

RESEARCH ARTICLE

Lemon juice: as a natural, environmentally benign and efficient catalyst for Acetylation of Amines and Salicylic acid

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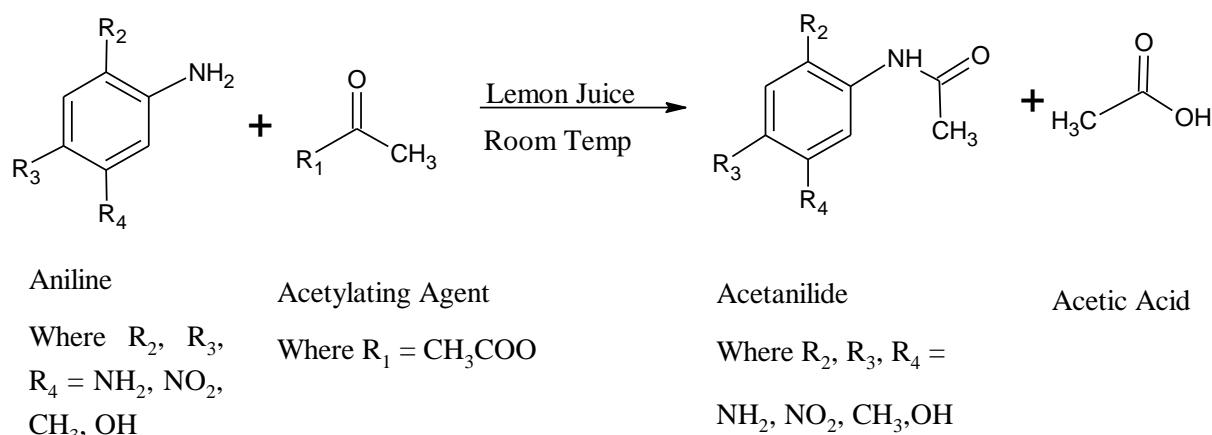
Manuscript Details	ABSTRACT
<p>Received : 25.07.2016 Revised : 22.08.2016 Accepted: 30.08.2016 Published: 18.09.2016</p> <p>ISSN: 2322-0015</p> <p>Editor: Dr. Arvind Chavhan</p> <p>Cite this article as: Chavhan Dasharath M, Patil Shrikant S and Khandekar Snehal R. Lemon juice: as a natural, environmentally benign and efficient catalyst for Acetylation of Amines and Salicylic acid. <i>Int. Res. Journal of Science & Engineering</i>, 2016,4 (3-4):85-89.</p> <p>Copyright: © Author(s), This is an open access article under the terms of the Creative Commons Attribution Non-Commercial No Derivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.</p>	<p>Lemon juice containing citric acid acts as a natural acid catalyst in Acetylation of amines and hydroxyacids such as salicylic acid. Acetylation of different amines and salicylic acid were carried out by using lemon juice 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 magnetic stirring at room temperature and under solvent free condition. The present methodology illustrates the efficient acetylation of primary amines and Salicylic acids by lemon juice by means of acetic anhydrides under weakly acidic condition at room temperature.</p> <p>Keywords: Lemon juice, acetylation, citric acid, amines, salicylic acid.</p> <p>INTRODUCTION</p> <p>Amino group an important functional group found in natural product and plant extract. It plays numerous biological roles in animal and plant body like protein synthesis as it constitutes the major proportion of amino acid. Acetylation of amino group is an important and frequently utilized method and fundamental transformation in organic chemistry. (Greene <i>et al.</i>, 1999, Pearson <i>et al.</i>, 1999) amino groups Acetylation constitutes the fundamentals of many preparations of natural and synthetic products such as perfumes, flavors, food additives, cosmetics, pharmaceuticals, plasticizers, and polymers. Knowing the importance of protection amine functional group during the multi-steps organic synthesis, the various methods for the protection of amino groups of amines using varieties of reagent and catalysts such as Cu(OTf)₂, (Saravanan and Singh, 1999) basic alumina, (Paul <i>et al.</i>, 2002) In (OTf)₃, (Chauhan <i>et al.</i>, 2000) montmorillonite K-10 and KSF, (Li <i>et al.</i>, 1997) ruthenium (III) chloride, (De 2004) and zeolite H-FER (Chavan <i>et al.</i>, 2001) in the presence of acetic anhydride and with various reagents under microwave irradiation, (Lidstrom <i>et al.</i> 2001) by utilising the basic catalyst such as pyridine, 4-pyrrolidinopyridine, and 4-dialkyl-</p>

aminopyridine. (Hofle *et al.*, 1978) similarly other catalyst like N-acyl-N-(2,3,4,5,6-pentafluoro-phenyl) methane sulfonamides, (Kondo *et al.* 2000) ortho-substituted N,N-diacetylaniline, (Murakami *et al.*, 1997) poly (3-acyl-2-oxazolone), (Kunieda *et al.*, 1982) and N-acetyl-N-acyl-3-aminoquinazolinones. (Atkinson *et al.* 1996) At the same time, selective N-acetylation of the primary amine moiety in the presence of secondary amine moiety can also be achieved by these methods. Latest literature survey revealed the use of molecular iodine, (Ahmed and Van Lier 2006) 3-nitro benzene boronic acid, (Tale and Adude 2006) and La(NO₃)₃·6H₂O, (Srikanth *et al.*, 2006)

However, the most common acetylating reagents used are acetyl chloride, acetic acid, acetic anhydride or any other protic acid. In spite of these ways of interest, due to the importance of acetylation of amino group innovation of inexpensive and green catalyst is still in demand.

A variety of methods are now available for acetylation. Most of them have certain demerits such as use of expensive, toxic catalyst, long reaction times, harsh reaction conditions and non-satisfactory yield of the desired products. With increasing environmental concerns and the regulatory constraints, the development of environmentally benign organic reactions has become a crucial and demanding area in modern organic chemical research. We wish to report a practical and convenient method for the preparation of amide, using lemon juice, a natural acid catalyst.

The present research work described a highly efficient and eco-friendly protocol for acetylation under aqueous condition at room temperature using lemon juice.



MATERIAL AND METHODS

Merck, pre-coated Silica gel 60 F254 (Aluminum sheets) plates were used for analytical TLC. IR spectra were recorded on FTIR spectrophotometer. ¹H NMR spectra were recorded (in CDCl₃ /DMSO-d₆) on 400 MHz spectrometer using TMS as an internal standard.

Preparation of catalyst

Take the fresh lemon wash it thoroughly with water and cut it. Pilled the cutted lemon collect the juice in beaker filter the juice with funnel by using simple filter paper. Use this lemon juice as a catalyst for acetylation of amino groups

Synthesis of n-phenylacetamide (1a)

Aniline 1 mmol was added into the water 5mL containing 0.5 ml lemon juice with constant stirring at room temperature. Add 2.5 mmol of acetic anhydride drop wise to avoid the complete hydrolysis of acetic anhydride with constant stirring. Completion of the reaction was monitored by TLC (ethylacetate:hexane = 20:80) separated solid product was extracted with diethyl ether and recrystallized from hot distilled water.

IR (KBr, cm⁻¹): 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.

Figure 1

RESULTS AND DISCUSSION

The efficiency of lemon 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. Salicylic acid does not easily undergo acetylation it required the longer reaction time produces the product with very low yield at higher temperature..

Table 1: N-Acetylation of Amines of amines

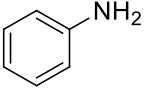
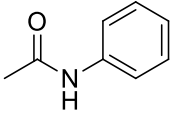
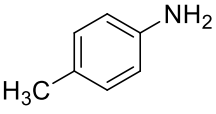
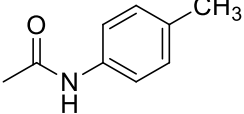
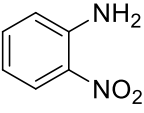
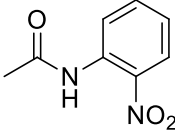
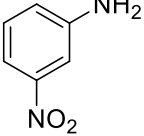
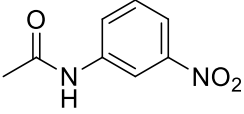
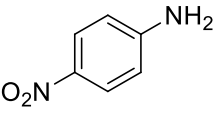
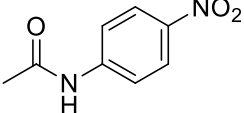
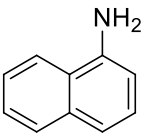
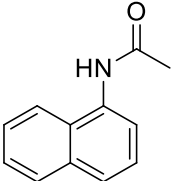
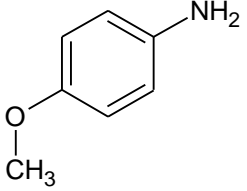
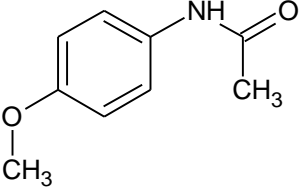
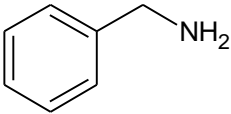
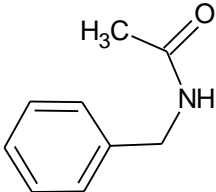
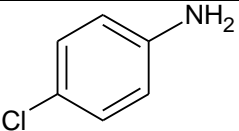
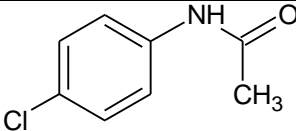
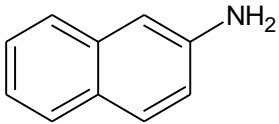
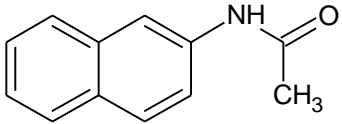
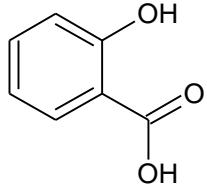
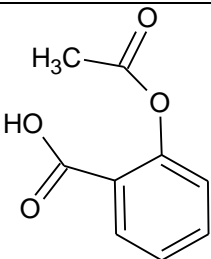
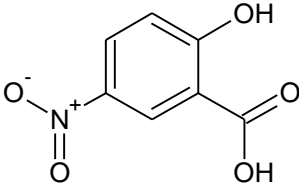
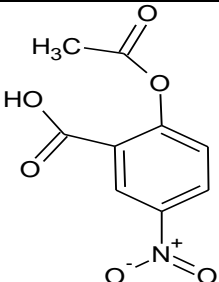
Sr. No.	Substrate	Product	Reaction time in min	aYield %	Melting Point
1a.			12	93	112-114
1b.			10	95	149-150
1c.			16	82	90-92
1d.			12	90	152-154
1e.			15	89	213-215
1f.			11	97	155-157
1g.			20	87	129-131

Table 1: continued...

Sr. No.	Substrate	Product	Reaction time in min	aYield %	Melting Point
1h.			20	75	57-59
1i.			15	80	177-178
1j.			18	90	168-170
1k.			30	65	135
1l.			25	70	287

CONCLUSION

In conclusion acetylation of different amines and salicylic acid were carried out by using lemon juice 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 magnetic stirring at room temperature and under solvent free condition. The present methodology illustrates the efficient acetylation of primary amines and Salicylic acids by lemon 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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