2,4,6-Triphenylpyridine as a Neutral Leaving Group in the Palladium(0)-Catalyzed Allylation of Nucleophiles

M. Moreno-Mañas,* L. Morral and R. Pleixats

Department of Chemistry, Universitat Autònoma de Barcelona, Bellaterra, 08193-Barcelona, Spain

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Palladium(0)-catalyzed allylation of nucleophiles such as morpholine, sodium dimethyl malonate and 2,6-dimethylaniline can be achieved under very mild conditions using *N*-allyl-2,4,6-triphenylpyridinium tetrafluoroborates as allylating reagents in reactions in which 2,4,6-triphenylpyridine acts as the neutral leaving group.

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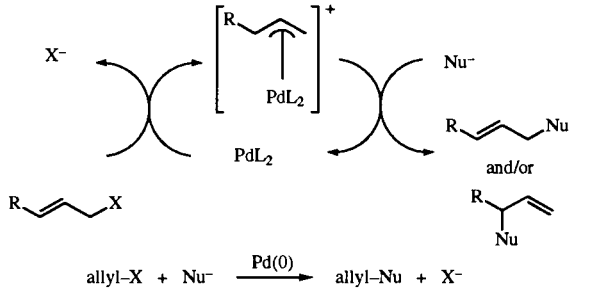
Introduction.

The palladium(0)-catalyzed allylation of nucleophiles (the Tsuji-Trost reaction) is a powerful method which has gained high recognition due to its versatility, broad scope, and easy experimental procedure [1]. The catalytic cycle is represented in Scheme 1; an allyl system reacts with palladium(0) species to form a strongly electrophilic cationic η^3-allylpalladium complex, which is attacked by nucleophiles to form the final product or products, the catalytic species being recovered. Although many leaving groups X have been reported in the literature, the acetoxy (AcO-) and the alkoxycarbonyloxy (RO-CO-O-) groups remain the most popular since the corresponding acetates and mixed carbonates are very reactive and easily available. Ammonium salts have also been used in the Tsuji-Trost reaction as the source of the cationic complex, which means that amines can be useful leaving groups [2,3].

Scheme 1

Catalytic cycle of the palladium(0)-catalyzed allylation of nucleophiles (the Tsuji-Trost reaction).

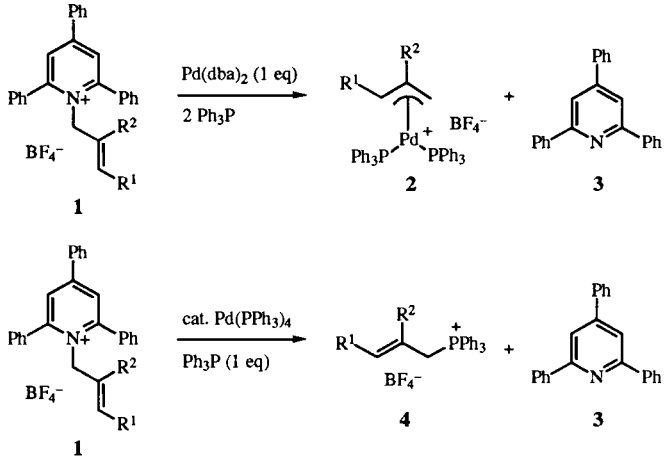


On the other hand Katritzky and coworkers have studied the nucleophilic displacements on pyridinium salts, pyridines acting as neutral leaving groups [4]. In particular, 2,4,6-triphenylpyridine has been extensively used as a highly efficient leaving group.

In the course of our investigations on structural features of cationic η^3-allylpalladium complexes [5] we required an experimentally simple method to prepare complexes **2** (Scheme 2). We found that they could be prepared simply by treating 2,4,6-triphenylpyridinium tetrafluoroborates, **1**, with one equivalent of dibenzylideneacetonepalladium(0) in the presence of two equivalents of monodentate phosphine or one equivalent of bidentate phosphine [5,6], as shown in Scheme 2. Moreover, if the amount of palladium is kept catalytic but the amount of phosphine remains stoichiometric, allyltriphenylphosphonium tetrafluoroborates **4** are isolated in good yields (Scheme 2) [6]. In other words, these studies show that pyridinium salts **1** are excellent substrates in the Tsuji-Trost reaction, 2,4,6-triphenylpyridine, **3**, acting as the neutral leaving group. However, this research was aimed to the preparation of the cationic complexes **2** rather than to explore the possibilities of pyridinium salts in the Tsuji-Trost reaction. Now, we present the preliminary results from the reactions of two different *N*-allylpyridinium salts with a selection of carbon and nitrogen nucleophiles confirming these possibilities.

Scheme 2

Uses of 2,4,6-triphenylpyridine as a neutral leaving group in Pd(0)-mediated reactions (Ref 6).

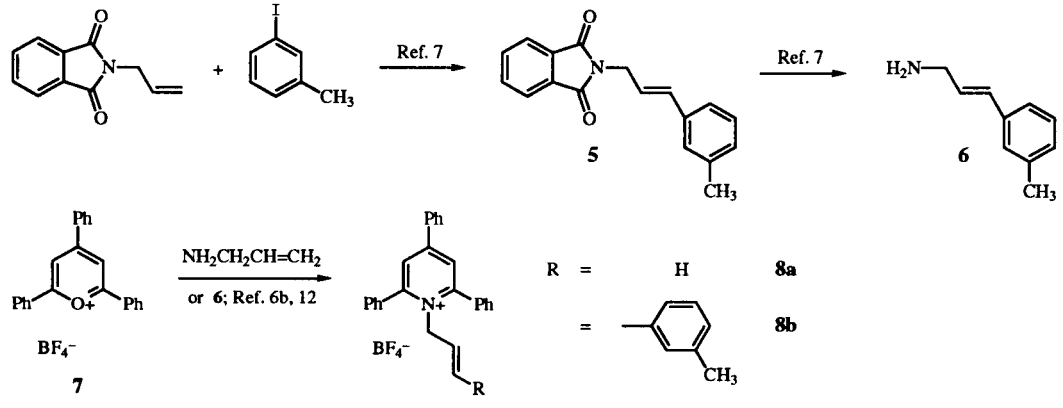


Results.

2,4,6-Triphenylpyrilium tetrafluoroborate, **7**, was treated with allylamine or with *m*-methylcinnamylamine, **6**, by the general method described by Katritzky [4] (Scheme 3) to afford pyridinium tetrafluoroborates **8a,b**. The cinnamylamine **6** was prepared by Heck reaction between *N*-allylph-

Scheme 3

Preparation of *N*-allyl-2,4,6-triphenylpyridinium tetrafluoroborates.

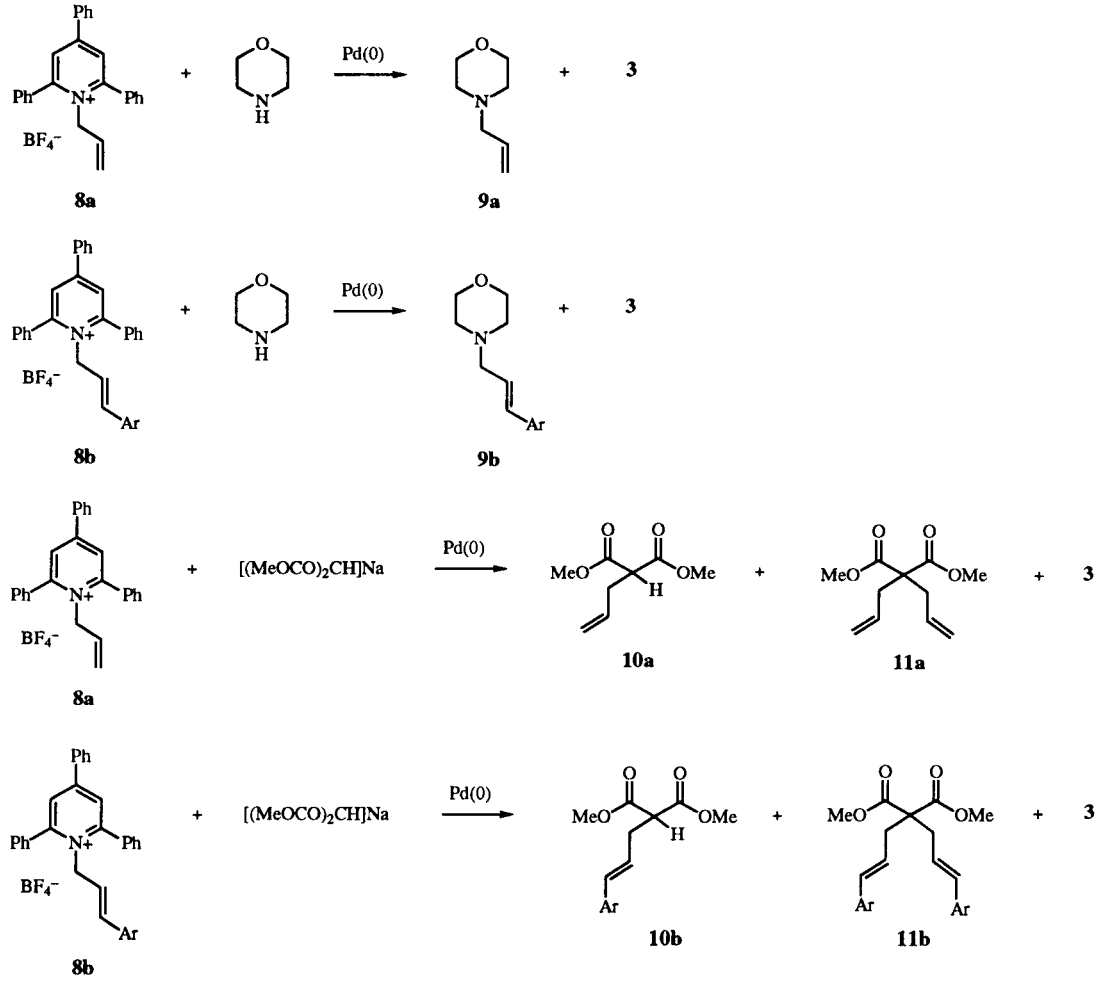


thalimide and *m*-methyliodobenzene to give **5** according to a general method described by Malek and Moormann [7]. Deprotection to the free amine **6** was achieved by the reaction of **5** with hydrazine.

First, we studied the reactions of **8a** and **8b** with morpholine under tetrakis(triphenylphosphine)palladium(0) catalysis (Scheme 4). They gave *N*-allylmorpholine, **9a**, and *N*-(*m*-methylcinnamyl)morpholine, **9b**, working even

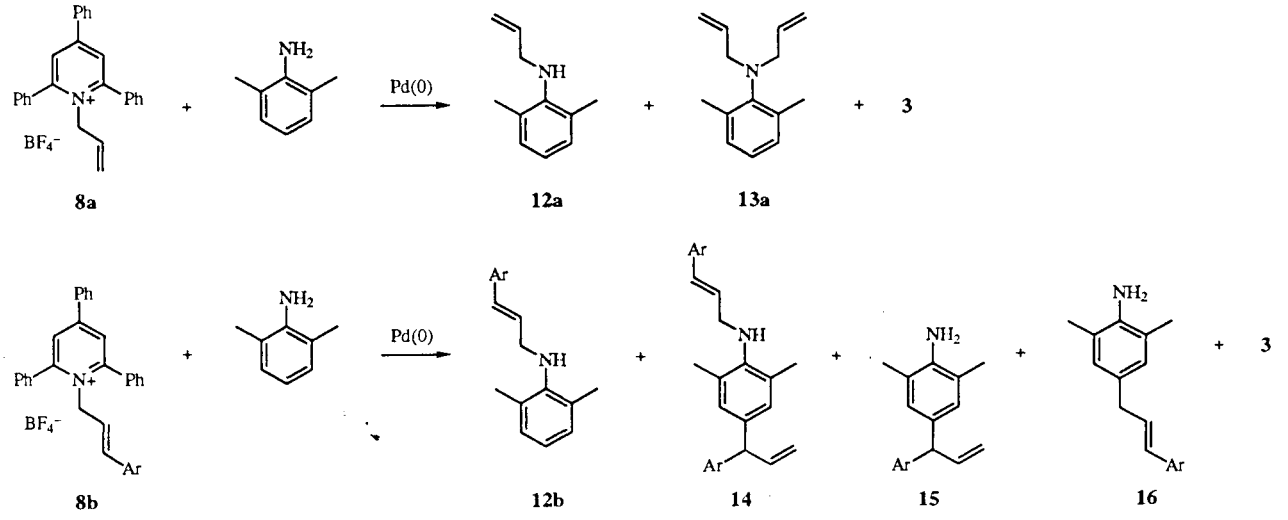
Scheme 4

Pd(0)-Catalyzed reactions of *N*-allyl-2,4,6-triphenylpyridinium tetrafluoroborates with morpholine and sodium dimethyl malonate.



Scheme 5

Pd(0)-Catalyzed reactions of *N*-allyl-2,4,6-triphenylpyridinium tetrafluoroborates with 2,6-dimethylaniline



at room temperature. This is in sharp contrast with the rather severe conditions required in Katritzky's uncatalyzed methodology.

The reaction at room temperature of **8a** with one equivalent of the sodium salt of dimethyl malonate generated with sodium hydride, afforded a mixture of dimethyl allylmalonate, **10a**, and dimethyl diallylmalonate, **11a**, which were separated by column chromatography (Scheme 4). Two equivalents of **8b** were used in its reaction at room temperature with dimethyl malonate to obtain directly **11b** as the major compound. This was achieved by previously forming the sodium salt of dimethyl malonate and adding a second equivalent of sodium hydride to the reaction medium. The expected **11b**, accompanied by minor amounts of **10b**, was efficiently formed (Scheme 4).

Although phenols are allylated at oxygen under palladium(0) catalysis [8], we are not aware of the use of anilines as nucleophiles in the Tsuji-Trost reaction. Therefore we decided to explore the behavior of a severely hindered aniline such as 2,6-dimethylaniline in order to force allylation to occur at the ring carbon atoms. However, the reaction of 2,6-dimethylaniline with **8a** under tetrakis(triphenylphosphine)palladium(0) catalysis gave a mixture of *N*-allyl-2,6-dimethylaniline, **12a**, and *N,N*-diallyl-2,6-dimethylaniline, **13a**, (Scheme 5) no products from allylation at the ring being detected.

Nevertheless, the reaction between **8b** and 2,6-dimethylaniline gave different results, a complicated mixture of different allylation compounds being formed (Scheme 5). Upon repeated purification procedures reasonably pure samples of the most abundant reaction products were isolated and spectroscopically characterized. The compounds isolated were: 2,6-dimethyl-*N*-(*m*-methylcinnamyl)aniline, **12b**; 2,6-dimethyl-*N*-(*m*-methylcinnamyl)-4-(1-(*m*-methylphenyl)allyl)aniline, **14**; 2,6-dimethyl-4-(1-(*m*-methylphenyl)allyl)aniline, **15**; and 2,6-dimethyl-4-(*m*-methylcinnamyl)aniline, **16**. The structures of products **12b** and **14-16** are based in their pmr spectra as indicated in the Experimental. This result is most unusual. In fact cinnamyl derivatives have been extensively used when studying regioselectivity at the nucleophile in the palladium-catalyzed allylation of ambident nucleophiles since they are not only very reactive but because they give regioselectively allylation at the less substituted terminal carbon atom of the cinnamyl system (linear and not branched allylation products) [9]. Therefore, the formation of **14** and **15** is unexpected according to the available information [10]. Product **16** could have been formed either by direct Pd-catalyzed *C*-allylation or from **12b** by a double [3.3] sigmatropic Claisen plus Cope rearrangement. The double rearrangement requires an intermediate featuring a branched chain at C-2 of the aromatic ring. The formation of both **14** and **15** has a different explanation, and it is probably related to the ability of amines to coordinate the metal in cationic η^3-allylpalladium complexes. This ability permits the Pd-catalyzed allylation of amines by migration of the amine from palladium to carbon [11]. Further studies on this problem are in course.

Blank experiments were performed between **8a** and all three studied nucleophiles, all conditions being the same but in the absence of tetrakis(triphenylphosphine)palladium(0). No reaction or only traces (for 2,6-dimethylaniline) of final products were detected.

EXPERIMENTAL

The pmr (cmr) spectra were registered at 250 MHz (62.5 MHz) using tetramethylsilane as the internal standard. Mass spectra were determined under electron impact at 70 eV. All manipulations concerning Pd-catalyzed allylations were performed under nitrogen. Sodium hydride suspensions were washed with anhydrous hexanes. Column chromatographies were performed using silica-gel (35-70 microns). Yields are not optimized.

m-Methylcinnamylamine (**6**).

N-(*m*-Methylcinnamyl)phthalimide (**5**) was prepared in 74% yield by the Heck reaction between 3-methyl-1-iodobenzene and *N*-allylphthalimide according to the general method described by Malek and Moormann [7]. It had mp 107°; ir (potassium bromide): 1770, 1704, 1320, 974, 955, 706 cm^{-1}; pmr (deuteriochloroform): 2.30 (s, 3H), 4.42 (dd, J = 6.6 and 1.2 Hz, 2H), 6.23 (dt, J = 15.7 and 6.6 Hz, 1H), 6.62 (d, J = 15.7 Hz, 1H), 6.99-7.20 (m, 4H), 7.65-7.74 (m, 2H), 7.80-7.88 (m, 2H); cmr (deuteriochloroform): 21.2, 39.6, 122.4, 123.2, 123.6, 127.1, 128.4, 128.6, 132.1, 133.8, 133.9, 136.1, 138.0, 167.9.

Anal. Calcd. for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 77.83; H, 5.29; N, 4.86.

The free amine **6** was prepared from **5** by standard treatment with hydrazine hydrate in ethanol. Amine **6** had pmr (deuteriochloroform): 1.60 (s, 2H), 2.32 (s, 3H), 3.44 (d, J = 5.7 Hz, 2H), 6.28 (dt, J = 15.9 and 5.7 Hz, 1H), 6.45 (d, J = 15.9 Hz, 1H), 6.94-7.23 (m, 4H); ms: m/z 147 (M, 100), 146 (58), 132 (79), 131 (33), 130 (59), 129 (48), 128 (23), 117 (24), 115 (74), 91 (48), 77 (29), 65 (28), 63 (26), 56 (57), 51 (28).

N-Allyl-2,4,6-triphenylpyridinium Tetrafluoroborate (**8a**).

It was prepared by the method of Katritzky as previously described [6b, 12]. It had mp 156-157° (lit [12], mp 164-166°); ir (potassium bromide): 1619, 1552, 1051, 897, 761, 698 cm^{-1}; pmr (deuteriochloroform): 4.47 (d, J = 17.2 Hz, 1H), 4.96-5.06 (m, 3H), 5.40-5.57 (m, 1H), 7.38-7.58 (m, 9H), 7.65-7.75 (m, 6H), 7.80 (s, 2H); cmr (deuteriochloroform): 56.9, 120.1, 126.5, 128.0, 129.0, 129.0, 129.6, 130.1, 130.9, 132.0, 132.4, 133.8, 155.9, 156.8.

N-(*m*-Methylcinnamyl)-2,4,6-triphenylpyridinium Tetrafluoroborate (**8b**).

It was prepared in 69% yield as for **8a**. The salt **8b** had mp 126-127°; ir (potassium bromide): 1624, 1566, 1054, 957, 765, 701 cm^{-1}; pmr (deuteriochloroform): 2.26 (s, 3H), 5.17 (d, J = 6.2 Hz, 2H), 5.55 (d, J = 15.8 Hz, 1H), 5.73 (dt, J = 15.8 and 6.2 Hz, 1H), 6.83-7.15 (m, 4H), 7.40-7.60 (m, 9H), 7.66-7.79 (m, 6H), 7.82 (s, 2H); cmr (deuteriochloroform): 21.2, 57.2, 119.9, 123.7, 126.5, 127.2, 128.0, 128.5, 129.0, 129.1, 129.4, 129.6, 131.0, 132.0, 132.7, 133.9, 134.7, 136.1, 138.2, 156.0, 156.8.

N-Allylmorpholine (**9a**).

A solution of pyridinium salt **8a** (2.40 g, 5.5 mmoles) in anhydrous tetrahydrofuran (15 ml) was added to a solution of tetrakis(triphenylphosphine)palladium(0) (265 mg, 0.23 mmole) in the same solvent (20 ml). This mixture was added to morpholine (400 mg, 4.59 mmoles) in anhydrous tetrahydrofuran (15 ml). The new mixture was stirred for 20 minutes at room temperature, then it was filtered and the filtrate was evaporated. The residue was taken in dichloromethane and the organic solution washed with aqueous sodium hydrogen carbonate and water. The organic layer was concentrated and added to methanol (100 ml) to afford a precipitate of 2,4,6-triphenylpyridine (**3**) (1.014 g) which was filtered off. Naphthalene-1,5-disulfonic acid (1.29 g, 3.4 mmoles) in methanol (20 ml) was added to the filtrate. No precipitate of the corresponding salt was formed and, therefore, the mixture was evaporated and the residue was dissolved in dichloromethane. This organic solution was extracted with aqueous sodium hydrogen carbonate, washed with water, dried and evaporated. The residue consisted of amine **9a** impurified with residual **3**. Distillation gave pure **9a** (23%), bp 80-85°(oven temperature)/80 mmHg; ir (film): 1645, 1118, 926, 903, 739 cm^{-1}; pmr (deuteriochloroform): 2.37 (t, J = 4.7 Hz, 4H), 2.92 (dt, J = 6.6 and 1.1 Hz, 2H), 3.65 (t, J = 4.7 Hz, 4H), 5.05-5.18 (m, 2H), 5.78 (ddt, J = 16.8, 10.2 and 6.6 Hz, 1H); cmr (deuteriochloroform): 53.5, 62.0, 66.8, 118.1, 134.5. The preparation of this compound by a different method was previously described and the pmr spectra are coincidental [13].

N-(*m*-Methylcinnamyl)morpholine (**9b**).

A solution of pyridinium salt **8b** (1.98 g, 3.8 mmoles) in anhydrous tetrahydrofuran (15 ml) was added to a solution of tetrakis(triphenylphosphine)palladium(0) (199 mg, 0.17 mmole) in the same solvent (20 ml). This mixture was added to morpholine (300 mg, 3.4 mmoles) in anhydrous tetrahydrofuran (15 ml). The new mixture was stirred for 30 minutes at room temperature, then it was filtered and the filtrate was evaporated. The residue was taken in dichloromethane and the organic solution washed with aqueous sodium hydrogen carbonate and with water. The organic layer was evaporated and the residue was chromatographed through a column of silica gel with ethyl acetate and mixtures of ethyl acetate and methanol of increasing polarity. 2,4,6-Triphenylpyridine (**3**) was eluted first followed by a mixture of **9b** and unreacted **8b**. Distillation afforded pure **9b** (353 mg, 47%) which had bp 150-160° (oven temperature)/0.4 mm Hg; ir (film): 1453, 1118, 969, 866, 795, 768, 693 cm^{-1}; pmr (deuteriochloroform): 2.32 (s, 3H), 2.49 (t, J = 4.7 Hz, 4H), 3.13 (dd, J = 6.8 and 1.3 Hz, 2H), 3.72 (t, J = 4.7 Hz, 4H), 6.23 (dt, J = 15.9 and 6.8 Hz, 1H), 6.49 (d, J = 15.9 Hz, 1H), 7.00-7.23 (m, 4H); cmr (deuteriochloroform): 21.3, 53.6, 61.3, 66.9, 123.4, 125.7, 127.0, 128.2, 128.4, 133.4, 136.6, 138.0; ms: m/z 217 (M, 33), 131 (69), 129 (24), 116 (29), 115 (40), 112 (100), 91 (39), 86 (25), 56 (46).

Anal. Calcd. for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found: C, 76.71; H, 8.94; N, 6.33.

Dimethyl Allylmalonate (**10a**) and Dimethyl Diallylmalonate (**11a**).

A solution of **8a** (1.6 g, 3.7 mmoles) and tetrakis(triphenylphosphine)palladium(0) (177 mg, 0.153 mmole) in anhydrous tetrahydrofuran (35 ml) was added to sodium dimethyl malonate (from sodium hydride (147 mg of 55% suspension, 3.37 mmoles) and dimethyl malonate (400 mg, 3.03 mmoles)) in the same solvent (15 ml). After 20 minutes at room temperature the mixture was filtered, the filtrate was evaporated and the residual oil was chromatographed through a column of silica-gel using mixtures of hexanes-diethyl ether. Triphenylpyridine was eluted first followed by **11a**, **10a** and dimethyl malonate.

Dimethyl allylmalonate (**10a**) (66%) had ir (film): 1754, 1738, 1643, 999, 924 cm^{-1}; pmr (deuteriochloroform): 2.59 (ddt, J = 7.7, 6.6 and 1.3 Hz, 2H), 3.41 (t, J = 7.7 Hz, 1H), 3.68 (s, 6H), 5.00 (ddd, J = 10.2, 2.9 and 1.3 Hz, 1H), 5.06 (ddd, J =

17.2, 2.9 and 1.3 Hz, 1H), 5.71 (ddt, J = 17.2, 10.2 and 6.6, 1H); cmr (deuteriochloroform): 32.7, 51.3, 52.3, 117.5, 133.8, 169.2. The preparation of this compound by a different method was previously described and the pmr spectra are coincident [14].

Dimethyl diallylmalonate (**11a**) (7%) had ir (film): 1737, 1642, 997, 923 cm^{-1}; pmr (deuteriochloroform): 2.60 (dt, J = 7.4 and 1.1 Hz, 4H), 3.67 (s, 6H), 5.01-5.11 (m, 4H), 5.61 (ddt, J = 17.3, 9.7 and 7.4 Hz, 2H); cmr (deuteriochloroform): 36.9, 52.3, 57.6, 119.2, 132.2, 171.1. The preparation of this compound by a different method was previously described and the spectroscopic data are coincident [15].

Dimethyl (*m*-Methylcinnamyl)malonate (**10b**) and Dimethyl Bis(*m*-methylcinnamyl)malonate (**11b**).

A solution of **8b** (2.38 g, 4.55 mmoles) and tetrakis(triphenylphosphine)palladium(0) (131 mg, 0.113 mmoles) in anhydrous tetrahydrofuran (20 ml) was added to sodium dimethyl malonate (from sodium hydride (238 mg of 55% suspension, 5.45 mmoles) and dimethyl malonate (300 mg, 2.27 mmoles)) in the same solvent (15 ml). The mixture was maintained for three hours at room temperature, then filtered and the filtrate was concentrated and poured into methanol (100 ml). The precipitated triphenylpyridine (**3**) was filtered out, and the filtrate was evaporated to dryness, the residue was dissolved in chloroform and the organic solution was washed with water, dried and evaporated. The residue was chromatographed through silica-gel using hexanes-ethyl acetate (95:5). The remaining **3** was eluted first, followed by **11b** (552 mg, 62%), a mixture of **10b** and **11b** (68 mg) and pure **10b** (23 mg, 4%).

Compound **10b** presented pmr (deuteriochloroform): 2.31 (s, 3H), 2.74 (dt, J = 7.3 and 1.1 Hz, 2H), 3.47 (t, J = 7.3 Hz, 1H), 3.73 (s, 6H), 6.06 (dt, J = 15.7 and 7.3 Hz, 1H), 6.39 (d, J = 15.7 Hz, 1H), 6.98-7.21 (m, 4H).

Compound **11b** had mp 81-82°; ir (potassium bromide): 1724, 1208, 979, 767, 697 cm^{-1}; pmr (deuteriochloroform): 2.33 (s, 6H), 2.83 (dd, J = 7.5 and 1.1 Hz, 4H), 3.73 (s, 6H), 6.05 (dt, J = 15.7 and 7.5 Hz, 2H), 6.43 (d, J = 15.7 Hz, 2H), 7.00-7.22 (m, 8H); cmr (deuteriochloroform): 21.3, 36.7, 52.4, 58.3, 123.4, 123.6, 126.9, 128.2, 128.4, 134.2, 137.0, 138.0, 171.2.

Anal. Calcd. for $C_{25}H_{28}O_4$: C, 76.50; H, 7.19. Found: C, 76.38; H, 6.97.

N-Allyl-2,6-dimethylaniline (**12a**) and *N,N*-Diallyl-2,6-dimethylaniline (**13a**).

A solution of **8a** (1.724 g, 4.0 mmoles) and tetrakis(triphenylphosphine)palladium(0) (191 mg, 0.165 mmole) in anhydrous tetrahydrofuran (35 ml) was added to a solution of 2,6-dimethylaniline (400 mg, 3.3 mmoles) in the same solvent (15 ml). The mixture was refluxed for 48 hours, then filtered and the filtrate was evaporated. The residue was taken in dichloromethane and the organic solution was washed with aqueous sodium hydrogen carbonate and with water, concentrated and poured into methanol (30 ml). The precipitated solid **3** was filtered off and the filtrate was evaporated to afford a residue which was chromatographed through a column of silica-gel with mixtures of hexanes-dichloromethane of increasing polarity to afford **13a** (55 mg, 8%) and **12a** (46 mg) as pure compounds, a mixture of both (450 mg), and unreacted 2,6-dimethylaniline (100 mg). The fractions containing the mixture of **13a** and **12a** were chromatographed again with hexanes-diethyl ether as eluent to afford **13a** contaminated with triphenylpyridine (62 mg, <16% overall yield) and **12a** (273 mg, 60% overall yield).

Compound **12a** had ir (film): 3380, 1642, 1474, 993, 920, 764 cm^{-1}; pmr (deuteriochloroform): 2.31 (s, 6H), 2.88 (s, 1H), 3.61 (dt, J = 6.0 and 1.2 Hz, 2H), 5.13 (ddd, J = 10.2, 2.9, and 1.2 Hz, 1H), 5.28 (ddd, J = 17.2, 2.9 and 1.6 Hz, 1H), 6.01 (ddt, J = 17.2, 10.2, and 6.0 Hz, 1H), 6.84 (t, J = 7.3 Hz, 1H), 7.01 (d, J = 7.3 Hz, 2H); cmr (deuteriochloroform): 18.4, 51.2, 115.8, 121.9, 128.7, 129.4, 136.7, 145.8. The preparation of this compound by a different method was previously described and the pmr spectra are coincidental [16].

Compound **13a** had ir (film): 1640, 1592, 1473, 991, 917, 769 cm^{-1}; pmr (deuteriochloroform): 2.29 (s, 6H), 3.62 (br d, J = 6.7 Hz, 4H), 5.01 (br dd, J = 10.1 and 3.0 Hz, 2H), 5.10 (ddd, J = 17.0, 3.0 and 1.4 Hz, 2H), 5.82 (ddt, J = 17.0, 10.1, and 6.7 Hz, 2H), 6.90-7.02 (m, 3H); cmr (deuteriochloroform): 19.6, 55.9, 115.9, 125.0, 128.7, 136.9, 137.5, 148.1; ms: m/z 201 (M, 62), 174 (37), 172 (21), 160 (32), 158 (24), 145 (42), 144 (75), 133 (31), 132 (100), 131 (27), 130 (23), 118 (21), 117 (40), 105 (27), 91 (23), 79 (24), 77 (40), 41 (35). The preparation of this compound by a different method was previously described [16].

Reaction of **8b** with 2,6-Dimethylaniline under Pd(0)-Catalysis.

A solution of **8b** (2.37 g, 4.5 mmoles) and tetrakis(triphenylphosphine)palladium(0) (119 mg, 0.103 mmoles) in anhydrous tetrahydrofuran (35 ml) was added to a solution of 2,6-dimethylaniline (250 mg, 2.06 mmoles) in the same solvent (15 ml). The mixture was refluxed for 24 hours, then more tetrakis-(triphenylphosphine)palladium(0) (120 mg) was added and the refluxing time extended for additional 24 hours. The mixture was then filtered and the filtrate was evaporated. The residue was taken in dichloromethane and the organic solution was washed with aqueous sodium hydrogen carbonate and with water, dried and evaporated. The residue was chromatographed through a column of silica-gel with hexanes and hexanes-ethyl acetate mixtures. No pure products could be isolated and the collected fractions were put together in four main groups which were evaporated and studied as follows:

Group 1 contained 2,4,6-triphenylpyridine (**3**) and 2,6-dimethyl-*N*-(*m*-methylcinnamyl)aniline (**12b**) (*ca.* 14%). The mixture was dissolved in chloroform and the solution poured into methanol. Compound **3** precipitated, the filtrate was evaporated and the residue was distilled to afford fairly pure **12b** which showed bp 200-240° (oven temperature)/0.4 mm Hg; ir (film): 3370, 1597, 1474, 966, 766, 693 cm^{-1}; pmr (deuteriochloroform): 2.30 (s, 6H), 2.32 (s, 3H), 2.95 (s, 1H), 3.72 (dd, J = 6.2 and 1.4 Hz, 2H), 6.33 (dt, J = 15.7 and 6.2 Hz, 1H), 6.57 (d, J = 15.7 Hz, 1H), 6.83 (t, J = 7.3 Hz, 1H), 7.00 (d, J = 7.3 Hz, 2H), 7.02-7.21 (m, 4H); cmr (deuteriochloroform): 18.5, 21.3, 50.8, 70.7, 122.0, 123.4, 127.0, 127.8, 128.2, 128.4, 128.8, 129.6, 131.4, 136.9, 138.0, 145.8; ms: m/z 251 (M, 17), 132 (25), 131 (100), 91 (26).

Group 2 contained 53 mg (*ca.* 7%) of 2,6-dimethyl-*N*-(*m*-methylcinnamyl)-4-(1-(*m*-methylphenyl)allyl)aniline (**14**), which had ir (film): 3374, 1484, 967, 775, 696 cm^{-1}; pmr (deuteriochloroform): 2.26 (s, 6H), 2.30 (s, 3H), 2.33 (s, 3H), 2.79 (s, 1H), 3.69 (dd, J = 6.2 and 1.3, 2H), 4.55 (d, J = 7.3 Hz, 1H), 4.98 (dt, J = 17.1 and 1.3 Hz, 1H), 5.16 (dt, J = 10.2 and 1.3 Hz, 1H), 6.27 (ddd, J = 17.1, 10.2, and 7.3 Hz, 1H), 6.32 (dt, J = 15.8 and 6.2 Hz, 1H), 6.56 (d, J = 15.8 Hz, 1H), 6.83 (s, 2H), 6.95-7.23 (m, 8H); cmr (deuteriochloroform): 18.6, 21.3, 21.4, 29.6, 50.9, 54.4, 115.6, 123.4, 125.5, 126.9, 127.0, 127.9, 128.1,

128.2, 128.4, 128.8, 129.2, 129.6, 131.3, 136.9, 136.9, 137.8, 138.0, 141.2, 143.7, 144.0; ms: m/z 381 (M, 20), 131 (100).

Group 3 contained 90 mg of a mixture of 2,6-dimethylaniline and allylation products. It was not further studied.

Group 4 contained a mixture (87 mg, 17%) of 2,6-dimethyl-4-(*m*-methylcinnamyl)aniline (**16**) and 2,6-dimethyl-4-(1-(*m*-methylphenyl)allyl)aniline (**15**) which had ir (film): 3463, 3382, 1625, 1603, 1487, 967, 780, 696 cm^{-1}; pmr (deuteriochloroform): from **15**: 2.11 (s, 6H) or 2.13 (s, 6H), 2.29 (s, 3H) or 2.30 (s, 3H), 3.35 (br s, 2H), 4.52 (d, J = 7.3 Hz, 1H), 4.96 (dt, J = 17.2 and 1.3 Hz, 1H), 5.14 (dt, J = 10.0 and 1.3 Hz, 1H), 6.17-6.43 (m, 1H), 6.75 (s, 2H) or 6.80 (s, 2H), 6.94-7.20 (m, 4H), from **16**: 2.13 (s, 6H) or 2.11 (s, 6H), 2.30 (s, 3H) or 2.29 (s, 3H), 3.35 (br s, 2H), 3.38 (d, J = 5.8 Hz, 2H), 6.39 (d, J = 15.7 Hz, 1H), 6.17-6.37 (m, 1H), 6.80 or 6.75 (s, 2H), 6.94-7.20 (m, 4H); ms of **15**: m/z 252 (M+1, 20), 251 (M, 100), 236 (68), 224 (24), 160 (28), 145 (21), 144 (22), 130 (20), 129 (30); ms of **16**: m/z 252 (M+1, 23), 251 (M, 100), 236 (64), 144 (23), 134 (29), 129 (39).

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REFERENCES AND NOTES

[1] For reviews see: [a] B. M. Trost and T.-R. Verhoeven, Organopalladium Compounds in Organic Synthesis and in Catalysis, Vol **8**, Chapter 57, in Comprehensive Organometallic Chemistry, G. Wilkinson, F. G. A. Stone and E. W. Abel, eds, Pergamon Press, 1982, pp 799-938; [b] S. A. Godleski, Nucleophiles with Allyl-Metal Complexes, Vol **4**, Chapter 3.3, in Comprehensive Organic Synthesis, B. M. Trost and I. Fleming, eds, Pergamon Press, 1991, pp 585-661; [c] R. F. Heck, Palladium Reagents in Organic Synthesis, Chapter 5, Academic Press, London, 1985; [d] G. Consiglio and R. M. Waymouth, *Chem. Rev.*, **89**, 257 (1989); [e] C. G. Frost, J. Howarth and J. M. J. Williams, *Tetrahedron: Asymmetry*, **3**, 1089 (1992); [f] J. Tsuji, Palladium Reagents and Catalysis, John Wiley & Sons, Chichester, 1995; [g] P. J Harrington, Transition Metal Allyl Complexes: Pd, W, Mo-assisted Nucleophilic Attack, Vol **12**, Chapter 8.2, in Comprehensive Organometallic Chemistry II, E. W. Abel, F. G. A. Stone and G. Wilkinson, eds, Pergamon Press 1995, pp 797-904.

[2] For recent examples of amines as leaving groups in the Tsuji-Trost reaction see: [a] M. Grellier, M. Pfeffer and G. van Koten, *Tetrahedron Letters*, **35**, 2877 (1994); [b] T. Doi, A. Yanagisawa, M. Miyazawa and K. Yamamoto, *Tetrahedron: Asymmetry*, **6**, 389 (1995); [c] S. Lemaire-Audoire, M. Savignac, J. P. Genêt and J.-M. Bernard, *Tetrahedron Letters*, **36**, 1267 (1995); [d] S. Lemaire-Audoire, M. Savignac, C. Dupuis and J. P. Genêt, *Bull. Soc. Chim. France*, **132**, 1157 (1995).

[3] For nickel-catalyzed coupling of allylamines with boronic acids see: B. M. Trost and M. D. Spagnol, *J. Chem. Soc., Perkin Trans. 1*, 2083 (1995).

[4] For reviews see: [a] A. R. Katritzky, *Tetrahedron*, **36**, 679 (1980); [b] A. R. Katritzky and C. M. Marson, *Angew. Chem., Int. Ed. Engl.*, **23**, 420 (1984); [c] A. R. Katritzky and G. Musumarra, *Chem. Soc. Rev.*, **13**, 47 (1984).

[5a] R. Malet, M. Moreno-Mañas, T. Parella and R. Pleixats, *Organometallics*, **14**, 2463 (1995); [b] R. Malet, M. Moreno-Mañas, T. Parella and R. Pleixats, *J. Org. Chem.*, **61**, 758 (1996).

[6a] R. Malet, M. Moreno-Mañas and R. Pleixats, *Organometallics*, **13**, 397 (1994); [b] R. Malet, M. Moreno-Mañas and R. Pleixats, *An. Quím. Int. Ed.*, **92**, 25 (1996).

[7] N. J. Malek and A. E. Moormann, *J. Org. Chem.*, **47**, 5395 (1982).

[8] C. Goux, M. Massacret, P. Lhoste and D. Sinou, *Organometallics*, **14**, 4585 (1995), and references cited therein.

[9] M. Moreno-Mañas and R. Pleixats, *Adv. Heterocyclic Chem.*, **66**, 73 (1996).

[10] For the formation of a branched minor product in the palladium-catalyzed cinnamylation of a pyrazolone see: M. Moreno-Mañas, M. Pérez and R. Pleixats, *Tetrahedron*, **50**, 515 (1994).

[11] B. M. Trost and E. Keinan, *J. Am. Chem. Soc.*, **100**, 7779 (1978).

[12] A. R. Katritzky and O. Rubio, *J. Org. Chem.*, **49**, 448 (1984).

[13] M. Baboulène, J.-L. Torregrosa, V. Speziale and A. Lattes, *Bull. Soc. Chim. France*, II-565 (1980).

[14a] G. Fournet, G. Balme and J. Gore, *Tetrahedron*, **46**, 7763 (1990); [b] W. Oppolzer and A. Fürstner, *Helv. Chim. Acta*, **76**, 2329 (1993).

[15] S-W. Zhang, T. Mitsudo, T. Kondo and Y. Watanabe, *J. Organomet. Chem.*, **450**, 197 (1993).

[16] H. Bader and H.-J. Hansen, *Helv. Chim. Acta*, **62**, 2613 (1979).