

Palladium-Catalyzed Reaction of Propargyl Nucleophiles with α -Sulfonyl α,β -Unsaturated Ketones: A Single-Step Synthesis of Furo[3,4-*c*] Heterocyclic Derivatives

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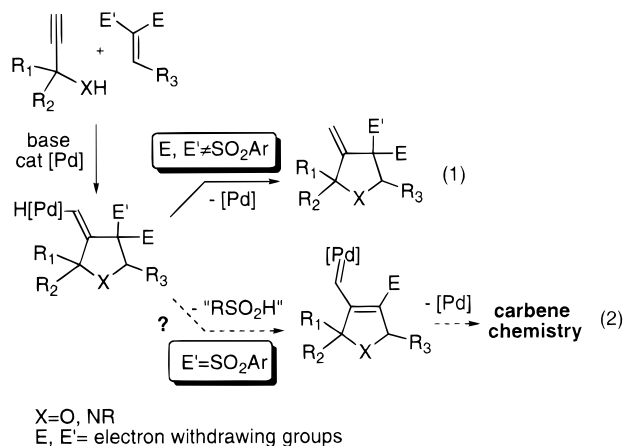
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The search for new methodologies that allow the rapid construction of polycyclic structures in a single operation is, today, an important challenge for synthetic organic chemists.¹ In this area, reactive transition metal carbene complexes, generated in catalytic reactions, have emerged as extremely valuable intermediate species in the design of consecutive cyclization processes.² These catalytic metal carbenes have usually been generated by exposure of α -diazocarbonyl compounds to metal complexes or salts.³ Like free carbenes, they have been involved in a wide range of synthetic transformations, such as self-dimerization, cyclopropanation, and various insertion reactions. Coordination of the carbene with the metal tempers its reactivity and imparts greater selectivity to the reaction. Remarkably, the observed selectivities may be strongly influenced by the nature of the coordinated metal complex.⁴

In recent years, our research efforts have been concerned with the elaboration of tandem or cascade reactions⁵ involving palladium-mediated Wacker-type cyclization processes, which were devised in our laboratory.⁶ Recently, a new methodology based on a Michael addition–carbocyclization sequence has permitted the systematic formation of highly functionalized tetrahydrofurans and pyrrolidines simply through the joining of two readily available components, a propargylic alcohol (or amine) as the Michael donor and an arylidene (or alkylidene) malonate as the Michael acceptor (Scheme 1, eq 1).^{7,8} A study of the synthetic utility of sulfone-based activated olefins as versatile multi-coupling reagents for

Scheme 1



the construction of more elaborate heterocycles was then undertaken. Previous work⁹ suggested that the particular ability of the sulfonyl group to act as a leaving group may change the reaction pathway by generating carbene palladium complexes. These metal-stabilized carbenes may then be involved in further transformations, thus imparting increased complexity to the reaction products (Scheme 1, eq 2).¹⁰

Of particular interest was the design of selective intramolecular processes aimed at the construction of polycyclic systems. The possibility of directing our strategy toward the synthesis of furan-based bicyclic compounds was first investigated with this aim. Furans are common substructures in many natural products that exhibit interesting biological activities and can be found in numerous commercial products, including pharmaceuticals, fragrances, and dyes.¹¹ They are also valuable building blocks in organic synthesis.^{11,12} The 6π -electrocyclization of alkenone carbenes¹³ is an interesting method for synthesizing furans.¹⁴ It is of particular importance in the preparation of 3,4-disubstituted furans, which are rather difficult to obtain by other means.^{14,15} It was reasoned that, if alkenone carbenes could be generated by applying the tandem Michael addition–

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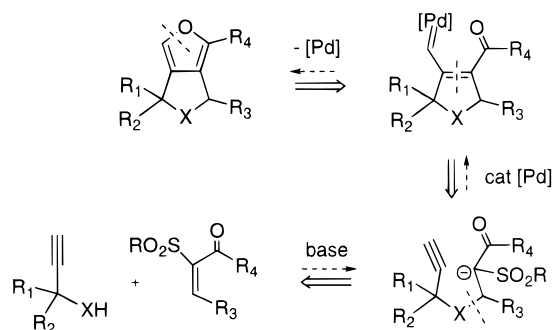
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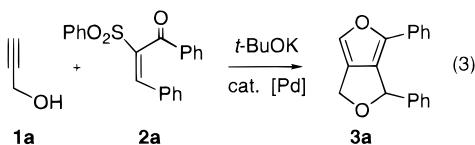
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Scheme 2. Retrosynthesis

carbocyclization to arylidene β -ketosulfones, then internal trapping of the carbene by the carbonyl oxygen would produce a variety of furo[3,4-*c*]furans and furo[3,4-*c*]pyrroles (Scheme 2).¹⁶ The successful execution of this strategy is reported.

The reaction of propargyl alcohol **1a** and α -phenylsulfonyl chalcone **2a** was the first to be investigated. From previous work, it was thought that a stoichiometric amount of ^tBuOK would be required as the base if the expected reaction were to take place efficiently.⁹ The desired furofuran **3a** was obtained by simple treatment of a solution of **1a** (1.5 equiv) with the chosen base (1.1 equiv) and subsequent addition of the Michael acceptor **2a** together with a catalytic amount (5 mol %) of a palladium complex (eq 3).



Poor to moderate yields were obtained, depending on the nature of the catalyst and solvent used (Table 1). The best results were obtained with Pd(PPh₃)₂X₂ (X = Cl or OAc) as the catalyst in ethereal solvents under reflux (Table 1, entries 2, 3, 8, and 9). Under these conditions, essentially complete and clean reactions were observed. Polymerization of the Michael acceptor would possibly account for the moderate yields obtained under such conditions. However, substantial amounts of this material, together with small quantities of the open-type molecule resulting from simple 1,4-conjugate addition, were recovered when the reaction did not proceed efficiently (Table 1, entries 4–7 and 10).

Attention was then focused on the reactivity of various Michael acceptors that differed in the nature of the substituent on the sulfone in order to probe possible electronic or steric effects in the preceding reaction. Reactions were conducted under the above optimized conditions (Table 1, entry 3). Not surprisingly, substituting the phenyl moiety for electron-donating groups such as methyl or *tert*-butyl resulted in a dramatic decrease in the rate of the reaction, and large amounts of starting material were recovered from the reaction mixture (Table 2, entries 2 and 3). The trifluorosulfonyl moiety is a better electron-withdrawing group and a better leaving group

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Table 1. Reaction between α -Phenylsulfonyl Chalcone (2a) and Propargyl Alcohol with Different Catalysts in Various Solvents^a

entry	catalyst	solvent	<i>T</i> (°C)	time (h)	yield (%)
1	Pd(OAc) ₂ (PPh ₃) ₂	THF	20	– ^b	–
2	Pd(OAc) ₂ (PPh ₃) ₂	THF	70	4	52
3	PdCl ₂ (PPh ₃) ₂	THF	70	3	57
4	PdCl ₂ (dppf)	THF	70	4 ^c	27
5	[PdCl(allyl)] ₂	THF	70	4 ^c	18
6	Pd(PPh ₃) ₄	THF	70	4 ^c	15
7	PdCl ₂ (CH ₃ CN) ₂	CH ₃ CN	80	5 ^{c,d}	9 ^e
8	PdCl ₂ (PPh ₃) ₂	dioxane	100	3.5	51 ^e
9	PdCl ₂ (PPh ₃) ₂	DME	85	5	49 ^e
10	PdCl ₂ (PPh ₃) ₂	DMF	100	4 ^c	17 ^e

^a Reactions conducted on half-millimolar scale using ^tBuOK as base. ^b Proceeded slowly. Only small amounts of the expected product were formed after prolonged reaction times (>24 h). ^c The reaction ceased after less time than the time allotted. Small amounts of both the Michael acceptor and the Michael adduct were recovered from the reaction. ^d Unidentified side products were also formed. ^e Yields were not improved at lower temperatures.

Table 2. Influence of the Nature of the Sulfonyl Group on the Reaction between α -Sulfonyl Chalcones and Propargyl Alcohol^a

entry	sulfonyl	yield (%)	recovered M. A. ^b
1 ^c	PhSO ₂	57	trace
2	MeSO ₂	10	32
3	^t BuSO ₂	<5	43
4	CF ₃ SO ₂	47	16

^a Reactions conducted for 3 h in refluxing THF using PdCl₂(PPh₃)₂ as catalyst. ^b MA = Michael acceptor. ^c Result from Table 1, entry 3.

than alkyl (or aryl) sulfones. Such features would be expected to favor the initial Michael addition, as well as the expulsion of the sulfonyl group. Reaction did indeed occur, leading to the expected furofuran, albeit in a yield lower than that obtained with a phenylsulfonyl group (Table 2, entry 4). The lower reactivity observed in this case could be due to a better stabilization of the enolate intermediate, which would be less prone to cyclization.

The scope of the reaction was thus investigated on phenylsulfonyl derivatives. The results are summarized in Table 3. A range of furofurans were obtained in moderate to good yields. The reaction tolerates various substitution patterns of the α,β -unsaturated ketones, both alkyl and aryl substituents giving comparable results (Table 3, entries 1–7). Remarkably, even hindered nucleophiles participate efficiently (Table 3, entry 8). Finally, the methodology was successfully extended to the synthesis of furopyrroles (Table 3, entries 9 and 10).

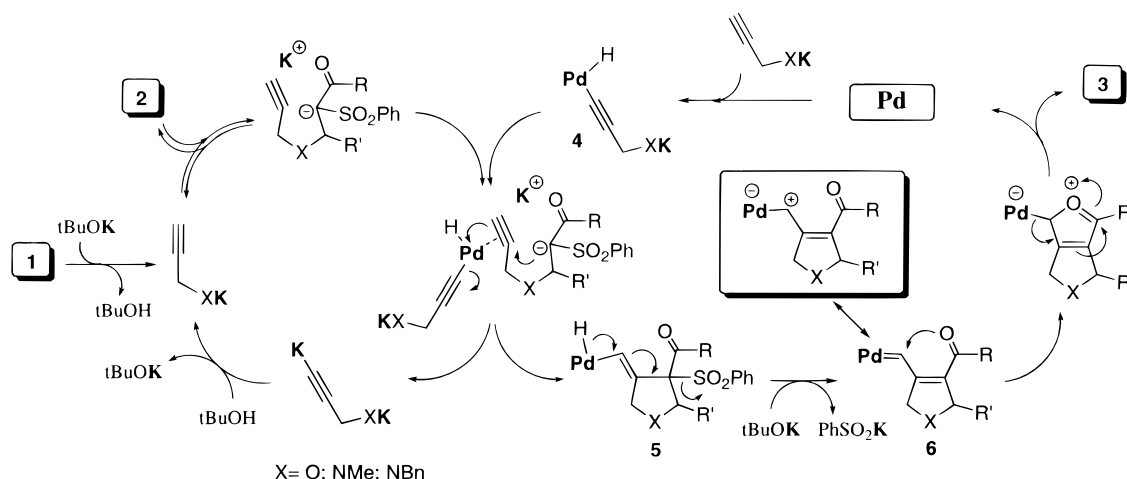
According to our mechanistic understanding of the reaction, the arylidene β -ketosulfone behaves here as a multi-coupling reagent. It acts initially as a Michael acceptor and then as a nucleophilic ionic center. The cyclization is believed to be promoted by a σ -alkynyl palladium(II) (or IV) hydride species (**4**) resulting from insertion of the metal into the C–H bond of the terminal acetylene (Scheme 3).¹⁷ This would lead to an intermediate species **5**. At this stage, the well-known ability of the sulfonyl moiety to act as a leaving group would trigger the generation of a palladium carbene (**6**) via what appears to be a unique example of sulfinic acid elimination. As illustrated in the first catalytic cycle (Scheme

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Table 3. Palladium-Catalyzed Cyclization of Propargyl Nucleophiles with α -Sulfonyl- α,β -unsaturated Ketones^a

Entry	Nucleophile	Acceptor	furan	yield (%) ^b	Entry	Nucleophile	Acceptor	furan	yield (%) ^b
1				57	6				47
2				52	7				45
3				58	8				50
4				42	9				54
5				60	10				52

^a Reactions conducted on half-millimolar scale in refluxing THF. Ratio of **1**:^tBuOK: PdCl₂(PPh₃)₂ = 1.5:1:1.2:0.05. ^b Yields refer to pure isolated products.

Scheme 3

3), the first cyclization reaction would require only catalytic quantities of ^tBuOK in order to proceed, as this base should be continuously regenerated during this process. It seems reasonable, therefore, to suggest that the base intervenes also in the second cyclization reaction, possibly by abstracting the hydrogen of the intermediate Pd(II or IV)–H species to form the palladium carbene. This would produce potassium sulfinate as a side product, hence the need for stoichiometric quantities

of base. The electrophilic vinylidene palladium **6** is then attacked by the oxygen of the adjacent ketone, leading to **3** in a 6 π -electrocyclization process at the end of which the catalyst is recycled.

In conclusion, an efficient single-step synthesis of a new class of furofurans and furopyrroles from the easily available propargyl alcohols (or amines) and arylidene (or alkylidene) β -ketosulfones has been developed. Further investigations will focus on the potential utility of

this reaction in natural product synthesis, in particular syntheses of lignans. When considering the diversity of reactions that commonly involve electrophilic carbenes, we believe that the chemistry described herein will be useful for the construction of more complex molecules.

Experimental Section

General Methods. Unless otherwise noted, all reactions were carried out under a nitrogen atmosphere in oven-dried glassware using standard syringe, cannula, and septa techniques. Commercial reagents and solvents were used as purchased, except for tetrahydrofuran, which was distilled over calcium hydride. Thin-layer chromatography was carried out on Merck silica 60/F-254 aluminum-backed plates. Flash chromatography was performed using Merck silica gel 60 (40–63 μm). Melting points are uncorrected. NMR spectra were recorded in CDCl_3 . Chemical shifts (δ) are quoted in parts per million. J values are given in hertz.

General Procedure for the Cyclization of α -Phenylsulfonyl- α,β -Unsaturated Ketones with Propargyl Nucleophiles. To potassium *tert*-butoxide (60 mg, 0.6 mmol) in THF (1.5 mL) was added the propargyl alcohol or amine (0.75 mmol), and the resulting mixture was stirred at room temperature for 10 min. The Michael acceptor (0.5 mmol) and $\text{PdCl}_2(\text{PPh}_3)_2$ (17.5 mg, 0.025 mmol) were then successively added, and the reaction mixture was heated under reflux for 3 h. The reaction was then quenched with a saturated aqueous solution of ammonium chloride, and the organic material was extracted with ethyl acetate. The organic layer was dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by chromatography on silica gel (eluent, ethyl acetate/petroleum ether).

1,6-Diphenyl-1H,3H-furo[3,4-*c*]furan (3a): 57%; solid; mp 96–98 °C; ^1H NMR (CDCl_3 , 300 MHz) δ 7.45–7.10 (m, 11H), 6.16 (s, 1H), 5.02 (d, $^2J = 11.4$, 1H), 4.92 (d, $^2J = 11.4$, 1H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 144.0, 139.7, 133.3, 130.1, 129.9, 128.8, 128.7, 128.6, 127.9, 127.2, 124.4, 79.9, 64.9. HRMS m/z calcd for $\text{C}_{18}\text{H}_{14}\text{O}_2$, 262.0994; found, 262.0982.

1-(3,4-Dioxymethylene)phenyl-6-phenyl-1H,3H-furo[3,4-*c*]furan (3b): 52%; solid; mp 143–145 °C; ^1H NMR (CDCl_3 , 300 MHz) δ 7.35–7.13 (m, 6H), 6.92 (dd, $J = 8.1$ and 1.5, 1H), 6.81 (d, $J = 1.5$, 1H), 6.78 (d, $J = 8.1$, 1H), 6.07 (s, 1H), 5.93 (bs, 1H), 5.92 (bs, 1H), 4.99 (d, $^2J = 11.8$, 1H), 4.88 (d, $^2J = 11.8$, 1H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 148.2, 148.0, 143.9, 133.8, 133.3, 130.1, 129.9, 128.6, 127.2, 124.4, 121.8, 108.2, 108.1, 101.2, 79.8, 64.7. Anal. Calcd for $\text{C}_{19}\text{H}_{14}\text{O}_4$: C, 74.50; H, 4.61. Found: C, 74.77; H, 4.57.

1-(4-Fluoro)phenyl-6-phenyl-1H,3H-furo[3,4-*c*]furan (3c): 58%; solid; mp 73–75 °C; ^1H NMR (CDCl_3 , 300 MHz) δ 7.40–7.00 (m, 10H), 6.16 (s, 1H), 5.00 (d, $^2J = 11.4$, 1H), 4.90 (d, $^2J = 11.4$, 1H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 165.4, 160.4, 144.0, 135.6, 135.5, 133.2, 130.0, 129.9, 129.8, 129.7, 128.6, 128.5, 127.3, 124.4, 115.9, 115.5, 79.2, 64.8. Anal. Calcd for $\text{C}_{18}\text{H}_{13}\text{FO}_2$: C, 77.13; H, 4.67. Found: C, 76.83; H, 4.37.

1-Cyclohexyl-6-phenyl-1H,3H-furo[3,4-*c*]furan (3d): 42%; solid; mp 81–83 °C; ^1H NMR (CDCl_3 , 300 MHz) δ 7.55 (d, $J =$

8.5, 2H), 7.39 (m, 2H), 7.25 (m, 2H), 7.12 (s, 1H), 5.17 (d, $J = 3.0$, 1H), 4.82 (s, 2H), 1.85–1.00 (m, 10H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 143.2, 133.1, 130.8, 129.9, 128.7, 128.4, 127.1, 124.7, 82.4, 65.4, 43.1, 30.4, 26.7, 26.6, 26.4, 26.1. Anal. Calcd for $\text{C}_{18}\text{H}_{20}\text{O}_2$: C, 80.56; H, 7.51. Found: C, 80.34; H, 7.47.

1-Phenyl-6-isopropyl-1H,3H-furo[3,4-*c*]furan (3e): 60%; liquid; ^1H NMR (CDCl_3 , 300 MHz) δ 7.34 (m, 5H), 7.05 (s, 1H), 5.93 (s, 1H), 4.96 (d, $^2J = 11.4$, 1H), 4.85 (d, $^2J = 11.4$, 1H), 2.78 (sept, $J = 7.0$, 1H), 1.03 (d, $J = 7.0$, 3H), 1.01 (d, $J = 7.0$, 3H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 150.8, 141.6, 131.4, 128.6, 128.4, 128.3, 127.6, 126.7, 79.2, 64.9, 27.6, 21.1, 20.6. HRMS m/z calcd for $\text{C}_{15}\text{H}_{16}\text{O}_2$, 228.1150; found, 228.1140.

1-Phenyl-6-(4-nitro)phenyl-1H,3H-furo[3,4-*c*]furan (3f): 47%; solid; mp 139–141 °C; ^1H NMR (CDCl_3 , 300 MHz) δ 8.05 (d, $J = 8.8$, 2H), 7.45–7.35 (m, 8H), 6.16 (s, 1H), 5.05 (d, $^2J = 11.4$, 1H), 4.93 (d, $^2J = 11.4$, 1H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 146.1, 141.9, 138.9, 135.5, 134.2, 133.0, 132.2, 129.0, 127.9, 124.5, 124.1, 80.0, 65.0. Anal. Calcd for $\text{C}_{18}\text{H}_{13}\text{NO}_4$: C, 70.35; H, 4.26; N, 4.56. Found: C, 70.46; H, 4.41; N, 4.56.

1-Phenyl-6-(4-methoxy)phenyl-1H,3H-furo[3,4-*c*]furan (3g): 45%; solid; mp 60–62 °C; ^1H NMR (CDCl_3 , 300 MHz) δ 7.55–7.15 (m, 8H), 6.79 (d, $J = 8.8$, 2H), 6.14 (s, 1H), 5.00 (d, $^2J = 11.4$, 1H), 4.93 (d, $^2J = 11.4$, 1H), 3.75 (s, 3H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 158.8, 144.0, 139.9, 133.2, 129.2, 128.8, 128.6, 127.9, 126.9, 125.8, 123.2, 114.1, 79.8, 64.9, 55.3. Anal. Calcd for $\text{C}_{19}\text{H}_{16}\text{O}_3$: C, 78.06; H, 5.52. Found: C, 78.33; H, 5.30.

1,6-Diphenyl-7,7-dimethyl-1H,3H-furo[3,4-*c*]furan (3h): 50%; solid; mp 70–72 °C; ^1H NMR (CDCl_3 , 300 MHz) δ 7.45–7.05 (m, 11H), 6.16 (s, 1H), 1.61 (s, 6H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 143.5, 141.7, 140.2, 130.1, 129.3, 128.7, 128.5, 128.4, 128.3, 127.0, 124.4, 79.9, 79.0, 29.8, 29.4. Anal. Calcd for $\text{C}_{20}\text{H}_{18}\text{O}_2$: C, 82.73; H, 6.25. Found: C, 82.49; H, 6.18.

N-Methyl-1,6-diphenyl-1H,3H-furo[3,4-*c*]pyrrole (3i): 54%; solid; mp 78–80 °C; ^1H NMR (CDCl_3 , 300 MHz) δ 7.35–7.25 (m, 5H), 7.22 (s, 1H), 7.15–7.05 (m, 5H), 4.62 (s, 1H), 4.16 (d, $^2J = 12.1$, 1H), 3.62 (d, $^2J = 12.1$, 1H), 2.45 (s, 3H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 144.1, 140.3, 131.2, 130.7, 130.4, 129.6, 129.0, 128.6, 128.2, 128.0, 126.7, 124.6, 69.3, 52.4, 39.7. Anal. Calcd for $\text{C}_{19}\text{H}_{17}\text{NO}$: C, 82.88; H, 6.22; N, 5.09. Found: C, 82.48; H, 6.29; N, 4.89.

N-Benzyl-1,6-diphenyl-1H,3H-furo[3,4-*c*]pyrrole (3j): 52%; solid; mp 123–125 °C; ^1H NMR (CDCl_3 , 300 MHz) δ 7.45–7.05 (m, 16H), 4.93 (s, 1H), 3.97 (d, $^2J = 12.1$, 1H), 3.91 (d, $^2J = 13.2$, 1H), 3.62 (d, $^2J = 13.2$, 1H), 3.58 (d, $^2J = 12.1$, 1H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 144.2, 140.9, 139.3, 131.1, 130.9, 130.5, 129.7, 129.3, 128.7, 128.5, 128.3, 128.2, 128.0, 127.0, 126.7, 124.6, 67.2, 56.8, 49.6. HRMS m/z calcd for $\text{C}_{25}\text{H}_{21}\text{NO}$, 351.1623; found, 351.1622.

Supporting Information Available: General procedure and characterization for α -sulfonyl α,β -unsaturated ketones and copies of ^1H NMR spectra for compounds **3a–3j**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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