Soapnut Extract Catalyzed Eco-Friendly synthesis of Acyl Amines

Santosh B. Pore

Department of Chemistry, S. G. M. College, Karad (India) – 415124
Email: *santoshbpore[at]gmail.com*

Abstract: ***A general, simple, efficient, cost-effective and green procedure for acylation of amines has been developed by treatment with acetic anhydride, efficiently catalyzed by using intact plant material (aqueous extract of pericarp of Sapindus trifoliatus fruit). Reactions proceed with very good to excellent yields at room temperature.***

Keywords: Acylation, Soapnut, Surfactant

1. Introduction

Environmental and economic considerations make it urgent to redesign important chemical processes using appropriate catalysts to achieve higher yields [1]. The selection of a particular catalyst is a matter for the chemistry laboratory. Several types of substances such as acids, bases, clays, enzymes, ionic liquids and supercritical solvents have been used to catalyze reactions. This is due to the problems associated with common catalysts such as their hazardous nature, high cost, tedious implementation, difficult handling, the need for large amounts of organic solvents during and after the reaction and most importantly, their adverse effects on the environment. In order to overcome the specific catalytic gap used in organic synthesis, we looked naturally to get help. Nature is full of numbers and diverse plants, many of which contain pharmacology and biological chemicals [2]. Intact plant systems represent a unique class of potential biocatalysts for reactions of exogenous organic substrates [3]. Synthetic processes using these materials are more efficient and produce less waste than traditional chemicals and solvents.

A number of synthetic reactions, such as the asymmetric reduction of aliphatic, aromatic and azido ketones [4], synthesis of organochalcogen-α-methylbenzyl alcohols [5], oxidation of recemic 1-phenylethanol [6], hydrolysis of recemic mixtures of chiral esters [7], aliphatic and aromatic aldehydes and ketones were reduced using coconut juice (Cocos nucifera) [8] and efficiently obtained using intact plant material as a biocatalyst. The sensual group, especially the amino group, is one of the most basic and most frequently used conversions in organic synthesis to provide useful and effective protective protocols in multi-stage synthetic processes. The most effective basic catalysts include 4 (dimethylamino) pyridine (DMAP) [10] ZrO $(Otf)_2$ [10d], and strong acids. Powerful acid catalysts [11a] Naic acid catalyst] $Sc(OTf)_3$ [11b], $In(OTf)_3$ [11c], $Bi(OTf)_3$ [11d], and yttrium zirconium Lewis acid [11e]. Some of these reagents and catalysts produce waste products, as do some reactions involving organic solvents, which are often toxic and polluting and therefore currently unacceptable. One of the major factors for an environmentally friendly solution chemical process is the choice of cheap, safe and non-toxic solvents. Since water is abundant in nature, it is the first choice. Therefore, the development of effective and convenient synthetic methodology, intact plant materials are saturated with water, used as catalysts, and are important areas of research. Like our interests in the green chemical process, in consideration of the importance of environmental factors and environmental factors, this article reports Amin Acacia about aquatic fruits that meet many of the above requirements. As a continuation of our research activities [12-13] dedicated to green chemistry, we have studied the pericarp of the fruit of Sapindus trifoliatus (soapnut) for use in the synthesis of imine formation [14]. We report here on the acylation of amines in the presence of an aqueous extract of Sapindus trifoliatus under mild conditions and in a much shorter time frame.

Therefore, the need for a practical, efficient and more environmentally friendly alternative for this important transformation prompted us to disclose a simple acylation procedure catalyzed by an aqueous extract of fruits of soapnut.

2. Materials and Methods

General

All reported yields are based on isolated compounds. Melting points were determined with a Buchi melting point apparatus and are uncorrected. TLC separations were carried out on silica gel plates with UV indicator from Aldrich; visualization was by UV fluorescence or by staining with iodine vapor. ^{1}H NMR spectra were recorded on a Bruker Avon 300 MHz spectrometer using DMSO as solvent. Tetramethylsilane (TMS) was used as an internal standard. Infrared spectra were recorded on a Perkin-Elmer One FTIR spectrometer. The samples were examined as KBr discs ~5 % w/w. All chemicals were purified prior to use.

Plant Material and Aqueous Extract

Dried fruits of Sapindus trifoliatus were purchased from local markets and identified by the Department of Botany, Shivaji University, Kolhapur, India. The dry pericarp of the fruits (100 g) was soaked in water (400 ml) for12 h. The material was then macerated with the water in which it was soaked and filtered. The filtrate, i.e., the aq. extract, was kept below 58 and used as catalyst for 15 d.

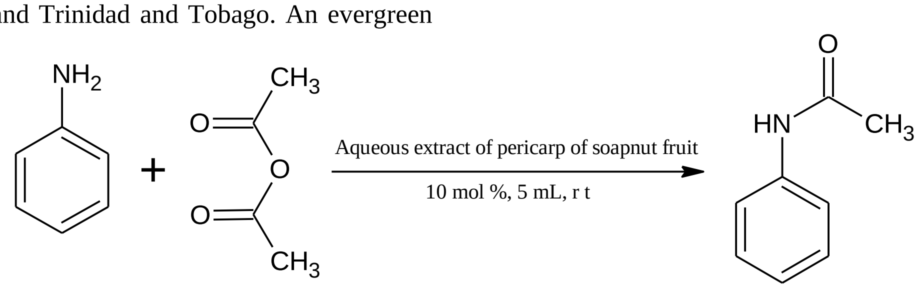
General procedure for the acylation of amines

A mixture of aniline (1 mmol), acetic anhydride (1.05 mmol) and aqueous extract of pericarp of Sapindus trifoliatus fruit as a catalyst (10 %, 5 ml) was stirred at room temperature for an appropriate time (Table 2). After completion of the reaction as indicated by TLC (hexane/ethyl acetate 8:2), reaction mixture was washed by cold water. The reaction mixture was filtered by whatman filter paper and the remaining solid material was washed with cold water. The solid product was recrystallized to give pure product.

3. Results and Discussion

To begin with, the pericarp of Sapindus trifoliatus (soapnut) fruit was chosen for experiment. Soapnut is commonly known as ‘Ritha’ in Hindi. Sapindus trifoliatus, the South India soapnut or three-leaf soapberry, is a species of flowering plant in the family Sapindaceae, native to Pakistan, India, Bangladesh, the Andaman Islands, Myanmar, and Sri Lanka, and introduced to eastern tropical Africa, Rodrigues, and Trinidad and Tobago. An evergreen tree reaching 25 m (82 ft), its seeds are rich in saponins, and are both collected in the wild and cultivated to make soap for washing fabrics, washing hair, for promoting hair growth, as an expectorant, emetic and pugitive [15]. Aqueous extract of this fruit has been in use as detergent since a long time in India. Various properties of Sapindus trifoliatus fruit are due to presence of saponins in it [16]. The structures of different saponins present in the fruit have been recently established [17] and it is found that they have surfactant properties similar to dodecylbenzene sulfonates [18]. The aqueous extract of pericarp of fruits shows acidic pH (3.86) which is due to presence of an acid with molecular formula $C_{30}H_{48}O_5$ corresponding to pentacyclic triterpenes [21]. These interesting properties of Sapindus trifoliatus fruit prompted us to use it as catalyst in acylation of amines.

Herein we report a general, rapid, and one-pot convenient procedure for N-acetylation of amines using acetic anhydride under room temperature catalyzed by aqueous extract of soapnut pericarp (Scheme -1).



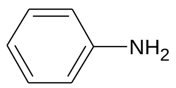
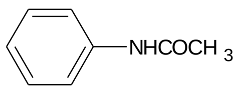
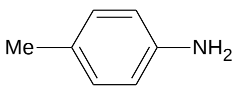
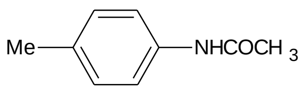
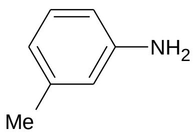
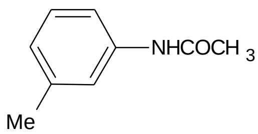
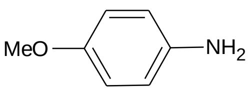
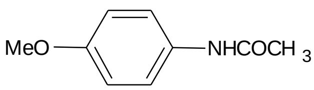
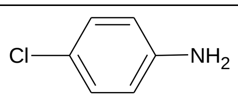
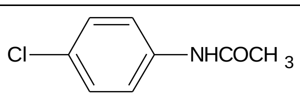
1 2 3

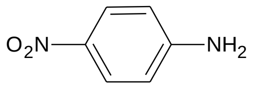
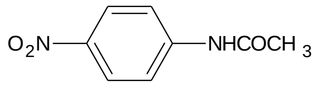
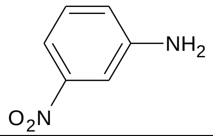
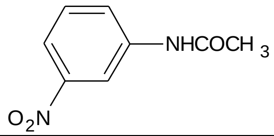
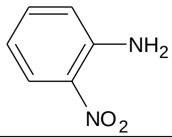
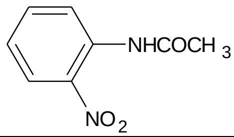
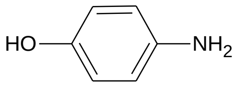
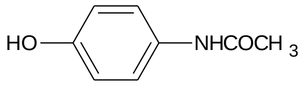
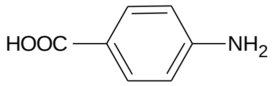
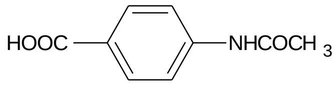
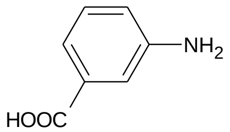
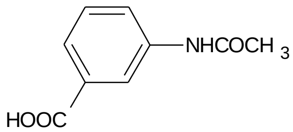
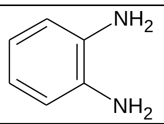
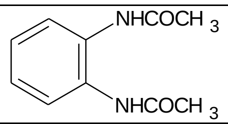
Scheme 1: Acylation of amines catalyzed by aq. extract of soapnut pericarp

Table 1: Effect of concentration of aqueous extract of Soapnut pericarp

Entry	Conc. of aq. extract of Soapnut pericarp (w/v)	Reaction Time (min.)	Yield (%)
1	2.5	60	75
2	5	30	95
3	10	30	95
4	20	30	95
5	30	30	95

Table 2: Acylation of aromatic amines catalyzed by aqueous extract of soapnut

Entry	Amine	Time (min.)	Product	Yield [a, b] (%)
1		30		95
2		20		95
3		20		90
4		15		90
5		45		95

6		60		85
7		60		85
8		45		85
9		20		90
10		45		85
11		45		85
12		30		90

a Products were compared with IR and ^{1}H NMR data of authentic sample.
b Isolated yield after purification.

The general efficiency of this reaction is evident from the fact that a variety of aromatic amines react in excellent yields within short time; aniline is acylated within 5 min. First, we have tried to optimize the reaction conditions for acetylation of aniline at different concentrations of the catalyst (Table-1). It gives good results at 5%, 10%, 20% and 30% aqueous extract of pericarp of soapnut fruits. Therefore, use of 10%, 5ml aqueous extract with 1 mmol of aniline and 1.05 mmol of acetic anhydride at room temperature gave 95% of acetanilide. Similarly, we obtained good to excellent yields of the product by reaction of differently substituted anilines under identical reaction conditions (Table-2). The reactants were solubilized in a very short time and it was exciting to observe that the reaction occurred immediately on stirring the reaction mixture at room temperature. The reaction was completed within 30min and desired acetanilide was obtained in 95% isolated yield. The rate enhancement in aqueous extract of pericarp of soapnut fruits can be attributed to its surfactant property and acidic pH. The saponins which are highly acidic solubilize the reactant species by hydrogen bond formation in aqueous medium. This increases number of favorable collisions between the reactant species. Further encapsulation of hydrophobic end of the product in micellar cages drives the equilibrium towards product side which increases the speed as well as yields of products. This remarkable activation in reaction rate, prompted us to explore the potential of this protocol for the synthesis of acylation of amines.

4. Conclusion

In conclusion, we have developed a simple, convenient and efficient synthetic protocol for the acylation of amines using a catalytic amount of aqueous extract of pericarp of Soapnut fruits. Thus, aqueous extract of pericarp of Soapnut fruits as a catalyst could be viable, economic and ecofriendly catalyst. Another advantage of this method is excellent yields in shorter reaction time with high purity of the products.

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