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**MICROWAVE PROMOTED REDUCTIVE COUPLING OF CARBONYL
COMPOUNDS TO BIS(TRIMETHYLSILYL) PINACOLS UNDER
SOLVENT-FREE CONDITIONS**

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Abstract : Reductive coupling of carbonyl compounds was performed with trimethylchlorosilane (TMS-Cl) on montmorillonite K10 clay in conventional microwave oven in short time with quantitative yields of bis(trimethylsilyl) pinacols.

The reductive coupling of carbonyl compounds to give pinacols is an important method for the formation of vicinally functionalized C-C bonds. It is well established that pinacolization of carbonyl compounds can be effected by either anionic or radical route. Majority of pinacolic couplings occur via radical-radical coupling, and generally afford a mixture of *d,l* and *meso* diols¹.

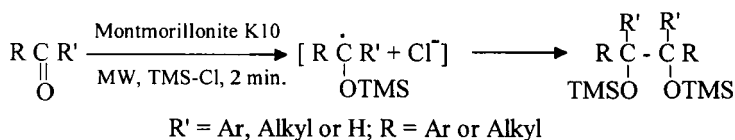
Montmorillonite clays as catalysts have received considerable attention in recent years due to their characteristic properties and the ease of set-up and work-up^{2,3}.

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In continuation of our interest in the development of environmentally benign synthetic method using microwave (MW) irradiation under solvent-free conditions, we wish to report a mild, convenient and heterogeneous catalytic methodology for the solventless synthesis of bis(trimethylsilyl) pinacols^{4,5}.

It is known that aldehydes and ketones are transformed into pinacols with Li or Mg in HMPT or THF in the absence of water after 6-8 hours at 50 °C, or with other methods described in the literature^{1,6}. Yanada reported that the reductive coupling of aromatic aldehydes and ketone proceeded with SmI₂ and Ti(OⁱPr)₄ in methanol⁷. The reductive coupling of aryl aldehydes were also reported in the presence of Ti(III) complexes⁸.

Microwave heating has been used for a wide variety of application, including the rapid synthesis of organic compounds. By heating TMS-Cl and aldehydes or ketones on montmorillonite K10 clay in conventional microwave oven, various bis(trimethylsilyl) pinacols were synthesized in a very short time with quantitative conversion of carbonyl compound. Aromatic aldehydes and ketone are reduced by this method to give silylated pinacol coupling products with good yields. In the case of aliphatic ketones, the coupling products were produced with lower yields. We assume that the reaction probably proceeds via a radical-radical route as it is shown in **Scheme 1**. The ratio of *d,l* / *meso* was determined by ¹H NMR analysis⁹.

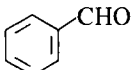
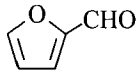
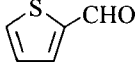
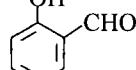
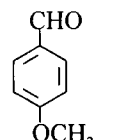
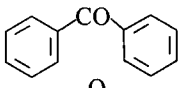



Scheme 1

Experimentals

^1H NMR spectra were recorded in CDCl_3 on Bruker AC 80 spectrometer, using TMS as internal standard. IR spectra were obtained on Matt Son 1000 Unicam FTIR spectrometer.

Table 1 Coupling of Carbonyl Compounds in the Presence of TMS-Cl, Montmorillonite Under MW Irradiation

Entry	Carbonyl Comp.	<i>d,l</i> / <i>meso</i> ratio	Yield (%)
1		0.62	85
2		0.71	90
3		1.0	80
4		1.75	81
5		1.23	82
6		-	68
7		-	66
8	$\text{CH}_3\text{COCH}_2\text{CH}_3$	0.58	56

In a typical experiment, a mixture of aldehyde or ketone (2 mmole), TMS-Cl (2.2 mmol) and montmorillonite K10 clay (ca. 1 gr) in a teflon container was placed in microwave oven. After 1.5-2 min., the K10 clay was washed with dichloromethane and the solvent was evaporated to afford the bis(trimethylsilyl) pinacols. The results with different aldehydes and ketones are listed in **Table 1**.

In summary, the use of montmorillonite K10 clay provides a significant new, effective, environmentally compatible, and practical method for coupling of aldehydes and should find wide applications and ketones in the synthetic organic chemistry.

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