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AN EASY AND EFFICIENT ACCESS TO BIS-ALLYLOXY-ARENES

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Abstract: Bis-allyloxy-arenes were prepared in very good yields by reaction of the bis-hydroxy-arene on the appropriate allyl carbonate at room temperature in the presence of a palladium(0) catalyst.

Allylic aryl ethers are very valuable synthons in organic chemistry. They are for exemple key precursors for the Claisen rearrangement.[1] The allyl group has also been used as protection of phenolic groups.[2] The most widely used methodology for the preparation of these substrates is the alkylation of suitable allylic halides with the corresponding phenol in the presence of potassium carbonate or sodium hydride. These strategies were also applied to the preparation of some bis-allyloxy arenes. However this methodology suffers from long reaction time, heating, and very often moderate chemical yields. One of the by-products is the *C*-alkylated product formed *via* the Claisen rearrangement due to the reaction temperature.

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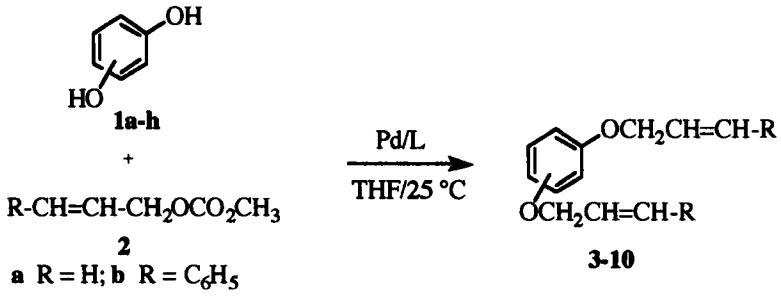
We recently shown that allylic aryl ethers were conveniently prepared in high yields and under very mild conditions *via* palladium(0)-catalyzed arylation of allylic carbonates under very mild conditions.[3] We expected that this procedure could be also conveniently used for the preparation of some bis-allyloxy-arenes (Scheme).



Scheme

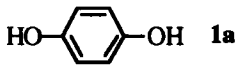
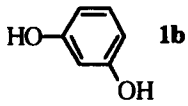
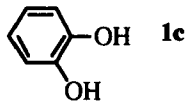
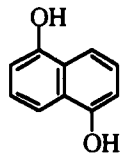
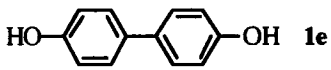
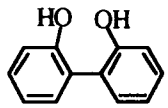
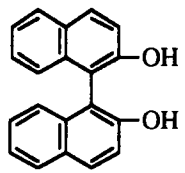
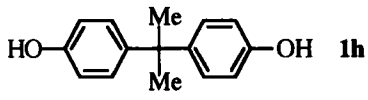
1,4-Dihydroxybenzene **1a** reacted with an excess of allyl methyl carbonate **2a** in THF in the presence of a catalytic amount of palladium(0) at room temperature to give the 1,4-bis-allyloxy-benzene **3a** in 96% yield (Table, entry 1). Extension of this methodology to 1,3- and 1,2-dihydroxybenzene **1b** and **1c** gave the 1,3- and 1,2-bis-allyloxy-benzene **4a** and **5a** in 95% and 96% yield, respectively (Table, entries 3 and 5). The substitution of allyl methyl carbonate **2a** by *(E)*-cinnamyl methyl carbonate **2b** allowed the preparation of the bis-cinnamyloxy-benzene **3b**, **4b**, and **5b** in 96%, 96%, and 79% yield, respectively (Table, entries 2, 4, 6). The same yields were obtained when the reaction was carried out at 60 °C.

Dihydroxynaphtalene **1d** reacted with methyl allyl carbonate **2a** at room temperature to give the bis-allyloxy-naphtalene **6a** in 99% yield (Table, entry 8). Performing the reaction at 60 °C gave a mixture of compounds, some of them resulting probably from a Claisen rearrangement.[3e]

Biphenyl-diols **1e** and **1f** gave also the expected bis-allyloxy- and bis-cinnamyloxy-biphenyl derivatives **7a**, **8a**, and **8b** in 98%, 99%, and 95% yield, respectively, at room temperature (Table, entries 8-10). Again for **1f**, performing the reaction at 60 °C gave a mixture of compounds.

Binaphtol **1g** gave bis-allyloxy-naphtalene **9a** and bis-cinnamyloxy-naphtalene **9b** in 100% and 81% yield, respectively, when the reaction was performed at room temperature (Table, entries 11,12), although a mixture of compounds was obtained at 60 °C.

Table. Palladium-catalyzed allylation of bisphenols

Entry	Phenol	Carbonate	Compound (Yield %)
1	 **1a**	**2a**	**3a** (96)
2		**2b**	**3b** (96)
3	 **1b**	**2a**	**4a** (95)
4		**2b**	**4b** (96)
5	 **1c**	**2a**	**5a** (96)
6		**2b**	**5b** (79)
7	 **1d**	**2a**	**6a** (99)
8	 **1e**	**2a**	**7a** (98)
9	 **1f**	**2a**	**8a** (99)
10		**2b**	**8b** (95)
11	 **1g**	**2a**	**9a** (100)
12		**2b**	**9b** (81)
13	 **1h**	**2a**	**10a** (98)
14		**2b**	**10b** (97)

Finally bisphenol **1h** gave compounds **10a** and **10b** in 98% and 97% yield, respectively.

In conclusion, various bis-allyloxy-arenes could be prepared in nearly quantitative yields at room temperature by the condensation of the corresponding bis-hydroxy-arene and the appropriate allylic carbonate in the presence of a palladium complex.

EXPERIMENTAL

All manipulations involving palladium catalysis were carried out in Schlenk tubes under an inert atmosphere. Tetrahydrofuran was distilled from sodium/benzophenone. ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were obtained using a Brüker AM 200 spectrometer. Chemical shifts are reported on the δ scale with reference to tetramethylsilane as an internal standard. Silica gel column chromatography was carried out using Merck silica gel 60 Gerudan (40-63 μm). 1,2-Bis-allyloxy-benzene (**3a**),[4] 1,3-bis-allyloxy-benzene (**4a**),[5] 1,4-bis-allyloxy-benzene (**5a**),[6] 1,5-bis-allyloxy-naphtalene (**6a**),[7] 4,4'-bis-allyloxy-biphenyle (**7a**),[8] 2,2'-bis-allyloxy-biphenyle (**8a**),[9] 2,2'-bis-allyloxy-1,1'-binaphtyle (**9a**)[10] and 2,2-bis-(4-allyloxyphenyl)propane (**10a**),[11] have already been described.

General procedure for the synthesis of ***3-10****.*

The catalytic system was prepared by stirring for 1 h in a Schlenk tube under argon $Pd_2(dba)_3$ or dipalladium tris(benzylidenacetone) (22.9 mg, 0.025 mmol) and 1,4-bis(diphenylphosphino)butane or dppb (42.6 mg, 0.1 mmol) in tetrahydrofuran (5 mL). This solution was added under argon to a Schlenk tube containing the unsaturated carbonate (3 mmol) and the phenol (1 mmol) in tetrahydrofuran (5 mL). The solution was stirred at 25 °C and the reaction followed by TLC. After 24 h, removal of the solvent followed by column chromatography on silica gel gave the desired allyloxybenzene.

1,2-Bis-*(E)*-cinnamyloxy-benzene (3b): white solid; mp: 121-123°C; R_f = 0.77 (hexane-ethyl acetate 4:1); ^{1}H NMR (200 MHz, $CDCl_3$) δ: 4.79 (dd, J = 5.7, 1.3 Hz, 4 H, OCH_2), 6.47 (dt, J = 16.0, 5.7 Hz, 2 H, =C*H*CH_2), 6.75 (d, J = 16.0 Hz, 2 H, -CH=), 6.95 (m, 4 H, H_{arom}), 7.23-7.42 (m, 10 H, H_{arom}); ^{13}C (50 MHz, $CDCl_3$) δ: 69.9 (CH_2), 114.5, 121.4, 124.8, 126.6, 127.8, 128.5, 132.9, 136.5 and 148.7 (=CH-, C_{arom}). Anal. calcd. for $C_{24}H_{22}O_2$ (342.42): C 84.18, H 6.48, found: C 83.92, H 6.70.

1,3-Bis-*(E)*-cinnamyloxy-benzene (4b): white solid; mp: 103-104°C; R_f = 0.61 (hexane-ethyl acetate 4:1); ^{1}H NMR (200 MHz, $CDCl_3$) δ: 4.69 (dd, *J* = 5.7, 1.3 Hz, 4 H, OCH_2), 6.41 (dt, *J* = 16.0, 5.7 Hz, 2 H, =C*H*CH_2), 6.58 (m, 3 H, H_{arom}), 6.74 (d, *J* = 16.0 Hz, 2 H, -CH=), 7.16-7.44 (m, 11 H, H_{arom}); ^{13}C (50 MHz, $CDCl_3$) δ: 68.7 (CH_2), 102.1, 107.2, 124.4, 126.6, 127.9, 128.6, 129.9, 133.1, 136.4 and 159.9 (=CH-, C_{arom}). Anal. calcd. for $C_{24}H_{22}O_2$ (342.42): C 84.18, H 6.48, found: C 84.04, H 6.61.

1,4-Bis-*(E)*-cinnamyloxy-benzene (5b): white solid; mp: 177-179°C; R_f = 0.91 (CH_2Cl_2); ^{1}H NMR (200 MHz, DMSO-d_6) δ: 4.66 (dd, *J* = 5.7, 1.3 Hz, 4 H, OCH_2), 6.43 (dt, *J* = 16.2, 5.7 Hz, 2 H, =C*H*CH_2), 6.74 (bd, *J* = 16.2 Hz, 2 H, -CH=), 6.94 (s, 4 H, H_{arom}), 7.26-7.39 (m, 6 H, H_{arom}), 7.46-7.50 (m, 4 H, H_{arom}); ^{13}C (50 MHz, $CDCl_3$) δ: 69.4 (CH_2), 115.9, 124.8, 126.6, 127.9, 128.6, 132.9, 135.4 and 154.0 (=CH-, C_{arom}). Anal. calcd. for $C_{24}H_{22}O_2$ (342.42): C 84.18, H 6.48, found: C 84.15, H 6.37.

2,2'-Bis-*(E)*-cinnamyloxy-biphenyl (8b): white solid; mp: 87-89°C; R_f = 0.58 (hexane/ethyl acetate 4:1); ^{1}H NMR (200 MHz, DMSO-d_6) δ: 4.63 (dd, *J* = 4.9, 1.5 Hz, 4 H, OCH_2), 6.23 (dt, *J* = 16.0, 4.9 Hz, 2 H, =C*H*CH_2), 6.49 (dt, *J* = 16.0, 1.5 Hz, 2 H, -CH=), 6.96-7.07 (m, 4 H, H_{arom}), 7.17-7.36 (m, 14 H, H_{arom}); ^{13}C (50 MHz, $CDCl_3$) δ: 68.8 (CH_2), 112.5, 120.7, 124.9, 126.3, 127.5, 128.5, 131.3, 131.5, 136.6 and 156.2 (=CH-, C_{arom}). Anal. calcd. for $C_{30}H_{26}O_2$ (418.54): C 86.09, H 6.26, found: C 86.19, H 6.24.

2,2'-Bis-*(E)*-cinnamyloxy-1,1'-binaphtyl (9b): white solid; mp: 181-182°C; R_f = 0.98 (CH_2Cl_2); ^{1}H NMR (200 MHz, DMSO-d_6) δ: 4.65 (d, *J* = 4.8 Hz, 4 H, OCH_2), 6.03 (dt, *J* = 15.9, 4.8 Hz, 2 H, =C*H*CH_2), 6.23 (dt, *J* = 15.9, 1.5 Hz, 2 H, -CH=), 7.06-7.47 (m, 18 H, H_{arom}), 7.84-7.97 (m, 4 H, H_{arom}); ^{13}C (50 MHz, $CDCl_3$) δ: 69.8 (CH_2), 116.0, 120.7, 123.7, 125.0, 126.3, 127.4, 127.9, 128.3, 129.2, 129.4, 131.4, 134.1, 136.5 and 154.0 (=CH-, C_{arom}). Anal. calcd. for $C_{40}H_{34}O_2$ (546.71): C 87.88, H 6.27, found: C 88.02, H 6.10.

2,2-Bis[4-*(E)*-cinnamyloxyphenyl]propane (10b): white solid; mp: 116-118°C; R_f = 0.77 (hexane/ethyl acetate 4:1); ^{1}H NMR (300 MHz, DMSO-d_6) δ: 1.66 (s, 6 H, CH_3), 4.68 (dd, *J* = 5.6, 1.5 Hz, 4 H, OCH_2), 6.43 (dt, *J* = 15.8,

5.9 Hz, 2 H, =C*H*CH_2), 6.73 (d, J = 15.8 Hz, 2 H, -CH=), 6.86 (m, 4 H, H_{arom}), 7.15 (m, 4 H, H_{arom}), 7.24-7.44 (m, 10 H, H_{arom}); ^{13}C (75.5 MHz, $CDCl_3$) δ: 31.1 (CH_3), 41.8 (CMe_2), 68.7 (CH_2), 114.2, 124.8, 126.7, 127.8, 127.9, 128.6, 132.9, 136.6, 143.4 and 156.6 (=CH-, C_{arom}). Anal. calcd. for $C_{33}H_{32}O_2$ (460.62): C 86.05, H 7.00, found: C 86.10, H 7.12.

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