Palladium-Catalyzed C-Phenylation of Methyl Acrylate with Triphenylbismuth Dicarboxylates

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Abstract—A new catalytic reaction of C-phenylation of methyl acrylate with bismuth derivatives $Ph_3Bi(O_2CR)_2$ (R = H, Me, Et, Bu, CF₃, Ph) or Ph_3BiCl_2 in a 3 : 1 ratio was studied. The reaction was performed in the presence of 4 mol % palladium compounds $PdCl_2$, $Pd(OAc)_2$, $Pd_2(dba)_3$, $Pd(Ph_3P)_2Cl_2$, and $PdLCl_2$ (L = dppm, dppe, dppp, dppb, dppf, binap, xantphos) at 50°C in CH₃CN, DMF, THF, or CH₂Cl₂ and gave methyl cinnamate (yield up to 85% based on the starting bismuth compound), diphenyl (up to 138%), and benzene (up to 59%).

Organobismuth compounds are mild reagents for formation of C-C bonds in reactions with phenols, enols, β -diketones, and β -keto esters [1, 2]. C-Phenylation of unsaturated compounds with bismuth derivatives was performed for the first time by Asano [3]. In that study, styrene was converted into stilbene by the reaction with Ph₃Bi in the presence of a stoichiometric amount of $Pd(OAc)_2$ at 50°C. The same system was later used for phenylation of octene, ethyl acrylate [4], and methyl acrylate [5]. The interest in couplings of organobismuth compounds in the presence of catalytic amounts of palladium compounds recently increased. Among such reactions are C-phenylation of alkenes with bismuthonium salts [6] or diphenylbismuth chloride [7] and carbonylation of triphenylbismuth to obtain ketones [8]. In all the coupling reactions, diphenyl was formed in significant amounts as by-product. The homocoupling of organometallic compounds of Bi(III, V) to diaryls in the presence of palladium compounds was specially studied in [9, 10].

We found recently that triarylantimony dicarboxylates are efficient and mild agents for C-arylation of unsaturated compounds. In an argon atmosphere, one phenyl group is transferred to the unsaturated compound, and in an oxygen atmosphere, two phenyl groups are transferred [11, 12]. Proceeding with these studies, we tested in similar reactions triphenylbismuth dicarboxylates and compared them with the corresponding antimony derivatives. For this purpose, we prepared the compounds Ph_3BiX_2 in one step by the reactions of Ph_3Bi with acids in the presence of *t*-BuOOH (20°C, 24 h):

 $\begin{array}{l} {\rm Ph_{3}Bi+2HX+t\text{-}BuOOH} \longrightarrow {\rm Ph_{3}BiX_{2}+t\text{-}BuOH+H_{2}O}, \\ {\rm X} \ = \ {\rm O_{2}CH} \ (85\%), \ {\rm OAc} \ (80\%), \ {\rm O_{2}CEt} \ (70\%), \ {\rm O_{2}CBu} \\ (62\%), \ {\rm O_{2}CCF_{3}} \ (40\%), \ {\rm O_{2}CPh} \ (65\%). \end{array}$

The resulting bismuth derivatives were used for C-phenylation of methyl acrylate in the presence of catalytic amounts of palladium. The reaction of triphenylbismuth dipropionate with methyl acrylate I was performed in the presence of catalytic amounts of PdCl₂ in acetonitrile at 50°C for 3 h. The reactant ratio was $Ph_3Bi(O_2CEt)_2$: I: PdCl₂ = 1:3:0.04. $Ph_3Bi(O_2CEt)_2$ was chosen as the starting organometallic compound taking into account high phenylating activity of the corresponding antimony derivative under similar conditions [11, 12]. Methyl acrylate I is a convenient model compound. It is very reactive and is selectively phenylated at the trans position to methyl cinnamate II. Ester I was taken in a threefold excess relative to the organometallic compounds, because all the three phenyl groups in triphenylbismuth dicarboxylate can be involved in the reaction:

$$\begin{array}{c} Ph_{3}Bi(O_{2}CEt)_{2} + CH_{2}=CHCO_{2}Me\\ \mathbf{I}\\ \hline \mathbf{I}\\ \hline \frac{PdCl_{2}}{CH_{3}CN} \end{array} PhCH=CHCO_{2}Me + Ph_{2} + PhH.\\ \mathbf{II} \qquad \mathbf{III} \qquad \mathbf{IV} \end{array}$$

We obtained the following phenyl-containing compounds: methyl cinnamate **II** (cross-coupling product, yield 53%), diphenyl **II** (homocoupling product, yield 105%), and a small amount of benzene (yield 6%) (Table 1, run no. 1). Here and hereinafter, the yield is given in mol % based on the starting organometallic compound.

The first step of the process involves generation of the active catalyst species Pd(0) in the course of the metal interchange of PdX_2 with the starting organometallic compound, C-phenylation of ester I, and decomposition of palladium hydride in accordance with scheme I. Then Pd(0) enters into the redox reaction with Ph_3BiX_2 to form the phenylpalladium intermediate PhPdX, which then either phenylates ester I to compound II with the release of acid HX or undergoes metal interchange with the starting organometallic compound to form a diphenylpalladium intermediate whose decomposition without participation of ester I gives diphenyl [scheme (2)]:

$$Ph_{3}BiX_{2} + PdX_{2} \longrightarrow Ph_{2}BiX_{3} + [PhPdX], \quad (1)$$

$$CH_{2}=CHCO_{2}Me + [PhPdX]$$

$$\longrightarrow PhCH=CHCO_{2}Me + [HPdX], \quad [HPdX] \longrightarrow Pd(0) + HX, \quad Ph_{3}BiX_{2} + Pd(0) \xrightarrow{-Ph_{2}BiX} PhPdX$$

$$CH_{2}=CHCO_{2}Me \longrightarrow PhCH=CHCO_{2}Me + Pd(0), \quad (2)$$

Influence of the kind of the catalyst. The results of experiments with different salts and complexes of Pd(0, II) as catalysts are given in Table 1. With $Pd_2(dba)_3$ (dba is dibenzylideneacetone), the selectivity was approximately the same as with PdCl₂ (yield of II 70%, yield of diphenyl 112%; Table 1, run no. 2). With Pd(OAc)₂, the phenylation was less efficient (yield of II 29%, yield of III 123%; Table 1, run no. 3). The presence of the monodentate ligand Ph_3P in the coordination sphere of Pd drastically decreased the yield of the target product II (to 6%), but exerted no effect on the yield of the homocoupling product (Table 1, run no. 4). With excess Ph₃P (4 mol per mole of Pd), no compound II was obtained at all, and the yield of III increased to 138%, approaching the theoretical maximum of 150% (Table 1, run no. 5). Thus, triphenylphosphine does not suppress the catalytic homocoupling of the organobismuth compound but suppresses the concurrent catalytic cross-coupling with ester I [scheme (2)].

The effect of diphosphines is more complex. Diphosphines are arranged in Table 1 (run nos. 6–13) in the order of increasing bite angle α [13]. With the aim to improve the selectivity of the process, we tested the following ligands: dppm, bis(diphenylphosphino)-methane, α 72°; dppe, 1,2-bis(diphenylphosphino)ethane, α 85°; dppp, 1,3-bis(diphenylphosphino)propane, α 91°; binap, α 92°; dppf, 1,1'-bis(diphenylphosphino)ferrocene, α 96°; dppb, 1,4-bis(diphenylphosphino)butane, α 99°; and xantphos, α 111°.

In this series, dppe occupies a particular place: It catalyzes neither homo- nor cross-coupling (Table 1, run no. 8). This ligand forms a very stable five-mem-

Table 1. Influence of the kind of the catalyst on the product yields in phenylation of methyl acrylate I with the system $Ph_3Bi(O_2CEt)_2$ -[Pd], $1:0.04^a$

Run no.	Catalyst	Yield, % ^b		
		II	Ph ₂	PhH
1	PdCl ₂	53	105	6
2	$Pd_2(dba)_3$	70	112	3
3	$Pd(OAc)_2$	29	123	Traces
4	$Pd(PPh_3)_2Cl_2$	6	109	5
5	$PdCl_2 + 4PPh_3$	0	138	5
6	$PdCl_2 + dppm$	43	127	5
7	$PdCl_2 + 2dppm$	7	131	4
8	$PdCl_2 + dppe$	9	11	Traces
9	$PdCl_2 + dppp$	15	82	6
10	$PdCl_2 + dppb$	26	98	13
11	$PdCl_2 + dppf$	21	107	11
12	$PdCl_2 + binap$	49	92	29
13	$PdCl_2$ + xantphos	32	121	11

^a The reactions were performed in CH₃CN at 50°C for 3 h in the presence of air. ^b Based on Ph₃Bi(O₂CEt)₂.



bered chelate ring with Pd. Such an anomalous behavior of dppe is well-known [13].

With the other diphosphines, the yield of **III** remained high (82–127%), but the yield of **II** decreased. This trend was particularly pronounced with dppf and dppb (yield of **II** 21 and 26%, respectively; Table 1, run nos. 11, 10) and less pronounced with binap and dppm (49 and 43%, respectively; Table 1, run nos. 12, 6). It is interesting that with a twofold excess of dppm the yield of **II** drastically decreases (to 7%), and compound **III** becomes the prevailing reaction product (131%, Table 1, run no. 7). This fact can be accounted for as follows. The four-membered chelate ring formed by dppm with Pd is highly strained. The strain is eliminated by the ring opening, leaving a site for the coordination of methyl acrylate:



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Table 2. Influence of the acid residue X in the starting organometallic compound on the product yields in phenylation of methyl acrylate I with the system $Ph_3BiX_2-PdCl_2$, $1:0.04^a$

Dun no	Х	Yield, %		
Kun no.		II	Ph ₂	PhH
1	O ₂ CH	70	46	59
2	OÃc	26	127	3
3	O_2CEt	53	105	6
4	0 ₂ CBu	57	100	18
5	$O_2 CCF_3$	59	55	41
6	O_2 CPh	85	75	54
7 ^b	O_2 CPh	37	86	6
8 ^c	$O_2^{-}CPh$	31	126	4
9 ^d	CĨ	72	51	18
				1

^a The reactions were performed in CH₃CN at 50°C for 3 h in air. ^b Reaction in the presence of K₂CO₃, 1 mol per mole of organometallic compound. ^c Reaction in the presence of Et₃N, 1 mol per mole of organometallic compound. ^d PhCl (20%) was also detected.

With a twofold excess of dppm, this vacancy is occupied by the second dppm molecule:



It should be noted that the yield of **IV** was low (0-29%) with all the palladium catalysts.

Thus, $PdCl_2$ and $Pd_2(dba)_3$ are the most efficient catalysts for C-phenylation of **I** with triphenylbismuth dicarboxylates, as well as with triphenylantimony dicarboxylates [12]. In the subsequent experiments we used $PdCl_2$ as a simpler and cheaper catalyst.

Solvent effect. As solvents for the reaction system $Ph_3Bi(O_2CPh)_2$: **I** : $PdCl_2 = 1:3:0.04$, we used, along with CH_3CN , also CH_2Cl_2 , THF, and DMF. The reaction was performed at 50°C for 3 h. In CH_2Cl_2 , THF, and DMF, the yield of **II** was considerably lower than in CH_3CN : 11, 30, 32, and 85%, respectively; the yield of **III** remained approximately the same (68–77%), and the yield of benzene **IV** was 23, 18, 4, and 54%, respectively. Thus, in acetonitrile the extent of the reaction and the yield of **II** were the highest. In this respect, compounds $Ph_3Bi(O_2CR)_2$ are similar to $Ph_3Sb(O_2CR)_2$ [12].

The influence of the acid residue X in the starting organobismuth compound was studied with the system $Ph_3BiX_2 : I : PdCl_2 = 1 : 3 : 0.04$ as example. The

reaction was performed at 50°C for 3 h in acetoninitrile. All the triphenylbismuth dicarboxylates entered into C-phenylation of methyl acrylate (Table 2). The yields of **II** were the highest with the diformate and dibenzoate (70 and 85%, respectively), with moderate yields of **III** (46 and 75%; Table 2, run nos. 1, 6). Approximately equal yields of II, 53-59%, were obtained with triphenylbismuth dipropionate, divalerate, and bis(trifluoroacetate) (Table 2, run nos. 3-5). The diacetate, Ph₃Bi(OAc)₂, appeared to be the least efficient: The yield of **II** was the lowest (26%), and the yield of IV, the highest (127%) (Table 2, run no. 2). Thus, under the reaction conditions, the activity of C-phenylating agents Ph₃Bi(O₂CR)₂ does not correlate with the strength of acids RCO₂H. The similar pattern was observed previously with $Ph_3Sb(O_2CR)_2$ [12].

With the derivatives of strong acids (formic, trifluoroacetic, benzoic), the yields of benzene **IV** reach 41-59% and approach the yields of the cross- and homocoupling products (Table 2, run nos. 1, 5, 6). Benzene is a secondary product of the reaction of Bi(III) phenyl compounds with acids formed by scheme (1):

$$Bi(III)-Ph + HX \longrightarrow Bi(III)-X + PhH.$$

To decrease the yield of benzene, the reaction with triphenylbismuth dibenzoate was performed in the presence of bases, K₂CO₃ and Et₃N, added to neutralize the acid. In these cases, indeed, the yield of benzene decreased from 54 to 6 and 4%, respectively. However, the yield of **II** decreased also (from 85 to 37 and 31%), and the yield of **III** increased from 75 to 86 and 126% (Table 2, run nos. 7, 8). The decreased yield of methyl cinnamate in the presence of Et₃N may be due to the fact that Et₃N, like Ph₃P, is a strong electron-donor ligand for Pd. It occupies sites in the palladium coordination sphere, preventing approach of the olefin to PhPdX. In this case, the yield of Ph_2 increases, similarly to the experiment with the addition of Ph_3P . With K_2CO_3 , an exchange reaction with Ph₃Bi(O₂CPh)₂, yielding weakly reactive triphenylbismuth carbonate, is possible:

$$Ph_3Bi(O_2CPh)_2 + K_2CO_3 \longrightarrow Ph_3BiCO_3 + 2PhCO2K.$$

Thus, additions of bases Et_3N and K_2CO_3 sharply decrease the yield of benzene but also negatively affect the main C-phenylation process.

An unexpected result was obtained in experiments on phenylation of **I** with Ph_3BiCl_2 . The yield of **II** was high (72%), and the yield of **III** was considerably lower (51%). Also we detected benzene (18%) and chlorobenzene (20%) (Table 2, run no. 9). Previously we found that triphenylantimony dihalides, in contrast to carboxylates, showed no reactivity in C-phenylation [12].

Thus, we found that triphenylbismuth dicarboxylates catalytically C-phenylate methyl acrylate in the presence of Pd(0, II) compounds under mild conditions; the yield of the target product is up to 85% based on the starting organometallic compound. The reactions involving $Ph_3Bi(O_2CR)_2$ and $Ph_3Sb(O_2CR)_2$ are characterized by similar influence of the palladium catalyst, acid residue in the organometallic compound, and solvent on the yield of the phenylation product. However, there are some differences.

(1) The organobismuth compounds are more reactive. The elimination of phenyl groups is complete in 3 h at 50°C. This is due to the lower strength of the Bi–C bond [14].

(2) Being more active, compounds $Ph_3Bi(O_2CR)_2$ are less selective than $Ph_3Sb(O_2CR)_2$. Whereas the antimony derivatives yield methyl cinnamate as a single phenylation product, the bismuth derivatives also yield diphenyl and benzene.

(3) Introduction of tertiary mono- and bidentate phosphine ligands into the coordination sphere of palladium results in complete loss of the reactivity of $Ph_3Sb(O_2CR)_2$ [12], whereas with $Ph_3Bi(O_2CR)_2$ in most cases the cross-coupling rate only decreases to a certain extent depending on the structure of the phosphine and the homocoupling rate remains unchanged. This distinction is caused by the weaker steric demands of the homocoupling compared to cross-coupling.

(4) Whereas the bismuth compounds Ph_3BiX_2 are active with both X = chloride and X = carboxylate, the compounds Ph_3SbX_2 are active only with X = carboxylate, because only the carboxy group renders anchimeric assistance in the slow step of the metal interchange involving Pd and Sb [12].

EXPERIMENTAL

The volatile products were analyzed by GLC on an LKhM-80 chromatograph equipped with a flameionization detector; carrier gas He. Benzene was determined with a 300-cm column, stationary phase 15% dinonyl phthalate on Chromaton N-AW-DMCS, 80°C; methyl cinnamate and diphenyl were determined with a 240-cm column, stationary phase 15% Apiezon L on Chromaton N-AW-DMCS, 220°C; chlorobenzene was determined with the same column at 130°C.

t-BuOOH, Pd(OAc)₂, Pd₂(dba)₃, and Pd(Ph₃P)₂Cl₂ were prepared according to [15–18], respectively.

 $PdCl_2$, dppm, dppe, dppp, dppb, dppf, binap, and xantphos are commercially available. Methyl acrylate was shaken with an alkali until the yellow color disappeared, dried over Na_2SO_4 , and distilled. All the solvents were purified by distillation.

Ph₃Bi(O₂CH)₂. To a solution of 2.2 g of triphenylbismuth in 20 ml of Et_2O , we added 0.38 ml of formic acid, after which we added slowly with cooling 0.53 ml of *t*-BuOOH. The mixture was left for 24 h in the dark at room temperature. The crystalline precipitate thus obtained was filtered off on a glass frit, dried, and recrystallized from methylene chloride– hexane, 1:4; yield 2.1 g (80%), mp 150–152°C (with decomposition) {published data [2]: mp 140– 150°C (with decomposition)}.

The other organobismuth compounds were prepared similarly: triphenylbismuth diacetate, mp 187– 189°C (published data [2]: 187–189°C); triphenylbismuth dipropionate, mp 156°C (published data [2]: 157–159°C); triphenylbismuth divalerate, mp 89°C (published data [2]: 91°C); triphenylbismuth bis(trifluoroacetate), mp 143–144°C (published data [2]: 143– 144°C); triphenylbismuth dibenzoate, mp 166–168°C (published data [2]: 167–169°C).

Reaction of $Ph_3Bi(O_2CH)_2$ with methyl acrylate and $PdCl_2$ (1:3:0.04) in acetonitrile at 50°C for 3 h in air. A mixture of 0.265 g of $Ph_3Bi(O_2CH)_2$, 0.0036 g of $PdCl_2$, 0.135 ml of methyl acrylate, and 6 ml of acetonitrile was placed in a 50-ml ampule with a silicone stopper and heated in an oven at 50°C for 3 h. Then the liquids were distilled off under reduced pressure. The residue was passed through a silica gel column using hexane–ethyl acetate, 4 : 1, as eluent. The condensate and filtrate were analyzed by GLC for the content of volatiles.

The phenylation with the other organometallic compounds and in other solvents was performed similarly.

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