

Organic salts with acetic acid tags: As multi-purpose catalysts

Compiled by Mahmoud Zarei

Mahmoud Zarei was born in Hamedan, Iran in 1986. He received his B.Sc. in Pure Chemistry (2010) from Islamic Azad University Arak and M.Sc. in Organic Chemistry (2013) at Bu-Ali Sina University, Iran. Also, he received his Ph.D. in Organic Chemistry (2017) under the supervision of Prof. Mohammad Ali Zolfigol. He is currently working towards his Postdoctoral under the supervision of Prof. Mohammad Ali Zolfigol. His research interest is the synthesis, characterization and applications of homogeneous and heterogeneous reagent and catalyst in organic synthesis.

Department of Chemistry, Faculty of Science, University of Qom, Qom, 3716146611, Iran.

Email: mahmoud8103@yahoo.com, mahmoud8103@gmail.com



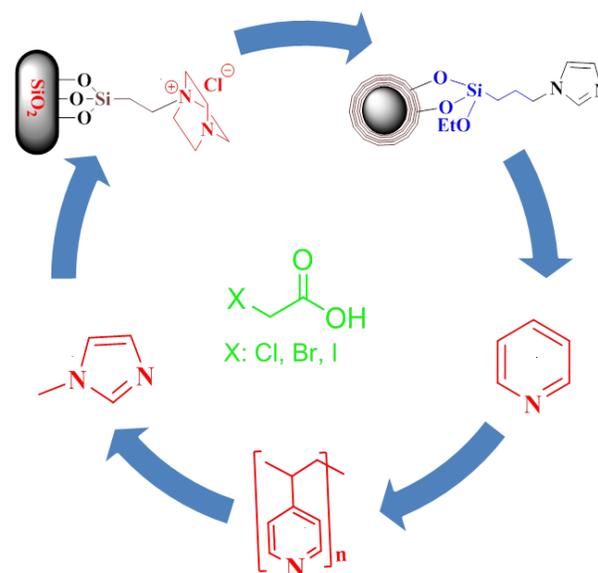
This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research.

Introduction

Acetic acid and its derivatives are very important materials with significant applications in both the industrial and academic communities. These are used in various industries especially food and pharmaceutical industries, due to their non-toxicity as pH regulators, catalysts and preservatives in food products [1].

In recent years, ionic liquids (ILs) and molten salts (MSs) with acetic acid moieties such as pyridine, imidazole, nano-magnetic Fe_3O_4 and poly 4-vinylpyridine based salts have been used as Brønsted acidic homogenous and heterogeneous versatile catalysts for various purposes [2].

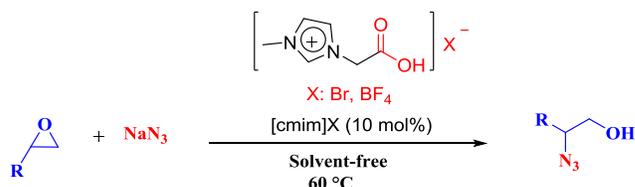
In this spotlight, we have reviewed ionic liquids (ILs) and molten salts with acetic acid tags as efficient catalysts for the synthesis of azido alcohols, α -ariloxy alcohols, tetrahydrobenzo[b]pyrans, 2-amino benzo[h]chromene, spiropyran, bis-coumarins, 4,4'-(arylmethylene)-bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)s, naphthodipyran and amidoalkyl phenols.



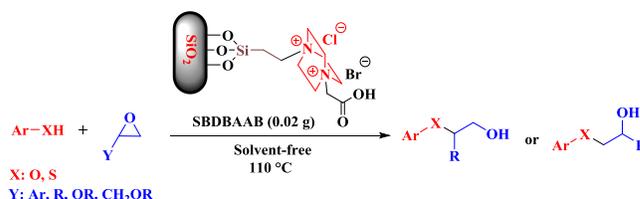
Scheme 1. Structures of ionic liquids (ILs) and molten salts (MSs) with acetic acid tags.

Abstracts

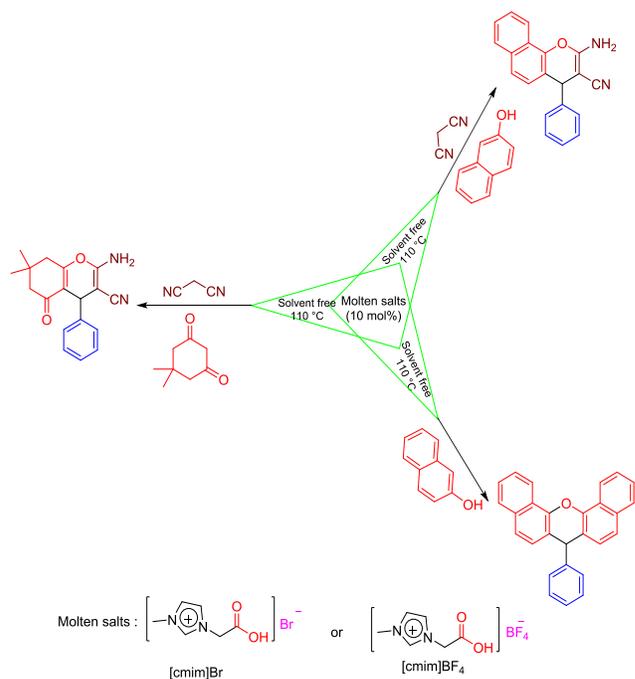
(A) The catalytic activities of the acetic acid functionalized 1-methyl-1*H*-imidazolium salts such as [cmim]Br and [cmim]BF₄ have been studied as novel catalysts for the ring opening of epoxides by the one-pot reaction of various epoxides and sodium azide at 60 °C under solvent-free condition [3].



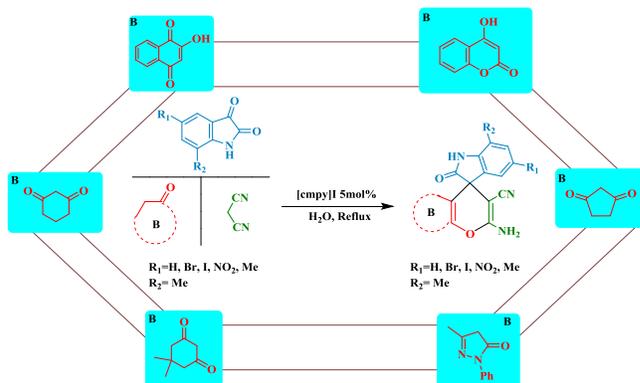
(B) In 2019, Zolfigol *et al.* have introduced a novel solid acid namely Silica-bonded 1,4-diazabicyclo[2.2.2]octane-acetic acid bromide (SBDBAAB) as a highly efficient and reusable catalyst for the regioselective synthesis of novel α -ariloxy alcohols by the reaction of epoxide and phenols under solvent-free conditions in excellent yields and short reaction times [4].



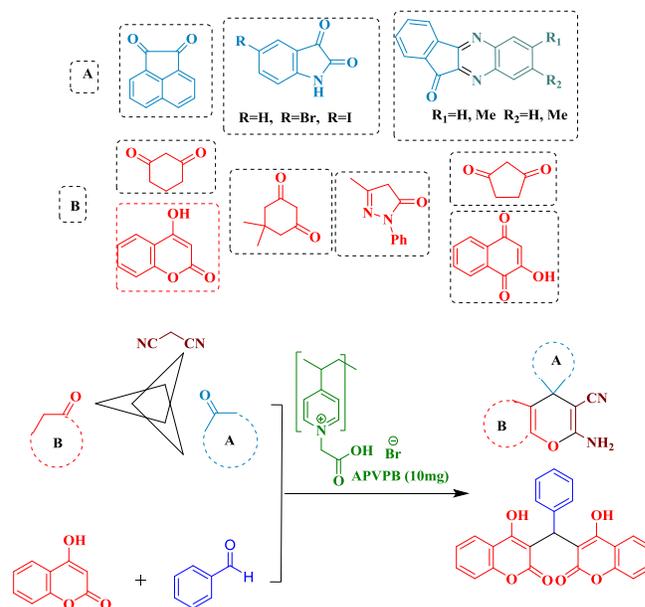
(C) Acetic acid functionalized imidazolium salts 1-carboxymethyl-3-methylimidazolium bromide ([cmim]Br) and 1-carboxymethyl-3-methylimidazolium tetrafluoroborate ([cmim][BF₄]) as novel, recyclable and ecofriendly catalysts for the preparation of 14-aryl-14*H*-dibenzo[*a,j*]xanthene under solvent-free conditions in excellent yields and short reaction times. Furthermore, Acetic acid functionalized imidazolium salts were also used for the synthesis of tetrahydrobenzo[*b*]pyrans and 2-amino benzo[*h*]chromene derivatives. A simple, efficient, clean reaction, short reaction times, high yields, easy preparation and high TOF (turn over frequency) values of the catalyst in comparison with other reported catalysts are some advantages of the described catalysts [5].



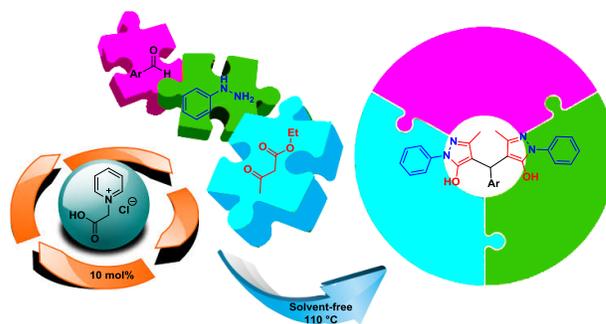
(D) The catalytic activity of the 1-(carboxymethyl)pyridinium iodide [cmpyl]I, as a highly efficient, reusable nanostructured, mild and green catalyst in the synthesis of spiropyrans with the one-pot domino reaction between satin derivatives or acenaphthenquinone, with malononitrile, and 1,3-dicarbonyl compounds under aqueous media has been studied [6].



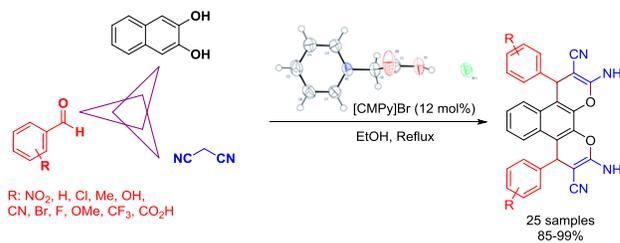
(E) Acetic acid functionalized poly(4-vinylpyridinium) bromide (APVPB) as an efficient nano catalyst has been used for the synthesis of spiropyran compounds *via* various carbonyl compounds (**A**) and α -methylene carbonyl compounds (**B**) as an activated carbonyl compound and malononitrile in water under reflux conditions. The described catalyst has been also used for the synthesis of bis coumarins derivatives under solvent-free conditions [7]. The reported spiropyran compounds have been suggested as alternative systems and candidates for medicinal and agricultural applications.



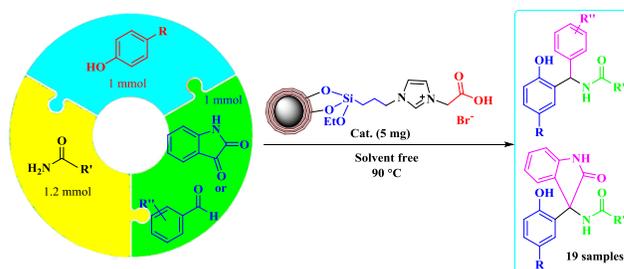
(F) Acetic acid functionalized pyridinium salt (1-(carboxymethyl) pyridinium chloride {[cmpy]Cl}) as an efficient catalyst has been successfully used for the synthesis of 4,4'-(arylmethylene)-bis(3-methyl-1-phenyl-1H-pyrazol-5-ols) under solvent-free conditions. The obtained products are interesting bioactive compounds, which had been prepared in excellent yields and very short reaction times [8].



(G) In another exploration, naphthodipyrans have been introduced as a category compounds which have been prepared from the condensation of naphthalene-2,3-diol, malononitrile and various aromatic aldehydes in the presence of a catalytic amount of 1-(carboxymethyl) pyridinium bromide [CMPy]Br under solvent free conditions [9].



(H) Zolfigol *et al.* have introduced [Fe₃O₄@SiO₂-(CH₂)₃-im-CH₂CO₂H]Br as an efficient nano-magnetic catalyst, for the reaction of various amides (benzamide, acetamide and urea), aryl aldehydes, phenolic compounds or isatin under solvent-free conditions for preparation of amidoalkyl phenols in high yields and short reaction times [10].



References

- [1] (a) J. Barclay, *Br. Med. J.* 2 (1866) 512. (b) N. Shibata, *Gan to Kagaku Ryoho.* 25 (1998) 751-755. (c) M. J. Page, S. Green, M. A. Mrocki, S. J. Surace, J. Deitch, B. McBain, N. Lyttle, R. Buchbinder, *Cochrane Database Syst. Rev.* 6 (2016) CD012225. (d) T. P. Habif, *Clinical dermatology: A color guide to diagnosis and therapy*, Elsevier, 2009, p. 367.
- [2] (a) P. Wasserscheid, T. Welton, *Ionic Liquids in Synthesis*, Wiley-VCH: Weinheim, 2008. (b) P. Wasserscheid, W. Keim, *Angew. Chem. Int. Ed.* 39 (2000) 3772-3789. (c) A.R. Moosavi-Zare, M.A. Zolfigol, M. Zarei, A. Zare, V. Khakyzadeh, A. Hasaninejad, *Appl. Catal. A* 467 (2013) 61-68. (d) A.R. Moosavi-Zare, M.A. Zolfigol, M. Zarei, A. Zare, V. Khakyzadeh, *J. Mol. Liq.* 186 (2013) 63-69. (e) M.A. Zolfigol, A.R. Moosavi-Zare, M. Zarei, C. R. Chim. 17 (2014) 1264-1267. (f) A.R. Moosavi-Zare, M.A. Zolfigol, M. Zarei, E. Noroozizadeh, M.H. Beyzavi, *RSC Adv.* 6 (2016) 89572-89577. (g) M. Zarei, E. Noroozizadeh, A.R. Moosavi-Zare, M.A. Zolfigol, *J. Org. Chem.* 83 (2018) 3645-3650. (h) H. Ghaderi, M.A. Zolfigol, Y. Bayat, M. Zarei, E. Noroozizadeh, *Synlett* 27 (2016) 2246-2250.
- [3] S. Rezayati, E. Salehi, R. Hajinasiri, S. Afshari Sharif Abad, *C. R. Chim.* 20 (2017) 554-558.
- [4] M. Zarei, E. Noroozizadeh, O. Khaledian, A. R. Moosavi-Zare, M. A. Zolfigol, *J. Mol. Struct.* 1175 (2019) 428-438.
- [5] (a) A. R. Moosavi-Zare, M. A. Zolfigol, O. Khaledian, V. Khakyzadeh., *Chin. J. Catal.* 35 (2014) 573-578 (b) A. R. Moosavi-Zare, M. A. Zolfigol, O. Khaledian, V. Khakyzadeh, M. Darestani Farahani, H. Gerhardus Kruger. *New J. Chem.* 38 (2014) 2342-2347. (c) A. R. Moosavi-Zare, M. A. Zolfigol, O. Khaledian, V. Khakyzadeh, M. Darestani farahani, M. H. Beyzavi, H. Gerhardus Kruger. *Chem. Eng. J.* 248 (2014) 122-127.
- [6] A. R. Moosavi-Zare, M. A. Zolfigol, R. Salehi-Moratab, E. Noroozizadeh., *Can. J. Chem.* 95 (2016) 194-198.
- [7] (a) A. R. Moosavi-Zare, M. A. Zolfigol, E. Noroozizadeh, M. Zarei, R. Karamian, M. Asadbegy, *J. Mol. Catal. A: Chem.* 425 (2016) 217-228. b) E. Noroozizadeh, A. R. Moosavi-Zare, M. A. Zolfigol, M. Zarei, R. Karamian, M. Asadbegy, S. Yari, S. H. Moazzami Farida. *J. Iran. Chem. Soc.* 15 (2018) 471-481.
- [8] A. R. Moosavi-Zare, M. A. Zolfigol, E. Noroozizadeh, O. Khaledian, B. Shirmardi Shaghasem. *Res. Chem. Intermed.* 42 (2016) 4759-4772.
- [9] M. Rajabi-Salek, M. A. Zolfigol, M. Zarei, E. Noroozizadeh, I. Mohammadpoor-Baltork, H. Amiri Rudbari. *ChemistrySelect* 3 (2018) 12791-12796.
- [10] J. Afsar, A. Khazaei, M. Zarei, M. A. Zolfigol. *ChemistrySelect* 4 (2019) 1122-1126.