First $TaCl_5$-SiO_2 Catalyzed Prins Reaction : Comparative Study of Conventional Heating vs Microwave Irradiation#

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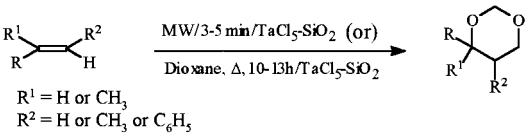
Abstract : $TaCl_5$-SiO_2 catalyzed Prins reaction has been achieved for the first time using microwave irradiation.

The condensation of olefins with aldehydes (mostly formaldehyde), generally called the Prins reaction,[1a,b] is the only organic transformation wherein a new C-C bond together with 1,3-diol formation is achieved. This reaction is catalyzed by mineral acids,[2] however some literature reports have been documented wherein milder Lewis acids[3] have also been utilized. Recent additions[4] include solid catalysts such as resin,[5] Zeolite[6] and K_{10} clay.[7]

Our interest in the development of new methodologies for 1,3-diol formation en-route to biologically important hydroxyl compounds has prompted us to study the $TaCl_5$-SiO_2 catalyzed Prins reaction of olefins and formaldehyde (Scheme and Table), the results being presented herein.



R^1 = H or CH_3
R^2 = H or CH_3 or C_6H_5

Scheme

The present study has unequivocally confirmed that the conventional refluxing temperature and longer reaction times required for Prins reaction are totally avoided using microwave irradiation, which is becoming an alternate and substitute-heating source.

When the commercially available styrene, **1a** (0.01 mol), paraformaldehyde (0.01 mol) and $TaCl_5$-SiO_2[7,8] (0.001 mol) were admixed efficiently and exposed to Microwaves at 600 watts for 3 min, an excellent yield of 1,3-diol derivative **2a** was obtained after filtration through a small pad of silica gel. This reaction, however, took approximately 12 h of refluxing in dioxane and a tedious workup before 80% yield of **2a** was isolated.

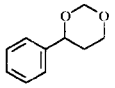
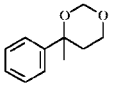
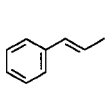
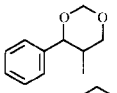
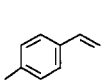
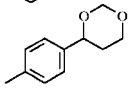
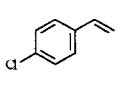
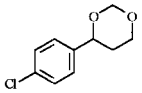
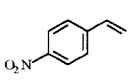
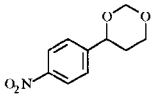
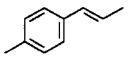
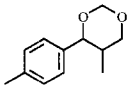
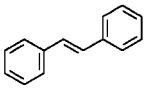
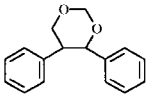
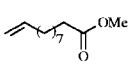
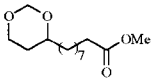
α-Methyl styrene **1b** (entry-b), β-methyl styrene, **1c** (entry-c), *p*-methyl styrene **1d** (entry-d), *p*-chloro styrene **1e** (entry-e), *p*-nitro styrene **1f** (entry-f), *p*-methyl-β-methyl styrene **1g** (entry-g), stilbene **1h** (entry-h), and undecenoate **1i** (entry-i) were similarly transformed to corresponding 1,3-diol derivatives (2a-i) after irradiation with microwaves for 3-5 minutes. All the reactions were also conducted in conventional round bottomed flasks with refluxing in dioxane. Invariably the products obtained by microwave irradiation were purified with more ease.

In conclusion a thorough and comparative study of Prins reaction catalyzed by $TaCl_5$-SiO_2 under both solvent and solvent free conditions have been studied for the first time.

Typical Experimental Procedure

(a) Microwave Irradiation: Styrene (1.04 g, 0.01 mol) and paraformaldehyde (0.9 g, 0.01 mol) were absorbed on activated silica gel (2g, 100-200 mesh, dried overnight at 110°C) and stirred at room temperature for 1 hr. under N_2 atmosphere. To this $TaCl_5$-SiO_2 (0.37 g, 10 mole percent) was added and admixed thoroughly and irradiated in a microwave oven (600 watts) for 3 min. This mixture was cooled to room temperature, charged on a small silica pad and eluted with n-hexane/ethyl acetate mixture (80/20). Removal of volatiles furnished 1,3-dioxane derivative (**2a**, 1.48 g, 90%).

Table . Prins reaction Catalyzed by $TaCl_5$-SiO_2

Entry	Substrate (1)	Product* (2)	Reaction time & Yield (%) Microwave Irradiation**	Conventional heating***
a			3 min (90)	12 h (80)
b			3 min (88)	10 h (82)
c			3 min (86)	10 h (80)
d			3 min (88)	10 h (80)
e			4 min (85)	12 h (78)
f			5 min (80)	13 h (70)
g			3 min (90)	10 h (80)
h			4 min (85)	13 h (78)
i			4 min (78)	13 h (70)

* : All the products were characterized by 1H NMR and elemental analysis and also by comparision with literature data[5,6,7,10]

** : Microwave irradiation was carried out at 600 watts.

*** : Refluxed in dioxane for given time.

b) Conventional Method : Styrene (1.04 g, 0.01 mol) was added to a mixture of paraformaldehyde (0.9 g, 0.01 mol) and $TaCl_5$-SiO_2 (0.37 g, 10 mol percent) in dioxane and it was refluxed for 12 hr. at 110°C under N_2 atmosphere. On completion, the reaction mixture was poured into water and extracted with ethyl acetate. Standard workup and removal of volatiles afforded 1,3-dioxane derivative (**2a**, 1.32 g, 80%).

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