7.72 (m, 5H). ^{13}C NMR (CDCl$_3$, 100 MHz) ∂ 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. MS *m/z* 214 (M$^+$), HRMS calc. For $C_{15}H_{18}O$ 214.1358, found 214.1354.

Bifuran (entry-10).

^{1}H NMR (CDCl$_3$, 400 MHz) ∂ 0.89 (t, J = 7.2 Hz, 6H), 1.35 (m, 8H), 1.67 (m, 4H), 2.66 (t, J = 7.4 Hz, 4H), 5.97 (s, 2H), 7.12-7.70 (m,10H). ^{13}C NMR (CDCl$_3$, 100 MHz) ∂ 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. MS *m/z* 426 (M$^+$), HRMS calc. For $C_{30}H_{34}O_2$ 426.2559, found 426.2554.

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18. All new products were characterized by their spectral and analytical data.