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CHEMOSELECTIVE SILYLATION OF ALCOHOLS[1]

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ABSTRACT : Hexamethyldisilazane (HMDS) in pesence of a catalytic amount of Envirocat EPZG[R] silylates different alcohols in high yields with absolute chemoselectivity.

Trimethylsilylation is used extensively for protection and derivatization of most functional groups to increase volatility for gas chromatography and mass spectrometry.[2] One of the reported most common reagents for silylation is hexamethyldisilazane (HMDS) which is cheap and commercially available reagent. Its handling does not need special precaution and the reaction work-up is not time consuming. The main drawback of this reagent is its poor silylating power, which needs forceful conditions in many

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instances and reactions with tertiary alcohols do not take place.[3] The activity of HMDS has been increased drastically by using some catalysts but usually low selectivity and long reaction time, with some exceptions[4] have been reported in the literature.

We now report chemoselective silylation of alcohols with HMDS by using new heterogeneous catalyst, Envirocat EPZG^R (scheme I).

$$\underset{\mathbf{1}}{2ROH} + Me_3SiNHSiMe_3 \xrightarrow[CH_3CN,\ 25\ ^oC]{\text{Envirocat EPZG}^R} \underset{\mathbf{2}}{2R\text{-}OSiMe_3} + NH_3$$

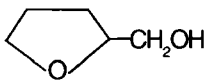
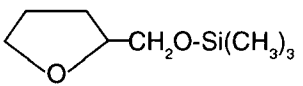
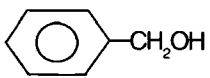
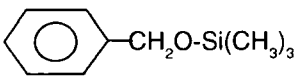
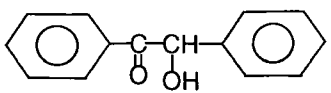
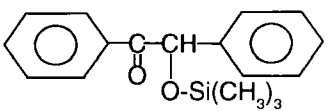
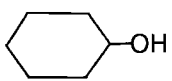
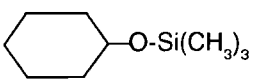
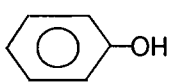
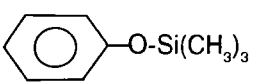
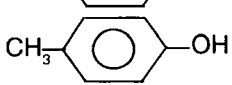
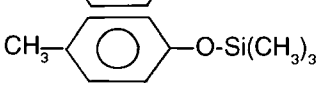
Scheme I

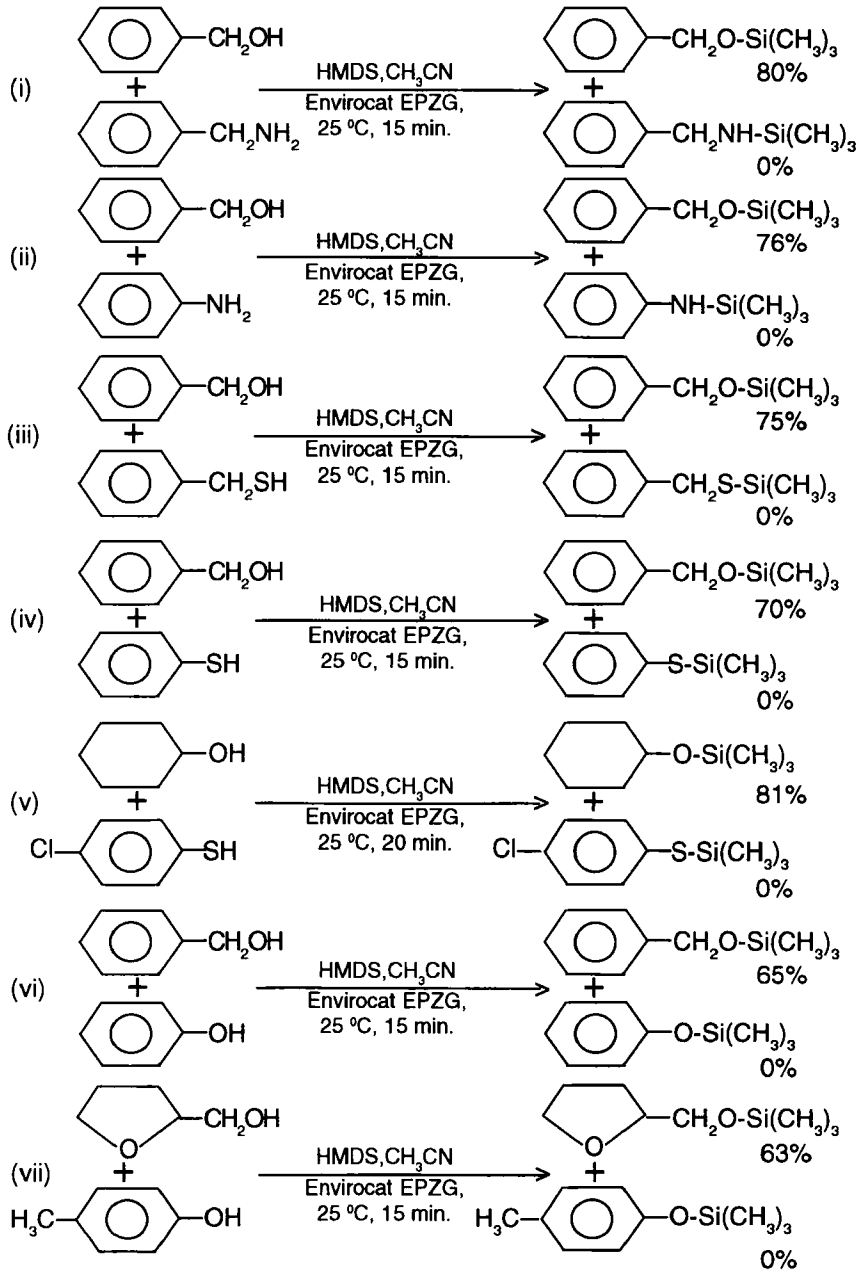
In recent years there has been considerable growth in interest in the catalysis of organic reactions by inorganic reagents supported on high surface area inorganic materials.[5] Envirocat^R a new family of supported regents is a significant breakthrough in environmentally-friendly chemistry. Envirocat EPZG^R is one of the supported catalyst which have both Bronsted and Lewis acid characteristics. Recently Envirocat EPZG^R has been successfully used for synthesis of conjugated nitroolefins.[7]

HMDS by using a catalytic amount of Envirocat EPZG^R silylates different types of alcohols in presence of amines or thiols or phenols in high yields with absolute chemoselectivity. The results are presented in table and scheme II. Reaction times are drastically decreased to few minutes and reaction work-up is exceedingly simple which involves merely filtration. Even tertiary alcohol undergoes silylation with HMDS under mild condition.

In conclusion HMDS and a catalytic amount of Envirocat EPZG^R serves as an efficient reagent for chemoselective silylation of primary, secondary and tertiary alcohols in presence of amines thiols and phenols under mild conditions.

Table : Silylation of alcohols and phenols by using HMDS in presence of Envirocat EPZG[R]

Entry	Substrate	Reaction condition,°C	Reaction time	Product[a]	Yield[b] (%)
1	$CH_3(CH_2)_2CH_2OH$	25	35 min.	$CH_3(CH_2)_2CH_2O\text{-}Si(CH_3)_3$	92
2		25	60 min.		70
3		25	15 min.		72
4		85	30 min.		97
5		25	20 min.		85
6	$(CH_3)_3\text{—}OH$	25	15 min.	$(CH_3)_3\text{—}O\text{-}Si(CH_3)_3$	91
7		85	6 h		96
8		85	4 h		94



Scheme II

Experimental: Envirocat EPZG^R was procured from Contract Chemicals,Merseyside England LY34 9HY and activated 1 h prior to use by azeotropic drying. Products were characterised by their physical constants and spectral characteristics (IR and ^{1}H NMR).

General Procedure for Silylation: A mixture of alcohol or phenol (10 mmol) in acetonitrile (15 mL), HMDS (5 mmol) and Envirocat EPZG^R (100 mg) was stirred at 25 ^{0}C for the time specified in table. The reaction was monitored by TLC. After completion of the reaction, mixture was filtered and catalyst was washed with ether (10x3 mL). Removal of the solvent under reduced pressure furnished product in good yield. Products were characterised by their physical constants, spectral characteristics (IR, ^{1}H NMR) and comparison with authentic samples.

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References and footnotes:

1. Solid Supported Reactions and Reagents Part 18, For part 17 see, Bandgar, B. P. and Thite, C. S., Synth. Commun., in press.
2. Green, T. W. and Wuts, P. G. M. Protective Groups in Organic Synthesis, 2nd Ed., John Wiley, New York **1990.**
3. Bruynes , C. A. and Jurriens, T. K. *J. Org. Chem.* **1982**, *47*, 3966 and references cited therein.
4. Cossy, J. and Pale, P. *Tetrahedron Lett.* **1987**, 6039.
5. Clark, J. H.; Kybett, A. P. and Macaquarrie, D. J. Supported Reagents, VCH, New York **1992.**
6. Contract Chemicals, England "Envirocats- Supported Reagents : Product Information" **1994.**

7. Bandgar, B. P., Zirange, M. B. and Wadgaonkar, P. P. *Synlett.* **1996**,149.

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