

Tonsil Clay as a Green Catalyst for Rapid and Efficient Reduction of Aldehydes and Ketones with NaBH₃CN

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Reduction of aldehydes and ketones to the corresponding alcohols in the presence of sodium cyanoborohdride as reductive agent and Tonsil clay as catalyst under solvent-free conditions was investigated. Tonsil (catalyst) decreased the reduction time of each aldehyde and ketone to proportional alcohols in comparison with their reduction in the absence of catalyst with high degree of purity of alcohols. Reduction reactions were carried out in solvent-free condition in less than 15 min at room temperature. All obtained alcohols from reduction of related carbonyl compounds were detected by FT-IR and ¹H/¹³C NMR spectra.

Keywords: Sodium cyanoborohdride, Tonsil clay, Reduction, Aldehyde, Ketone, Alcohols, Green chemistry

INTRODUCTION

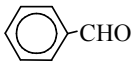
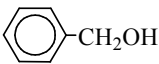
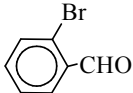
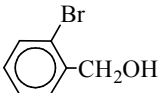
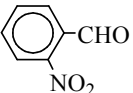
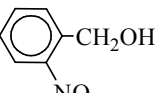
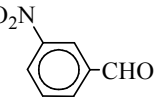
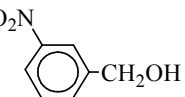
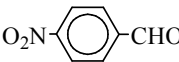
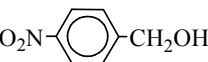
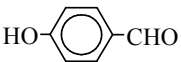
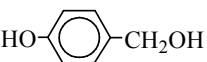
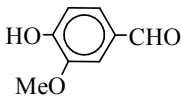
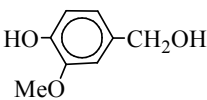
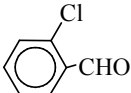
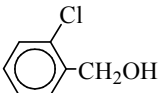
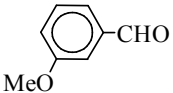
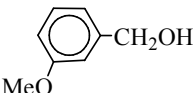

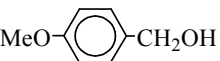
Reduction of functional groups is one of the most practical reactions in organic synthesis and a wide range of reducing agents have been introduced for this purpose [1]. In the early twentieth century, some metal powders such as zinc, sodium and iron in acetic acid were used for reduction of functional groups such as aldehyde, ketone and ester. Later, sodium in ethanol, sodium hydroxide and zinc in ethanol were used. The preparation and use of LiAlH₄ and NaBH₄ in the first half of the twentieth century opened a new window in this field. Among the gentle and potent reducing agents for functional groups, lithium aluminum hydride and sodium borohydride are the most used and most popular reactants in synthetic organic laboratories. Lithium aluminum hydride is the strongest reducing agent that has the ability to reduce all organic groups. Therefore, it is very difficult to use this reagent for selective reduction of multi-functional molecules. In the other words, sodium borohydride is a gentle mild reducing agent initially selected for functional groups in protonated solvents.

NaBH₃CN is a safe substance for the environment where NaBH₄ is rapidly hydrolyzed and degraded. NaBH₃CN is a stable and selective reducing agent that has been used in many organic syntheses [2].

Solid organic reactions have recently received careful attention with advantages (a simply work-up procedure, energy saving, avoidance of solvent waste, dangers and toxicity) over the solution reactions [3]. The application of catalysis has provided a fundamental means towards pollution prevention and waste minimization. Green chemistry is the design of chemical products and processes to reduce or eliminate the use and generation of hazardous substances. Performing chemical reactions on a solid phase is a method in which molecules are bonded onto a solid surface and the reaction is step-by-step in a reaction mixture. Compared with conventional synthesis in liquid phase chemistry, the advantages of this method are the easy separation of the reaction product, shorter times, greater safety, economic benefits and environmental interactions. The literature review shows that Tonsil clay as an inexpensive and readily available reagent has been widely used in organic transformations [4-14]. Therefore, in continued use of Tonsil clay in organic reactions with our

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Table 1. Solvent Free Reduction of Aldehydes with NaBH₃CN/Tonsil Clay System at Room Temperature with 1/3 Ratio of Subs/NaBH₃CN

Entry	Substrate	Product	Time (min)	Yield (%) ^a
1			3	96
2			5	93
3			3	95
4			3	97
5			3	98
6			8	91
7			10	96
8			5	98
9			6	95
10			6	94

^aYields refer to isolated pure products.

research group [4], we decided to examine the reducing capability of NaBH₃CN/Tonsil system for reduction of carbonyl group of aldehydes and ketones under solvent-free

conditions. Clays are very cheap, commercially available, green and heterogeneous reagents that have been used in various organic transformations such as Biginelli

condensation [5], Baeyer-Villiger oxidation of ketones [6], anti-Markonikov hydroamination of α,β -ethylenic compounds [7], epoxidation of alkene and hydroxylation of alkanes [8], synthesis of 1,2,3,4-tetrahydrocarbazoles and indoles [9], Friedel-Crafts type benzylation reactions [10], ring opening of epoxides with thiols [11], synthesis of bis-phthalimides [12], synthesis of 2-aryl-1-aryl-1*H*-1,3-benzimidazole [13] and Michael reaction of amines [14], among others. The aim of this work is reduction of aldehydes and ketones in the presence of reactive reagent of sodium cyanoborohydride and Tonsil clay. This study aims to achieve high utilization, simplicity of work and reduction of the reaction time under solvent-free conditions.

EXPERIMENTAL

Tonsil, inexpensive Bentonitic clay, is readily available commercially. This clay was shown to have the following composition (in %): SiO₂: 74.5, Al₂O₃: 9.3, MgO: 0.4, Fe₂O₃: 1.3, CaO: 4.0, K₂O: 0.4 and H₂O: 9.7 [15]. All reagents and solvents were purchased from commercial sources with the best quality and were used without further purification. IR and ¹H/¹³C NMR spectra were recorded on Thermo Nicolet Nexus 670 FT-IR and 300 MHz Bruker spectrometers, respectively. All yields refer to isolated pure products. TLC was applied for the purity determination of substrates, products and reaction monitoring over silica gel 60 F₂₅₄ aluminium sheet. All the products were identified by comparison of their spectral data and/or melting point with those reported in the literature [16,17].

General Procedure for Solvent-Free Reduction of Aldehydes and Ketones

In a clean and dry mortar, a mixture of 1 mmol of an aldehyde or a ketone and 0.1 g of Tonsil clay was ground. NaBH₃CN (0.188 g, 3 mmol) was then added and grinding of the reaction mixture was continued, the progress of the reaction was monitored by TLC (CCl₄/Et₂O: 5/2). The milling cycle was repeated, if necessary, until the reaction was completed. After completion of the reaction, the mixture was washed with CH₂Cl₂ (3 × 5 ml) and then filtered. The extracts were combined and dried over anhydrous Na₂SO₄. Evaporation of the solvent under

reduced pressure afforded the resulting alcoholic product in high yield (Tables 1, 2).

Caution. Considering to evolution of a small amount of HCN gas in these reactions, it is highly recommended to perform all reactions under a good fuming hood or conducting the gas to a KOH solution via a sealed system.

RESULTS AND DISCUSSION

Sodium cyanoborohydride has developed suitable methods for the reduction of organic functional groups such as carbonyl group in aldehydes and ketones. In order to achieve simpler, less costly and more environmentally friendly methods and to overcome the disadvantages of sodium cyanoborohydride at low pH values, we decided to investigate the reduction process for aldehydes and ketones in the solid phase, along with the use of Tonsil as the catalyst. Despite the Lewis and Brønsted-Lowry acid character of the studied clay, its acidity is very low in comparison with sulfuric or triflic acids [18] and without losing the reducing power of NaBH₃CN. The reactions were carried out quantitatively at room temperature.

All solvent free reactions were completed in less than 15 min affording the corresponding alcohols in high yield (Tables 1, 2).

CONCLUSIONS

Solid phase reaction with Tonsil is an effective and simple method for reduction of carbonyl groups. The procedure includes milling a mixture of NaBH₃CN, Tonsil clay and carbonyl group compounds in the absence of any organic solvent. The reaction is promoted in 3-15 min at room temperature. The advantages of NaBH₃CN/Tonsil system in reduction of aldehydes and ketones were examined by comparison with those of reported for NaBH₃CN/acidic MeOH (2N, HCl) [18]. Tables 1 and 2 show that the reducing potential of NaBH₃CN in Tonsil clay is more efficient than that in acidic/MeOH. Good yields, low reaction times, simple reaction procedure and work-up as well as the benefits of solvent-free reaction conditions are the advantages of this method.

Table 2. Solvent Free Reduction of Ketones with NaBH₃CN/Tonsil Clay System at Room Temperature with 1/3 Ratio of Subs/NaBH₃CN

Entry	Substrate	Product	Time (min)	Yield (%) ^a
1			9	98
2			10	96
3			15	95
4			10	98
5			8	97

^aYields refer to isolated pure products.

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