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New Preparative Method of Aryl Tosylates by Using Organobismuth Reagents

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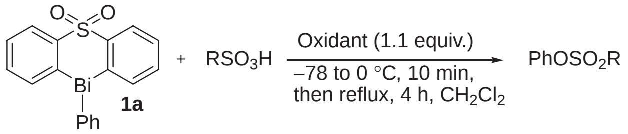
A new method for the preparation of aryl tosylates by using pentavalent bismuth is described. Treatment of 10-arylphenothiabismine 5,5-dioxides, *m*-chloroperoxybenzoic acid (MCPBA) and *p*-toluenesulfonic acid monohydrate in dichloromethane affords aryl tosylates in good to high yields.

Aryl tosylates are common reagents in organic synthesis not only as protected substrates of phenolic hydroxy group[1] but also as starting materials of various reactions. They recently become more attractive in transition-metal-catalyzed cross-coupling reactions because of their increased stability compared with aryl triflate, and it was reported that aryl tosylates were applicable for palladium- and nickel-catalyzed Suzuki–Miyaura[2] and Kumada coupling reaction,[3] and palladium-catalyzed alkoxycarbonylation.[4]

The most general procedure for the preparation of aryl tosylates is to react phenols with toluene-4-sulfonyl chloride (TsCl) in the presence of organic bases such as pyridine or Et_3N. Recently, solvent-free tosylation of phenols by using polyoxometalates as catalyst[5] or microwave activation[6] was reported, whereas general procedures without using phenols are not known yet.

Organobismuth reagents are well studied as mild oxidants and arylation reagents.[7] It is also reported from our laboratory that pentavalent organobismuths are effective for N-arylation of pyridin-2(1*H*)-ones, O-phenylation of tertiary alcohols and oxidative coupling reaction of carbonyl compounds.[8] These reactions are attributed to the unique character of valency change from Bi^{V} to Bi^{III}. Thus, two ligands on the pentavalent bismuth are coupled accompanied with reductive elimination to generate trivalent bismuth simultaneously. Ligand coupling reactions of pentavalent bismuth dihalides or diacetates are reported,[7a,7d,7e] while those of pentavalent bismuth ditosylates were not known. Then, we would like to report a synthesis of aryl tosylates by using a novel ligand coupling reaction of pentavalent bismuth ditosylates generated in situ. First, heterocyclic bismuth **1a** was selected as a model substrate of aryl donor in consideration of that reactivity and selectivity reported by Suzuki's group.[9] They reported that heterocyclic pentavalent bismuth dichloride such as 10-dichloro-10-(4′-methylphenyl)phenothia-$10^{\lambda}5$-bismine 5,5-dioxide prepared from **1b** was quite unstable to form 4-chlorotoluene quantitatively by reductive elimination and that only 4-methylphenyl group participated in the reductive elimination while heterocyclic bismuth part remained unchanged.

Table 1. Reaction of **1a** with various oxidants and sulfonic acids



Entry	RSO_3H/equiv.	Oxidant	Yield/%
1	$TsOH{\cdot}H_2O$/2.2	*t*-BuOOH	ND[b]
2	$TsOH{\cdot}H_2O$/2.2	$(PhCOO)_2$	ND
3	$TsOH{\cdot}H_2O$/2.2	CH_3COOOH	49
4	$TsOH{\cdot}H_2O$/2.2	MCPBA	87
5[a]	$TsOH{\cdot}H_2O$/2.2	MCPBA	48
6	$TsOH{\cdot}H_2O$/1.1	MCPBA	63
7	$TsOH{\cdot}H_2O$/2.8	MCPBA	91
8	MsOH/2.8	MCPBA	80
9	TfOH/2.2	MCPBA	29

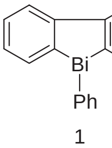
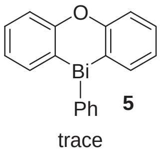
[a] Reaction was carried out at rt for 30 h. [b] Not Detected.

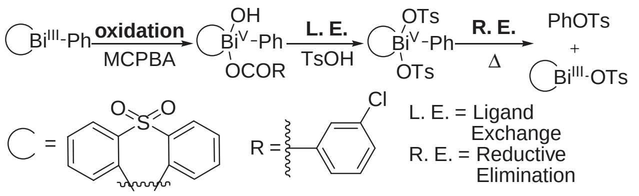
In the first place, the effects of oxidants and sulfonic acids were examined. The results of the reaction carried out by using 10-phenylphenothiabismine 5,5-dioxide[9] (**1a**), 1.1 equiv. of oxidants in the presence of some sulfonic acids in CH_2Cl_2 are summarized in Table 1. When *tert*-butyl hydroperoxide and benzoyl peroxide were used as an oxidant, the expected phenyl tosylate was not obtained (Entries 1 and 2). Instead, the desired phenyl tosylate was respectively obtained in 49 and 87% yields when an oxidant such as peracetic acid or MCPBA was used (Entries 3 and 4). The reaction was sluggish when carried out at room temperature (Entry 5). The yield of PhOTs decreased to 63% yield when the amount of $TsOH{\cdot}H_2O$ was reduced to 1.1 equiv. (Entry 6). In the view of reproducibility, it was found that the amount of $TsOH{\cdot}H_2O$ was needed more than 2 equiv., and the best result was obtained by using 2.8 equiv. of $TsOH{\cdot}H_2O$ (Entry 7). Next, other sulfonic acids were examined, and it was observed that methanesulfonic acid (MsOH) gave the desired phenyl mesylate in 80% yield (Entry 8). On the other hand, trifluoromethanesulfonic acid (TfOH) gave the desired phenyl triflate in only 29% yield because **1a** was decomposed by TfOH (Entry 9).

In the next place, reactivity of other bismuth reagents was examined (see Table 2). This reaction proceeded only when **1a** was used. It is, therefore, assumed that triphenylbismuthane (**3**), phenylbiphenyl-2,2′-ylenebismuthane[10] (**4**) and 10-phenyl-

Table 2. Effect of organobismuth reagents

$$Bi^{III} + \underset{(2.2\ \text{equiv.})}{TsOH{\cdot}H_2O} \xrightarrow[\text{then reflux, 4 h, } CH_2Cl_2]{\text{MCPBA (1.1 equiv.)}\atop -78 \text{ to } 0\ ^{\circ}\text{C, 10 min,}} \underset{\mathbf{2a}}{PhOTs}$$

Entry	1	2	3	4
Bi^{III}	Ph_3Bi **3**	 **4**	 **5**	**1a**
Yield/%	ND	1	trace	87

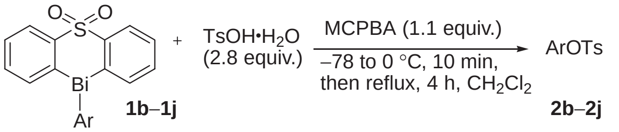


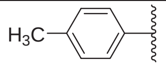
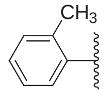
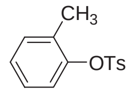
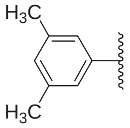
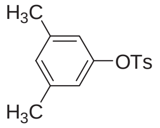
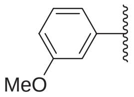
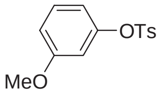
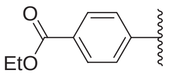
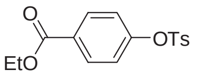
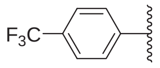
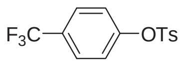
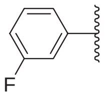
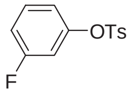
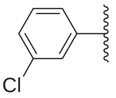
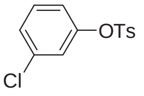
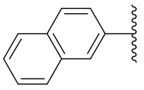
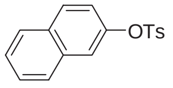
Scheme 1. Plausible mechanism for the formation of the phenyl tosylate.

phenoxabismine[9] (**5**) are oxidized by MCPBA and that subsequent ligand exchanges to disulfonate occurred. On the other hand, final reductive elimination step did not proceed effectively (Scheme 1). It is thought that this unique reactivity might be caused by the transannular interaction of **1a** between bismuth and the sulfonyl oxgen atom as was indicated by Suzuki's group. Furthermore, coupled compounds with *m*-chlorobenzoic acid or the diphenyl sulfone part were not detected since phenyl tosylate was obtained selectively in this reaction.

Finally, the reaction of various 10-arylphenothiabismine 5,5-dioxides under optimized conditions was examined, and results are summarized in Table 3. Trivalent bismuth compounds (**1b**–**1j**) were synthesized by way of the substitution reaction of aryl Grignard reagents with 10-iodophenothiabismine 5,5-dioxide. Electron-rich aryl groups having methyl or methoxy substituents were applicable to this reaction and the desired aryl tosylates (**2b**–**2e**) were obtained in high yields (Entries 1–4). On the other hand, electron-poor aryl groups having ethoxycarbonyl, trifluoromethyl substituents or halogen were tolerated to afford the expected aryl tosylates (**2f**–**2i**) in moderate to good yields (Entries 5–8). 2-Naphthyl tosylate (**2j**) was also obtained in 86% yield (Entry 9). These reactions are carried out easily since there was no need to isolate unstable pentavalent bismuth compared with trivalent bismuth reagents which are purified regardless of temperature and moisture.

Table 3. Synthesis of aryl tosylates by using optimized conditions



Entry		Ar		Product	Yield/%[a]
1	**1b**		**2b**		83
2	**1c**		**2c**		81
3	**1d**		**2d**		88
4	**1e**		**2e**		85
5	**1f**		**2f**		76
6[b]	**1g**		**2g**		79
7[c]	**1h**		**2h**		72
8[b]	**1i**		**2i**		73
9	**1j**		**2j**		86

[a]Isolated yield. [b]Reflux 10 h. [c]Reflux 8 h.

It is noted that synthesis of aryl tosylates by using novel ligand coupling between aryl group and tosyloxy group on the pentavalent bismuth was established. Because preparations of sulfonyl chlorides or phenols in advance are not needed, this coupling reaction is an alternative method for the preparation of aryl sulfonates. It is interesting to note that the transannular interaction between bismuth and the sulfonyl oxygen atom of 10-arylphenothiabismine 5,5-dioxides brought about extremely unique ligand coupling reaction in organobismuth chemistry.

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