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Synthesis of Novel Imidazolium and Benzimidazolium Salts from Halomethyl Derivatives of 4-Pyrones

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Abstract: A series of mono- and bis-benzimidazolium and imidazolium salts of 4-pyrone derivatives has been synthesized in good yields, by various quaternization reactions of halomethyl derivatives of 4*H*-pyran-4-ones. These salts can be used as novel precursors of functionalized *N*-heterocyclic carbenes and some of them as novel ionic liquids.

Keywords: 4-pyrones, benzimidazolium salts, imidazolium salts, KI, kojic acid, substitution reactions.

INTRODUCTION

Imidazolium and benzimidazolium salts are an important class of quaternary ammonium compounds (QACs) which have extensively achieved considerable attention in different chemical, biochemical and industrial areas [1-7]. Deprotonation of *N*,*N*′-disubstituted derivatives of these salts, generates *N*-heterocyclic carbenes (NHCs) species. These nucleophilic carbenes as excellent ligands of metal ions are widely used in coordination chemistry [8, 9]. Resulting metal-NHC complexes have found great applications in medicinal chemistry [10] and as catalysts in many carbon-carbon bond forming reactions [11-16]. Furthermore, applications of NHC precursors as organocatalysts in many organic transformations have rapidly increased [17, 18].

Moreover, the imidazolium salts can serve as ionic liquids as environmentally benign solvents due to their interesting properties such as thermal stability, non-flammability, very low vapor pressure and reusability [19, 20]. 4-Pyrones and their heterocyclic derivatives constitute an important class of biologically active natural and synthetic products, continuing to attract interest [21-24]. Since a variety of heterocycles with tethered imidazolium or benzimidazolium groups have been synthesized and used as carbene ligands, [25-29], and through our recent attempts for the synthesis of heterocyclic and polyfunctional frameworks of 4-pyrones [30, 31], we were interested in the preparation of imidazolium and benzimidazolium salts based on 4-pyrone structures. Herein we report synthesis of some of these salts starting from various halomethyl derivatives of 4-pyrones.

RESULTS AND DISCUSSION

Schemes **1** and **2** show the substitution reactions of halomethyl derivatives **1a-f**. These starting compounds were prepared from benzylic halogenations of the corresponding 4-pyrones according to the literatures [32]. Treatment of halomethyl derivatives **1a-d** with commercial *N*-methylimidazole in acetonitrile at 25 ºC for 24 hr, resulted in the formation of salts **2a-d**, which were obtained in good yields and simple workup. The 4-(bromomethyl)phenyl derivatives **1e,f** also react similarly to afford imidazolium salts **2e,f**. To evaluate the possibility of reducing the melting points of these compounds to achieve the new ionic liquids, anion exchange reactions of these salts with $AgBF_4$ were carried out according to a known procedure [42], to furnish the corresponding imidazolium tetrafluoroborates **3a-f** (Schemes **1**, **2**).

Table **1** shows the yields and uncorrected melting points of imidazolium salts. According to the table, the salts obtained from protected kojic acid, **2b**, **3b**, as well as ionic derivatives bearing phenyl group, **3d-f,** melt below 100 °C or near room temperature. Due to the influence of miscibility of these salts in their applications, we also examined the miscibility of all synthesized salts in water and conventional organic solvents (Table **2**). As shown in the table, good miscibility in water and methanol was observed for these salts.

We then examined the reactions of *N*-alkylbenzimidazoles with 2-halomethyl-4-pyrones (Scheme **1**). At first, treatment of **1a,c** with *N*-alkylbenzimidazoles in boiling acetonitrile resulted in trace amounts of salts even after extended time. But the addition of potassium iodide (KI, 1.1 eq.) to the mixture, led to the progress of the reactions and the benzimidazolium salts **2g-l** were obtained after 10 h at 70°C in good yields (Table **3**). Employment of KI as activator for *N*′-alkylation of *N*-alkylimidazoles with alkylchlorides has also been reported [6]. The utilized *N*-alkylbenzimidazoles, were prepared from alkylation of benzimidazole according to the reported procedures [43, 44].

In order to obtain more interesting compounds from the standpoint of coordination chemistry, we then decided to synthesize the 4-pyrone-bridged bis imidazolium and benzimidazolium salts. For this purpose we used 2,6-bis [(4-bromomethyl)phenyl)]-4-pyrone **4** [45]. Again, treatment of

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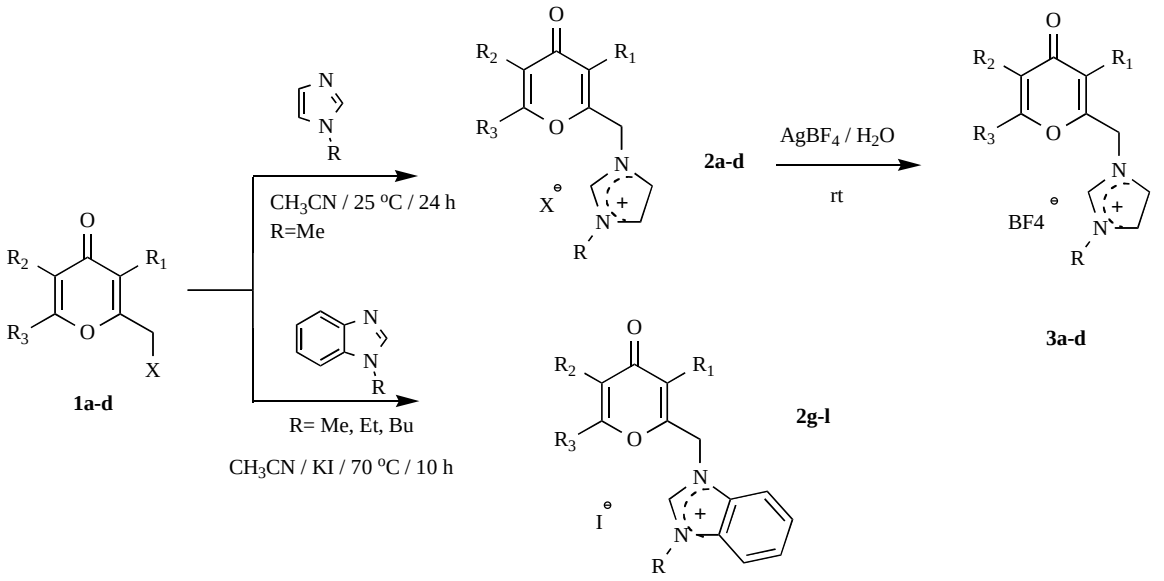
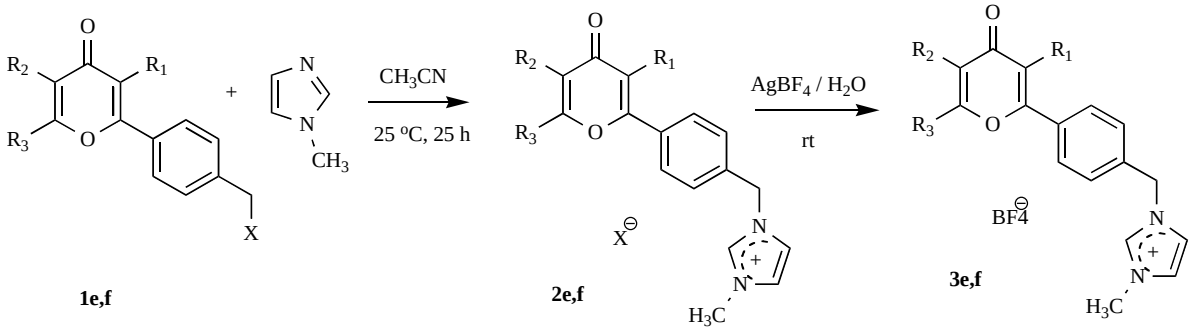


Scheme 1. Reactions of *N*-methylimidazole and *N*-alkylbenzimidazoles with 2-halomethyl-4-pyrones and anion exchanging of imidazolium products.



Scheme 2. Reactions of *N*-methylimidazole with 2-[(4-bromomethyl)phenyl]-4-pyrones and anion exchanging of imidazolium products.

Table 1. Synthesis of Imidazolium Salts 2a-f and 3a-f.

Entry	R_1	R_2	R_3	X	1	2[a] (Mp ºC, Yield %)	3[b] (Mp ºC, Yield %)
1	H	OH	H	Cl	**1a**	**2a** (237-239, 88)	**3a** (132-134, 92)
2	H	OCH_2Ph	H	Cl	**1b**	**2b** (93-95, 83)	**3b** (31-32, 90)
3	H	H	Ph	Br	**1c**	**2c** (218-220, 85)	**3c** (123-124, 92)
4	Ph	Ph	CH_3	Br	**1d**	**2d** (190-191, 83)	**3d** (98-99, 90)
5	H	H	CH_3	Br	**1e**	**2e** (177-179, 88)	**3e** (91-93, 89)
6	H	H	Ph	Br	**1f**	**2f** (138-139, 86)	**3f** (60-62, 91)

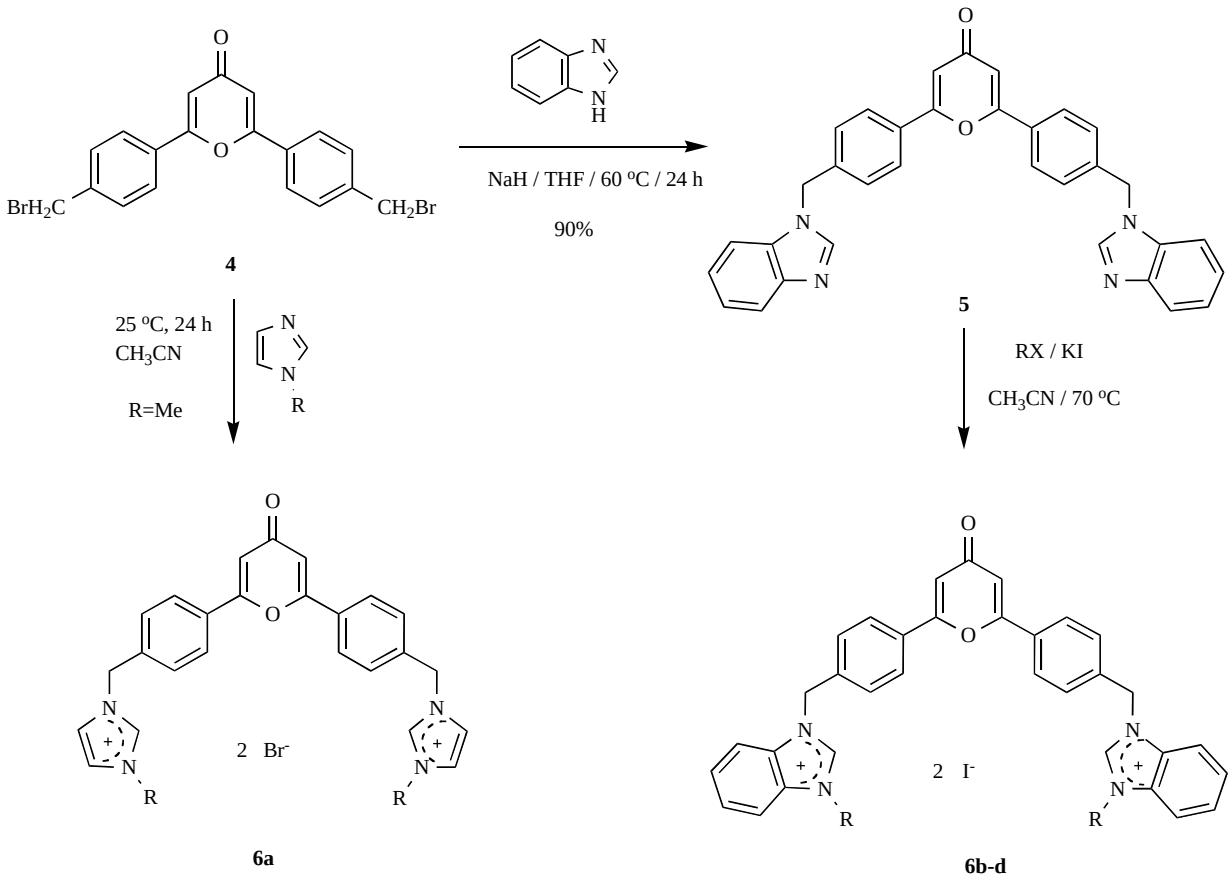
Conditions: [a] 1-methylimidazole (2.2 mmol), **1a-f** (2 mmol), acetonitrile (15 ml), r.t., 24 h. [b:] **2a-f** (1 mmol), $AgBF_4$ (2 mmol), H_2O (14 ml), r.t., 1 h.

dibromide **4** with *N*-methylimidazole in acetonitrile at 25 ºC for 24 h, resulted in the formation of **6a** (Scheme **3**). For synthesis of the corresponding bis-benzimidazolium salts, we used an indirect route. Treatment of **4** with 2 equiv. of benzimidazole in the presence of sodium hydride in THF at 60°C for 24 h gave the bis(benzimidazolyl) derivative **5** in 90% yield (Scheme **3**). Reactions of **5** with alkyl halides such as methyl iodide, ethyl bromide and n-butyl bromide in hot acetonitrile, again resulted in the formation of trace amounts of salts even after prolonged time. Addition of potassium iodide (2.0 eq.) to the reaction mixture, expedited the reactions and the bis-benzimidazolium iodides **6b-d** were

Table 2. Miscibility of Imidazolium Salts 2a-f, 3a-f.

Salt	Miscibility in Solvents					
	H_2O	MeOH	CH_3CN	$CHCl_3$	EtOAc	THF
2a	m	m	pm	im	im	im
2b	m	m	pm	im	im	im
2c	m	m	pm	im	im	im
2d	m	m	m	pm	pm	im
2e	m	m	pm	im	im	im
2f	m	m	pm	im	im	im
3a	m	m	m	pm	pm	im
3b	m	m	m	im	im	im
3c	m	m	m	pm	pm	im
3d	pm	m	m	m	m	im
3e	pm	m	m	pm	pm	im
3f	m	m	m	im	im	im

m: miscible, pm: partly miscible, im: immiscible



Scheme 3. Synthesis of 4-pyrone-bridged bis imidazolium and benzimidazolium salts.

achieved at 70°C in 74-84% yields (Scheme **3**). Table **4** shows the yields and melting points of the 4-pyrone-bridged salts.

CONCLUSION

In conclusion, we have designed and synthesized a series of novel imidazolium and benzimidazolium salts containing

Table 3. Synthesis of Benzimidazolium Salts 2g-l.

Entry	1	R	2 (Mp °C, Yield %)
1	**1a**	Me	**2g** (200-202, 88)
2	**1c**	Me	**2h** (199-201, 67)
3	**1a**	Et	**2i** (150-152, 68)
4	**1c**	Et	**2j** (150-152, 73)
5	**1a**	Bu	**2k** (158-160, 90)
6	**1c**	Bu	**2l** (218-220, 87)

Conditions: **1a,c** (2 mmol), *N*-alkylbenzimidazoles (2.2 mmol), acetonitrile (15 ml), KI (2.2 mmol), 70°C, 10 h.

Table 4. Synthesis of Salts 6a-d.

Entry	R	6 (Mp °C, Yield %)
1	Me	**6a** (209-211, 74)
2	Me	**6b** (198-200, 74)
3	Et	**6c** (238-240, 80)
4	Bu	**6d** (278-280, 84)

Conditions: for **6a:** dibromide **4** (1 mmol), 1-methylimidazole (1.1 mmol), acetonitrile (15 ml), r.t., 24 h., for **6b-d**: compound **5** (2 mmol), alkylhalides (12 mmol), KI (4 mmol), acetonitrile (10 ml), 70°C, 48 h.

a 4-pyrone moiety, by reaction of different halomethyl derivatives of 4-pyrones with *N*-methyl imidazole and *N*-methyl benzimidazoles, followed by anion exchanging of imidazolium salts with $AgBF_4$. These salts can be used as novel precursors of *N*-heterocyclic carbenes and some of them as novel ionic liquids. Solubility of all imidazolium salts has been studied in water and conventional organic solvents and remarkable results have been obtained. We have also synthesized the 4-pyrone bridged bis-imidazolium and benzimidazolium salts, from dibromide **4** in one or two steps respectively. Spectroscopic data of the selected salts are reported [47-49].

CONFLICT OF INTEREST

The author(s) confirm that this article content has no conflicts of interest.

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REFERENCES

[1] Lee, J.P.; Yoo, B.; Suresh, T.; Kim, K.J. Novel silane-substituted benzimidazolium iodide as gel electrolute for dye-sensitized solar cells. *Electrochimica Acta*, **2009**, *54*, 4365-4370.

[2] Xia, M.; Shi, C.; Sun, R.; Cai, M.; Liu, Z. Solvent-free synthesis of alkylbenzimidazolium iodides and their applications in dye-sensitized solar cells. *Solar Energy*, **2010**, *84*, 1828-1832.

[3] Shimakawa, Y.; Morikawa, T.; Sakaguchi, S. Facile route to benzyls from aldehydes *via* NHC-catalyzed benzoin condensation under metal-free conditions. *Tetrahedron Lett*., **2010**, *51*, 1786-1789.

[4] Kim, S.Y.; Kim. S.; Park, M.J. Enhanced proton transport in nanostructured polymer electrolyte/ionic liquid membranes under water-free conditions. *Nat. Commun*., **2010**, 1-7.

[5] Sun, P.; Armstrong, D.W. Ionic liquids in analytical chemistry. *Analytica Chimica Acta*, **2010**, *661*, 1-16.

[6] Oertel, A.M.; Ritleng, V.; Chetcuti, M.J. *N′*-activation of *N*-arylimidazoles: facile syntheses of *N*-alkyl-*N′*-arylimidazolium iodides from less expensive chloro substrates. *Synthesis*, **2009**, 1647-1650.

[7] Shibata, N.; Okamoto, M.; Yamamoto, Y.; Sakaguchi, S. Reversal of stereoselectivity in the Cu-catalyzed conjugate addition reaction of dialkylzinc to cyclic enone in the presence of a chiral azolium compound. *J. Org. Chem.*, **2010**, *75*, 5707-5715.

[8] Hahn, F.E.; Jahnke, M.C. Heterocyclic carbenes: synthesis and coordination chemistry. *Angew. Chem. Int. Ed*., **2008**, *47*, 3122-3172.

[9] Diez-Gonzalez, S.; Marion, N.; Nolan, S.P. *N*-Heterocyclic carbenes in late transition metal catalysis. *Chem. Rev*., **2009**, *109*, 3612-3676.

[10] Teyssot, M.L.; Jarrousse, A.S.; Manin, M.; Chevry, A.; Roche, S. Metal-NHC complexes: a survey of anti-cancer properties. *Dalton Trans*., **2009**, 6894-6902.

[11] Gulcemal, S.; Kahraman, S.; Daran, J.C.; Cetinkaya, E. The synthesis of oligoether- substituted benzimidazolium bromides and their use as ligand precursors for the Pd- catalyzed Heck coupling in water. *J. Organometal. Chem*., **2009**, *694*, 3580-3589.

[12] Demir, S.; Ozdemir, I.; Cetinkaya, B. Synthesis and catalytic activity of novel xylyl-linked benzimidazolium salts. *Appl. Organometal. Chem*., **2009**, *23*, 520-523.

[13] Zou, G.; Huang, W.; Xiao, Y.; Tang, J. Heck reaction catalysed by palladium supported with an electron-rich benzimidazolylidene generated *in situ*: remarkable ligand electronic effects and controllable mono- and di-arylation. *New J. Chem*., **2006**, *30*, 803-809.

[14] Altava, B.; Burguete, M.I.; Karbass, N.; Luis, S.V. Palladium *N*-methylimidazolium supported complexes as efficient catalysts for the Heck reaction. *Tetrahedron Lett*., **2006**, *47*, 2311.

[15] Yiğit, B.; Yiğit, M.; Özdemir, I.; Çetinkaya, E. The Synthesis of Some Benzimidazolium Salts and Use as Carbene Precursors in the Heck and Suzuki Reactions. *Heterocycles*, **2010**, *81*, 943-953.

[16] Doğan, Ö.; Gürbüz, N.; Özdemir, İ.; Çetinkaya, B.; Şahin, O. Synthesis, characterization and catalytic activity of novel *N*-heterocyclic carbene-palladium complexes. *Dalton trans*., **2009**, *35*, 7087-7093.

[17] Shimakawa, Y.; Morikawa, T.; Sakaguchi, S. Facile route to benzils from aldehydes *via* NHC-catalyzed benzoin condensation under metal-free conditions. *Tetrahedron Lett*., **2010**, *51*, 1786-1789.

[18] Enders, D.; Niemeier, O.; Henseler, A. Organocatalysis by *N*-Heterocyclic carbenes. *Chem. Rev*., **2007**, *107*, 5606-5655.

[19] Plechkova, N.V.; Rogers, R.D.; Seddon, K.R. Ionic liquids: from knowledge to application (Book Review). *J. Am. Chem. Soc.*, **2010**, *132*, 12518.

[20] Giernoth, R. Task-specific ionic liquids. *Angew. Chem. Int. Ed*., **2010**, *49*, 2834-2839.

[21] Wilk, W.; Waldmann, H.; Kaiser, M. γ-Pyrone natural products-A privileged compound class provided by nature. *Bioorg. Med. Chem*., **2009**, *17*, 2304-2309.

[22] Yan, Y.L.; Cohen, S.M. Efficient Synthesis of 5-amido-3-hydroxy-4-pyrones as inhibitors of matrix metalloproteinases. *Org. Lett*., **2007**, *9*, 2517-2520.

[23] South, M.S., Ma, C.C.; Koeller, K.J., Rahman, H.K.; Neumann, W.L. Polycyclic aryl and heteroaryl substituted 4-pyrones useful for selective inhibitors of the coagulation cascade. U.S. Patent 6,916,847 B2, July 12, 2005, *Chem. Abstr*, **2001**, *135*, 303776e.

[24] Sengoku, T.; Takemura, T.; Fukasawa, E.; Kigoshi, H. Aldol-type reaction of a 4-pyrone: a straightforward approach to 4-pyrone containing natural products. *Tetrahedron Lett*., **2009**, *50*, 325-328.

[25] Jahnke, M.C.; Hussain, M.; Hupka, F.; Cavell, K.J. Synthesis of pyrazine-bridged diimidazolium salts and their application in palladium catalyzed Heck-type coupling reactions. *Tetrahedron*, **2009**, *65*, 909-913.

[26] Zhang, X.; Gu, S.; Xia, Q.; Chen, W. New structural motifs of silver and gold complexes of pyridine-functionalized benzimidazolylidene ligands. *J. Organometal. Chem*., **2009**, *694*, 2359-2367.

[27] Lee, H.M.; Chiu, P.L.; Hu, C.H.; Lai, C.L. Synthesis and structural characterization of metal complexes based on pyra-

zole/imidazolium chlorides. *J. Organometal. Chem.*, **2005**, *690*, 403-414.

[28] Nielsen, D.J.; Cavell, K.J., Viciu, M.S., Nolan, S.P. Furan- and thiophene-functionalised bis-carbene ligands: Synthesis, silver(I) complexes, and catalysis. *J. Organometal. Chem.*, **2005**, *690*, 6133-6142.

[29] Scheele, U.J.; Dechert, S.; Meyer, F. A versatile access to pyridazines with tethered imidazolium groups-new precursors for mono- and binucleating NHC/pyridazine hybrid ligands. *Tetrahedron Lett.*, **2007**, *48*, 8366-8670.

[30] Shahrisa, A.; Ghasemi, Z.; Saraei, M. Synthesis of 2,6-Bis(1*H*-indole-6-yl)-4*H*-pyran-4-ones *via* Leimgruber–Batcho Indole Synthesis. *J. Heterocycl. Chem.*, **2009**, *46*, 273-277.

[31] Shahrisa, A.; Ghasemi, Z. Synthesis of fused pyrimidone derivatives of 4-pyrones from the acetates of Baylis-Hillman adducts. *Chem. Hetrocycl. Comp*., **2010**, *46*, 30-36.

[32] 2-Chloromethyl-5-hydroxy-4-pyrone **1a** (chlorokojic acid) and 5-bezyloxy-2-chloromethyl-4-pyrone **1b** were prepared from chlorination of commercially available kojic acid and kojic acid-benzyl ether respectively according to the literature [33]. Kojic acid-benzyl ether itself was achieved by benzylation of phenolic OH of kojic acid [34]. 2-Bromomethyl-6-phenyl-4-pyrone **1c** was synthesized by heating of 2-hydroxymethyl-6-phenyl-4-pyrone in HBr/H_2SO_4 at 70 °C for 18 h which itself was prepared from reduction of the corresponding ethoxycarbonyl derivative [35]. Bromides **1d-f** were obtained from benzylic bromination of the corresponding 4-pyrones in the presence of NBS (1 eq.) and catalytic amounts of benzoyl peroxide (BPO) in boiling CCl_4 for 48 h [36]. 2,6-Dimethyl-3,5-diphenyl-4-pyrone, required for preparation of **1d**, was itself prepared according to the reported procedure [37]. The starting 4-pyrones, required for preparation of **1e,f**, were achieved through dehydrative cyclization of related 1,3,5-triketones in the presence of conc. H_2SO_4, as a significant procedure for the synthesis of a variety of 4-pyrone structures [38-41].

[33] Tam, T. F.; Li, W. Processes for the manufacturing of 3-hydroxy-*N*,1,6-trialkyl-4-oxo-1,4-dihydropyridine-2-carboxamide. U.S.Patent 6,426,418 B1, July 30, **2002**, *Chem. Abstr*, *137*, 12089q.

[34] Kazuo, M.; Masanao, S.; Shoichiro, O.; Yutaka, W. Ascorbic acid-Kojic acid conjugate and production. Jpn. Patent JP08081462, March 26, **1996**. *Chem. Abstr*., *125*, 58988u.

[35] Rudas, M.; Fejes, I.; Nyerges, M.; Toke, L. Substituent effects on the 4π + 2π cycloadditions of 4*H*-pyran-4-one derivatives. *J. Chem. Soc. Perkin Trans. 1*, **1999**, *9*, 1167-1172.

[36] Shahrisa. A.; Saraei. M. Synthesis of pyrone carbaldehydes, pyrone sulfonium ylides and related epoxides. *J. Heterocycl. Chem*., **2009**, *46*, 268-272.

[37] Emmick, T.L.; Latsinger, R.L. 2,6-Dimethyl-3,5-diphenyl-4*H*-pyran-4-one. *Organic synthesis*, **1968**, collective vol. v. Wiley, 450-452.

[38] Sakakura, A.; Watanabe, H.; Ishihara, K. Rate-accelerating effect by the neighboring-group participation of protecting groups in the dehydrative cyclization of 1,3,5-triketones. *Org. Lett*., **2008**, *10*, 2569-2572.

[39] Tyvorskii, V.I.; Bobrov, D.N.; Kulinkovich, O.G. New synthetic approaches to 2-perfluoroalkyl-4*H*-pyran-4-ones. *Tetrahedron*, **1998**, *54*, 2819-2826.

[40] Arimoto, H.; Nishiyama, S.; Yamamum, S. Mild conditions for cyclization of β-triketides to the corresponding γ-pyrones carrying adjacent chiral centers toward biomimetic synthesis of fully substituted γ-pyrone-containing natural products. *Tetrahedron Lett*., **1990**, *31*, 5619-5620.

[41] Shahrisa, A.; Hemmati, S. Chemistry of pyrones: Part I-Synthesis of triketones and triketoesters and related 4*H*-pyran-4-ones. *Indian J. Chem*., **2000**, *39B*, 190-197.

[42] Wilkes, J.S.; Zaworotko, M.J. Air and water stable 1-ethyl-3-methylimidazolium based ionic liquids. *J. Chem. Soc., Chem. Commun*., **1992**, 965-967.

[43] Liu, Q.X.; Zhao, X.J.; Wu, X.M.; Guo, J.H. New mercury(II) and silver(I) complexes containing NHC metallacrown ethers with the π–π stacking interaction *J. Organometal. Chem*., **2007**, *692*, 5671-5679.

[44] Starikova, O.V.; Dolgushin, G.V.; Larina, L.I.; Komarova, T.N. Synthesis of new stable carbenes from the corresponding 1,3-dialkylimidazolium and benzimidazolium salts *ARKIVOC*, **2003**, (xiii), 119-124.

[45] 2,6-bis[(4-bromomethyl)phenyl)]-4-pyrone **4** was prepared by benzylic bromination of 2,6-bis(4-methylphenyl)-4-pyrone in the presence of NBS (2 eq.) and catalytic amounts of benzoyl peroxide (BPO) in boiling CCl_4 for 48 h [46]. 2,6-Bis(4-methylphenyl)-4-pyrone was itself prepared through dehydrative cyclization of 1,5-bis(4-methylphenyl)-1,3,5-pentane-trione in the presence of conc. H_2SO_4 [38-41].

[46] Marei, M.G.; Mishrikey, M.M.; El-Kholy, I.E.S. Synthesis of a new series of 4-pyrones. *Indian J. Chem.*, **1987**, 26B, 163-5. *Chem. Abstr*., **108**, 5817e.

[47] *General procedure for preparation of compounds **2a-f** and **3a-f**.* To a stirred solution of 1-methylimidazole (0.18 gr, 2.2 mmol) in dry acetonitrile (5 ml) was added dropwise a solution of bromomethyl derivative **1a-f** (2 mmol) in dry acetonitrile (10 ml). The reaction mixture was stirred at room temperature for 24 h and then concentrated under reduced pressure. Ethyl acetate (20 ml) was added to the mixture and after stirring for 10 min, the precipitated solid was filtered. The solid product washed twice with EtOAc (10 ml) to remove remaining starting materials and then was kept at 45 °C under vacuum for 12 h. Imidazolium bromides **2a-f** were produced in 83-88% yields. For preparation of salts **3a-f**, a solution of $AgBF_4$ (2 mmol) in distilled water (7 ml) was added to a solution of imidazolium salts **2a-f** (1 mmol) in H_2O (7 ml)(as well as 2 ml acetonitrile in the case of **2d,e**). The mixture was stirred at rt for 1 h and then white precipitate was filtered. The filtrate was allowed to stand overnight at room temperature. The solution was passed through filter paper to removed small amounts of solid impurities. Water was removed under reduced pressure by rotary evaporator and acetonitrile (10 ml) was added to the residue. Insoluble black precipitate was filtered and the filtrate was dried over $MgSO_4$. Acetonitrile was removed under reduced pressure. Imidazolium tetrafluoroborates **3a-f** were obtained in 89-92% yields. *Data for* 1-[(5-Hydroxy-4-oxo-4*H*-pyran-2-yl)methyl]-3-Methyl-imidazolium tetrafluoroborate **3a**: Gray solid, yield 92%, mp 132-134°C; FT-IR(KBr), ν: 3223 (OH), 3135, 3085, 2987, 2943, 1648, 1616, 1445, 1270 cm^{-1}; ^1H NMR(400 MHz, D_2O), δ: 3.88 (s, 3H, N-CH_3), 5.48 (s, 2H, CH_2-N), 6.52 (s, 1H, H-3 pyrone), 7.78 (s, 1H, imidazolium-H), 7.84 (s, 1H, imidazolium-H), 9.34 (s, broad, 1H, OH), 8.09 (s, 1H, H-6 pyrone), 9.35 (s, 1H, H-2 imidazolium) ppm; ^{13}C NMR(100 MHz, D_2O), δ: 36.0, 48.8, 113.5, 122.7, 124.1, 137.5, 140.1, 146.1, 159.5, 173.6 ppm; Elemental analysis: calculated for $C_{10}H_{11}BF_4N_2O_3$, C 40.84, H 3.74, N 9.53; found, C 40.63, H 3.55, N 9.78. *Data for* 1-[(5-Benzyloxy-4-oxo-4*H*-pyran-2-yl)methyl]-3-Methyl-imidazolium tetrafluoroborate **3b**, Bright brown solid, yield 90%, mp 31-32°C; FT-IR(KBr), ν: 3098, 2930, 1648, 1623, 1434, 1220 cm^{-1}; ^1H NMR (400 MHz, D_2O), δ: 3.87 (s, 3H, N-CH_3), 4.92 (s, 2H, OCH_2Ph), 5.47 (s, 2H, CH_2-N), 6.52 (s, 1H, H-3 pyrone), 7.33-7.39 (m, 5H, Ph-H), 7.75 (s, 1H, imidazolium-H), 7.82 (s, 1H, imidazolium-H), 8.22 (s, 1H, H-6 pyrone), 9.31 (s, 1H, H-2 imidazolium), ppm; ^{13}C NMR(100 MHz, D_2O), δ: 36.0, 48.6, 70.6, 114.6, 122.7, 124.1, 128.1, 128.3, 128.5, 135.9, 137.6, 141.5, 146.9, 159.8, 172.8 ppm; Elemental analysis: calculated for $C_{17}H_{17}BF_4N_2O_3$, C 53.15, H 4.43, N 7.29; found, C 53.42, H 4.31, N 7.42.

[48] *General procedure for preparation of compounds **2g-l.*** To a stirred mixture of 2-halomethyl-4-pyrones **1a** or **1c** (2 mmol) and potassium iodide (2.2 mmol), in dry acetonitrile (10 mL), was added dropwise a solution of *N*-alkylbenzimidazoles (alkyl=Me, Et, n-Bu) (2.2 mmol) in dry acetonitrile (5 ml). The mixture was heated at 70°C for 10 h and then concentrated by rotary evaporator. Ethyl acetate (20 mL) was added to the residue and after stirring for 10 min, the precipitated product was filtered, washed with ethyl acetate (2×10 mL) and dried *in vacuo* to give the products **2g-l**. *Data for* 1-[(5-Hydroxy-4-oxo-4*H*-pyran-2-yl)methyl]-3-Methyl-benzimidazolium iodide **2g**, White solid, yield 88%, mp 200-202 °C; FT-IR (KBr), ν: 3423 (OH), 3142, 3086, 2987, 1644 (pyrone C=O), 1617, 1585, 1364 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6), δ: 4.11 (3H, s, N-CH_3), 5.83 (2H, s, CH_2-N), 6.68 (1H, s, H-3 pyrone), 7.69−7.73 (2H, m, H-5,6 benzimidazolium), 8.04-8.13 [3H, m, (2H, H-4,7 benzimidazolium), (1H, H-6 pyrone)], 9.43 (1H, s, OH), 9.91 (1H, s, H-2 benzimidazolium) ppm; ^{13}C NMR (100 MHz, DMSO-d_6), δ: 33.7, 46.9, 113.5, 113.6, 114.0, 126.9, 127.2, 130.9, 131.9, 140.3, 143.6, 146.2, 159.2, 173.8 ppm; Elemental analysis: calculated for $C_{14}H_{13}IN_2O_3$, C 43.76, H 3.39, N 7.29; found, C 44.08, H 3.27, N 7.33. *Data for* 1-Methyl-3-[(4-oxo-6-phenyl-4*H*-pyran-2-yl)methyl]-benzimidazolium iodide **2h**, White

solid, yield 67%, mp 199-201 °C; FT-IR (KBr), ν: 3390 (OH), 3038, 2898, 1654 (pyrone C=O), 1622, 1567, 1451, 1194 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6), δ: 4.12 (3H, s, N-CH_3), 5.93 (2H, s, CH_2-N), 6.62 (1H, d, *J*=1.6 Hz, pyrone-H), 6.91 (1H, d, *J*=1.9 Hz, pyrone-H), 7.46-7.56 (3H, m, phenyl-H), 7.71-7.77 (2H, m, H-5,6 benzimidazolium), 7.80 (2H, d, *J*=7.3 Hz, phenyl-H), 8.05 (1H, d, *J*=6.4 Hz, H-7 benzimidazolium), 8.23 (1H, d, *J*=7.8 Hz, H-4 benzimidazolium), 9.96 (1H, s, H-2 benzimidazolium) ppm; ^{13}C NMR(100 MHz, DMSO-d_6), δ: 33.8, 47.0, 110.9, 113.7, 114.0, 115.1, 126.2, 126.9, 127.1, 129.2, 130.4, 131.2, 131.9, 132.0, 143.7, 160.3, 163.3, 178.8 ppm; Elemental analysis: calculated for $C_{20}H_{17}IN_2O_2$, C 54.07, H 3.83, N 6.31; found, C 54.34, H 3.75, N 6.37.

[49] *Preparation of* 1,1′-Dimethyl-3,3′-{[4-(2,6-diyl-4-oxo-4*H*-pyran)diphenyl]dimethyl}-dibenzimidazolium diiodide **6a** was similar to **2a-f**. *Preparation of* 2,6-Bis [4-(1-benzimidazolylmethyl)phenyl]-4*H*-pyran-4-one **5**: To a stirred suspension of sodium hydride 80% (0.25 g, 8.5 mmol) in THF (15 ml) was added a solution of benzimidazole (1.0 g, 8.5 mmol) in THF (10 mL) under Ar. After stirring at room temperature for 0.5 h, a solution of 2,6-bis[4-(bromomethyl)phenyl]-4*H*-pyran-4-one **4** (1.82 g, 4.2 mmol) in THF (20 ml) was added dropwise to the mixture. The mixture was stirred at 60 °C under Ar for 24 h, and then concentrated by a rotary evaporator. Water (150 ml) was added to the residue and after stirring, the mixture was left at rt for 24 h. The precipitate was filtered, washed with acetone (10 ml) and dried *in vacuo* to give 1.9 g, 90% yield of **5** as white solid, mp 250-252 °C; FT-IR (KBr), ν: 3115, 2972, 2861, 1643 (pyrone C=O), 1600, 1422, 1383, 1259, 944 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6), δ: 5.65 (4H, s, CH_2-N), 6.96 (2H, s, pyrone-H), 7.24-7.26 (4H, m, H-5,6 benzimidazole), 7.45 (4H, d, *J*=8.0, aryl-H), 7.55-7.57 (2H, m, H-7 benzimidazole), 7.69-7.71 (2H, m, H-4 benzimidazole), 8.00 (4H, d, *J*=8.0, aryl-H), 8.65 (2H, s, H-2 benzimidazole) ppm; ^{13}C NMR (100 MHz, DMSO-d_6), δ: 47.3, 110.8, 110.9, 119.5, 121.9, 122.7, 126.5, 128.0, 130.3, 133.6, 140.4, 143.4, 144.3, 161.9, 178.9 ppm. Elemental analysis: calculated for $C_{33}H_{24}N_4O_2$, C 77.94, H 4.76, N 11.02; found, C 77.68, H 4.73, N 11.21. *General procedure for preparation of compounds* **6b-d,** A stirred mixture of compound **5** (1.0 g, 1.97 mmol), fresh distilled alkyl halide (12 mmol), potassium iodide (0.66 g, 4 mmol), in dry acetonitrile (10 ml), was heated at 70°C for 48 h. The mixture was then concentrated by rotary evaporator and ethyl acetate (20 ml) was added to the residue. After stirring for 10 min, the precipitated product was filtered, washed with ethyl acetate (3×20 ml) and dried *in vacuo* to give the products **6b-d**. *Data for* 1,1′-Dimethyl-3,3′-{[4-(2,6-diyl-4-oxo-4*H*-pyran)diphenyl]dimethyl}-dibenzimidazolium diiodide **6b,** Yellow solid, 74% yield; mp 198-200 °C. FT-IR (KBr), ν: 3046, 2996, 1644 (pyrone C=O), 1604, 1566, 1456, 1259, 947 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6), δ: 4.12 (6H, s, N-CH_3), 5.89 (4H, s, CH_2-N), 7.05 (2H, s, pyrone-H), 7.63-7.72 [8H, m, (4H, aryl-H), (4H, H-5,6 benzimidazolim)], 7.93 (2H, d, *J*=8.0 Hz, H-7 benzimidazolim), 8.05-8.09 [6H, m, (4H, aryl-H), (2H, H-4 benzimidazolim)], 9.88 (2H, s, H-2 benzimidazolium) ppm; ^{13}C NMR (400 MHz, DMSO-d_6), δ: 33.5, 49.3, 111.4, 113.6, 113.9, 126.7, 126.8, 128.9, 130.7, 131.2, 132.1, 137.4, 143.2, 162.0, 179.0 (pyrone C=O) ppm; F Elemental analysis: calculated for $C_{35}H_{30}I_2N_4O_2$, C 53.05, H 3.79, N 7.07; found, C 53.32, H 3.63, N 6.76.