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Chemoselective conversion of aromatic epoxide and 1,2-diol to 1,3-dioxane derivatives with phenyltrimethylammonium tribromide in the presence of a catalytic amount of antimony(III) bromide

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Abstract—*trans*-Stilbene oxide was oxidatively converted to 2-phenyl-1,3-dioxanes with phenyltrimethylammonium tribromide in the presence of various 1,3-diols and a catalytic amount of $SbBr_3$ in DMSO at room temperature. Aromatic 1,2-diol, such as hydrobenzoin, was similarly converted to 2-aryl-1,3-dioxane derivatives under the same reaction conditions.

As antimony halides are effective for organic synthesis as a weak Lewis acid and are easier to handle than other metal halides such as $AlCl_3$ and $TiCl_4$, several transformations of organic compounds with antimony halides as a catalyst have been developed.[1,2] In a previous letter, the combination of antimony halides and complex metal hydrides was reported to be more effective for the conjugate reduction of 2-butene-1,4-diones and the reductive debromination of aromatic α-bromo ketones in comparison with those of reagents and other metal halides, $AlCl_3$, $CuCl_2$, and $FeCl_3$.[3a,b] Antimony halide–Bu_4NI was also reported to be useful for the reductive ring-opening of 2,3-epoxy-1,4-butanediones to 2-hydroxy-1,4-butanediones.[3c]

On the other hand, phenyltrimethylammonium tribromide (PTAB) is known to be a convenient reagent for brominating organic compounds and is useful for the synthesis of many functional compounds in organic chemistry.[4–6] PTAB–$SbBr_3$ or PTAB–$CuBr_2$ was reported to be convenient and chemoselective for the oxidation of secondary alcohols to the respective ketones. Further, PTAB was found to be useful for the chemoselective conversion of 3-alkoxyfurans to 2-alkoxy-3(2*H*)-furanones.[7] Therefore, there has been much interest in further applications for other organic synthesis with the combination of PTAB and antimony halide. The reaction of *trans*-stilbene oxide with PTAB and $SbBr_3$ in DMSO was carried out and predominantly afforded 2-phenyl-1,3-dioxane in the presence of 1,3-propanediol. In the presence of various 1,3-diols, the reaction of *trans*-stilbene oxide with PTAB–$SbBr_3$ in DMSO was carried out to clarify the limitations and chemoselectivity of this oxidative transformation of *trans*-stilbene oxide to 2-phenyl-1,3-dioxane. *trans*-Stilbene oxide was found to be easily oxidized and chemoselectively transformed to the respective 1,3-dioxanes without being overoxidized to benzoic acid. As there are still continuing developments in the chemoselective acetalization of aldehyde and functional compounds,[8] the PTAB–$SbBr_3$ system is supposed to be an alternative favorable method for the oxidative acetalization. We would like to report the results of our studies concerning the conversion of *trans*-stilbene oxide and aromatic 1,2-diols to 2-aryl-1,3-dioxanes.

The reaction of *trans*-stilbene oxide **1**, chosen as a representative epoxide for this study, with PTAB–$SbBr_3$ in various stoichiometric ratios was carried out. The results are summarized in Table 1. At a molar ratio of 1:3:7 of stilbene oxide **1**, PTAB, and 1,3-propanediol in the presence of a catalytic amount of $SbBr_3$ in DMSO, 2-phenyl-1,3-dioxane **4a** was obtained in good yield (run 1). The following experiments were carried out to test the effects of PTAB and $SbBr_3$ on the transformation of stilbene

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Keywords: Epoxide; 1,2-Diol; 1,3-Dioxane; Phenyltrimethylammonium tribromide; Antimony(III) bromide.

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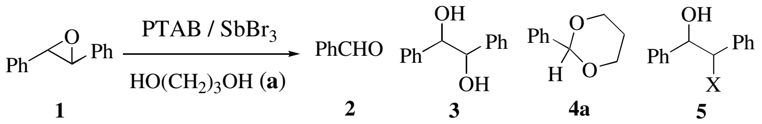
Table 1. Reaction of *trans*-stilbene oxide **1** with PTAB–$SbBr_3$[a]



Run	Molar ratio/**1**			Solvent[b]	Time (h)	Products, yield (%)				
	PTAB	$SbBr_3$	$HO(CH_2)_3OH$ (**a**)			**2**	**3**	**4a**	**5**	**1**
1	3.0	0.2	7.0	A	48	2[c]	—	85	—	—
2	3.0	—	7.0	A	38	—	45	—	—	48
3	—	0.2	7.0	A	34	—	89	—	—	—
4	3.0	0.2	7.0	B	48	—	—	—	85[d]	—
5	4.0	0.2	—	B	69	—	—	—	73[d]	—[e]
6	3.0	0.2	7.0	C	46	—	—	—	56[f]	—[g]
7	3.0	0.2	7.0	D	43	—	—	—	30[f]	—[h]
8	3.0	0.2	7.0	E	46	—	—	40	33[f]	—
9	2.0	0.2	7.0	A	40	2[c]	26[c]	71	—	—
10	1.0	0.2	7.0	A	40	2[c]	31[c]	67	—	—

[a] Substrate (**1**): 0.25 mmol; solvent: 8 mL; temp: room temperature.
[b] A = DMSO, B = MeOH, C = CH_2Cl_2, D = C_6H_{14}, E = DMF.
[c] Yields were also determined by ^1H NMR analysis of crude products.
[d] **5a**: X = OMe.
[e] Benzil (4%) and diphenylacetaldehyde (13%) were obtained.
[f] **5b**: X = Br.
[g] 2-Diphenylmethyl-1,3-dioxane (27%).
[h] 2-(3-Hydroxypropoxy)-1,2-diphenylethanol (44%).

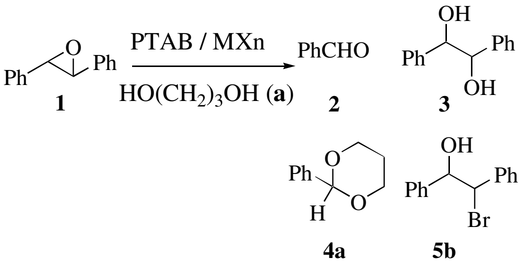
oxide **1** to 1,3-dioxane **4a**. In the absence of $SbBr_3$, hydrobenzoin **3** was afforded besides recovered epoxide **1**. 1,3-Dioxane **4a** was not obtained (run 2). In the absence of PTAB, hydrobenzoin **3** was obtained similarly (run 3). Further, in the absence of 1,3-propanediol, the reaction of epoxide **1** with PTAB–$SbBr_3$ took place to give a mixture of hydrobenzoin **3** (60%), diphenylacetaldehyde (6%), and benzaldehyde **2** (14%) under the same reaction conditions.[9] Consequently, both $SbBr_3$ and PTAB in the presence of 1,3-propanediol were confirmed to be essential for the oxidative conversion of epoxide **1** to 1,3-dioxane **4a**.

The reaction of **1** with PTAB–$SbBr_3$ was carried out in various solvents, MeOH, CH_2Cl_2, C_6H_{14}, and DMF to examine the solvent effect of DMSO in this system. In MeOH, epoxide **1** was not transformed into 1,3-dioxane and dimethylacetal, while methoxyalcohol **5a** was obtained (run 4). Methoxyalcohol **5a** and benzil were similarly obtained in MeOH without 1,3-propanediol. Dimethylacetal was not afforded (run 5).

Bromoalcohol **5b** was mainly obtained accompanied by 2-diphenylmethyl-1,3-dioxane in CH_2Cl_2 (run 6). In hexane, a mixture of bromoalcohol **5b** and 2-(3-hydroxypropoxy)-1,2-diphenylethanol was afforded (run 7). A mixture of 1,3-dioxane **4a** and bromoalcohol **5b** was afforded in DMF (run 8). In the present experiments, DMSO turned out to be the most useful solvent for the conversion of epoxide **1** to 1,3-dioxane **4a** in various solvents. Further, the reaction of **1** in the presence of $SbBr_3$ and 1,3-propanediol was carried out with 1.0–2.0 M equiv of PTAB over **1** to make clear the optimum amount of PTAB in this system. The yield of 1,3-dioxane **4a** was not fully satisfactory, accompanied by hydrobenzoin **3** (runs 9 and 10). More than 2.0 M equiv of PTAB over epoxide **1** was confirmed to be needed for obtaining 1,3-dioxane **4a** in high yields.[10]

To clarify the effect of $SbBr_3$, the reaction of epoxide **1** was also carried out in the presence of a catalytic amount of various other metal halides. The results are shown in Table 2. In the presence of $BiBr_3$, $CuBr_2$, $FeCl_3$, and $CoCl_2$, 2-phenyl-1,3-dioxane **4a** was not

Table 2. Reaction of *trans*-stilbene oxide **1** with PTAB–MXn in DMSO-1,3-propanediol[a]



Run	MXn	Time (h)	Products, yield (%)			
			2	**3**	**4a**	**5b**
1	$SbBr_3$	70	2[b]	—	85	—
2	$BiBr_3$	40	5[b]	89	—	—
3	$CuBr_2$	63	10	70	—	—
4	$FeCl_3$	38	—	83	—	8[b]
5	$CoCl_2$	95	—	80	—	—
6	$SbCl_3$	48	3[b]	—	90	—

[a] Substrate (**1**): 0.25 mmol; PTAB: 0.75 mmol; MXn: 0.05 mmol; 1,3-propanediol (**a**): 1.75 mmol; DMSO: 8 mL; temp: room temperature.
[b] Yields were also determined by ^1H NMR analysis of crude products.

obtained in high yields, predominantly accompanied by hydrobenzoin **3** (runs 2–5). On the contrary, 1,3-dioxane **4a** was obtained in 90% yield in the presence of $SbCl_3$ instead of $SbBr_3$ under the same reaction conditions (run 6). Antimony halides, $SbBr_3$ and $SbCl_3$, were confirmed to be effective for the conversion of stilbene oxide **1** to 1,3-dioxane **4a** with PTAB in DMSO.

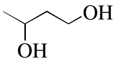
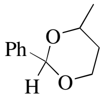
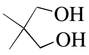
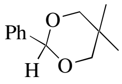
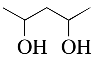
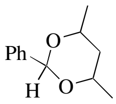
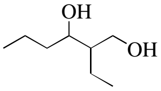
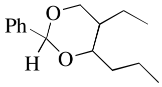
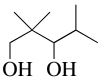
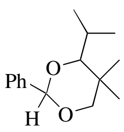
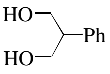
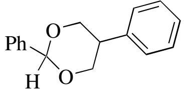
The reaction of epoxide **1** was carried out in the presence of various 1,2-diols and monools instead of 1,3-propanediol to clarify the limitations and chemoselectivity of the oxidative conversion of epoxide to 1,3-dioxane **4a** in this system. The reaction of epoxide **1** with PTAB–$SbBr_3$ in the presence of methyl alcohol, propyl alcohol, and isopropyl alcohol took place to give benzaldehyde **2**. The corresponding dialkylacetals were not afforded. Epoxide **1** was also converted to hydrobenzoin **3** with 1,2-diols, such as ethyleneglycol, 1,2-propanediol, and 1,2-butanediol. Even in the presence of glycerine, hydrobenzoin **3** was obtained. The respective 1,3-dioxane and 1,3-dioxolane were not afforded either. Accordingly, this PTAB–$SbBr_3$ in DMSO system was found to be a chemoselective method for oxidative conversion of aromatic epoxide into 2-aryl-1,3-dioxane in the presence of 1,3-propanediol.

Further, the reaction of monosubstituted aromatic and aliphatic epoxides was also carried out to examine the utility of this method. The reaction of styrene oxide with PTAB–$SbBr_3$ in DMSO took place to give a mixture of 1-phenyl-1,2-ethanediol (38%) and 2-bromo-2-phenylethanol (32%) under the same reaction conditions. 1,3-Dioxane **4a** was not afforded. Monosubstituted aliphatic epoxide, 1-dodecene oxide, was also converted to 1-bromo-2-dodecanol (75%) predominantly.[11] It was suggested that the monosubstituted aromatic and aliphatic epoxides were not oxidized to the corresponding aldehydes by this method. Therefore, the monosubstituted aromatic and aliphatic epoxides were not converted to the corresponding 1,3-dioxanes. In the present experiments, this system was confirmed to be applicable for oxidative conversion of disubstituted aromatic epoxide into 2-aryl-1,3-dioxane in the presence of 1,3-propanediol.

To examine the limitations of this transformation, the reaction of **1** was carried out in the presence of various 1,3-diols (**b**–**g**) under the same reaction conditions. The results are shown in Table 3. In both straight and branched aliphatic 1,3-propanediols (**b**–**f**), the corresponding 1,3-dioxane derivatives **4b**–**f** were afforded in good yields as expected (runs 1–5). Even in aromatic 1,3-propanediol (**g**), 1,3-dioxane (**4g**) was obtained in moderate yield under the same reaction conditions (run 6). The system PTAB–$SbBr_3$ in DMSO-1,3-diol was supposed to be useful for the oxidative transformation of disubstituted aromatic epoxide to various 2-aryl-1,3-dioxanes.

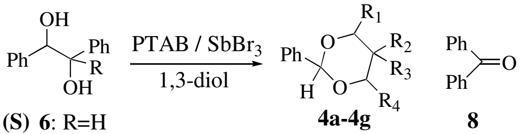
In addition, the reaction of aromatic compounds **6**, **7** was carried out with PTAB–$SbBr_3$ in the presence of various 1,3-diols (**a**–**g**) to examine the application of this method for other organic compounds. The results are shown in Table 4. *meso*-Hydrobenzoin **6** was transformed to the corresponding 1,3-dioxanes **4a**–**g** in 1,3-diols (**a**–**g**), as expected (runs 1–7). The reaction of 1,1,2-triphenyl-1,2-ethanediol **7** afforded the respective 1,3-dioxanes **4a**–**g** and benzophenone **8** (runs 8–14). These results suggested that the PTAB–$SbBr_3$ system acetalized aldehyde to 1,3-dioxanes chemoselectively.

Table 3. Conversion of *trans*-stilbene oxide **1** to various 1,3-dioxanes **4b**–**g** with PTAB–$SbBr_3$ in DMSO[a]

Run	1,3-Diol (**b**–**g**)		Molar ratio/1	Time (h)	Yields (%)		
1		**b**	6.0	43		**4b**	88
2		**c**	4.0	39		**4c**	85
3		**d**	6.0	40		**4d**	81
4		**e**	4.0	39		**4e**	92
5		**f**	2.5	46		**4f**	91
6		**g**	2.0	46		**4g**	79

[a] Substrate (**1**): 0.25 mmol; PTAB: 0.75 mmol; $SbBr_3$: 0.05 mmol; $PhCH_2(Et)_3NCl$: 0.25 mmol; DMSO: 8 mL; temp: room temperature.

Table 4. Conversion of aromatic 1,2-diols **6**, **7** to 1,3-dioxanes **4a**–**g** and benzophenone **8** with PTAB–$SbBr_3$ in DMSO[a]



(S) **6**: R=H
7: R=Ph

4a-4g

8

Run	S	1,3-Diol (a–g)		Time (h)	Products, yield (%)		
		Molar ratio/S			4a–g		8
1	**6**	**a**	7.0	70	**4a**	96	
2	**6**	**b**	7.0	19	**4b**	96	
3	**6**	**c**	7.0	70	**4c**	86	
4	**6**	**d**	6.0	40	**4d**	95	
5	**6**	**e**	2.5	37	**4e**	87	
6	**6**	**f**	3.0	61	**4f**	94	
7	**6**	**g**	3.0	42	**4g**	80	
8	**7**	**a**	7.0	70	**4a**	83	87
9	**7**	**b**	6.0	41	**4b**	84	88
10	**7**	**c**	3.0	42	**4c**	86	89
11	**7**	**d**	3.0	42	**4d**	85	89
12	**7**	**e**	2.0	41	**4e**	84	86
13	**7**	**f**	2.0	42	**4f**	84	86
14	**7**	**g**	2.0	42	**4g**	85	89

[a] Substrate (**S**): 0.25 mmol; PTAB: 0.75 mmol; $SbBr_3$: 0.05 mmol; $PhCH_2(Et)_3NCl$: 0.25 mmol; DMSO: 8 mL; temp: room temperature.

To make sure the chemoselectivity for acetalization of aldehyde to 1,3-dioxanes, the following experiments were carried out with PTAB–$SbBr_3$–DMSO in the presence of various alcohols. Benzaldehyde **2** was acetalized with PTAB–$SbBr_3$ in DMSO in the presence of 1,3-propanediol as expected, while benzophenone **8** was not acetalized. Further, benzaldehyde **2** was predominantly converted to 1,3-dioxane in the presence of both methanol and 1,3-propanediol. Benzaldehyde dimethylacetal was not obtained. Benzaldehyde dimethylacetal was exchanged with acetal into 1,3-dioxane **4a** with PTAB–$SbBr_3$ in the presence of 1,3-propanediol in DMSO.[12] These results accounted for the chemoselective acetalization of aldehyde to 1,3-dioxane by PTAB–$SbBr_3$ in DMSO.

In conclusion, the PTAB–$SbBr_3$ in DMSO-1,3-diol system was found to be a chemoselective method for the oxidative transformation of disubstituted aromatic epoxide and 1,2-diols into 1,3-dioxanes without overoxidation to carboxylic acid. Furthermore, this system was also confirmed to be an alternative mild and chemoselective procedure for the acetalization of aldehydes to 1,3-dioxanes without dehydrating at room temperature.[13,14]

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9. *trans*-Stilbene oxide **1** was easily converted to benzaldehyde **2** (79%) with PTAB–$SbBr_3$ in the presence of 1.0 M equiv of benzyltriethylammonium chloride over epoxide **1** in DMSO for 20 h at room temperature. Benzyltriethylammonium chloride was found to promote the oxidation of disubstituted aromatic epoxides and diols to corresponding aldehydes: Sayama, S. Unpublished results.
10. *cis*-Stilbene oxide was converted to 2-phenyl-1,3-dioxane **4a** (45%) at 55 °C for 2 h. At room temperature, *cis*-stilbene oxide was not easily converted to **4a** (9%) with PTAB–$SbBr_3$ in the presence of 1,3-propanediol, accompanied by hydrobenzoin (60%). On the contrary, *trans*-4-chlorostilbene oxide was converted to 2-phenyl-1,3-dioxane **4a** (81%) and 2-(4-chlorophenyl)-1,3-dioxane (81%) under the same reaction conditions. Consequently, *trans*-epoxides were more smoothly oxidized and converted to the corresponding 1,3-dioxanes by this method than *cis*-epoxides.

11. For bromoalcohol examples by alternative method, see Ref. 3c.
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13. Typical procedure: to a solution of $SbBr_3$ (18 mg, 0.05 mmol) in DMSO (8 mL) were added PTAB (282 mg, 0.75 mmol) and *trans*-stilbene oxide **1** (49 mg, 0.25 mmol). 1,3-Propanediol (133 mg (127 μL), 1.75 mmol) was added. After stirring for 48 h at room temperature, the reaction mixture was treated with 0.5 M aq $Na_2S_2O_3$ and extracted with ethyl acetate. The organic layer was washed with 0.5 M aq $Na_2S_2O_3$ and successively saturated aq NaCl, and dried with $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by column chromatography on silica gel (Wakogel C-200) with CCl_4 and $CHCl_3$ (9:1, v/v). 2-Phenyl-1,3-dioxane **4a** (70 mg, 0.42 mmol) was obtained in 85% yield. Similarly, in the presence of 1.0 M equiv of benzyltriethylammonium chloride (56 mg, 0.25 mmol) over *trans*-stilbene oxide **1** (49 mg, 0.25 mmol), *trans*-stilbene oxide **1** was also converted to 2-phenyl-1,3-dioxane **4a** (70 mg, 0.42 mmol) with PTAB–$SbBr_3$ in DMSO under the same reaction conditions. For the effect of benzyltriethylammonium chloride, see Ref. 9.
14. Typical procedure for the preparation of 2-phenyl-1,3-dioxane from *meso*-hydrobenzoin: to a solution of $SbBr_3$ (18 mg, 0.05 mmol) in DMSO (8 mL) were added PTAB (282 mg, 0.75 mmol) and *meso*-hydrobenzoin **6** (53 mg, 0.25 mmol). 1,3-Propanediol (133 mg (127 μL), 1.75 mmol) was added. After stirring for 70 h at room temperature, the reaction mixture was treated with 0.5 M aq $Na_2S_2O_3$ and extracted with ethyl acetate. The organic layer was washed with 0.5 M aq $Na_2S_2O_3$ and successively saturated aq NaCl, and dried with $MgSO_4$. After removal of the solvent in vacuo, the residue (83 mg) was purified by column chromatography on silica gel (Wakogel C-200) with CCl_4 and $CHCl_3$ (9:1, v/v). 2-Phenyl-1,3-dioxane **4a** (79 mg, 0.48 mmol) was obtained in 96% yield.