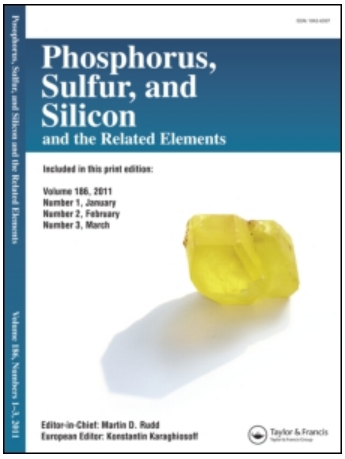

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Silylation of Alcohols and Phenols Using Hexamethyldisilazane Catalyzed by *N,N'*-Diiodo-*N,N'*-1,2-ethanediyl Bis(*p*-toluenesulfonamide) Under Solvent-Free and Microwave Conditions

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SILYLATION OF ALCOHOLS AND PHENOLS USING HEXAMETHYLDISILAZANE CATALYZED BY *N,N′*-DIIODO-*N,N′*-1,2-ETHANEDIYL BIS(*p*-TOLUENESULFONAMIDE) UNDER SOLVENT-FREE AND MICROWAVE CONDITIONS

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N,N′-Diiodo-N,N′-1,2-ethanediyl bis(p-toluenesulfonamide) (NIBTS) is an effective catalyst for the silylation of alcohols and phenols using hexamethyldisilazane under solvent-free and microwave conditions.

Supplemental materials are available for this article. Go to the publisher's online edition of* Phosphorus, Sulfur, and Silicon and the Related Elements *to view the free supplemental file.

Keywords Alcohols; HMDS; microwave irradiation; NIBTS; phenols; silylation; solvent-free

INTRODUCTION

The silylation of organic compounds is widely applied for the protection of hydroxyl group in organic synthesis.[1–3] Several methods are available for silylation of a hydroxy functional group using a variety of silylating agents.[2,4–6] 1,1,1,3,3,3-Hexamethyldisilazane (HMDS) is convenient as a silylating agent, because it is a stable, commercially available, cheap reagent and gives ammonia as the only byproduct. In addition, silylation with HMDS is nearly neutral and does not need special precautions. However, the main drawback of HMDS is its poor silylating power, which needs forceful conditions and long reaction times in many cases.[7] A variety of catalysts such as $(CH_3)_3SiCl$,[8] sulfonic acids,[9] $ZnCl_2$,[10] K-10 montmorillonite,[11] $LiClO_4$,[12] $H_3PW_{12}O_{40}$,[13] iodine,[14] nitrogen-ligand complexes of metal chlorides,[15] zirconium sulfophenyl phosphonate,[16] TBAPINO,[17] $ZrO(OTf)_2$,[18] $Fe(F_3CCO_2)_3$,[19] ZnO,[20] $NaHSO_4{\cdot}SiO_2$,[21] sulfonic acid-functionalized ordered nanoporous silica,[22] alumina sulfuric acid,[23] silica sulfuric acid,[24] indium tribromide,[25] and KBr[26] have

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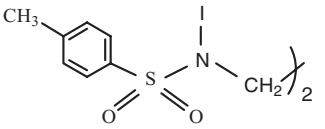


NIBTS

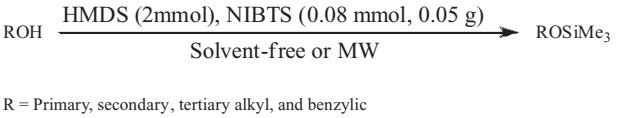
Figure 1 Structure of *N,N′*-diiodo-*N,N′*-1,2-ethanediylbis(p-toluenesulfonamide).

been developed for the activation of HMDS. Although these procedures provide an improvement, many of these catalysts need long reaction times, drastic reaction conditions, tedious workup, or are moisture-sensitive or expensive. Hence, introduction of new methods to circumvent these problems are still in demand.

RESULTS AND DISCUSSION

With our interest in the application of *N,N'*-diiodo-*N,N'*-1,2-ethanediyl *bis*(*p*-toluene sulfonamide) (NIBTS)[27] (Figure 1) as a mild catalyst in organic synthesis, in this article we report a simple method for the silylation of alcohols and phenols in the presence of NIBTS as an effective catalyst with HMDS under solvent-free and microwave irradiation conditions.

The reaction of alcohols and phenols with HMDS in the presence of NIBTS brings about *o*-silylation without side-product formation (Scheme 1).



R = Primary, secondary, tertiary alkyl, and benzylic

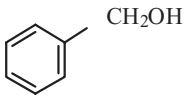
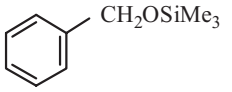
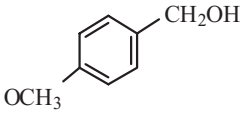
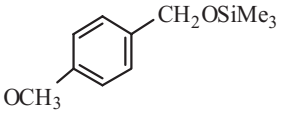
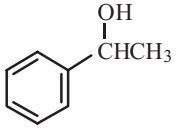
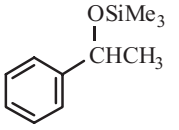
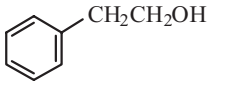
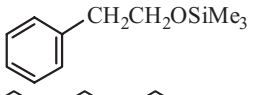
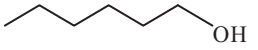
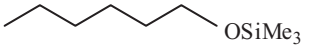
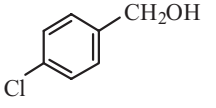
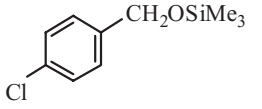
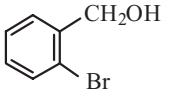
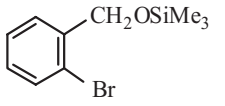
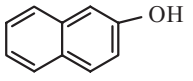
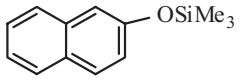
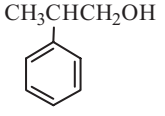
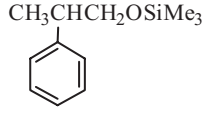
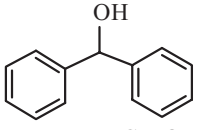
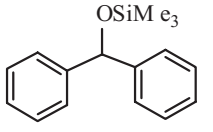
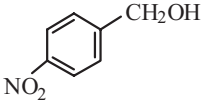
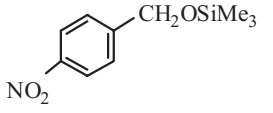
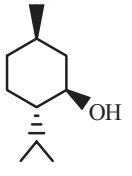
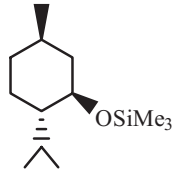
Scheme 1

First we carried out the reaction of benzyl alcohol with HMDS in the presence of NIBTS under solvent-free and microwave conditions (see Scheme S1, available online in the Supplemental Materials). We found a good yield obtained in 0.05 g (8 mol%) of NIBTS in solvent-free and microwave irradiation conditions (Table I). As shown in Table II, treatment of a variety of alcohols and phenols with HMDS in the presence of

Table I The effect of the amount of NIBTS on the reaction of benzyl alcohol and HMDS under solvent-free and MW conditions

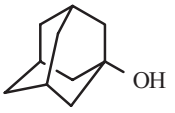
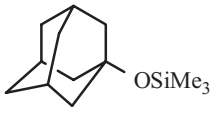
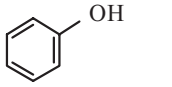
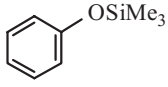
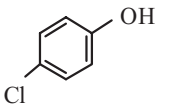
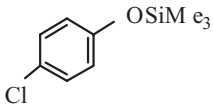
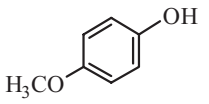
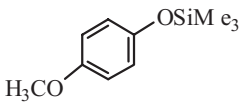
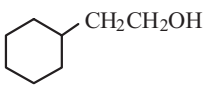
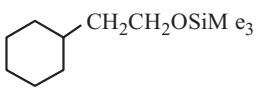
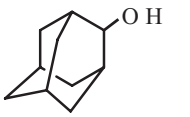
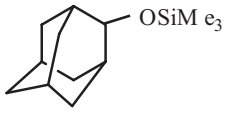
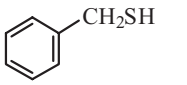
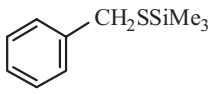
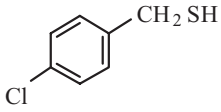
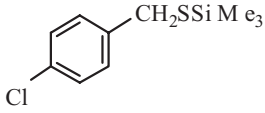
	Solvent-free		Microwave	
NIBTS (g)	Time (min)	Yield (%)	Time (min)	Yield (%)
0.01	5	Very low	1	Very low
0.02	5	75	1	60
0.03	5	75	1	80
0.04	5	86	1	93
0.045	5	90	1	96
0.05	5	95	1	98

Table II Silylation of alcohols and phenols using HMDS in the presence of NIBTS under solvent-free and MW conditions

Entry	Substrate	Product	Yield (%)/ Time (min)	Yield (%)/ Time (min)	References
1			95/5	98/1	18
2			96/12	100/1	18
3			80/40	87/16	18
4			94/12	96/3	18
5			80/60	90/10	18
6			93/9	96/1	18
7			95/10	97/4	28
8			80/219	88/1	18
9			92/30	96/7	28
10			92/15	95/5	18
11			88/230	81/12	28
12			76/115	87/10	14

(Continued on next page)

Table II Silylation of alcohols and phenols using HMDS in the presence of NIBTS under solvent-free and MW conditions *(Continued)*

Entry	Substrate	Product	Yield (%)/ Time (min)	Yield (%)/ Time (min)	References
13			88/35	90/6	18
14			87/46	94/3	29
15			90/110	95/1	29
16			84/24	93/6	30
17			86/130	80/8	18
18			67/440	90/12	28
19			12/—[a]	10/—[a]	—
20			12/—[a]	30/—[a]	—

[a]No reaction.

NIBTS gave the corresponding trimethylsilyl ethers in good to excellent yields. Primary and secondary benzylic alcohols and phenols were all protected using NIBTS in excellent yields under solvent-free or microwave conditions. Primary benzylic alcohols (with electron-releasing and electron-withdrawing groups) and aliphatic (linear, cyclic) alcohols were trimethylsilylated with excellent yield. We also found that hindered tertiary alcohols such as adamantanol (Table II, entry 13) were silylated in high yields. We found that NIBTS was not suitable for the silylation of thiols under solvent-free and microwave conditions (Table II, entries 18 and 19), as this reagent converted thiols to disulfides instead of to silyl thiols (Scheme S2, available online in the Supplemental Materials).

Our experiments also indicated that NIBTS is a reusable catalyst; after five runs, the catalytic activity was almost the same as fresh catalyst. Thus, after the successful silylation of benzyl alcohol in the first run under microwave irradiation (98%), the *N,N′*-diiodo-*N,N′*-1,2-ethanediyl bis(*p*-toluenesulfonamide) (NIBTS) catalyst was subjected to a second run reaction, from which it gave the product in 98% yield. The average chemical yield for five consecutive runs was 96% (see Table S1 online in the Supplemental Materials).

In conclusion, we have introduced the catalytic reagent *N,N′*-diido-*N,N′*-1,2-ethanediyl *bis* (*p*-toluenesulfonamide) (NIBTS) as the activator of HMDS for the protection of a various alcohols and phenols under solvent-free or microwave irradiation conditions. The catalyst is heterogeneous, non-corrosive, and environmentally benign. Isolation of products involved simple extraction and evaporation of the solvent.

EXPERIMENTAL

General Method for the Silylation of Alcohols and Phenols Using HMDS and NIBTS Under Solvent-Free Conditions

Alcohol or phenol (1 mmol), NIBTS (0.05 g, 0.08 mmol), and HMDS (2 mmol) were added to a mortar, and the mixture was pulverized vigorously with a pestle. The reaction was monitored by TLC (8:2, *n*-hexane:acetone). After completion of the reaction, CH_2Cl_2 (15 mL) was added, and the catalyst was removed by filtration. The organic phase was dried over anhydrous Na_2SO_4 (1 g). Evaporation of the solvent under reduced pressure gave the product. Further purification was achieved by distillation or recrystallization to afford pure silyl ethers (Table I).

General Method for the Silylation of Alcohols and Phenols Using HMDS and NIBTS Under Microwave Irradiation

Alcohol or phenol (1 mmol), NIBTS (0.05 g, 0.08 mmol), and HMDS (2 mmol) were added to a round-bottomed flask (25 mL). The flask was placed in a bath containing SiO_2 to enable absorption of additional microwave irradiation. The flask was irradiated in a microwave oven at a power output with (900 W) (LG Co. microwave, 230 V $\sim$ 50 Hz, RF output 900 W). After completion of the reaction [1–16 min, Table I, monitored by TLC (8:2, *n*-hexane:acetone)], CH_2Cl_2 (15 mL) was added, and the catalyst was removed by filtration. The organic phase was dried over anhydrous Na_2SO_4 (1 g). Evaporation of the solvent under reduced pressure gave the product. Further purification was achieved by distillation or recrystallization to afford pure silyl ethers (Table I).

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