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1,1'-(Ethane-1,2-diyl)dipyridinium bistribromide (EDPBT) as an organocatalyst for the silylation/desilylation reaction

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ABSTRACT

1,1'-(Ethane-1,2-diyl)dipyridinium bistribromide (**EDPBT**) was used as a chemoselective and effective organocatalyst for the silylation of hydroxyl groups as well as desilylation of trimethylsilyl ethers under mild conditions at room temperature with good to excellent yields.

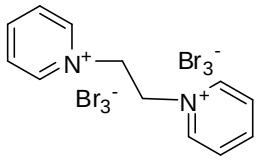
Keywords: Silylation, Hydroxyl group, 1,1'-(Ethane-1,2-diyl)dipyridinium bistribromide, Trimethylsilyl ethers, Desilylation.

1. Introduction

Development of efficient catalytic system for the selective organic transformation is currently one of the challenging tasks in synthetic organic chemistry [1]. In recent years, the search for environmentally benign chemical processes or methodologies has received much attention from chemists, because they are essential for the conservation of the global ecosystem. Catalytic oxidation is a valuable process because the use of stoichiometric reagents that are often toxic poses inherent limitations from both economical and environmental viewpoints regarding product purification and waste management [2-4].

Organic tribromide reagents (OTBs) are preferable as oxidants to molecular bromine, owing to the hazards associated with elemental bromine. Several tribromides have been reported i.e., tetramethylammonium tribromide [5], phenyltrimethylammonium tribromide [6,7], cetyltrimethylammonium tribromide, tetrabutylammonium trihromide [8], 1,8-diazabicyclo[5,4,0]-tetrabutylammonium tribromide [9], pyridine hydrobromide perbromide [10], hexamethylenetetramine-bromine [11] and DABCO-bromine [12]. Recently some ionic liquid tribromides (IL-Br_3^-) for the preparation of bromoesters from aromatic aldehydes [13] and bromination of aromatic substrates [14] were reported. It would be extremely useful to develop further synthetic protocols for the synthesis of OTBs [15]. In 2007, $\{[K.18\text{-crown-6}]Br_3\}_n$ was reported as a unique tribromide type and columnar nanotube-like structure [16].

1,1'-(Ethane-1,2-diyl)dipyridinium bistribromide [**EDPBT**] is a stable and suitable oxidant that can be prepared easily. Easy work-up and the stability of this reagent makes it safe and convenient source of active bromine in comparison to liquid bromine which is a highly toxic oxidizing agent. This reagent is transformed during alternative to other *N*-halo reagents [17]. Recently, this regent was used for the convenient oxidation of urazoles to their corresponding triazolinediones [18].



EDPBT

2. Results and Discussion

In continuation of our studies on using of tribromide reagents [16, 18], *N*-halo compounds [19], catalytic reactions [20-22] and silylation of hydroxyl groups [23], we found that **EDPBT** could be used as a catalyst for the silylation of hydroxyl groups under mild conditions.

The trimethylsilylation of hydroxyl groups is easily carried out at room temperature under mild conditions in the presence of **(EDPBT)** as active catalyst (Figure 1).

$$ROH + HMDS \xrightarrow[CH_3CN;\ rt]{EDPBT\ (Cat.)} ROSiMe_3 + NH_3$$

R= primary, secondary, tertiary alkyl, and aryl

Figure 1.

First, conversion of benzyl alcohol (1 mmol) to its corresponding benzyl silylether with this catalyst (**EDPBT**) (0.0015 mmol) and HMDS (0.8 mmol) in the presence of various solvents (Table 1) was studied. The results show that amongst these solvents; acetonitrile is the best solvent in terms of time and product yield.

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Table 1.
Silylation of benzyl alcohols with HMDS (0.8 mmol) in the presence of **EDPBT**, (**II**) (00015 mmol) at room temperature.

Entry	Solvent[a]	Time (min)	GC yield (%)
1	*n*-Hexane	300	90
2	CH_2Cl_2	300	100
3	$CHCl_3$	300	100
4	EtOAc	300	95
5	Et_2O	300	66
6	CH_3CN	10	100
7	THF	300	77
8	Acetone	20	--

Next, a range of silylethers under the following reaction conditions was prepared: hydroxyl compound (1 mmol), HMDS (0.8-1.8 mmol), **EDPBT** (0.0015 mmol), and acetonitrile (4 mL) (Table 2).
A wide range of various hydroxyl groups undergo silylation by this procedure to provide the corresponding trimethylsilyl ethers in good to excellent yields. Benzylic alcohols, phenols, and primary alcohols generally are faster than secondary and tertiary alcohols. Then, selective silylation of different binary mixtures of alcohols and also alcohols in the presence of amine or thiols was investigated. This method was shown to be highly selective for the primary alcohols such as benzyl alcohol and 1-octanol. The primary alcohols were completely converted to the corresponding silylethers, while tertiary alcohols were not converted to the corresponding silylated products (0% yield). Also, the chemoselectivity of **EDPBT** in the silylation method was explored. Figure 2 clearly shows that alcohols in the presence of amines or thiols were completely converted to the corresponding trimethylsilyl ethers as sole product (Figure 2).
To show the efficiency of the **EDPBT** in comparison with older reported procedures in the literature, table 3 compares some of our results with DABCO-bromine [23], sulfonic acid-functionalized [24], DBDEB [25], $Mg(OTf)_2$ [26] and H-β zeolite [27] respect to reaction times and yields of obtained products (Table 3).
Also, for the comparison of **EDPBT** with some other tribromides, we applied our reaction protocols for the silylation of 4-chlorobenzyl alcohol in the presence of some reported tribromides. As shown in Table 4, **EDPBT** has some advantages to other in terms of reaction time and simplicity of work-up procedure.
In all studied reactions, fast evaluation of ammonia gas was observed. Thus, according to the observation due to the reaction and previously experiences [16,18], a reasonable mechanism was proposed in which the generation of NH_3 and catalytic role of **EDPBT** (as a Br^+ source) in a catalytic cycle are clarified (Figure 3) [25,28].
In continuation of our researches on the deprotection reactions [29-31], we decided to study the ability of **EDPBT** as catalyst in regeneration of the parent alcohols from the corresponding trimethylsilyl ether. Therefore, in this part of the work, **EDPBT** was successfully used as a suitable catalyst for the conversion of several trimethylsilyl ethers to the corresponding alcohols in the presence of wet SiO_2 (60% w/w) in high yields at room temperature (Figure 4). The results are summarized in Table 5.

3. Conclusion

A practical, efficient and convenient method for the silylation of hydroxyl compounds as well as deprotection of trimethylsilyl ethers is described. Very low molar ratio of the **EDPBT** in comparison to previously reported catalysts is a main advantage of the described method. Therefore, we think this method, in addition to the current methodologies, can be suitable for the silylation of hydroxyl groups and regeneration of parent alcohols from corresponding trimethylsilyl ethers.

4. Experimental

General: Chemicals were purchased from Fluka, Merck and Aldrich chemical companies. The products were characterized by comparison of their spectral (IR and ^{1}H-NMR) and physical data with those authentic samples which were produced by other reported procedures [23]. 1,1'-(Ethane-1,2-diyl)dipyridinium bistribromide (**EDPBT**) was prepared according to recently reported procedure by Kavala *et al* [17]. GC analysis was run with Shimadzu GC-14A. TLC was performed on Silica gel polygram SIL G/UV 254 plates.

General procedure for the silylation of alcohols

To a stirring solution of compound containing hydroxyl group (1 mmol) and HMDS (0.8-1.8 mmol) in CH_3CN (4 mL) was added **EDPBT** (0.0015 mmol) and stirred at room temperature for the time specified in Table 2. The reaction was followed by GC (or TLC, *n*-hexane/EtOAc, 9:1). After completion of the reaction, the reaction mixture was passed through a short pad of silica gel. Evaporation of the solvent under reduced pressure gave pure products.

General procedure for deprotection of trimethylsilyl ethers

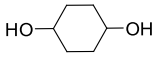
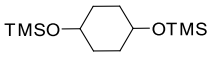
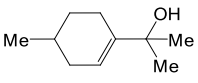
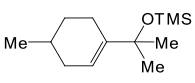
A mixture of the trimethylsilyl ethers (1 mmol; see Table 5 for substrates and stirring times), CH_3CN (4 ml), **EDPBT** (0.0015 mmol) and wet SiO_2 (0.2 g) was stirred at room temperature for the specified time. The reaction was monitored by TLC using a 9:1 mixture of *n*-hexane/EtOAc as an eluent. After completion of the reaction the mixture was filtered and the solid residue was washed with CH_3CN. The filtrate was dried over anhydrous Na_2SO_4 (3 g) and filtered off after appropriate time. Preparative thin layer chromatography on short pad of silica gel with CH_3CN afforded pure products in 78-90% yields.

Spectroscopic data for selected products:

Entry 1: ^{1}H NMR (90 MHz, $CDCl_3$): δ = 0.19 (s, 9H), 4.72 (s, 2H), 7.341 (s, 5H,). IR (KBr): 2953, 1450, 1249, 1093 and 1033 cm^{-1}.
Entry 7: ^{1}H NMR (90 MHz, $CDCl_3$): δ = 0.144 (s, 9H), 2.90 (t, 2H), 3.85 (t, 2H,) and 7.29 (s, 5H). IR (KBr): 3025, 2956, 1497, 1251, 1095 and 841 cm^{-1}.
Entry 9: ^{1}H NMR (90 MHz, $CDCl_3$): δ = 0.24 (s, 9H), 6.87-7.2 (m, 5H). IR (KBr): 3040, 2961, 1597, 1493, 1253, 918 and 844 cm^{-1}.
Entry 16: ^{1}H NMR (90 MHz, $CDCl_3$): δ = 0.121 (s, 9H), 0.67-1.5 (m, 33H), 2.17 (m, 10H,), 3.48 (b, 1H) and 5.34 (b, 1H). ^{1}H NMR (22.5 MHz, $CDCl_3$): δ = 0361, 11.938, 18.838, 19.432, 21.192, 22.837, 22.648, 24.0, 28.053, 32.059, 35.894, 36.353, 37.527, 39.953, 42.431, 42.844, 50.362, 56.919, 72.455, 121.329, 141.397.

Table 2.

Silylation of alcohols, phenols and naphthols (1 mmol), with HMDS (0.8-18 mmol) in the presence of T **EDPBT** (0.0015-0.002 mmol), and acetonitrile (4 mL) at room temperature

Entry	Substrate	Product	EDPBT (mmol)	HMDS (mmol)	Time (min)	Yield[a] (%)
1	Ph-CH_2OH	Ph-CH_2OTMS	0.0015	1.1	10	100
2	4-Br-Ph-CH_2OH	4-Br-Ph-CH_2OTMS	0.0015	0.8	10	98
3	4-Cl-Ph-CH_2OH	4-Br-Ph-CH_2OTMS	0.0015	0.8	10	100
4	2,4-Cl_2-Ph-CH_2OH	2,4-Cl_2-Ph-CH_2OTMS	0.0015	0.8	10	100
5	4-F-Ph-CH_2OH	4-F-Ph-CH_2OTMS	0.0015	0.9	10	90
6			0.0015	0.8	15	90
7	Ph-CH_2CH_2OH	Ph-CH_2CH_2OTMS	0.0015	0.9	10	98
8	*n*-$C_8H_{17}OH$	*n*-$C_8H_{17}OTMS$	0.0015	0.8	5	100
9	Ph-OH	Ph-OTMS	0.0015	1.1	20	88
10	4-OMe-Ph-OH	4-OMe-Ph-OTMS	0.0015	1.1	60	--
11	4-F-Ph-OH	4-F-Ph-OTMS	0.0015	1.1	30	--
12	2-NO_2-Ph-OH	2-NO_2-Ph-OTMS	0.0015	1.1	60	--
13	4-NO_2-Ph-OH	4-NO_2-Ph-OTMS	0.0015	1.1	60	--
14	4-NH_2-Ph-OH	4-NH_2-Ph-OTMS	0.0015	1.1	60	--
15	Cyclohexyl-OH	Cyclohexyl-OTMS	0.0015	0.8	10	100
16	Cholesteryl-OH	Cholesteryl-OTMS	00.002	1.5	15	96[c, d]
17	Cyclodecanyl-OH	Cyclodecanyl-OTMS	0.0015	0.8	15	100
18			0.0015	1.8	30	--
19	$(Ph)_2$-CH-OH	$(Ph)_2$-CH-OTMS	0.0015	0.9	20	--
20	Indanyl-OH	Indanyl-OTMS	0.0015	0.8	5	97
21	2-Adamantanyl-OH	2-Adamantanyl-OTMS	00.002	1.5	10	90
22	Ph-CH_2-$C(CH_3)_2$-OH	Ph-CH_2-$C(CH_3)_2$-OTMS	0.0015	0.8	60	--
23			0.0015	0.8	80	98
24	2-Furyl-CH_2-OH	2-Furyl-CH_2-OTMS	0.0015	0.8	20	100
25	2-Pyridyl-CH_2-OH	2-Pyridyl-CH_2-OTMS	0.0015	0.9	15	97
26	2,4,6-$(CH_3)_3$-Ph-OH	2,4,6-$(CH_3)_3$-Ph-OTMS	0.0015	1.1	15	88[c]
27	4-CHO-Ph-OH	4-CHO-Ph-OTMS	0.0015	1.1	60	--
28	2-Naphthyl-OH	2-Naphthyl-OTHS	0.0015	1.1	50	--

[a:] GC yield [b:] Uncompleted reaction [c:] Isolated yield [d:] In the CH_2Cl_2

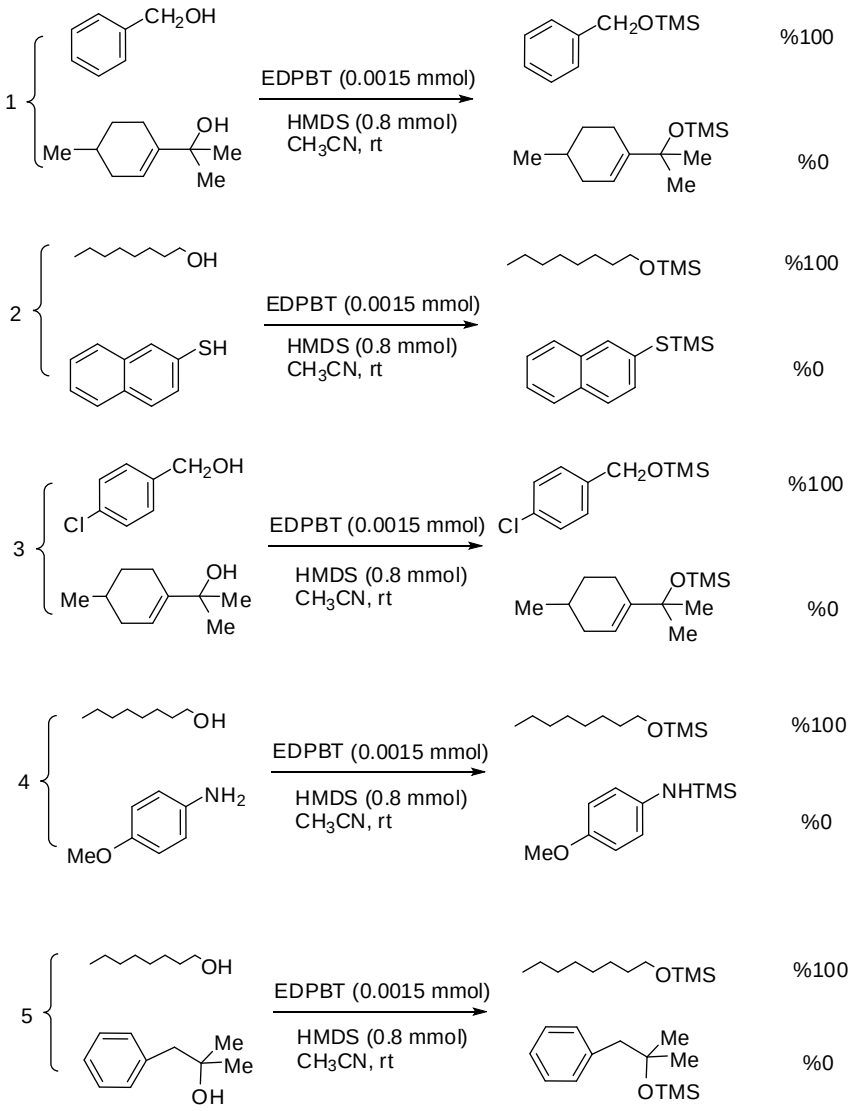


Figure 2.

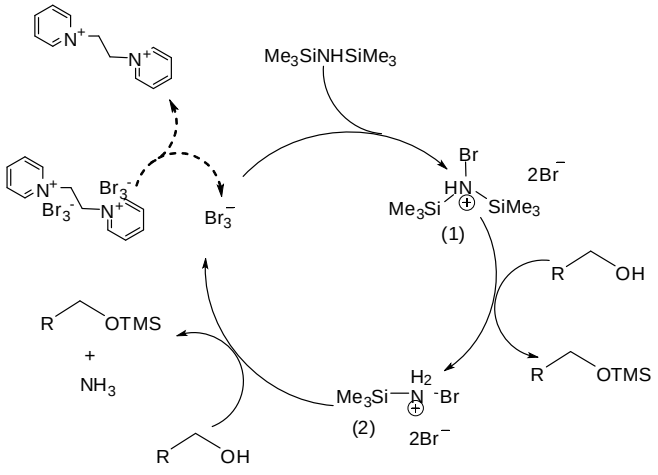


Figure 3.

Table 3.

Comparison of the results **EDPBT** with various reported catalysis in the synthesis of trimethylsilylether using HMDS.

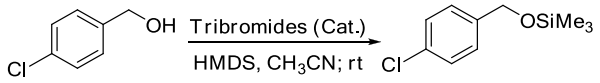
Entry	Substrate	Time (min)/ yield (%)[a]					
		EDPBT	TCCA	sulfonic acid-functionalized	DBDEB	$Mg(OTf)_2$	H-β zeolite
1	Ph-CH_2OH	10/100[b]	240/90	55/99[b]	30/95	38/95	300/95
2	Ph-OH	20/88	10.8/92	120/90[b]	-	60/70	600/87
3	Cyclohexyl-OH	10/100[b]	90/85	60/92[b]	150/96	-	700/95
4	*n*-$C_8H_{17}OH$	5/100[b]	240/87	-	180/87	50/95	-
5	Ph-CH_2CH_2OH	10/100[b]	160/90	40/100[b]	-	-	-

[a:] Isolated yield.

[b:] GC Yield.

Table 4.

Comparison between **EDPBT** and some reported tribromides in the silylation of 4-chlorobenzyl alcohol



Entry	Tribromide[ref]	Time (min)	Yield(%)	
			GC	Isolated
1	EDPBT	10	100	93
2	DABCO-bromine[12]	15	100	85
3	HMTAB[11]	15	100	90
4	Py-HBr_3[10]	15	100	82

IR (Nojul): 2853, 1468, 1378, 1245, 1085 and 840 cm^{-1}. MS: *m/e* (relative intensity): 460 (*M* + 2), 459 (*M* + 1), 458 (*M*), 443, 386, 368, 329, 255, 247, 213, 149, 129, 73.

Entry 19: ^1H NMR (90 MHz, $CDCl_3$): δ = 0.39 (s, 9H), 6.06 (s, 1H), and 7.61 (m, 10H,). IR (KBr): 2855, 1463, 1377, 1250, 1098 and 841 cm^{-1}.

Entry 28: ^1H NMR (90 MHz, $CDCl_3$): δ = 0.463 (s, 9H) and 7.17-7.80 (m, 7H). IR (Nojul): 1632, 1600, 1468, 1255, 970 and 847 cm^{-1}.

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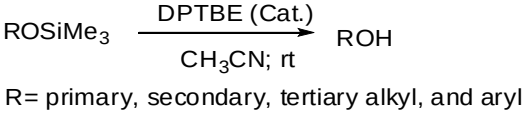

Figure 4.

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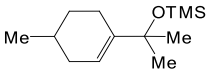
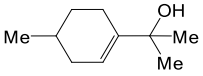
Table 5.

Deprotection of silylethers (1 mmol) in the presence of **EDPBT** (0.0015 mmol), wet SiO_2 (60% w/w, 0.2 g) and acetonitrile (4 mL) at room temperature

Entry	Substrate	Product	Time (min)	Yield(%)[a]
1	Ph-CH_2OTMS	Ph-CH_2OH	10	90
2			15	80
3	Ph-CH_2CH_2OH	Ph-CH_2CH_2OH	35	79
4	Cyclodecanyl-OTMS	Cyclodecanyl-OH	120	90
5	4-Cl-Ph-CH_2OTMS	4-Cl-Ph-CH_2OH	110	82
6	4-OMe-Ph-CH_2OTMS	4-OMe-Ph-CH_2OH	15	90
7	*n*-C_8H_{17}OTMS	*n*-C_8H_{17}OH	100	80
8	2,4-Cl_2-Ph-CH_2OTMS	2,4-Cl_2-Ph-CH_2OH	120	78

[a:] Isolated yield

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