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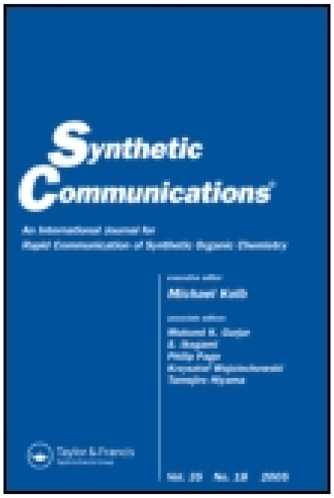

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Synthesis of Unsymmetrical Divinylbenzenes by Palladium Catalyzed Sequential Heck Reactions Starting from Carboxybenzenediazonium Salts

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ABSTRACT

Six *p*-, *m*- and *o*-unsymmetrical divinylbenzenes **5a**, **5b**, **6a**, **6b**, **6c** and **7a** are synthesized from *p*-, *m*- and *o*- carboxybenzenediazonium tetrafluoroborates via sequential Heck reactions in good overall yield.

Key Words: Divinylbenzenes; Arenediazonium salt; Heck reaction.

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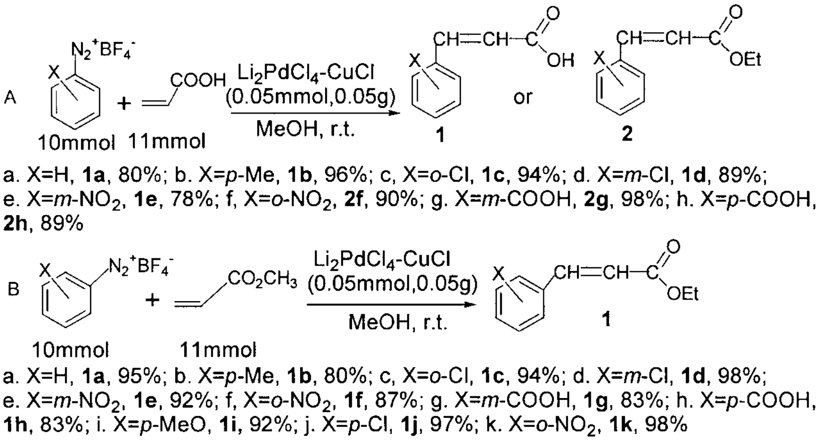
Palladium catalyzed arylation reactions of olefins (the Heck reaction[1]) conventionally use aryl halides (mainly iodides and bromides) as arylating reagents and require the addition of a base and a ligand (usually monodentate phosphines) in the reaction mixture. The use of other arylation reagents such as arenesulfonyl chlorides,[2] aryl triflates,[3] aryl perfluoroalkanesulfonates,[4] aroyl chlorides[5] and arenediazonium salts[6–9] have also been reported. Of all these alternative arylating reagents, arenediazonium salts and aroyl chlorides are more attractive considering (1) the easy availability of the aryl substrates with diversified substitution pattern, (2) the high reactivity and (3) that the arenediazonium salts are cheaper than the aryl bromides and iodides (as a matter of fact, the later are often prepared from the corresponding arenediazonium salts).

Although the Heck reaction has mainly been employed in the synthesis of 1-arylolefins, there is also a potentiality to use it for the synthesis of unsymmetrical divinylbenzenes which are important synthetic targets in view of their relation with poly(*p*-phenylenevinylenes) and nonlinear optical materials. Heck originally explored this possibility with bromoiodobenzenes.[10] Since then, the choice of arylating reagents applicable to the synthesis of unsymmetrical divinylbenzenes has been largely expanded. The significant difference in the reactivity of different leaving groups (Br^-, I^-, SO_2Cl^-, OH^-, $ROSO_2{}^-$, $COCl^-$, N_2, etc.), in participating the rate determining oxidative addition with palladium(0) can be made use of to achieve sequential Heck reactions at the same aromatic substrate to introduce two different vinyl groups. However, these potentialities have not been widely explored. Spencer explored the use of bromoaroyl chloride,[11] albeit in limited scope, partly because of the difficulties in obtaining the regioisomeric halogenoarenes. Very recently, Sengupta reported the application of iodoarenediazonium salt for the synthesis of *para*- and *ortho*-divinylbenzenes.[12] Considering the easy availability and the low cost of the arylating reagent, as well as the convenience and versatility of the method, we envision that the arenediazonium salt-aroyl chloride combination as in **1** (Sch. 1) is an advantageous choice of arylating reagents for these sequential Heck reactions. Reported here is the synthesis of divinylbenzenes starting from the corresponding carboxybenzenediazonium salts via sequential arylation reactions.

Arylation of acrylic acid and its esters by Heck reaction for the preparation of cinnamic acid and its esters is of important synthetic value and has been extensively investigated with aryl iodides[13] and bromides[14] under various conditions. The use of aroyl chlorides[5] and arenediazonium salts[6–8] has also been reported. More than a decade ago, we reported a modification of the arenediazonium salt Heck reaction by using a bimetallic Li_2PdCl_4–CuCl catalyst system with methanol as solvent, in which the arenediazonium salts react with acrylic acid and methyl acrylate at room temperature to give cinnamic acid and their esters in high yield (Eq. (1)).[7a] Neither base nor ligand is needed in the reactions. The simple reaction conditions, short reaction time (usually completed within 30 min), the small loading of the palladium catalyst (0.5 mmol%, as compared to the no less than 1–2 mmol% in other routine practice with arenediazonium salt as arylating reagent and 1–2 mmol% in the aryl iodide and bromide reaction) and its easy availability makes the procedure an exceedingly convenient and practical procedure for rather large scale preparations.

This procedure is now used in our syntheses of divinylbenzenes, starting from the carboxybenzenediazonium salts **1a**, **2a** and **3a** prepared from the corresponding aminobenzoic acids by routine diazotization procedures. The *o*-, *m*- and *p*-divinylbenzenes **5a–b**, **6a–c** and **7a** were synthesized by reaction sequences as outlined in Sch. 1.

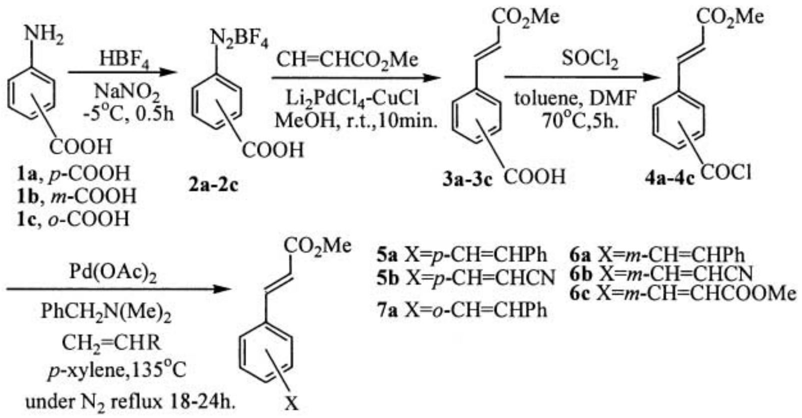
The first alkenylation reaction takes place at the diazonium salt with Li_2PdCl_4–CuCl (molar ratio 1:10) as catalyst in the presence of methyl acrylate in methanol with smooth evolving of nitrogen. The yields are in all cases high, ranging from 83% for the *p*-isomer to 98% for the *o*-isomer. It is known that arenediazonium salts can take part in Meerwein reaction with acrylic acid or methyl acrylate in aqueous acetone with CuCl as catalyst to give 3-aryl-2-chloropropanoic acid or



a. X=H, **1a**, 80%; b. X=*p*-Me, **1b**, 96%; c, X=*o*-Cl, **1c**, 94%; d. X=*m*-Cl, **1d**, 89%; e. X=*m*-NO_2, **1e**, 78%; f, X=*o*-NO_2, **2f**, 90%; g. X=*m*-COOH, **2g**, 98%; h. X=*p*-COOH, **2h**, 89%

a. X=H, **1a**, 95%; b. X=*p*-Me, **1b**, 80%; c, X=*o*-Cl, **1c**, 94%; d. X=*m*-Cl, **1d**, 98%; e. X=*m*-NO_2, **1e**, 92%; f, X=*o*-NO_2, **1f**, 87%; g. X=*m*-COOH, **1g**, 83%; h. X=*p*-COOH, **1h**, 83%; i. X=*p*-MeO, **1i**, 92%; j. X=*p*-Cl, **1j**, 97%; k. X=*o*-NO_2, **1k**, 98%

Equation 1.



Scheme 1.

methyl 3-aryl-2-chloropropanoate in moderate yield by a free radical mechanism.[15,16] However, in the present case, the arylation reactions could not proceed in the absence of Li_2PdCl_4, and typical Heck arylation products were obtained. Other solvents have also been tried, and it turns out that the reaction could not take place in MeCN, probably because of the strong coordination ability of this nitrile solvent to the palladium(II).[17] In acetone, acetone–dichloromethane (1:1, V/V), ethyl acetate or in aqueous solution, the reactions proceed only sluggishly with incomplete nitrogen evolution.

These alkenylated benzoic acids were then transformed into their benzoyl chloride **4a**, **4b** and **4c** by warming in toluene with thionyl chloride in 92%, 89% and 90% yield respectively. The second vinyl functionality was introduced by reaction of **4a**, **4b** and **4c** with the corresponding olefin with palladium acetate $Pd(OAc)_2$ as catalyst and *N*,*N*-dimethylbenzylamine (1.1 equiv. mol) as a base in refluxing *p*-xylene. The divinylbenzenes were obtained by flash chromatography. The yields are given in Table 1. The overall yields starting from the carboxy-arenediazonium salts are 57 and 64% for the two *p*-isomers **5a** and **5b**, 47, 44 and 31% for the three *m*-isomers **6a**, **6b** and **6c** and 40% for the *o*-isomer **7a**, respectively (see the Experimental).

The large coupling constant (~18 Hz) between the vicinal olefinic protons in the ^{1}H NMR spectra of these divinylbenzenes obtained after chromatographic separation on silica gel column indicated that they all have *E*-, *E*-configuration, although the ^{1}H NMR spectra of the crude reaction mixture revealed the presence of other geometric isomers

Table 1. Synthesis of divinylbenzenes **5**, **6** and **7** from vinylbenzoic acids **3**.[a]

		Divinylbenzene[c]		
		Second alkene		
Vinylbenzoic acid	Vinylbenzoyl chloride[b]	$PhCH{=}CH_2$	$CH_2{=}CHCN$	$CH_2{=}CHCO_2CH_3$
3a	**4a** (92)	**5a** (75)	**5b** (84)	
3b	**4b** (89)	**6a** (76)	**6b** (71)	**6c** (50)
3c	**4c** (90)	**7a** (45)		

[a] In parenthesis are the yield (%) of isolated pure product.

[b] General synthetic procedures for **4**: the alkenylated benzoic acid, $SOCl_2$ and DMF were mixed in toluene and stirred at 70°C for 4 h. The reaction mixture was concentrated in vacuo and the product collected by filtration. The crude product was recrystallized from petroleum ether (b.p. 60–90°C) to furnish the pure aroyl chloride. For reaction scales, see Experimental.

[c] General synthetic procedures for the divinylbenzenes: $Pd(OAc)_2$ (2–4 mmol%) and *N*,*N*-dimethyl benzylamine were added to a mixture of the corresponding aroyl chloride and styrene in *p*-xylene. The reaction mixture was stirred for 18–24 h at 135°C and was then diluted with water and extracted with $CHCl_3$ (3×40 mL). The organic layer was dried with $MgSO_4$ and concentrated in vacuo. The residue was subjected to column chromatographic separation on a silica gel column with petroleum ester (b.p. 60–90°C)-ethyl acetate as eluent to give the product. For reaction scales, see Experimental.

which were transformed to the *E*-, *E*-isomer during the chromatographic separation.

In conclusion, the easier availability and cheapness of the starting material[1] comparing with bromoiodobenzenes, bromoaroyl chlorides or iodoarenediazonium salts, in combination with the convenient reaction conditions, the use of Pd(II) instead of Pd(0) and the small loading of the Pd(II) catalyst, as well as the good overall yield of the divinylbenzenes make carboxybenzenediazonium salts an advantageous versatile arylating reagent for practical and efficient synthesis of regioisomeric symmetric and unsymmetrical divinylbenzenes.

EXPERIMENTAL

Melting points were uncorrected. Proton NMR were recorded on a Bruker AC-300 spectrometer at 300 MHz in $CDCl_3$. *J* values are given in Hz. Infrared spectra were taken with a Shimadzu IR 408 spectrometer in KBr pellets. Mass spectra were recorded with a VG ZAB-HS spectrometer.

Arenediazonium fluoroborates were prepared by literature procedures.[18] Methanol (A.R. grade) was refluxed with magnesium and distilled. Alkenes, toluene, *p*-xylene and *N*,*N*-dimethyl benzylamine were purified by distillation before use. Other reagents (CP or AR grade) were used as received without further purification. Methanol solution of Li_2PdCl_4 was prepared by stirring dry LiCl (0.84 g, 20 mmol) and $PdCl_2$ (1.77 g, 10 mmol) in methanol (100 mL) overnight.

General Procedure for the Synthesis of Divinylbenzenes

Li_2PdCl_4 (0.05 mmol) and CuCl (0.05 g, 0.5 mmol) were added to a mixture of the carboxy-benzenediazonium salt (2.36 g, 10 mmol) and methyl acrylate (0.946 g, 11 mmol) in MeOH (5 mL). The reaction mixture was stirred for about 30 min at room temperature until nitrogen evolution ceased. The mixture was then cooled to 0°C. The solid product was collected by filtration. The filtrate was then concentrated, cooled and filtered again to give another crop of product. The general procedures for the preparations of the aroyl chlorides **4a–c** and of the divinylbenzenes are given in Table 1.

Preparation of 5a: The *p*-carboxycinnamic acid **3a** was obtained in 83% yield. Reaction of **3a** (6.97 g, 31.7 mmol) with $SOCl_2$ (2.75 mL, 37.9 mmol) and DMF (0.09 mL) in toluene (50 mL) for 5 h afforded **4a** (6.53 g, 92%). Refluxing **4a** (2.25 g, 10 mmol) with styrene (1.4 mL, 11 mmol) in *p*-xylene (20 mL) in the presence of $Pd(OAc)_2$ (2 mg, 0.009 mmol) and $PhCH_2NMe_2$ (1.65 mL, 11 mmol) at 135°C under a nitrogen atmosphere for 24 h gave **5a** (1.98 g, 75%). The overall yield starting from arenediazonium salts is 57%.

***E*,*E*-Methyl 4-styrylcinnamate (5a):** M.p. 182–183°C (yellow solid from petroleum ether (b.p. 60–90°C)–ethyl acetate) (lit. 184–186°C[10a]) IR 1716, 1634, 1598, 1438, 1172, 972, 820 cm^{-1}. ^1H NMR: δ 3.83 (s, 3H, CH_3), 6.47 (d, $J = 16.3$ Hz, 1H), 7.20 (d, $J = 16.3$ Hz, 1H), 7.11 (d, $J = 16.3$ Hz, 1H), 7.71 (d, $J = 16.2$ Hz, 1H), 7.30–7.56 (m, 9H, ArH). MS: m/z 264 [M^+] (100), 232 (5), 178 (19), 127, 77. Anal. found: C, 81.78; H, 6.04; calcd. for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10.

Preparation of 5b: Refluxing **4a** (2.25 g, 10 mmol) with acrylonitrile (0.73 mL, 11 mmol) in *p*-xylene (20 mL) in the presence of $Pd(OAc)_2$ (2 mg, 0.009 mmol) and $PhCH_2NMe_2$ (1.65 mL, 11 mmol) at 135°C under a nitrogen atmosphere for 18 h gave **5b** (1.79 g, 84%). Overall yield starting from arenediazonium salts is 64%.

***E*,*E*-Methyl 4-(2-cyanoethenyl)cinnamate (5b):** M.p. 126–128°C (white solid from petroleum-ether (b.p. 60–90°C)–ethyl acetate) (lit. 121–122°C[11]). IR: 2210, 1709, 1632, 1426, 1328, 1171, 1121, 973, 814 cm^{-1}. ^{1}H NMR: δ 3.83 (s, 3H, CH_3), 5.94 (d, $J = 16.7$ Hz, 1H), 7.41 (d, $J = 16.7$ Hz, 1H), 6.50 (d, $J = 16.0$ Hz, 1H), 7.68 (d, $J = 16.0$ Hz, 1H), 7.47–7.58 (m, 4H, ArH). MS: *m*/*z* 213 [M^+] (77), 182 (100), 154, 127, 101, 77. Anal. found: C, 73.10; H, 5.13; N, 6.39; calcd. for $C_{13}H_{11}NO_2$: C, 73.22; H, 5.20; N, 6.57.

Preparation of 6a: The *m*-carboxycinnamic acid **3b** was obtained in 70% yield. Reaction of **3b** (5.15 g, 25 mmol) with $SOCl_2$ (2.18 mL, 30 mmol) and DMF (0.01 mL) in toluene (20 mL) for 5 h afforded **4b** (4.98 g, 89%). Refluxing **4b** (2.25 g, 10 mmol) with styrene (1.4 mL, 11 mmol) in *p*-xylene (20 mL) in the presence of $Pd(OAc)_2$ (2 mg, 0.009 mmol) and $PhCH_2NMe_2$ (1.65 mL, 11 mmol) at 135°C under nitrogen for 18 h gave **6a** (2.01 g, 76%). The overall yield starting from **2b** is 47%.

***E*,*E*-Methyl 3-styrylcinnamate (6a):** M.p. 140–141°C (white solid from petroleum-ether (b.p. 60–90°C)–ethyl acetate) IR: 1717, 1642, 1436, 1321, 1174, 986, 967, 801, 752, 6939 cm^{-1}. ^{1}H NMR: δ 3.85 (s, 3H, CH_3), 6.51 (d, $J = 16.2$ Hz, 1H), 7.14 (d, $J = 16.4$ Hz, 1H), 7.15 (d, $J = 16.4$ Hz, 1H), 7.74 (d, $J = 16.2$ Hz, 1H), 7.30–7.67 (m, 9H, ArH). MS: *m*/*z* 264 [M^+] (100), 232 (13), 203 (54), 178 (28). Anal. found: C, 81.47; H, 5.98; calcd. for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10.

Preparation of 6b: Refluxing **4b** (2.25 g, 10 mmol) with acrylonitrile (0.73 mL, 11 mmol) in *p*-xylene (20 mL) in the presence of $Pd(OAc)_2$ (4 mg, 0.018 mmol) and $PhCH_2NMe_2$ (1.65 mL, 11 mmol) at 135°C under a nitrogen atmosphere for 24 h gave **6b** (1.51 g, 71%). The overall yield starting from **2b** is 44%.

***E*,*E*-Methyl 3-(2-cyanoethenyl)cinnamate (6b):** M.p. 114–115°C (white solid from petroleum-ether (b.p. 60–90°C)–ethyl acetate) IR: 2212, 1710, 1639, 1618, 1314, 1179, 1197, 987, 854, 791, 677 cm^{-1}. ^{1}H NMR: δ 3.84 (s, 3H, CH_3), 5.95 (d, $J = 16.8$ Hz, 1H), 7.69 (d, $J = 16.2$ Hz, 1H), 6.49 (d, $J = 16.2$ Hz, 1H), 7.40–7.62 (m, 5H, ArH). MS: *m*/*z* 213 [M^+] (38), 182, 154 (100), 127 (42). Anal. found: C, 73.15; H, 5.02; N, 6.87; calcd. for $C_{13}H_{11}NO_2$: C, 73.22; H, 5.20; N, 6.57.

Preparation of 6c: Refluxing **4b** (2.25 g, 10 mmol) with methyl acrylate (0.99 mL, 11 mmol) in *p*-xylene (20 mL) in the presence of $Pd(OAc)_2$ (2 mg, 0.009 mmol) and $PhCH_2NMe_2$ (1.65 mL, 11 mmol) at 135°C under a nitrogen atmosphere for 24 h gave **6c** (1.23 g, 50%). The overall yield starting from **2b** is 31%.

***E*,*E*-Dimethyl 3,3′-(1,3-phenylene)*bis*-2-propanoate (6c):** M.p. 134–136°C (white solid from petroleum-ether (b.p. 60–90°C)–ethyl acetate) (lit. 138°C[19]). IR: 3030, 2954, 1731, 1642, 1577, 1437, 1321, 1170, 979, 857, 795, 672 cm^{-1}. ^{1}H NMR: δ 3.83 (s, 6H, CH_3), 6.49 (d, $J = 16.0$ Hz, 2H), 7.70 (d, $J = 16.0$ Hz, 2H), 7.40–7.66 (m, 4H, ArH). MS: m/z 246 [M$^+$] (0.91), 206 (4.09), 189 (100), 157, 118, 102, 77. Anal. found: C, 68.06; H, 5.39; calcd. for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73.

Preparation of 7a: The *o*-carboxycinnamic acid **3c** was obtained in 98% yield. Reaction of **3c** (6.97 g, 31.7 mmol) with $SOCl_2$ (2.75 mL, 37.9 mmol) and DMF (0.09 mL) in toluene (50 mL) for 5 h give **4c** (6.39 g, 90%). Refluxing **4c** (2.25 g, 10 mmol) with styrene (1.4 mL, 11 mmol) in *p*-xylene (20 mL) with $Pd(OAc)_2$ (4 mg, 0.018 mmol) and $PhCH_2NMe_2$ (1.65 mL, 11 mmol) at 135°C under nitrogen for 24 h gave **7a** (1.19 g, 45%). The overall yield starting from **2c** is 40%.

***E,E*-Methyl 2-styrylcinnamate (7a):** Yellow oil. IR: 1710, 1630, 1595, 1320, 965, 760, 690 cm^{-1}. ^{1}H NMR: δ 3.83 (s, 3H, CH_3), 6.46 (d, $J = 15.9$ Hz, 1H), 7.19 (d, $J = 16.2$ Hz, 1H), 7.10 (d, $J = 16.2$ Hz, 1H), 7.71 (d, $J = 15.9$ Hz, 1H), 7.30–7.57 (m, 9H, ArH). MS: m/z 264 [M$^+$], 232, 205 (100), 178, 161, 131, 91, 77. Anal. found: C, 81.67; H, 6.02; calcd. for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10.

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