Efficient Synthesis of *p*-Vinyl-*trans*-Stilbene

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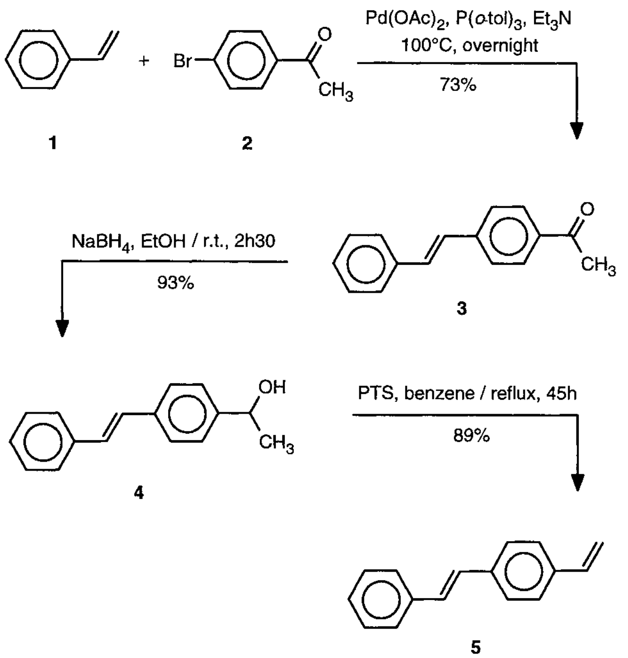
Dedicated to the memory of Prof. Dr. N. Alexandrou, The Aristotelion University of Thessaloniki, Greece

p-Vinyl-*trans*-stilbene was synthesized in three steps with 60 % overall yield. The repetition of these steps to obtain longer oligomers is only limited by the poor solubility of the products.

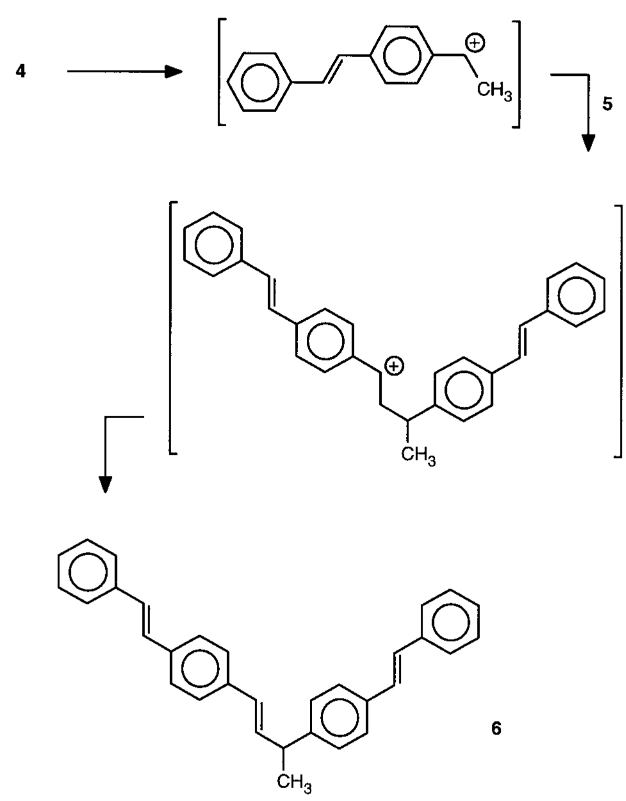
(*E*)-1-Ethenyl-4-(2-phenylethenyl)benzene [(*E*)-4-vinylstilbene], commonly named *p*-vinyl-*trans*-stilbene (PVTS), is a molecule that has been used for a long time in various applications. Its vinylic end group undergoes radical polymerization very readily, giving linear polymer chains with pendant stilbene groups. Such polymers, or copolymers obtained by copolymerization with another monomer, have been studied extensively, for example for scintillation properties,[1] for the possibility of polyanion formation,[2] or for the photochromic properties of the stilbene side groups.[3] More recently, a new application of PVTS was reported in the development of polymers for light emitting diodes:[4] by grafting the molecule on to a partially brominated polystyrene, a polymer bearing blue light emitting chromophores as side chains is obtained. In the course of our work on the preparation of luminescent oligomers, polymers and copolymers based on poly(*p*-phenylenevinylene) (PPV), we have been confronted with the need for PVTS and related compounds. Many synthetic routes to the PVTS molecule have been reported,[1-4] but they all include numerous steps, delicate procedures, and are characterized by poor overall yield (< 35 %). We present here an easy procedure for the preparation of PVTS in three steps (Scheme 1), with an excellent overall yield (> 60 %), starting from readily available and inexpensive commercial compounds.



Scheme 1

The first step consists of a palladium catalyzed Heck coupling[5] between styrene (**1**) and bromoacetophenone **2**, with palladium(II) acetate and tris(2-tolyl)phosphane as catalyst and co-catalyst, respectively, in triethylamine. The reaction is performed in a capped heavy-walled Pyrex tube, since it is known that pressure has a positive effect on the coupling yield.[6] 1-[(*E*)-4-(2-Phenylethenyl)-phenyl]ethanone [(*E*)-4-acetylstilbene, **3**] is obtained in 73 % yield. The Heck reaction is known to give pure *E* double bonds,[5] and this is confirmed by the ^{1}H NMR spectrum of the compound. In the second step, the ketone function is reduced to the corresponding alcohol **4** using sodium borohydride[7] with a yield of 93 %. This alcohol is finally dehydrated to the vinyl function by the action of 4-toluenesulfonic acid (PTS).[7] The reaction is performed in refluxing benzene, in a Dean–Stark apparatus in order to continuously remove the water formed by the reaction. PVTS **5** is obtained in 89 % yield, which means that the whole procedure has an overall yield of 60 %.

The last step (dehydration) is the most critical and the method employed[7] had to be adapted in order to obtain such good yields. There are a few critical points that must be discussed. First, catalytic quantities of PTS have to be used. If more than 1 mol% of PTS is added, the reaction becomes faster but a side product is formed. This compound was isolated and could be identified as a dimer of PVTS. The formation of this product can be understood by considering the mechanism depicted in Scheme 2. The dehydration of the alcohol **4** proceeds through formation of a carbocation intermediate. A PVTS molecule **5** can react with that species to give a dimer carbocation, which eventually leads to the PVTS dimer **6**. The higher the initial concentration of PTS, the higher the concentration of the carbocation species, and therefore the probability of the side reaction occurring becomes higher. Second, the workup of the reaction must also be carried out very carefully to avoid polymerization of the very reactive monomer. If the solvent is removed directly after the reaction is finished, the solution turns blue and a mixture of polymeric product and PVTS dimer is finally obtained. To avoid this cationic polymerization and dimerization, addition of methanol to the reaction mixture prior to solvent evaporation, in order to destroy any carbocations that could still be present, proved to be sufficient. Finally, the removal of the solvent must be performed at room temperature (under vacuum). Heating of the solution results in thermal polymerization, and only polymeric material is collected. This problem can possibly also be avoided by using a polymerization inhibitor. When all these precautions are taken the pure monomer can be obtained in very good yield.



Scheme 2

We are currently working on the extension of this procedure in order to obtain longer oligo(*p*-phenylenevinylene)s. The sequence of three reactions can be repeated with PVTS as starting material instead of styrene to give a PPV trimer. The problem is that all the compounds are poorly soluble because of their increased size and rigid character which makes their purification difficult. It is therefore necessary to work with substituted derivatives.

In conclusion, we have developed a very easy and convenient route to synthesize PVTS in high yield. By working with substituted molecules, the sequence of reactions can be repeated to obtain longer PPV oligomers.

NMR spectra (^{1}H and ^{13}C) were recorded on a Varian Gemini 200 MHz spectrometer using $CDCl_3$ as solvent and internal standard ($\delta = 7.27$ for ^{1}H and $\delta = 77.0$ for ^{13}C). ^{13}C NMR spectra were measured with attached proton test. Figure 1 shows the NMR spectra assignments (R = acetyl, hydroxyethyl or vinyl). Et_3N was dried over KOH, EtOH was dried over molecular sieves and benzene was dried over sodium. Column chromatography was performed on Merck Kieselgel 60 (230–400 mesh).

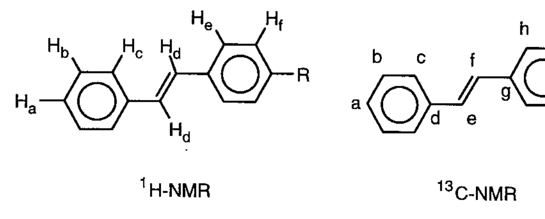


Figure 1

1-[(*E*)-4-(2-Phenylethenyl)phenyl]ethanone [(*E*)-4-Acetylstilbene, 3]:
A mixture of styrene (**1**, 1.4 mL, 12.5 mmol), 1-(4-bromophenyl)ethanone (**2**, 2 g, 10 mmol), $Pd(OAc)_2$ (22.5 mg, 0.1 mmol), tris(2-tolylphosphane (61 mg, 0.2 mmol) and Et_3N (5 mL, 36 mmol) was prepared in a heavy-walled Pyrex tube. The tube was capped under argon and heated overnight at 100 °C. After cooling, the solid reaction product was stirred in 5% HCl soln (200 mL) and collected by filtration. The gray solid was washed with H_2O, then dissolved in $CHCl_3$ (20 mL) and the solution filtered carefully. The solvent was evaporated and the residue recrystallized from EtOH (75 mL) to give **3** as a pale yellow powder; yield: 1.6 g (73%).

^{1}H NMR: $\delta = 2.6$ (3 H, s, C*H*$_3$), 7.2 (2 H, d, H_d *trans*), 7.25–7.45 (3 H, m, H_a and H_b), 7.55 (2 H, d, H_c), 7.6 (2 H, d, H_e), 7.96 (2 H, d, H_f).

^{13}C NMR: $\delta = 26.5$ (CH_3), 126.5 (C_c), 126.8 (C_h), 127.4 (C_e or C_f), 128.3 (C_a), 128.77 (C_i), 128.84 (C_b), 131.4 (C_f or C_e), 136 (C_j), 136.5 (C_d), 142 (C_g), 197 (*C*O).

1-[(*E*)-4-(2-Phenylethenyl)phenyl]ethanol [(*E*)-4-(1-Hydroxyethyl)stilbene, 4]:
A solution of **3** (1.5 g, 6.76 mmol) in dry EtOH (100 mL) was stirred at r.t. and $NaBH_4$ (0.6 g, 5.8 mmol) was added slowly. The mixture was stirred at r.t. for 2.5 h. A 5% HCl soln (10 mL) was added slowly. After cooling the solution was filtered and the solvent evaporated. The crude solid was washed with H_2O and dried, giving **4** as a white powder; yield: 1.4 g (93%).

^{1}H NMR: $\delta = 1.5$ (3 H, d, C*H*$_3$), 1.8 (1 H, s, O*H*), 4.9 (1 H, q, C*H*–O), 7.12 (2 H, s, H_d *trans*), 7.25–7.43 (5 H, m, H_a, H_b, and H_f), 7.51 (2 H, d, H_e), 7.55 (2 H, d, H_c).

^{13}C NMR: $\delta = 25.1$ (CH_3), 70.2 (*C*H–O), 125.7 (C_i), 126.5 (C_c), 126.6 (C_e and C_f), 127.6 (C_h), 128.2 (C_a), 128.9 (C_b), 136.6 (C_d), 137.5 (C_g), 145.2 (C_j).

(*E*)-1-Ethenyl-4-(2-phenylethenyl)benzene [(*E*)-4-Vinylstilbene, 5]:
A solution of **4** (1.1 g, 4.9 mmol) and 4-toluenesulfonic acid (PTS) (10 mg, 0.05 mmol) in dry benzene (100 mL) was heated under reflux for 45 h in a Dean–Stark apparatus. MeOH (10 mL) was added to the solution which was then evaporated without heating. The solid product was purified by column chromatography on silica gel ($CHCl_3$/hexane, 50 : 50) giving **5** as a white powder; yield: 0.9 g (89%).

^{1}H NMR: $\delta = 5.28$ (1 H, d, C=C*H*$_2$ *trans*), 5.78 (1 H, d, C=C*H*$_2$ *cis*), 6.74 (1 H, dd, C*H*=C), 7.13 (2 H, s, H_d *trans*), 7.25–7.5 (5 H, m, H_a, H_b, and H_f), 7.52 (2 H, pseudo d, H_e), 7.56 (2 H, pseudo d, H_c).

^{13}C NMR: $\delta = 113.7$ (C=*C*H$_2$), 126.5 (C_c), 126.7 (C_e and C_f), 127.6 (C_h), 128.3 (C_a), 128.6 (C_i), 128.7 (C_b), 136.4 (*C*H=C), 136.9 (C_d), 137.3 (C_g and C_j).

MS: *m*/*z* calcd for $C_{16}H_{14}$, 206.11; Found, 206.16.

Anal.: $C_{16}H_{14}$: Calcd C 93.15, H 6.85; Found C 92.45, H 6.83.

1-[(*E*)-1-Methyl-3-{4-[(*E*)-2-phenylethenyl]phenyl}-2-propenyl]-4-[(*E*)-2-phenylethenyl]benzene [(*E*)-4-[(*E*)-1-methyl-3-[(*E*)-4-styrylphenyl]allyl]stilbene, 6]:
This compound was obtained in the synthesis of **5** when higher concentrations of PTS were used. It was isolated in the same way as **5**.

^{1}H NMR: $\delta = 1.5$ (3 H, d, C*H*$_3$), 3.7 (1 H, m, C*H*–CH$_3$), 6.4 [2 H, d, C*H*=C*H*–CH(CH$_3$)], 7.15 (4 H, d, H_d), 7.20–7.43 (10 H, m, H_a, H_b, and H_f), 7.43–7.57 (8 H, m, H_c and H_e).

^{13}C NMR: $\delta = 21.1$ (CH_3), 42.4 (*C*H–CH$_3$), 126.44, 126.68, 127.48, 127.54, 127.66, 128.21, 128.32, 128.43, 128.65, 135.1, 135.4, 136.1, 136.9, 137.4, 145.1.

MS: *m*/*z* calcd for $C_{32}H_{28}$, 412.22; Found 412.12.

Anal. ($C_{32}H_{28}$): Calcd C 93.15, H 6.85; Found C 91.25, H 6.84.

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