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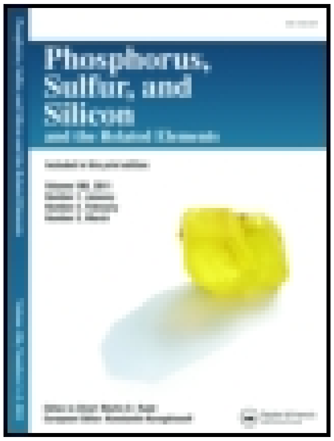

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Silylation of Hydroxy Groups with HMDS Under Microwave Irradiation and Solvent-Free Conditions

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SILYLATION OF HYDROXY GROUPS WITH HMDS UNDER MICROWAVE IRRADIATION AND SOLVENT-FREE CONDITIONS

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(Received August 7 2001.)

Phenols and alcohols are silylated with hexamethyldisilazane (HMDS) under microwave irradiation in solvent-free condition in good to excellent yields.

Keywords: Phenols; silylation of alcohols

Many chemical conversions and multiple synthesis sequences often require protection of hydroxy groups. The trimethylsilyl group is one of the most widely used protecting groups in organic synthesis and is often used to prepare silyl ethers as volatile derivatives of alcohols and phenols.[1–5] Several silylating reagents are available for this conversion, including trimethylsilyl halides in the presence of a tertiary amine[6,7] or lithium sulfide,[8] hexamethyldisilazane,[9] hexamethyldisiloxane (HMDSO) in acidic media,[10] allylsilazane,[11,12] and so on.[13,14] HMDS is an inexpensive and commercially available reagent; its handling does not require special precautions and the work up of the reaction mixture is easy and rapid. The major disadvantage and drawback of this reagent is its poor silylating power, which needs special conditions in most cases. Several catalysts such as trimethylchlorosilane,[15] sulfuric acid, amines or trimethylsilyl amide,[16] imidazole,[17] zinc chloride,[18] metalloporphirins,[19,20] and very recently iodine[21] in CH_2Cl_2, have been used for silylation with HMDS. Although these methods resulted in improved reaction conditions in many cases, several hours are still necessary for complete reaction.

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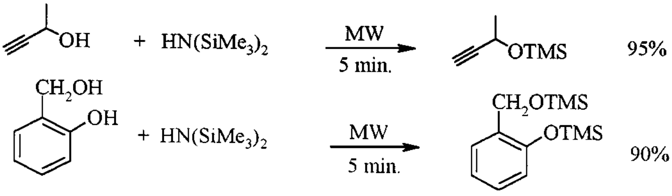
Microwave irradiation is a very useful technique in organic synthesis,[22–27] and microwave heating under solvent-free conditions has attracted much attention in recent years.[28]

RESULTS AND DISCUSSION

In conjunction with our recent work on microwave-assisted reaction under solvent-free condition,[29,30] we now have found that phenols and alcohols may be silylated by using HMDS under dry and nonpolluting conditions. When a phenol or an alcohol is treated with neat HMDS under microwave irradiation, the corresponding silyl ethers were obtained. To establish the generality of this method, the reaction was conducted with a variety of phenols and alcohols. Table I summarizes the data for the preparation of silyl ethers, which were obtained in good to excellent yields. In contrast, by the use of classical heating, silylation of *o*-cresol with HMDS gave a low yield (ca. 20%) of silylated product after 4 h. To examine relatively large scale synthesis, when 10 mmol of 1-naphthol were irradiated in a conventional microwave oven for 8 min, 1-trimethylsiloxynaphalene was obtained in 90% isolated yield.



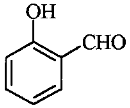
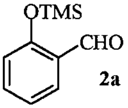
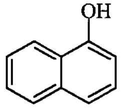
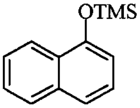
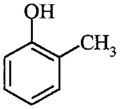
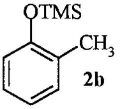
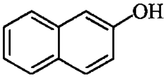
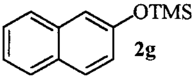
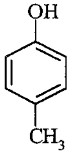
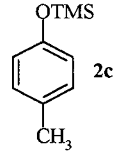
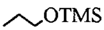
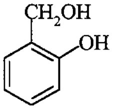
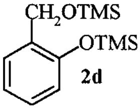
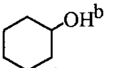
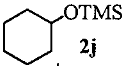
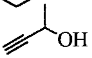
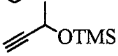
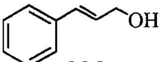
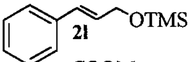
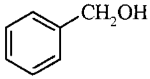
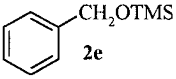
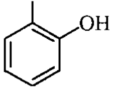
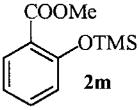
SCHEME 1

In conclusion, domestic microwave irradiation under a solvent-free condition provides a mild and excellent method for silylation of phenols and alcohols in a short time and relatively large scale, using inexpensive and easy to handle HMDS as silylating agent with high yields.

EXPERIMENTAL

All chemicals were used as received without further purification. All products were identified with their NMR and IR spectroscopic data.

TABLE I Silylation of Alcohols and Phenols with HMDS in Solvent-Free Condition and Under Microwave Irradition[a]

Substrate	Product	Yield	Substrate	Product	Yield
	 **2a**	96		 **2f**	95
	 **2b**	90		 **2g**	95
	 **2c**	92		 **2h**	95
			1-Octanol[b]	$CH_3(CH_2)_6CH_2OTMS$ **2i**	63
	 **2d**	90		 **2j**	62
				 **2k**	95
				 **2l**	95
	 **2e**	88		 **2m**	82

[a] Reaction time: 5 min, except where stated;
[b] Reaction time: 10 min.

General Procedure for the Preparation of Silylated Phenols or Alcohols

The phenol or alcohol (2 mmol) and HMDS (2 mmol) were placed in a 10 mL beaker. The beaker was put into a 50 mL Teflon vessel and was irradiated in a conventional microwave oven at 450 W; the reaction was monitored by gas liquid chromatography (GLC). After the completion of the reaction (Table I), the crude material was purified by distillation with a bulb-to-bulb distillation unit to the corresponding silyl ether. The yields shown in Table I are isolated yields. All products gave satisfactory spectral data in accordance to the proposed structures.[4,8,11,31] Spectral data of the new compounds are: **2d**, ^1H NMR, δ, ($CDCl_3$), 0.2 (s, 9H), 0.3 (s, 9H), 4.7 (s, 2H), 7.4 (m, 4H); ^{13}C NMR, δ, ($CDCl_3$), −0.5 (CH_3), 0.4 (CH_3), 59.6 (CH_2), 118.4 (CH), 121.3 (CH), 127.5 (CH), 127.6 (CH), 131.6 (C), 152.1 (C); IR, (neat), 1250, 842 cm^{-1}. **2m**, ^1H NMR, δ, ($CDCl_3$), 0.2 (s, 9H), 3.8 (s, 3H), 7.3 (m, 4H); IR (CCl_4), 1253, 849 cm^{-1}.

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