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THE ACYLATION OF DIFFERENT AMINES WITH ACETIC ANHYDRIDE (ACYLATING AGENT) BY USING BIOCATALYST

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Abstract

A general, simple, efficient, cost-effective and green procedure for acylation of amines has been developed by treatment with acetic anhydride is efficiently catalyzed by using fruit juices. Reactions proceed with very good to excellent yields at room temperature.

Keywords: *efficient, cost-effective, fruit juices, excellent yields.*

INTRODUCTION

Environmental and economical considerations prompt an argent need to redesign the important chemical process using suitable catalyst and achieve better yields [1]. The choice of the particular catalyst is a matter of chemical institution. Several types of substances such as acids, bases, clays, enzymes, ionic liquids and supercritical solvents have been employed to catalyze reactions. This is due to problems associated with prevailing catalysts like hazardous nature, high cost, tedious work up, difficult to handle, requirement of large quantities of organic solvents during and after the reaction and above all, their detrimental effects on environment. In an attempt to overcome some of the deficiencies of catalysts used in organic synthesis, we looked to nature for help. Nature abounds in number and variety of plants, many of which contain chemical constituents that are pharmacologically and biologically important [2]. Intact plant systems represent a unique class of potential biocatalysts for the reactions of exogenous organic substrates [3]. The synthetic transformations using these materials are more efficient and generate less waste than the conventional chemical reagents and solvents. Recognizing their inherent green aspects, number of synthetic reactions such as asymmetric reduction of aliphatic, aromatic and azidoketones [4], synthesis of organochalcogeno-α-methyl benzyl alcohols [5], oxidation of

recemic 1-phenyl ethanol [6] and hydrolysis of recemic mixture of chiral esters [7], aliphatic and aromatic aldehydes and ketones was reduced using coconut juice (*Cocos nucifera*),
[8] have been effaciously achieved using intact plant materials as biocatalysts.

The acylation of functional groups, especially amino groups is one of the most basic and frequently used transformations in organic synthesis as it provides a useful and efficient protection protocol in a multistep synthetic process [9]. The most efficient base catalysts are 4-(dimethylamino) pyridine (DMAP) [10a], phosphines, [10b], [10c] ZrO(OTf)2 [10d], Iodine [10e] and the powerful acid catalysts employed include Me3SiOTf [11a]. Sc(OTf)3 [11b], In(OTf)3 [11c], Bi(OTf)3 [11d] and yttria-zirconica based Lewis acid [11e]. Some of these reagents and catalysts lead to waste as well as some reactions involving organic solvents, often toxic and polluting, hence unacceptable in the present days. One of the major factors for a green chemical process in solution involves the choice of cheap, safe and non-toxic solvents. Water being abundant in nature is the first choice. Thus, development of an efficient and convenient synthetic methodology, the intact plant materials are soaked in water and it is used as a catalyst is an important area of research. Considering the importance of acylation and environmental factors as well as our interest in green chemical processes, we report in this paper acylation of amines in an aqueous extract of strawberry, karwand (*Carissa carandas*) and kiwi (*actinida deliciosa*), which fulfills many of the above requirements.

In continuation of our research work devoted to the green chemistry [12-13], we have investigate the pericarp of *Sapindus trifoliatus* fruits were used in the synthesis of imine formation [14], we report herein the synthesis of acylation of amines in the presence of aqueous extract of *fruit juices* under mild condition within much lesser time.

Thus, a need for a practical, efficient and greener alternative for this important transformation prompted us to disclose here a simple procedure for acylation catalyzed by aqueous extract of strawberry(*Fragaria ananassa)*, karvand (*Carissa carandas*) and kiwi (*actinida deliciosa)* fruit.

MATERIALS AND METHODS

Facile and green synthetic approaches are important issues in organic synthesis.

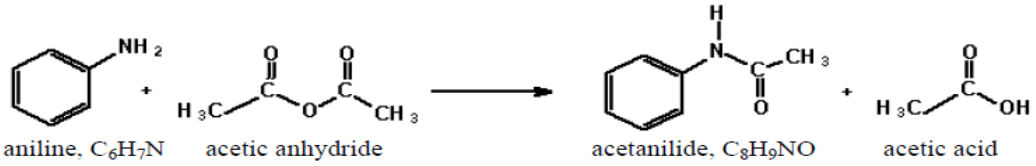
Green chemistry has become a motivational and inspirational tool for organic chemists to develop mild and benign pathways for the synthesis of biologically active compounds. The naturally available fruit juice as a biocatalyst in synthesis fulfills almost all the terms and conditions of green chemistry and attracted the interest of researchers. The best thing is that

most of fruits are easily available, cheap and can be easily extracted. The purpose of this review is to look out present aspects of fruit juice in organic transformations.

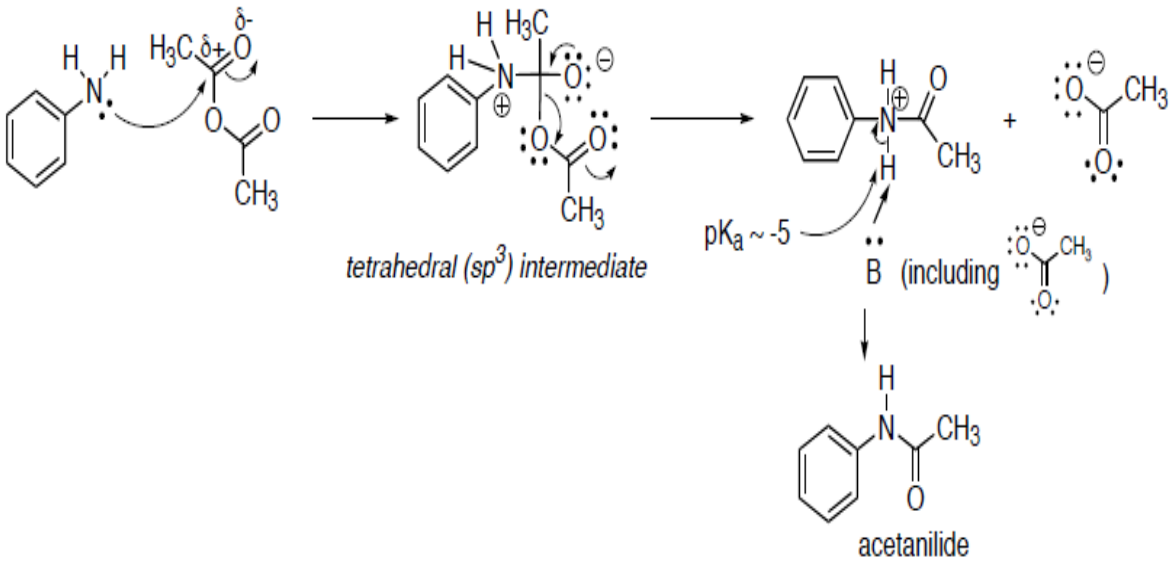
General procedure for the acylation of amines

A mixture of aniline (10 mmol), acetic anhydride (10 mmol) and aqueous extract of desired fruit juices as a catalyst (1ml) was stirred at room tempreture 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 what man filter paper; the remaining solid material was washed with cold water. The solid product was recrystallized to give pure product.

REACTION:



MECHANISM OF THE REACTION



PREPARATION OF CATALYST

Fruit juice of strawberry

The garden strawberry was first bred in Brittany, France, in the 1750s via a cross of Fragaria virginiana from eastern north America and Fragaria chiloensis, which was brought from chile by Amedee-Francois Frezier in 1714.

Composition of Strawberry

Amount per 100 grams

- Polyunsaturated fat - 0.2g
- Sodium - 1mg
- Potassium - 135mg
- Total Carbohydrate - 8gm
- Sugar - 4.9gm
- Protein – 0.7gm

The strawberry fruit is higher in Vitamin C, approximately 97%

General Procedure for Extraction of Strawberry Juice

The fruit was sliced and the fruit slices crushed in a motor pestle for few minutes to get the semisolid mass which was then filtered through to get liquid strawberry juice which worked as acid catalyst in organic reaction.

Fruit juice of kiwi

It is green on the inside with small black seeds. The kiwi has furry brown skin that is edible but is usually removed. The kiwifruit, native to northern China, first arrived in New Zealand at the turn of the 20th century; it was then known as the Chinese gooseberry. When the time came to export the fruit, to avoid the high duties charged on berries, the name was changed to the kiwi fruit.

Composition of kiwi fruit

Per medium fruit, the kiwifruit contains

- Protein - 1.14g
- Calcium - 34mg
- Iron - 0.31mg
- Magnesium - 17mg
- Phosphorus - 34mg
- Potasium - 312mg
- Sodium - 3mg
- Zinc – 0.14mg
- The fuzzy little kiwi also packs in the vital nutrients vitamin E, copper, vitamin K, choline, magnesium, and phosphorus. The kiwifruit is higher in vitamin C per ounce than most other fruits.

General Procedure for Extraction of Kiwi juice The skin of Kiwi fruit was peeled using knife. Then the fruit was sliced and the fruit slice crushed in a motor pestle for few minutes to get the semisolid mass which was then filtered through to get liquid kiwi juice which worked as acid catalyst in organic reactions.

Fruit juice of Karvand

Karvand is a plant found all over India in the temperate climate. The plant produces berry sized fruits which are green when unripe and turns into reddish black when ripe. The ripe fruit exudes white latex when severed from the branch. Karvand- Carissa Carandas is an Ayurvedic plant used for the treatment of acidity, indigestion, fresh and infected wounds, skin diseases, urinary disorders and diabetic ulcer.

Composition of karvand fruit

- Energy - 42 Equals
- Moisture – 91 gm
- Protein – 1 gm
- Fat – 3 gm

- Mineral -1 gm
- Fibre – 1 gm
- Carbohydrates – 3 gm
- Calcium – 21 mg
- Phosphorous – 28 mg

General Procedure for Extraction of Karvand juice

The skin of Karvand was peeled using knife. Then the fruit was sliced and the fruit slices crushed in a mortar pestle for few minutes to get the semisolid mass which was then filtered through to get liquid Karvand juice which worked as acid catalyst in organic reactions.

EXPERIMENTAL CHARACTERISATION

Acetanilide:

IR (neat): 3294, 3022, 2937, 1620, 1530, 1393.

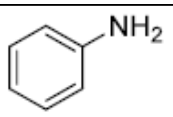
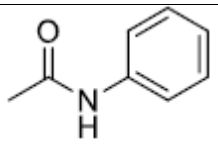
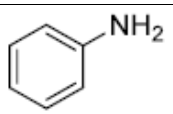
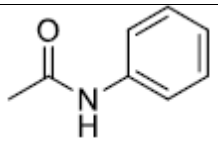
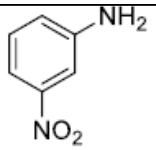
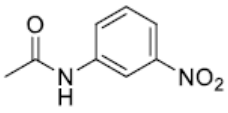
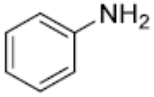
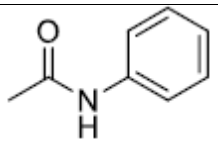
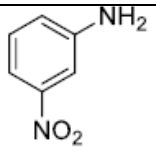
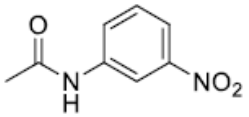
1H NMR (300 MHz, CdCl3): δ 8.3 (S, 1H, exchangeable with D2O), δ 7.5 (dd, 2H), δ 7.3-7.2 (m, 1H), δ 2.2 (S, 3H).

Elemental Analysis: C, 71.08; H, 6.70; N, 10.35; O, 11.86.

RESULTS AND DISCUSSION

The efficiency of fruit juice in aqueous phase to carry out the acetylation of amino group indicates the juice contain the citric acid when the citric acid in aqueous condition come in contact with amine and acetic anhydride formation of acetylated products takes place, citric acid serves as active weak water soluble catalyst as it is partially soluble in water. In the reported methodology Figure 1, the acetylation of aniline as a model reaction. From table 1 it is observed that the aromatic amino group without substitution takes less time to convert into the product, the electron donating group lowers the reaction time and convert the product into higher yield while the compound containing electro withdrawing groups takes longer time to convert into the product with lower yield.

Table1:Acetylation of amines

Fruit Juices	Substrate	Product	Reaction Time in Min	Yield %	Melting Point
Strawberry Juice			12	75%	112-114
Kiwi Juice			15	69%	112-114
			15	71%	152-154
Karvand Juice			10	73%	112-114
			10	72%	152-154

CONCLUSION

In conclusion acetylation of different amines were carried out by using different fruit juices and acetic anhydride as an acetylating agent, reaction proceeds under normal reaction condition with the formation of product in high yield. The reactions were carried out with stirring at room temperature and under solvent free condition. The present methodology illustrates the efficient acetylation of primary amines with different fruit juice by means of acetic anhydrides under weakly acidic condition at room temperature. The present study offers the new researcher and chemist an alternative method for acetylation of amines. The catalyst does not harm to environment it is eco-friendly and cheaply available.

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