

Poly(*N,N'*-dibromo-*N*-ethyl-benzene-1,3-disulfonamide) and *N,N,N',N'*-Tetrabromobenzene-1,3-disulfonamide as Effective Catalysts for Conversion of Aldehydes to 1,1-Diacetates and Acetals

R. Ghorbani-Vaghei*, M. Amiri, N. Moshfeghifar, H. Veisi and S. Akbari Dadamahaleh
Department of Organic Chemistry, Faculty of Chemistry, Bu-Ali Sina University, Hamadan, Iran

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Poly(*N,N'*-dibromo-*N*-ethyl-benzene-1,3-disulfonamide) [PBBS] and *N,N,N',N'*-tetrabromobenzene-1,3-disulfonamide [TBBDA] are effective catalysts for easy preparation of 1,1-diacetates from aldehydes and acetic anhydride, and for easy preparation of acetals using diols under microwave irradiation in the presence of SiO₂.

Keywords: Aldehydes, Acetic anhydride, Diols, Microwave irradiation, TBBDA, PBBS

INTRODUCTION

The protection of aldehydes as acetates is an interesting feature in organic chemistry [1]. They are stable in neutral and basic media [2], and can be used as starting materials for the synthesis of valuable intermediates for Dils-Alder cycloaddition reactions [3], acetoxydienes from α,β -unsaturated aldehydes [3,4], and vinyl acetates such as 2,2-dichlorovinylacetate [4a,b]. The preparation of 1,1-diacetates is carried out under the catalysis of strong protic acids such as H₃PO₄ and CH₃SO₃H [5], and Nafion-H [6], or Lewis acids, such as Me₂S⁺Br⁻ [7], InCl₃/Al₂O₃ [8], Bi(OTf)₃ [9], I₂ [10], FeCl₃ [11]. In recent years, several catalysts have been employed for this reaction such as Zeolites [12], CAN [13], clay [14a,b], NBS [15], TiCl₃(OTf) [16], and dodecatungstophosphate (AlPW₁₂O₄₀) [17].

Acetalization is a well-known synthetic procedure for the protection of carbonyl groups in multistage synthesis [18], and is achieved by treatment of aldehydes or ketones with alcohols or diols and dehydrating agents in the presence of Bronsted or Lewis acids such as In(OTf)₃ [19], ammonium triflate [20],

H₃PW₁₂O₄₀ [21], novel brønsted acid (PDA) [22], *N,N'*-bis[3,5-bis(trifluoromethyl)phenyl]thiourea [23], 1-butyl-3-methylimidazolium tetrachlorogallate [24], Zr(HSO₄)₄ [25], 2,4,4,6-tetrabromo-2,5-cyclohexadienone (TABCO) [26], SiO₂Cl [27], LiOTf [28], Ti⁴⁺-Montmorillonite [29] and I₂ [30].

In this work, we used poly(*N,N'*-dibromo-*N*-ethyl-benzene-1,3-disulfonamide) [PBBS] and *N,N,N',N'*-tetrabromobenzene-1,3-disulfonamide [TBBDA] as effective catalysts for easy preparation of 1,1-diacetates from aldehydes and acetic anhydride, and for easy preparation of acetals using diols under microwave irradiation in the presence of SiO₂.

EXPERIMENTAL

Typical Procedure for Conversion of Benzaldehyde to 1,1-Diacetates Using TBBDA under Reflux Condition

To a magnetically stirred solution of benzaldehyde (1 mmol) and freshly distilled acetic anhydride (1.5 mmol), TBBDA (1 mmol) was added and the mixture was stirred under reflux condition until complete disappearance of the aldehyde starting material (as monitored by TLC). After completion, the reaction was quenched with water (25 ml),

*Corresponding author. E-mail: rgvaghei@yahoo.com

and the mixture was extracted with CH_2Cl_2 (25 ml). The organic layer was separated, and dried over Na_2SO_4 . Evaporation of the solvent under reduced pressure gave the pure 1,1-diacetate (Table 1).

General Procedure for Conversion of Aldehydes to Acetals Using TBBDA under Microwave Irradiation and Reflux Conditions

Aldehydes (1 mmol), TBBDA 0.082 g (0.15 mmol), 1,2-ethane diol (3 mmol) and SiO_2 (1 g) were mixed together and irradiated with microwaves for the appropriate reaction times as indicated in Table 3. After completion of the reaction, CH_2Cl_2 (25 ml) was added to the reaction mixture and SiO_2 was separated by simple filtration followed by the addition of H_2O (20 ml) to the mixture. Organic layer was separated and dried over anhydrous Na_2SO_4 (5 g) which, after evaporation of the solvent under vacuum, gave the desired acetals in high yields (Table 3).

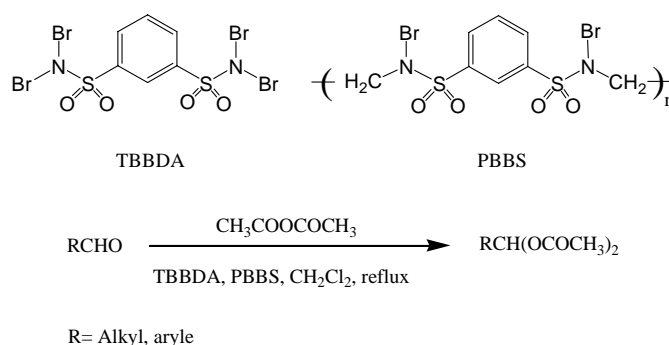
RESULTS AND DISCUSSION

Our interest in the application of poly-(*N,N'*-dibromo-*N*-ethyl-benzene-1,3-disulfonamide), [PBBS] and *N,N,N',N'*-tetrabromobenzene-1,3-disulfonamide [TBBDA] [35], in

organic synthesis has been previously reported [31-38]. We now report a mild and efficient method for conversion of aldehydes to 1,1-diacetates, in the presence of TBBDA and PBBS with acetic anhydride.

Both TBBDA and PBBS bear bromine atoms which are attached to nitrogen atoms adjacent to $-\text{SO}_2-$ groups. This generating Br^+ *in situ*, a strong Lewis acid, or an electrophilic species can catalyze generation of 1,1-diacetate from aldehydes and acetals from carbonyl compounds (Scheme 1).

By using TBBDA or PBBS as catalysts, various aromatic and aliphatic aldehydes were acylated to 1,1-diacetates in good to high yields under reflux conditions without by-products (Table 1).



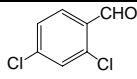
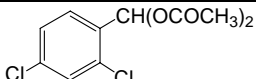
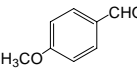
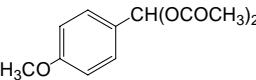
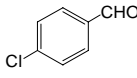
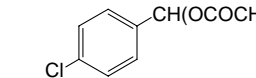
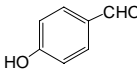
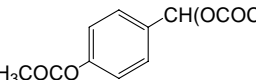
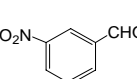
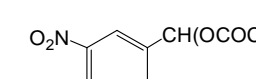

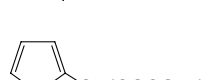
Scheme 1

Table 1. Acylation of Carbonyl Compounds Catalyzed by TBBDA and PBBS in CH_2Cl_2 under Reflux Condition

Entry	Substrate	Product	TBBDA		PBBS	
			Time (h)	Yield (%) ^a	Time (h)	Yield (%) ^a
1			1	90	2.3	85
2			2	90	2.4	90
3			2	90	2.5	80
4			2.1	85	2.25	75
5			3	90	3.4	85

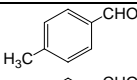
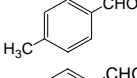
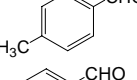
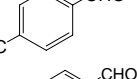
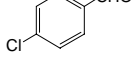
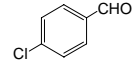
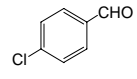
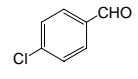
Poly(*N,N'*-dibromo-*N*-ethyl-benzene-1,3-disulfonamide)

Table 1. Continued

6			1.45	95	2.2	80
7			3	80	3	70
8			1.3	95	2	90
9			2.2	80	3	75
10			1	95	1.1	90
11			1	90	1.2	80

^aProducts were characterized by their physical properties, comparison with authentic samples, and by spectroscopic methods (IR, ¹H NMR).

Table 2. Comparison of the Effect of Catalysts for Gem-Diacetate Synthesis from 4-Methylbenzaldehyde and 4-Chlorobenzaldehyde

Entry	Substrate	Catalysts	Time (h)	Yield (%)	Ref.
1		TBBDA ^a	2	90	-
2		PBBS ^b	2.4	90	-
3		NBS	9	93	[15]
4		Bi(OTf) ₃	3.5	87	[9]
5		(CAN) ^c	4	97	[13]
6		Me ₂ S ⁺ Br Br ⁻	3.5	84	[7]
7		TBBDA	1.3	95	-
8		PBBS ^b	2	90	-

^a*N,N,N',N'*-Tetrabromobenzene-1,3-disulfonamid. ^bPoly(*N,N'*-dibromo-*N*-ethyl-benzene-1,3-disulfonamide). ^cCeric ammonium nitrate.

The advantages of TBBDA or PBBS over reported catalysts for the acylation of *p*-chlorobenzaldehyde, and *p*-methylbenzaldehyde are shown in Table 2. It is noteworthy that some of the previously reported methods require longer reaction times.

We found that aliphatic aldehydes acylated slower than aromatic aldehydes. Therefore, the method was selective for aromatic aldehydes in the presence of aliphatic aldehydes. From a mixture of benzaldehyde (1 mmol) and *n*-octanal (1 mmol) with acetic anhydride (1.2 mmol) in the presence of catalysts under reflux condition, 80% of benzaldehyde and 25% of *n*-octanal were acylated to 1,1-diacetates (Scheme 2).

It was also found that TBBDA and PBBS were efficient

catalysts for the conversion of aldehydes to their acetals in the presence of SiO₂ under microwave irradiation (Scheme 3). Our experiments showed that acetalization of aldehydes in the presence of SiO₂, and in the absence of TBBDA and PBBS under microwave irradiation, afforded low yields of acetals (10-20%).

It is noteworthy that various types of aromatic aldehydes, either electron-withdrawing or electron-releasing, were converted to their acetals with high chemoselectivity without overoxidation of aldehydes to carboxylic acids (Table 3). Aliphatic aldehydes also produced their corresponding acetals in good yields under the same reaction condition (Table 3, entry 10).

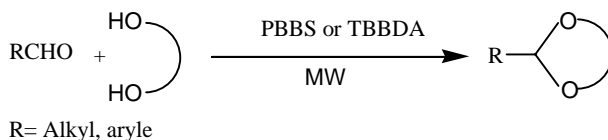
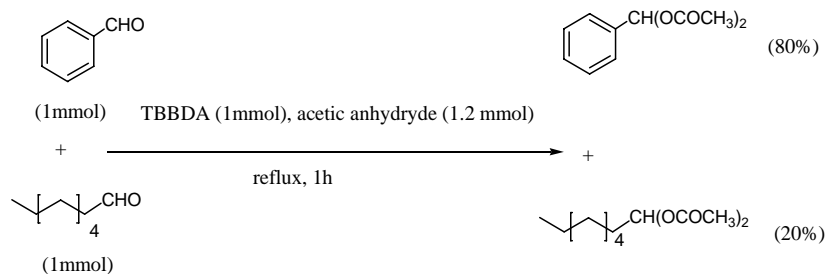
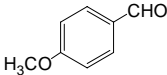
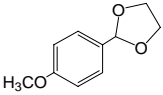
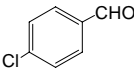
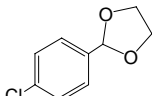
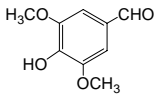
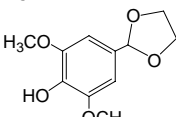
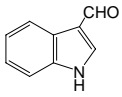
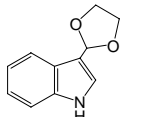
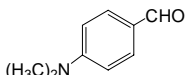
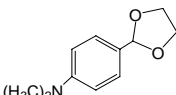
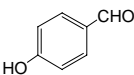
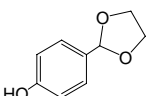
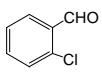
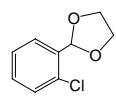
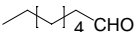
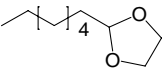
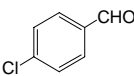
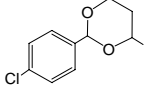
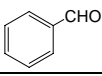
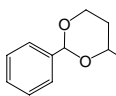


Table 3. Acetalization of Aldehydes Using TBBDA and PBBS in the Presence of Diols under Microwave Irradiation and Reflux Condition

Entry	Substrate	Product	TBBDA		PBBS	
			Time (min/h)	Yield (%) ^a	Time (min/h)	Yield (%) ^a
1			8	90	5	85
2			9	85	10	70

Table 3. Continued

3			10	80	10	60
4			5	95	5	75
5			7	75	12	85
6			8	75	10	60
7			6	60	8	60
8			10	85	6	75
9			4	90	5	80
10			10	60	12	50
11			2.4 h	75	3 h	70 ^b
12			1.25 h	85	2 h	80 ^b

^aProducts were characterized by their physical properties, comparison with authentic samples, and by spectroscopic methods (IR, ¹H NMR). ^bAldehydes (1 mmol), TBBDA or PBBS (0.18 mmol, 0.1 g), 1,3-butanediol (2 mmol), CH₃CN (5 ml), under reflux condition.

CONCLUSIONS






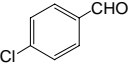
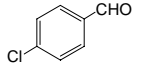
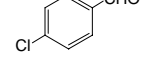
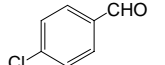
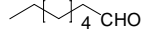
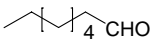
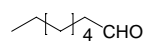
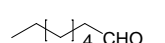
In this study, we have introduced other useful catalytic applications of TBBDA and PBBS for the generation of 1,1-diacetates from aromatic aldehydes under reflux conditions, and acetals from carbonyl compounds in the presence of SiO₂ under microwave irradiation. Preparation of the catalysts is easy and not a time consuming process. Work-up of the

reaction mixture was also easy and yields of the products are high.

ACKNOWLEDGMENTS

We are thankful to Bu-Ali Sina University, Center of Excellence and Development of Chemical Methods (CEDCM) for financial support.

Table 4. Comparison of the Effect of Catalysts for Acetals Synthesis from Aldehydes

Entry	Substrate	Catalysts	Time (min/h)	Yield (%)	Ref.
1		TBBDA	8	90	-
2		PBBS	5	85	-
3		<i>N,N'</i> -bis[3,5-bis(trifluoromethyl) phenyl]thiourea	9.2 h	92	[23]
4		Ti ⁴⁺ -Montmorillonite	1 h	>99	[29]
5		I ₂	7	85	[30]
6		TBBDA	5	95	-
7		PBBS	5	75	-
8		I ₂	7	90	[30]
9		<i>N,N'</i> -bis[3,5-bis(trifluoromethyl) phenyl]thiourea	2.5 h	87	[23]
10		TBBDA	10	60	-
11		PBBS	12	50	-
12		<i>N,N'</i> -bis[3,5-bis(trifluoromethyl) phenyl]thiourea	3.8 h	89	[23]
13		Ti ⁴⁺ -Montmorillonite	1 h	99	[29]

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