# Palladium-Catalyzed Rearrangement of 2-Alkynyl Aryl Ketones to Substituted Furans

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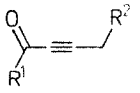
1,4-Diaryl- and 1,4-diaryl-2-alkyl-3-butyn-1-ones can be rearranged catalytically by treatment with $Pd(dba)_2/PPh_3$ to give 2,5-substituted and 2,3,5-trisubstituted furans in 26–38% yields.

A number of methods have been reported for the synthesis of substituted furans.[1-6] In our previous paper[7] we found that aryl 1-alkynyl ketones **(1)** are able to rearrange to 2,5-disub-



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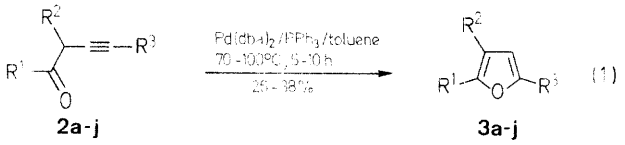
stituted furans in the presence of palladium catalyst. It has been reported that 2-alkynyl ketones **(2)** are able to be converted to allenyl ketones[8,9] which are the proposed intermediates of the rearrangement of **1**.[7] It was of interest to find out if ketones **2** could undergo the same rearrangement under similar conditions. 2,5-Diphenylfuran has been prepared from 1,4-diphenyl-3-butyn-1-one by hydrogenation, epoxidation, and acid-catalyzed rearrangement in 59% overall yield.[10] We here report the rearrangement of 2-alkynyl aryl ketones **2** to either 2,5-diaryl- or 3-alkyl-2,5-diarylfurans **3** by palladium catalyst.

**Table.** Palladium-Catalyzed Rearrangement of 2-Alkynyl Aryl Ketones **2**

| Product | Reaction Conditions (h, °C) | Yield[a] (%) | m.p. (°C) | Molecular Formula[b] or m.p. (°C) reported | MS *m/e* ($M^+$, %) | $^1$H-NMR ($CCl_4$/TMS)[c] $\delta$ |
|---|---|---|---|---|---|---|
| **3a** | 8, 100 | 29 | 101–102 | $C_{17}H_{14}O$ (234.3) | 234 (100) | 2.35 (s, 3H, $CH_3$); 6.6 (s, 2H); 7.0–7.8 (m, 9$H_{arom}$) |
| **3b** | 5, 100 | 30 | 126–127 | 123[14] | 254 (100) | 6.6 (s, 2H)[d]; 7.1–7.8 (m, 9$H_{arom}$) |
| **3c** | 10, 100 | 33 | 126–127 | 123[14] | 254 (100) | 6.6 (s, 2H); 7.1–7.8 (m, 9$H_{arom}$) |
| **3d** | 7, 100 | 28 | 169–170 | 167–168[5], 168–169[11] 169–170[12] | 288 (100) | 6.4 (s, 2H); 7.0–7.5 (m, 8$H_{arom}$) |
| **3e** | 9, 70 | 38 | 110–111.5 | $C_{16}H_{10}Cl_2O$ (289.1) | 288 (100) | 6.7 (s, 2H); 7.1–7.8 (m, 8$H_{arom}$) |
| **3f** | 10, 100 | 34 | 97–98 | $C_{17}H_{12}O_3$ (264.3) | 264 (100) | 5.85 (s, 2H, $CH_2$); 6.3–6.6 (m, 2H); 6.65–7.7 (m, 8$H_{arom}$) |
| **3g** | 10, 80 | 36 | 108–108.5 | $C_{16}H_{11}FO$ (238.2) | 238 (100) | 6.53 (s, 2H); 6.76–7.7 (m, 9$H_{arom}$) |
| **3h** | 10, 100 | 35 | 87–88 | 88[5] 88–89[10,11] | 220 (100) | 6.6 (s, 2H); 7.1–7.9 (m, 10$H_{arom}$) |
| **3i** | 5, 70 | 28 | 57–58 | 58–59[13] | 234 (100) | 2.2 (s, 3H, $CH_3$); 6.4 (s, 1H); 7.0–7.8 (m, 10$H_{arom}$) |
| **3j** | 6, 70 | 26 | 43.5–44.5 | $C_{19}H_{18}O$ (262.3) | 262 (100) | 1.05 (t, 3H, $CH_3$); 1.45–2.0 (m, 2H); 2.55 (t, 2H); 6.4 (s, 1H); 6.9–7.7 (m, 10$H_{arom}$) |

[a] Yield of isolated product.
[b] Satisfactory microanalyses obtained: C ±0.39, H ±0.23.
[c] Varian EM-360A spectrometer.
[d] $^{13}$C-NMR ($CDCl_3$/TMS): $\delta$ = 107.3, 107.7, 123.8, 124.9, 127.5, 128.4, 128.7, 128.9, 130.3, 130.5, 152.3, 153.7.

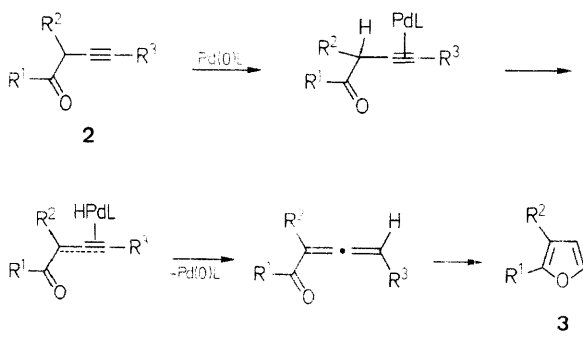



(1)

**2a-j** **3a-j**

dba = dibenzylideneacetone

| 2, 3 | $R^1$ | $R^2$ | $R^3$ |
|---|---|---|---|
| **a** | 4-$CH_3C_6H_4$ | H | $C_6H_5$ |
| **b** | 4-$ClC_6H_4$ | H | $C_6H_5$ |
| **c** | $C_6H_5$ | H | 4-$ClC_6H_4$ |
| **d** | 4-$ClC_6H_4$ | H | 4-$ClC_6H_4$ |
| **e** | 3,4-$Cl_2C_6H_3$ | H | $C_6H_5$ |
| **f** |  | H | $C_6H_5$ |
| **g** | 4-$FC_6H_4$ | H | $C_6H_5$ |
| **h** | $C_6H_5$ | H | $C_6H_5$ |
| **i** | $C_6H_5$ | $CH_3$ | $C_6H_5$ |
| **j** | $C_6H_5$ | *n*-$C_3H_7$ | $C_6H_5$ |




**2** **3** (2)

A possible mechanism of this rearrangement is as follows: by means of palladium-catalyst, the 2-alkynyl ketones **2** are first rearranged to allenyl ketones which are then cyclized to furans.[3]

**2-(4-Chlorophenyl)-5-phenylfuran (3b); Typical Procedure:**
A mixture of $Pd(dba)_2$ (1–2 mol%), 1-(4-chlorophenyl)-4-phenyl-3-butyn-1-one (**2b**; 200 mg), $PPh_3$ (1–2 mol%), and toluene (1 mL) is heated under nitrogen at 100 °C for 5 h. After cooling, the mixture is directly purified by TLC on silica gel (eluent: petroleum ether); yield of **3b**: 60 mg (30%); m.p. 126–127 °C.

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