Palladium-Catalyzed Cyclocarbonylation of *o*-Ethynylphenols and Vinyl Triflates To Form 3-Alkylidene-2-coumaranones

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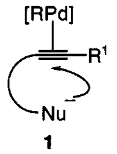
Keywords: Cyclocarbonylation / Alkynes / Catalysis / Palladium / Vinyl triflates

o-Ethynylphenols react with vinyl triflates, in the presence of tetrakis(triphenylphosphane)palladium(0) and under carbon monoxide, to form 3-alkylidene-2-coumaranones in good yield.

The palladium-catalyzed cyclization of alkynes bearing a nucleophilic center close to the carbon−carbon triple bond and unsaturated halides/triflates or allyl esters is a versatile and convenient process for the preparation of carbo-[1] and heterocycles.[2,3] The reaction is considered to proceed through the intramolecular regioselective nucleophilic attack across the carbon−carbon triple bond activated by coordination to a palladium atom bearing a carbon unit, as illustrated for **1**, followed by a reductive elimination step that produces the functionalized cyclic derivative and regenerates the active catalytic species. When the reaction with unsaturated halides or triflates is carried out in the presence of carbon monoxide, the activation of the carbon−carbon triple bond appears to involve the intervention of σ-acylpalladium complexes.[2i,2l,2m]



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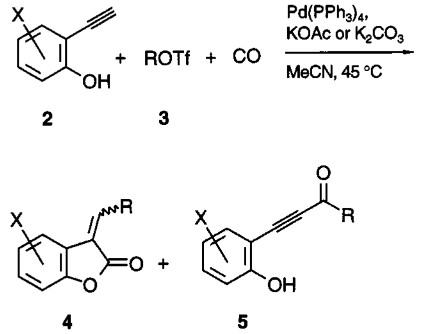
R = aryl, vinyl, alkynyl, allenyl, allyl, acyl
R^1 = alkyl, vinyl, aryl, H
Nu = C, N, O

During our investigations of this chemistry, we have found that *o*-ethynylphenols **2** and vinyl triflates **3**, when treated under the same reaction conditions employed earlier by us for the carbonylative cyclization of *o*-(arylethynyl)phenols with vinyl triflates and producing 3-acyl-2-arylbenzo[*b*]furans,[2l] follow a complete different course and afford the 3-alkylidene-2-coumaranones **4** (Scheme 1).

Treatment of *o*-ethynylphenol (**2a**) (1.5 equiv) with 3,3,5,5-tetramethylcyclohex-1-en-1-yl triflate (**3a**) in the presence of $Pd(PPh_3)_4$ (0.05 equiv.) and KOAc in MeCN under carbon monoxide at 45 °C for 4 h resulted in the formation of 3-(3,3,5,5-tetramethylcyclohex-1-en-1-yl)methylidene-2-coumaranone (**4a**) in 64% yield of an approximately 85:15 (*E*)/(*Z*) mixture of isolated isomers. The stereoisomeric ratio was assigned on the basis of NOE studies.[4] The carbonylative coupling derivative, 1-(3,3,5,5-tetramethylcyclohex-1-en-1-yl)-3-(*o*-hydroxyphenyl)propynone (**5a**) was also obtained in 27% yield. The reaction gave **4a** in 71% yield with K_2CO_3 as the base (3 h). However, with other vinyl triflates, this base has not consistently given the best results: For example, **4b** was isolated in 61% yield [ca. 82:18 (*E*)/(*Z*) mixture] with KOAc and in 54% yield [ca. 83:17 (*E*)/(*Z*) mixture] with K_2CO_3. We generally used KOAc. No attempts have been made to determine the amount of the carbonylative coupling derivative formed with each vinyl triflate.



Scheme 1. Palladium-catalyzed cyclocarbonylation of *o*-ethynylphenols **2** with vinyl triflates **3**

A reasonable rationale for the production of **4** from **2** and **3** is outlined in Scheme 2. The reaction is envisioned to involve the key intermediate **9**, which may arise from the palladium complex **8** through the displacement of one ligand from the palladium center by the carbon−carbon triple bond (pathway a) or from the palladium complex **7** through the intramolecular nucleophilic attack of the phenolic oxygen atom on the carbonyl ligand (pathway b). It is well known that coordinated carbonyl groups can be subject to attack by nucleophiles[5] (the nucleophilic attack of the oxygen atom on the carbonyl ligand is also involved in the formation of **8**). The carbonylpalladium fragment of **9** then adds intramolecularly to the triple bond. Numerous precedents[6,7] of related reactions suggest that this addition proceeds with *syn* stereochemistry. The resulting σ-vinylpalladium intermediate **10** undergoes the reductive elimination of Pd^0 to give the 2-coumaranone derivative **4** and the active catalyst.

Although this mechanism is reminiscent of the cyclocarbonylation of ethynylalcohols catalyzed by $PdCl_2$,[8] the dramatic difference in our results due to the involvement of

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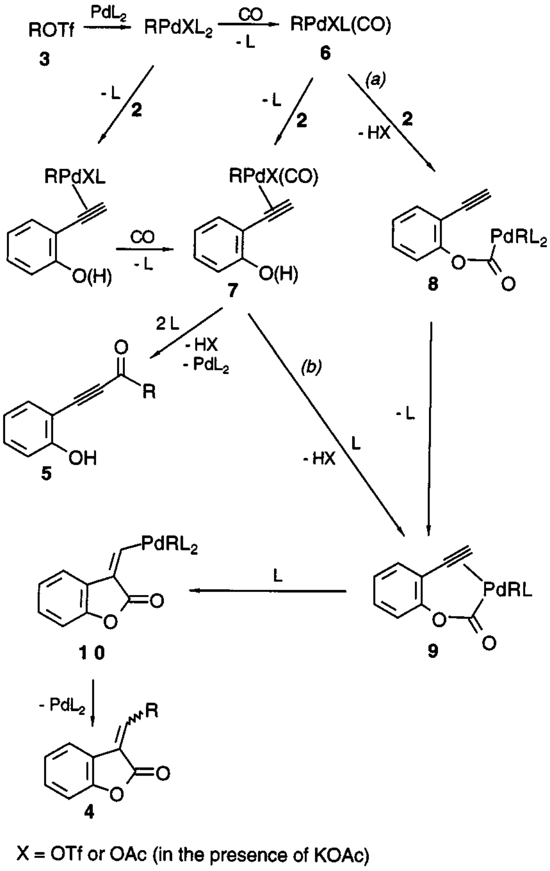
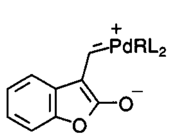
Pd^{II} species bearing a carbon framework which allows the cyclocarbonylation to combine with the formation of an additional carbon–carbon bond is remarkable.



Scheme 2. Suggested mechanism for the palladium-catalyzed cyclocarbonylation of *o*-ethynylphenols **2** with vinyl triflates **3**

Since this mechanistic proposal supports the concept of a *syn* addition to the triple bond to produce (*Z*)-alkylidenecoumaranone derivatives **4′′** the question arises as to how (*E*) isomers **4′** are produced. In fact, apart from the steroidal triflates **3f** and **3g**, which afford (*Z*) isomers as the sole (entries 8, 9, 12) or the main (entry 14) products, all the other examples we examined gave preferentially the (*E*) isomers. Control experiments argue in favor of the view that (*E*) isomers are generated through a thermal isomerization of the reductive elimination product arising from the *syn* adduct formed initially. Indeed, the same 85:15 (*E*)/(*Z*) mixture was obtained by treating both pure (*E*)-3-[(3,3,5,5-tetramethylcyclohex-1-en-1-yl)methylidene]-2-coumaranone (**4′a**) and the pure (*Z*) isomer **4′′a** in CD_3CN at 45°C for 1 h (reactions were monitored by NMR). In addition, an 85:15 (*E*)/(*Z*) ratio was observed on prolonging the reaction time of **2a** with **3a** to 24 h and monitoring the reaction at intervals (after 1, 2, 4, 6 and 24 h). These data clearly point out the ease with which addition products undergo a *cis*/*trans* isomerization and suggest that the observed stereochemistry is dependent on the relative thermodynamic stabilities of the *cis* and *trans* derivatives. At the moment, however, the origin of these different stabilities is unclear and no clear-cut rule can be suggested as to when the (*E*) or (*Z*) isomer predominates. It may be added that the thermal isomerization argument does not exclude the possibility that a *cis*/*trans* isomerization of the vinyl ligand formed initially by a *syn* addition can contribute to the product distribution. As proposed by Alper[9] for the appearance of *cis* and *trans* isomers of the products following the addition of a (hydroxycarbonyl)palladium unit to a carbon–carbon triple bond, this *cis*/*trans* isomerization could involve contributions from a zwitterionic resonance form of type **11**.[10]



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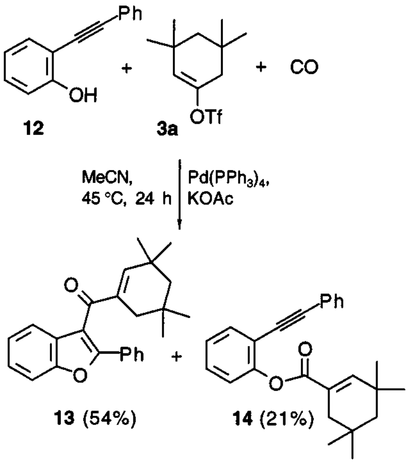
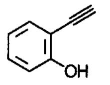
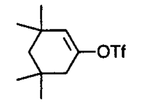
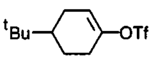
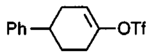
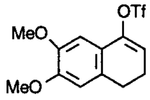
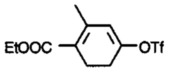
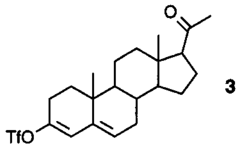
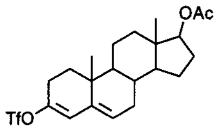
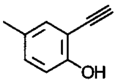
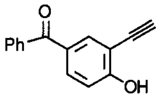
The divergent behavior of *o*-ethynyl- and *o*-(arylethynyl)phenols[4] is worth noting. For example, treatment of *o*-(phenylethynyl)phenol (**12**) and 3,3,5,5-cyclohex-1-en-1-yl triflate (**3a**) under our usual conditions gives the 3-acylbenzo[*b*]furan **13** along with the ester **14**; none of the products arising from the cyclocarbonylation path are discernible (Scheme 3).



Scheme 3. Palladium-catalyzed reaction of *o*-(phenylethynyl)phenol (**12**) with 3,3,5,5-tetramethylcyclohex-1-en-1-yl triflate (**3a**) under 1 atm of carbon monoxide

Apparently, the substitution pattern of the acetylenic moiety plays a key role in the product selectivity. A combination of electronic and steric effects could account for this. As to the electronic effects, semiempirical calculations[11] have shown that the highest negative charge is on the terminal carbon atom in **2a** and on the carbon atom linked to the *o*-hydroxyphenyl fragment in **12**. Therefore, to the extent that the charge distribution in the more polarized η^2-alkynepalladium intermediates reflects the charge distribution in the starting alkynes, the higher electrophilic character of the carbon atom bearing the phenyl group might favor the cyclization of **12** to the benzo[*b*]furan **13** through a mechanism similar to that proposed for the related cyclization of *o*-alkynyltrifluoroacetanilides to 2-substituted-3-acylindoles.[2i] Conversely, electronic factors might hamper the nucleophilic attack of the oxygen atom on the terminal carbon atom of **7** and favor the nucleophilic

Table 1. Palladium-catalyzed cyclocarbonylation of *o*-ethynylphenols **2** with vinyl triflates **3**[a]

entry	*o*-ethynylphenol **2**	vinyl triflate **3**	reaction time (h)	overall yield (%)[b]	of **4**	*E*:*Z* (**4'**:**4"**) ratio[c]
1	 **2a**	 **3a**	4	64	**4a**	85:15[d]
2	**2a**	**3a**	3	71[e]	**4a**	81:19
3	**2a**	 **3b**	3	61	**4b**	80:20
4	**2a**	**3b**	4	54[e]	**4b**	83:17
5	**2a**	 **3c**	8	52	**4c**	80:20
6	**2a**	 **3d**	2	71	**4d**	100:0
7	**2a**	 **3e**	3	45	**4e**	70:30
8	**2a**	 **3f**	1.5	61	**4f**	0:100
9	**2a**	 **3g**	2	79	**4g**	0:100
10	 **2b**	**3b**	4	40	**4h**	90:10
11	**2b**	**3d**	3	58	**4i**	100:0
12	**2b**	**3f**	2	59	**4j**	0:100
13	 **2c**	**3b**	8	50	**4k**	81:19
14	**2c**	**3f**	8	70	**4l**	20:80

[a] Unless otherwise stated, reactions were carried out in MeCN at 45°C, under a balloon of carbon monoxide, using the following molar ratios: **3**/**2**/KOAc/Pd(PPh_3)$_4$ = 1:1.5:2.5:0.5. – [b] Yields refer to single runs and are given for isolated products. – [c] Unless otherwise stated, (*E*)/(*Z*) ratios were calculated by NMR analysis. – [d] NMR analysis of the reaction mixture after work-up and the isolation of the stereoisomers **4'a** and **4''a** gave the same (*E*)/(*Z*) ratio. – [e] In the presence of K_2CO_3 (5 equiv.).

attack on the carbonyl ligand to give **9**. The conversion of this complex (which could be generated even from **6**; Scheme 2) into **10** through the addition of the carbonylpalladium moiety to the carbon–carbon triple bond might be favored by the low steric hindrance towards the incoming palladium fragment. With the analogous complex derived from **12**, the steric congestion between the bulky phenyl substituent[6i] and the palladium fragment might hinder the addition and direct the reaction towards the formation of the ester product through a reductive elimination path.

In conclusion, the chemistry outlined here provides an example of unusual cyclization of alkynes containing proximate nucleophiles promoted by organopalladium complexes and, from a synthetic point of view, a new and direct method for the preparation of functionalized coumaranones by palladium-catalyzed cyclocarbonylation of readily available precursors.

Experimental Section

Melting points were determined with a Büchi apparatus and are uncorrected. Vinyl triflates **3a**–**g** were prepared according to ref.[12] and were purified by chromatography on silica gel with *n*-hexane/EtOAc mixtures as eluent. *o*-Ethynylphenols **2a**–**c** and *o*-(phenylethynyl)phenol (**12**) were prepared according to the procedure given in ref.[21] All of the other starting materials, catalysts, ligands, bases, and solvents (anhydrous solvents included) are commercially available and were used as purchased, without further purification. Reaction products were purified on axially compressed columns, packed with SiO_2 25−40 μm (Macherey Nagel), connected to a Gilson solvent delivery system and to a Gilson refractive index detector, and with *n*-hexane/EtOAc mixtures as eluent. ^1H- (200 MHz) and ^{13}C-NMR (50.3 MHz) spectra ($CDCl_3$, unless otherwise stated; TMS as internal standard) were recorded with a Bruker AM 200 spectrometer. IR spectra were recorded with a Nicolet 5DX FT/IR spectrometer. MS spectra were recorded with a Hewelett Packard HP 5980A spectrometer equipped with a Data System 5934A. All the isolated new products gave satisfactory microanalyses.

General Procedure for the Preparation of 3-Alkylidene-2-coumaranones 4: This is exemplified by the reaction of 3,3,5,5-tetramethylcyclohex-1-en-1-yl triflate (**3a**) with *o*-ethynylphenol (**2a**): To a stirred solution of **3a** (0.150 g, 0.52 mmol) in MeCN (4 mL), were added **2a** (0.092 g, 0.78 mmol), $Pd(PPh_3)_4$ (0.030 g, 0.03 mmol), and KOAc (0.255 g, 2.60 mmol). The flask was purged with carbon monoxide for a few seconds and connected to a balloon of carbon monoxide. The reaction mixture was stirred at 45°C for 4 h. After cooling, the reaction mixture was diluted with ethyl acetate, washed with water, dried with Na_2SO_4 and concentrated under reduced pressure. The residue was purified by chromatography on silica gel with a 96:4 v/v *n*-hexane/EtOAc mixture as eluent to afford (*E*)-3-(3,3,5,5-tetramethylcyclohex-1-en-1-yl)methylidene-2-coumaranone (**4′a**) (0.080 g, 54% yield), (*Z*)-3-(3,3,5,5-tetramethylcyclohex-1-en-1-yl)methylidene-2-coumaranone (**4′′a**) (0.014 g, 10% yield) and 1-(3,3,5,5-tetramethylcyclohex-1-en-1-yl)-3-(*o*-hydroxyphenyl)propynone (**5a**) (0.040 g, 27% yield).

4′a: Oil. − IR (liquid film): $\tilde{\nu}$ = 1782, 1604, 749 cm^{-1}. − ^1H NMR: δ = 7.84 (d, J = 7.8 Hz, 2 H), 7.36−7.07 (m, 4 H), 6.283 (s, 1 H), 2.15 (s, 2 H), 1.48 (s, 2 H), 1.17 (s, 6 H), 1.06 (s, 6 H). − ^{13}C NMR: δ = 169.7 154.2, 146.0, 145.0, 130.8, 129.9, 123.6, 123.5, 122.5, 119.1, 111.1, 49.1, 42.0, 33.9, 30.9, 30.8, 29.7. − MS; *m/z* (%): 282 (47) [M^+], 239 (28), 121 (100). − $C_{19}H_{22}O_2$ (282.4): calcd. C 80.80, H 7.86; found C 80.89, H 7.88.

4′′a: Oil. − IR (liquid film): $\tilde{\nu}$ = 1788, 1603, 749 cm^{-1}. − ^1H NMR: δ = 7.26−7.07 (m, 6 H), 6.31 (s, 1 H), 2.44 (s, 2 H), 1.41 (s, 2 H), 1.13 (s, 6 H), 1.01 (s, 6 H). − MS; *m/z* (%): 282 (69) [M^+], 239 (33), 136 (100). − $C_{19}H_{22}O_2$ (282.4): calcd. C 80.80, H 7.86; found C 80.88, H 7.84.

5a: M.p. 129−131°C. − IR (KBr): $\tilde{\nu}$ = 3294, 2194, 1604, 755 cm^{-1}. − ^1H NMR: δ = 7.49 (dd, J = 7.7 Hz, J = 1.6 Hz, 1 H), 7.38 (td, J = 7.7 Hz, J = 1.9 Hz, 1 H), 7.18 (s, 1 H), 7.02 (d, J = 7.6 Hz, 1 H), 6.94 (td, J = 7.6 Hz, J = 0.9 Hz, 1 H), 2.11 (s, 2 H), 1.44 (s, 2 H), 1.19 (s, 6 H), 1.00 (s, 6 H). − ^{13}C NMR: δ = 180.3, 159.1, 156.0, 136.8, 133.3, 120.5, 116.0, 106.9, 92.5, 87.4, 49.5, 35.7, 34.3, 30.6, 30.2, 29.6. − MS; *m/z* (%): 282 (51) [M^+], 267 (36), 145 (100). − $C_{19}H_{22}O_2$ (282.4): calcd. C 80.80, H 7.86; found C 80.91, H 7.84.

Acknowledgments

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[1] For carbocyclizations of alkynes promoted by σ-organopalladium complexes, see: G. Fournet, G. Balme, B. Van Hemelryck, J. Gore, *Tetrahedron Lett.* **1990**, *31*, 5147−5150. − G. Fournet, G. Balme, J. Gore, *Tetrahedron* **1991**, *47*, 6293−6304. − D. Bouyssi, G. Balme, J. Gore, *Tetrahedron Lett.* **1991**, *32*, 6541−6544. − I. Coudanne, G. Balme, *Synlett* **1998**, 998−1000. − X. Marat, N. Monteiro, G. Balme *Synlett* **1997**, 845−847.

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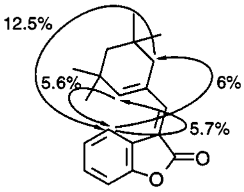
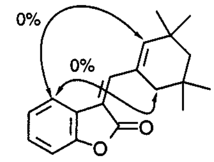
[4] The relevant NOE effects for the determination of the stereochemistry of **4′a** and **4′′a**, presented by arrows, are as follows:



4'a



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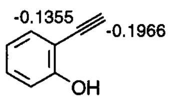
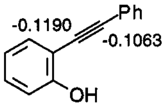
[11] Mopac 6.0 residual charge data for acetylenic carbon atoms of **2a** and **12**, using the Hamiltonian AM 1 of substructures with optimized bond lengths, bond angles, and torsional angles, are as follows:



2a



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