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Efficient Synthesis of 1,4-Dialkoxy and 1,4-Dialkyl Substituted 2,5-Divinylbenzenes via the Stille Reaction

Walid A. Daoud*,† **and Michael L. Turner**††

Department of Chemistry, University of Sheffield,
Sheffield, S3 7HF, UK

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An efficient palladium catalyzed cross coupling of tributyl(vinyl)stannane with dialkoxy and dialkyl substituted 1,4-dihalobenzenes is described. This single-step coupling provides an efficient synthesis of functionalized 2,5-divinylbenzenes, which are useful precursors of 1,4-phenylenevinylene copolymers.

Conjugated polymers, and in particular poly(1,4-phenylenevinylene) derivatives,[1,2] have attracted considerable current interest due to their processing ability and electroluminescent properties. These polymers have been prepared by a number of different methods, using a variety of precursors.[3] Recently synthetic methods employing transition metal catalyzed C–C bond forming reactions, such as the Heck reaction, have been reported. These methods have expanded the range of accessible polymer architectures.[4] Suitable precursors include highly functionalized 1,4-dihalobenzenes that may be condensed with 1,4-divinylbenzene in a palladium catalyzed Heck reaction to give a wide range of substituted phenylenevinylene copolymers.[5,6] Dialkyl substituted divinylbenzenes undergo metathesis polycondensation in the presence of a metal alkylidene complex to give oligomeric all-trans phenylenevinylene derivatives. These compounds were prepared in low overall yield from the corresponding dicyanobenzenes using a five-step procedure involving a Wittig reaction.[7,8] The cross coupling of tributyl(vinyl)stannane with various organic electrophiles, such as aryl halides in the presence of a palladium catalyst, has been demonstrated by Stille[9] and others[10] to be a highly efficient method for the preparation of styrene derivatives. However, the coupling of tributyl(vinyl)stannane with aryl halides substituted with electron-donating groups is reported to be not favored and gives a low yield of coupled products.[11] Recently, Littke and Fu reported a successful cross coupling of electron-rich monohaloaryls such as *p*-chloroanisole and *p*-chloroaniline with organotin compounds in the presence of $\mathrm{P}^t\mathrm{Bu}_3$ as a ligand for palladium and CsF to activate the tin reagent.[10c] According to these authors, the presence of an *o*-methyl group to the halide caused a steric hindrance, which resulted in a lower yield. Herein we report on the use of the Stille methodology in an efficient, yet simple, synthesis of 1,4-dialkoxy and 1,4-dialkyl substituted 2,5-divinylbenzenes in the presence of *trans*-di(μ-acetato)-bis[*o*-(di-*o*-tolylphosphino)-benzyl]dipalladium(II) (Fig. 1) as a palladium catalyst and without the use of any other additives.

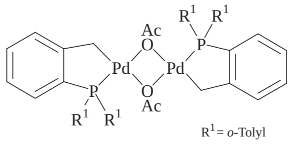

Fig. 1. Chemical structure of palladacycle catalyst.

1,4-Dialkylbenzene **1** ($\mathrm{R}^1 = \mathrm{R}^2 = \mathrm{C}_{16}\mathrm{H}_{33}$) was synthesized in good yield (60%) by a nickel catalyzed cross-coupling of a Grignard reagent with dibromobenzene (Scheme 1). The corresponding 1,4-dialkoxybenzenes **1** ($\mathrm{R}^1 = \mathrm{R}^2 = \mathrm{OC}_{12}\mathrm{H}_{25}$ or $\mathrm{OC}_{16}\mathrm{H}_{33}$; $\mathrm{R}^1 = \mathrm{OC}_{12}\mathrm{H}_{25}$, $\mathrm{R}^2 = \mathrm{OCH}_3$) were obtained from hydroquinone (67 and 64%, respectively) or 4-methoxyphenol (82%) by a Williamson ether synthesis with an alkyl bromide. The iodination of **1** with iodine and iodic acid gave **2** in 60% after extensive purification.[5]

The reaction of **2** with tributyl(vinyl)stannane[12] in the presence of a palladium catalyst required high temperatures (>80 °C) and extended reaction times. The products, 1,4-dialkyl and 1,4-dialkoxy substituted 2,5-divinylbenzenes **3**, were isolated (55%) in the necessary purity for polymerization reactions by column chromatography and recrystallization. To ensure that the products are free of any organotiniodide impurities, it was necessary to treat the reaction mixture with potassium fluoride to precipitate insoluble tributyltinfluoride, which may be removed by filtration through Celite.

A range of reaction conditions were employed to optimize the yield of **3**. The best conversions were obtained using a palladacycle catalyst, *trans*-di(μ-acetato)-bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II), prepared from palladium acetate and tri(*o*-tolyl)phosphine in toluene at a temperature below reflux.[13] This palladacycle catalyst was found to be more stable at high temperatures than tetrakis(triphenylphosphine)palladium. No reaction was detected at reaction temperatures below 80 °C, and at temperatures close to toluene reflux (110 °C) the reaction time was much reduced, but the isolated yield was very low (25%). The highest isolated yield (55%) of pure product **3** was obtained after 40 h at 90 °C. The cross coupling of tributyl(vinyl)stannane with analogous substituted dibromobenzenes was also possible. However, a higher reaction temperature (100 °C) was required to achieve complete conversion and it was necessary to add an extra equivalent of the catalyst after 40 h in order to isolate 45% of the coupled product after 90 h.

To summarize, 1,4-dialkoxy and 1,4-dialkyl substituted 2,5-divinylbenzenes can be prepared in good yield and high purity by the palladium catalyzed cross-coupling of tributyl(vinyl)stannane and disubstituted dihalobenzenes. These compounds are useful as monomers for 1,4-phenylenevinylene copolymers; studies of their polymerization reactions are under investigation.

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† Present address: Nanotechnology Centre, ITC, The Hong Kong Polytechnic University, Hung Hom, Hong Kong

†† Present address: Department of Chemistry, University of Manchester, M13 9PL, UK

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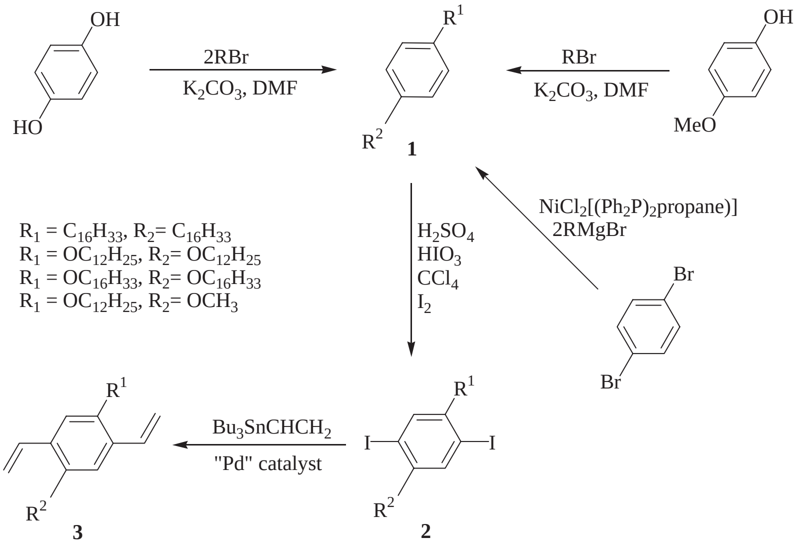

Scheme 1. Preparation of divinyl substituted benzenes via the Stille reaction.

Experimental

Preparation of 2,5-Bis(dodecyloxy)-1,4-diiodobenzene. A 250 mL flask was charged with iodine (1.14 g, 4.5 mmol), 1,4-bis(dodecyloxy)benzene (2.23 g, 5 mmol), iodic acid (0.527 g, 3 mmol), CCl_4 (4 mL), glacial acetic acid (18 mL), 0.65 mL H_2SO_4, and 3 mL of deionized water. The resulting mixture was heated to 75 °C for 3 h. After this time, a solution of sodium thiosulfate was added to remove any unreacted iodine. The solution was extracted with dichloromethane and washed three times with a 5% NaOH solution, followed by washing three times with water. The organic layer was dried over $MgSO_4$ and the solvent removed under reduced pressure. The product, 2,5-bis(dodecyloxy)-1,4-diiodobenzene, was isolated by two recrystallization steps from ethanol to give an overall yield of 60%. ^1H NMR ($CDCl_3$) δ 7.28 (s, 2H, arom.), 3.92 (t, 4H, $J = 6.4$ Hz, α-OCH_2), 1.5–1.2 (m, 40H, aliph.), 0.8 (t, 6H, $J = 6.6$ Hz, $-CH_3$).

Preparation of 1,4-Bis(dodecyloxy)-2,5-divinylbenzene. Two mole equivalents of tributyl(vinyl)stannane (0.6 mL, 1.93 mmol) were added to a solution of 2,5-bis(dodecyloxy)-1,4-diiodobenzene (0.64 g, 0.92 mmol) in 50 mL of toluene. To this, (10 mg, 0.0094 mmol) of the isolated palladacycle catalyst was added. The reaction mixture was stirred at 90 °C for 3 h, after which an additional amount (10 mg) of the catalyst was added, and the mixture was heated at 90 °C for 36 h. The reaction mixture was allowed to cool to room temperature and a solution of potassium fluoride and ether was added and stirred for 3 h. The resulting solution was filtered through Celite to remove solid tributyltinfluoride and the catalyst residues. The solvents were removed under reduced pressure and the crude product was purified by column chromatography on silica gel using hexane/DCM 6:1 as the eluent. Recrystallization of the product from cold ethanol gave 0.25 g (55% yield) of 1,4-bis(dodecyloxy)-2,5-divinylbenzene. ^1H NMR ($CDCl_3$) δ 7.0 (m, 2H, $-CH{=}CH_2$), 6.9 (s, 2H, arom.), 5.65 (dd, 2H, $^{trans}J = 17.8$ Hz, $^{cis}J = 1.42$ Hz, *cis*-$CH{=}CH_2$), 5.2 (dd, 2H, $^{trans}J = 11.3$ Hz, $^{cis}J = 1.42$ Hz, *trans*-$CH{=}CH_2$), 3.9 (t, 4H, $J = 6.4$ Hz, α-OCH_2), 1.55–1.25 (m, 40H, aliph.), 0.8 (m, 6H, $-CH_3$). ^{13}C NMR ($CDCl_3$) δ 150.4, 131.5, 127.1, 114, 110.5, 69.3, 31.9, 29.6, 29.3, 26.1, 22.7, 14.1. Analytical data for $C_{34}H_{58}O_2$: EI-MS m/z 498 (M+ 100%), 330 (7%). Found (calcd): C, 81.64 (81.86); H, 11.94 (11.72)%.

1-Dodecyloxy-4-methoxy-2,5-divinylbenzene. ^1H NMR ($CDCl_3$) δ 7.2 (m, 2H, $-CH{=}CH_2$), 7.0 (s, 2H, arom.), 5.6 (dd, 2H, $^{trans}J = 17.7$ Hz, $^{cis}J = 1.36$ Hz, *cis*-$CH{=}CH_2$), 5.25 (dd, 2H, $^{trans}J = 11.1$ Hz, $^{cis}J = 1.4$ Hz, *trans*-$CH{=}CH_2$), 3.9 (t, 2H, $J = 6.4$ Hz, α-OCH_2), 3.75 (s, 3H, $-OCH_3$), 1.55–1.25 (m, 20H, aliph.), 0.8 (t, 3H, $J = 6.5$ Hz, $-CH_3$). ^{13}C NMR ($CDCl_3$) δ 151.8, 151.2, 131.5, 131.4, 127.1, 126.9, 114.3, 114, 110.7, 109.1, 69.4, 56.3, 31.9, 29.6, 29.4, 26.1, 22.7, 14.1. Analytical data for $C_{23}H_{36}O_2$: EI-MS m/z 344 (M+ 100%). Found (calcd): C, 79.34 (79.73); H, 10.51 (10.46)%.

1,4-Dihexadecyl-2,5-divinylbenzene. ^1H NMR ($CDCl_3$) δ 7.2 (s, 2H, arom.), 6.9 (dd, 2H, $^{trans}J = 17.3$ Hz, $^{cis}J = 11$ Hz, $-CH{=}CH_2$), 5.6 (dd, 2H, $^{trans}J = 17.3$ Hz, $^{cis}J = 1.46$ Hz, *cis*-$CH{=}CH_2$), 5.2 (dd, 2H, $^{trans}J = 11$ Hz, $^{cis}J = 1.46$ Hz, *trans*-$CH{=}CH_2$), 2.5 (m, 4H, α-CH_2), 1.55–1.25 (m, 56H, aliph.), 0.65 (t, 6H, $J = 6.6$ Hz, $-CH_3$). ^{13}C NMR ($CDCl_3$) δ 138, 135.6, 134.4, 126.6, 114.6, 33, 31.9, 31.3, 29.7, 29.5, 22.7, 14.1. Analytical data for $C_{42}H_{74}$: EI-MS m/z 579 (M+ 100%), 552.6 (12%). Found (calcd): C, 86.44 (86.69); H, 13.15 (12.8)%.

1,4-Bis(hexadecyloxy)-2,5-divinylbenzene. ^1H NMR ($CDCl_3$) δ 7.2 (s, 2H, arom.), 6.9 (m, 2H, $-CH{=}CH_2$), 5.6 (dd, 2H, $^{trans}J = 17.7$ Hz, $^{cis}J = 1.46$ Hz, *cis*-$CH{=}CH_2$), 5.2 (dd, 2H, $^{trans}J = 15$ Hz, $^{cis}J = 1.46$ Hz, *trans*-$CH{=}CH_2$), 2.5 (t, 4H, $J = 6.4$ Hz, α-CH_2), 1.55–1.25 (m, 56H, aliph.), 0.65 (t, 6H, $J = 6.5$ Hz, $-CH_3$). ^{13}C NMR ($CDCl_3$) δ 150.6, 131.6, 127.1, 113.9, 110.5, 69.3, 31.9, 29.7, 29.4, 29.4, 26.1, 22.7, 14.1. Analytical data for $C_{42}H_{74}O_2$: EI-MS m/z 610 (M+ 100%). Found (calcd): C, 81.97 (82.22); H, 12.55 (12.13)%.

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References

1 J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, and A. B. Holmes, *Nature*, **539**, 347 (1990).

2 R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes. R. N. Marks, C. Taliani, D. D. C. Bradley, D. A.

Dos Santos, L. L. Brédas, M. Löglund, and W. R. Salaneck, *Nature*, **397**, 121 (1999).

3 A. Kraft, A. C. Grimsdale, and A. B. Holmes, *Angew. Chem., Int. Ed.*, **37**, 402 (1998).

4 a) W. Heitz, *Pure Appl. Chem.*, **67**, 1951 (1995), and references therein. b) H. P. Weitzel and K. Mullen, *Macromol. Chem. Phys.*, **191**, 2837 (1990). c) M. Suzuki, J. C. Lim, and T. Saegusa, *Macromolecules*, **23**, 1574 (1990). d) S. T. Pasco, P. M. Lahti, and F. E. Karasz, *Macromolecules*, **32**, 6933 (1999). e) Q. Chu, Y. Pang, L. Ding, and F. E. Karasz, *Macromolecules*, **36**, 3848 (2003).

5 Z. N. Bao, Y. Chen, R. B. Cai, and L. P. Yu, *Macromolecules*, **26**, 5281 (1993).

6 a) D. K. Fu, B. Xu, and T. M. Swager, *Tetrahedron*, **53**, 15487 (1997). b) A. Hilberer, H. J. Brouwer, B. J. Vanderscheer, J. Wildeman, and G. Hadziioannou, *Macromolecules*, **28**, 4525 (1995). c) H. Li, C. Xiang, Y. Li, S. Xiao, H. Fang, and D. Zhu, *Synth. Met.*, **135–136**, 483 (2003).

7 E. Thorn-Csanyi and P. Kraxner, *Makromol. Chem., Rapid Commun.*, **19**, 223 (1998).

8 E. Thorn-Csanyi and P. Kraxner, *Makromol. Chem. Phys.*, **198**, 3827 (1997).

9 D. R. McKean, G. A. Parrinello, F. Renaldo, and J. K. Stille, *J. Org. Chem.*, **52**, 422 (1987).

10 a) B. Gómez-Lor, A. M. Echavarren, and A. Santos, *Tetrahedron Lett.*, **38**, 5347 (1997). b) J. N. G. Pillow, P. L Burn, I. D. W. Samuel, and M. Halim, *Synth. Met.*, **102**, 1468 (1999). c) A. F. Littke and G. C. Fu, *Angew. Chem., Int. Ed.*, **38**, 2411 (1999). d) I. C. Grig-Alexa, A. L. Finaru, L. Ivan, P. Caubère, and G. Guillaumet, *Tetrahedron Lett.*, **45**, 2343 (2004).

11 For an excellent review see: a) V. Farina, V. Krishnamurthy, and W. J. Scott, *Org. React.*, **50**, 1 (1997). b) J. K. Stille, *Angew. Chem., Int. Ed. Engl.*, **25**, 508 (1986).

12 D. Seyferth and F. G. A. Stone, *J. Am. Chem. Soc.*, **79**, 515 (1957).

13 W. A. Herrmann, C. Brossmer, K. Ofele, C. P. Reisinger, T. Priermeier, M. Beller, and H. Fischer, *Angew. Chem., Int. Ed. Engl.*, **34**, 1844 (1995).