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^tOOH (1 to 2 mol) and a palladium salt ($PdCl_2$, Li_2PdCl_4; 0.04 mol) in AcOH at 50 °C. The yield of methyl cinnamate is two moles per mole of the starting Ph_3Sb.

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

Earlier,[1] triphenylantimony dicarboxylates $Ph_3Sb(O_2CR)_2$ 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^0 to Pd^{II}.

However, high yields of *C*-phenylation products of styrene,[2] 1-octene, ethyl acrylate,[3] methyl acrylate,[4] and vinylsilanes[5] with triphenylantimony can be attained only when Pd^{II} salts are used in stoichiometric amounts (mole per mole of Ph_3Sb).

In the present work, *C*-phenylation of methyl acrylate with triphenylantimony was catalyzed by *tert*-butyl hydroperoxide, which effectively oxidizes Ph_3Sb into $Ph_3Sb(OAc)_2$ in AcOH.[6]

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).[1]

Results and Discussion

The reaction of Ph_3Sb, methyl acrylate, Bu^tOOH, and $PdCl_2$ (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_3Sb). The same reaction without hydroperoxide gives only 0.02 mole of methyl cinnamate.

Hydroperoxide in the presence of acetic acid oxidizes Sb^{III}.[6]

$$\begin{aligned} &Ph_3Sb + Bu^tOOH + 2\,AcOH \longrightarrow \\ &\longrightarrow Ph_3Sb(OAc)_2 + Bu^tOH + H_2O \end{aligned} \tag{1}$$

Phenylpalladium acetate PhPdOAc formed *in situ* from $Ph_3Sb(OAc)_2$ phenylates methyl acrylate according to Equations (2)—(4).[4]

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$$\mathrm{Ph_3Sb(OAc)_2 + Pd^0} \longrightarrow$$
$$\longrightarrow \mathrm{[PhPdOAc] + Ph_2SbOAc} \tag{2}$$

$$\mathrm{[PhPdOAc] + CH_2{=}CHCO_2Me} \longrightarrow$$
$$\longrightarrow \mathrm{PhCH{=}CHCO_2Me + [HPdOAc]} \tag{3}$$

$$\mathrm{[HPdOAc]} \longrightarrow \mathrm{Pd^0 + AcOH} \tag{4}$$

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 Ph_2SbX type can, in the presence of oxygen, *C*-phenylate unsaturated compounds with Pd^{II} salts as catalysts.[1,7]

We found that Ph_3Sb can release two Ph groups when an excess of Bu^tOOH is used (2 mol). A more efficient catalyst for this reaction is Li_2PdCl_4. For instance, the yield of methyl cinnamate in the reaction of Ph_3Sb with methyl acrylate in the presence of Bu^tOOH and Li_2PdCl_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 Bu^tOOH oxidizes Sb^{III} into Sb^{V} (Eq. (5)) to give diphenylantimony triacetate, which can react with Pd^0 (Eq. (6)).

$$\mathrm{Ph_2SbOAc + Bu^tOOH + 2\ AcOH} \longrightarrow$$
$$\longrightarrow \mathrm{Ph_2Sb(OAc)_3 + Bu^tOH + H_2O} \tag{5}$$

$$\mathrm{Ph_2Sb(OAc)_3 + Pd^0} \longrightarrow$$
$$\longrightarrow \mathrm{[PhPdOAc] + PhSb(OAc)_2} \tag{6}$$

Phenylpalladium acetate phenylates methyl acrylate (see Eq. (3)), while $PhSb(OAc)_2$ 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 Ph_3Sb with methyl acrylate in the presence of Bu^tOOH and Li_2PdCl_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 Ph_3Sb.

Hence, in the presence of stoichiometric amounts of Bu^tOOH, Ph_3Sb 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).[8]

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 Ph_3Sb and Li_2PdCl_4 were performed as described earlier;[1] Bu^tOOH (99% purity) was prepared according to the known procedure.[9] Before use, methyl acrylate was washed with an alkaline solution until the yellow color of the aqueous layer disappeared, then with water, dried over Na_2SO_4, and distilled.

Reaction of Ph_3Sb with methyl acrylate in AcOH in the presence of Bu^tOOH and $PdCl_2$. *tert*-Butyl hydroperoxide (45 mg, 0.5 mmol) was added to a stirred solution of Ph_3Sb (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 Ph_3Sb was completely consumed (TLC data), $PdCl_2$ (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 Ph_3Sb, GLC data). When the reaction was carried out under argon, the tube was degassed and filled with argon before sealing.

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