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Palladium-catalyzed heteroannulation of catechol with functionalized propargylic carbonates: Influence of the functional group on the regioselectivity of the cyclization

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Abstract

The palladium(0)-catalyzed annulation of catechol with propargylic carbonates bearing different functionalized groups (hydroxy, *tert*-butyldimethylsilyloxy, ester, diethylamino) afforded functionalized 2,3-dihydro-2-ylidene-1,4-benzodioxin isomers. The regioselectivity of the cyclization depends strongly on the nature of the substituent and on the chain length between the triple bond and the function.

Keywords: Palladium(0)-annulation; Propargylic carbonate; Catechol; 2,3-Dihydro-1,4-benzodioxin; Regioselectiviy

1. Introduction

The palladium-catalyzed allylic substitution reaction is now a well established procedure that is widely applied in organic synthesis [1]. In this reaction, control of regio- and stereoselectivity is a great challenge. Generally the palladium-catalyzed reaction of unsymmetrical allylic acetates afforded a mixture of two regioisomers. It has been shown that the appropriate choice of the reaction conditions and the ancillary ligands on palladium play an important role in determining the regiocontrol of the substitution reaction. If steric hindrance at one terminus of the allyl moiety directs the substitution away from that terminus, the use of polarizing functional groups such as carbonyl, amine, acetate, alkoxide, alcohol, thioether, silyl, or even alkene, adjacent to the η^3-allyl complex, could control the regioselectivity of the allylic substitution [2–7].

We recently published a very easy access to 2,3-dihydro-2-ylidene-1,4-benzodioxins via a palladium-catalyzed heteroannulation of catechol with unfunctionalized propargylic carbonates [8], the major regioisomer resulting generally from the attack of the oxygen nucleophile on the more electrophilic terminus of the intermediate η^3-allyl-palladium complex. In this study we report our results concerning the palladium-catalyzed condensation of catechol with functionalized propargylic carbonates.

2. Experimental

2.1. Materials

All commercially available reagents were used as received. All reactions were monitored by TLC analysis (TLC plates GF_{254} Merck). Air- and moisture-sensitive reactions were performed under inert atmosphere techniques. Melting points were determined on a Büchi apparatus and are uncorrected. Column chromatographies were performed on silica gel 60 (230–240 mesh, Merck). NMR spectra were recorded with a Bruker AMX 300 spectrometer and referenced as following: ^{1}H (300 MHz), internal $SiMe_4$ at $\delta = 0.00$ ppm, ^{13}C (75 MHz), internal standard at $\delta = 77.23$ ppm. Exact mass spectra were recorded on a Finnigan Mat 95 XL spectrometer. Compounds **2a** [9], **2b** [10], **2c** [11], **2d** [12], **5** [13], **7** [14], and **9** [15] were prepared according to literature procedures. Compounds **11b** and **12b** have already been described [8d].

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2.2. General procedure for the synthesis of propargylic carbonates **3**, **6**, **8**, and **10**

To a solution of propargylic alcohol **2**, **5**, **7**, or **9** (17.8 mmol), pyridine (5.6 g, 71.4 mmol), and dimethylaminopyridine (436 mg, 3.6 mmol), in CH_2Cl_2 (40 mL), was added at 0 °C methyl chloroformate (6.7 g, 71.4 mmol). After being stirred for 24 h at rt, water (30 mL) was added, and the mixture was extracted with diethyl ether (3× 30 mL). Evaporation of the solvent under reduced pressure gave an oil. Purification of this oil by chromatography on silica using petroleum ether/EtOAc as the eluent gave the corresponding propargylic carbonate **3**, **6**, **8**, or **10**.

2.2.1. 5-[(tert-Butyldimethylsilyl)oxy]pent-2-yn-1-yl methyl carbonate (**3b**)

Yield 98%; colorless oil; R_f 0.62 (petroleum ether/EtOAc 5:1); ^{1}H NMR ($CDCl_3$): δ 0.08 (s, 6H, $SiCH_3$), 0.90 (s, 9H, CMe_3), 2.45 (tt, J = 7.1, 2.2 Hz, 2H, CH_2), 3.73 (t, J = 7.1 Hz, 2H, CH_2OTBDMS), 3.81 (s, 3H, CH_3), 4.73 (t, J = 2.2 Hz, 2H, CH_2O); ^{13}C NMR ($CDCl_3$): δ −5.0, 18.7, 23.5, 26.2, 55.3, 56.4, 61.9, 74.9, 85.8, 155.7. Anal. Calcd for $C_{13}H_{24}O_4Si$: C, 57.32; H, 8.88. Found: C, 57.63; H, 9.04.

2.2.2. 6-[(tert-Butyldimethylsilyl)oxy]hex-2-yn-1-yl methyl carbonate (**3c**)

Yield 90%; colorless oil; R_f 0.65 (petroleum ether/EtOAc 5:1); ^{1}H NMR ($CDCl_3$): δ 0.06 (s, 6H, $SiCH_3$), 0.90 (s, 9H, CMe_3), 1.72 (tt, J = 7.0, 6.7 Hz, 2H, CH_2), 2.32 (tt, J = 7.0, 2.0 Hz, 2H, CH_2), 3.68 (t, J = 6.0 Hz, 2H, CH_2OTBDMS), 3.82 (s, 3H, CH_3), 4.73 (t, J = 2.0 Hz, 2H, CH_2O); ^{13}C NMR ($CDCl_3$): δ −5.0, 15.6, 18.7, 26.3, 31.7, 55.4, 56.6, 61.8, 73.9, 88.4, 155.7. Anal. Calcd for $C_{14}H_{26}O_4Si$: C, 58.70; H, 9.15. Found: C, 59.16; H, 9.06.

2.2.3. 7-[(tert-Butyldimethylsilyl)oxy]hept-2-yn-1-yl methyl carbonate (**3d**)

Yield 91%; colorless oil; R_f 0.62 (petroleum ether/EtOAc 5:1); ^{1}H NMR ($CDCl_3$): δ 0.01 (s, 6H, $SiCH_3$), 0.85 (s, 9H, CMe_3), 1.45–1.75 (m, 4H, CH_2), 2.20 (tt, J = 6.7, 2.2 Hz, 2H, CH_2), 3.58 (t, J = 5.9 Hz, 2H, CH_2OTBDMS), 3.76 (s, 3H, CH_3), 4.98 (t, J = 2.2 Hz, 2H, CH_2O); ^{13}C NMR ($CDCl_3$): δ −5.0, 18.7, 18.9, 25.2, 26.3, 32.2, 55.3, 56.6, 62.9, 73.9, 88.6, 155.7. Anal. Calcd for $C_{15}H_{28}O_4Si$: C, 59.96; H, 9.39. Found: C, 60.15; H, 9.55.

2.2.4. 4-Methoxybut-2-yn-1-yl methyl carbonate (**6**)

Yield 86%; colorless oil; R_f 0.56 (petroleum ether/EtOAc 4:1); ^{1}H NMR ($CDCl_3$): δ 3.37 (s, 3H, CH_3), 3.81 (s, 3H, CH_3), 4.13 (br s, 2H, CH_2), 4.79 (br s, 2H, CH_2); ^{13}C NMR ($CDCl_3$): δ 55.1, 55.6, 57.6, 59.8, 80.0, 83.5, 155.3. HRMS-FAB (CI): Calcd for $C_7H_{11}O_4$ $[M+H]^+$: 159.0657. Found: 159.0655.

2.2.5. Methyl 4-(methoxycarbonyloxy)but-2-ynoate (**8**)

Yield 56%; colorless oil; R_f 0.55 (petroleum ether/EtOAc 7:3); ^{1}H NMR ($CDCl_3$): δ 4.85 (s, 2H, CH_2), 3.84 (s, 3H, CH_3), 3.80 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$): δ 53.3, 54.9, 55.8, 78.6, 80.8, 153.5, 155.3. Anal. Calcd for $C_7H_8O_5$: C, 48.84; H, 4.68. Found: C, 48.52; H, 4.75.

2.2.6. 4-(Diethylamino)but-2-yn-1-yl methyl carbonate (**10**)

Yield 36%; colorless oil; R_f 0.37 (hexane/EtOAc 1:1); ^{1}H NMR ($CDCl_3$): δ 1.06 (t, J = 7.2 Hz, 6H, CH_3), 2.53 (q, J = 7.2 Hz, 4H, CH_2), 3.46 (t, J = 1.9 Hz, 2H, CH_2), 3.81 (s, 3H, OCH_3), 4.76 (t, J = 1.9 Hz, 2H, CH_2); ^{13}C NMR ($CDCl_3$): δ 13.0, 41.3, 47.6, 55.5, 56.3, 78.3, 83.2, 155.6. HRMS-FAB (CI): Calcd for $C_{10}H_{17}NO_3$ $[M+H]^+$: 200.1287. Found: 200.1289.

2.3. General procedure for the synthesis of ω-hydroxy propargylic carbonates (**4**)

A solution of propargylic silyl ether **3** (0.9 mmol) and $Bu_4NF{\cdot}3xH_2O$ (0.46 g, 1.8 mmol) in THF (8 mL) was stirred at rt for 1 h. After evaporation of the solvent, the residue was diluted with diethyl ether (10 mL), and the ethereal solution washed with water (3× 4 mL). Evaporation of the solvent gave a residue that was purified by column chromatography over silica eluting with petroleum ether/ethyl acetate to afford the corresponding ω-hydroxy propargylic carbonate **4**.

2.3.1. 5-Hydroxypent-2-yn-1-yl methyl carbonate (**4b**)

Yield 55%; colorless oil; R_f 0.74 (EtOAc + 0.5% Et_3N); ^{1}H NMR ($CDCl_3$): δ 2.50 (tt, J = 6.4, 2.2 Hz, 2H, CH_2), 2.69 (br s, 1H, OH), 3.72 (t, J = 6.4 Hz, 2H, CH_2OH), 3.81 (s, 3H, CH_3), 4.73 (t, J = 2.2 Hz, 2H, CH_2O); ^{13}C NMR ($CDCl_3$): δ 22.4, 26.2, 55.5, 61.0, 75.5, 85.5, 155.7. Anal. Calcd for $C_7H_{10}O_4$: C, 53.15; H, 6.37. Found: C, 53.22; H, 6.33.

2.3.2. 6-Hydroxyhex-2-yn-1-yl methyl carbonate (**4c**)

Yield 73%; colorless oil; R_f 0.76 (EtOAc); ^{1}H NMR ($CDCl_3$): δ 1.62 (br s, 1H, OH), 1.78 (tt, J = 7.0, 6.1 Hz, 2H, CH_2), 2.37 (tt, J = 7.0, 2.1 Hz, 2H, CH_2), 3.73 (t, J = 6.1 Hz, 2H, CH_2OH), 3.82 (s, 3H, CH_3), 4.73 (t, J = 2.1 Hz, 2H, CH_2O); ^{13}C NMR ($CDCl_3$): δ 15.6, 31.3, 55.4, 56.5, 61.7, 74.3, 88.0, 155.7. Anal. Calcd for $C_8H_{12}O_4$: C, 55.80; H, 7.02. Found: C, 55.76; H, 7.05.

2.3.3. 7-Hydroxyhept-2-yn-1-yl methyl carbonate (**4d**)

Yield 64%; colorless oil; R_f 0.73 (EtOAc + 0.5% Et_3N); ^{1}H NMR ($CDCl_3$): δ 1.46–1.63 (m, 4H, CH_2), 1.99 (bs, 1H, OH), 2.18 (tt, J = 6.7, 2.2 Hz, 2H, –CH_2–C≡), 3.56 (t, J = 5.9 Hz, 2H, CH_2OH), 3.72 (s, 3H, CH_3), 4.63 (t, J = 2.2 Hz, 2H, CH_2O); ^{13}C NMR ($CDCl_3$): δ 18.9, 25.9, 32.0, 53.4, 56.6, 62.5, 74.0, 88.5, 155.7. Anal. Calcd for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 57.33; H, 7.59.

2.4. 4-Hydroxybut-2-yn-1-yl methyl carbonate (**4a**)

To a solution of but-2-yn-1,4-diol (3 g, 34.8 mmol) in THF (100 mL) was slowly added NaH (835 mg, 34.8 mmol), followed by methyl chloroformate (3.29 g, 34.8 mmol). After being stirred for 12 h, the mixture was treated with water (30 mL), and the solvent was evaporated. The residue was extracted by diethyl ether (3× 30 mL), and the organic layers were dried over sodium

sulfate. Evaporation of the solvent under reduced pressure followed by column chromatography gave compound **4a** as an oil (1.5 g, yield 30%). R_f 0.5 (petroleum ether/EtOAc 2:1); ^{1}H NMR ($CDCl_3$): δ 3.80 (s, 3H, CH_3), 3.96 (br s, 1H, OH), 4.29 (br s, 2H, CH_2OH), 4.78 (br s, 2H, CH_2); ^{13}C NMR ($CDCl_3$): δ 55.4, 56.0, 78.8, 86.3, 155.6. HRMS-FAB (CI): Calcd for $C_6H_9O_4$ $[M+H]^+$: 145.0501. Found: 145.0500. The NMR data are in agreement with the literature [16].

2.5. General procedure for the palladium-catalyzed annulation reaction

A mixture of $Pd_2(dba)_3$ (20.8 mg, 2.2×10^{-2} mmol) and dppb (38.8 mg, 9.1×10^{-2} mmol) in THF (7 mL) was stirred under a nitrogen atmosphere at rt for 30 min. This catalyst solution was added to a mixture of benzene-1,2-diol (100 mg, 0.9 mmol) and the corresponding propargylic carbonate (1.1 mmol). The resulting solution was stirred at the indicated temperature for 24 h. The solvent was evaporated and the residue chromatographed over silica eluting with petroleum ether/ethyl acetate to afford the corresponding 2,3-dihydro-1,4-benzodioxine. The ratio of the two regioisomers was determined by ^{1}H NMR.

2.5.1. (3-Methylidene-2,3-dihydro-1,4-benzodioxin-2-yl) methanol (**11a**)

Colorless oil; R_f 0.52 (petroleum ether/EtOAc 3:1); ^{1}H NMR ($CDCl_3$): δ 2.00 (br s, 1H, OH), 3.77 (dd, J = 11.9, 4.8 Hz, 1H, CH_2O), 3.87 (dd, J = 11.9, 7.4 Hz, 1H, CH_2O), 4.36 (d, J = 2.2 Hz, 1H, =CH_2), 4.53 (dd, J = 7.4, 4.8 Hz, 1H, OCH<), 4.76 (d, J = 2.2 Hz, 1H, =CH_2), 6.80–6.90 (m, 4H, H_{arom}); ^{13}C NMR ($CDCl_3$): δ 62.2, 74.0, 92.7, 116.8, 117.8, 122.9, 123.0, 141.8, 142.4, 149.8. HRMS-FAB (CI): Calcd for $C_{10}H_{11}O_3$ $[M+H]^+$: 179.0708. Found: 179.0708.

2.5.2. 2-[1,4-Benzodioxin-2(3H)-ylidene]ethanol (**12a**) (as a 75:25 Z/E mixture)

R_f 0.28 (petroleum ether/EtOAc 3:1); ^{1}H NMR ($CDCl_3$): δ 1.80 (br s, 1H, OH), 4.25 (d, J = 7.7 Hz, 0.5H, (*E*) CH_2OH), 4.43 (d, J = 7.0 Hz, 1.5H, (*Z*) CH_2OH), 4.49 (s, 1.5H, (*Z*) OCH_2), 4.70 (s, 0.5H, (*E*) OCH_2), 5.00 (t, J = 7.0 Hz, 0.75H, (*Z*) =CH–), 5.58 (t, J = 7.7 Hz, 0.25H, (*E*) =CH–), 6.80–7.20 (m, 4H, H_{arom}); ^{13}C NMR ($CDCl_3$): δ 55.8 (*E*), 56.8 (*Z*), 65.0 (*E*), 65.9 (*Z*), 106.5 (*E*), 106.7 (*Z*), 116.5 (*E*), 116.6 (*Z*), 117.0 (*Z*), 117.4 (*E*), 122.2, 122.4, 122.5, 142.4, 143.9, 144.5. The NMR data are in agreement with the literature [8].

2.5.3. 2-(Methoxymethyl)-3-methylene-2,3-dihydro-1,4-benzodioxine (**11c**) and 2-(methoxyethylidene)-2,3-dihydro-1,4-benzodioxine (**12c**)

Colorless oil; HRMS-FAB (EI): Calcd for $C_{11}H_{12}O_3$ $[M]^+$: 192.0786; Found: 192.0789.

Compound ***11c*** *(in the mixture).* R_f 0.60 (petroleum ether/EtOAc 8:1); ^{1}H NMR ($CDCl_3$): δ 3.45 (s, 3H, CH_3), 3.67 (dd, J = 10.5, 5.1 Hz, 1H, CH_2O), 3.75 (dd, J = 10.5, 7.0 Hz, 1H, CH_2O), 4.46 (d, J = 2.1 Hz, 1H, =CH_2), 4.73 (dd, J = 7.0, 5.1 Hz, 1H, OCH<), 4.84 (d, J = 2.1 Hz, 1H, =CH_2), 6.90–7.00 (m, 4H, H_{arom}); ^{13}C NMR ($CDCl_3$): δ 59.5, 71.6, 72.4, 92.0, 116.2, 117.6, 122.2, 122.5, 141.9, 142.1, 150.1.

Compound ***12c*** *(in the mixture) as a 85:15 Z/E mixture.* R_f 0.48 (petroleum ether/EtOAc 8:1); ^{1}H NMR ($CDCl_3$): δ 3.35 (s, 0.45H, (*E*) CH_3), 3.38 (s, 2.55H, (*Z*) CH_3), 4.00 (d, J = 7.7 Hz, 0.3H, (*E*) CH_2OCH_3), 4.22 (d, J = 7.0 Hz, 1.7H, (*Z*) CH_2OCH_3), 4.49 (s, 1.7H, (*Z*) OCH_2), 4.68 (s, 0.3H, (*E*) OCH_2), 4.91 (t, J = 7.0 Hz, 0.85H, (*Z*) =CH–), 5.50 (t, J = 7.7 Hz, 0.15H, (*E*) =CH–), 6.85–7.10 (m, 4H, H_{arom}); ^{13}C NMR ($CDCl_3$): δ 58.0 (*E*), 58.4 (*Z*), 60.8 (*E*), 65.4 (*Z*), 65.5 (*Z*), 66.7 (*E*), 104.0 (*E*), 104.4, (*Z*), 116.9 (*E*), 117.0 (*Z*), 117.8 (*Z*), 117.6 (*E*), 122.5 (*E*), 122.7 (*E* + *Z*), 122.8 (*Z*), 142.9 (*Z*), 143.1 (*E*), 144.3 (*E*), 144.4 (*Z*), 145.7 (*Z*), 147.9 (*E*).

2.5.4. tert-Butyl(dimethyl)[2-(3-methylene-2,3-dihydro-1,4-benzodioxin-2-yl)ethoxy]silane (**11e**) and {[3-(1,4-benzodioxin-2(3H)-ylidene)propyl]oxy}(tert-butyl)dimethylsilane (**12e**)

Colorless oil; Anal. Calcd for $C_{17}H_{26}O_3Si$: C, 66.62; H, 8.55. Found: 66.73; H, 8.69.

Compound ***11e*** *(in the mixture).* R_f = 0.73 (petroleum ether/EtOAc 9:1); ^{1}H NMR ($CDCl_3$): δ 0.09 (s, 6H, $SiCH_3$), 0.92 (s, 9H, CMe_3), 1.93–2.02 (m, 2H, CH_2), 3.63–3.93 (m, 2H, CH_2O), 4.41 (d, J = 1.9 Hz, 1H, =CH_2), 4.71 (t, J = 6.2 Hz, 1H, OCH<), 4.76 (d, J = 1.9 Hz, =CH_2), 6.88–7.00 (m, 4H, H_{arom}); ^{13}C NMR ($CDCl_3$): δ −5.0, 18.7, 26.3, 34.6, 58.9, 70.3, 100.0, 116.5, 117.9, 122.3, 122.6, 142.6, 142.7, 144.4.

Compound ***12e*** *(in the mixture) as a 90:10 Z/E mixture.* R_f = 0.62 (petroleum ether/EtOAc 9:1); ^{1}H NMR ($CDCl_3$): δ 0.09 (s, 6H, $SiCH_3$), 0.92 (s, 9H, CMe_3), 2.29 (m, 0.2H, (*E*) =CH–CH_2), 2.49 (m, 1.8H, (*Z*) =CH–CH_2), 3.63–3.93 (m, 2H, CH_2O), 4.48 (s, 0.2H, (*E*) OCH_2C=), 4.64 (s, 1.8H, (*Z*) OCH_2C=), 4.71 (t, J = 6.2 Hz, 0.1H, (*E*) =CH–), 4.81 (t, J = 7.3 Hz, 0.9H, (*Z*) =CH–), 6.88–7.00 (m, 4H, H_{arom}); ^{13}C NMR ($CDCl_3$): δ −4.9, 18.7, 26.3, 28.2, 62.9, 65.7, 104.8, 116.9, 117.7, 122.4, 143.3, 144.2, 153.0.

2.5.5. 3-(3-Methylene 2,3-dihydro-1,4-benzodioxin-2-yl)propan-1-ol (**11f**)

Colorless oil; R_f 0.6 (petroleum ether/EtOAc 1:1); ^{1}H NMR ($CDCl_3$): δ 1.68–1.97 (m, 4H, CH_2), 3.58 (t, J = 6.0 Hz, 2H, CH_2OH), 4.38 (d, J = 1.9 Hz, 1H, =CH_2), 4.48 (br t, J = 6.5 Hz, 1H, OCH<), 4.74 (d, J = 1.9 Hz, 1H, =CH_2), 5.38 (br s, 1H, OH), 6.70–7.00 (m, 4H, H_{arom}). HRMS-FAB (EI): Calcd for $C_{12}H_{14}O_3$ $[M]^+$: 206.0943. Found: 206.0944.

2.5.6. tert-Butyl(dimethyl)[3-(3-methylene-2,3-dihydro-1,4-benzodioxin-2-yl)propoxy]silane (**11g**) and {[4-(1,4-benzodioxin-2(3H)-ylidene)butyl]oxy}(tert-butyl)dimethylsilane (**12g**)

Colorless oil; R_f = 0.69 (petroleum ether/EtOAc 14:1). Anal. Calcd for $C_{18}H_{28}O_3Si$: C, 67.46; H, 8.81. Found: 67.70; H, 8.99.

Compound ***11g*** *(in the mixture).* ^{1}H NMR ($CDCl_3$): δ 0.07 (s, 6H, $SiCH_3$), 0.91 (s, 9H, CMe_3), 1.60–1.93 (m, 4H, CH_2), 3.65–3.75 (m, 2H, CH_2O), 4.40 (d, J = 1.9 Hz, 1H, =CH_2), 4.48 (br t, J = 6.6 Hz, 1H, OCH<), 4.75 (d, J = 1.9 Hz, 1H, =CH_2),

6.88–7.00 (m, 4H, H_{arom}); ^{13}C NMR ($CDCl_3$): δ −4.9, 18.7, 26.4, 28.2, 28.8, 62.9, 73.5, 91.0, 116.4, 117.8, 122.3, 122.6, 142.7, 142;8, 143.3.

*Compound **12g** (in the mixture) as a 90:10 Z/E mixture*. ^1H NMR ($CDCl_3$): δ 0.07 (s, 6H, $SiCH_3$), 0.91 (s, 9H, CMe_3), 1.60–1.93 (m, 2H, CH_2), 2.33 (dt, J = 7.3, 7.3 Hz, 2H, =CH–CH_2), 3.65–3.75 (m, 2H, CH_2O), 4.46 (bs, 1.8H, (*Z*) OCH_2–C=), 4.65 (br s, 0.2H, (*E*) OCH_2–C=), 4.75 (d, J = 7.3 Hz, 1H, =CH–), 6.88–7.00 (m, 4H, H_{arom}); ^{13}C NMR ($CDCl_3$): δ −4.9, 18.7, 26.4, 29.4, 31.4, 64.4, 108.3, 117.0, 117.7, 122.2, 122.4, 142.7, 142.8, 143.3, 153.1

2.5.7. 4-(3-Methylene-2,3-dihydro-1,4-benzodioxin-2-yl)butan-1-ol (**11h**) and 5-[1,4-benzodioxin-2(3H)-ylidene]pentan-1-ol (**12h**)

Colorless oil; R_f = 0.55 (petroleum ether/EtOAc 1:1). HRMS-FAB (IE): Calcd for $C_{13}H_{16}O_3$ $[M]^+$: 220.1099. Found: 220.1099.

*Compound **11h** (in the mixture)*. ^1H NMR ($CDCl_3$): δ 1.34–1.82 (m, 6H, CH_2), 1.89 (br s, 1H, OH), 3.54 (t, J = 5.3 Hz, 2H, CH_2O), 4.27 (d, J = 1.9 Hz, 1H, =CH_2), 4.34 (dd, J = 8.2, 5.3 Hz, 1H, OCH<), 4.64 (d, J = 1.9 Hz, 1H, =CH_2), 6.75–6.95 (m, 4H, H_{arom}).

*Compound **12h** (in the mixture)*. ^1H NMR ($CDCl_3$): δ 1.34–1.82 (m, 4H, CH_2), 1.89 (br s, 1H, OH), 2.18 (dt, J = 7.3, 7.3 Hz, 2H, =CH–CH_2), 3.54 (t, J = 5.3 Hz, 2H, CH_2O), 4.31 (br s, 2 H, OCH_2–C=), 4.62 (t, J = 7.3 Hz, 1H, =CH–), 6.75–6.95 (m, 4H, H_{arom}).

2.5.8. tert-Butyl(dimethyl)[4-(3-methylene 2,3-dihydro-1,4-benzodioxin-2-yl)butoxy]silane (**11i**) and {[5-(1,4-benzodioxin-2(3H)-ylidene)pentyl]oxy}(tert-butyl)dimethylsilane (**12i**)

Colorless oil; R_f = 0.78 (petroleum ether/EtOAc 9:1). Anal. Calcd for $C_{19}H_{30}O_3Si$: C, 68.22; H, 9.04. Found: 68.27; H, 9.19.

*Compound **11i** (in the mixture)*. ^1H NMR ($CDCl_3$): δ 0.00 (s, 6H, $SiCH_3$), 0.85 (s, 9H, CMe_3), 1.41–1.61 (m, 4H, CH_2), 1.67–1.83 (m, 2H, CH_2–CH<), 3.58 (t, J = 5.8 Hz, 2H, CH_2O), 4.31 (d, J = 1.9 Hz, 1H, =CH_2), 4.40 (br t, J = 6.6 Hz, 1H, OCH<), 4.68 (d, J = 1.9 Hz, 1H, =CH_2), 6.82–6.88 (m, 4H, H_{arom}); ^{13}C NMR ($CDCl_3$): δ −4.9, 18.7, 22.2, 26.4, 31.5, 32.8, 63.3, 73.8, 91.0, 116.4, 117.8, 122.3, 122.6, 142.7, 142.8, 153.2.

*Compound **12i** (in the mixture)*. ^1H NMR ($CDCl_3$): δ 0.00 (s, 6H, $SiCH_3$), 0.85 (s, 9H, CMe_3), 1.41–1.61 (m, 4H, CH_2), 1.67–1.83 (m, 2H, =CH–CH_2), 3.58 (t, J = 6.2 Hz, 2H, CH_2O), 4.36 (br s, 2 H, OCH_2–C=), 4.68 (m, 1H, =CH–), 6.82–6.88 (m, 4H, H_{arom}); ^{13}C NMR ($CDCl_3$): δ −4.9, 18.7, 24.0, 26.0, 26.4, 63.4, 65.8, 108.7, 117.0, 117.7, 122.2, 122.4, 143.2, 143.4, 144.5.

2.5.9. Methyl (2E)-[1,4-benzodioxin-2(3H)-ylidene]acetate (**13**)

Yield 84%; colorless oil; R_f = 0.69 (petroleum ether/EtOAc 95:5); ^1H NMR ($CDCl_3$): δ 3.75 (s, 3H, CH_3), 5.27 (br s, 2H, OCH_2), 5.70 (br s, 1H, =CH–), 6.97–7.05 (m, 4H, H_{arom}); ^{13}C NMR ($CDCl_3$): δ 51.8, 61.8, 98.5, 117.0, 117.7, 123.1, 124.1, 142.1, 144.6, 161.4, 167.5. These data are in agreement with the literature [17].

2.5.10. [2-(1,4-Benzodioxin-2(3H)-ylidene)ethyl] diethylamine **14** and N-ethyl-N-[(3-methylene-2,3-dihydro-1,4-benzodioxin-2-yl)methyl]ethanamine **15**

Yield 98%.

*Compound **14** (in the mixture) as a 85:15 Z/E mixture*. Colorless oil; R_f = 0.1 (EtOH). ^1H NMR ($CDCl_3$): δ 0.99 (t, J = 7.2 Hz, 6H, CH_3), 2.48 (q, J = 7.2 Hz, 4H, CH_2CH_3), 3.07 (d, J = 7.7 Hz, 0.3H, (*E*) CH_2N), 3.30 (d, J = 7.1 Hz, 1.7H, (*Z*) CH_2N), 4.38 (s, 1.7H, (*Z*) OCH_2), 4.54 (s, 0.3H, (*E*) OCH_2), 4.75 (t, J = 7.1 Hz, 0.85H, (*Z*) =CH–), 5.31 (t, J = 7.7 Hz, 0.15H, (*E*) =CH–), 6.77–6.84 (m, 4H, H_{arom}); ^{13}C NMR ($CDCl_3$): δ 11.8 (*Z*), 12.0 (*E*), 46.1 (*Z*), 46.7 (*E*), 47.0 (*Z*), 48.2 (*E*), 60.8 (*E*), 65.5 (*Z*), 103.9 (*Z*), 104.6 (*E*), 116.8 (*E*), 116.9 (*Z*), 117.5 (*E*), 117.7 (*Z*), 122.0 (*E*), 122.5 (*Z*), 122.6 (*E*), 143.0 (*Z*), 143.3 (*E*), 144.2 (*E*), 146.0 (*E*) 144.3 (*Z*), 145.6 (*Z*). HRMS-FAB (CI): Calcd for $C_{14}H_{20}NO_2$ $[M+H]^+$: 234.1494. Found: 234.1496.

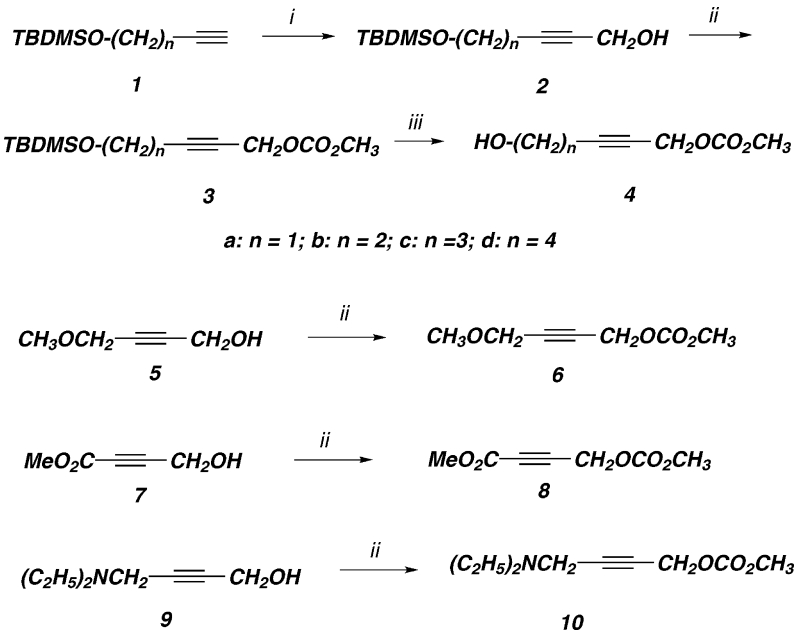
*Compound **15***. Colorless oil; R_f = 0.55 (EtOH). ^1H NMR ($CDCl_3$): δ 0.93 (t, J = 7.2 Hz, 6H, CH_3), 2.55 (q, J = 7.2 Hz, 4H, CH_2CH_3), 2.65 (dd, J = 14.1, 4.9 Hz, 1H, CH_2N), 2.77 (dd, J = 14.1, 7.5 Hz, 1H, CH_2N), 4.35 (d, J = 2.1 Hz, 1H, =CH_2), 4.56 (dd, J = 7.5, 4.9 Hz, 1H, CHO), 4.68 (d, J = 2.1 Hz, 1H, =CH_2), 6.79–6.83 (m, 4H, H_{arom}); ^{13}C NMR ($CDCl_3$): δ 11.0, 47.0, 53.0, 71.8, 90.5, 115.1, 116.7, 120.9, 121.3, 140.7, 141.2, 150.5. HRMS (EI): Calcd for $C_{14}H_{19}NO_2$ $[M]^+$: 233.1416. Found: 234.1418.

3. Results and discussion

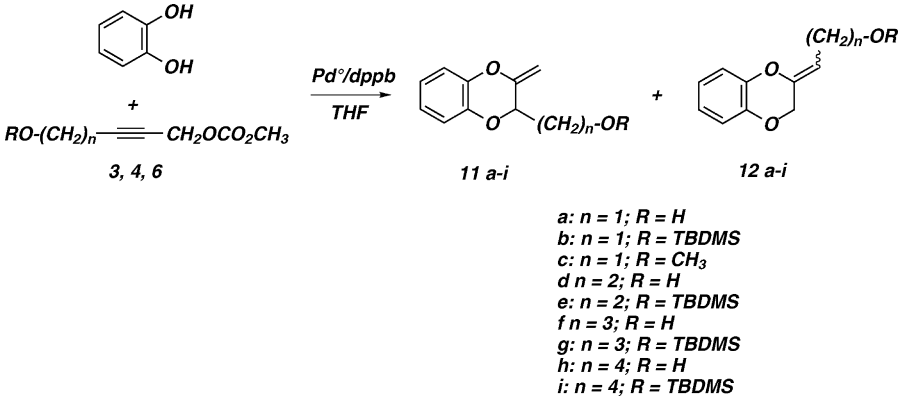
The preparation of the starting propargylic carbonates **3a–d**, bearing a *t*-BuMe_2SiO group, **4a–d**, bearing a hydroxyl group, **6** bearing a methoxy group, and **8** and **10**, bearing, respectively, an ester and a tertiary amino group, is shown in Scheme 1. Acetylenic silyl ethers **1a–d** were quantitatively obtained from commercially available acetylenic alcohols by reaction with *t*-BuMe_2SiCl (TBDMSCl) in the presence of pyridine and DMAP (dimethylaminopyridine). Compounds **1a–d** were converted to the corresponding hydroxy acetylenic derivatives **2a–d** by hydroxymethylation [*n*-BuLi, $(CH_2O)_n$]. Reaction of these acetylenic alcohols **2a–d** with methyl chloroformate in the presence of pyridine afforded the acetylenic carbonates **3a–d**, whose deprotection using $Bu_4NF{\cdot}3xH_2O$ gave the corresponding propargylic alcohols **4a–d** in quite good yields. Carbonates **6**, **8**, and **10**, were obtained by reaction of the corresponding functionalized acetylenic alcohols **5**, **7**, and **9**, with methyl chloroformate in the presence of pyridine.

The reaction of catechol with propargylic carbonates **3**, **4**, and **6** (Scheme 2), was carried out in THF in the presence of a palladium complex generated *in situ* by mixing $Pd_2(dba)_3$ with dppb [or 1,4-bis(diphenylphosphino)butane] at 25 or 50 °C. The results are summarized in Table 1, and the proposed mechanism for this cyclization is shown in Scheme 3.

We first studied the palladium-catalyzed annulation of hydroxyl protected propargylic carbonates with catechol. We have previously shown that the palladium-catalyzed annulation



Scheme 1.

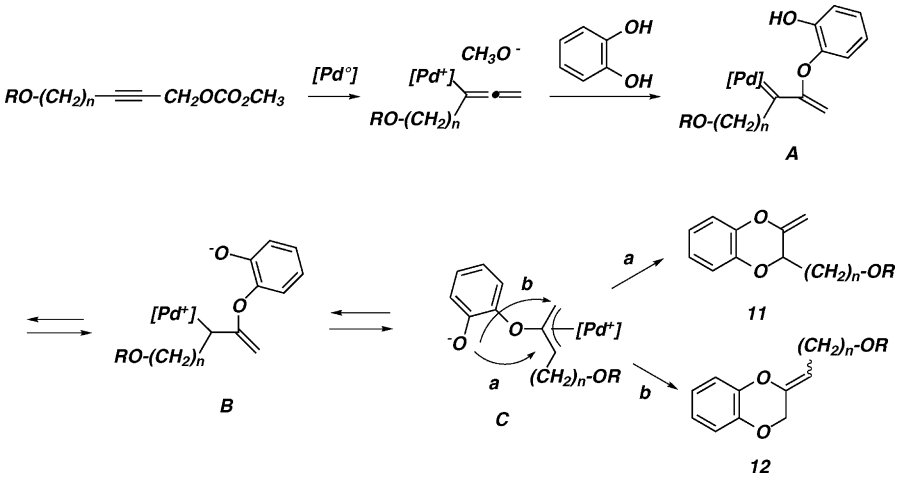


Scheme 2.

Table 1
Palladium-catalyzed heteroannulation of catechol with functionalized propargylic carbonates **3**, **4**, and **6**[a]

Entry	Carbonate	T (°C)	Yield (%)[b]	Compounds[c]
1	**4a**	25	56	**11a** (65%) + **12a** (35%) (Z/E = 75/25)
2	**3a**	25	97	**11b** (31%) + **12b** (69%) (Z/E = 90/10)
3	**6**	25	72	**11c** (22%) + **12c** (78%) (Z/E = 85/15)
4	**4b**	50	No reaction	
5	**3b**	25	58	**11e** (74%) + **12e** (26%) (Z/E = 90/10)
6	**3b**	50	85	**11e** (75%) + **12e** (25%) (Z/E = 90/10)
7	**4c**	25	No reaction	
8	**4c**	50	18	**11f**
9	**3c**	25	66	**11g** (82%) + **12g** (18%) (Z/E = 90/10)
10	**3c**	50	95	**11g** (80%) + **12g** (20%) (Z/E = 90/10)
11	**4d**	25	13	**11h** (93%) + **12h** (7%)
12	**4d**	50	90	**11h** (94%) + **12h** (6%)
13	**3d**	25	75	**11i** (82%) + **12i** (18%)
14	**3d**	50	90	**11i** (87%) + **12i** (13%)

[a] [Carbonate]/[catechol]/[$Pd_2(dba)_3$]/[dppb] = 50:40:1:4; THF as the solvent.
[b] After column chromatography.
[c] Determined by ^{1}H NMR on the crude mixture.



Scheme 3.

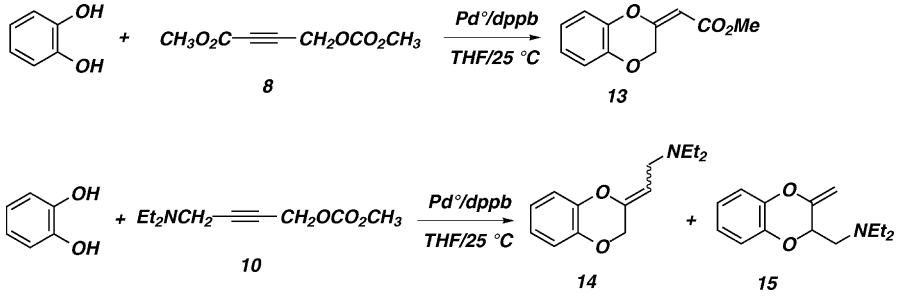
of 4-[(*tert*-butyldimethylsilyl)oxy]but-2-yn-1-yl methyl carbonate (**3a**) with catechol gave a 31:69 mixture of 2,3-dihydro-1,4-benzodioxines **11b** and **12b**, in 97% chemical yield (Table 1, entry 2), the major isomer of compound **12b** having the *Z*-stereochemistry (*Z*/*E* = 9:1) [8d]. The formation of the major compound **12b** resulted from the attack of the oxygen nucleophile at the less substituted terminus of the η^3-allyl intermediate, or at the terminus of the allyl fragment distal to the heteroatom, according to the mechanism previously proposed (Scheme 3, path b). The palladium-catalyzed annulation of catechol with 4-methoxycarbonate **6** gave also a 22:78 mixture of the two regioisomers **11c** and **12c** in 72% chemical yield (Table 1, entry 3), the regioisomer **12c** being again the major one.

When propargylic carbonate **3b**, bearing the protected hydroxyl group two atoms away from the π-allyl moiety was used, a mixture of the two 2,3-dihydro-1,4-benzodioxines **11e** and **12e** was also obtained in 58% yield, this yield being increased to 85% when the reaction was performed at 50 °C (Table 1, entries 5 and 6). However we observed now that the major regioisomer was compound **11e**, resulting from the attack of the oxygen nucleophile at the more substituted terminus of the intermediate η^3-allyl complex (Scheme 3, path a). The same behaviour was observed when carbonates **3c** and **3d**, bearing the protected oxygenated functional group three and four atoms away from the π-allyl moiety, were used (Table 1, entries 9, 10, 13, and 14). Regioisomers **11g** and **11i**, resulting from the attack at the more substituted terminus of the η^3-allyl complex, were obtained as the major compounds: **11g/12g** = 82:18 at 25 °C and 80:20 at 50 °C, **11i/12i** = 82:18 at 25 °C and 87:13 at 50 °C; it is to be noted that the yields were almost quantitative when the reaction was performed at 50 °C.

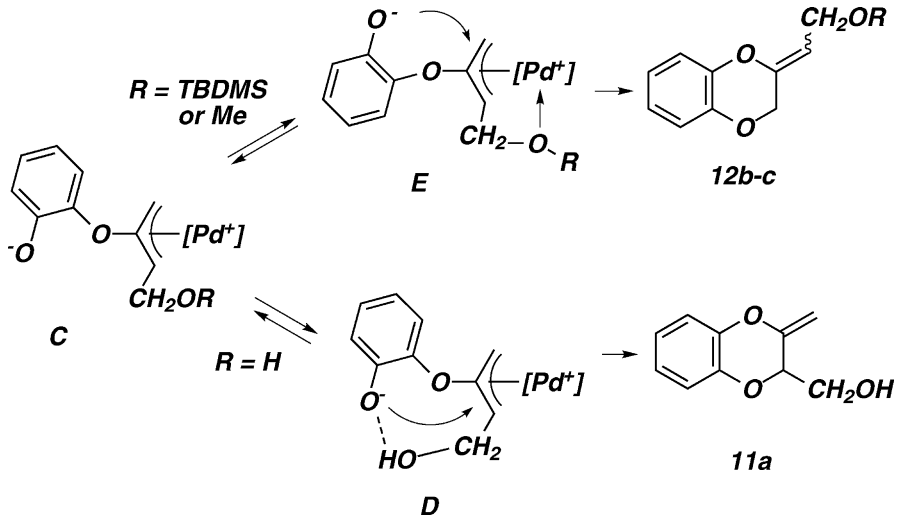
Reaction of hydroxy propargylic carbonate **4a** with catechol afforded the corresponding 2,3-dihydro-1,4-benzodioxines **11a** and **12a** in 56% chemical yield (Table 1, entry 1); however we noticed that the major regioisomer was now compound **11a** (65%), resulting from the substitution at the terminus of the allylic moiety proximal to the hydroxyl group, according to path a (Scheme 3). Surprisingly, condensation of catechol with carbonates **4b** and **4c**, having two and three methylene units between the hydroxyl function and the triple bond, gave no reaction at all at 25 °C. Increasing the reaction temperature to 50 °C allowed the formation of compound **11f**, although in low yield (18% yield only), when no reaction occurred starting from carbonate **4b** (Table 1, entries 4, 7, and 8).

Finally, the palladium-catalyzed condensation of hydroxycarbonate **4d** with catechol occurred at 25 °C in 13% yield, this value increasing to 90% when the reaction was performed at 50 °C (Table 1, entries 11 and 12). The major 2,3-dihydro-1,4-benzodioxine was regioisomer **11h** (about 94%) resulting from the attack of the oxygen nucleophile at the more substituted termini of the η^3-allyl intermediate (Scheme 3, path a).

The palladium-catalyzed annulation was extended to methyl 4-(methoxycarbonyloxy)but-2-ynoate (**8**) (Scheme 4). Only cyclized compound **13**, resulting from the attack of the oxygen nucleophile at the terminus of the allylic moiety distal to the ester group, according to path b (Scheme 3), was formed in



Scheme 4.



Scheme 5.

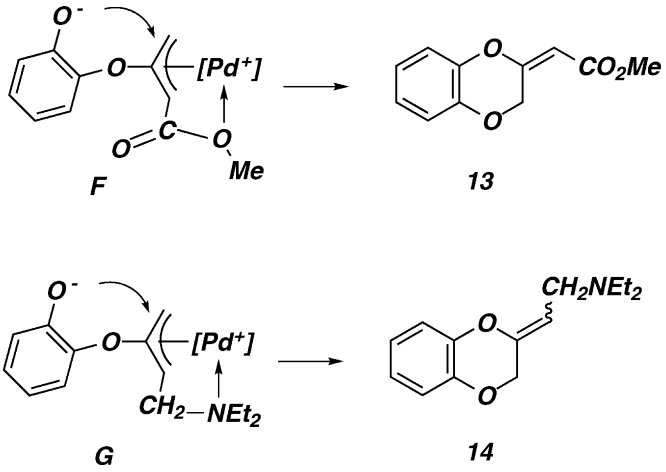
84% yield. The *E*-stereochemistry of this isomer was assigned by NOE experiments: no exaltation of the signal of the ethylenic proton at $\delta = 5.70$ ppm was observed by irradiation of the signal of the $-CH_2-$ at $\delta = 5.27$ ppm, and reversely; moreover, the ^{13}C NMR spectrum was in agreement with the literature data for this compound [17].

Finally, palladium-catalyzed reaction of 4-(diethylamino) but-2-yn-1-yl methyl carbonate (**10**) with catechol afforded a 70:30 mixture of regioisomers **14** and **15** in 98% chemical yield (Scheme 4). The major isomer **14** resulted from the attack of the oxygen nucleophile at the terminus of the intermediate allylic complex distal to the amino group, according to path b.

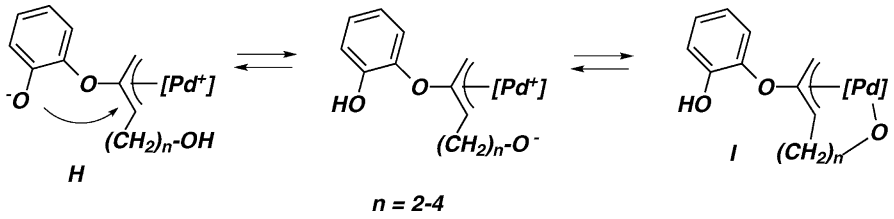
It has been shown that polar substituents in the allylic position of a π-allylic complex favor the attack of the nucleophile such as carbon or nitrogen nucleophiles at the terminus distal to this substituent, leading to a product with a 1,4-relationship between this polar group and the nucleophile [3a,3b,3d,18,19]. However it was also recently showed that the palladium-catalyzed allylic substitution of diene monoepoxides or of substrates possessing an adjacent amide functional group with amines had a quite different behaviour, a high level of regioselectivity in favor of the introduction of the amine function proximal to the hydroxyl or amino function being observed [2c–d,7,20].

In the case of the palladium-catalyzed condensation of propargylic carbonates **3a**, **4a**, and **6**, with catechol, we observed that the regioselectivity of the attack of the oxygen nucleophile on the intermediate π-allyl complex, and so of the cyclization reaction, depends strongly on the nature of the substituent of the oxygen atom. Carbonate **4a**, having a free hydroxyl group in the allylic position of the intermediate η^3-allylic complex, afforded compound **11a** as the major regioisomer, resulting of the attack of the phenoxide at the terminus proximal to this hydroxyl function, when the reverse regioselectivity was observed for carbonate **3a** (or **6**) having a protected hydroxyl function, compound **12b** (or **12c**) being now the major regioisomer. This different behaviour could be explained as shown in Scheme 5. When carbonate **4a** was used, the intermediate carbene–palladium complex **A** afforded the zwitterionic η^3-allyl complex **C** by proton transfer from the phenol to the carbene complex. Once the nucleophile is deprotonated, it forms a hydrogen bond with the hydroxyl function (complex **D**) and so reacts at the nearest electrophilic carbon, due to a proximity effect, which is the one proximal of the hydroxyl function, leading to the formation of regioisomer **11a** as the major compound [7]. When carbonate **3a** or **6** was used, the regioselectivity of the cyclization could be due to the complexation of the oxygen to the palladium allowing the formation of intermediate **E**. This complexation could induced a distortion of the η^3-allylic intermediate, and the attack of the nucleophile would occur at the terminus of the π-allyl distal to the ether function, which is the less bound to the metal [19], affording compound **12b** or **12c** as the major regioisomer.

Formation of compound **13** as the unique regioisomer, and compound **14** as the major regioisomer, in the palladium-catalyzed heteroannulation of carbonates **8** and **10**, respectively, could also be rationalized by the complexation of the ester (complex **F**) and amino group (complex **G**) to the palladium, allowing



Scheme 6.



Scheme 7.

the attack at the terminus of the π-allyl distal to these functions (Scheme 6).

Carbonates **4b–d** gave very low yields in cyclized products at room temperature, or no reaction at all. Performing the reaction at 50 °C gave the 2,3-dihydro-2-ylidene-1,4-benzodioxins in high yields (up to 90%) only for carbonate **4d**. This quite different behaviour could be explained by the formation of an intermediate palladium complex **I** (Scheme 7). This complex would be stable at room temperature, and so the reaction could not occur. However at 50 °C, when $n = 4$, it would be in equilibrium with complex **H**. In this complex **H**, the attack occurs at the more electrophilic terminus of the π-allyl intermediate which is the more proximal in this case of the hydroxyl function [8], even if hydrogen bond with this hydroxyl function seems unlikely.

The cyclization of carbonates **3b–d** afforded 2,3-dihydro-2-ylidene-1,4-benzodioxins **11** as the major regioisomer. One reason could be that the complexation of palladium by the oxygen, if it occurs, did not induced any distortion in the π-allyl intermediate, due to the length of the tether between the oxygen and the allylic moiety. In this case the internal attack of the nucleophile occurred on the more electrophilic terminus of the π-allyl intermediate, as shown previously. It is to be noticed that this regioselectivity is in agreement with that reported in the literature in the case of the external palladium-catalyzed substitution of allylic acetates bearing a thioether group in the homoallylic position ($n = 2$), but in contrast with the results published when the length between the oxygen and the π-allyl complex increased ($n = 2$) [2b].

4. Conclusion

In conclusion, the regioselectivity of the palladium(0)-catalyzed annulation between catechol and propargylic carbonates bearing a *tert*-butyldimethylsilyloxy group depends strongly on the chain length between the triple bond and the silyloxy group. 2,3-Dihydro-2-methylene-1,4-benzodioxin was the major regioisomer formed, except starting from 4-[(*tert*-butyldimethylsilyl)oxy]but-2-yn-1-yl methyl carbonate, where it was the minor one. This regioisomer was always obtained as the major isomer starting from hydroxy propargylic carbonate; however the chain length between the triple bond and the hydroxyl function seems crucial for the cyclization. Using the propargylic carbonate bearing an ester or a diethylamino function afforded the 1,4-benzodioxin-2(3*H*)-ylidene derivative as the major regioisomer.

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