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An Environmentally Friendly and Efficient Green Method for Acylation

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ABSTRACT

Green chemistry is the development of chemical products and processes that minimize or eliminate the usage or synthesis of harmful substances. Green chemistry involves a chemical product's whole life cycle, including design through production, usage, and disposal. A variety of chemical reactions rely heavily on the acylation of phenols and amines. Acetylation reactions are typically carried out with an excess of acetic anhydride (Ac_2O) in solvent-free conditions or with stoichiometric quantities of Ac_2O in organic solvents; both processes require the addition of basic or acid catalysts to facilitate esterification. As a result, they generally produce huge amounts of waste, enhancing the process's E-factor. Therefore is in particular important to discover sustainable ways to accomplish acetylation reactions in high yields. In this review, we have studied different green acetylation reactions.

INTRODUCTION:

Various industries use harmful and toxic chemicals that harm the environment. These chemicals have an adverse impact on human health. Two decades ago, the chemistry community discovered a new branch of chemistry that is safe for both human health and the environment. This novel approach is known as green. Chemistry aims to reduce toxic chemical compounds, by-products, reagents, and solvents to human health and the environment through engineering and techniques. Green Chemistry involves synthesizing, processing, and using chemicals in a way that minimizes or eliminates dangers to humans and the environment. Green Chemistry, which has the spirit of sustainable development, was booming.[1]

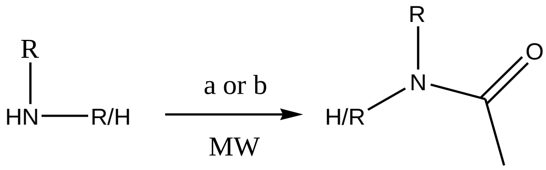
The first principle illustrates the fundamental idea of Green Chemistry preventing pollution for the environment. The other principles focus on matters such as atom economy, toxicity, solvents, energy consumption, and the use of raw materials from renewable resources.[2]

N-acylation procedures have widespread applications in the organic chemistry, biology, pharmaceutical, and agricultural industries.[3-5]

Acylation with acetyl chloride and acetic anhydride is a frequently used method. However, N-acylation via acyl chloride and/or acid anhydride has been associated with various limitations.[6-7]

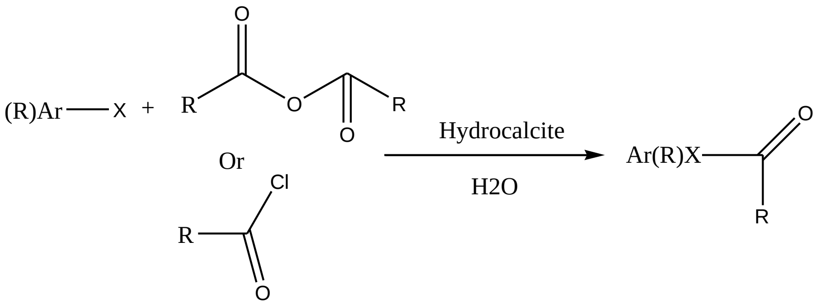
Green methods for Acetylation:

1. G. Brahmachari et al. synthesised and reported various N-acetylated derivatives by using zinc acetate as a selective N-acetylating agent without the use of any solvent in a closed vessel by exposing them to microwave irradiation. It has also been noted that the Using a catalytic quantity of this reagent in acetic acid allows for smooth N-acetylation of various amines, and the reaction is chemo-selective to phenols, thiols, acids, and alcohols. This approach for chemo-selective N-acetylation of amines utilising zinc acetate in acetic acid under microwave irradiation is simple, efficient, cost-effective, and ecologically safe. The process is quick and produces high yields without the need for any additional solvents.[8]



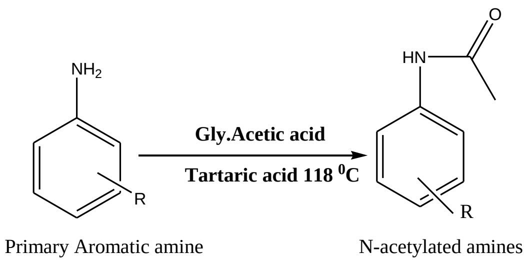
R=alkyl/aryl/benzyl, A-Zinc Acetate, b-Acetic acid-zinc acetate

2. Massah AR et al. synthesized amides and esters in water with hydrotalcite at room temperature. It is a gentle, efficient, and ecologically friendly technique for synthesizing various amines and phenols, resulting in moderate to high yields with minimal work-up.[9]

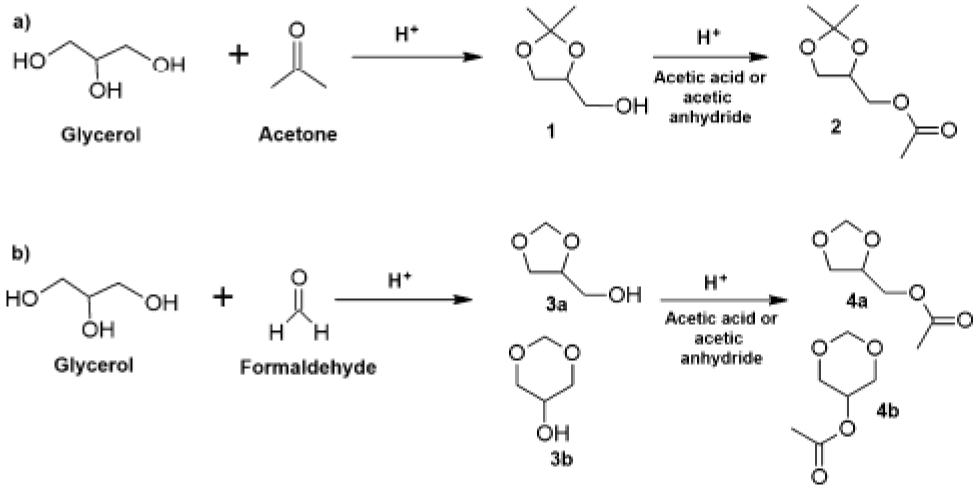


X=O,N,H

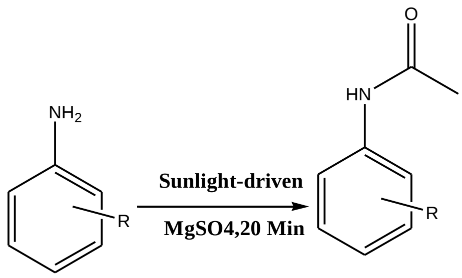
3. Pasricha S et al. synthesized various acetylated primary aromatic amines by using the tartaric acid-glacial acetic acid system, which is to be a simple, affordable, and ecologically friendly catalyst for the N-acetylation of primary aromatic amines.[10]



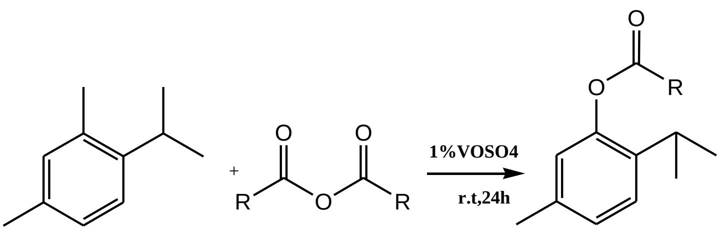
4. Dodson JR et al. described a solvent-less, heterogeneously catalysed technique for the acetylation of both solketal and glycerol in novel products. The process was optimised by investigating the effects of acetylating reagents (acetic acid and acetic anhydride), reagent molar ratios, and a variety of commercial solid acid catalysts (Amberlyst-15, Zeolite Beta, K-10 Montmorillonite, and Niobium Phosphorate) on conversion and selectivity.[11]



5. Gupta A, Sidhwani IT, et al. reported a sustainable approach for the synthesis of industrially relevant acetanilide moieties in the presence of sunlight utilizing MgSO4 as a Lewis acid catalyst with high selectivity, a short reaction time, and outstanding yields.[12]

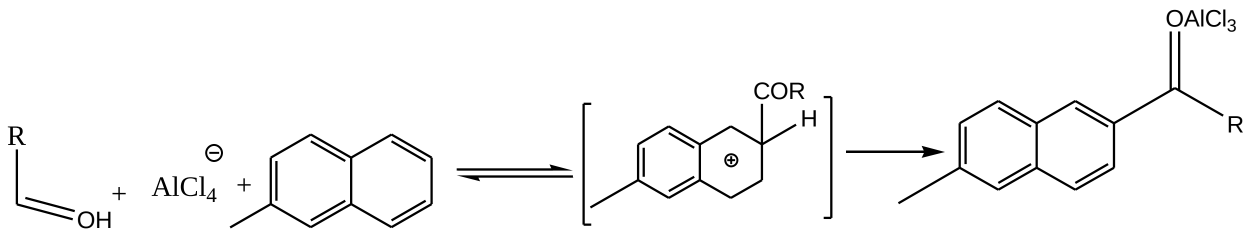


6. Valentini F.et al. converted Thymol, a naturally occurring phenol, to the equivalent physiologically active ester with high yields in the presence of 1% VOSO4. The procedure may be used to efficiently synthesize additional thymyl esters as well as acetyl alcohols, aryl and alkyl thiols.[13]

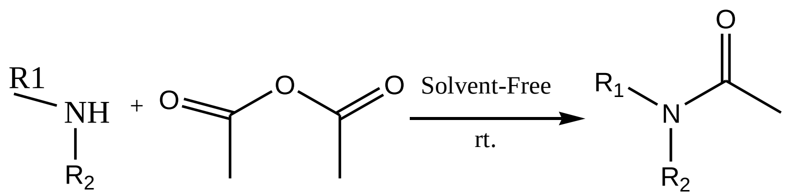


7. Li W. et al. synthesized various derivatives by using acid chloride as the acylating agent and solvent to achieve an efficient and solvent-free acylation of 2-methylnaphthalene (2-

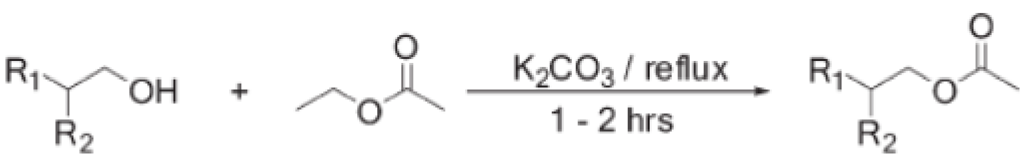
MN). The catalyst, reactant ratio, mixing temperature, reaction temperature, and reaction time were all examined for their effects on product yield and selectivity.[14]



8. Ouarna S. et al. reported an environmentally friendly, easy, mild, selectively specific, and highly efficient technique for the acylation of main and secondary amine functions in a variety of structurally and electrically aliphatic and aromatic compounds is developed, yielding their corresponding N-Ac derivatives. The key advantages of this procedure are mild circumstances, simplicity, and ease of work-up.[15]

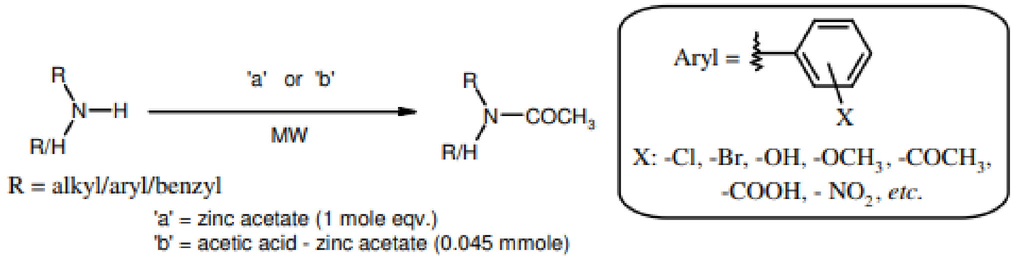


9. N. Mallesha et al reported a facile and selective acetylation of primary alcohols in the presence of other reactive functionalities such as secondary alcohol, phenol, acetonide, and amine by employing mild ethyl acetate as an acetyl-transfer agent and solid potassium carbonate as a catalyst.[16]

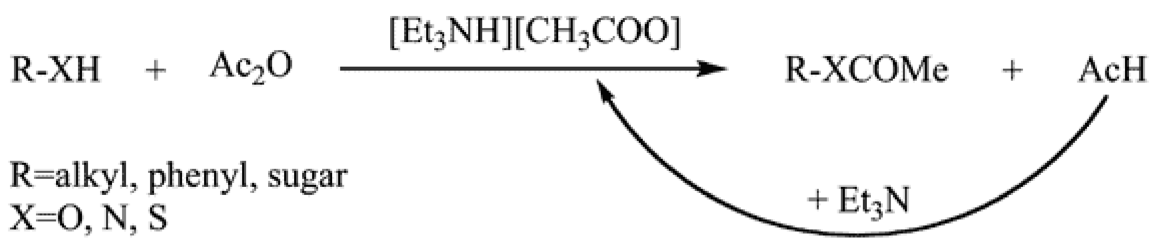


10. Brahmachari G. et al. reported microwave acetylation with zinc acetate. It has also been discovered that a catalytic amount of this reagent in acetic acid is sufficient for the smooth operation of N-acetylation of a variety of structurally different amines and that the reaction is chemoselective in terms of phenols, thiols, acids, and alcohols. This paper describes a simple, efficient, cost-effective, and environmentally friendly alternative approach for

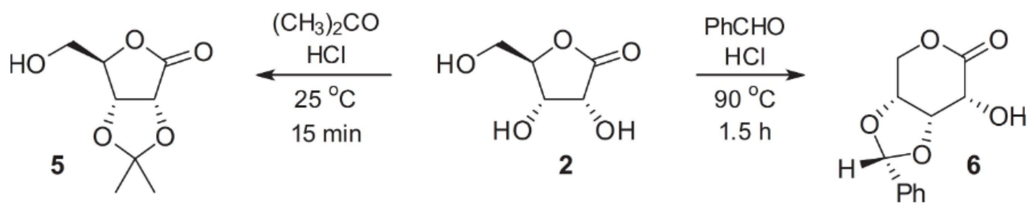
chemoselective N-acetylation of amines that employs a catalytic quantity of zinc acetate in acetic acid under microwave irradiation. The reaction requires no additional solvent and is quick, with good to exceptional yields.[17]



11. Lafuente L et al. synthesized acetylated derivatives by using the ionic liquid triethylammonium acetate (TEAA) as an effective solvent for the acetylation of alcohols, amines, oximes, and thiols to their corresponding acetyl compounds with only a 10% excess of acetic anhydride. Furthermore, TEAA is not only an affordable and recyclable solvent, but it also acts as an anomeric selective catalyst in the per-acetylation of sugar moieties.[18]

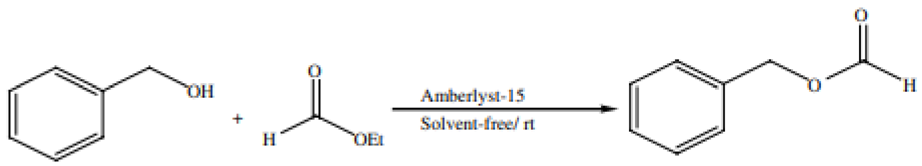


12. Cardozo HM et al. acetylated D-ribono-1,4-lactone and representative carbohydrates using acetic anhydride and molecular sieves in the absence of a solvent. This green acetylation technique was extended to D-ribonolactone derivatives and natural carbohydrates. To show the synthetic usefulness of the approach, 2,3,5-tri-O-acetyl-D-ribonolactone was used.[19]



13. AS Singh et al. reported various derivatives by using, reacting alcohols with ethyl formate using Amberlyst-15, a solid acidic resin catalyst. The catalyst may acetylate alcohols with

ethyl acetate at reflux temperatures. This approach has benefits over standard techniques due to its simplicity, reusability, nontoxicity, and catalyst stability.[20]



14. JR Dodson et al. reported a solvent less heterogeneously catalyzed technique for acetylating both solketal and glycerol formal to new compounds. The process was optimized by investigating the influence of acetylating reagents (acetic acid and acetic anhydride), reagent molar ratios, and a range of commercial solid acid catalysts (Amberlyst-15, zeolite Beta, K-10 Montmorillonite, and niobium phosphate) on conversion and selectivity. Using acetic anhydride as the acetylation reagent and a 1:1 molar ratio with all catalysts resulted in high conversions (72-95%) and selectivities (86-99%) to the desired products. [21]

REFERENCES:

1. Maity G, Ghosha AK, Ghosh PK. Green Chemistry: Synthesis of organic compounds through green approach. J. Indian Chem. Soc. 2020 Dec;97(12c):2897-902.
2. Deligeorgiev T, Gadjev N, Vasilev A, Kaloyanova S, Vaquero JJ, Alvarez-Builla J. Green chemistry in organic synthesis. Mini-Reviews in Organic Chemistry. 2010 Feb 1;7(1):44-53.
3. Savanur HM, Malunavar SS, Prabhala P, Sutar SM, Kalkhambkar RG, Laali KK. Synthesis of diverse libraries of carboxamides via chemoselective N-acylation of amines by carboxylic acids employing Brønsted acidic IL [BMIM (SO3H)][OTf]. Tetrahedron letters. 2019 Oct 17;60(42):151159.
4. Humphrey JM, Chamberlin AR. Chemical synthesis of natural product peptides: coupling methods for the incorporation of noncoded amino acids into peptides. Chemical Reviews. 1997 Oct 1;97(6):2243-66.
5. Scozzafava A, Owa T, Mastrolorenzo A, Supuran CT. Anticancer and antiviral sulfonamides. Current medicinal chemistry. 2003 Jun 1;10(11):925-53.
6. Katritzky AR, He HY, Suzuki K. N-acylbenzotriazoles: neutral acylating reagents for the preparation of primary, secondary, and tertiary amides. The Journal of organic chemistry. 2000 Dec 1;65(24):8210-3.
7. Mali SM, Bhaisare RD, Gopi HN. Thioacids mediated selective and mild N-acylation of amines. The Journal of organic chemistry. 2013 Jun 7;78(11):5550-5.
8. Brahmachari G, Laskar S, Sarkar S. A green approach to chemoselective N-acetylation of amines using catalytic amount of zinc acetate in acetic acid under microwave irradiation.
9. Massah AR, Toghyani M, Najafabadi BH. Green and efficient method for the acylation of amines and phenols in the presence of hydrotalcite in water. Journal of Chemical Research. 2012 Oct;36(10):603-5.
10. Pasricha S, Rangarajan TM. Green Acetylation of Primary Aromatic Amines.
11. Dodson JR, Leite TD, S. Pontes N, Peres Pinto B, Mota CJ. Green acetylation of solketal and glycerol formal by heterogeneous acid catalysts to form a biodiesel fuel additive. ChemSusChem. 2014 Sep;7(9):2728-34.
12. Gupta A, Sidhwani IT, Gupta R, Monga Y, Sharma RK. Sunlight-driven N-acetylation of anilines: a green chemistry approach. New Journal of Chemistry. 2023;47(37):17229-33.
13. Valentini F, Galloni P, Brancadoro D, Conte V, Sabuzi F. A stoichiometric solvent-free protocol for acetylation reactions. Frontiers in Chemistry. 2022 Mar 9;10:842190.

14. Li W, Jin H, Yang S, Guo X, He G, Zhang R. An environmentally friendly acylation reaction of 2-methylnaphthalene in solvent-free condition in a micro-channel reactor. Green Processing and Synthesis. 2019 Jan 28;8(1):474-9.
15. Ouarna S, K'tir H, Lakrout S, Ghorab H, Amira A, Aouf Z, Berredjem M, Aouf NE. An eco-friendly and highly efficient route for N-acylation under catalyst-free conditions. system. 2015;21:22.
16. Mallesha N, Rao SP, Suhas R, Gowda DC. A green method for selective acetylation of primary alcohols using ethyl acetate and solid potassium carbonate. Journal of Chemical Research. 2011 Sep;35(9):536-9.
17. Brahmachari G, Laskar S, Sarkar S. A green approach to chemoselective N-acetylation of amines using catalytic amount of zinc acetate in acetic acid under microwave irradiation.
18. Lafuente L, Diaz G, Bravo R, Ponzinibbio A. Efficient and selective N-, S-and O-acetylation in TEAA ionic liquid as green solvent. Applications in synthetic carbohydrate chemistry. Letters in Organic Chemistry. 2016 Mar 1;13(3):195-200.
19. Cardozo HM, Ribeiro TF, Sá MM, Sebrão D, Nascimento MG, Silveira GP. Molecular Sieves Mediated Green Per-O-Acetylation of Carbohydrate Templates and Lipase Catalyzed Regioselective Alcoholysis of 2, 3, 5-Tri-O-Acetyl-D-Ribonolactone. Journal of the Brazilian Chemical Society. 2015;26:755-64.
20. Singh AS, Bhanage BM, Nagarkar JM. Formylation and acetylation of alcohols using Amberlyst-15® as a recyclable heterogeneous catalyst. Green Chemistry Letters and Reviews. 2012 Mar 1;5(1):27-32.
21. Dodson JR, Leite TD, S. Pontes N, Peres Pinto B, Mota CJ. Green acetylation of solketal and glycerol formal by heterogeneous acid catalysts to form a biodiesel fuel additive. ChemSusChem. 2014 Sep;7(9):2728-34.