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Application of Halide Molten Salts as Novel Reaction Media for *O*-Glycosidic Bond Formation

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In this study we have explored the application of halide molten salts as reaction media for *O*-glycosidic bond formation under basic conditions and mild heating. Eighteen different room-temperature ionic liquids and molten salts, representing four different classes of cations (i.e. imidazolium, pyridinium, pyrrolidinium and ammonium), were screened in the glycosidation reaction of *p*-nitrophenol with aceto-bromo-α-D-galactose. 1-Butyl-4-methylimidazolium chloride (BMIM·Cl) gave the best results and was applied in the reactions of other phenolic substrates to give the products with up to 80 % yields. All the reactions were highly selective to give the β-anomers, and the molten salt BMIM·Cl could easily be reused with no apparent loss in activity.

Introduction

The formation of *O*-glycosidic linkages often presents numerous challenges that include issues with stereoselectivity and limited substrate specificity, yet these reactions are critically important in developing biologically active molecules. Carbohydrate-based drugs are now, more than ever, exciting targets for drug design due to recent advances in understanding carbohydrate-binding proteins such as lectins and proteoglycans.[1] Examples of successful carbohydrate-based drugs with one or more glycosidic linkages include acarbose,[2,3] a glycosidase inhibitor; fondaparinux,[4,5] an effective anticoagulant; and doxorubicin,[6] a chemotherapeutic agent. Further development of biologically active carbohydrates predicates the need for broad, efficient, and selective methods to construct glycosidic bonds.

A variety of donors have been used to chemically construct glycosides and oligosaccharides. Thioglycosides[7] and trichloroacetimidates[8] (TCA) are excellent donors that are commonly employed,[9] and both may be activated for glycosidation in the presence of a Lewis acid at low temperatures. Glycosyl halides are also utilized to construct glycosidic bonds, and glycosyl bromides and chlorides may be activated under traditional Koenigs–Knorr conditions[10] in the presence of a base such as silver carbonate. Some of the drawbacks to all these donors may include the need for low reaction temperatures, use of inert conditions and molecular sieves, lengthy preparation of the donor, and careful handling and storage of moisture-sensitive donors.

Ionic liquids (ILs) or molten salts have emerged as a new class of compounds with unique properties that have been applied in organic chemistry. For example, they have been used in asymmetric and enzymatic catalysis,[11–14] in chiral resolution,[15,16] in extraction,[17] and in a wide variety of reactions as solvents.[18–24] Lately, there has been growing interest in their medicinal applications.[25,26] One attractive feature of ILs that distinguishes them from typical organic solvents is the potential to tailor their physiochemical properties.[12,27–29] Recently, the use of highly polar room-temperature ionic liquids (RTILs) in glycosidation reactions has been of great interest as many of these reactions proceed through a cationic oxocarbenium ion that may interact with the anionic counterpart of the IL.[30] There are excellent examples in the literature detailing the use of ILs in glycosidation reactions as either a promoter in a typical organic solvent, such as dichloromethane (DCM) or acetonitrile, or as the sole reaction medium. A wide variety of carbohydrate donors, such as TCAs, thioglycosides, and glycosyl fluorides have been condensed with acceptors in RTILs. As examples, Toshima et al. described highly efficient methods for both *O*- and *C*-aryl glycosidation of glycosyl fluorides using 1-hexyl-4-methylimidazolium triflate (HxMIm·OTf) with HOTf and 1-hexyl-4-methylimidazolium tetrafluoroborate (HxMIm·BF_4) with HBF_4, respectively.[30–32] Galan and co-workers[33] reported use of 1-butyl-3-methylimidazolium triflate (BMIm·OTf) as a promoter with both thioglycosides and TCAs.

Whereas numerous other examples exist, to the best of our knowledge, there has been no report of the use of glycosyl bromides in traditional Koenigs–Knorr-type reactions with an IL solvent. Although considered less stable than their fluoride counterpart, glycosyl bromides offer several

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advantages over other donors. For example, they do not require lengthy preparations and are commercially available. Quite often, the commercially available material is inexpensive, as is the case for acetobromo-α-D-glucose and -galactose. This may be particularly attractive to chemists focused on target-oriented synthesis or those less experienced in handling carbohydrates as they can circumvent donor preparation.

Results and Discussion

Towards the goal of developing a straightforward and efficient methodology for coupling bromide donors, we herein report the evaluation of Koenigs–Knorr-type couplings of glycosyl bromides in a series of molten salts. As a model reaction for glycosidic bond formation, we chose to study the well-reported coupling of acetobromo-α-D-galactose with *p*-nitrophenol.[34–37] Whereas there have been several studies detailing this transformation, obtaining the high reported yields often requires technical complications such as resin-based suspension of the phenol, ball-mill mechanical stirring, or overhead stirring.[38,39] In our initial study, we screened a series of RTILs containing three different types of cations with different combinations of anions at 25 °C by utilizing silver carbonate to promote the glycosidation (Scheme 1 and Table 1). We were pleased to find that the glycosidation product was formed in low to moderate yields, even under conditions that had not been optimized. In all cases, the isolated products were obtained as the β-anomer as a result of anchimeric assistance. Among the imidazolium-based RTILs, the hydrophobic ILs 1-butyl-3-methylimidazolium bis(triflic)imide (BMIm·Tf_2N) and 1-butyl-3-methylimidazolium hexafluorophosphate (BMIm·PF_6) outperformed the hydrophilic ILs 1-butyl-3-methylimidazolium triflate (BMIm·OTf) and 1-butyl-3-methylimidazolium tetrafluoroborate (BMIm·BF_4) (Table 1, compare Entries 1 and 2 with 3 and 4). Interestingly, this trend was not observed for pyridinium-based ILs, where the hydrophobic IL *N*-hexylpyridinium bis(triflic)-imide (HxPy·Tf_2N) and the hydrophilic IL *N*-butylpyridinium tetrafluoroborate (BPy·BF_4) both gave similar yields (Table 1, Entries 5 and 6). We also carried out the same reaction in the pyrrolidinium-based IL *N*-butyl-*N*′-methylpyrolidinium triflate (BMPr·OTf), and it is noteworthy that this is the first report of a pyrrolidinium-based IL being used in a glycosidation reaction.

In an attempt to optimize the reaction conditions, we decided to increase the reaction temperature to 80 °C for three leading RTILs: BMIm·PF_6, BPy·BF_4 and BMPr·OTf.

Table 1. Glycosidation of acetobromo-α-D-galactose and *p*-nitrophenol in RTILs.[a]

Entry	IL	Yield [%][b]
1	BMIm·Tf_2N	33
2	BMIm·PF_6	36
3	BMIm·OTf	16
4	BMIm·BF_4	21
5	HxPy·Tf_2N	35
6	BPy·BF_4	37
7	BMPr·OTf	35

[a] All reactions were performed neat in the RTILs (1.5 g) in the presence of Ag_2CO_3 (2 equiv.), acetobromo-α-D-galactose (1 equiv.), and *p*-nitrophenol (2 equiv.) at room temperature for 2 h. [b] Isolated yields after purification by column chromatography.

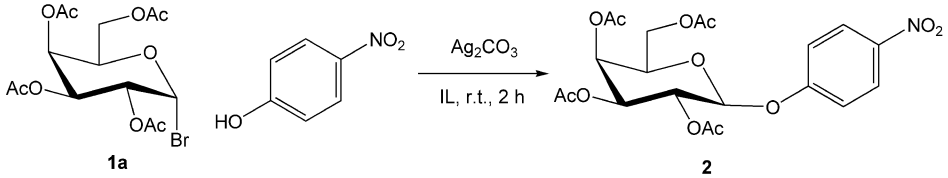
In general, at high temperature the reactions proceeded quickly, and the yields were also improved for BMIm·PF_6 and BPy·BF_4 (compare Table 2, Entries 1 and 5 with Table 1, Entries 2 and 4). In all cases, decomposition of the glycosyl bromide to the anomeric hydroxide (40% recovered for BMIm·PF_6) was observed during the course of reaction by thin layer chromatography (TLC).

Table 2. Glycosidation of acetobromo-α-D-galactose and *p*-nitrophenol in RTILS and molten halide salts at 80 °C.[a]

Entry	IL	Yield [%][b]
1	BmIm·PF_6	38
2	BMIm·Cl	70
3	BMIm·Br	69
4	BMIm·I	54
5	BPy·BF_4	44
6	EtPy·Cl	54
7	EtPy·Br	58
8	BMPr·OTf	30
9	BMPr·Cl	49
10	EtMPr·Br	66
11	NH_4Cl	24
12	TBACl	57
13	TBAB	54
14	TBAI	54

[a] All reactions were performed neat in the IL (1.5 g) in the presence of Ag_2CO_3 (2 equiv.), acetobromo-α-D-galactose (1 equiv.), and *p*-nitrophenol (2 equiv.) at room temp. for 15 min followed by 80 °C for 15 min. [b] Isolated yields after purification by column chromatography.

The success of these reactions at 80 °C prompted us to explore halide salts that exist as solids at 25 °C but as liquids at elevated temperatures. Surprisingly, there is only one report in the literature of a glycosidation reaction in a halide molten salt, and the study describes *O*-glycoside



Scheme 1. Glycosidation of acetobromo-α-D-galactose and *p*-nitrophenol in ILs.

formation by a Ferrier rearrangement.[40] We screened a panel of heterocyclic and ammonium salts as solvents for the Koenigs–Knorr-type coupling of acetobromo-α-D-galactose with *p*-nitrophenol. We were delighted to observe moderate to good conversion (54–70%) of the starting material to the corresponding *O*-aryl glycoside for three common imidazolium halides, i.e. 1-butyl-3-methylimidazolium chloride (BMIm·Cl), 1-butyl-3-methylimidazolium bromide (BMIm·Br) and 1-butyl-3-methylimidazolium iodide (BMIm·I) (Table 2, Entries 2, 3 and 4). Similar to these observations, the yields were higher in molten pyridinium and pyrrolidinium halides (Table 2, Entries 6, 7, 9 and 10) as compared to their RTIL counterparts (Table 2, Entries 5 and 8). The reaction could also be performed in ammonium chloride with 27% yield (Table 2, Entry 11), and the yields were significantly increased to 54–57% with tetrabutylammonium halides (Table 2, Entries 12–14). Whereas there are myriads of examples in the literature of ammonium halides as phase-transfer catalysts for glycosidation reactions,[36,37] to the best of our knowledge, this is the first report of the use of ammonium salts as reaction media in glycosidic bond formation. It is worth mentioning here that pyrrolidinium and ammonium halides have melting points higher than 80 °C; however, after addition of silver carbonate and phenol, the reaction mixture became semisolid at 25 °C and finally changed to a viscous liquid when stirred at 80 °C. It is also worth noting that preliminary screening of the reaction under microwave conditions did not improve the conversion. For example, when **1a** was treated with *p*-nitrophenol, silver carbonate, and BMIm·Cl in a CEM microwave reactor at 50 °C and 60 W for 1 min, only 40% of the glycosylated product was recovered. Increasing the temperature to 80 °C at 60 W resulted in 28% of product, and 80 °C at 200 W provided complete decomposition of the starting material. In all these cases, the starting material was completely consumed, and a complex mixture of polar baseline material, which was not recovered, was observed by TLC.

As BMIm·Cl performed the best of all the screened salts, it was selected for further optimization, and we evaluated the effect of the stoichiometry of the base and phenol on the reaction yield. For example, when we systematically increased the amount of phenol from 1 to 3 equiv., the product yield enhanced significantly from 52 to 80% (Table 3, Entries 1–4). A similar effect was observed when the stoichiometry of base was examined: the yields increased from 30% with 0.5 equiv. of base to 80% with 2 equiv. of base (Table 3, Entries 3 and 5–7). We also attempted to screen a variety of bases for this reaction (viz. NaH, LiOH, K_2CO_3, Cs_2CO_3 and Ag_2O). However, all of them resulted in decomposition of the starting glycosyl halide to the anomeric hydroxide except silver oxide (Ag_2O), which gave the same product yield as silver carbonate. It appears that, as in the case of the traditional Koenigs–Knorr reaction, the use of heavy metal ions[10] in molten halide salts drives the conversion of the glycosyl halide to the oxocarbenium ion, although the exact role of the molten halide salt still remains unclear.

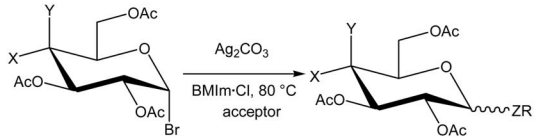
Table 3. Effect of base and phenol stoichiometry on the glycosidation in BMIm·Cl.[a]

Entry	Ag_2CO_3 [equiv.]	*p*-$O_2NC_6H_4OH$ [equiv.]	Yield [%][b]
1	2	1	52
2	2	2	69
3	2	3	80
4	2	4	77
5	0.5	3	30
6	1	3	62
7	3	3	78

[a] All reactions were performed neat in BMIm·Cl (1.5 g) in the presence of Ag_2CO_3, acetobromo-α-D-galactose (1 equiv.), and *p*-nitrophenol at room temp. for 15 min followed by 80 °C for 15 min. [b] Isolated yields after purification by column chromatography.

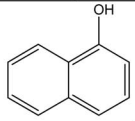
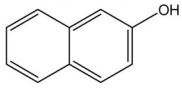
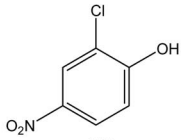
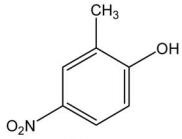
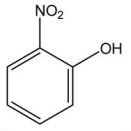
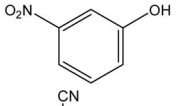
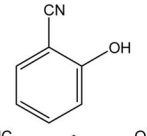
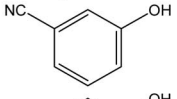
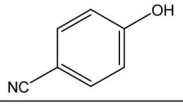
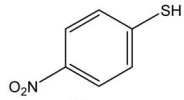
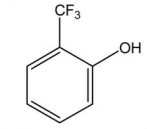
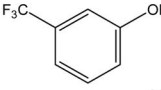
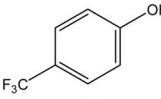
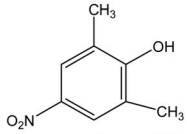
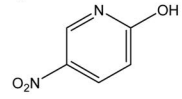
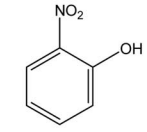
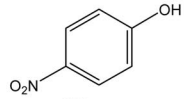
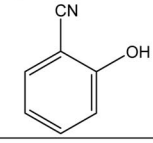
With a method in hand, we proceeded to survey a variety of acceptors to examine the scope and specificity of the reaction in molten BMIm·Cl. Both electron-rich and electron-deficient aromatic alcohols were treated with either acetobromo-α-D-galactose or -glucose in the presence of silver carbonate at 80 °C (Table 4). As expected and evident from the literature,[37,41] galactose **1a** proved to be a more reactive donor than the corresponding glucose **1b** (Table 4, Entries 5 & 7 and 16 & 18). Interestingly, in many cases (Table 4, Entries 3–8, 10, 11, 15–17), the α-glycoside was obtained in addition to the β-product, and the α/β ratios ranged from 0.08 to 0.37. A number of reports with similar donors and acceptors in the literature demonstrate kinetically controlled formation of only the β-glycoside product.[36,37,42] However, in our case, isolation of the thermodynamic α-product[43] may in part be explained by the high temperature employed for the reaction in molten halide salts. A trend in conversion can clearly be demonstrated by comparing the yields of phenols substituted with a strong electron-withdrawing group to the yields of those substituted with a moderate or weak one. Electron-deficient phenols that were substituted at the *o*- and *p*-positions gave higher yields than the corresponding *m*-analog. Since electron-deficient phenols are more easily converted into the corresponding silver salts, it is possible that BMIm·Cl plays a role in facilitating this conversion by stabilizing the salt. Interestingly, the combination of molten BMIm·Cl and silver carbonate results in the quick evolution of a gas, which indicates an interaction between the base and the molten salt. Recent reports detail the isolation of N-heterocyclic carbene (NHC) complexes upon treatment of imidazolium salts with silver oxide;[44–46] thus, we analyzed a sample of BMIm·Cl/Ag_2CO_3 by ^1H and ^{13}C NMR spectroscopy, which revealed a mixture of two species. As expected, one component was identified as BMIm·Cl by comparison with a pure compound, and the other we have characterized as a silver–NHC complex based on the C-2 chemical shift of $\delta = 179.47$ ppm, which is typical for imidazolylidene species. This component also has two doublet signals in the imidazolium region as opposed to three signals for BMIm·Cl in the ^1H NMR spectrum, which supports loss of the 2-H proton and formation of the silver–carbene (see Supporting In-

Table 4. Summary of glycosidation reactions in molten BMIm·Cl.[a]



1a: X = H, Y = OAc
1b: X = OAc, Y = H

Z = O or S
R = aryl

Entry	Donor	Acceptor	Product	Yield [%][b]	α/β ratio[c]
1	**1a**		**3**	40	β only
2	**1a**		**4**	13	β only
3	**1a**		**5**	65	15:85
4	**1a**		**6**	65	13:87
5	**1a**		**7**	81	9:91
6	**1a**		**8**	58	5/95
7	**1a**		**9**	78	8:92
8	**1a**		**10**	54	10:90
9	**1a**		**11**	62	β only
10	**1a**		**12**	27	27:73
11	**1a**		**13**	61	10:90
12	**1a**		**14**	38	β only
13	**1a**		**15**	44	β only
14	**1a**		**16**	66	β only
15	**1a**		**17**	21	24:76
16	**1b**		**18**	66[d]	19:81
17	**1b**		**19**	70[d]	20:80
18	**1b**		**20**	52	β only

[a] All reactions were performed neat in BMIm·Cl (1.5 g) in the presence of Ag_2CO_3 (2 equiv.), acetobromo-α-D-galactose **1a** or -galactose **1b** (1 equiv.), and acceptor (3 equiv.) at room temp. for 15 min followed by 80 °C for 15 min. [b] Isolated yields after purification by column chromatography. [c] Determined by NMR spectroscopy (^{1}H and HSQC data). [d] Reaction performed with Ag_2O.

formation). In-depth studies of these species are ongoing and will be reported in due course.

In addition to substrate screening, we also examined the potential to recycle the molten halide salt in our model reaction of **1a** with *p*-nitrophenol. After completion of the reaction, ethyl acetate and water were added to the mixture. The products were extracted into ethyl acetate, and BMIm·Cl was recovered by concentrating the aqueous layer. The recovered molten salt was reused twice for the same reaction without apparent loss in the product yield (Table 5). The detailed protocol for this process is given in the Supporting Information.

Table 5. Recycling of BMIm·Cl from glycosidation of **1a** to **2**.

No. of cycle	Isolated yield [%]
0	80
1	75
2	76

Conclusions

We have shown that molten halide salts are suitable reaction media for the glycosidation of acetobromo-α-D-galactose and -glucose under basic conditions. The reaction

is straightforward and employs inexpensive, commercially available donors, and very little decomposition of the glycosyl bromide was observed even in the absence of molecular sieves and/or inert conditions. The commercial availability of the glycosyl bromide makes it an attractive substrate in certain settings where timelines can preclude lengthy syntheses of glycosyl donors. In addition, the ability to recycle the molten salt and to perform the reaction at elevated temperatures results in a flexible, cost-efficient glycosidation method.

Supporting Information (see footnote on the first page of this article): Additional data (^{1}H NMR, ^{13}C NMR, GCOSY, GHSQC, and HRMS) relating to compounds **2**–**20** and protocols for the glycosidation reaction in molten halide salts and RTILs; Figure S1 contains NMR spectroscopic data of BMIm·Cl and the mixture of BMIm·Cl and silver–NHC complex.

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