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A highly efficient ultrasound-promoted synthesis of 2,3-disubstituted benzo[*b*]furans *via* intramolecular C–C bond formation in ionic liquid[bmim]BF_4 at room temperature†

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An efficient ultrasound-promoted synthesis of 2,3-disubstituted benzo[*b*]furans in the ionic liquid [bmim]BF_4 at room temperature is reported. 5-*exo*-*dig* carbanion–yne intramolecular cyclization is mediated using anhydrous K_3PO_4 as a mild, inexpensive base under atmospheric conditions giving the title benzo[*b*]furans in excellent yields. Ionic liquid [bmim]BF_4 has been used both as a reaction medium, as well as a catalyst for the C–C bond formation.

Introduction

Intramolecular cyclizations forming C–C bonds have become one of the most efficient methods for the synthesis of carbocyclic and heterocyclic compounds.[1a,b] A number of methodologies using transition metal catalyzed annulations,[2–4] intramolecular Heck reaction,[5,6] carbocyclization of *gem*-dihaloalkenes,[7a–c] sequential Sonogashira coupling[8] *etc.* have been utilized for the formation of diverse heterocyclic compounds. 2,3-functionalized benzo[*b*]furans have been widely studied as they constitute important units in many natural products and biologically active compounds.[9,10] Their potential in chemistry and biology has consistently stimulated the search for new methods for their synthesis. In the literature, there are various methods for benzo[*b*]furan synthesis *via* C–O bond formation,[11–16] but very few are available *via* C–C bond formation.[17,18] Moreover, many of these methods use very expensive reagents, specific PTCs (phase transfer catalysts), harsh reaction conditions and tedious work-up procedures. These drawbacks prompted us to develop a mild and greener approach towards the synthesis of 2,3-disubstituted benzo[*b*]furans at room temperature using ultrasonication (US) as the energy source.

Ultrasound-assisted organic synthesis as a green approach is a powerful technique employed for organic reactions leading to higher yields, shorter reaction times, milder conditions and higher analytical purity.[19a–d] It is considered a processing aid in terms of energy conservation and waste minimization compared with traditional methods. Sonochemistry (use of ultrasound in chemistry) offers the synthetic chemist the advantage of chemical activation through cavitation and provides a source of energy, which can be used to enhance a variety of chemical reactions. The strong acceleration of the reaction rate by ultrasonic irradiation is based on the cavity effect and hot spot formation.[20a,b] The cavity effect is defined as the phenomenon of formation, growth and eventual collapse of small bubbles within a liquid. As these bubbles are small and rapidly collapse, the temperature and pressure within the bubble during a collapse is very high, thus, each cavitation bubble acts as a micro-reactor that offers the opportunity of speeding up reactions to take place in an absolutely safe manner. In addition, the reactions are carried out at room temperature under atmospheric conditions. In order to avoid the disadvantages of volatile and toxic organic solvents, ionic liquids (ILs) have shown great promise as non-volatile solvents and are being increasingly explored as an eco-friendly medium for clean synthesis. They are easy to recycle and possess no effective vapour pressure.[21,22] This communication is the first report of a highly efficient and environmentally benign protocol for the ultrasound-assisted synthesis of a variety of 2,3-disubstituted benzo[*b*]furans in high yields. The intramolecular C–C bond formation leading to the heterocycle is catalyzed by a mild base potassium phosphate[23–25] in the ionic liquid [bmim]BF_4, (1-butyl 3-methyl imidazolium tetrafluoroborate) under ultrasound irradiation at room temperature. Ionic liquid [bmim]BF_4 has been used both as a reaction medium, as well as the catalyst for the intramolecular carbanion–yne cyclization (Scheme 1).

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Scheme 1 Synthesis of 2,3-disubstituted benzo[*b*]furans: K_3PO_4 mediated intramolecular C–C bond formation in ionic liquid.

Results and discussion

The study was initiated by conducting the intramolecular cyclization of simple 1-phenyl-2-(2-(phenylethynyl)phenoxy) ethanone **1a** using *t*-BuOK (potassium tertiary butoxide) as a base in THF under ultrasound irradiation at room temperature. To our delight the reaction was neat and completed in 30 min yielding the desired benzo[*b*]furan **2a** in 80% yield (Table 1, entry 1). Encouraged by this result we decided to choose **1a** as a template for the screening of different solvents and bases for the optimization of reaction conditions. A change of solvent from THF to DMF or DMSO prolonged the reaction time to 1 h (entry 2 and 3). Changing the base to cesium carbonate and conducting the reaction in THF, acetonitrile or acetonitrile–water mixture gave no reaction (entry 4–6). Addition of a catalytic amount of PTC, (tetrabutyl ammonium bromide or iodide) in conjunction with cesium carbonate again failed to initiate any reaction (entry 7). However, to our surprise, the addition of a catalytic amount of DABCO (1,4-diazabicyclo[2.2.2]octane) along with cesium carbonate in dichloromethane completely changed the course of the reaction, it was complete in 45 min and benzo[*b*]furan was isolated in 80% yield (entry 8). Use of strong bases like KOH or NaOH formed complex mixtures of unidentifiable compounds from which the desired compound could not be isolated. Use of moderate bases like Na_2CO_3 or K_2CO_3 gave either low yields or negligible formation of benzo[*b*]furans (entry 9, 10). These observations led to the belief that for solvents basicity is more important than polarity. Since the use of strong bases led to complex mixtures, it was thought to study the effect of a mild base synergistically with a moderately basic solvent. Anhydrous potassium phosphate has been utilized as an auxiliary mild base in homogeneous metal-catalyzed reactions, particularly in the presence of base-sensitive functional groups in a number of C–C bond forming reactions.[26–28] In this analogy, we conducted our reaction using potassium phosphate in DMF and surprisingly the desired benzo[*b*]furan **2a** was isolated in 81% yield (entry 11). Thus, on comparing the results, K_3PO_4 was found to be the most efficient base and upon examining the influence of the amount of anhydrous K_3PO_4 on the reaction, it was found that approximately 2.5–3.0 equiv. of base was necessary for the completion of the reaction in less time. A change of solvent to THF or DMSO did not have any significant effect on the reaction. In order to avoid the use of toxic DMF and applying a greener approach, the same reaction was performed in ionic liquid [bmim]BF_4. The reaction was almost quantitative in 30 min, as observed by TLC (thin layer chromatography) and 2,3-disubstituted benzo[*b*]furan **2a** was isolated in >95% yield through column chromatography (entry 12). To investigate the use of other ionic liquids, as different combinations of anions and cations lead to different ionic liquids with different polarities, the reaction was tried in [bmim]PF_6 (1-butyl 3-methyl imidazolium hexafluorophosphate), [bmim]OH (1-butyl 3-methyl imidazolium hydroxide) and [bpy]BF_4 (*N*-butyl pyridinium tetrafluoroborate) (entry 13–15). It was found that the reaction worked best in [bmim]BF_4. In the case of [bmim]PF_6 the product was isolated in >80% yield, but the time needed for the completion of the reaction was prolonged to 1 h, presumably due to the hydrophobic nature of this ionic liquid.[29] In our case, since the reaction is conducted under atmospheric conditions it is more compatible in hydrophilic ionic liquid, [bmim]BF_4. As compared to other cation-based ILs, such as pyridinium, thiazolium, pyrazolium *etc.*,imidazolium cations exhibit higher ionic conductivities and lower viscosity.[30] As shown in the mechanism of our reaction (Scheme 4) the imidazolium cation binds to the carbanion formed and stabilizes the intermediates (i & ii). This binding of the imidazolium cation is presumably facilitated due to the availability of a hydrogen bond donor site at C-2 of the imidazolium ring flanked by two N-atoms resulting in the strong solute solvent interactions and acceleration of the reaction rate. This is further supported by the results obtained using the pyridinium cation-based ionic liquid that lacks a H-donor site and thus affords the product in lower yields with increased reaction time (entry 15).

Table 1 Synthesis of 2,3-disubstituted benzo[*b*]furans under ultrasonic irradiation. Optimization of reaction conditions, solvents and bases

Entry	Base [a]	Solvent	Method/Time	Yield (%) (**2a**)
1	*t*-BuOK	THF	US[b]/30 min	80
2	*t*-BuOK	DMF	US/1 h	90
3	*t*-BuOK	DMSO	US/1 h	90
4	Cs_2CO_3	THF	US/5 h	N. R[c]
5	Cs_2CO_3	CH_3CN	US/5 h	N. R
6	Cs_2CO_3	CH_3CN/H_2O	US/5 h	N. R
7	Cs_2CO_3/PTC[d]	CH_3CN/H_2O	US/5 h	N. R
8	Cs_2CO_3/DABCO[e]	DCM	US/45 min	80
9	KOH or NaOH	CH_3CN/H_2O	US/2 h	C. M[f]
10	Na_2CO_3 or K_2CO_3	CH_3CN/H_2O	US/5 h	N. R
11	K_3PO_4	DMF	US/1 h	81
12	K_3PO_4	[bmim]BF_4	US/30 min	96
13	K_3PO_4	[bmim]OH	US/1 h	80
14	K_3PO_4	[bmim]PF_6	US/1 h	84
15	K_3PO_4	[bpy] BF_4	US/1 h	68
16	K_3PO_4	[bmim]BF_4	50 °C/1 h	C. M
17	K_3PO_4	[bmim]BF_4	RT[g]/4 h	40
18	K_3PO_4	[bmim]BF_4	MW/15 min	85

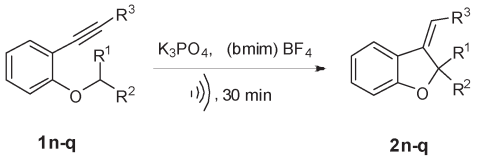
[a] 2.5–3 equivalent of bases were used. [b] Ultrasonic irradiation. [c] No reaction. [d] 10 mol % of phase transfer catalyst were used. [e] 1 : 1 ratio of base and DABCO were used. [f] Complex mixture. [g] Room temperature.

To explain the promotional effect of ultrasonic irradiation, the same reaction was performed in [bmim]BF_4 under conventional heating and stirring at 50 °C. Though the reaction was complete in 1 h, it showed a complex mixture (Table 1, entry 16) from which the desired compound could not be isolated. Similarly, when the reaction was carried out at room temperature, it was incomplete even after 4 h of stirring (entry 17). Thus, having accomplished the optimization of reaction conditions, it was thought to compare the reaction under another green condition *i.e.*, microwave irradiation (MW), the reaction was complete in a shorter time of 15 min, but the cyclized product was isolated in 85% (entry 18). The results are summarised in Table 1.

Next, equipped with the optimized experimental conditions, substrate generality of the reaction was investigated under the same reaction conditions to study the effect of substituents R^1 and R^2 present on the aryl rings (Table 2). Presence of an electron-donating methoxy or electron-withdrawing halogen group on either acetylenic aryl ring or alkoxyaryl ring facilitated formation of benzofurans in excellent yields (entries 1b–f). The reactions were neat and products could be easily isolated/purified by simple filtration through a short column of silica gel. Even dihalo and trimethoxy groups were well tolerated (entries 1g–i). When aryl acetylene was replaced with trimethylsilyl acetylene, the reaction again progressed well with subsequent desilylation of the TMS group during the cyclization process (entry 1j–m).

Further modifications in the molecular structure were carried out by subsequently replacing the hydrogens at the alpha position to the carbonyl carbon by one and two ester groups, respectively (Scheme 2).

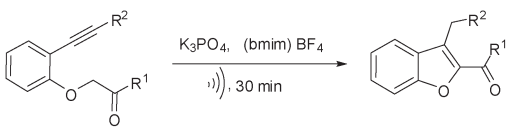
In this case the reaction time was increased up to 45 min. This increase in reaction time is presumably due to the decreased acidity of α-hydrogens adjacent to an ester group as compared to that adjacent to a carbonyl group. Also, the compounds formed were benzo[*b*]furan isomers and not benzo[*b*]furans because due to the lack of α-hydrogen, the molecules could not be aromatized to benzofurans. The results are shown in Table 3.



Scheme 2 C–C bond formation in ester analogues.

In the analogy of carbanion-yne cyclization, we thought of extending the same reaction protocol to carbanion–ene molecular framework and study the cyclization of (*E*)-2-(5-methoxy-2-styrylphenoxy)-1-phenylethanone **3**. In this case the reaction was complete in 4 h. A white solid was isolated (80%) by purification through column chromatography along with a phenolic compound. Spectral analyses confirmed the structure of **4** as 2-aroyl-3-benzyl-6-methoxy-2,3-dihyrobenzofuran and **5** as (*E*)-2-styrylphenol (Scheme 3).The results are again contrary to a published report wherein chroman derivatives are formed through 6-*endo-trig* cyclization using *t*-BuOK as a base with 2-phenylvinylphenoxy and 2-phenylallylphenoxy substrates under reflux conditions.[31] With the above observations, we also tried the cyclization of **3** by changing the mild base, anhydrous K_3PO_4, to *t*-BuOK. No benzo[*b*]furan was formed, instead the phenacyl group was completely knocked out forming (*E*)-2-styrylphenol as the sole product. Interestingly, if the same reaction was performed under conventional heating at 80 °C in K_3PO_4/[bmim]BF_4, it resulted in substantially low yields of **4** (40%) and increased formation of **5** (>50%). This may be explained due to the decreased activity of the olefinic double bond (styryl substrate), as compared to the more reactive alkyne substrate requiring more time for cyclization to benzo[*b*]furan, whereas, strong basic conditions or heating facilitates the hydrolysis of the phenacyl group. The reason for 5-*exo-dig* cyclization in our study taking precedence over 6-*endo-trig* cyclization may be due to subsequent stabilization of the carbanion formed with the aryl rings

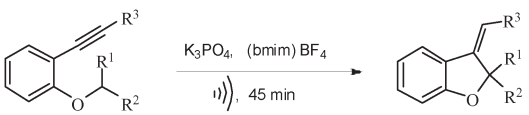
Table 2 Synthesis of 2,3-disubstituted benzo[*b*]furans. The effect of substituent groups



Entry	R^1	R^2	Product	Yield (%)[a]
1a	Ph	Ph	2a	96
1b	4-MeOPh	Ph	2b	95
1c	Ph	4-MeOPh	2c	96
1d	4-MeOPh	4-MeOPh	2d	96
1e	Ph	4-BrPh	2e	95
1f	4-BrPh	44-MeOPh	2f	96
1g	3,4,5-OMePh	Ph	2g	94
1h	3,4-ClPh	Ph	2h	95
1i	3,4-ClPh	4-MeOPh	2i	97
1j	Ph	$Si(Me)_3$	2j(R^2 = H)	97
1k	4-MeOPh	$Si(Me)_3$	2k(R^2 = H)	94
1l	4-BrPh	$Si(Me)_3$	2l(R^2 = H)	94
1m	3,4,5-OMePh	$Si(Me)_3$	2m(R^2 = H)	93

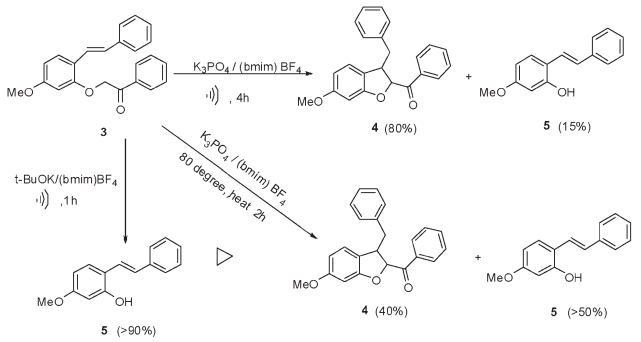
[a] Isolated yields.

Table 3 Synthesis of 2,2,3-trisubstituted benzo[*b*]furan isomers



Entry	R^1	R^2	R^3	Product	Yields (%)[a]
1n	CO_2Et	Ph	Ph	2n	87
1o	CO_2Et	Ph	4-MeOPh	2o	85
1p	CO_2Et	CO_2Et	Ph	2p	82
1q	CO_2Et	CO_2Et	4-MeOPh	2q	80

[a] Isolated Yields.

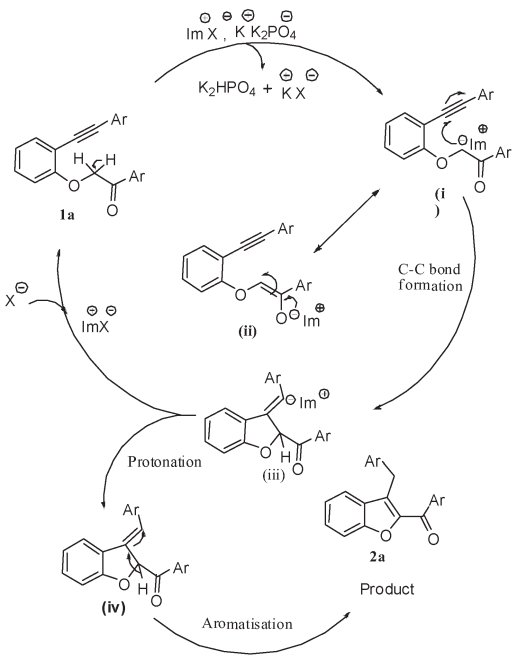


Scheme 3 Cyclization of styrylphenoxy phenyl ethanones.

attached to double or triple bonds under mild basic conditions.

The reaction protocol as described above is highly efficient, involves the use of an inexpensive base K_3PO_4 and employs an ultrasonic cleaning bath as the cheapest source of ultrasonic irradiation. Furthermore, a very small amount of ionic liquid (1 ml $mmol^{-1}$) is required for the reaction, that works both as a solvent, as well as a catalyst. The cost analysis of the reaction protocol as compared to other reported methods makes it quite economical due to the recyclability of the ionic liquid. The recycling procedure involves filtration of the reaction mixture to remove the residual base and washing with diethyl ether (15 ml × 3). The product along with the impurities is isolated from the diethyl ether layer by drying over anhydrous Na_2SO_4 and evaporation under reduced pressure. The ionic liquid thus separated was dried under a vacuum overnight at 80 °C for reuse in the next reaction. The same process is adopted after each reaction and the recovered ionic liquid was successively used for four consecutive cycles without any significant loss in the efficiency of the solvent. Moreover, the new reaction procedure was not found to be sensitive to the quality and type of the reagents or solvents which were used, such as those commercially available without further purification. All of the reactions were carried out under atmospheric conditions and therefore, in the hydrophilic ionic liquid [bmim]BF_4 no extra precaution was needed for the exclusion of moisture.

Based on these results a possible mechanism is postulated for the intramolecular cyclization, as shown in Scheme 4. Abstraction of an α-proton by potassium phosphate results in carbanion generation (i), which is stabilized by the imidazolium cation of the ionic liquid (ii). The nucleophilic attack by the anion on alkynyl carbon induces intramolecular *5-exo-dig* cyclization forming the intermediate (iii). Subsequent proton transfer leads to aromatization affording the stabilized 2,3-disubstituted benzo[*b*]furan **2a** in excellent yields.



Scheme 4 Proposed mechanism for K_3PO_4/[bmim]BF_4 mediated C–C bond formation/cyclization.

Conclusion

In conclusion, we have developed a convenient and highly efficient ultrasound-promoted synthesis of 2,3-disubstituted benzo[*b*]furans in ionic liquid at room temperature and under mild basic conditions. The reaction is tolerant to both electron-donating, as well as electron-withdrawing substituents, and can be used to access 2,3-functionalized benzo[*b*]furans in good to excellent yields through either carbanion–yne or carbanion–ene carboannulation.

Experimental

General procedure for the synthesis of 2a

To a mixture of compound **1a** (312 mg, 1 mmol) in 1 ml of ionic liquid [bmim]BF_4, anhydrous potassium phosphate (636 mg, 3 mmol) was added and the reaction mixture irradiated under ultrasonic condition for 30 min. After completion of the reaction, as monitored by TLC, the product was extracted with diethyl ether (15 ml × 3) leaving behind the ionic liquid that was further used in another reaction cycle. The combined organic layer was finally washed with water, dried over Na_2SO_4 and concentrated under reduced pressure to give a solid residue. The pure product **2a** was isolated by simple filtration/purification over a small column of silica gel, using EtOAc/hexane, as a white solid, m.p. 110–112 °C. ^{1}H NMR (300 MHz,$CDCl_3$) δ 8.15–8.13 (d, J = 7.1 Hz ,2H), δ 7.66–7.48 (m, 6H), 7.40–7.38 (d, J = 7.1 Hz, 2H), 7.31–7.18 (m, 4H), 4.57 (s, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 185.9, 154.5, 148.4, 139.7, 137.8, 132.8, 129.2, 128.8, 128.6, 128.5, 128.4, 128.2, 126.4, 123.6, 122.2, 112.4, 30.5. IR (KBr, cm^{-1}): 1641, 1550, 1262, 1218, 1018, 769. ESI-MS: (m/z) = 313 $[M + H]^+$.

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