

# SYNLETT Spotlight 298

## Silica-Supported Perchloric Acid (HClO<sub>4</sub>-SiO<sub>2</sub>)

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Dedicated to my parents



This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

### Introduction

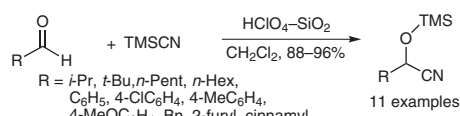
Heterogeneous catalysts have gained much importance in recent years due to economic and environmental benefits.<sup>1</sup> These catalysts make synthetic processes clean, safe, high-yielding, and inexpensive.<sup>2</sup> A tremendous interest has sparked in various chemical transformations promoted by catalysts under heterogeneous conditions. Recently, silica-supported perchloric acid (HClO<sub>4</sub>-SiO<sub>2</sub>), synthesized by Chakraborti et al.<sup>3</sup> has been found to be an efficient and recyclable heterogeneous catalyst for various organic transformations, such as synthesis of bis-indolylmethanes, bis-indolylglycoconjugates, 1,4-dihydropyridines, coumarins via Pechmann condensation, 1,3-dithiolane/dithiane, transformation of thioglycosides to

their corresponding 1-*O*-acetates, Ferrier rearrangement of glycols, acetal/ketal formation and chemoselective carbon-sulfur bond formation. It is also used in carbon-carbon bond formation between aldehydes and cyanides. Further, it is easy to handle, stable, and environmentally safe. Thus, silica-supported perchloric acid is a versatile organic reagent used as an acid catalyst.

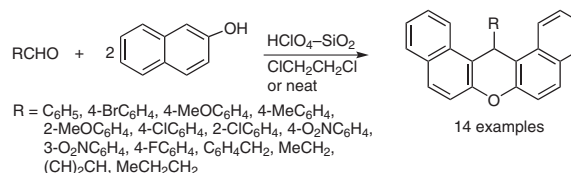
For the preparation of silica-supported perchloric acid HClO<sub>4</sub> (as a 70% aqueous solution) was added to the suspension of silica gel in diethyl ether. The mixture was concentrated and the residue heated at 100 °C for 72 h under vacuum to afford HClO<sub>4</sub>-SiO<sub>2</sub> as a free flowing powder.<sup>3</sup>

### Abstracts

(A) The Winkler reaction,<sup>4</sup> the addition of cyanide to carbonyl, which allows the preparation of cyanohydrin, is one of the old carbon-carbon bond-forming reactions. Heydari et al. carried out the Winkler reaction by using HClO<sub>4</sub>-SiO<sub>2</sub> to act as a highly effective catalyst.<sup>5</sup>



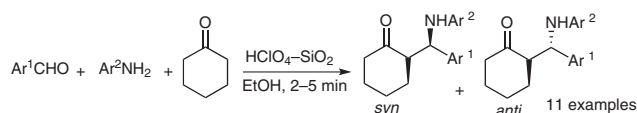
(B) Xanthenes and benzoxanthenes are cited as active oxygen heterocycles possessing anti-bacterial, anti-inflammatory, and antiviral properties. They are also utilized in photodynamic therapy.<sup>6</sup> Bigdeli et al. and Das et al. synthesised these molecules by using HClO<sub>4</sub>-SiO<sub>2</sub> as catalyst.<sup>7,8</sup>



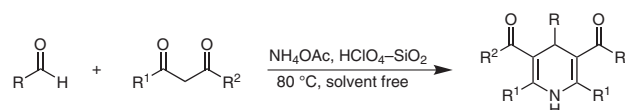
(C) Quinolines are useful as drugs and pharmaceuticals. HClO<sub>4</sub>-SiO<sub>2</sub> can be applied for the development of simple, convenient, and high-yielding syntheses.<sup>9</sup>



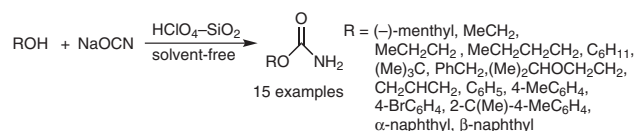
(D) The Mannich reaction<sup>10</sup> is an important carbon-carbon bond forming reaction and used for the synthesis of β-amino carbonyl compounds, which are important synthetic intermediates for various pharmaceuticals and natural products. Bigdeli et al. applied HClO<sub>4</sub>-SiO<sub>2</sub> in a one-pot, three-component Mannich reaction.<sup>11</sup>



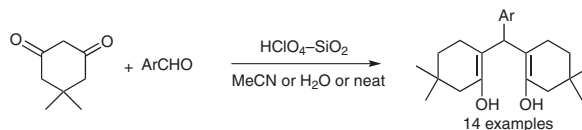
(E) HClO<sub>4</sub>-SiO<sub>2</sub> can be applied for the synthesis of 1, 4- dihydropyridines.<sup>12</sup>



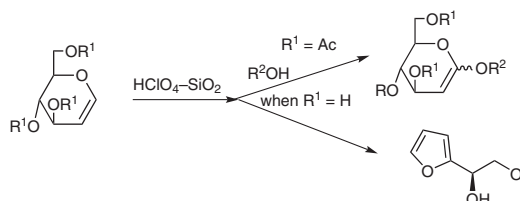
(F) Carbamates (urethanes) are common components of agrochemicals, such as herbicides, fungicides, and pesticides as well as drug intermediates in the pharmaceuticals industry. Their ability to cyclize to heterocyclic compounds is widely exploited in organic synthesis. Modarresi-Alam et al. developed a novel and highly efficient method for the synthesis of various primary carbamates by using  $\text{HClO}_4\text{-SiO}_2$  as an effective reagent.<sup>13</sup>



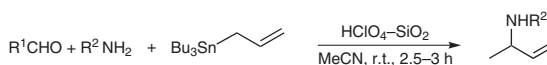
(G) One-pot Knoevenagel condensation, Michael addition, and cyclodehydration of dimedone and aldehydes in acetonitrile, aqueous and solvent free conditions was carried out by using this catalyst to give 1,8-dioxo-octahydroxanthenes.<sup>14</sup>



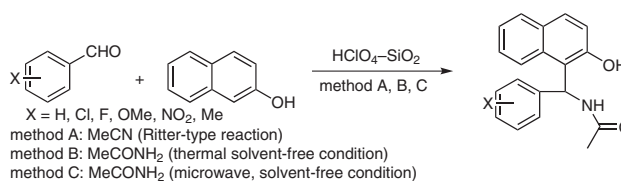
(H) 2,3-Unsaturated-*O*-glycosides are useful chiral intermediates in the synthesis of biologically active compounds, such as glycopeptide building blocks, oligosaccharides, and modified carbohydrates.  $\text{HClO}_4\text{-SiO}_2$  allows the reaction of primary, secondary, and allylic alcohols, phenols, and thiophenols with 3,4,6-tri-*O*-acetyl-D-glucal to yield the corresponding 2,3-unsaturated-*O*-glycosides in good to excellent yields and in short reaction times with high a selectivity.<sup>15</sup>



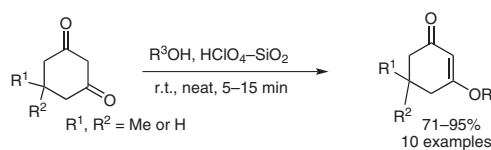
(I) Nagarapu et al. applied  $\text{HClO}_4\text{-SiO}_2$  for the synthesis of various homoallylic amines.<sup>16</sup>



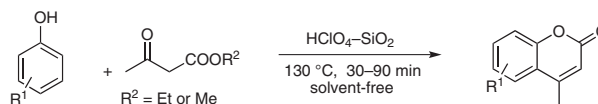
(J) Recently, Shaterian et al. developed a new synthesis for amidoalkyl by the reaction of aryl aldehyde, 2-naphthol, and acetonitrile or acetamide in the presence of  $\text{HClO}_4\text{-SiO}_2$ .<sup>17</sup>



(K) The conversion of cyclic diketones into keto enol ethers was previously carried out by treatment with alcohols in the presence of a catalyst, such as  $\text{TiCl}_3$ ,  $\text{I}_2$ ,  $\text{B}(\text{C}_6\text{F}_5)_3$ ,  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ , and  $\text{Yb}(\text{OTf})_3$ . However, the application of an improved heterogeneous catalyst in the preparation of keto enol ethers is felt to be highly useful and practical catalysts.<sup>18</sup>



(L) The Pechmann condensation<sup>19</sup> is one of the most common procedures for the preparation of coumarin and its derivatives. This method involves the reactions between a phenol and a  $\beta$ -keto ester in the presence of an acidic catalyst. Maheswara et al. applied  $\text{HClO}_4\text{-SiO}_2$  under solvent-free conditions to carry out Pechmann condensation.<sup>20</sup>



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