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Palladium(II)-catalyzed phenylation of unsaturated compounds using phenylantimony chlorides under air☆

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Abstract

Diphenylantimony chloride and phenylantimony dichloride, mainly the former, react smoothly with alkenes in acetonitrile at r.t. in the presence of a catalytic amount of $Pd(OAc)_2$ under air to afford the corresponding phenylated alkenes (Heck-type reaction). The addition of AgOAc as reoxidant is not necessary for this reaction in sharp contrast to similar reactions using triarylstibines. The oxygen absorption is confirmed in this catalytic reaction and the reaction does not proceed catalytically in palladium(II) under inert gases, such as nitrogen or argon. Even under air the addition of a radical scavenger stopped the reaction. The regeneration of PhPdOAc species from Ph_2SbCl, HPdOAc species and oxygen is proposed as a key step in the catalytic cycle where oxygen-containing radical species might be present as intermediates. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Antimony; Palladium; Oxygen; Heck reaction

1. Introduction

The chemistry of organoantimony compounds has been developed and the potentiality of such compounds in organic synthesis is currently increasing [1]. The authors have recently reported [2] that triarylstibines (Ar_3Sb) reacted with enones and enals in the presence of a catalytic amount of $Pd(OAc)_2$ together with the reoxidant AgOAc to afford the conjugate addition products (the formal hydroarylated compounds to an olefinic part) in good yield, while similar reactions proceeded even in the absence of AgOAc when diarylantimony chlorides and arylantimony dichlorides were used. They have also disclosed that triphenylstibine reacted with several alkenes other than enones and enals to give the corresponding phenylated alkenes via the so-called Heck-type reaction [3] under the same conditions (with AgOAc and cat. $Pd(OAc)_2$) [2]. In the course of further studies, they found that the above phenylation reaction of alkenes proceeded also catalytically in $Pd(OAc)_2$, but without AgOAc, when diphenylantimony chloride and phenylantimony dichloride were employed in lieu of triphenylstibine. This paper reports here on the details of these reactions as one of the C–C bond forming reactions using organoantimony compounds [4–8] together with some mechanistic considerations on the reaction pathway. It is worth noting that pentavalent phenylantimony compound (Ph_5Sb) reacted with allyl acetate or allyl phenyl ether to afford allylbenzene in the presence of a catalytic amount of a transition metal salt such as $Pd(PPh_3)_4$ or $Pd(OAc)_2$ [9].

2. Results and discussion

2.1. Pd(II)-catalyzed phenylation of unsaturated compounds

When 2-propen-1-ol (allyl alcohol) (**1a**) was treated with 1.2 equimolar amounts of diphenylantimony chlo-

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☆ Dedicated to the memory of the late Professor Rokuro Okawara.

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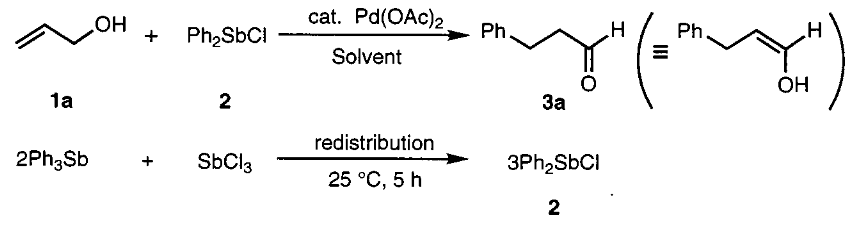


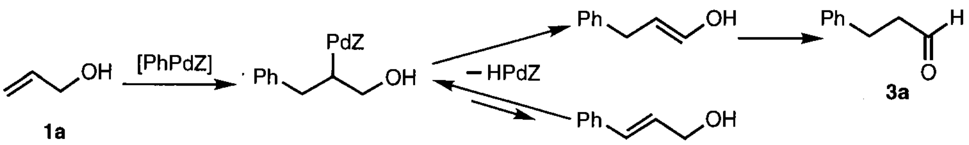
Scheme 1.

ride (**2**), prepared in situ from Ph_3Sb:$SbCl_3$ (2:1) according to the literature method [10], in the presence of a catalytic amount of $Pd(OAc)_2$ (0.1 equimolar amount) at 25°C for 24 h under air, 0.73 equimolar amounts of 3-phenylpropanal (**3a**) were obtained (73% yield on the basis of the amount of **1a** employed) (Scheme 1). When an excess amount of **1a** (five equimolar amounts) was employed, the yield of **3a** was 1.15 equimolar amounts and less than the amount of **2** employed (1.2 equimolar amounts), showing that only one phenyl group out of the two of **2** was used in this reaction. At shorter reaction times than 24 h, the yield became lower. The formation of **3a**, not 3-phenyl-2-propen-1-ol, by Heck-type phenylation of **1a** has been known (Scheme 2) [3]. Optimum reaction conditions for this phenylation reaction were examined by using **1a** as a substrate (Table 1). In respect to the amount of catalyst, the best result was obtained when 3 mol% $Pd(OAc)_2$ was used. In the reaction using either 10 or 1 mol% $Pd(OAc)_2$, the product yield was lower. As a solvent, acetonitrile (CH_3CN) and tetrahydrofuran (THF) were revealed to be the solvent of choice. The product yield was much lower in methanol and acetone. The reaction proceeded smoothly at 25°C, while either at lower (0°C) or higher (50°C) temperature, the product yield decreased considerably. Thus, it was decided to apply to other alkenes the reaction conditions using 3 mol% of $Pd(OAc)_2$ and acetonitrile as a solvent at 25°C under air.

From various alkenes, such as **1a**, 3-buten-2-ol (**1b**), 2-methyl-2-propen-1-ol (**1c**), 2-buten-1-ol (**1d**), allyl acetate (**1h**), 3-acetoxy-1-butene (**1i**), styrene (**1m**), α-methylstyrene (**1n**), β-methylstyrene (**1o**), allylbenzene (**1p**), acrylonitrile (**1q**) and methyl acrylate (**1r**), the corresponding phenylation products were produced in good to excellent yield (Table 2, runs 1–4, 8, 9 and 13–18). Each reaction was stopped when the amount of phenylation product did not increase more by GLC monitoring. On the other hand, from 3-methyl-2-buten-1-ol (**1e**), cinnamyl alcohol (**1f**) and 2-cyclohexen-1-ol (**1g**), the corresponding products were obtained only in low yield (runs 5–7), while the formation of phenylated products was not observed from 1-acetoxy-2-cyclohexene (**1j**) and 1-acetoxy-3-methyl-2-butene (**1k**) (runs 10 and 11). From allyl phenyl ether (**1l**) an isomeric mixture of two phenylated alkenes [($\mathbf{3l_1}$), ($\mathbf{3l_2}$)] was obtained (run 12). When α,β-unsaturated ketone, 3-buten-2-one (**1s**), was used, the expected phenyl-substituted product (4-phenyl-3-buten-2-one) was not formed, but the product (**3b**) due to a formal Michael-type conjugate addition of benzene to an alkene part was produced as we have already noted in acetic acid as solvent [2] (run 19). The formation of a slight amount of biphenyl (< 10%; one equimolar amount of biphenyl to Ph_2SbCl corresponds to 100%) and white precipitates (described below) were observed in all cases. When the reaction of two equimolar amounts of reactive substrate **1r** with one equimolar amount of Ph_2SbCl was carried out, 1.17 equimolar amounts of **3r** were obtained (58.5% yield on the basis of **1r**), showing that, in this case, a slightly more than one phenyl group out of the two of **2** were transferred to **1r**.

All the above described reactions were carried out under air. However, the different result was obtained when the reaction was carried out under nitrogen. Thus, when **1a** was treated with **2** in acetonitrile in the presence of 3 mol% of $Pd(OAc)_2$ at 25°C for 24 h under nitrogen atmosphere, **3a** was obtained only in 1.6% yield (Table 3). A similar catalytic reaction under oxygen afforded the product **3a** in 87% yield with 6% yield of biphenyl, and therefore, it became clear that the presence of oxygen was inevitable for this catalytic reaction. Actually, when the amount of oxygen consumed in the phenylation of **1a** under oxygen was measured, it was revealed that an equimolar amount of oxygen to the phenylation product was consumed (see Section 4). In the presence of a stoichiometric amount of $Pd(OAc)_2$ (one equimolar amount), on the other hand, **3a** was obtained in 79% yield together with biphenyl (35% yield on the basis of Ph_2SbCl) in spite of the lack of oxygen. It was also revealed that even under air the addition of a radical scavenger, galvinoxyl, prevented the reaction almost completely. The result indicated that a free radical species may be involved in this catalytic phenylation reaction under air.

As to the palladium catalysts, palladium(0) complexes, such as tris(dibenzylideneacetone)dipalladium and tetrakis(triphenylphosphine)palladium were inactive. Even with $Pd(OAc)_2$ no reaction occurred, when triethylamine was added in the reaction system, the addition of which being known to give a naked palladium(0) species (Table 3) [4]. These results show that Pd(0) is not effective for this reaction.



Scheme 2.

When phenylantimony dichloride ($PhSbCl_2$), prepared in situ from one equimolar amount of Ph_3Sb and two equimolar amounts of $SbCl_3$ according to the same method for Ph_2SbCl [10], was reacted with an equimolar amount of **1a** under the above described optimum conditions (with 3 mol% $Pd(OAc)_2$ in acetonitrile at 25°C for 24 h under air), the yield of product **3a** was only 9%. Even by use of 10 mol% of the catalyst the product yield was 39%. These results show that a phenyl transfer ability is quite low in the case of $PhSbCl_2$ compared with Ph_2SbCl (**2**) in accord with the evidence shown above that a transfer of more than one phenyl group from **2** is quite slow.

Diphenylbismuth chloride (an analog of Ph_2SbCl), prepared from Ph_3Bi and $BiCl_3$ [11], was also applied to this reaction. Table 4 summarizes the results of the reactions with several substrates such as allyl alcohol (**1a**), allyl acetate (**1h**) and allylbenzene (**1p**), where only in the case of **1a**, the corresponding phenylation product was obtained. Compared with the case of Ph_2SbCl, much more biphenyl was produced when Ph_2BiCl was used, in accord with a report of a facile formation of biphenyl from Ph_2BiCl [4]. Although Ph_2BiCl was effective for phenylation of **1a**, the phenylation did not proceed well with many other arylmetal chlorides, such as Ph_2TlCl, Ph_3SnCl and Ar_2TeCl_2 under these reaction conditions. Thus, by use of Ph_2TlCl, only a trace amount of the corresponding phenylation product was detected by GLC together with 6% of biphenyl. In the case of Ph_3SnCl, the amount of the detected phenylation product was equal to that of $Pd(OAc)_2$ employed and biphenyl was not detected by GLC, while in the case of Ar_2TeCl_2 no products were detected.

Table 1
Palladium(II)-catalyzed phenylation of allyl alcohol (**1a**) with Ph_2SbCl under various conditions[a]

$Pd(OAc)_2$ (mol%)	Solvent	Temperature (°C)	Yield of **3a**[b] (%)
10	CH_3CN	25	73
3	CH_3CN	25	94
1	CH_3CN	25	80
3	CH_3CN	0	50
3	CH_3CN	50	65
10	THF	25	79
1	THF	25	80
10	Toluene	25	60
10	Acetone	25	44
10	AcOH	25	23
10	MeOH	25	10

[a] Ph_3Sb (0.8 mmol), $SbCl_3$ (0.4 mmol), **1a** (1.0 mmol), solvent (10 ml), at 25°C.

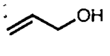
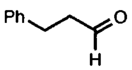
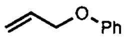
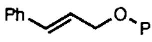
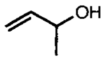
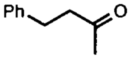
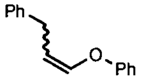
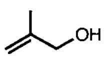
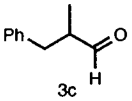
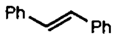
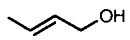
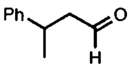
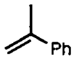
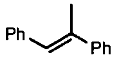
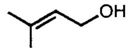
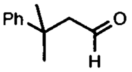
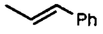
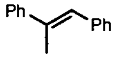
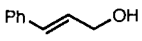
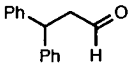
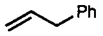
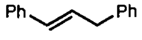
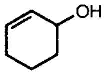
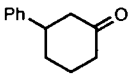
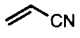
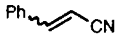
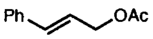
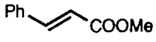
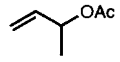
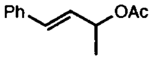
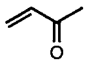
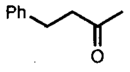
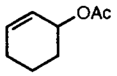
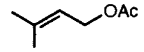
[b] Determined by GLC on the basis of **1a**.

2.2. Plausible reaction pathway

The active species of a Heck reaction has been generally accepted as a phenylpalladium species, and actually Russell and co-workers have recently reported that aromatic protons of the phenyl on palladium appeared at 7.11 and 6.66 ppm [12]. On the other hand, the protons of the phenyl moiety attached to antimony usually appeared in the range 7.3–8.3 ppm [13] and are distinguishable from the protons of the phenyl moiety on palladium. The NMR spectroscopic studies were carried out to know whether oxygen is needed in the step of the formation of a phenylpalladium species or not. The proton NMR spectrum ($CDCl_3$) of the oil, prepared by keeping a mixture of Ph_3Sb (two equimolar amounts) and $SbCl_3$ (one equimolar amount) at 25°C for 5 h, showed large multiplet peaks at 7.64 (2H) and 7.43 (3H) ppm together with small multiplet peaks at 7.88 and 7.58 ppm, those at 7.45 and 7.34 ppm and those at 8.23 and 7.53 ppm. The former large peaks correspond to Ph_2SbCl, while the latter three small peaks correspond to $PhSbCl_2$, Ph_3Sb and Ph_3SbCl_2, respectively [13]. When $Pd(OAc)_2$ (0.25 equimolar amounts) was added to the $CDCl_3$ solution of this oil (mainly Ph_2SbCl) under air, two new peaks appeared at 7.04 and 6.72 ppm, probably due to the formation of a phenylpalladium species. Even when a completely deaerated $CDCl_3$ solution of Ph_2SbCl (one equimolar amount) was added to $Pd(OAc)_2$ (0.25 equimolar amounts) in an NMR tube under nitrogen, the NMR spectrum of the resultant yellow solution showed signals of the corresponding aromatic protons of the phenyl on palladium. Therefore, it is clear that oxygen does not play a role in producing a phenylpalladium species.

By considering the above ^1H-NMR spectral data together with the necessity and consumption of oxygen in this reaction, a plausible catalytic reaction pathway for phenylation is presented in Scheme 3. First, a phenylpalladium species [PhPd(OAc)] (**4**), produced by transmetallation between diphenylantimony chloride (**2**) and $Pd(OAc)_2$, adds to an alkene (**1**) to afford an

Table 2
Palladium(II)-catalyzed phenylation of alkenes with Ph_2SbCl[a]

Run	Alkene	Reaction time (h)	Product	Yield[b] (%)	Run	Alkene	Reaction time (h)	Product	Yield[b] (%)
1	 **1a**	21	 **3a**	94(91)	12	 **1l**	8	 **3l$_1$**	40
2	 **1b**	23	 **3b**	58(48)				 **3l$_2$**	33 (*E*/ *Z* = 15/85][c]
3	 **1c**	44	 **3c**	89(67)	13	 **1m**	19	 **3m**	100
4	 **1d**	24	 **3d**	58(42)	14	 **1n**	72	 **3n**	62
5	 **1e**	24	 **3e**	(12)	15	 **1o**	24	 **3n**	90(76)
6	 **1f**	24	 **3f**	Trace	16	 **1p**	6	 **3p**	71
7	 **1g**	100	 **3g**	13(11)	17	 **1q**	64	 **3q**	(100) [*E*/ *Z* = 80/20][c]
8	 **1h**	6	 **3h**	92(74)	18	 **1r**	9	 **3r**	100(100)
9	 **1i**	10	 **3i**	72(63)	19	 **1s**	9	 **3b**	62
10[d]	 **1j**	–							
11[d]	 **1k**	–							

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[a] Ph_3Sb (0.8 mmol), $SbCl_3$ (0.4 mmol), alkene (1.0 mmol), $Pd(OAc)_2$ (3 mol%), CH_3CN (10 ml), at 25°C.

[b] GLC yield on the basis of alkene employed. Isolated yield is shown in parentheses.

[c] *E*/*Z* ratio was determined by GLC and ^1H-NMR.

[d] $Pd(OAc)_2$ (0.1 mmol, 10 mol%) was used.

alkylpalladium species (**5**). A β-hydride elimination from **5** gives the product (**3**) and a hydridopalladium species (**6**). This pathway from **4** to **6** has already been well-established in a Heck reaction. Species **6** is ordinarily known to give palladium(0) and acetic acid by reductive elimination and the phenylation reaction does not proceed any more without a reoxidant. In this catalytic phenylation, however, species **4** should be regenerated by participation of oxygen as the reaction does not proceed catalytically in the absence of oxygen. The speculative process of this regeneration step is shown in Scheme 4 on the basis of oxygen uptake in the reaction as well as the presence of a free radical species. First and most importantly, antimony has a hyperva-

Table 3
The effect of atmosphere and palladium catalysts[a]

Run	Catalyst (mol%)	Atmosphere	Additive	Yield (%)[b]	
				3-Phenylpropanal (**3a**)	Biphenyl
1	$Pd(OAc)_2$ (3)	Air	–	94	12
2	$Pd(OAc)_2$ (3)	N_2	–	1.6	13
3	$Pd(OAc)_2$ (100)	N_2	–	79	35
4	$Pd(OAc)_2$ (3)	O_2	–	87	6
5	$Pd(OAc)_2$ (3)	Air	Galvinoxyl[c]	Trace	Trace
6	$Pd_2(dba)_3$ (10)	Air	–	0	8
7	$Pd(PPh_3)_4$ (10)	Air	–	0	16
8	$Pd(OAc)_2$ (10)	Air	Et_3N[d]	0	0
9	–	Air	–	0	0

[a] Ph_3Sb (0.8 mmol), $SbCl_3$ (0.4 mmol), **1a** (1.0 mmol), solvent (10 ml), at 25°C.

[b] Determined by GLC on the basis of **1a** and **2**, respectively.

[c] Galvinoxyl (5 mol%) was added.

[d] Triethylamine (2.0 mmol) was added.

lent nature; a co-ordination number of $SbCl_3$ is 8, while that of $PhSbCl_2$ is 5, as shown by X-ray analysis [14]. Ph_2SbCl should also be a hypervalent compound. Species **6** can be co-ordinated by 2 mol of Ph_2SbCl to provide a complex **A** in which the electron density of the antimony atom becomes lower than that of the free Ph_2SbCl. Therefore, the antimony atom of the complex **A** can interact more easily with oxygen's lone pair. The co-ordination of oxygen is followed by homolytic fission of the Sb–C1 bond because of the radical character of oxygen. A chlorine atom abstracts the hydrogen attached to the neighboring Pd atom, and both HCl and biradical species are generated. After the intramolecular phenyl transfer, the biradical species reacts with **2** to generate complex **B** and $PhSbO_2$, the latter of which being a polymeric compound and hardly soluble in all organic solvents [15]. The formation of white to grey precipitates was always observed after the reaction. In spite of several attempts to characterize these precipitates using IR, MS, EPMA, XRD and the combustion analysis (see Section 4), however, the exact nature of them is not yet clear; probably a mixture of $PhSbO_2$, $PhSb(OH)Cl$, $PhSbCl_2$ and so on.

3. Conclusion

In conclusion, diphenylantimony chloride reacted with many alkenes in the presence of a catalytic amount of palladium(II) acetate under air to afford the corresponding Heck-type phenylated products, while the re activity of phenylantimony dichloride was much lower. The presence of oxygen is inevitable for this catalytic reaction and a phenylpalladium species might be reproduced from a hydridopalladium species via oxygen participating radical pathway. The reaction seemed to be characteristic for Ph_2SbCl, because the reaction did not proceed catalytically with many other similar chlorides of the corresponding Group 13–16 elements except for the combination of Ph_2BiCl and allyl alcohol.

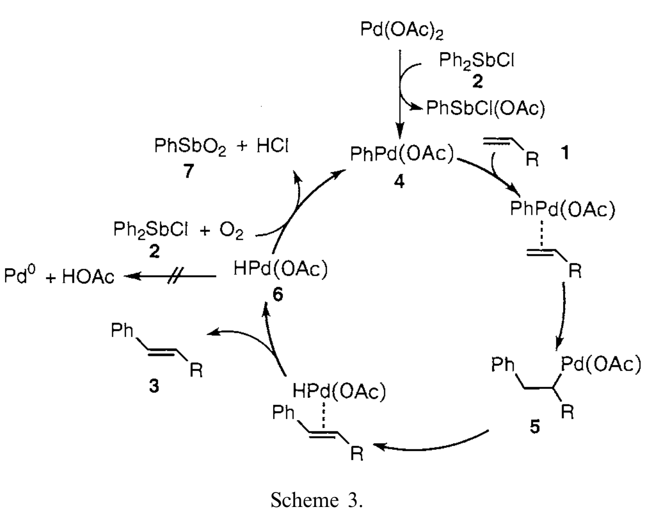
Table 4
Palladium(II)-catalyzed phenylation with Ph_2BiCl[a]

Alkene	Catalyst (mol%)		Yield (%)	
			Phenylation product[b]	Biphenyl[c]
1a	$Pd(OAc)_2$ (10)	**3a**	57	70
1h	$Pd(OAc)_2$ (10)	**3h**	0	19
1p	$Pd(OAc)_2$ (10)	**3p**	0	54
1a	$Pd(OAc)_2$ (3)	**3a**	61	51
1a	–	**3a**	0	5

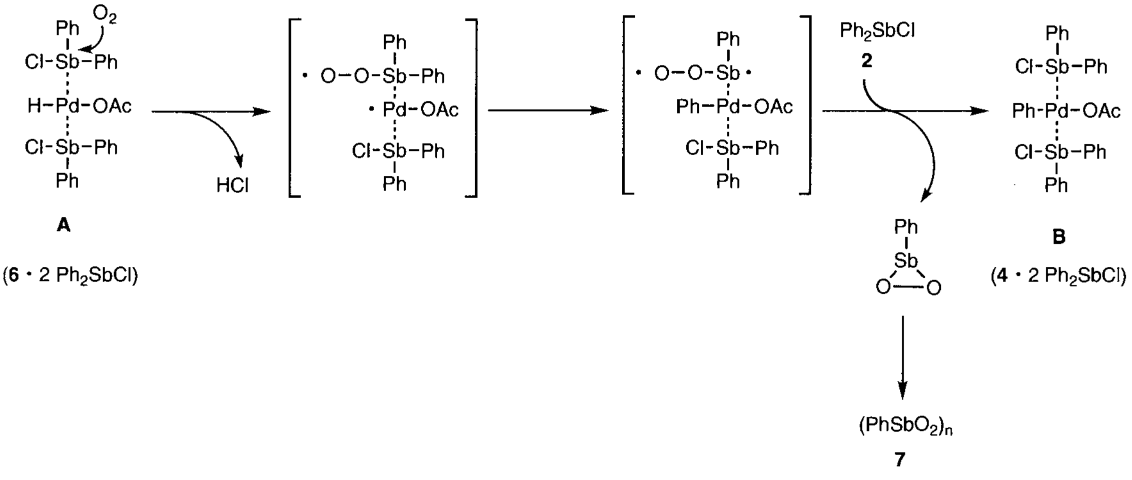
[a] Ph_2BiCl (1.2 mmol), alkene (1.0 mmol), CH_3CN (10 ml), at 25°C, 24 h.

[b] Isolated yield.

[c] Determined by GLC on the basis of Ph_2BiCl.



Scheme 3.



Scheme 4.

4. Experimental

^{1}H- and ^{13}C-NMR spectra were measured on JEOL EX-400 and JEOL JNM-GSX270 spectrometers for solutions in $CDCl_3$ with Me_4Si as an internal standard. Melting points were determined on a Yanaco MP-J3 micro-melting point apparatus and uncorrected. MS spectra were obtained on a Shimadzu QP-5000S spectrometer at an ionizing voltage of 70 eV. GLC analyses were carried out with Shimadzu GC-14A instrument equipped with a CBP 10-S25-050 (Shimadzu, fused silica capillary column, 0.33 mm × 25 m, 5.0 mm film thickness) column using helium as carrier gas. GLC yields were determined using dibenzyl as an internal standard. Analytical thin layer chromatographies (TLC) were performed with silica gel 60 Merck F-254 plates. Column chromatographies on SiO_2 were performed with Wakogel C-300. Elemental analyses were performed at the Microanalytical Center of Kyoto University. The electron probe microanalysis (EPMA) was performed with JEOL X-ray microanalyzer JXA-840A instrument. For ion chromatography and inductively coupled plasma (ICP), Dionex Co. (Tokyo), Dx-500 type and Seiko Instruments and Electronics Ltd., SPS 1700VR type were employed, respectively. X-ray powder diffraction (XRD) data were obtained on MAC Science Co. (Tokyo), MXP-18 system using Cu–K_α radiation and an energy dispersive detector.

4.1. Materials

Commercially available organic and inorganic compounds were used without further purification. Diphenylantimony chloride (**2**) was prepared in situ by the known disproportionation method between triphenylstibine and antimony(III) chloride [10]. Ph_2BiCl [11], Ph_2TlCl [16] and Ar_2TeCl2 [17] were prepared by the known methods, respectively. Ph_3SnCl was commercially available. All allylic alcohols, allylic acetates and other unsaturated compounds were commercial products except for 3-acetoxy-1-butene (**1i**), 3-acetoxy-1-cyclohexene (**1j**) and 4-acetoxy-2-methyl-2-butene (**1k**), which were synthesized by acylation of the corresponding alcohols. All transition metal salts were commercial products, except for $[Pd(PPh_3)_4]$, which was prepared by a known method [18].

4.2. Reaction procedure

4.2.1. General procedure for Pd(II)-catalyzed reaction of unsaturated compounds with diphenylantimony chloride

Diphenylantimony chloride (1.2 mmol) was prepared in situ by stirring triphenylstibine (0.8 mmol) and antimony(III) chloride (0.4 mmol) in the absence of solvent for 5 h at 25°C [10]. Then, a solution of unsaturated compound (1 mmol) and palladium(II) acetate (6.9 mg, 0.03 mmol) in acetonitrile (10 ml) was added to the above prepared Ph_2SbCl and the mixture was stirred at 25°C for an appropriate time. The precipitated white to grey solids were filtered off and the filtrate was poured into brine (30 ml) and extracted with diethyl ether (30 ml). The organic extract was washed with water and dried over anhydrous $MgSO_4$. Removal of the solvent under reduced pressure usually left an almost colorless oil, which was separated and purified by column chromatography using ethyl acetate/hexane mixture as an eluent to give the Heck-type product. For obtaining GLC yield, a similar reaction was carried out in the presence of an appropriate amount of dibenzyl as an internal standard. The yield of the precipitated solid was usually around 150 mg. All the products were known compounds and only ^{1}H-NMR spectroscopic data are shown below except for the compounds **3b**, **3d**,

3h, **3m**, **3n**, **3q** and **3r**, which are commercial products.

3-Phenylpropanal (**3a**): 91% yield; an oil; ^{1}H-NMR $\delta = 2.78$ (2H, td, $J = 7.7$, 1.4 Hz), 2.97 (2H, t, $J = 7.7$ Hz), 7.18–7.30 (5H, m) and 9.83 (1H, t, $J = 1.4$ Hz).

2-Methyl-3-phenylpropanal (**3c**): 67% yield; an oil; ^{1}H-NMR $\delta = 1.09$ (3H, d, $J = 6.9$ Hz), 2.60 (1H, dd, $J = 12.6$, 7.8 Hz), 2.68 (1H, m), 3.09 (1H, dd, $J = 12.6$, 5.0 Hz), 7.16–7.33 (5H, m) and 9.72 (1H, d, $J = 1.4$ Hz).

3-Methyl-3-phenylbutanal (**3e**): 12% yield; an oil; ^{1}H-NMR $\delta = 1.45$ (6H, s), 2.66 (2H, d, $J = 3.0$ Hz), 7.20–7.39 (5H, m) and 9.49 (1H, t, $J = 3.0$ Hz).

3-Phenylcyclohexanone (**3g**): 11% yield; an oil; ^{1}H-NMR $\delta = 1.74$–1.92 (2H, m), 2.07–2.19 (2H, m), 2.32–2.62 (4H, m), 2.96–3.04 (1H, m) and 7.21–7.37 (5H, m).

(*E*)-3-Acetoxy-1-phenyl-1-butene (**3i**): 63% yield; an oil; ^{1}H-NMR $\delta = 1.41$ (3H, d, $J = 6.6$ Hz), 2.08 (3H, s), 5.53 (1H, dq, $J = 6.9$, 6.6 Hz), 6.19 (1H, dd, $J = 16.0$, 6.9 Hz), 6.60 (1H, d, $J = 16.0$ Hz) and 7.24–7.40 (5H, m).

(*E*)-Cinnamyl phenyl ether (**3l$_1$**) and (*E*,*Z*)-phenyl-3-phenyl-1-propenyl ether (**3l$_2$**): **3l$_2$** was isolated as an *E*/*Z* mixture; **3l$_1$** (a white solid as a pure form) was identified by the ^{1}H-NMR spectrum of a mixture of **3l$_1$** and **3l$_2$**. **3l$_1$**: ^{1}H-NMR $\delta = 4.71$ (2H, d, $J = 5.9$ Hz), 6.43 (1H, dt, $J = 16.1$, 5.9 Hz), 6.74 (1H, d, $J = 16.1$ Hz) and 6.94–6.99, 7.25–7.44 (10H, m). (*E*)-**3l$_2$**: an oil; ^{1}H-NMR $\delta = 3.38$ (2H, dd, $J = 7.5$Hz and $^4J = 1.4$ Hz), 5.54 (1H, dt, $J = 12.1$, 7.5 Hz), 6.51 (1H, dt, $J = 12.1$ Hz and $^4J = 1.4$ Hz) and 6.97–7.09, 7.16–7.46 (10H, m). (*Z*)-**3l$_2$**: an oil; ^{1}H-NMR $\delta = 3.58$ (2H, dd, $J = 7.6$ Hz and $^4J = 1.4$ Hz), 5.04 (1H, td, $J = 7.6$, 6.0 Hz), 6.50 (1H, dt, $J = 6.0$ Hz and $^4J = 1.4$ Hz) and 6.97–7.09, 7.16–7.46 (10H, m).

(*E*)-1,3-Diphenyl-1-propene (**3p**): an oil; ^{1}H-NMR $\delta = 3.55$ (2H, d, $J = 6.2$ Hz), 6.37 (1H, dt, $J = 15.9$, 6.2 Hz), 6.47 (1H, d, $J = 15.9$ Hz) and 7.21–7.37 (10H, m).

4.2.2. The procedure for NMR spectroscopic study

In an NMR tube Pd(OAc)$_2$ (1.89 mg, 8.4 μmol) was placed under N$_2$. The in situ prepared Ph$_2$SbCl (10.6 mg, 34 μmol) was dissolved in degassed CDCl$_3$ (0.5 ml), and the mixture was deaerated by suction under cooling with liquid nitrogen. The deaerated solution was then added to Pd(OAc)$_2$ in the NMR tube under N$_2$, and the ^{1}H-NMR analysis was carried out.

4.2.3. The procedure for measurement of oxygen consumption

Diphenylantimony chloride (1.2 mmol) was prepared in situ by stirring triphenylstibine (282.5 mg, 0.8 mmol) and antimony(III) chloride (91.2 mg, 0.4 mmol) in the absence of solvent for 5 h at 25°C [10]. Then, the internal standard dibenzyl (50.0 mg) and palladium(II) acetate (6.9 mg, 0.03 mmol) were added to the flask containing the above prepared Ph$_2$SbCl and the flask was deaerated and then filled with oxygen. A syringe filled with 50 ml of oxygen was connected to the flask in which the reaction was carried out by adding solution of allyl alcohol (**1a**) (58.1 mg, 1 mmol) in acetonitrile (10 ml) under stirring. After 2 h, the 18 ml of oxygen in the syringe was consumed, which corresponds to 0.74 mmol (25°C, 1 atm) and the oxygen consumption did not increase any more. The GLC yield of 3-phenylpropanal (**3a**) was 72% (0.72 mmol).

4.2.4. Attempts to characterize the precipitates formed after the reaction

The IR spectrum of the dried precipitates showed the band at 457 cm^{-1}, which can probably be assigned to Sb–O [19], as well as the bands corresponding to monosubstituted phenyl group. The combustion analysis showed H% 1.85, C% 24.72 and O% 11.80 and these values were lower than those expected from PhSbO$_2$ (H% 2.18, C% 31.22, O% 13.86). In the mass spectrum analysis (FAB) the value of 365 was observed as a parent peak and also the fragment peaks clearly showed the presence of antimony considered from their ratio of isotopes. Further, EPMA analysis of another lot showed the presence of both antimony and chlorine and the ICP analysis of Sb and the ion chromatography analysis of Cl revealed them to be 63.8% and 8.96%, respectively, the ratio of which being 2:1. The XRD analysis showed that the precipitates were amorphous and not crystalline inorganic compounds such as SbCl$_3$ and Sb$_2$O$_3$.

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