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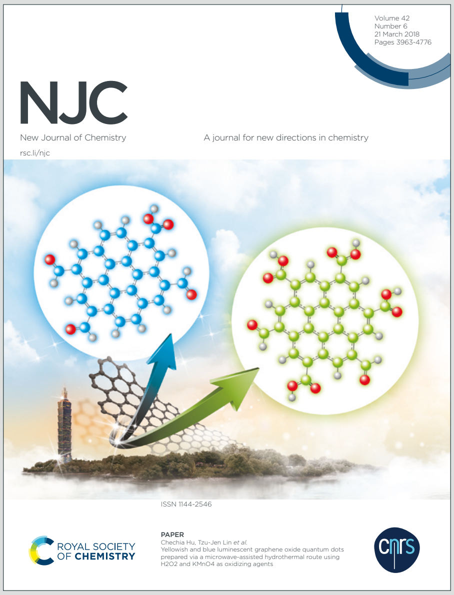

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ARTICLE

Anion Functionalized Ionic liquid From Artificial Sugar: A Sustainable Pathway for Diverse Bis-enol Derivatives

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Himani Sharma,[a] Suman Srivastava*[a]

An Artificial Sugar Saccharine based anion-functionalized ionic liquid [Bmim]Sac was synthesized and used for new and straightforward strategies for the construction of diverse range of bis-enol. The advantage of this methodology is use of non-toxic, inexpensive and reusable catalyst, and high atom economy, and easy purification makes this an efficient process. Besides, a probable mechanism describing dual activation of ionic liquid as well as dual hydrogen bonding of saccharinate anion has been proposed.

Introduction,

Diversity-oriented synthesis offers a unique approach for the synthesis of structurally diverse bioactive skeletons by varying substrate functionalities and molecular building blocks.[1] Recently green chemistry approach has profoundly influenced the Diversity-oriented synthesis by considering its environmental compatibility. Hence, diversity-oriented synthesis carried out with readily available environmentally benign solvents and reagents is attractive. In this context, functionalized ionic liquids have appeared as an important and essential replacement for toxic, hazardous, flammable, and highly volatile organic solvents as well as catalyst.[2] Functionalized ionic liquid is an effort to take advantage of the potential "design" capacity of Functionalized ionic liquids and allowing them as working systems rather than just reaction media.[3] ILs can be functionalized by designing different cations and anions on the basis of requirement.[4] Since anion plays an important role in ionic liquid catalysis, recently several anion functional ionic liquids, were synthesized and used for the gas capture[5] and basic catalytic reaction.[6]

Biscoumarin and Aryl/alkylbispyranylmethane are renowned as significant organic natural products with excellent potent of therapeutic applications in the field of medicinal and biological chemistry.[7] Biscoumarin derivatives such as Acenocoumarol, Phenprocoumon, Warfarin, and Dicoumarol are anticoagulant agents that act as vitamin K antagonists (Figure1).[8-9] Aryl/alkylbispyranylmethane bearing 4-hydroxy pyran-2-one structural moieties such as Phaeolschidins and 5-substituted pyrimidine nucleoside with arylbispyranylmethane moiety can act as anti-oxidant and antiviral agent respectively (Figure 1).[10] On the basis of above said importance of bisenols, development of mild, efficient, and ecofriendly synthetic methodology is essential. Biscoumarin have been synthesized through the catalyzed domino reaction with a variety of catalysts including I_2,[11] $RuCl_3.nH_2O$,[12] n-dodecylbenzenesulfonic acid,[13] Nano silica chloride,[14] Sodium dodecyl sulfate (SDS),[15] heteropoly acids,[16] cellulose sulfuric acid,[17] Zn(proline)$_2$,[18] CuO-CeO_2 nanocomposite catalyst[19] Propane-1,2,3-triyltris(hydrogen sulfate).[20] A variety of catalyst have been also used for the synthesis of Aryl/alkylbispyranylmethane such as organic bases,[21] nano magnetic core-shell catalysts,[22] $Fe_3O_4@SiO_2/(CH_2)_3$-[Imidazolium-SO_3H]Cl.[23]

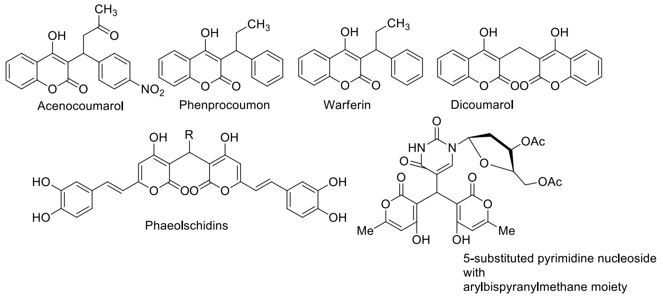

Figure1. Bioactive agents bearing Biscoumarin and Aryl / alkylbispyranylmethane structural scaffolds

A variety of ionic liquids[24-30] has also been used for the synthesis of biscoumarin and Aryl/alkylbispyranylmethane. Recalling the previously developed methods and their shortcomings, some of which have included the application of hazardous organic solvents, low yield, strongly acidic conditions, expensive moisture-sensitive catalysts, extended reaction times, high reaction temperatures, and also tedious work-up conditions, it is still necessary to develop a non-toxic, green, reusable catalytic system for the synthesis of Bisenol scaffolds. From previously published work for synthesis of Bisenol, it is also evident that there is yet a scope of common

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[a] *Department of Applied Sciences, National Institute of Technology, Delhi. NILERD campus, Sec A-7, Narela, Delhi, India, 110040, Email: sumanbhu08@gmail.com*

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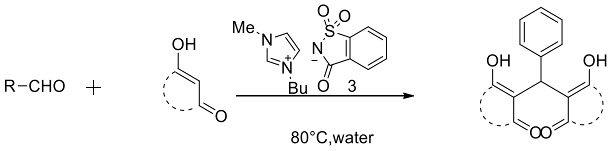
methodology for various bisenol scaffolds.[27, 31] In continuation to developing diversity oriented synthesis[32] and green multicomponent methodology,[33] we herein report synthesis of a large collection of bisenol derivatives such as biscoumarin, arylbispyranylmethane and tetraketones using green anion functionalized ionic liquid synthesized from simple, bio-renewable starting such as Saccharine.[34]

Saccharine is one of the most widely explored, cheapest, readily available substrates and due to its non toxic properties,[35a] it can be used for synthesis of anion functionalized ionic liquid. Since anion play an essential structural element in altering the technical properties of ionic liquid. Therefore, the selection of saccharine based anion with non toxic potential proved to be far superior than the anions such as BF_4^- , $(CF_3SO_2)_2N^-$ which have high toxic potentials.[35b,35c] In addition, 1-butyl-3-methyl-imidazolium cation with a short alkyl side chain (C = 4) was chosen because ionic liquids with longer alkyl side chains (C>6) proved to cause high toxicities.[35d] Owing to the wide application of bis-enol derivatives, we were interested in exploring saccharine based ionic liquid for the synthesis of bisenol as a novel and green methodology. Present report focuses on the bisenol synthesis through domino Knoevenagel-Michael reaction of aldehyde, and 4-hydroxycoumarin/4-hydroxy-6-methyl-2 pyrone /Dimidone /Cyclohexanone 1,3- dione in the presence of [Bmim]Sac as a catalyst in water (scheme 1).

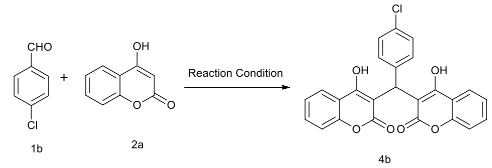


Scheme 1. Synthesis of Bisenol scaffolds under mild and eco-friendly conditions

Results and discussion,

[Bmim]Sac was synthesized via reaction of sodium saccharinate with [Bmim]Br in dry acetone at room temperature. To optimise the reaction condition, the reaction of 4-Cl-benzaldehyde and 4-hydroxycoumarin as a model reaction in the presence of different amount of [Bmim]Sac was studied. In absence of [Bmim]Sac, only a trace amount of 4b was obtained even at 100 °C (Table 1, entry 6). The amount of catalyst and reaction temperature was optimized using same model reaction. Initially, model reaction was performed in neat ionic liquid at room temperature and it was found that 40 mol% of catalyst (Table 1, entry 7) is sufficient to achieve the target compound in 60% yield at room temperature. On increasing the temperature from 50 ˚C to 80˚C, yield increases progressively (Table 1, entry 8-11), and we found that the reaction accomplished in short duration in presence of only 30 mol% of catalyst at 80˚C (Table 1, entry 12). Further increase in the temp up to 100 °C doesn't have any effect on yield (Table 1, entry 13). But in presence of water, 10 mol% of ionic liquid is sufficient to complete the reaction in 10 min (Table 1, entry 14). The presence of water gave the most excellent result with respect to both time and yield (Table 1, entry 14). This may be due to structural and dynamical changes in IL-water solution.[36] Therefore, 10 mol% [Bmim]Sac in the presence of water and 80˚C was selected as the optimal reaction condition. In order to show the merit of our procedure, we have performed synthesis of Biscoumarin using other ionic liquid (Table 1, entry 1, 2, 3, 4, and 5). The results were summarized in Table 1.

Table 1 Reaction condition optimization in presence of different ionic liquids for the synthesis of Biscoumarin



S. No	Ionic liquid , Temp and amount of catalyst[a]	Time	Yield(%)[b]
1	[Bmim]Br, 80°C, 20 mol%	5h	**30**
2	[Bmim]OH 80°C, 20 mol%	5h	65
3	$[Bmim]BF_4$ 80°C, 20 mol%	5h	70
4	$[Bmim]\ SO_3H$, 80°C, 20 mol%	5h	72
5	$[Bmim]PF_6$, 80°C, 20 mol%	5h	75
6	-, 100**°C,**	24h	trace
7	[Bmim]Sac, RT, 40 mol%	5h	60
8	[Bmim]Sac, 50˚C, 40 mol%	12h	62
9	[Bmim]Sac, 60˚C, 40 mol%	12h	65
10	[Bmim]Sac, 70˚C, 40 mol%	12h	70
11	[Bmim]Sac, 80˚C, 40 mol%	45min	85
12	[Bmim]Sac, 80˚C, 30 mol%	45min	85
13	[Bmim]Sac, 100˚C, 30 mol%	45min	85
14	**[Bmim]Sac, 80˚C, 10 mol%, water**	**10 min**	**96**

[a]Reaction Conditions: 4-Cl benzaldehyde (1.0 mmol), 4-hydroxycoumarin (2a, 2.0 mmol), [b]Isolated yield

Next, the substrate tolerance of this catalyst for synthesis of Bisenol was investigated using different veriety of aldehydes and cyclic active methylene compounds under optimized conditions. Results displayed in scheme 3 shows that various aromatic aldehydes either with electron donating or electron withdrawing substituent groups reacts smoothly with cyclic active methylene compounds to give the target compounds in good to excellent yields. Heteroaromatic aldehydes such as thiophene-2-carbaldehyde and furan-2-carbaldehyde were competent to undergo condensation with 4-hydroxy coumarin and isolating the corresponding biscoumarin in quantitative yield (scheme 3, 4j, 4k, 4u). To further evaluate the scope of substrate, we investigated the catalytic activity of [Bmim]Sac for synthesis of aryl/alkyl bispyranylmethane as well as tetraketones derivatives (scheme 2). For this, we replaced 4-hydroxy coumarin with 4-hydroxy-6-methyl-2-pyrone/ dimedone/ 1,3-cyclohexanedione in condensation reaction with substituted aldehyde and the results are summarized in (scheme 2 and 3).

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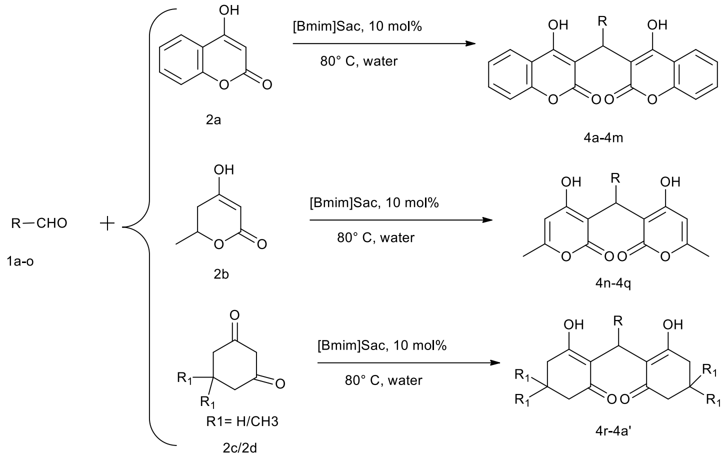
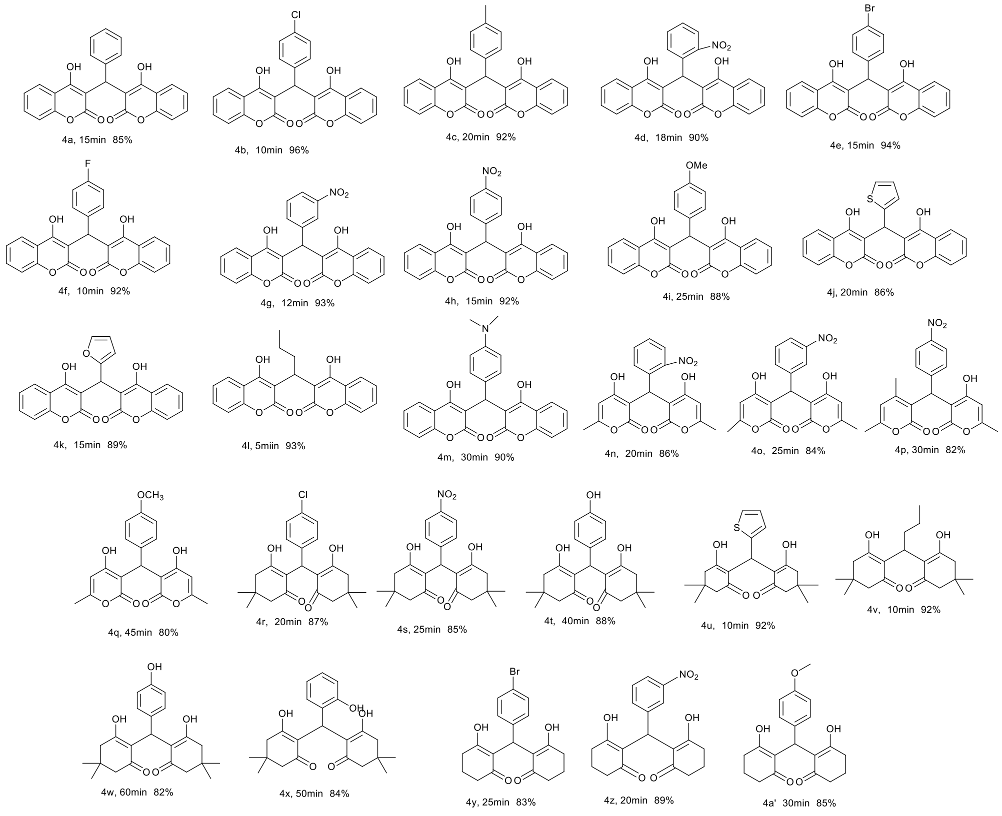
Scheme 2. Domino Knoevenagel-Michael reaction of substituted aldehydes **1a-o** with 4-hydroxycoumarin/4-hydroxy-6-methyl-2-pyrone/ dimedone/ 1,3-cyclohexanedione **2a-d,** catalyzed by [Bmim]Sac[a]



Scheme 3. Synthesis of biscoumarin, bispyranylmethane and tetraketones via optimized reaction conditions.



[a]*Reaction Conditions*: Substituted aldehyde (1.0 mmol), 4-hydroxycoumarin/4-hydroxy-6-methyl-2-pyrone/dimedone/1,3-cyclohexanedione(2.0 mmol), [Bmim]Sac (0.1 mmol).; [b]Isolated yield.

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Aliphatic aldehyde such as n-Butyraldehyde afforded target product in excellent yield with very short reaction time (scheme 2, 4l and 4v). In most of the cases, the solid products obtained were just filtered off the reaction mixture or in some cases extracted with ethyl acetate and water and later recrystallized from ethanol to obtain the pure product. The plausible reaction for [Bmim]Sac catalyzed one-pot Knoevenagel-Michael reaction mechanism was proposed and is illustrated in Figure. 2. The process represents a typical domino reaction by dual activation by ionic liquid. The carbonyl group of aldehyde was activated by formation of hydrogen bonds with C-2 hydrogen of [Bmim] cation of ionic liquid, and saccharinate anion of IL activated OH of 4-hydroxy-coumarin as a hydrogen bond acceptor.

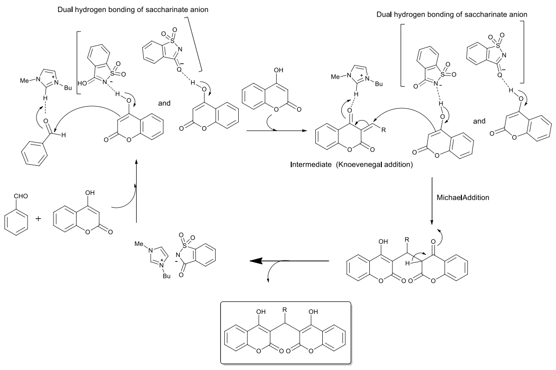

Figure 2: Plausible mechanism via dual activation of [Bmim]Sac and dual hydrogen bonding of saccharinate anion

This dual activation led to addition of one molecule of 4-hydroxycoumarin to one aldehyde molecule. Then, intermediate which was also activated by the [Bmim] cation of ionic liquid and then reacted with another molecule of 4-hydroxycoumarin activated by anion of ionic liquid, leading to target compound with high efficiency. In this catalytic procedure, [Bmim] cation and the anion have a synergetic effect on substrates, and also dual hydrogen bonding ability of saccharinate anion[35a] is a possible reason why this catalytic system could reduce reaction duration significantly.

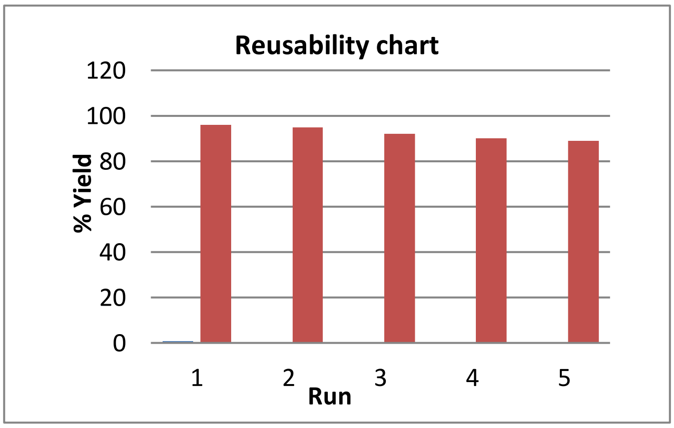

Figure 3. Reusability chart

The reusability of the [Bmim]Sac was also investigated using reaction between 4-Cl benzaldehyde and 4-hydroxycoumarin as a model system. After the completion of reaction as monitored by TLC, water was added to the reaction mixture. The solid precipitate was filtered and the filtrate containing water and the ionic liquid catalyst was dried and subsequently used for the next run. It was shown that after five cycles the catalytic activity had a low decrease (Figure 3), suggesting the good recyclability of this ionic liquid for Bisenol synthesis. Also after five cycles of reusability, IR and NMR characterization of ionic liquid was performed which is similar to fresh IL indicating purity and activity of Ionic liquid (See supporting information, Fig 3-6).

Conclusions

Artificial sweetener saccharine based ionic liquid was found to be an efficient catalyst for the synthesis of Bis-enol derivatives. The attractive features of this method include milder and cleaner reaction conditions, higher yields and purity of the product and an easier work-up and isolation of products. In addition, this ionic liquid catalyst is easy to prepare, and its raw materials such as saccharine are highly biocompatible biodegradable and non toxic, which make the preparation and utilization procedures more safe and green.

Conflicts of interest

"There are no conflicts to declare".

Acknowledgements

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An Artificial Sugar Saccharine based anion-functionalized ionic liquid [Bmim]Sac was synthesized and used for new and straightforward strategies for the construction of diverse range of bis-enol.