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Bromodimethylsulfonium bromide (BDMS) in ionic liquid: a mild and efficient catalyst for Beckmann rearrangement

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ABSTRACT

Bromodimethylsulfonium bromide (BDMS)-catalyzed Beckmann rearrangement of a variety of ketoximes has been carried out in the imidazolium-based ionic liquid [bmim]PF_6 under mild conditions without using any additional cocatalyst or solvent to afford excellent conversion and selectivity. The ionic liquid is recovered and reused for up to three runs without any loss of efficiency.

In general, amides are potential precursors for the synthesis of various natural products as well as synthetic intermediates for medicinal compounds and materials.[1] The Beckmann rearrangement (BKR)[2] is an important reaction for transformation of ketoximes into amides, which has been successfully utilized to produce ε-caprolactam and laurolactam in industry. This reaction generally requires high reaction temperature and a large amount of a strong Brønsted acid and dehydrating media.[3] Thus, the reaction leads to large amounts of by-product precluding its application to sensitive substrates. To avoid these requisite harsh conditions, several methodologies under vapour phase,[4] solvent-free,[5] supercritical water,[6] or liquid phase[7–9] conditions have been developed. Of the liquid phase processes, cyanuric chloride (CNC),[8f] 1,3,5-triazo-2,4,6-triphosphorine-2,2,4,4,6,6-chloride (TAPC),[9a] sulfamic acid,[8g] chlorosulfonic acid,[9b] bis(2-oxo-3-oxazolidinyl) phosphinic chloride (BOP-Cl),[9c] diethyl chlorophosphate,[9d] $HgCl_2/CH_3CN$,[9e] bis(trichloromethyl) carbonate/DMF,[9f] *p*-toluenesulfonyl chloride (TsCl),[9g] trifluoroacetic acid,[9h] *p*-toluenesulfonic acid (TsOH),[9i] and mesitylenesulfonyl chloride[9j] catalyzed BKR are elegant and recent approaches. However, some of these variants suffer from drawbacks such as toxicity, the use of toxic solvents, expensive reagents, production of considerable amounts of by-products, long reaction times and low yields. Therefore, the development of a simple, mild, inexpensive catalyst for highly efficient and selective catalytic BKR process is still in demand.

Among the various possibilities for realizing these reactions under milder conditions, the use of room-temperature ionic liquids (ILs) instead of the more common polar media has been reported.[10] Ionic liquids have negligible vapour pressure and excellent thermal stability that combined with easy preparation, recycling, and good solvating ability of a wide range of substrates and catalysts, make them viable ecosustainable solvents for a number of stoichiometric and catalytic processes.[11] This class of novel solvents is attracting increasing popularity as a potential green alternative to conventional volatile organic media (DMF, CH_3CN, etc.) in view of the projected advantages such as environmental compatibility, reusability, greater selectivity, operational simplicity, non-corrosive nature, and ease of isolation.[11]

Bromodimethylsulfonium bromide (BDMS),[12] a commercially available light orange solid compound, has attracted considerable interest in the field of organic chemistry after the discovery by Meerwein,[12c] due to its easy handling, low cost, as well as its easy access and varied applications both as a catalyst[13] and as an effective reagent.[14]

However, its synthetic utility as a catalyst for the BKR has not been explored until now. Very recently, we have demonstrated the virtue of this reagent for the conversion of aldoximes and primary carboxamides to the corresponding nitriles.[15a] In continuation of the research directed towards the development of new and efficient synthetic methodologies,[15] we sought to explore the advantages of this reagent further for other important transformations. In this report, we present our results on the first highly effective BDMS-catalyzed BKR of ketoximes to the corresponding amides in which the molar ratio of BDMS and oxime was 0.20:1.

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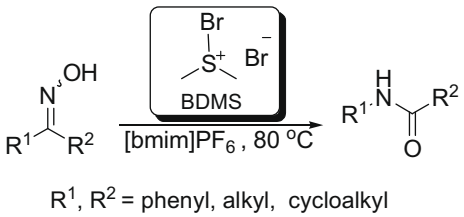
Thus, it is a green process for preparation of amides from ketoximes precluding the use of any additional Lewis or Bronsted acids as a cocatalyst, toxic organic solvents and without producing any significant corrosive waste (Scheme 1).

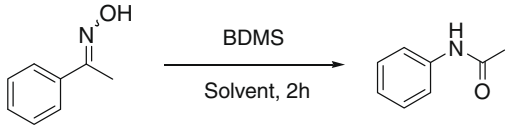
To optimize the reaction conditions and find the right solvent using acetophenone oxime as a model substrate, few experiments were carried out with different solvents at varied reaction temperature and mol % of catalyst as illustrated in Table 1. BDMS was found to be an effective reagent for BKR in polar nucleophilic organic solvents (CH_3CN and CH_3NO_2) as indicated in Table 1 (entries 5 and 6). However, in order to make BKR catalytic we chose to perform the same reaction in ionic liquid and to our delight, it was found that the treatment of acetophenone oxime with catalytic amount of BDMS (20 mol %) in [bmim]PF_6 at 80 °C afforded acetanilide in a selectivity of 99% with almost complete conversion (Table 1, entry 9), whereas the same reaction in other ionic liquids such as [bmim]Br, [bmim]Cl, and [bmim]BF_4 accomplished the rearrangement far less effectively with 0–30% conversion (Table 1, entries 7, 8 and 10). The above reaction condition was appropriate for the transformation because lowering the reaction temperature from 80 to 50 °C and decreasing the amount of catalyst from 20 to 10 mol % lowered the substrate conversion rate (Table 1, entries 9, 11 and 12). No conversion was observed in the absence of BDMS (Table 1, entry 13).

To explore the generality and scope of the BKR catalyzed by BDMS, various ketoximes as substrates were examined at 80 °C



Scheme 1. Beckmann rearrangement.

Table 1
BDMS-catalyzed Beckmann rearrangement of acetophenone oxime in different solvents[a]



Entry	Solvent	Reaction temp (°C)	Conversion[b] (%)	Selectivity[c] (%)
1	THF	Reflux	20	0
2	CH_3NO_2	80	30	86
3	DCE	Reflux	25	0
4	CH_3CN	Reflux	39	98
5	CH_3CN[d]	Reflux	100	98
6	CH_3NO_2[d]	80	96	86
7	[bmim]Br	80	30	54
8	[bmim]Cl	80	20	0
9	[bmim]PF_6	80	100	99
10	[bmim]BF_4	80	—	—
11	[bmim]PF_6	50	40	96
12	[bmim]PF_6[e]	80	61	98
13	[bmim]PF_6[f]	80	—	—

[a] Reaction condition: 135.0 mg (1 mmol) acetophenone oxime, 44.4 mg (0.2 mmol) BDMS, solvent (2 mL).
[b] Conversion (%) of acetophenone oxime as determined by GC analysis.
[c] Selectivity for acetanilide.
[d] 222 mg (1 mmol) BDMS was used.
[e] 22.2 mg (0.1 mmol) BDMS was used.
[f] In the absence of BDMS.

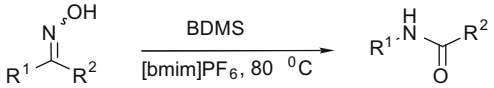
in [bmim]PF_6 for 1–6 h (Table 2). Moderate to good results were obtained over BKR of acetone, 2,4-dimethylpentanone, cyclopentanone, and cyclohexanone oximes (entries 1–4). The conversion of all these oximes was nearly 100%, however, the selectivities were only 80%, 76%, 72%, and 69%, respectively. Based on the qualitative analysis by GC–MS, it could be known that their main by-products were the corresponding ketones and only trace amounts of dimeric oximes were observed (0.2%). Much better results could be obtained if aryl ketoximes were used as substrates in BKR.

The conversions of aromatic ketoximes, for example, 2-, 3-, 4-methoxyacetophenone oximes, 2-, 4-haloacetophenone oximes, 4-nitroacetonephenone oxime and symmetrical and unsymmetrical benzophenone oximes were 94–100% with selectivities >94% (entries 5–15). Usual migratory aptitude of BKR is followed with the listed substrates. For example, in all cases of substituted acetophenone oximes (entries 5 and 7–12), only migration of the aryl group is observed without any product from migration of the methyl group. In the reactions of the unsymmetrical benzophenone oxime (4-fluorophenyl)-phenylmethanone oxime gave a mixture of isomeric amides *N*-(4-fluorophenyl)benzamide and 4-fluoro-*N*-phenylbenzamide in the ratio of 0.8:1.0 (entry 14). Similarly, (4-methoxyphenyl)-phenylmethanone oxime produced *N*-(4-methoxyphenyl)benzamide and 4-methoxy-*N*-phenylbenzamide as an isomeric mixture in the ratio of 1.0:0.7 (entry 15). However, if the migratory aptitudes of the two substituents are close, mixture of products was obtained. Pivalophenone oxime (entry 6) as anticipated produces both *N*-*tert*-butylbenzamide and pivalanilide, but the migration of phenyl group is still favored over that of the *tert*-butyl group by a factor of 4. These results imply that electron-rich aryl groups have better migrating aptitude than the alkyl groups toward the oximino nitrogen terminus and thus, cationic species of the oximino nitrogen terminus is involved (vide infra). In conformity with the earlier observations on the BKR, we also found that electron-donating groups on the aromatic ring (entries 7–9, 15) facilitate the reaction, and electron-withdrawing groups (entries 10–12, 14) retard it. It has been recognized that BKR is stereospecific and generally the group *anti* to the hydroxyl group on the ketoxime selectively migrates. This behaviour has also been used to assign *syn* or *anti* configuration of oximes. The starting oximes used in the present study were mixtures of *syn* and *anti* isomers (where applicable), but in most cases a majority of a single amide isomer was obtained as the product, which is favoured based on the migratory aptitude. This indicates that BDMS is also capable of catalyzing the *syn*–*anti* isomerization of oximes under the conditions of BKR. The equilibrium among involved isomers is faster than the rearrangement so that the product composition is determined by the relative rates of migration of the involved groups and is independent of the stereochemistry of the starting oximes.

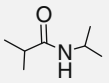
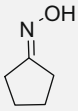
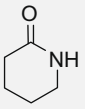
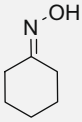
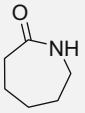
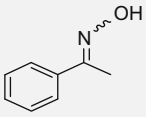
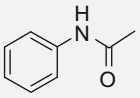
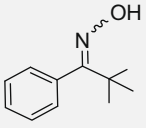
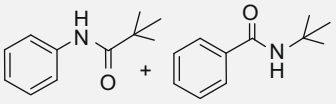
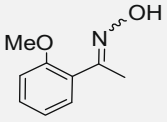
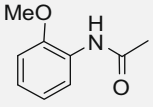
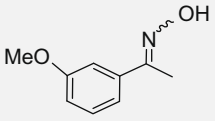
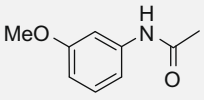
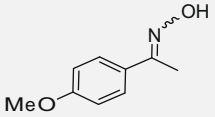
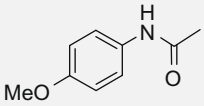
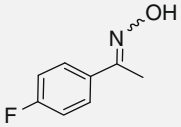
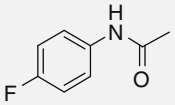
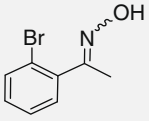
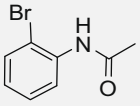
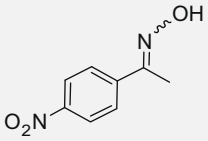
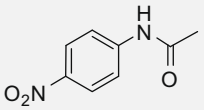
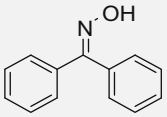
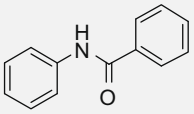
After isolation of products (amides/lactams), the ionic liquid [bmim]PF_6 was easily recovered, and reused[16] without any significant loss of activity. For example, the acetophenone oxime rearranged to the corresponding amide in similar yields and purity of the first run over three cycles (91%, 88%, 90%, respectively). Based on the fact that BDMS can be in situ generated from DMSO and HBr,[17] a plausible catalytic cycle for BDMS-mediated Beckmann rearrangement is outlined in Scheme 2.

In conclusion, we have disclosed a mild and green procedure for obtaining amides/lactams from the corresponding ketoximes via Beckmann rearrangement employing BDMS in the ionic liquid [bmim]PF_6 under catalytic conditions in the absence of any additional cocatalyst or solvent. The operational simplicity, general applicability, use of inexpensive and commercially available catalyst, relatively fast reaction rate, high yields and recyclability of the ionic liquid makes this protocol an attractive and valid alternative to existing methodologies. The present work has opened up a new aspect of the synthetic utility of BDMS.

Table 2
Beckmann rearrangement of ketoximes/lactams to amides in [bmim]PF_6 using 20 mol % BDMS as the catalyst[a]

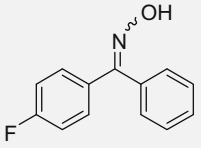
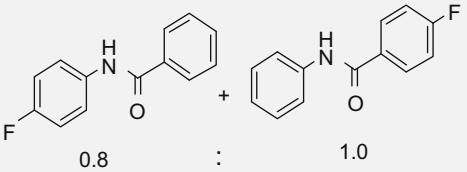
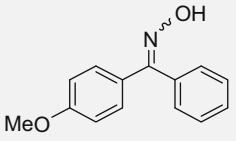
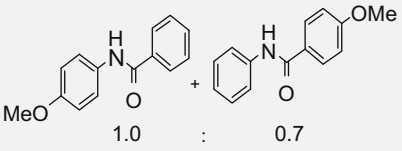


R^1, R^2 = Phenyl, alkyl and cycloalkyl

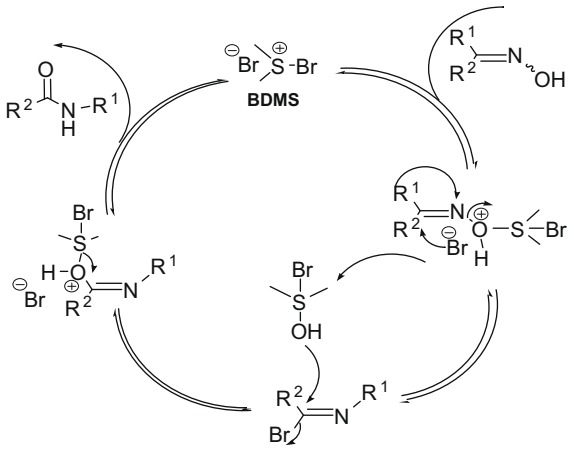
Entry	Ketoxime	Amide/lactam	Time (h)	Conversion[b] (%)	Selectivity[c] (%)	Yield[d,e] (%)
1			2	99	80	71
2			2.5	99	76	68
3			3	99	72	64
4			3	99	69	60
5			2	100	99	94
6		 5.3 : 1	2	98	97	81[f]
7			1	100	99	91
8			1.2	100	99	88
9			1	100	99	90
10			3	98	98	86
11			2.7	98	96	84
12			6	97	94	81
13			2	100	98	95

(*continued on next page*)

Table 2 (*continued*)

Entry	Ketoxime	Amide/lactam	Time (h)	Conversion[b] (%)	Selectivity[c] (%)	Yield[d,e] (%)
14		 0.8 : 1.0	3	99	97	84[f]
15		 1.0 : 0.7	1.5	100	97	87[f]

[a] See Ref. 16 for general procedure.
[b] Conversion (%) of ketoxime as determined by GC analysis.
[c] Selectivity for amides/lactams.
[d] All the products are known compounds[8c,9e] and were characterized by comparison of their mp, TLC, IR and ^{1}H NMR data with those of authentic samples.
[e] Yields of the isolated pure compounds.
[f] Overall yield of isomeric mixture.



Scheme 2. A plausible catalytic cycle for BDMS-catalyzed Beckmann rearrangement.

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16. *General procedure for bromodimethylsulfonium bromide (BDMS)-catalyzed Beckmann rearrangement*: A stirred solution of ketoxime (1 mmol) and BDMS (0.2 mmol) in 2 mL of [bmim]PF_6 was heated at 80 °C for 1.5–6 h (Table 2). The reaction progress was monitored by TLC. Upon completion, the reaction mixture was cooled to rt and extracted with ether (4 × 10 mL). The combined organic phase was dried over $MgSO_4$, filtered and evaporated under reduced pressure. The resulting crude product was purified by silica gel column chromatography (EtOAc/hexane 3:7) to give the corresponding amide. The structure of the products was confirmed by comparison of their mp, TLC, IR or ^{1}H NMR data with authentic samples obtained commercially or prepared by literature method. The residue of the ionic liquid was dissolved in CH_2Cl_2, filtered on Celite. The filtrate was washed with water followed by saturated aqueous K_2CO_3 solution in order to remove residual acid and other impurities and dried under vacuum to afford the ionic liquid [bmim]PF_6, which was used in subsequent runs.
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