Catalytic *C*-phenylation of methyl acrylate with tetraphenylantimony(v) halides and carboxylates

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Catalytic *C*-phenylation of methyl acrylate to methyl cinnamate with the Ph_4SbX complexes (X = F, Cl, Br, OH, OAc, O_2CEt) in the presence of the palladium compounds $PdCl_2$, $Pd(OAc)_2$, $Pd_2(dba)_3$, $Pd(Ph_3P)_2Cl_2$, and $Pd(dppf)Cl_2$ (dba is dibenzylideneacetone and dppf is bis(diphenylphosphinoferrocene)) was studied in organic solvents (MeCN, THF, DMF, MeOH, and AcOH). The highest yield of methyl cinnamate (73% based on the starting organometallic compound) was obtained for the $Ph_4SbCl—PdCl_2$ (1 : 0.04) system in acetonitrile.

Key words: phenylation, methyl acrylate, tetraphenylantimony complexes, palladium compounds, Heck reaction.

Triphenylantimony is used in the *C*-phenylation of unsaturated compounds (Heck reaction) in the presence of equimolar amount of palladium diacetate.[1—4] Unlike triphenylantimony, triphenylantimony dicarboxylates $Ph_3Sb(O_2CR)_2$ provide phenylatation of methyl acrylate in high yields in the presence of catalytic amounts of palladium compounds. The organic Sb^V derivatives act as both the sources of the Ph groups and the oxidants of Pd^0 to Pd^{II}. Triphenylantimony dihalides have no phenylating ability.[5]

It was of interest to use in these reactions triphenylantimony(v) compounds Ph_4SbX, which are accessible, highly soluble, and stable to the air oxygen and moisture. The involvement of all four Ph groups in the phenylation of an organic substrate could be expected.

The purpose of this work is to synthesize phenylating agents (*viz.*, tetraphenylantimony halides and carboxylates) and to study their efficiency in the palladium-catalyzed *C*-phenylation of methyl acrylate compared to the known reactive Ph_3SbX_2 compounds.

Results and Discussion

Tetraphenylantimony complexes Ph_4SbX were synthesized by neutralization of the stibonium base Ph_4SbOH with the corresponding acids. Hydrochloric acid was used in an equimolar amount in a dilute aqueous solution. Excess acetic and propionic acids were taken as solvents. Tetraphenylantimony fluoride, chloride, and propionate were obtained in the individual states, whereas tetraphenylantimony acetate was prepared as the crystal solvate $Ph_4SbOAc \cdot AcOH$. According to the published data,[6—8] this complex can have different structures depending on the method of synthesis: trigonal-bipyramidal in which the AcOH molecule is bound by the hydrogen bond to the acetate group at the pentacoordinated antimony atom[6,7] and octahedral with hexacoordinated antimony, where the metal atom is bound to two symmetrically arranged acetate groups in the eight-membered cycle.[8]

The complex obtained has the characteristic features of both structures. For example, the IR spectrum of $Ph_4SbOAc \cdot AcOH$ in Nujol or KBr pellets exhibits the bands of stretching vibrations of the COO group bound to the Sb atom: $\nu_{as}(COO)$ = 1560 cm^{-1} and $\nu_s(COO)$ = 1400 cm^{-1}. In addition to these bands, the spectrum contains distinct absorption bands of acetic acid, which is not bound to the metal: $\nu_{as}(COO)$ = 1730 cm^{-1} and $\nu_s(COO)$ = 1270 cm^{-1}. At the same time, the ^1H NMR spectrum in $CDCl_3$ contains a singlet of the Me protons of two identical acetate groups δ = 1.82 (s, 6 H) and a multiplet of protons of four Ph groups δ = 7.70—7.20 (m, 20 H). Probably, when the crystalline complex is dissolved in $CDCl_3$, the coordination antimony polyhedron is rearranged, and the acetate groups become identical in the NMR spectrum. When the $Ph_4SbOAc \cdot AcOH$ adduct is stored in air, the AcOH molecule is eliminated to form Ph_4SbOAc.[7]

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The model reaction of *C*-phenylation of methyl acrylate by the most accessible Ph_4SbBr in the presence of $PdCl_2$ (molar ratio 3 : 1 : 0.04) in acetonitrile at 50 °C for 6 h was showed[9] to occur *via* Scheme 1.

Scheme 1

$$H_2C{=}CH{-}CO_2Me \xrightarrow[MeCN,\ 50\ ^\circ C,\ 6\ h]{Ph_4SbBr + Pd} Ph_3Sb + PhCH{=}CH{-}CO_2Me + HBr$$

The yield of methyl cinnamate based on the starting organometallic compound (OMC) reaches 57% under these conditions. The organoantimony nonvolatile residue contains triphenylantimony and unreacted Ph_4SbBr.

The catalyst structure affects the yield of the main product. The most often applied palladium catalysts were used. The yields of methyl cinnamate (% based on OMC) in the *C*-phenylation of methyl acrylate by the $Ph_4SbBr{-}Pd^{0,II}$ (1 : 0.04) system (MeCN, 50 °C, 6 h) are presented below (dba is dibenzylideneacetone, and dppf is bis(diphenylphosphino)ferrocene). In the case of $Pd(OAc)_2$, biphenyl was additionally formed (9% based on OMC).

Pd complex	Yield
$PdCl_2$	57
$Pd(OAc)_2$	33
$Pd_2(dba)_3$	21
$Pd(Ph_3P)_2Cl_2$	0
$Pd(dppf)Cl_2$	0

As can be seen, palladium dichloride is most efficient in the phenylation of Ph_4SbBr. The yield of methyl cinnamate is much lower when the $Pd(OAc)_2$ or Pd^0 dibenzylideneacetone complex are used. In addition, biphenyl, the by-product of homocoupling, was formed in the case of $Pd(OAc)_2$. The introduction of phosphine ligands, such as PPh_3 and bis(diphenylphosphino)ferrocene, into the coordination sphere of palladium completely stops the phenylation of an unsaturated compound (see above). The same influence of the structure of the Pd compounds has been found[10] in the phenylation of methyl acrylate with the $Ph_3Sb(O_2CEt)_2$ derivative.

It is known that polar electron-donating solvents capable of coordinating to the Pd atom are used, as a rule, in the Heck reaction. For example, in the reaction of Ph_4SbBr under study, the N-donating solvents DMF and especially MeCN were most efficient. Compared to them, O-donating THF, AcOH, and MeOH were inefficient. The starting OMC and $PdCl_2$ catalysts were completely dissolved in all the solvents listed. The yields of methyl cinnamate (% based on OMC) in methyl acrylate *C*-phenylation with the $Ph_4SbBr{-}PdCl_2$ (1 : 0.04) system (50 °C, 6 h) in various solvents are presented below. Biphenyl (9% based on OMC) was additionally formed in the case of THF.

Solvent	Yield
MeCN	57
DMF	25
MeOH	7
THF	6
AcOH	6

When $Ph_3Sb(O_2CEt)_2$ was used as the phenylating agent in the catalytic reaction, the ratio of activities of the solvents was quite different: THF ≈ DMF > MeCN ≈ ≈ AcOH > MeOH.[10]

The influence of the X acido ligands in the starting Ph_4SbX on the yield of the products of methyl acrylate phenylation was studied. As can be seen from the data in Table 1, among tetraphenylantimony halides, the yield of methyl cinnamate is maximal in the case of tetraphenylantimony chloride (73%) and decreases on going to bromide and fluoride. The low yield of the phenylation product (7%) is observed along with a considerable amount of biphenyl (32%, see Table 1) when Ph_4SbOH is used. The reactions with Sb^V acetate and propionate were inefficient: the yield of methyl cinnamate was 21—28%. The lower reactivity of tetraphenylantimony carboxylates compared to that in the case of halides was unexpected when compared with the Ph_3SbX_2 derivatives. As we have shown previously,[5] triphenylantimony dicarboxylates are much more reactive than the corresponding dihalides.

Thus, the results obtained indicate that tetraphenylantimony(v) halides, similarly to the previously studied triphenylantimony(v) dicarboxylates,[5] can enter under mild conditions into the palladium-catalyzed reaction of methyl acrylate *C*-phenylation with the yield up to 73%. The Pd^0 complex is the active form of the catalyst according to Scheme 2.

In the first step of oxidative addition, the phenylpalladium intermediate is formed and then it performs phenylation of the unsaturated compound at the C—H bond.

Table 1. Yield of methyl cinnamate in the *C*-phenylation of methyl acrylate by the $Ph_4SbX{-}PdCl_2$ (1 : 0.04) system (MeCN, 50 °C, 6 h)

Ph_4SbX	Yield (% based on OMC)	
	Methyl cinnamate	Ph_2
Ph_4SbCl	73	—
Ph_4SbBr	57	—
Ph_4SbF	29	—
Ph_4SbOAc	21	—
Ph_4SbO_2CEt	28	1
Ph_4SbOH	7	32

Scheme 2

$$Pd^0 + Ph_4SbCl \longrightarrow PhPdCl + Ph_3Sb$$

$$PhPdCl + H_2C{=}CHCO_2Me \longrightarrow PhCH{=}CHCO_2Me + Pd^0 + HCl$$

The introduction of phosphine results in the formation of very stable complexes, the ligand exchange between palladium and antimony is violated, and the reactions stops (see above).

The substantial difference found for the influence of the X acido ligand and the solvent on methyl acrylate *C*-phenylation when Ph_4SbX and Ph_3SbX_2 are used can be explained as follows. First, the Ph_4SbX complexes, especially halides, are ionic compounds and can dissociate in polar media.[8] Unlike them, the Ph_3SbX_2 compounds are covalent. This should affect the rate and mechanism of the oxidative addition step (see Scheme 2). Second, in the case of Ph_4SbX, the reaction produces Ph_3Sb. This compound, being an analog of Ph_3P, is also capable of deactivating the palladium catalyst and decreasing the rate of phenylation in different solvents.[10] Unlike this, the reaction of Ph_3SbX_2 affords the Ph_2SbX compounds, which do not deactivate the catalyst because of the weak donor ability.

Thus, Ph_4SbBr and especially Ph_4SbCl in the presence of catalytic amounts of $PdCl_2$ can act as mild and selective agents of *C*-phenylation of methyl acrylate involving one Ph group. The structure of the acido ligand at the Sb atom and the solvent have a strong effect on the yield of methyl cinnamate. The character of this effect differs from that found previously for the Ph_3SbX_2 compounds.

Experimental

^{1}H NMR spectra were recorded on a Bruker Avance DPX-200 instrument in $CDCl_3$ using Me_4Si as internal standard. IR spectra were obtained on a Specord M-80 spectrophotometer in the 4000—400 cm^{-1} interval in KBr pellets and in Nujol suspension between two KBr optical windows. GLC analysis of volatile products was carried out on an LKhM-80 chromatograph (flame-ionization detector, helium as carrier gas, column 100 cm, 15% Apieson-L on Chromaton N-AW, 220 °C). Silica gel 60 Merck was used in column chromatography.

Tetraphenylantimony(v) Ph_4SbBr was synthesized according to a previously described procedure[8] by the reaction of Ph_3Sb with PhBr in the presence of $AlBr_3$ in 43% yield or in the presence of $AlCl_3$ in 25% yield, m.p. 211 °C (*cf.* Ref. 8: m.p. 210—215 °C). ^{1}H NMR, δ: 7.90—7.44 (m, Ph). IR, ν/cm^{-1}: 460 (ν(Sb—C)).

Tetraphenylhydroxoantimony(v) Ph_4SbOH was prepared by the treatment of a hot saturated aqueous solution of Ph_4SbBr [11] with a 12% aqueous ammonia excess in 90% yield.

Tetraphenylchloroantimony(v) Ph_4SbCl was synthesized according to a previously described procedure[11] from Ph_4SbOH in 70% yield, m.p. 208 °C (*cf.* Ref. 8: m.p. 202—205; 208—210 °C). ^{1}H NMR, δ: 7.90—7.44 (m, Ph). IR, ν/cm^{-1}: 460 (ν(Sb—C)).

Tetraphenylfluoroantimony(v) Ph_4SbF was prepared using a known procedure[12] in 76% yield, m.p. 161 °C (*cf.* Ref. 12: m.p. 162—163 °C).

Tetraphenylpropionatoantimony(v) Ph_4SbO_2CEt was synthesized by the dissolution of Ph_4SbOH (0.7 g) in propionic acid (2 mL) with heating on a water bath at 60 °C. The solution was concentrated on a water bath under a reduced pressure, toluene (2 mL) was added, and the solvent was evaporated again. The yield of Ph_4SbO_2CEt was 96.5%, m.p. 120 °C (*cf.* Ref. 13: m.p. 122 °C). ^{1}H NMR, δ: 7.70—7.30 (m, 20 H, Ph); 1.95 (q, 2 H, CH_2); 0.83 (t, 3 H, Me). IR, ν/cm^{-1}: 1520 (ν_{as}(COO)); 1360 (ν_s(COO)); 670 (ν(Sb—O)); 470 (ν(Sb—C)).

Tetraphenylacetatoantimony(v) (crystal solvate with AcOH) $Ph_4SbOAc \cdot AcOH$ was synthesized similarly to Ph_4SbO_2CEt in 83% yield, m.p. 112—114 °C (*cf.* Refs.: m.p. 112—113 °C,[8] 108—110 °C [7]). ^{1}H NMR, δ: 7.70—7.30 (m, 20 H, Ph); 1.82 (s, 6 H, Me). IR, ν/cm^{-1}: 3200—2400 (ν(O—H)); 1730 (ν_{as}(COO)); 1560 (ν_{as}(COO)); 1400 (ν_s(COO)); 1270 (ν_s(COO)); 670 (ν(Sb—O)); 460 (ν(Sb—C)). $Ph_4SbOAc \cdot AcOH$ was stored in air for 25 days and dried under reduced pressure to give Ph_4SbOAc, m.p. 132 °C (*cf.* Ref. 14: m.p. 131 °C).

Commercial compounds $PdCl_2$, $Pd(dppf)Cl_2$, and $Pd(Ph_3P)_2Cl_2$ were used without purification. $Pd(OAc)_2$ was prepared by the oxidation of palladium black with HNO_3 in AcOH for 30 h in 80% yield after recrystallization from AcOH.[15] $Pd_2(dba)_3(CHCl_3)$ was synthesized by the reduction of Pd with MeOH in the presence of dibenzylideneacetone[16] in 66% yield. Methyl acrylate was washed with an alkali solution until the yellow coloration stopped, dried above Na_2SO_4, and distilled.

Reaction of Ph_4SbBr with methyl acrylate and $Pd(OAc)_2$ in MeCN. An ampule was loaded with Ph_4SbBr (0.5 mmol) and methyl acrylate (1.5 mmol), and then a solution of $Pd(OAc)_2$ (0.02 mmol) in acetonitrile (4 mL) was added.[17] The ampule was sealed and heated at 50 °C for 6 h. Then the ampule was opened, and the solvent was condensed off into a trap filled with liquid nitrogen.

A hexane—ethyl acetate (5 : 1) eluent was added to the solid residue, and the resulting mixture was passed through a column with silica gel to remove inorganic products. Methyl cinnamate[18] (0.17 mmol) and biphenyl (0.043 mmol) were determined in the filtrate by GLC.

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References

1. R. Asano, I. Moritani, Y. Fujiwara, and S. Teranishi, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 2910.
2. K. Kawamura, K. Kikukawa, M. Takagi, and T. Matsuda, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 2021.

3. K. Kikukawa, K. Ikenaga, F. Wada, and T. Matsuda, *Tetrahedron Lett.*, 1984, **25**, 5789.
4. A. V. Gushchin, D. V. Moiseev, and V. A. Dodonov, *Zh. Obshch. Khim.*, 2002, **72**, 1669 [*Russ. J. Gen. Chem.*, 2002, **72** (Engl. Transl.)].
5. A. V. Gushchin, D. V. Moiseev, and V. A. Dodonov, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 1230 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 1291].
6. S. P. Bone and D. B. Sowerby, *Phosphorus, Sulfur, Silicon, Relate Elem.*, 1989, **45**, 23.
7. V. S. Senchurin, Author´s Abstract, Ph. D. (Chem.) Thesis, Blagoveshchensk State Pedagogical Institute, Irkutsk, 2002, 19 pp. (in Russian).
8. K. A. Kocheshkov, A. P. Skoldinov, and N. N. Zemlyanskii, *Metody elementoorganicheskoi khimii. Sur´ma, vismut* [*Methods of Organoelement Chemistry. Antimony, Bismuth*], Nauka, Moscow, 1976, 483 pp. (in Russian).
9. D. V. Moiseev, A. V. Gushchin, V. A. Dodonov, E. V. Grunova, and P. Yu. Rakcheev, *Tez. dokl. Mezhdunar. konf. "Metalloorganicheskie soedineniya — materialy budushchego tysyacheletiya" (III Razuvaevskie chteniya)* [*Proc. Intern. Conf. "Organometallic Compounds — Materials of the Future Century"*] *(Nizhnii Novgorod, May 29 — June 2, 2000)*, Nizhnii Novgorod, 2000, 106 (in Russian).
10. A. V. Gushchin, D. V. Moiseev, Yu. B. Malysheva, and V. A. Dodonov, *New Approaches in Coordination and Organometallic Chemistry. Look from 21-th Century (Nizhny Novgorod, June 1—6, 2002)*, Nizhny Novgorod, 2002, 53.
11. G. Kalfoglou and L. H. Bowen, *J. Phys. Chem.*, 1969, **73**, 2728.
12. G. Doleschall, N. A. Nesmeyanov, and O. A. Reutov, *J. Organomet. Chem.*, 1971, **30**, 369.
13. O. K. Sharutina, V. V. Sharutin, V. S. Senchurin, G. K. Fukin, L. N. Zakharov, A. I. Yanovskii, and Yu. T. Struchkov, *Izv. Akad. Nauk, Ser. khim.*, 1996, 194 [*Russ. Chem. Bull.*, 1996, **45**, 186 (Engl. Transl.)].
14. O. K. Sharutina, Author´s Abstract, Doct. Sci. (Chem.) Thesis, Blagoveshchensk State Pedagogical Institute, Irkutsk, 2001, 50 pp. (in Russian).
15. T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer, and G. Wilkinson, *J. Chem. Soc.*, 1965, **6**, 3632.
16. T. Ukai, H. Kawazura, Y. Ishii, J. J. Bonnet, and J. A. Ibers, *J. Organomet. Chem.*, 1974, **65**, 253.
17. *Organikum. Organisch-Chemisches Grundpraktikum*, Von Uberarbeitete Auflage, Veb Deutscher Verlag der Wissenschaften, Berlin, 1964.

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