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Lewis acid-catalyzed Beckmann rearrangement of ketoximes in ionic liquids

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ABSTRACT

The Beckmann rearrangement of five ketoximes was done in 17 different ionic liquids by using four Lewis acids. The effect of the type of cation and the type of anion in the ionic liquid on the rate of the rearrangement reaction and product composition is compared and discussed. The effects of the hydrophobicity and the hydrogen bonding ability of ionic liquids on the rearrangement of ketoximes were investigated, as well as the catalytical activity of the Lewis acids.

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1. Introduction

Ionic liquids (ILs) have become very popular solvents in organic synthesis over the past decades [1,2]. They are suitable for many types of general and specific solute–solvent interactions, including ionic, π–π, hydrogen bonding, etc. [3]. ILs have been used in organic synthesis [4], biocatalysis [5], separations [6], polymer chemistry [7], nanomaterials [8], a.o. Less attention has been paid to their exploitation in the rearrangement reactions, albeit ILs have been used successfully in the Fries [9], the Michaelis-Arbuzov [10], the Ferrier [11], and the Claizen [12] rearrangement reactions a.o. Very promising results have been obtained for the Beckmann rearrangement reaction in ILs [13–21] but, to the best of our knowledge, there has been no report of the Beckmann rearrangement in ILs in the presence of Lewis acids. The formation of complex anions between the halide anions of ILs and Lewis acids is well documented [2], and modified ILs are regarded as solvents and catalysts for organic transformations. In this study, we investigated the Beckmann rearrangement of ketoximes in detail in order to understand the relationship between the structure of ILs, the type of Lewis acids, and the rate and the product distribution of the rearrangement.

2. Experimental

2.1. Materials and instruments

Gas chromatographic (GC) analysis was done on a Hewlett Packard 5890 instrument using a flame ionization detector with the following flow rates: hydrogen, 30 mL/min; air, 300 mL/min; and helium, 1.8 mL/min. A DB–5MS (30 m × 0.25 mm) column was used, the injection temperature was 250 °C, and the temperature regime of analysis was as follows: starting temperature 50 °C for 1 min, then 10 °C/min up to 250 °C, and a final temperature of 250 °C for 10 min. GC/MS analyses were performed with a Shimadzu GC 2010 gas chromatograph connected to a Shimadzu QP 2010 mass spectrometer, EI ionization with 70 eV energy, distribution in a splitless injector 1:30, and using automatic injector OAC 20i. The sample volume for all analyses was 1 μL. The ^{1}H NMR spectra were registered on a Varian Mercury BB 200 MHz instrument in $DCCl_3$ or DMSO-d_6 solutions. ILs 1-ethyl-3-methylimidazolium bromide ([emim][Br]), 1-butyl-3-methylimidazolium bromide ([bmim][Br]), 1-hexyl-3-methylimidazolium bromide ([hmim][Br]), 1-octyl-3-methylimidazolium bromide ([omim][Br]), 1-butyl-3-methylimidazolium chloride ([bmim][Cl]), 1-butyl-3-methylimidazolium iodide ([bmim][I]), 1-butylpyridinium bromide ([C_4Py][Br]), 1-heptylpyridinium bromide ([C_7Py][Br]), and tributyldodecylammonium bromide [$C_{4,4,4,12}$][Br] were prepared as described [22,23]. ILs with tetrafluoroborate and hexafluorophosphate anions were prepared from the corresponding bromides or chlorides by anion-exchange reactions with NH_4BF_4 and NH_4PF_6, respectively [22]. The IL tetrabutylammonium bromide ([$C_{4,4,4,4}$][Br]) was obtained from Aldrich.

2.2. Syntheses. General procedure. The Beckmann rearrangement of 4-chloroacetophenone oxime in an ionic liquid

[bmim][Br] (1150 mg; 5.25 mmol) and $SnCl_4$ (1991 mg; 10.50 mmol) were mixed together under argon and stirred at 120 °C for 30 min. 4-Chloroacetophenone oxime (746 mg; 4.38 mmol) was added to the stirred mixture. Samples (~1 mg)

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were taken from the mixture at 5 min, 15 min, 30 min, 1 h, 2 h, 3 h, and 4 h, treated with water, and extracted with diethyl ether (2 × 3 mL). The sample of the combined extracts was analyzed by GC. The chromatographic peaks were: (a) compared with peaks and retention times of individual substances; (b) characterized by MS. The results are given in Tables 1–3. Rearrangement reactions with other oximes, ionic liquids and Lewis acids were performed in a similar way and are given in Tables 1–3 and in Figs. 1–4.

3. Results and discussion

The Beckmann rearrangement needs the presence of an acid catalyst [24–30]; Lewis acids are highly soluble in ILs and therefore might be useful catalysts. The solution is accompanied by complex anion formations with halide anions of ILs, the molar ratio of partners being an important characteristic of the ILs obtained. In this study, the Lewis acids $AlCl_3$, $TiCl_4$, $SnCl_4$, and BF_3 were tested for suitability in the Beckmann rearrangement in the imidazolium, pyridinium and tetraalkylammonium-based ILs. Selected ILs contain cations and anions that might interact with the transition state of the rearrangement reaction. Imidazolium and pyridinium cations are expected to have a π–π interaction with the transition state of the rearrangement reaction, in contrast to the tetraalkylammonium, cation, which is not capable of it. The cations mentioned above might form hydrogen bonds with the transition state if they have sufficiently acidic C–H bonds, such as the C_2–H bond in the imidazolium cation. The cations might have different hydrophobicity if they contain sufficiently long alkyl groups attached to a nitrogen atom. The anions of the selected ILs are halides, and tetrafluoroborate and hexafluorophosphate were used to investigate the impact of the nucleophilicity of the anions in ILs. The ketoximes, acetophenone oxime, 4-methoxy acetophenone oxime, 4-chloroacetophenone oxime, 1-acetonaphthone oxime, and 2-acetonaphthone oxime, were investigated to make sure that the observed effects are general.

3.1. The impact of the type of cation in ionic liquids

The cation in ILs has an effect mainly on the rate of the Beckmann rearrangement. In this study, the effect was examined with 1-butyl-3-methylimidazolium ([bmim]), 1-heptylpyridinium ([C_7Py]), and tetrabutylammonium ([$N_{4,4,4,4}$]) bromides.

It is almost impossible to evaluate each of the above-mentioned interactions separately, and probably the best way to assess the solvent effect is the use of empirical solvatochromic measurements

Table 1
The Beckmann rearrangement of acetophenone oximes in ionic liquids with different cations.

Entry	Oxime	Ionic liquid	Lewis acid	T, °C/t (min)	Conversion (%)	Products (%)	
						2	**3**
1	**1a**	[bmim][Br]	$AlCl_3$	80/30	100	100	
2	**1a**		$TiCl_4$	80/30	100	98	2
3	**1a**		$SnCl_4$	120/180	68	88	12
4	**1a**		BF_3	120/180	78	88	12
5	**1a**	[bmmim][Br]	$AlCl_3$	80/30	100	100	
6	**1a**		$TiCl_4$	80/30	100	100	
7	**1a**		$SnCl_4$	120/180	79	100	
8	**1a**		BF_3	120/180	100	100	
9	**1a**	[C_7Py][Br]	$AlCl_3$	80/30	100	100	
10	**1a**		$TiCl_4$	80/30	100	100	
11	**1a**		$SnCl_4$	120/180	75	88	12
12	**1a**		BF_3	120/180	100	81	19
13	**1a**	[$N_{4,4,4,4}$][Br]	$AlCl_3$	80/30	99	100	
14	**1a**		$TiCl_4$	80/30	100	100	
15	**1a**		$SnCl_4$	120/180	96	95	15
16	**1a**		BF_3	120/180	99	91	9
17	**1b**	[bmim][Br]	$AlCl_3$	80/30	100	100	
18	**1b**		$TiCl_4$	80/30	100	100	
19	**1b**		$SnCl_4$	120/180	100	100	
20	**1b**		BF_3	120/180	100	97	3
21	**1b**	[C_7Py][Br]	$AlCl_3$	80/30	100	100	
22	**1b**		$TiCl_4$	80/30	100	100	
23	**1b**		$SnCl_4$	120/180	100	100	
24	**1b**		BF_3	120/180	100	98	2
25	**1b**	[$N_{4,4,4,4}$][Br]	$AlCl_3$	80/30	100	100	
26	**1b**		$TiCl_4$	80/30	100	98	2
27	**1b**		$SnCl_4$	120/180	100	100	
28	**1b**		BF_3	120/180	100	99	1
29	**1c**	[bmim][Br]	$AlCl_3$	80/30	100	100	
30	**1c**		$TiCl_4$	80/30	34	79	21
31	**1c**		$SnCl_4$	120/180	96	98	2
32	**1c**		BF_3	120/180	32	84	16
33	**1b**	[bmmim][Br]	$AlCl_3$	80/30	98	100	
34	**1c**		$TiCl_4$	80/30	100	93	7
35	**1c**		$SnCl_4$	120/180	100	100	
36	**1c**		BF_3	120/180	33	82	18
37	**1c**	[C_7Py][Br]	$AlCl_3$	80/30	80	91	9
38	**1b**		$TiCl_4$	80/30	100	97	3
39	**1c**		$SnCl_4$	120/180	96	96	4
40	**1c**		BF_3	120/180	38	82	18
41	**1b**	[$N_{4,4,4,4}$][Br]	$AlCl_3$	80/30	49	90	10
42	**1c**		$TiCl_4$	80/30	31	84	16
43	**1b**		$SnCl_4$	120/180	95	97	3
44	**1c**		BF_3	120/180	29	88	12

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