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Study of homo- and cross-coupling competition in the reaction of triarylbismuth(V) dicarboxylates with methyl acrylate in the presence of a palladium catalyst

Dmitry V. Moiseev [a,*], Yulia B. Malysheva [a], Andrey S. Shavyrin [b], Yury A. Kurskii [b], Aleksey V. Gushchin [a]

[a] Department of Organic Chemistry, Nizhny Novgorod State University, 23 Gagarin Avenue, 603950 Nizhny Novgorod, Russia
[b] G.A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, GSP-445, 49 Tropinin Street, 603950 Nizhny Novgorod, Russia

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Abstract

Triarylbismuth(V) derivatives $Ar_3Bi(O_2CR)_2$ (Ar = Ph, *m*-Tol, *p*-Tol; R = H, Me, Et, *n*-Bu, *t*-Bu, *n*-C_5H_{11}, CF_3, CH_2Cl, CCl_3, Ph) were prepared in good to excellent yields by reaction of Ar_3Bi with equimolar amounts of *t*-BuOOH in the presence of an acid. These compounds were tested in the C-arylation reaction of methyl acrylate, as a model substrate, in the presence of palladium catalyst (4 mol%). It was found that triphenylbismuth dicarboxylates are very active phenylating agents under mild conditions (20 °C). The effect of the carboxylic group, the effect of the nature of the palladium catalyst and the effect of oxygen on the reactivity of the organobismuth compounds and on the selectivity of the C-arylation reaction were studied. Methyl cinnamate, the C-phenylation product, and biphenyl, the homo-coupling by-product, were obtained in all cases. Triphenylbismuth divalerate $Ph_3Bi(O_2CBu)_2$ is the most reactive compound among the triphenylbismuth dicarboxylates studied.

Keywords: Bismuth(V); Arylation; Palladium; Homo-coupling; Cross-coupling

1. Introduction

Application of heteroatom-containing compounds in organic synthesis is a rapidly growing area of research. Recently, we showed that some types of organoantimony(V) derivatives are efficient agents in the palladium-catalyzed C-arylation reaction of unsaturated compounds under mild conditions. Triarylantimony(V) dicarboxylates $Ar_3Sb(O_2CR)_2$ in the presence of $PdCl_2$ arylate selectively unsaturated compounds with involvement of one aryl group of the antimony derivative under inert atmosphere and of two aryl groups in the presence of oxygen [1–3]. Tetraarylantimony(V) derivatives Ar_4SbX (X = Hal, O_2CR) perform the palladium-catalyzed C-phenylation reaction of unsaturated compounds with transfer of one aryl group of the antimony derivative [4]. However, in the presence of peroxide three aryl groups are involved in the reaction [1].

In continuation of our research, we studied the application of triarylbismuth dicarboxylates in the C-phenylation reaction. Due to the low energy of the C–Bi bond the organobismuth derivatives are highly reactive and could be applied for a new C–C bond formation under very mild conditions. Organobismuth compounds are currently receiving much interest [5]. There are several examples of palladium-mediated conversions of a C–Bi bond into a C–C bond. Cross-coupling have been observed in the reaction of Ar_3Bi with acyl chloride [6], aryl halides and triflates [7], allyl halides [8] and in the

* Corresponding author. Tel.: +7 831 2337865; fax: +7 831 2658592.
E-mail address: moisdv@mail.nnov.ru (D.V. Moiseev).

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reaction of organobismuth dialkoxides with aryl or alkenyl triflates and aryl halides [9,10]. Pentavalent triarylbismuth compounds Ar_3BiX_2 (X = Hal, OAc) have been used in the palladium-catalyzed cross-coupling reaction with hypervalent iodonium salts at room temperature [11]. The homo-coupling of organobismuth compounds has also been studied [6,12]. Triarylbismuth has been used in the carbonylation reaction as well [13]. Arylation of vinyl epoxides, diol acetonides and diol carbonates has been performed with both triarylbismuth(III) and triarylbismuth(V) dichloride or carbonate [14]. Several types of organobismuth(III) compounds have been tested in Heck-type reactions [15–17]. Bismuth ylides have been used to study a homo- and cross-coupling competition [18].

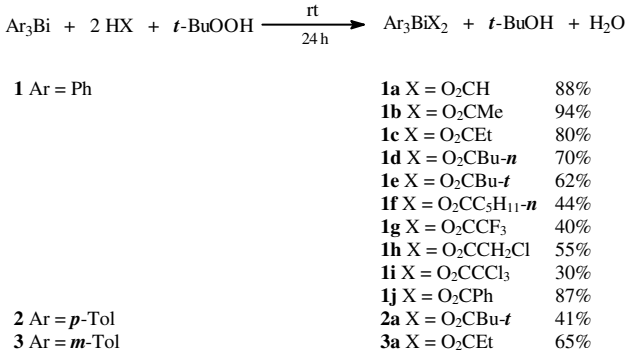
2. Results and discussion

2.1. Synthesis of Ar_3BiX_2

The organobismuth dicarboxylates $Ar_3Bi(O_2CR)_2$ were obtained in moderate to good yields by the one-step reaction of triarylbismuth with the appropriate carboxylic acid in the presence of equimolar amounts of peroxide (Scheme 1) [19].

2.2. Reaction of Ph_3BiX_2 with methyl acrylate at 50 °C

The organobismuth(V) dicarboxylates were tested in the Heck-type C-arylation reaction of methyl acrylate **4**, which was used as a model unsaturated substrate for the cross-coupling reaction, in the presence of catalytic amounts of various palladium complexes. To compare the reactivity of the organobismuth compounds with that of the corresponding organoantimony derivatives the reactions were initially carried out under the same conditions used for the antimony compounds: in acetonitrile at 50 °C for 3 h, under air with ratio between [Bi(V)], **4** and [Pd] of 1:3:0.04. The *trans*-arylation products, the cinnamic acid derivatives **5a**–**c**, and the biaryl



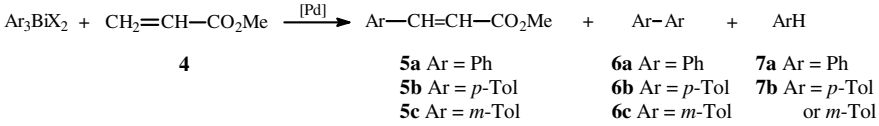
Scheme 1.

derivatives **6a**–**c**, the homo-coupling products, were found in all cases. In some cases formation of aromatic hydrocarbons (**7a**–**b**) also occurred (Scheme 2).

The nature of the palladium catalyst as well as the presence of additional ligands affect the yields of the reaction products (Table 1). In all cases the main reaction product is biphenyl **6a**. Among the catalysts studied in the C-phenylation reaction of **4** with triphenylbismuth dipropionate $Ph_3Bi(OEt)_2$ **1c** $PdCl_2$ is the most effective toward the formation of the cross-coupling product **5a** (53%) with a **5a/6a** ratio of 0.5 (Table 1, entry 1). The 100% yield of methyl cinnamate or benzene relates to the involvement of one phenyl group of the starting organometallic compounds, whereas the 100% yield of biphenyl relates to the involvement of two phenyl groups. Another palladium salt $Pd(OAc)_2$ shows the same activity in terms of phenyl group involvement (275%), but the selectivity of the C-phenylation process (or the **5a/6a** ratio) is lower (Table 1, entry 2) than that obtained with $PdCl_2$. The presence of triphenylphosphine in the coordination sphere of palladium does not affect the homo-coupling reaction (Table 1, entries 3 and 4). At the same time, the yield of **5a** decreases dramatically, and in the case of large excess of Ph_3P ligand the cross-coupling reaction is stopped completely (Table 1, entry 4). Under these conditions, the Ph_3P ligands bind too strongly to the palladium center to allow the exchange reaction with **4** to produce **5a**.

The use of diphosphines such as dppm [*bis*(diphenylphosphino)methane], dppe [1,2-*bis*(diphenylphosphino)ethane], dppp [1,3-*bis*(diphenylphosphino)propane], dppb [1,4-*bis*(diphenylphosphino)butane] also affects the reaction. In the case of dppm the total yield of the reaction is the highest (300%) and corresponds the full involvement of all phenyl groups of the starting compound **1c** (Table 1, entry 5). However, the selectivity of the cross-coupling process is lower (0.34) than that obtained using the $PdCl_2$ catalyst. The palladium catalyst with dppe ligand has the lowest activity. Methyl cinnamate **5a** and biphenyl **6a** were obtained in 9% and 11% yield, respectively (Table 1, entry 7). However, increasing the number of carbon atoms in the backbone chain of the diphosphine leads to higher activity of the catalyst. In the case of dppp and dppb the total involvement of phenyl groups under these conditions reaches 185% and 235%, respectively (Table 1, entries 8 and 9).

Such effect of the diphosphines is probably caused by the strain imposed by the respective bite-angles upon chelation of the phosphines to the palladium atom. In the case of dppe (bite-angle 85° [20–22]) the most stable palladium complex is formed. This complex is stable enough under these conditions to stop a catalytic cycle (Table 1, entry 7). In the case of dppm, the very strained bite-angle (72°) [20,21] causes the dissociation of one phosphorus atom. This allows a molecule of **4** to be coordinated to the palladium atom (Scheme 3, A). When



Scheme 2.

Table 1
Palladium catalyzed reaction of $Ph_3Bi(O_2CEt)_2$ **1c** with methyl acrylate **4** at 50 °C: influence of the nature of the catalyst[a]

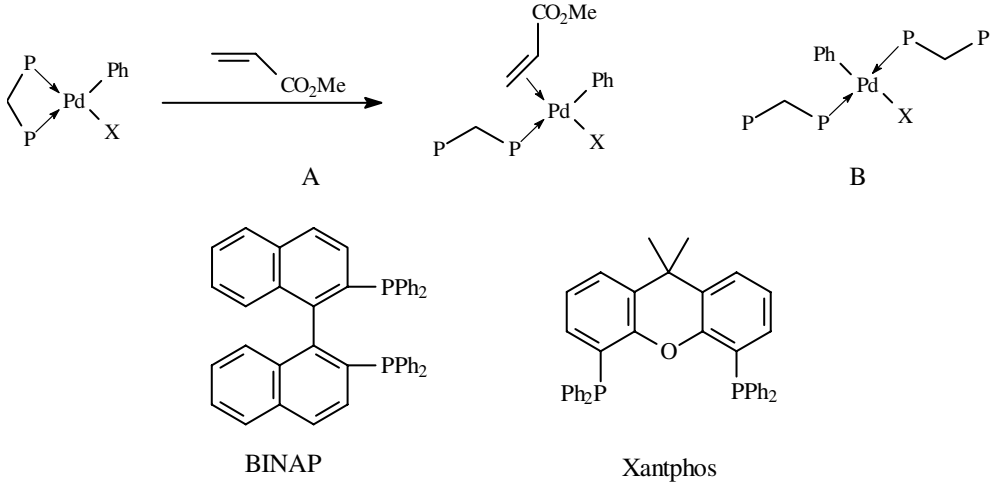
Entry	[Pd]	Yields[b](%)			**5a/6a** ratio	ΣPh (%)
		5a	**6a**	**7a**		
1	$PdCl_2$	53	105	6	0.50	269
2	$Pd(OAc)_2$	29	123	tr	0.24	275
3	$Pd(Ph_3P)_2Cl_2$	6	109	5	0.06	229
4	$PdCl_2$ + 6 Ph_3P	tr	104	0	–	208
5	$PdCl_2$ + dppm	43	126	5	0.34	300
6	$PdCl_2$ + 2 dppm	7	132	4	0.05	275
7	$PdCl_2$ + dppe	9	11	tr	0.82	31
8	$PdCl_2$ + dppp	15	82	6	0.18	185
9	$PdCl_2$ + dppb	26	98	13	0.27	235
10	$PdCl_2$ + BINAP	49	92	29	0.53	262
11	$PdCl_2$ + Xantphos	32	121	11	0.26	285

[a] The reactions were performed in CH_3CN at 50 °C for 3 h, under air with ratio between [Bi], **4** and [Pd] of 1:3:0.04.
[b] Yields were determined by GLC.

using a twofold excess of dppm this free coordination site is occupied by the second phosphine (Scheme 3, B) and the C-phenylation reaction is stopped (Table 1, entry 6). Diphosphines such as dppp and dppb (bite-angle 95° and 99° [21,22], respectively) also form strained and unstable complexes.

Ligands possessing a rigid structure like BINAP and xantphos were also tested. The BINAP ligand (92°) [20] gave the highest yield of **5a** (49%). The selectivity of the C-phenylation reaction was also high (0.53) (Table 1, entry 10). Besides, the highest yield of benzene **7a** (29%) was observed. The use of the xantphos ligand (111°) [20] decreased the selectivity of the C-phenylation reaction significantly. Methyl cinnamate **5a** and biphenyl **6a** were found in 32% and 121% yield, respectively (Table 1, entry 11). Thus, $PdCl_2$, employed alone, appears to be the most efficient catalytic species for this C-phenylation reaction.

Under the conditions used in the present study all triphenylbismuth dicarboxylates are reactive in the homo- and cross-coupling processes (Table 2). The selectivity of the reaction depends on the nature of the carboxylic group. The highest yield of **5a** (85%) with good selectivity (1.13) was observed in the case of triphenylbismuth dibenzoate $Ph_3Bi(O_2CPh)_2$ **1j** (Table 2, entry 5). However, benzene **7a** was also obtained in high yield (54%). In the cases of other derivatives of strong acids, such as the formate **1a** and the triflouroacetate **1g**, benzene was also found in high yield (59% and 41%, respectively) (Table 2, entries 1 and 7). Simultaneously, the selectivity of the C-phenylation reaction was high (1.52 and 1.07, respectively). The high yield of **7a** can be explained by dephenylation of the organobismuth(III) derivatives formed in the reaction with a strong acid generated during the course of the reaction. Indeed, addition of triethylamine as a base into the reaction mixture stopped the formation of benzene. However, unfortunately, the selectivity of the reaction concomitantly decreased dramatically from 1.13 to 0.25 (Table 2, entries 5 and 6). The divalerate **1d** showed similar activity to that of **1c** (Table 2, entries 3 and 4). In the case of the



Scheme 3.

Table 2
$PdCl_2$ catalyzed reaction of Ph_3BiX_2 with methyl acrylate **4** at 50 °C: influence of the nature of the substituent X[a]

Entry	X	Yields[b] (%)			**5a/6a** ratio	ΣPh (%)
		5a	**6a**	**7a**		
1	O_2CH (**1a**)	70	46	59	1.52	221
2	O_2CMe (**1b**)	26	127	3	0.20	283
3	O_2CEt (**1c**)	53	105	6	0.50	269
4	O_2CBu-*n* (**1d**)	57	100	18	0.57	275
5	O_2CPh (**1j**)	85	75	54	1.13	289
6[c]	O_2CPh (**1j**)	31	126	4	0.25	287
7	O_2CCF_3 (**1g**)	59	55	41	1.07	210
8[d]	Cl	72	51	18	1.41	212

[a] The reactions were performed in CH_3CN at 50 °C for 3 h, under air with ratio between [Bi], **4** and [Pd] of 1:3:0.04.
[b] Yields were determined by GLC.
[c] Addition of base Et_3N in amount of 1–1 mol of organobismuth compound.
[d] PhCl was found in 20% yield.

diacetate **1b** the lowest selectivity was observed (0.20). Biphenyl **6a** was the main product of the reaction (127%) (Table 2, entry 2). It was surprising that triphenylbismuth dichloride Ph_3BiCl_2 showed a high reactivity as well, unlike Ph_3SbCl_2, which was completely inactive in this reaction [2]. The C-phenylation product **5a** was obtained in 72% yield with good selectivity (1.41) (Table 2, entry 8). PhCl was also found as a by-product of the reaction in 20% yield. Thus, triphenylbismuth dibenzoate $Ph_3Bi(O_2CPh)_2$ **1j** is the best reagent among those studied for the C-phenylation reaction under these conditions.

Thus, all the organobismuth(V) dicarboxylates exhibited a very high reactivity toward both the palladium catalyzed C-phenylation reaction and the homocoupling process. Under these conditions (CH_3CN, 50 °C, 3 h, under air), generally, more than two phenyl groups are involved in the palladium-mediated processes. The phosphine ligands and the carboxylic group of the bismuth(V) derivative affect the competition between these two main processes. It was anticipated that these effects could be observed more clearly under milder conditions to understand a mechanism of the process, therefore investigations on the same reactions at room temperature were carried out, and the results are discussed in the following section.

2.3. Reaction of Ph_3BiX_2 with methyl acrylate at room temperature

Indeed, in the reaction of $Ph_3Bi(O_2CPh)_2$ **1j**, which showed the highest reactivity at 50 °C, with **4** at room temperature for 3.5 h the total involvement of phenyl groups in the reaction was 120% with almost the same selectivity (1.16) (Table 3, entry 1). When the reaction was performed for 24 h the total involvement increased to 227%. The yields of **5a** and **6a** were similar to those obtained at 50 °C (80% and 71%, respectively) (Table 3, entry 2). This reaction is less selective in the presence of other palladium catalyst. Palladium species such as $Pd_2(dba)_3$ and $Pd(OAc)_2$ showed the same activity in the production of **5a** (70%) but different selectivity (0.93 and 0.78, respectively) (Table 3, entries 3 and 4). In the case of Li_2PdCl_4 the products **5a** and **6a** were obtained in 58% and 84% yield, respectively (Table 3, entry 5). Addition of the phosphine ligands to the reaction decreases the yield of **5a**. In the case of dppm the yield of methyl cinnamate **5a** decreased from 80% in the absence of the ligand to 45%. At the same time the yield of **6a** increased from 71% to 87% (Table 3, entries 6 and 2). The addition of Ph_3P stops the reaction

Table 3
Palladium catalyzed reaction of $Ph_3Bi(O_2CR)_2$ (R = Ph or Et) with methyl acrylate **4** at room temperature: influence of the nature of the catalyst[a]

Entry	Triphenylbismuth compound	[Pd]	Yields[b] (%)			**5a/6a** ratio	ΣPh (%)
			5a	**6a**	**7a**		
1[c]	$Ph_3Bi(O_2CPh)_2$	$PdCl_2$	44	38	0	1.16	120
2		$PdCl_2$	80	71	5	1.13	227
3		$Pd_2(dba)_3$	70	75	tr	0.93	220
4		$Pd(OAc)_2$	70	90	tr	0.78	250
5		Li_2PdCl_4	58	84	tr	0.69	226
6		$PdCl_2$ + dppm	45	87	6	0.52	225
7		$Pd(Ph_3P)_2Cl_2$	0	0	0	–	0
8	$Ph_3Bi(O_2CEt)_2$	$PdCl_2$	58	96	12	0.60	262
9[d]		$Pd(Ph_3P)_2Cl_2$	4	104	12	0.04	224
10		$PdCl_2$ + dppm	12	88	0	0.14	188
11		$PdCl_2$ + BINAP	74	97	10	0.76	278
12		$PdCl_2$ + Xantphos	74	111	4	0.65	300

[a] The reactions were performed in CH_3CN at room temperature for 24 h, under air with ratio between [Bi], **4** and [Pd] of 1:3:0.04.
[b] Yields were determined by GLC.
[c] Reaction time was 3.5 h.
[d] Reaction time was 70 h.

completely (Table 3, entry 7). Benzene **7a** was found in negligible amount in all reactions of **1j** at room temperature, unlike in the reaction at 50 °C, where it was obtained in 54% yield (Table 2, entry 5).

To compare the activity of the palladium catalysts at room temperature and at 50 °C a number of reactions were carried out with the triphenylbismuth dipropionate $Ph_3Bi(O_2CEt)_2$ **1c**. $PdCl_2$ did not show significant changes in activity and selectivity. The yields of **5a** and **6a** were 58% and 96%, respectively (Table 3, entry 8). However, Ph_3P reduces the activity more effectively at room temperature than at 50 °C. Only after 3 days biphenyl **6a** was obtained as the main product in 104% yield. **5a** was obtained in 4% yield (Table 3, entry 9). In the case of dppm the yield of **5a** decreased from 43% at 50 °C to 12% at room temperature. The selectivity of the C-phenylation reaction also decreased from 0.34 to 0.14 (Table 1, entry 5, Table 3, entry 10). This fact can be explained by invoking higher stability of the bidentate palladium complex under milder conditions. The use of the rigid diphosphines such as BINAP or xantphos leads to improvement in the yield of **5a** and in the selectivity of the C-phenylation process. In the case of the BINAP ligand the yield of **5a** increased from 49% to 74%, the yield of **6a** almost did not change and was 97% (Table 1, entry 10, Table 3, entry 11). In the case of the xantphos ligand the yield of **5a** increased more significantly, from 32% to 74%. The yield of **6a** decreased slightly (Table 1, entry 11, Table 3, entry 12).

The carboxylic group affects the reactivity of organobismuth compounds and the selectivity of the C-phenylation process. To understand this effect triphenylbismuth dicarboxylates were tested in the C-phenylation reaction at room temperature. The triphenylbismuth divalerate $Ph_3Bi(O_2CBu\text{-}n)_2$ **1d** is the most reactive triphenylbismuth derivative among those studied. The total involvement of phenyl groups in this case is 298%. The cross- and homo-coupling products were obtained in 92% and 103% yield, respectively (Table 4, entry 4). The bismuth derivatives containing less carbon atoms in the carboxylic group showed lower reactivity. This reactivity decreased in the order: **1d** (298%) > **1c** (262%) > **1b** (248%) > **1a** (170%), and the yields of **5a** decreased correspondingly (92%, 58%, 34% and 38%, respectively). (Table 4, entries 1–4). However, the yields of **6a** did not change significantly in the cases of the valerate **1d**, propionate **1c** or acetate **1b**. Only in the case of the formate **1a** the yield decreased to 35%, but the yield of **7a** increased considerably (62%) (Table 4, entry 1). The reactivity of organobismuth compounds decreases also when derivatives containing more bulky carboxylic groups, $Ph_3Bi(O_2CBu\text{-}t)_2$ **1e** or $Ph_3Bi(O_2C\text{-}C_5H_{11}\text{-}n)_2$ **1f**, are used. In the case of **1e**, methyl cinnamate **5a** and biphenyl **6a** were obtained in 85% and 83% yield, respectively (Table 4, entry 5). In the case of **1f** the corresponding yields were 72% and 91%, respectively (Table 4, entry 6). The presence of electron-withdrawing atoms in the carboxylic group also decreases the reactivity of the organobismuth compound. The involvement of phenyl groups decreases in the order: acetate **1b** (248%) > monochloroacetate **1h** (203%) > trichloroacetate **1i** (39%) (Table 4, entries 2, 9 and 10). However, at the same time the selectivity of the C-phenylation reaction increases from 0.32 in the case of **1b** to 1.40 in the case of **1i**. The triphenylbismuth bis(triflouroacetate) $Ph_3Bi(O_2CCF_3)_2$ **1g** also showed low reactivity. The products **5a** and **6a** were obtained in 28% and 23% yield, respectively (Table 4, entry 8). Thus, the nature of the carboxylic group has a strong effect on the reactivity of the organobismuth compounds and on the selectivity of the C-phenylation reaction. Triphenylbismuth divalerate $Ph_3Bi(O_2CBu\text{-}n)_2$ is the most effective among triphenylbismuth(V) dicarboxylates studied in the reaction. The organobismuth derivatives containing the

Table 4
$PdCl_2$ catalyzed reaction of Ph_3BiX_2 with methyl acrylate **4** at room temperature: influence of the nature of the substituent X[a]

Entry	X	Yields[b] (%)			**5a/6a** ratio	ΣPh (%)
		5a	**6a**	**7a**		
1	O_2CH (**1a**)	38 (20)[c]	35 (25)	62 (51)	1.09 (0.80)	170 (121)
2	O_2CMe (**1b**)	34 (15)	107 (52)tr (14)	0.32 (0.28)	248 (133)	
3	O_2CEt (**1c**)	58 (39)	96 (69)	12 (16)	0.60 (0.57)	262 (193)
4	$O_2CBu\text{-}n$ (**1d**)	92 (53)	103 (69)	tr (28)	0.89 (0.77)	298 (219)
5	$O_2CBu\text{-}t$ (**1e**)	85 (54)	83 (45)	5 (31)	1.02 (1.20)	253 (175)
6	$O_2CC_5H_{11}\text{-}n$ (**1f**)	72	91	5	0.79	259
7	O_2CPh (**1j**)	80 (23)	71 (36)	5 (31)	1.13 (0.64)	227 (126)
8	O_2CCF_3 (**1g**)	28 (20)	23 (45)	0 (3)	1.22 (0.44)	74 (113)
9	O_2CCH_2Cl (**1h**)	53 (22)	57 (52)	33 (53)	0.93 (0.42)	203 (181)
10	O_2CCCl_3 (**1i**)	14 (15)	10 (14)	5 (8)	1.40 (1.07)	39 (51)
11[d]	Cl	54	39	10	1.38	227

[a] The reactions were performed in CH_3CN at room temperature for 24 h, under air with ratio between [Bi], **4** and [Pd] of 1:3:0.04.
[b] Yields were determined by GLC.
[c] Yields of products in the reaction under argon are indicated in brackets.
[d] Methyl hydrocinnamate and PhCl were found in 21% and 4% yield, respectively.

stronger electron-withdrawing carboxylic groups have the lowest reactivity. The selectivity of the C-phenylation reaction is higher at room temperature than that at 50 °C.

The effect of the solvent was studied in the reaction of the valerate **1d** with **4** (1:3). Acetonitrile has a determinant effect on the yield of the products (Table 4, entry 4). When DMF or THF were used the yield of **5a** decreased dramatically (31% and 23%, respectively). At the same time, however, the yields of **6a** are similar to those in acetonitrile, 84% and 100%, respectively. The yields of both products become lower in benzene, CH_2Cl_2 or hexane: 6–17% for the C-phenylation product, 34–78% for the biphenyl. Thus, acetonitrile is the best solvent for the C-phenylation reaction with the organobismuth compounds.

Oxygen plays an important role in the C-arylation reaction of olefins with triarylantimony dicarboxylates [2]. To establish the effect of oxygen on the C-phenylation process with triphenylbismuth dicarboxylates some reactions were carried out under inert atmosphere. The results of these reactions are shown in brackets in Table 4. The reactivity of the organobismuth compounds and the selectivity of the C-phenylation reaction decreased significantly in almost all cases. The reactivity of the triphenylbismuth dicarboxylates depends on the electron-withdrawing properties of the carboxylic group, as reflected by the pK_a values. Indeed, as it can be seen in Fig. 1, the involvement of phenyl groups of the starting organobismuth compounds both under air and inert atmosphere decreases according to the pK_a value. In the cases of the stronger acids the effect of oxygen is negative: the involvement of phenyl groups in the reactions with **1i** (pK_a = 0.70) and **1g** (pK_a = 0.23) is lower under air than that under argon. In the case of the weaker acids this effect is positive: the involvement of phenyl groups increases in the presence of oxygen. The effect of oxygen is more marked in the cases of acids with pK_a values higher than 4. Among all the organobismuth compounds studied, the valerate **1d** (pK_a = 4.82) showed the highest reactivity both under air and inert atmosphere (298% and 219%, respectively) (Table 4, entry 4). The propionate **1c** (pK_a = 4.87) and the pivalate **1e** (pK_a = 5.03) showed slightly lower reactivity both under air and argon (Table 4, entries 3 and 5). In the case of **1e**, an increased steric hindrance in the compound can account for this observation. Although the acetate **1b** (pK_a = 4.75) and the propionate **1c** have pK_a values close to that of **1d**, their lower reactivity is probably due to the lower solubility of the corresponding organobismuth(III) intermediates. The monochloroacetate **1h** (pK_a = 2.85) and the formate **1a** (pK_a = 3.75) are between the bismuth(V) derivatives of the stronger acids and of the weaker acids and the effect of oxygen is positive for both (Fig. 1). The activity of **1h** is higher under argon than that of the acetate **1b**, while the order is reversed under air.

2.4. Possible reaction pathways

The general mechanism of the Heck-type palladium catalyzed C-arylation reaction of alkenes is now well established [23,24]. The catalytic cycle includes four

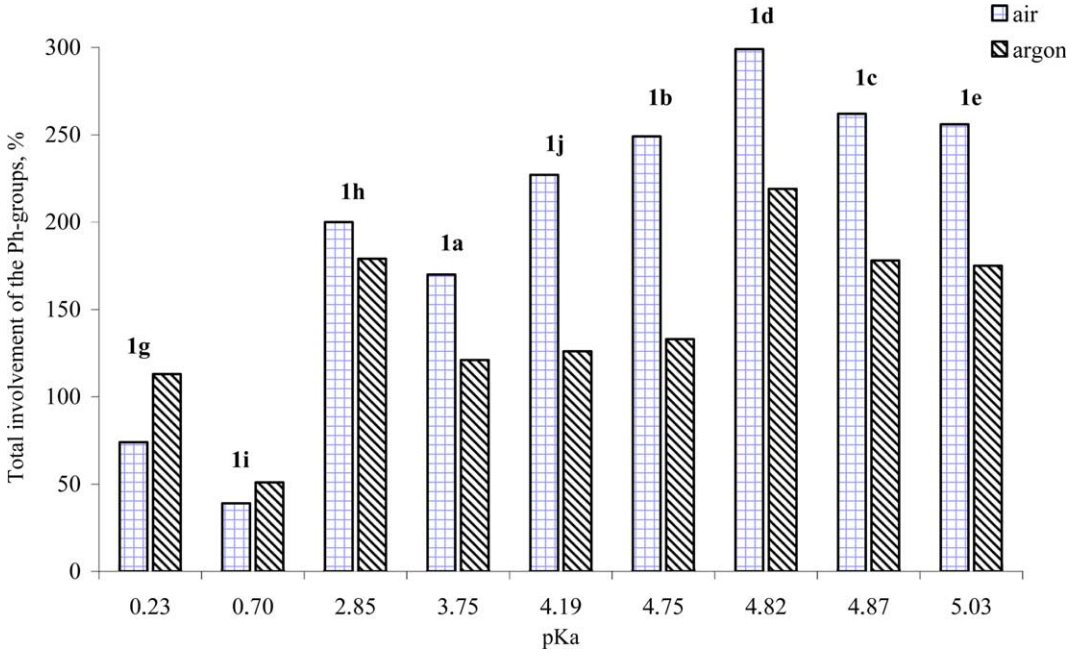
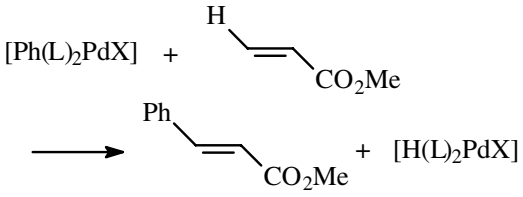


Fig. 1. Effect of the pK_a value of the acids included in the triphenylbismuth dicarboxylates and the reaction atmosphere on the total involvement of phenyl groups. The reactions were performed in CH_3CN at room temperature for 24 h with the ratio [Bi]:**4**:$PdCl_2$ (1:3:0.04).

main steps: activation of the catalyst, oxidative addition, migratory insertion and palladium hydride elimination [24]. Although the mechanism of the investigated reaction with triarylbismuth dicarboxylates is not fully elucidated, we assume that the key process, the C-phenylation reaction, occurs in a similar way to that for triarylantimony(V) dicarboxylates studied previously [1,2].

When Pd(II) salts are used as the catalyst, a transmetallation reaction to yield a phenylpalladium intermediate likely occurs in the first step (Eq. (1)). This intermediate participates directly in the C-phenylation reaction with formation of palladium hydride species (Eq. (2)), which are known to decompose by reductive elimination to an acid and an active $L_2Pd(0)$ species (Eq. (3)), where L can be phosphine, solvent, olefin or organobismuth(III) derivative. The $L_2Pd(0)$ species are oxidized by the initial organobismuth(V) compound to give again the phenylpalladium intermediate (Eq. (4)).

$$Ph_3BiX_2 + (L)_2PdX_2 \rightarrow [Ph(L)_2PdX] + Ph_2BiX_3 \quad (1)$$



(2)

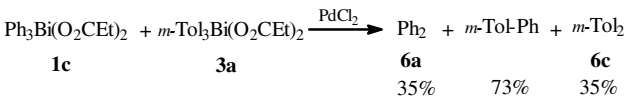
$$[H(L)_2PdX] \rightarrow (L)_2Pd + HX \quad (3)$$

$$Ph_3BiX_2 + (L)_2Pd \rightarrow [Ph(L)_2PdX] + Ph_2BiX \quad (4)$$

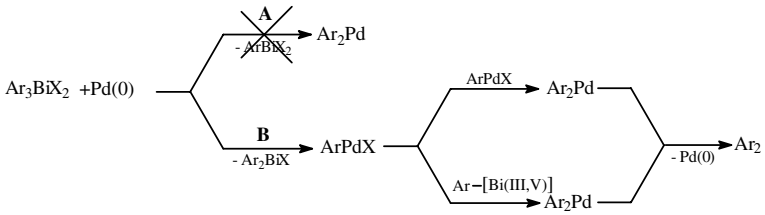
In the case of triarylantimony(V) derivatives the nature of the X group has a strong effect on the oxidative addition process. Palladium insertion along the Ph–Sb bond of triphenylantimony dicarboxylates occurs with the participation of a carboxylic group. Conversely, all halides Ph_3SbX_2 (X = F, Cl, Br) show a very low or no reactivity [2]. The triphenylbismuth(V) derivatives are more reactive due to the lower energy of the Ph–Bi bond. Ph_3BiCl_2 has a similar activity to that of the triphenylbismuth dicarboxylates (Tables 2 and 4). Another difference between antimony and bismuth derivatives is the effect of phosphines on the transmetallation and the oxidative addition steps. The presence of strongly binding ligands such as Ph_3P in the coordination sphere of palladium induces a substantial steric hindrance in both of these steps in the case of the triphenylantimony dicarboxylates and the reaction is stopped [2]. Contrast to that, as it can be seen in Tables 1 and 3, the presence of phosphine ligands affects the C-phenylation reaction of **4** with the triphenylbismuth dicarboxylates (Eq. (2)), decreasing the yield of **5a**, and does not affect the homo-coupling process. This fact indicates that the transmetallation and the oxidative addition take place even if the palladium catalyst contains bulky ligands. However, it should be noted that $Ph_3Bi(O_2CPh)_2$ **1j** does not react with the palladium complex containing Ph_3P as a ligand (Table 3, entry 7), unlike the triphenylbismuth dicarboxylates containing alkyl radical in a carboxylic group (Table 1, entry 3 and Table 3, entry 9).

According to the mechanism described above (Eq. (1)–(4)), one phenyl group of the triphenylbismuth derivative is involved in the C-phenylation reaction and the yield of **5a** could reach 100%. However, consumption of phenyl groups on side-reactions decreases this yield. The homo-coupling product, biphenyl **6a**, could be formed by several ways: the palladium-mediated reaction via the Ph_2Pd species or self-coupling of the organobismuth intermediates. The formation of R_2Pd type species in one stage was suggested in the homo-coupling reaction of R_2Te derivatives with palladium(0) [25]. To study the mechanism of the formation of **6a** the coupling reaction of the mixture of triphenylbismuth dipropionate $Ph_3Bi(O_2CEt)_2$ **1c** and tris(*meta*-tolyl)bismuth dipropionate *m*-$Tol_3Bi(O_2CEt)_2$ **3a** taken in a 1:1 ratio was carried out under typical conditions (acetonitrile, r.t., under air, $PdCl_2$ (4 mol%)). Three products were obtained: biphenyl **6a**, 3-methyl-biphenyl and 3,3′-dimethyl-biphenyl **6c**, in 35%, 73% and 35% yield, respectively (Scheme 4). This statistic distribution of the products (1:2:1), where 3-methyl-biphenyl being the major one, indicates two important points: no self-coupling takes place in the system, and diarylpalladium species are formed via two successive steps (Scheme 5, route **B**) (the homo-coupling products **6a** and **6c** would otherwise be the major ones (Scheme 5, route **A**)).

Another evidence for the formation of biaryl occurring via two successive steps is a decrease in the yield of **6a** in the C-phenylation reaction of **4** with **1c** under typical conditions with different **4**:**1c** ratios (Fig. 2). The yield of **6a** is reduced from 136% in the absence of **4** to 78% in the presence of a 10-fold excess of **4**. Simultaneously, the yield of the C-phenylation product **5a** increases from 0% to 79%, respectively. These facts indicate that the phenylpalladium species PhPdX is formed during the first stage and reacts either with **4** (Eq. (2)) or with the organobismuth compounds. Otherwise, the yields of the reaction products would be less significantly affected. According to the obtained results, the reaction rate of the PhPdX species with the initial **1c** (Eq. (5)) is higher than that with **4** (Eq. (2)). When **4** and **1c** were reacted in a 1:1 ratio, the C-phenylation product **5a** and biphenyl **6a** were obtained in 43% and 108% yield, respectively.



Scheme 4.



Scheme 5.

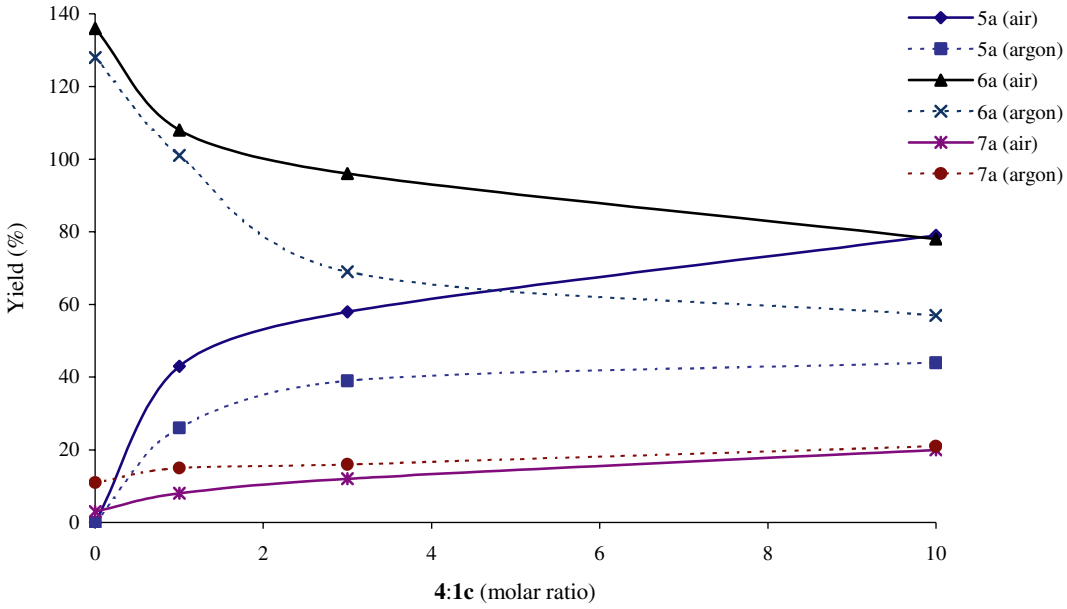


Fig. 2. Effect of the molar ratio **4**:**1c** on the yields of the reaction products (CH_3CN, r.t., 24 h, with 4 mol% of $PdCl_2$).

The same reactions were carried out under argon as well. As shown in Fig. 2, the yields of **5a** and **6a** were reduced. Of note, when an excess of **4** is used the total involvement of phenyl groups decreases both under air and under argon. In the former case this effect is negligible, from 275% in the absence of **4** to 255% in the presence of a 10-fold excess of it. Under argon, however, this effect is more pronounced, from 267% to 179%, respectively. This indicates that an oxygen-sensitive organobismuth intermediate is formed in the presence of a large excess of **4**. Analogously to the organoantimony derivatives it can be assumed that this intermediate may be the Ph_2BiX derivative formed according to Eq. (4). In the presence of a large excess of **4** the rate of the C-phenylation reaction (Eq. (2)) increases compared to that with the organobismuth compound (Eq. (5)) and the Ph_2BiX species accumulates in the reaction mixture. In the presence of oxygen Ph_2BiX is oxidized in the coordination sphere of palladium to a bismuth(V) derivative, which can oxidize Pd(0) to the PhPdX species. This process likely occurs via mechanism similar to that observed for the corresponding organoantimony derivative Ph_2SbX [1] (Eq. (6)). Indeed, when Ph_2BiCl and **4** (1:3) were reacted in CH_3CN at room temperature under argon in the presence of $PdCl_2$ (4 mol%), only trace amount of the products were found (the total involvement of the phenyl groups 6%). However, the same reaction carrying out in the presence of oxygen affords methyl cinnamate **5a**, biphenyl **6a** and benzene in the yield of 11%, 10% and 10%, respectively. When methyl acrylate **4** is absent or taken in a stoichiometric ratio (1:1) to Ph_3BiX_2, the reaction of PhPdX with the starting Ph_3BiX_2 (Eq. (5)) becomes the main pathway. According to this reaction the homo-coupling product **6a** can be obtained in 50% yield. The Ph_2BiX_3 species formed in this reaction are unstable and probably more reactive than the starting Ph_3BiX_2. No data supporting the existence of such organobismuth(V) derivatives could however be found in the literature. Ph_2BiX_3 species are able to oxidize the Pd(0) species into PhPdX (Eq. (7)), which reacts with **4** (Eq. (2)) or with the organobismuth(III) derivatives (Eqs. (8) and (9)), increasing the yield of the products.

$$PhPdX + Ph_3BiX_2 \rightarrow Ph_2 + Ph_2BiX_3 + Pd(0) \quad (5)$$

$$2Ph_2BiX + O_2 \xrightarrow{[Pd]} 2Ph_2Bi(O)X \xrightarrow{Pd^0} PhPdX + PhBiO \quad (6)$$

$$Ph_2BiX_3 + Pd(0) \rightarrow PhPdX + PhBiX_2 \quad (7)$$

$$PhPdX + Ph_2BiX \rightarrow Ph_2 + PhBiX_2 + Pd(0) \quad (8)$$

$$PhPdX + PhBiX_2 \rightarrow Ph_2 + BiX_3 + Pd(0) \quad (9)$$

However, the mechanism suggested above can explain the involvement of only two phenyl groups of the starting **1c** in the absence of oxygen. As it can be seen from the obtained results (Fig. 2) the total involvement of phenyl groups is more than 200% under argon when the **4**:**1c** molar ratio is 1:1 (243%) or when methyl acrylate is absent (267%). These results are similar to those of the corresponding reactions under air (267% and 275%, respectively). This can be explained by the participation of the Ph_2BiX_3 species formed according to Eq. (5), which should be a stronger oxidant than Ph_3BiX_2. Ph_2BiX_3 is able to oxidize the PhPdX intermediate to the palladium(IV) species Ph_2PdX_2 (Eq. (10)), which decomposes into **6a** and the palladium(II) salt PdX_2 (Eq. (11)). Thus, palladium(II) remains in the reaction mixture and can be involved in the transmetallation reaction with organobismuth derivatives. As a consequence, oxygen must not affect significantly the palladium-mediated process in the absence of olefin, which is what is being observed experimentally.

$$PhPdX + Ph_2BiX_3 \rightarrow Ph_2PdX_2 + PhBiX_2 \quad (10)$$

$$Ph_2PdX_2 \rightarrow Ph_2 + PdX_2 \quad (11)$$

Arylbismuth(III) derivatives can interact with acids to give benzene [26]. This reaction occurs easily with strong acids and requires heating in the cases of weak carboxylic acids. Triarylbismuth Ar_3Bi in the reaction with an acid, generally, converts into an $ArBiX_2$ species. To achieve full dearylation of Ar_3Bi the presence of a large excess of the acid is necessary [26c–e]. We suggest that the acid generated in the reductive elimination stage (Eq. (3)) can react with the organobismuth(III) intermediates Ph_2BiX to give **7a** (Eq. (12)). An increase in the yield of **7a** in almost all reactions carried out under argon confirms this suggestion because the bismuth(III) compounds are accumulated in the reaction mixture. It is interesting to note that the yield of **7a** under air is the highest in the cases of the bismuth(V) compounds containing the carboxylic acids with middle pK_a values (formate **1a** (62%) and monochloroacetate **1h** (33%)) (Table 4, entries 1 and 9). The organobismuth compounds containing other carboxylic acids, either stronger or weaker than the two above mentioned, provide significantly lower yields of **7a**. This indicates that the triphenylbismuth dicarboxylates containing these acids have transition properties in between those of the derivatives containing weaker or stronger acids. They are active like the derivatives containing the weaker acids, and the acids formed according to Eq. (3) are strong enough to provide the dephenylation of the bismuth(III) compound. The low activity of the derivatives containing stronger acids, **1g** and **1i**, and the corresponding very low yield of **7a** seem to suggest a different mechanism governs their participation in the palladium mediated processes.

$$Ph_2BiX + HX \rightarrow PhBiX_2 + PhH \quad (12)$$

Attempts to prove the mechanistic points discussed above by ^1H NMR spectroscopy were made in the C-arylation reaction of **4** with tris(*para*-tolyl)bismuth dipivalate *p*-$Tol_3Bi(O_2CBu\text{-}t)_2$ **2a**. This system was selected for the following reasons. The initial compounds as well as the organic products had clear and easily identifiable NMR signals. Moreover, we assume that the presence of the pivalic group will increase the solubility of the proposed organobismuth intermediates. D_3CCN was used as a solvent. The reaction was carried out under air at room temperature. After 1 h, the resonances of the starting **2a** disappeared completely [7.93 (d, *ortho*-protons), 7.43 (d, *meta*-protons), 2.37 (s, CH_3) and 0.97 (s, Bu-*t*) ppm]. At the same time a white solid precipitated in the NMR tube and the ^1H spectra showed a quite complicated pattern. Except for the strong resonances [doublets at 7.51 and 7.25 ppm] of tolyl groups of the C-arylation and biaryl products, upfield-shifted of those of the starting **2a**, only strong resonances of the tolyl group of a new species [doublets at 8.34 and 7.69 ppm], downfield-shifted significantly of those of the starting **2a**, were detected in the spectra. These resonances can be associated with the organobismuth(V) derivative *p*-$Tol_2Bi(O_2CBu\text{-}t)_3$, the *p*-Tol–Bi bond of which is more polar than that of **2a** due to the effect of three carboxylic groups. One more doublet due to *ortho*-protons of the tolyl group at 7.60 ppm, upfield-shifted of those of the starting **2a**, was observed in the spectra, and may correspond to an organobismuth(III) derivative. However, precipitation of a solid in the NMR tube did not allow for a quantitative determination of all species present in the reaction mixture.

The proposed bismuth intermediates such as Ar_2BiX_3, Ar_2BiX or $ArBiX_2$ are relatively unstable. They are able to react with other molecules of the organobismuth compounds in a ligand exchange type reaction or form insoluble oxo-complexes, which are probably inactive in the palladium-catalyzed reactions. These side-reactions affect the understanding of the whole mechanism of the participation of the triarylbismuth dicarboxylates in the palladium-mediated reactions described above. Further studies are now underway to better understand the various intertwined mechanistic facets of the catalytic reaction reported in this work.

3. Conclusion

Readily available triarylbismuth(V) dicarboxylates $Ar_3Bi(O_2CR)_2$ are very reactive reagents for the palladium-mediated formation of new C–C bonds. The Heck-type C-arylation reaction can be easily performed at room temperature in CH_3CN as the best solvent, with $PdCl_2$ (4 mol%) as the most effective catalyst. The homo-coupling process competes with the C-arylation reaction due to the low energy of the C–Bi bond. The nature of the carboxylic group affects the activity of the organobismuth derivatives and the competition between the C-arylation reaction and the homo-coupling process. When derivatives containing weak carboxylic acids were used in the reaction the highest reactivity of the triarylbismuth dicarboxylates was observed, with almost all three aryl groups involved in the reactions. Triarylbismuth divalerate $Ar_3Bi(O_2CBu\text{-}n)_2$ is the most effective in the C-arylation reaction. The derivatives containing strong acids showed the highest selectivity. The C-arylation reaction is significantly inhibited by the presence of strongly binding ligands on the palladium, such as phosphines. The reaction atmosphere also affects the reactions. The reactivity of triarylbismuth dicarboxylates and the selectivity of the C-arylation reaction decrease when the reactions are performed under argon.

Triarylbismuth(V) dicarboxylates $Ar_3Bi(O_2CR)_2$ are significantly more reactive than triarylantimony(V) dicarboxylates studied previously. However, the selectivity of the C-arylation is significantly higher in the case of the antimony derivatives. Unlike triphenylantimony dichloride, Ph_3BiCl_2 is active in the C-phenylation reaction. In the case of organoantimony(V) compounds the nature of the carboxylic group has a little effect on the reaction whereas it is important in the reactions with the organobismuth(V) derivatives. Oxygen and phosphine ligands affect the C-arylation reaction both with bismuth and with antimony derivatives.

4. Experimental

4.1. General methods

Gas chromatographic analyses were performed with a LKhM-80 chromatograph using helium as the carrier gas, column 300 cm length, 15%-DNF on the Chromaton N-AW-DMCS at 80 °C (for analyze of benzene) and column 240 cm length, 15%-Apiezon-L on the Chromaton N-AW-DMCS at 130 °C (for analyze of chlorobenzene) and 220 °C (for analyze of methyl cinnamate and biphenyl). ^{1}H NMR spectra were measured on a Bruker Avance DPX-200 spectrometer for solutions in $CDCl_3$, D_3CCN.

t-BuOOH was prepared by the method of Milas and Surgenor [27]. Commercial methyl acrylate was washed with an alkali solution until the yellow color disappeared, then dried with Na_2SO_4 and distilled. All solvents were distilled prior to use. $Pd(OAc)_2$ [28], $Pd_2(dba)_3$ [29], $Pd(Ph_3P)_2Cl_2$ [30] were prepared by the reported methods, and $PdCl_2$, dppm, dppe, dppp, dppb, BINAP, xantphos were commercially available. Ph_2BiCl was prepared by a treatment of Ph_3Bi and $BiCl_3$ in a 2:1 ratio in dry ether [31].

4.2. Preparation of $Ph_3Bi(O_2CH)_2$ 1a using t-BuOOH

t-BuOOH (5 mmol) was added dropwise to a stirred cold (5–10 °C) solution of Ph_3Bi (5 mmol) and HCOOH (10 mmol) in Et_2O (50 ml). The reaction mixture was kept in the dark for 24 h at room temperature. The solvent was distilled off under reduced pressure and the solid residue was purified by recrystallization ($CHCl_3$/hexane) to afford **1a** (2.1 g, 80%), m.p. 150–152 °C (decomp.) (lit. [32] 140–150 °C (decomp.)).

Other organobismuth compounds were prepared by the same procedure:

Triphenylbismuth diacetate **1b**: m.p. 187–189 °C (lit. [32] 187–189 °C).

Triphenylbismuth dipropionate **1c**: m.p. 156 °C (lit. [32] 157–159 °C).

Triphenylbismuth divalerate **1d**: m.p. 89 °C (lit. [32] 91 °C).

Triphenylbismuth dipivalate **1e**: m.p. 142 °C (lit. [32] 146–148 °C).

Triphenylbismuth dihexanoate **1f**: m.p. 73–76 °C; ^{1}H NMR: δ 8.16 (d, J = 7.3 Hz, 6H), 7.61–7.42 (m, 9H), 2.05 (t, J = 7.3 Hz, 4H), 1.45–1.30 (m, 4H), 1.18–0.86 (m, 8H), 0.73 (t, J = 7.3 Hz, 6H). Anal. Calc. for $C_{30}H_{37}O_4Bi$: C, 53.7; H, 5.6. Found: C, 53.5; H, 5.6%.

Triphenylbismuth bis(trifluoroacetate) **1g**: m.p. 143–144 °C (lit. [32] 143–144 °C).

Triphenylbismuth bis(monochloroacetate) **1h**: m.p. 110 °C (lit. [32] 155–156 °C); ^{1}H NMR: δ 8.18 (d; J = 7.3 Hz, 6H), 7.67 (t; J = 7.3 Hz, 6H), 7.54 (t; J = 7.3 Hz, 3H), 3.86 (s; 4H). Anal. Calc. for $C_{22}H_{19}Cl_2O_4Bi$: C, 42.1; H, 3.1. Found: C, 42.0; H, 3.1%.

Triphenylbismuth bis(trichloroacetate) **1i**: m.p. 158 °C (lit. [32] 158 °C).

Triphenylbismuth dibenzoate **1j**: m.p. 166–168 °C (lit. [32] 167–169 °C).

Tris(*para*-tolyl)bismuth dipivalate **2a**: m.p. 167–171 °C; ^{1}H NMR: δ 8.00 (d, J = 8.3 Hz, 6H), 7.34 (d, J = 8.3 Hz, 6H), 2.37 (s, 9H), 0.96 (s, 18H). Anal. Calc. for $C_{31}H_{39}O_4Bi$: C, 54.4; H, 5.7. Found: C, 54.4; H, 5.6%.

Tris(*meta*-tolyl)bismuth dipropionate **3a**: m.p. 90 °C; ^{1}H NMR: δ 7.95 (d, J = 8.3 Hz, 6H), 7.49 (t, J = 7.7 Hz, 3H), 7.28 (d, J = 7.3 Hz, 3H), 2.41 (s, 9H), 2.17–2.05 (m, 4H), 0.94 (t, J = 7.7 Hz, 6H). Anal. Calc. for $C_{27}H_{31}O_4Bi$: C, 51.6; H, 4.9. Found: C, 51.4; H, 4.9%.

Triphenylbismuth dichloride: m.p. 149–150 °C (lit. [32] 146–147 °C).

4.3. Typical procedure for the C-phenylation reaction

A mixture of $Ph_3Bi(O_2CH)_2$ (0.265 g, 0.5 mmol), $PdCl_2$ (3.6 mg, 0.02 mmol), methyl acrylate (0.135 ml, 1.5 mmol) in acetonitrile (6 ml) was placed in a 50 ml tube. The tube was sealed and the reaction mixture was kept at 50 °C for 3 h. The solvent was then evaporated under reduced pressure and analyzed by GLC. The solid residue was purified from inorganic products by elution through a short column on silica gel using a mixture of hexane–ethyl acetate (v/v 4:1) as the eluent. The filtrate was analyzed by GLC. Methyl cinnamate (0.057 g), biphenyl (0.035 g) and benzene (0.023 g) were found.

4.4. The C-phenylation reaction under argon

A mixture of $Ph_3Bi(O_2CH)_2$ (0.265 g, 0.5 mmol), $PdCl_2$ (3.6 mg, 0.02 mmol), methyl acrylate (0.135 ml, 1.5 mmol) in acetonitrile (6 ml) was placed in a 50 ml tube. The reaction mixture was degassed by repeated freeze–pump–thaw cycles and the tube was filled with argon. The tube was sealed and the reaction mixture was kept at room temperature for 24 h. The following procedure was the same as described above. Methyl cinnamate (0.016 g), biphenyl (0.019 g) and benzene (0.020 g) were found.

4.5. The reaction between $Ph_3Bi(O_2CEt)_2$ and m-$Tol_3Bi(O_2CEt)_2$

A mixture of $Ph_3Bi(O_2CEt)_2$ (0.147 g, 0.25 mmol), m-$Tol_3Bi(O_2CEt)_2$ (0.157 g, 0.25 mmol) $PdCl_2$ (3.6 mg, 0.02 mmol) in acetonitrile (6 ml) was placed in a 50 ml tube. The tube was sealed and the reaction mixture was kept at 20 °C for 24 h. The solvent was then evaporated under reduced pressure and analyzed by GLC. The solid residue was purified from inorganic products by elution through a short column on silica gel using a mixture of hexane–ethyl acetate (v/v 4:1) as the eluent. The solvent was evaporated from filtrate and residue was analyzed by ^1H NMR. Biphenyl (0.027 g), 3-methyl-biphenyl (0.061 g) and 3,3′-dimethyl-biphenyl (0.032 g) were found.

4.6. Procedure for ^1H NMR spectroscopic study

A mixture of p-$Tol_3Bi(O_2CBu\text{-}t)_2$ (0.086 g, 0.125 mmol), $PdCl_2$ (0.9 mg, 0.005 mmol), methyl acrylate (0.034 ml, 0.375 mmol) in D_3CCN (1 ml) was placed in NMR tube. The tube was sealed. The reaction was monitored by ^1H NMR within one day.

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