

## Brief Communications

### Catalytic system based on triphenylantimony and *tert*-butyl hydroperoxide for the Heck reaction

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Triphenylantimony was used as an efficient agent for *C*-phenylation of methyl acrylate in the presence of Bu<sup>t</sup>OOH (1 to 2 mol) and a palladium salt (PdCl<sub>2</sub>, Li<sub>2</sub>PdCl<sub>4</sub>; 0.04 mol) in AcOH at 50 °C. The yield of methyl cinnamate is two moles per mole of the starting Ph<sub>3</sub>Sb.

**Key words:** triphenylantimony, *tert*-butyl hydroperoxide, *C*-phenylation, methyl acrylate, palladium compounds, Heck reaction.

Earlier,<sup>1</sup> triphenylantimony dicarboxylates Ph<sub>3</sub>Sb(O<sub>2</sub>CR)<sub>2</sub> were reported to be efficient agents for palladium-catalyzed *C*-phenylation of methyl acrylate (Heck reaction). They also serve as sources of phenyl groups and oxidize Pd<sup>0</sup> to Pd<sup>II</sup>.

However, high yields of *C*-phenylation products of styrene,<sup>2</sup> 1-octene, ethyl acrylate,<sup>3</sup> methyl acrylate,<sup>4</sup> and vinylsilanes<sup>5</sup> with triphenylantimony can be attained only when Pd<sup>II</sup> salts are used in stoichiometric amounts (mole per mole of Ph<sub>3</sub>Sb).

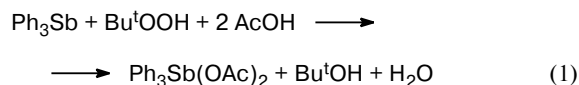
In the present work, *C*-phenylation of methyl acrylate with triphenylantimony was catalyzed by *tert*-butyl hydroperoxide, which effectively oxidizes Ph<sub>3</sub>Sb into Ph<sub>3</sub>Sb(OAc)<sub>2</sub> in AcOH.<sup>6</sup>

Note that the reaction mixture in AcOH is homogeneous; *i.e.*, antimony-containing products form no precipitates, in contrast to the reaction in other solvents (MeOH, MeCN).<sup>1</sup>

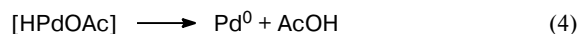
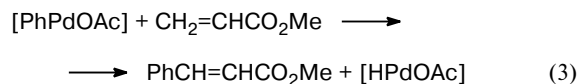
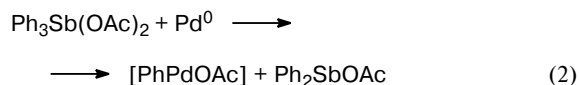
#### Results and Discussion

The reaction of Ph<sub>3</sub>Sb, methyl acrylate, Bu<sup>t</sup>OOH, and PdCl<sub>2</sub> (molar ratio 1 : 3 : 1 : 0.04) in naturally aerated AcOH at 50 °C for 6 h affords methyl cinnamate (1.2 moles per mole of the starting Ph<sub>3</sub>Sb). The same reaction without hydroperoxide gives only 0.02 mole of methyl cinnamate.

Hydroperoxide in the presence of acetic acid oxidizes Sb<sup>III</sup>.<sup>6</sup>

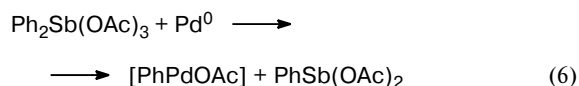
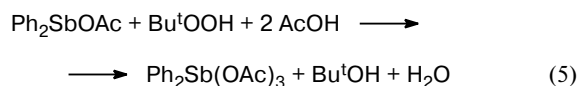


Phenylpalladium acetate PhPdOAc formed *in situ* from Ph<sub>3</sub>Sb(OAc)<sub>2</sub> phenylates methyl acrylate according to Equations (2)–(4).<sup>4</sup>



The above equations show that only one Ph group is involved in phenylation. The high yield of methyl cinnamate (> 1 mol) can be caused by the participation of atmospheric oxygen. It is known that antimony compounds of the  $\text{Ph}_2\text{SbX}$  type can, in the presence of oxygen, *C*-phenylate unsaturated compounds with  $\text{Pd}^{\text{II}}$  salts as catalysts.<sup>1,7</sup>

We found that  $\text{Ph}_3\text{Sb}$  can release two Ph groups when an excess of  $\text{Bu}^t\text{OOH}$  is used (2 mol). A more efficient catalyst for this reaction is  $\text{Li}_2\text{PdCl}_4$ . For instance, the yield of methyl cinnamate in the reaction of  $\text{Ph}_3\text{Sb}$  with methyl acrylate in the presence of  $\text{Bu}^t\text{OOH}$  and  $\text{Li}_2\text{PdCl}_4$  (molar ratio 1 : 3 : 2 : 0.04) in AcOH at 50 °C under argon is 1.59 mol after 12 h and 2 mol after 24 h (then the yield remains unchanged). Apparently, a second molecule of  $\text{Bu}^t\text{OOH}$  oxidizes  $\text{Sb}^{\text{III}}$  into  $\text{Sb}^{\text{V}}$  (Eq. (5)) to give diphenylantimony triacetate, which can react with  $\text{Pd}^0$  (Eq. (6)).



Phenylpalladium acetate phenylates methyl acrylate (see Eq. (3)), while  $\text{PhSb}(\text{OAc})_2$  is inert in that reaction.

In air, atmospheric oxygen and an excess of hydroperoxide produce a combined effect. The yield of methyl cinnamate in the reaction of  $\text{Ph}_3\text{Sb}$  with methyl acrylate in the presence of  $\text{Bu}^t\text{OOH}$  and  $\text{Li}_2\text{PdCl}_4$  (1 : 3 : 1 : 0.04) in AcOH at 50 °C is 1.64 mol after 12 h, while in the case of double excess of hydroperoxide, the yield was 1.89 mol per the starting  $\text{Ph}_3\text{Sb}$ .

Hence, in the presence of stoichiometric amounts of  $\text{Bu}^t\text{OOH}$ ,  $\text{Ph}_3\text{Sb}$  is an efficient reagent for palladium-catalyzed *C*-phenylation of methyl acrylate. The reaction occurs under mild conditions (50 °C), as distinct from those involving aryl halides (80–140 °C).<sup>8</sup>

## Experimental

GLC analysis of the methyl cinnamate obtained was carried out on an LKhM-80 chromatograph at 220 °C (flame ionization detector, helium as a carrier gas, column 0.3×100 cm with 15% Apieson-L on Chromaton N-AW). Column chromatography used Merck 60 silica gel. The synthesis and purification of  $\text{Ph}_3\text{Sb}$  and  $\text{Li}_2\text{PdCl}_4$  were performed as described earlier;<sup>1</sup>  $\text{Bu}^t\text{OOH}$  (99% purity) was prepared according to the known procedure.<sup>9</sup> Before use, methyl acrylate was washed with an alkaline solution until the yellow color of the aqueous layer disappeared, then with water, dried over  $\text{Na}_2\text{SO}_4$ , and distilled.

**Reaction of  $\text{Ph}_3\text{Sb}$  with methyl acrylate in AcOH in the presence of  $\text{Bu}^t\text{OOH}$  and  $\text{PdCl}_2$ .** *tert*-Butyl hydroperoxide (45 mg, 0.5 mmol) was added to a stirred solution of  $\text{Ph}_3\text{Sb}$  (177 mg, 0.5 mmol) and methyl acrylate (130 mg, 1.5 mmol) in 8 mL of AcOH in a 50-mL tube. Five to ten minutes later when  $\text{Ph}_3\text{Sb}$  was completely consumed (TLC data),  $\text{PdCl}_2$  (3.6 mg, 0.02 mmol) was added, and the tube was sealed. The reaction mixture was kept at 50 °C for 6 h. The solvent was removed under reduced pressure, and the residue was passed through a thin layer of silica gel in hexane–ether (4 : 1) to separate antimony and palladium compounds. The yield of methyl cinnamate was 97 mg (0.6 mmol) (1.2 mol per mole of the starting  $\text{Ph}_3\text{Sb}$ , GLC data). When the reaction was carried out under argon, the tube was degassed and filled with argon before sealing.

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