Facile Palladium-Catalyzed Carbonylation of Triarylstibines in the Presence of Ammonium Cerium(IV) Nitrate

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Synthetic applications of organoantimony compounds are increasing.[1] As part of our series of studies on the synthetic use of organoheteroatom compounds,[2] we have now found that triarylstibines react with carbon monoxide (CO) at atmospheric pressure in methanol in the presence of a catalytic amount of a palladium compound at room temperature to afford the corresponding methyl benzoates and benzophenones in almost quantitative yields. Interestingly, the use of ammonium cerium(IV) nitrate (CAN) was required. Various other oxidants such as $CuCl_2$, $K_2S_2O_8$, and *p*-benzoquinone were almost completely ineffective. Although Goel *et al.* reported that the reaction of palladium(II) chloride with 1 or 2 equiv of triphenylstibine in toluene under a CO atmosphere gave several carbonylated compounds including benzoic acid, quite severe reaction conditions (150–200 °C, CO or $CO/NO/N_2$ pressure of 150 atm) and a stoichiometric amount of $PdCl_2$ were necessary.[3]

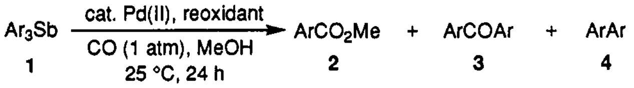
Treatment of triphenylstibine (**1a**) (0.5 mmol) with CO at atmospheric pressure in methanol in the presence of an equimolar amount of bis(benzonitrile)palladium(II) chloride at 25 °C for 24 h afforded methyl benzoate (**2a**) (43% yield) and benzophenone (**3a**) (11% yield) as the carbonylation products together with biphenyl (**4a**) (10% yield).[4] However, the addition of ammonium cerium(IV) nitrate (1.5 mmol) as a reoxidant allowed the amount of palladium to be reduced to 1 mol % based on the amount of stibine, and only carbonylation products **2a** and **3a** were formed in quantitative yields. This CAN-induced reaction also proceeded with other palladium(II) compounds as well as with palladium(0) complexes under similar conditions, but other reoxidants such as copper(II) chloride, copper(II) acetate, silver acetate, iron(III) chloride, $K_3Fe(CN)_6$, potassium persulfate ($K_2S_2O_8$), $K_2S_2O_8/AgNO_3$, DDQ, and *p*-benzoquinone in place of CAN were essentially ineffective for the carbonylation. With other easily available triarylstibines (**1b–g**), corresponding esters **2** and diaryl ketones **3** were also formed in almost quantitative yields (Scheme 1, Table 1). The application of our newly developed $PdCl_2(PhCN)_2$ catalytic system to tri(1-naphthyl)stibine (**1h**) resulted in formation of trace amounts of the corresponding carbonylated compounds, but with the use of Li_2PdCl_4 the expected methyl 1-naphthoate (**2h**) was obtained in moderate yield. A similar phenomenon was also observed with other trinaphthylstibines such as **1i** and **1j**. Among other compounds of group 15 elements, triphenylbismuthine was moderately reactive (**2a**, 16%; **3a**, 29%; **4a**, 31%), but triphenylarsine was almost unreactive (**2a**, 2%; **3a** and **4a**, 0%) under the present carbonylation conditions using 1 mol % $PdCl_2(PhCN)_2$ together with CAN.

Table 1. Palladium-Catalyzed Carbonylation of Triarylstibines[a]

triaryl-stibine	palladium salt (mol %)[b]	reoxidant	products and yield (%)[c] 2	3	4
1a	$PdCl_2(PhCN)_2$ (1)	CAN	89	11	0
1a	$PdCl_2$ (2)	CAN	84	16	0
1a	$PdCl_2(PPh_3)_2$ (3)	CAN	87	11	0
1a	Na_2PdCl_4 (2)	CAN	89	11	0
1a	Li_2PdCl_4 (3)[d]	CAN	84	15	0
1a	$Pd(OAc)_2$ (2)	CAN	79	19	0
1a	$Pd(PPh_3)_4$ (1)	CAN	86	9	0
1a	$Pd_2(dba)_3$ (1)	CAN	82	16	0
1a	$PdCl_2(PhCN)_2$ (1)	$CuCl_2$	2	0	5
1a	$PdCl_2(PhCN)_2$ (1)	AgOAc	2	0	0
1a	$PdCl_2(PhCN)_2$ (1)	$K_2S_2O_8$	0	0	2
1a	$PdCl_2(PhCN)_2$ (1)	$FeCl_3$	2	0	8
1a	$PdCl_2(PhCN)_2$ (1)	*p*-benzoquinone	0	0	4
1b	$PdCl_2(PhCN)_2$ (1)	CAN	71	24	0
1c	$PdCl_2(PhCN)_2$ (1)	CAN	81	15	0
1d	$PdCl_2(PhCN)_2$ (1)	CAN	69	27	0
1e	$PdCl_2(PhCN)_2$ (1)	CAN	46	14	0
1f	$PdCl_2(PhCN)_2$ (1)	CAN	79	19	0
1g	$PdCl_2(PhCN)_2$ (1)	CAN	77	19	0
1h[e]	Li_2PdCl_4 (5)[d]	CAN	33[f]	*g*	0
1i[e]	Li_2PdCl_4 (5)[d]	CAN	35[f]	*g*	0
1j[e]	Li_2PdCl_4 (5)[d]	CAN	37[f]	*g*	0

[a] All reactions were carried out with triarylstibine (**1**) (0.5 mmol) and a reoxidant (1.5 mmol) in MeOH (10 mL) at 25 °C for 24 h unless otherwise stated. [b] Based on triarylstibine. [c] GLC yield based on triarylstibine unless otherwise stated. 1.5 mmol of **2** and 0.75 mmol of **3** and **4** correspond to 100% yield, respectively. [d] Li_2PdCl_4 denotes a mixture of $PdCl_2$ and LiCl (1:2). [e] MeOH (20 mL). [f] Isolated yield. [g] Not determined. Even if it is present, it is only a trace amount.

Scheme 1



$$\underset{1}{Ar_3Sb} \xrightarrow[\text{CO (1 atm), MeOH; 25 °C, 24 h}]{\text{cat. Pd(II), reoxidant}} \underset{2}{ArCO_2Me} + \underset{3}{ArCOAr} + \underset{4}{ArAr}$$

a: Ar = Ph
b: Ar = 4-MeC_6H_4
c: Ar = 3-MeC_6H_4
d: Ar = 2-MeC_6H_4
e: Ar = 4-$MeOC_6H_4$
f: Ar = 4-ClC_6H_4
g: Ar = 3-ClC_6H_4
h: Ar = 1-naphthyl
i: Ar = 2-naphthyl
j: Ar = 6-methoxy-2-naphthyl

Although the exact mechanism of the reaction is not certain, the most plausible pathway seems to be the initial coordination of **1** to palladium(II) followed by aryl migration from antimony to palladium to produce an arylpalladium compound. The arylpalladium is then converted, after CO coordination, to an aroylpalladium compounds, which gives **2** and **3** via subsequent reaction with methanol or arylpalladium compound, respectively (Scheme 2). Coordination compounds such as $(Ph_3Sb)_2PdCl_2$[5] and $(Ph_3Sb)_2Pd_2(OAc)_4$[6] have already been isolated and characterized, and, in fact, we confirmed in a

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[1] For recent reviews see: (a) Freedman, L. D.; Doak, G. O. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Ed.; John Wiley & Sons, Inc.: New York, 1989; Vol. 5, pp 397–413. (b) Huang, Y. Z. *Acc. Chem. Res.* **1992**, *25*, 182.

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[4] Amounts of 1.5 mmol of **2a** and 0.75 mmol of **3a** and **4a** correspond to 100% yield, respectively.

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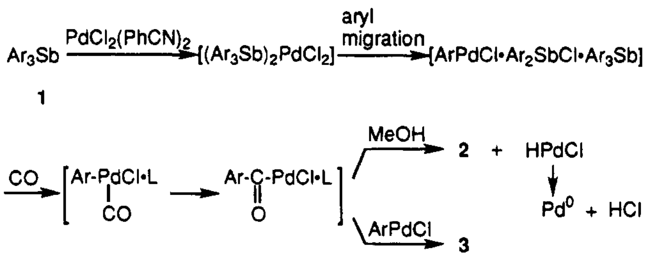
Scheme 2



separate experiment that $(Ph_3Sb)_2PdCl_2$ (0.25 mmol), prepared separately, reacted with CO to give the carbonylated products (**2a**, 12%; **3a** 9%) together with **4a** (14%).[4] When equimolar amounts of **1a** and **1b** (0.25 mmol each) were treated with CO (1 atm) under the conditions we employed, a mixture of **3a** (3.3%), phenyl 4-tolyl ketone (7.7%), and **3b** (3.7%)[7] was obtained together with the main products, the corresponding esters. The formation of the unsymmetrical ketone (crossover product) in this competitive reaction may support the existence of both aryl- and aroylpalladium(II) species during the reaction.[8] It is clear that CAN serves to reoxidize Pd(0) to Pd(II). However, as various other oxidants did not work well for this catalytic carbonylation, CAN must play an additional important role in the reaction. Although the exact function of CAN is not yet known, the following facts are worth noting: (1) other cerium compounds such as Ce_2O, $CeCl_3$, $Ce(OAc)_3{\cdot}H_2O$, and $CeF_4{\cdot}H_2O$ were completely ineffective, but $Ce(SO_4)_2{\cdot}nH_2O$ (n = 3−4) worked rather effectively (**2a**, 24%; **3a**, 28%); (2) that treatment of **1a** with an equimolar amount of CAN under an air or argon atmosphere at 25 °C for 24 h gave biphenyl in 5% yield shows that a C−Sb bond is cleaved, though slowly, by CAN even in the absence of a palladium salt; (3) treatment of **1a** with 1.5 mol equiv of CAN in methanol at 25 °C for 24 h followed by evaporation of the methanol left an uncharacterized white solid (mp > 250 °C), which did not show any spot due to Ph_3Sb by TLC, and the solid reacted with CO (1 atm) in the presence of $PdCl_2(PhCN)_2$ (1 mol %) over a period of 24 h to produce **2a** and **3a** in 74 and 18% yields, respectively.

The fate of antimony in the present carbonylation may be metallic antimony, as the formation of an 89% (1.335 mmol) yield of **2a** and an 11% (0.083 mmol) yield of **3a** from 0.5 mmol of **1a** (Table 1) indicates that all 3 phenyl groups are transferred to the product. However, metallic antimony might be reactive with oxygen and also with the oxidant CAN; therefore, we do not know yet the exact state of antimony after the reaction.

Experimental Section

General. ^1H (270 MHz) and ^{13}C (67.8 MHz) NMR spectra were recorded in $CDCl_3$. Melting points were uncorrected. GLC analyses were carried out with a CBP 10-S25-050 (fused silica capillary column, 0.33 mm × 25 m, 5.0 μm film thickness) column using helium as the carrier gas. GLC yields were determined using bibenzyl as an internal standard. The isolation of pure products was carried out via preparative TLC (silica gel 60 HF_{254}, Merck). Methanol was distilled from $Mg(OMe)_2$ ($Mg + I_2$). Commercially available organic and inorganic compounds were used without further purification except for $PdCl_2(PhCN)_2$, which was synthesized following a literature procedure.[9] Except for commercial triphenylstibine, triarylstibines **1b**,[10] **1c**,[11] **1d**,[11] **1e**,[12] **1f**,[13] **1g**,[13] **1h**,[14] and **1i**[15] were prepared by means of literature procedures. Authentic samples of compounds **2a−g** and **3a−g** were commercial products.

Synthesis of Tris(6-methoxy-2-naphthyl)stibine (1j). To a stirred solution of 2-bromo-6-methoxynaphthalene (7.113 g, 30 mmol) in ether (40 mL), cooled in an ice bath, was added by syringe n-BuLi (30 mmol, 1.6 M in hexane) under N_2. After the resulting yellow solution was stirred for 2 h at rt, it was cooled in an ice bath, and an ether (20 mL) solution of $SbCl_3$ (2.281 g, 10 mmol) was added using a dropping funnel over 30 min. The mixture was stirred for 5 h at rt and then poured slowly with stirring into 100 mL of ice and water. The cooled solution was filtered through a Buchner funnel, and the precipitate on the filter was washed with a small amount of $CHCl_3$. The filtrate was diluted with $CHCl_3$, and the aqueous phase was separated and extracted with $CHCl_3$ (3 × 50 mL). The combined organic phase was washed with brine (100 mL) and dried over Na_2SO_4. Evaporation of the solution under reduced pressure left a pale yellow solid, which was purified by recrystallization ($CHCl_3$/EtOH, 1/1) to give 2.077g (35%) of **1j** as a white, flaky solid: mp 178−180 °C; IR (KBr) 2950, 2925, 1620, 1265, 1215, 1020, 840 cm^{-1}; ^1H NMR δ 3.90 (s, 9H), 7.10−7.13 (m, 6H), 7.50 (dd, J = 8.1 and 1.1 Hz, 3H), 7.60−7.68 (m, 6H), 7.95 (s, 3H); ^{13}C NMR δ 55.3, 105.7, 118.9, 127.1, 129.4, 133.1, 134.6, 136.6, 158.1. Anal. Calcd for $C_{33}H_{27}O_3Sb$: C, 66.80; H, 4.59. Found: C, 66.64; H, 4.35.

Typical Procedure for Palladium-Catalyzed Carbonylation of Triarylstibines with Carbon Monoxide. Triphenylstibine (0.177 g, 0.5 mmol), bis(benzonitrile)palladium(II) chloride (0.002 g, 0.005 mmol), CAN (0.822 g, 1.5 mmol), and bibenzyl (an internal standard for GLC) were combined. The system was then flushed with CO from a CO balloon connected to the flask, and dry methanol (10 mL) was added by a syringe. After the initial red-orange solution was stirred for 24 h at 25 °C, a white precipitate was filtered off. The pale yellow filtrate was poured into brine (50 mL) and extracted with CH_2Cl_2 (2 × 30 mL). The combined organic phase was washed with water and dried over anhyd Na_2SO_4. GLC analysis revealed the presence of methyl benzoate (1.335 mmol, 89%) and benzophenone (0.083 mmol, 11%). Methyl esters **2h** (a pale yellow oil),[16] **2i** (a white solid, mp 73−74 °C; lit.[16] mp 76−76.5 °C), and **2j** (a white solid, mp 127−128 °C; lit.[17] mp 130−131 °C) were isolated by preparative TLC (EtOAc/hexane, 1/10). The compound ^1H and ^{13}C NMR and IR spectra matched those reported in the literatures.

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[7] An amount of 0.75 mmol of ketones corresponds to 100% yield.

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