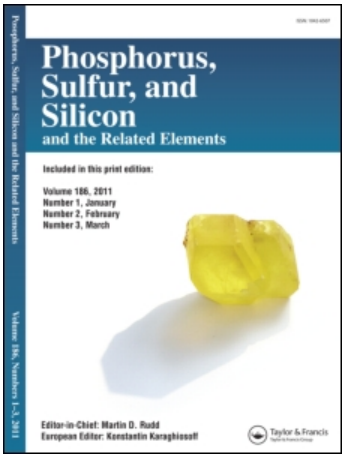

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N,N′-Dibromo-*N,N′*-1,2-ethanediylbis (Benzene Sulfonamide) as a Novel *N*-Bromo Reagent–Catalyzed Trimethylsilylation of Alcohols and Phenol With Hexamethyldisilazane in Both Solution and Solvent-Free Conditions

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Preparation and catalytic application of N,N′-dibromo-N,N′-1,2-ethanediylbis (benzene sulfonamide) for the trimethylsilylation of several of alcohols and phenols with hexamethyldisilazane in good to excellent yields under both solution and solvent-free conditions at r.t. is descried.

Keywords Alcohols; phenols; *N,N′*-dibromo-*N,N′*-1,2-ethanediylbis (benzene sulfonamide); hexamethyldisilazane; trimethylsilylation; solvent-free

INTRODUCTION

Functional-group manipulation through the protection–deprotection strategy is an unavoidable exercise in the synthesis of multifunctional target molecules. Among the various protecting groups used for hydroxyl function, the trimethylsilyl group is one of the popular methods.[1] Several methods have become available for trimethylsilylation of the hydroxy functional group using a variety of silylating

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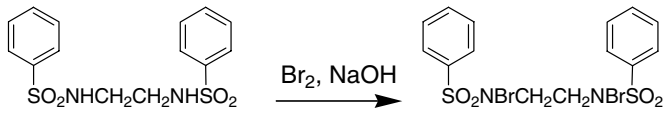
agents.[2–6] 1,1,1,3,3,3-hexamethyldisilazane (HMDS) is a stable, cheap, and commercially available compound that can be used for the preparation of trimethylsilyl ethers from hydroxy compounds, giving ammonia as the only byproduct. However, the major disadvantage and drawback of this reagent is its poor silylating power, which needs forceful conditions and long reaction times in many reactions.[7] Therefore, a variety of catalysts have been reported for the activation of HMDS.[8–20]

RESULTS AND DISCUSSION

The search for a new *N*-halo combination for the transformation of organic functional groups has been a matter of our continued interest.[21] We wish to report a new *N*–halo sulfonamide compound as a catalyst agent for mild, facile, high-yielding and homogeneous reaction conditions applied to the trimethylsilylation of alcohol and phenols. Therefore, we now introduce *N,N′*-dibromo-*N,N′*-1,2-ethanediylbis(benzene sulfonamide) **[BNBBS] 2**, which is a stable compound and can be stored and used after several months without any loss of activity. It is inexpensive and soluble in most organic solvents, and it is not explosive even when heated in solution. The reagent **2** was prepared similarly to a previously reported reagent[21a] from *N,N′*-1,2-ethanediylbis(benzene sulfonamide) **1** by the action of molecular bromine in an alkaline medium (Scheme 1).

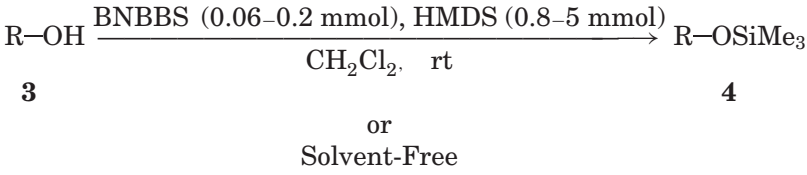


1 **2[BNBBS]**

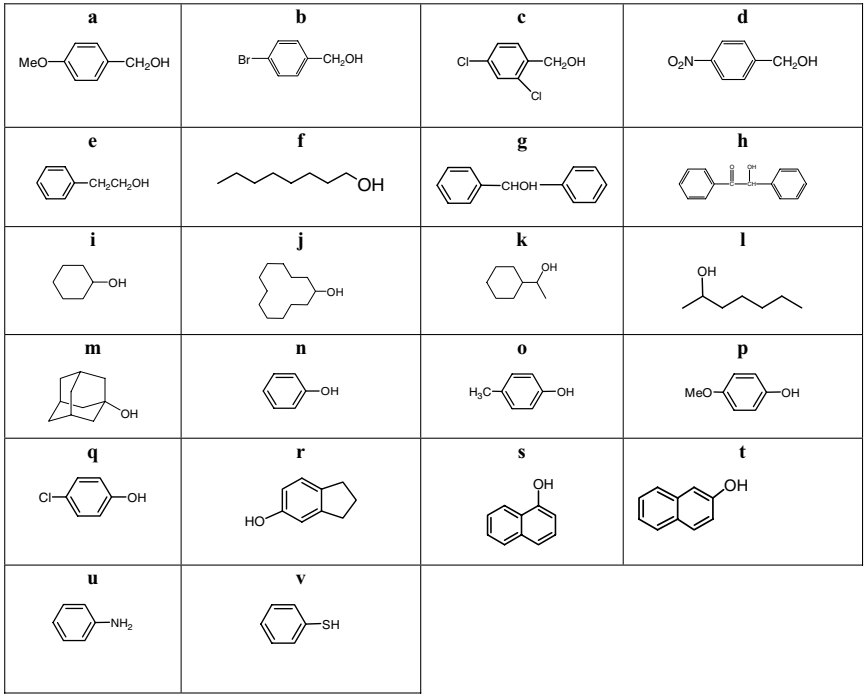
SCHEME 1

In this research, the catalytic application of BNBBS for the efficient trimetylsilylation of a wide range of alcohols and phenols using HMDS both in dichloromethane (**I**) and solvent-free (**II**) conditions have been investigated. The trimethylsilylation of thiols and amines by this protocol failed; starting materials were isolated from the mixture (Scheme 2 and Table I).

In order to show selectivity of this catalytic system, we tried several competitive reactions under similar conditions. In a binary



R = benzylic, linear, Cyclic, Aryl



SCHEME 2

mixture of 4-bromobenzyl alcohol (as a model for primary alcohol) and 1-adamantanol (as a model for tertiary alcohol), the primary alcohol was completely converted to the corresponding trimethylsilyl ether, while 0% conversion was observed for the tertiary alcohol (Table II, entry 1). Excellent selectivity was also observed for secondary alcohols in the presence of a tertiary alcohol (Table II, entry 2). Similarly, this method showed excellent selectivity for the trimethylsilylation of phenol in the presence of aniline or thiophenol (Table II, entries 3, 4).

TABLE I Trimethylsilylation of Alcohols and Phenols Using HMDS Catalyzed with BNBBS both in Dichloromethane (I) and Solvent-Free (II) Conditions at R.T.

Entry	Substrate	Product[a]	Subst/HMDS/ BNBBS		Time (h)		Yield (%)[b]	
			I	II	I	II	I	II
1	3a	4a	1:0.8:0.06	1:0.8:0.06	4	0.66	90	95
2	3b	4b	1:0.8:0.06	1:0.8:0.06	1	0.5	95	93
3	3c	4c	1:0.8:0.06	1:2:0.06	1	1	94	95
4	3d	4d	1:0.8:0.06	1:0.8:0.06	8	7	95	75
5	3e	4e	1:0.8:0.06	1:0.8:0.06	3	3.5	90	92
6	3f	4f	1:0.8:0.06	1:0.8:0.06	2.5	3.5	87	87
7	3g	4g	1:1:0.06	1:3:0.06	5	5.5	95	94
8	3h	4h	1:2:0.07	1:3:0.07	10	18	96	90
9	3i	4i	1:0.8:0.06	1:0.8:0.06	10	11	85	77
10	3j	4j	1:0.8:0.06	1:1.6:0.06	9	11.5	93	65
11	3k	4k	1:0.8:0.06	1:0.8:0.06	4	7.5	95	96
12	3l	4l	1:0.8:0.06	1:0.8:0.06	3	7.5	85	88
13	3m	4m	1:3:0.2	1:5:0.2	10	48	95	78
14	3n	4n	1:0.8:0.06	1:0.8:0.06	1.8	4	92	93
15	3o	4o	1:0.8:0.06	1:0.8:0.06	2	0.66	90	94
16	3p	4p	1:0.8:0.06	1:0.8:0.06	1.5	1.6	90	92
17	3q	4q	1:0.8:0.06	1:0.8:0.06	2	3.25	92	95
18	3r	4r	1:0.8:0.06	1:0.8:0.06	1.5	0.5	92	91
19	3s	4s	1:0.8:0.06	1:0.8:0.06	0.5	0.75	95	96
20	3t	4t	1:0.8:0.06	1:0.8:0.06	2	3	93	94
21	3u	4u	1:3:0.2	1:3:0.2	15	0	0	0
22	3v	4v	1:3:0.2	1:3:0.2	15	0	0	0

[a]All products were characterized by comparison of their spectral data (^{1}H- NMR, IR spectroscopy) with those of authentic samples.

[b]Yields of isolated product.

In order to learn the catalytic activity of BNBBS, we compared our obtained results for the trimethylsilylation of 1-*n*aphtol (as a model for phenols) with the best of the well-known data from the literature (Table III). However, we found that in some cases trimethylsilylation with phenols has been not reported;[16,8] has required forcing conditions,[19] prolonged reaction time,[19] and large amounts of catalyst;[18] and has obtained a low yield of product[19] or the need of volatile organic solvents.[19]

Other disadvantages of reported catalysts are moisture sensitivity,[18] toxicity, and corrosivity.[16]

The actual role of BNBBS in these reactions is not clear and should be studied in detail.

TABLE II Selective Reactions of Different Binary Mixtures With HMDS/ BNBBS at R.T.

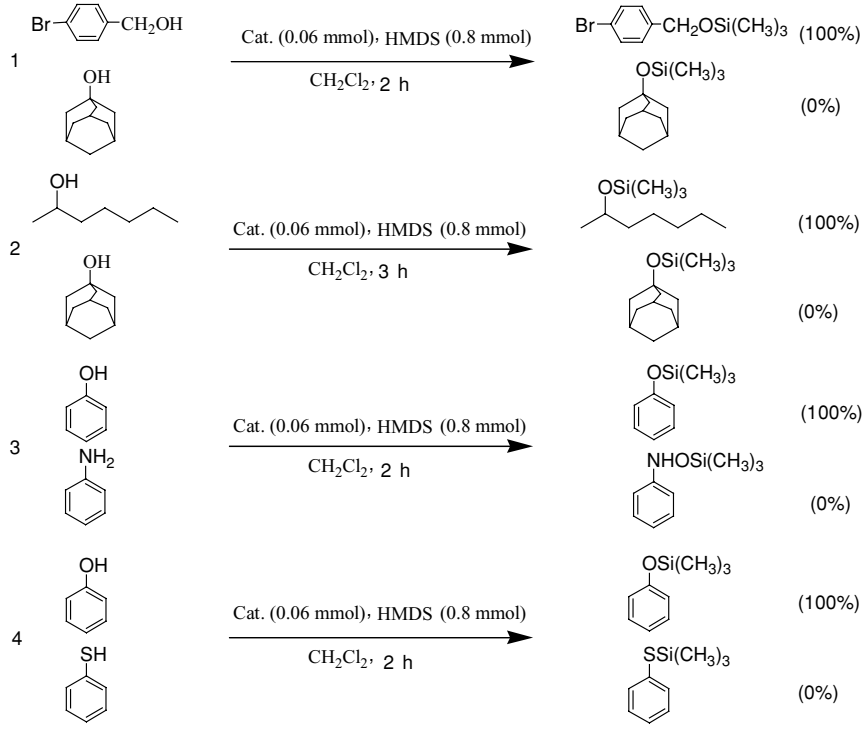
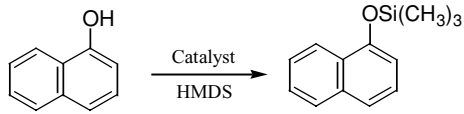


TABLE III Comparison of the Activity of Various Catalysts in the Trimethylsilylation of 1-*n*aphtol With HMDS



Entry	Catalyst	Condition	HMDS:Cat	Time	Yield (%)	Ref
1	BNBBS	Solvent-free, r.t.	0.8:0.06	45 min	96	This work
2	BNBBS	CH_2Cl_2, r.t.	0.8:0.06	30 min	95	This work
3	$CuSO_4.5H_2O$	CH_3CN, reflux	0.7:0.1	38 h	50	19
4	$LiClO_4$	Solvent-free, r.t.	0.7:0.5	20 min	80	18
7	I_2	CH_2Cl_2, r.t.	0.8:0.01	—	—	16
8	$Si(CH_3)_3Cl$	Solvent-free, 125°C	0.8:two drops	—	—	8

CONCLUSION

In summary, we have demonstrated that BNBBS is effective as a non-corrosive and practically neutral catalyst for the trimethylsilylation of a variety of alcohols and phenols using HMDS under mild conditions. The notable special features of this methodology are the simple reaction procedure, selectivity, excellent yields of products, easy work up, easy preparation of a catalyst, and low toxicity. The recovered starting martial 1 was rebrominated and was used many times without reducing activity.

EXPERIMENTAL

Preparation of *N,N′*-1,2-ethanediylbis (Benzene Sulfonamide) 1

Benzenesulfonyl chloride (30.0 g, 169.25 mmol) was placed in a beaker, ethylenediamine (8 mL, 78.9 mmol) was added dropwise (over 30 min), and the mixture was stirred with a glass rod. The mixture was heated (90°C) and stirred for 30 min. Distilled H_2O (100 mL) was added, and the precipitate filtered off. The crude product was recrystallized from EtOH; yield: (88%); m.p. 160°C.

IR (KBr) ν (cm^{-1}): 3319(m), 3272(s), 1583(w), 1327(s), 1156(s), 1092(s), 998(m), 906(m), 840(m), 754(s), 687(s). (w: weak, m: medium, s: strong).

^1H NMR ($CDCl_3$), δ (ppm): 3.28–3.56 (4H, d), 5.5 (2H, s), 7.5–7.9 (5H, m).

Preparation of *N,N′*-Dibromo-*N,N′*-1,2-ethanediylbis (Benzene Sulfonamide) 2

The sulfonamide 1 (10.0 g, 20 mmol) was dissolved in a slight molar excess of chilled aqueous NaOH solution (3 M) at r.t. and the solution was transferred to a beaker. A solution of Br_2 (3 mL, 58.4 mmol) in CCl_4 (6 mL) was added to the sulfonamide solution with vigorous stirring. Immediately a yellow precipitate began to form. The yellow precipitate was collected by suction on a Büchner funnel, washed with cold distilled H_2O (30 mL), and dried in a vacuum desiccator at r.t. for 6 h. The yield of the pure product was 83%. The product was stable at r.t. and was not sensitive to air.

IR (KBr) ν (cm-1): 2854(m), 1310(s), 1088(m), 841(m), 721(s), 687(m), 594(m). (w: weak, m: medium, s: strong).

1H NMR ($CDCl_3$), δ (ppm): 3.28–3.56 (4H, d), 7.66 (2H, d), 7.93 (2H, d).

General Procedure for the Trimethylsilylation of Alcohols and Phenols Using HMDS Catalyzed with BNBBS in Solution

Alcohol or phenol (1 mmol) was added to a mixture of HMDS (0.7 mmol) and BNBBS (0.06–0.1 mmol) in CH_2Cl_2 (7 mL), and then the mixture was stirred at r.t. for the specified time (Table I). The reaction was monitored by TLC (10:1, n-hexane:acetone). After completion of the reaction, the water (10 mL) was added to the reaction mixture to destroy the extra amounts of HMDS, and then the organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated, and then *n*-hexane (20 mL) was added to the residual mixture. Insoluble *N,N′*-1,2-ethanediylbis (benzene sulfonamide) was removed by filtration. Evaporation of *n*-hexane under reduced pressure gave the highly pure product without further purification.

Trimethylsilylation of Alcohols and Phenols Using HMDS Catalyzed with BNBBS under Solvent-Free Conditions: General Procedure

Alcohol or phenol (1 mmol) was added to a mixture of HMDS (0.8–5 mmol) and BNBBS (0.06–0.2 mmol), and then the mixture was stirred at r.t. for the appropriate reaction time (Table I). The reaction was monitored by TLC (10:1, n-hexane:acetone). After completion of the reaction, the resulting mixture was applied on a silica gel pad and was washed with a mixture of n-hexane/acetone (10:1). Evaporation of the solvent under reduced pressure gave the desired compound in a high purity.

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