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Tetrahedron Letters 46 (2005) 3823-3827

Tetrahedron Letters

## Efficient and selective hydroarylation of propiolic acids and their esters with arenes catalyzed by a PtCl<sub>2</sub>/AgOTf system

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> Received 3 February 2005; revised 23 March 2005; accepted 29 March 2005 Available online 13 April 2005

Abstract—PtCl<sub>2</sub>/AgOTf-catalyzed hydroarylation of ethyl propiolate proceeded effectively to give ethyl (2*Z*)-cinnamate derivatives in good to high yields, without the formation of diethyl (1*E*,3*Z*)-4-arylbuta-1,3-dicarboxylates that was observed in Pd(OAc)<sub>2</sub>-catalyzed reaction. Especially, PtCl<sub>2</sub>/AgOTf-catalyzed hydroarylation of propiolic acids proceeded effectively to give (2*Z*)-cinnamic acids exclusively.

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Catalytic C–H bond activation followed by functionalization has attracted much attention.<sup>1</sup> The process provides a direct and environmentally-benign transformation because it does not require pre-functionalization like halogenation. Hydroarylation of alkynes via aromatic C–H bond activation is one of the most atom-economic processes. The reaction has been studied widely by using various transition metal catalysts.<sup>2–10</sup>

$$Ar-H + = -CO_2Et \xrightarrow{Pd(OAc)_2} Ar \xrightarrow{CO_2Et} Ar \xrightarrow{CO_2Et} (1)$$

Previously, we reported the hydroarylation of alkynes by using a catalytic amount of  $Pd(OAc)_2$  in trifluoroacetic acid (TFA) as solvent (Eq. 1).<sup>2c-h,3</sup> The reaction gave aryl-substituted alkenes with high regio- and stereoselectivity in good to high yield. However, the hydroarylation of ethyl propiolate give diethyl (1*E*,3*Z*)-4arylbuta-1,3-diene-1,3-dicarboxylate derivatives along with the expected product, ethyl (2*Z*)-cinnamates, although the yields of the buta-1,3-diene-1,3-dicarboxylates were low.<sup>2c,3</sup> The formation of the buta-1,3-diene1,3-dicarboxylates caused decrease of the yield of the expected cinnamates because 2 equiv of ethyl propiolate is consumed by the formation of the buta-1,3-diene-1,3dicarboxylates. Therefore, a selective reaction that does not give the buta-1,3-diene-1,3-dicarboxylates is required for increasing the yield of the cinnamates. Nolan and co-workers reported that the N-heterocyclic carbene palladium complexes also catalyzed the hydroarylation reaction under the same reaction conditions as  $Pd(OAc)_2$  catalysis and the reaction gave the cinnamates selectively, suppressing the formation of the buta-1,3diene-1,3-dicarboxylates.<sup>2i</sup> We also showed that the hydroarylation of ethyl propiolate catalyzed by PtCl<sub>2</sub>/ AgOAc proceeds selectively, without the formation of the buta-1,3-diene-1,3-dicarboxylates.<sup>3</sup> In our continuous study of the hydroarylation, it was found that the activity of the PtCl<sub>2</sub>/AgOAc catalyst was low and should be improved. In this paper, we report a more efficient and active PtCl<sub>2</sub>/AgOTf catalyst in the hydroarylation of propiolates.



*Keywords*: Hydroarylation; Propiolic acid; Platinum chloride; Silver triflate; C–H Bond functionalization; Trifluoroacetic acid.

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<sup>0040-4039/\$ -</sup> see front matter @ 2005 Elsevier Ltd. All rights reserved. doi:10.1016/j.tetlet.2005.03.179

First, we investigated silver compounds as additives that were expected to react with PtCl<sub>2</sub>, affording a more cationic Pt species. This investigation was carried out in the reaction of ethyl propiolate (**2a**) with mesitylene (**1a**) that gave moderate yield in the case of the Pd(OAc)<sub>2</sub> catalyst (Eq. 2). The results are listed in Table 1.<sup>11</sup> The PtCl<sub>2</sub>/AgOAc-catalyzed reaction gave ethyl (2*Z*)-3-(2,4,6trimethylphenyl)propenoate (**3a**) and ethyl (2*Z*)-3-{3[(1Z)-2-ethoxycarbonylethenyl]-2,4,6-trimethylphenyl}propenoate (4a) in 36.4% and 1.0 % yield, respectively (entry 1), while the reaction did not proceed without catalyst (entry 2). The reaction did not gave diethyl (1E,3Z)-4-(2,4,6-trimethylphenyl)buta-1,3-diene-1,3-dicarboxylate (5a), similar to the previous report.<sup>3</sup> However, the yield and the conversion were low and almost same as those obtained when only  $PtCl_2$  was used

| Entry | Catalysts  | (Mol%)    | Conversion of 1a/% | Yields/           |                   | % <sup>b</sup> |  |
|-------|--|-----------|--------------------|-------------------|-------------------|----------------|--|
|       |  |           |                    | <b>3a</b>         | <b>4</b> a        | 5a             |  |
| 1     | PtCl <sub>2</sub> /AgOAc                           | (2.5/5.0) | 41.1               | 36.4              | 1.0               | 0              |  |
| 2     | None   |           | 0.7                | 0                 | 0                 | 0              |  |
| 3     | PtCl <sub>2</sub>                                  | (2.5)     | 43.2               | 39.2              | 1.9               | 0              |  |
| 4     | PtCl <sub>2</sub> /AgTFA <sup>c</sup>              | (2.5/5.0) | 43.6               | 40.5              | 1.3               | 0              |  |
| 5     | PtCl <sub>2</sub> /Ag <sub>2</sub> CO <sub>3</sub> | (2.5/2.5) | 50.9               | 43.5              | 1.9               | 0              |  |
| 6     | PtCl <sub>2</sub> /AgPF <sub>6</sub>               | (2.5/5.0) | 76.3               | 64.3              | 9.1               | 0              |  |
| 7     | PtCl <sub>2</sub> /AgBF <sub>4</sub>               | (2.5/5.0) | 78.0               | 65.6              | 10.8              | 0              |  |
| 8     | PtCl <sub>2</sub> /AgOTf                           | (2.5/5.0) | 83.8               | 67.4              | 15.7              | 0              |  |
| 9     | AgOTf  | (5.0)     | 20.3               | 13.3              | 0                 | 0              |  |
| 10    | $Pd(OAc)_2$  | (2.5)     | 72.9               | 51.0              | 2.1               | 9.6            |  |
| 11    | PtCl <sub>2</sub> /AgOTf                           | (2.5/5.0) | _                  | 85.7 <sup>d</sup> | 11.9 <sup>d</sup> | 0              |  |

Table 1. Pt(II)-catalyzed hydroarylation of ethyl propiolate (2a) with mesitylene (1a)<sup>a</sup>

<sup>a</sup> Reaction conditions: mesitylene (1a) (2 mmol), ethyl propiolate (2a) (2.4 mmol), catalysts, TFA (1 mL), room temperature, 15 h.

<sup>b</sup>GC yields based on 1a.

 $^{c}$  AgTFA = AgOCOCF<sub>3</sub>.

<sup>d</sup> 1a (4 mmol) and 2a (2 mmol) were used. The yields based on 2a.

| Entry | Ar–H         | Temp  | Time/h | Products and yields/% <sup>b</sup>                            |
|-------|--------------|-------|--------|---|
| 1     | H<br>1b      | RT    | 15     | Ar $3b$ CO <sub>2</sub> Et 91.1 (95.4) <sup>c</sup>           |
| 2     | H<br>1c      | RT    | 35     | $\operatorname{Ar}_{3c}$ CO <sub>2</sub> Et 64.5 <sup>d</sup> |
| 3     | H<br>1d      | RT    | 40     | Ar $CO_2Et \ 61.4 \ (61.6) \ (Z/E = 99/<1)$<br>3d             |
| 4     | H<br>H<br>Br | 40 °C | 48     | Ar $3e$ CO <sub>2</sub> Et 63.9 (64.9) <sup>e</sup>           |
| 5     | H<br>OH      | RT    | 48     | Ar $CO_2Et 76.2^{f}$  |

Table 2. Hydroarylation of ethyl propiolate (2a) with various arenes<sup>a</sup>

<sup>a</sup> Reaction conditions: PtCl<sub>2</sub> (0.05 mmol), AgOTf (0.10 mmol), arene (4 mmol), ethyl propiolate (2a) (2 mmol), TFA (1 mL).

<sup>b</sup> Isolated yields based on 2a. The yields in parentheses were determined by GC.

<sup>c</sup>CH<sub>2</sub>Cl<sub>2</sub> (0.25 mL) was added.

<sup>d</sup> CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) was added. **6b** was obtained in <8% yield.

<sup>e</sup> CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) and ClCH<sub>2</sub>CH<sub>2</sub>Cl (0.5 mL) were added. 4b and 6c were isolated in 4.4% and 12.8% yield, respectively.

<sup>f</sup>4c was isolated in 14.0% yield.



(entry 3). Addition of AgOCOCF<sub>3</sub> did not affect the reaction (entry 4). Ag<sub>2</sub>CO<sub>3</sub> slightly improved the yield and the conversion (entry 5). AgPF<sub>6</sub> and AgBF<sub>4</sub> were effective (entries 6 and 7) but AgOTf was the best additive among the Ag compounds tested (entry 8). PtCl<sub>2</sub>/AgOTf catalyst gave the highest conversion and yields among the employed Pd and Pt catalysts, revealing the effectivity of PtCl<sub>2</sub>/AgOTf catalyst. The reaction also proceeded by using only AgOTf in the absence of PtCl<sub>2</sub> (entry 9) but the yield was very low. This result suggests that the active catalyst is the Pt species generated from the reaction of AgOTf and PtCl<sub>2</sub>. The role of AgOTf is considered to transform insoluble  $PtCl_2$  to a soluble reactive, cationic Pt species.

Then, the reaction using  $PtCl_2/AgOTf$  catalyst was investigated to optimize the reaction conditions. Prolonged time improved the conversion of 1a to give a

| Entry | Ar–H | Temp  | Time/h | Products and isolated yields/% <sup>b</sup>   |  |
|-------|------|-------|--------|---|--|
| 1     | H    | 40 °C | 48     | $\begin{array}{ccc} Ph & Ph \\ & & 13.8^{\circ} \\ Ar & CO_2Et & Ar & CO_2H \\ \mathbf{7a} & \mathbf{8a} \end{array}$ |  |
| 2     | H    | RT    | 50     | $ \begin{array}{c} Ph & 13.6^d & Ph \\ & Ar & 7b & CO_2Et & Ar & 8b & CO_2H \\ \end{array} \\ \end{array} $           |  |

Table 3. Hydroarylation of ethyl phenylpropiolate<sup>a</sup>

<sup>a</sup> Reaction conditions: PtCl<sub>2</sub> (0.05 mmol), AgOTf (0.10 mmol), arene (4 mmol), ethyl phenylpropiolate (2b) (2 mmol), TFA (1 mL).

<sup>b</sup> The yields were based on **2b**.

<sup>c</sup> 1-Mesityl-1-phenylethene (9) was also obtained in 7.3% yield.

 $^{d}$  CH<sub>2</sub>Cl<sub>2</sub> (0.25 mL) was added. Ph— $\equiv$ CO<sub>2</sub>Et.

2b

Table 4. Hydroarylation of propiolic acids<sup>a</sup>

|       |               | Ar—H + R—<br>1   | ≡−CO <sub>2</sub> H −−<br>2 |        | Products                           |                   |
|-------|---------------|--|-----------------------------|--------|------------------------------------|-------------------|
| Entry | Ar–H          | R  | Temp                        | Time/h | Products and yields/% <sup>b</sup> |                   |
| 1     | H<br>1a       | Н<br>2с  | RT                          | 15     | 6a<br>Ar ⊂CO <sub>2</sub> H        | 94.3 <sup>c</sup> |
| 2     | H<br>1b       | Н<br>2с  | RT                          | 15     | Ar CO <sub>2</sub> H               | 95.7 <sup>d</sup> |
| 3     | H<br>Ic       | Н<br>2с  | 40 °C                       | 40     | Ar CO <sub>2</sub> H               | 76.7 <sup>e</sup> |
| 4     | H<br>1b       | Ph<br>2d   | RT                          | 48     | Ar CO <sub>2</sub> H               | 48.1 <sup>f</sup> |
| 5     | H<br>OH<br>1g | Н<br>2с  | RT                          | 25     | 0<br>10a                           | 86.1 <sup>g</sup> |
| 6     | MeO           | <sup><i>n</i></sup> C <sub>5</sub> H <sub>11</sub><br>2e | 40 °C                       | 45     | MeO                                | 92.8              |

<sup>a</sup> Reaction conditions: PtCl<sub>2</sub> (0.05 mmol), AgOTf (0.10 mmol), arene 1 (4 mmol), propiolic acids 2 (2 mmol), TFA (1 mL).

<sup>b</sup> Isolated yields based on **2**.

<sup>c</sup>1a (6 mmol) was used.

<sup>d</sup> CH<sub>2</sub>Cl<sub>2</sub> (0.25 mL) was added.

<sup>e</sup>ClCH<sub>2</sub>CH<sub>2</sub>Cl (0.75 mL) was added.

<sup>f</sup>CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) was added.

<sup>g</sup>CH<sub>2</sub>Cl<sub>2</sub> (0.75 mL) was added.

higher yield of 4a. Higher temperature also increased the conversion of 1a but the yields of 3a and 4a were decreased. This observation can be explained by hydrolysis of the ester products to acids at a higher temperature in TFA. Using an excess amount of 1a is effective for the selective formation of 3a. When the reaction of 1a (4 mmol) with 2a (2 mmol) was conducted under the same conditions, 3a and 4a were formed in 85.7% and 11.9% yields, respectively (entry 11).

Next, we examined the reaction with various arenes (Table 2).<sup>11</sup> The result showed that the reaction gave the hydroarylated products in good to excellent yields. Especially, electron-rich arene-like pentamethylbenzene (1b) gave high yield of the product 3b (entry 1). The reactions of naphthalene (1c) and *p*-xylene (1d) also gave adducts 3c and d in good yields (entries 2 and 3). This reaction is tolerant to unprotected OH and Br groups. The reaction of 1-bromo-2,4,6-trimethylbenzene (1e) and 2,4,6-trimethylphenol (1f) gave adducts 3e and f in good yields, together with bis-alkenylated products 4b and c (entries 4 and 5). In the case of 1e, higher temperature was required to improve the yield because of low reactivity of 1e (entry 4). The yields of 3 in  $PtCl_2/$ AgOTf catalysis were higher than those in  $Pd(OAc)_2$ catalysis.

Also, this reaction was applied to the reaction of internal alkyne, ethyl phenylpropiolate (2b) (Table 3). The reaction of 2b was slower than that of 2a and longer reaction time was required for high conversion of 2b. The reaction mainly gave products 8 which were formed by hydrolysis of 7 during the reaction, along with esters 7. In the case of mesitylene (1a), a small amount of decarboxylated product 9 was observed (entry 1).

Furthermore, we conducted the hydroarylation of propiolic acids because the prolonged reaction of ethyl propiolates mainly gave the hydrolysis products. This catalytic system was found to be effective for the reaction of propiolic acids (Table 4).<sup>12</sup> The reactions of propiolic acid (2c) gave the corresponding cinnamic acids 6 in good to high yields. The reactions of **1a** and **b** gave high yield of **6a** and **d**, respectively. In the case of mesitylene (1a), 3 equiv of 1a was used to increase the selectivity of **6a** (entry 1). The reaction of naphthalene (**1c**) at 40 °C gave **6b** in 76.7% yield (entry 3). The reaction of phenylpropiolic acid (2d) gave a moderate yield of 8b because of low solubility of 2d (entry 4). 2-Naphthol (1j) reacted with propiolic acid (2c), affording the corresponding coumarin 10a (entry 5). Alkyl-substituted propiolic acid, 2-octynoic acid (2e), also participated in the reaction (entry 6).

In conclusion, we have demonstrated selective and efficient hydroarylation of propiolates catalyzed by a PtCl<sub>2</sub>/ AgOTf system. In the case of ethyl propiolate, the PtCl<sub>2</sub>/AgOTf-catalyzed hydroarylation gave higher yield of cinnamates than the Pd(OAc)<sub>2</sub>-catalyzed reaction because of higher selectivity of the Pt catalyst. Especially, this catalyst was most effective for the reaction of propiolic acids. Further investigation of Pt-catalyzed hydroarylation of alkynes is now in progress.

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- 11. General procedure for PtCl<sub>2</sub>/AgOTf-catalyzed hydroarylation of propiolates: after a mixture of PtCl<sub>2</sub>, AgOTf, arene and TFA was stirred for 5 min at room temperature, propiolate was added to the mixture. The mixture was continuously stirred at the desired temperature. After a certain period, the reaction mixture was poured into water (20 mL), neutralized by NaHCO<sub>3</sub> and extracted with diethyl ether (20 mL) three times. The ethereal layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The residue was purified by column chromatography on silica gel using a mixture of ethyl acetate and hexane as eluent. <sup>1</sup>H and <sup>13</sup>C NMR spectra of **3a–f**, **4a**, **7a** and **b**, **8a** and **b** were identical to those in previous reports.<sup>3</sup>

Compound **4b**: oil <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.11 (t, J = 7.1 Hz, 6H, CH<sub>3</sub>), 2.02 (s, 3H, aryl-CH<sub>3</sub>), 2.32 (s, 6H, aryl-CH<sub>3</sub>), 4.02 (q, J = 7.1 Hz, 4H, OCH<sub>2</sub>), 6.14 (d, J = 11.7 Hz, 2H, vinyl), 7.04 (d, J = 11.7 Hz, 2H, vinyl). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  13.92, 17.82, 21.76, 60.06, 123.24, 125.87, 129.91, 133.52, 134.37, 144.04, 165.11. MS (EI, m/z): 396, 394 (M<sup>+</sup>). Compound **4c**: mp 109.3–111.5 °C <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.12 (t, J = 7.1 Hz, 6H, CH<sub>3</sub>), 1.99 (s, 3H, aryl-CH<sub>3</sub>), 2.10 (s, 6H, aryl-CH<sub>3</sub>), 4.03 (q, J = 7.1 Hz, 4H, OCH<sub>2</sub>), 4.53 (s, 1H, OH), 6.14 (d, J = 12.0 Hz, 2H, vinyl), 7.02 (d, J = 12.0 Hz, 2H, vinyl). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  13.11, 13.87, 17.22, 59.88, 119.49, 122.49, 122.58, 133.58, 144.46, 149.51, 165.32. MS (EI, m/z): 332 (M<sup>+</sup>).

12. General procedure for the hydroarylation using propiolic acids: after reaction, the reaction mixture was poured into water (20 mL), neutralized by NaHCO<sub>3</sub> and extracted with diethyl ether (20 mL). The ethereal layer was extracted with aqueous 2 N NaOH (10 mL) three times. A combined water layer was washed with diethyl ether (20 mL), acidified by aqueous HCl (60%) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL) three times. The CH<sub>2</sub>Cl<sub>2</sub> layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo, affording product. Compound 6a: mp 141.9-144.2 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) & 2.15 (s, 6H), 2.27 (s, 3H), 6.10 (d, J = 12.0 Hz, 1H), 6.84 (s, 2H), 7.11 (d, J = 12.0 Hz, 1H), 11.00 (s, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 20.00, 20.89, 122.07, 127.89, 131.99, 134.44, 136.92, 146.28, 171.10. MS (EI, *m*/*z*): 190 (M<sup>+</sup>). Compound **6b**: mp 156.8–157.8 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  6.21 (d, J = 12.0 Hz, 1H) 7.39– 7.53 (m, 4H), 7.66 (d, J = 12.0 Hz, 1H), 7.81–7.87 (m, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  121.37, 124.18, 125.08, 125.97, 126.44, 126.92, 128.62, 129.15, 130.91, 132.27, 133.22, 144.66, 170.30. MS (EI, m/z): 198 (M<sup>+</sup>). Compound 6d: 217–219 °C (sublimation) <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 2.13 (s, 6H, aryl-CH<sub>3</sub>), 2.19 (s, 6H, aryl-CH<sub>3</sub>), 2.22 (s, 3H, aryl-CH<sub>3</sub>), 6.12 (d, J = 12.0 Hz, 1H, vinyl), 7.20 (d, J = 12.0 Hz, 1H, vinyl), 10.42 (br s, 1H, COOH). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 16.35, 16.76, 17.62, 121.72, 129.87, 132.22, 132.38, 134.51, 148.28, 170.38. Compound 10a and b were reported in previous report.<sup>2h</sup>