Chemistry of Heterocyclic Compounds, Vol. 46, No. 2, 2010

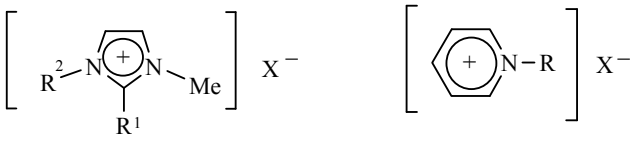
IMIDAZOLIUM AND PYRIDINIUM SALTS – SOLVENTS INFLUENCING THE RATE AND DIRECTION OF THE FRIES, BECKMANN, AND CLAISEN REARRANGEMENTS

S. Katkevica[1], A. Zicmanis[1]*, and P. Mekss[1]

The Fries, Beckmann, and Claisen rearrangements have been investigated in ionic liquid media. The effect of the structural elements of the latter on the direction of these rearrangements and the product yields has been studied.

Keywords: ionic liquids, imidazolium salts, pyridinium salts, Beckmann, Claisen, and Fries rearrangements.

Imidazolium and pyridinium salts are currently the most widely studied and used ionic liquids (IL) in organic synthesis and they are often simultaneously used as solvent and catalyst in very varied reactions [1-7]. With careful choice of substituents in the heterocyclic cations and the type of anions in the IL it is possible to change the rate, direction, and even mechanism of many organic reactions. The effect of heterocyclic salt IL on molecular rearrangements is rarely represented in the chemical literature and that has prompted us to a systematic investigation in this direction.



1a–j **2a–d**

1a–e R^1 = H, R^2 = Bu [bmim]; **a** X = Br, **b** X = Cl, **c** X = I, **d** X = BF_4, **e** X = PF_6;
f–h R^1 = H, X = Br, **f** R^2 = Et [emim], **g** R^2 = C_6H_{13} [hmim], **h** R^2 = C_8H_{15} [omim];
i R^1 = Me, R^2 = Bu, X = Br [bmmim]; **j** R^1 = H, R^2 = Et, X = OMs; **2a–c** R = C_7H_{15} [C_7Py];
a X = Br, **b** X = BF_4, **c** X = PF_6, **d** R = Me [mPy], X = OTs

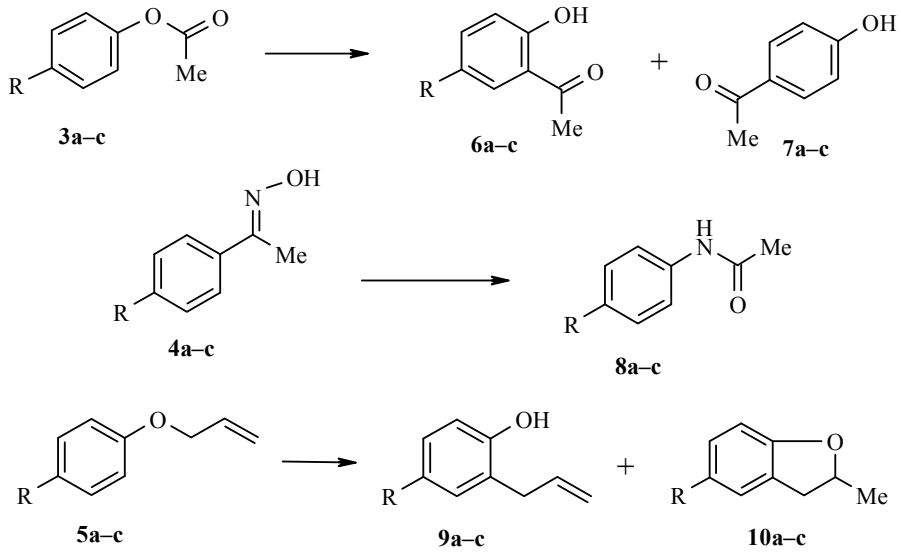
* To whom correspondence should be addressed, e-mail: zicmanis@latnet.lv.

[1] Faculty of Chemistry, University of Latvia, Riga LV-1586, Latvia.

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 195-208, February, 2010, Original article submitted May 30, 2008; revision submitted August 4, 2009.

In this work we have studied the electrophilic Fries rearrangement, the nucleophilic Beckmann rearrangement and the pericyclic Claisen rearrangement in IL media – the imidazolium **1** and pyridinium **2** salts. Esters **3a-c**, ketoximes **4a-c**, and the allyl aryl ethers **5a-c** respectively were used as substrates (see Scheme 1).

Scheme 1



3-10 a R = H, **b** R = OMe; **3**,**4**,**6-8 c** R = Cl; **5**,**9**,**10 c** R = NO_2

The Fries and Beckmann rearrangements were carried out in the presence of $AlCl_3$, $TiCl_4$, $SnCl_4$, and BF_3 (in the IL the molar fraction *X* of the Lewis acid was 0.67). It should be noted that only the use of $AlCl_3$ in IL has been reported in the literature [2, 8]. The Claisen rearrangement was studied without the use of a catalyst, the substrate being held in the IL medium at a temperature of 200ºC. In this study the dependence of the reaction rate and formation of products on the structural elements of the IL and the nature of the Lewis acid were examined.

The effect of the nature of the heterocyclic cation of the IL on the Fries, Beckmann, and Claisen rearrangements was examined through comparison of reactions in 1-butyl-3-methylimidazolium (**1a**) and 1-heptylpyridinium (**2a**) bromides.

The IL cations can react with polar reaction partners, electron pair donors and hydrogen bond acceptors while IL anions typically interact with electron pair acceptors and with hydrogen bond donors [9, 10].

The most important of the indicated reactions is likely the formation of hydrogen bonds between the IL cations and the reaction substrates, mainly between the hydrogen atom of the H-2 bond of the imidazolium ion and the hydrogen acceptor bonds of the reaction substrates. It is also important to take into account the additional interaction of the heterocyclic cation with the conjugated systems and the polarized parts of the reaction substrates (π-π interaction). It should be different in the IL with imidazolium **1** and pyridinium **2** series cations. In turn, the reaction of the bromide anion with the rearranging substrates is likely virtually the same in all IL used. For a quantitative discussion of the complex interactions an empirical scale of overall solvent polarity (the Reichardt constant E_T^N) [9, 11] has more often been used and is employed in our work.

The results of comparative experiments in which the effect has been studied of the structure of the IL cation **1a** and **2a** on the course of the Fries (substrates esters **3a-c**) and Beckmann rearrangement (substrates ketoximes **4a-c**), catalyzed by Lewis acids, and the results are presented in Table 1.

TABLE 1. Product Conversion and Content in the Reaction Mixture upon Fries and Beckmann Rearrangement in Ionic Liquids

Ionic liquid	Lewis acid	Fries rearrangement				Beckmann rearrangement		
		Experiment No.	Conversion, %*	**6**, %*	**7**, %*	Experiment No.	Conversion, %*[2]	**8**, %*[2]
		Substrate **3a**				Substrate **4a**		
[bmim][Br]	$AlCl_3$	1	100	53	35	25	100	100
(**1a**)	$TiCl_4$	2	100	28	0	26	100	98
	$SnCl_4$	3	98	8	0	27	68	88
	BF_3	4	82	0	0	28	78	88
$[C_7Py][Br]$	$AlCl_3$	5	95	52	31	29	100	100
(**2a**)	$TiCl_4$	6	100	25	0	30	100	100
	$SnCl_4$	7	100	15	0	31	75	88
	BF_3	8	57	0	0	32	100	81
		Substrate **3b**				Substrate **4b**		
[bmim][Br]	$AlCl_3$	9	100	66		33	100	100
(**1a**)	$TiCl_4$	10	100	83		34	100	100
	$SnCl_4$	11	68	23		35	100	100
	BF_3	12	38	0		36	100	97
$[C_7Py][Br]$	$AlCl_3$	13	98	82		37	100	100
(**2a**)	$TiCl_4$	14	100	75		38	100	100
	$SnCl_4$	15	50	40		39	100	100
	BF_3	16	48	0		40	100	98
		Substrate **3c**				Substrate **4c**		
[bmim][Br]	$AlCl_3$	17	59	97		41	100	100
(**1a**)	$TiCl_4$	18	67	100		42	34	79
	$SnCl_4$	19	1	100		43	96	98
	BF_3	20	18	0		44	32	84
$[C_7Py][Br]$	$AlCl_3$	21	94	98		45	80	91
(**2a**)	$TiCl_4$	22	81	62		46	100	97
	$SnCl_4$	23	10	100		47	96	96
	BF_3	24	62	0		48	38	82

* According to GLC data for the reaction mixture after being held for 3 h at 120ºC.

*[2] According to GLC data for the reaction mixture after being held for 3 h at 80ºC (with the use of $AlCl_3$ and $TiCl_4$) or for 3 h at 120ºC (with the use of $SnCl_4$ and BF_3).

High conversion of the starting material and selectivity of the reaction were found in almost all cases for the Fries and Beckmann rearrangements catalyzed by $AlCl_3$ and $TiCl_4$ (Table 1). Somewhat lower yields were attained using the ester **3c** and oxime **4c** (Table 1, experiments 17-24, 41-48). The Fries rearrangement of phenyl acetate (**3a**) to form *o*-acetylphenol (**6a**) and the *p*-isomer **7a** was seen only in reactions catalyzed by $AlCl_3$. With $TiCl_4$ and $SnCl_4$ catalysts only a small fraction of compound **3a** is converted to the hydroxyaryl ketone **6a** (Table 1, experiments 2, 3, 6, 7) and the major part is hydrolyzed to form phenol. With use of BF_3 the phenyl acetate (**3a**) does not generally rearrange (Table 1, experiments 4, 8). A higher reaction selectivity was seen in the Fries rearrangements of esters **3b** and **3c** in the presence of $TiCl_4$ and $SnCl_4$ but, as in the case of the phenyl acetate (**3a**) this reaction cannot be achieved using BF_3 as catalyst (Table 1, experiments 16, 24).

The rearrangement of ketoximes **4a-c** occurs readily in both IL **1a** and **2a** in the presence of $AlCl_3$ and $TiCl_4$ the yields of the amides obtained **8a-c** being almost quantitative (Table 1, experiments 25-48). By contrast

with aryl acetates, ketoximes rearrange in IL media even using $SnCl_4$ and BF_3. The reaction products show the presence of the corresponding acetophenones as the result of hydrolysis. Hence the Lewis acids BF_3 and $SnCl_4$ show different catalytic activity in the Fries and Beckmann rearrangements.

Figures 1 and 2 show graphically the effect of IL **1a** and **2a** and also of the different Lewis acids on the rate of reaction of the aryl acetates and ketoximes. The Fries rearrangements of phenyl acetate (**3a**) and 4-methoxyphenyl acetate (**3b**) occur rapidly (after 30-60 min) only with the most active of the catalysts $TiCl_4$ and $AlCl_3$ and the effect of both IL on the conversion of these esters can be considered as the same. An analogous conversion of 4-chlorophenyl acetate (**3c**) with $TiCl_4$ and $AlCl_3$ and also acetates **3a,b** with $SnCl_4$ and BF_3 occurs much more slowly and, only in these cases, can the effect of structural elements of the IL on the rate of the rearrangement be evaluated for now. The results of the majority of the experiments show a somewhat greater rate of rearrangement in the IL **2a** ([C_7Py][Br]) while the 4-chlorophenyl acetate (**3c**) shows the greatest substrate conversion for all four Lewis acids (Table 1, experiments 17-24). The rearrangement occurs at the highest rate in the presence of $TiCl_4$ (Fig. 1).

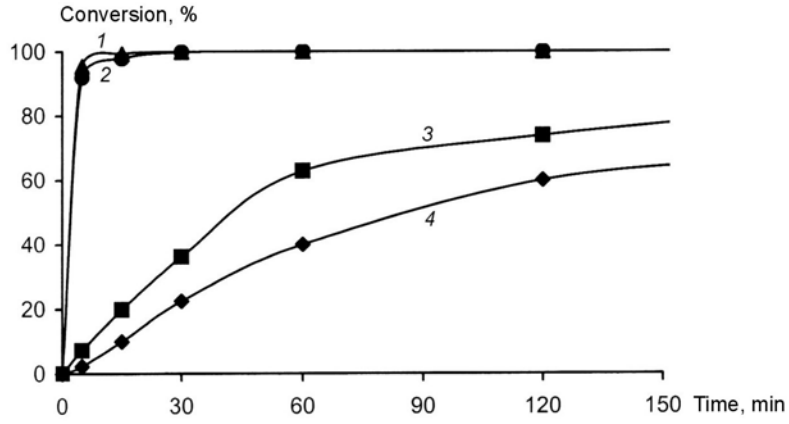


Fig. 1. $TiCl_4$-catalyzed Fries rearrangement of esters **3a** and **3c** at 120ºC: *1* – **3a**, [bmim][Br]; *2* – **3a** [C_7Py][Br]: *3* – **3c** [C_7Py][Br]; *4* – **3c** [bmim][Br].

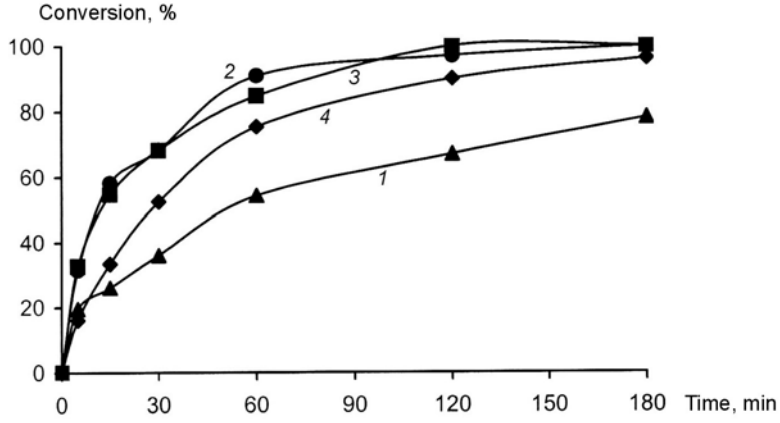


Fig. 2. BF_3- and $SnCl_4$-catalyzed Beckmann rearrangement of ketoximes **4a** and **4c** at 120ºC: *1* – **4a**, [bmim][Br]/BF_3; *2* – **4a**, [C_7Py][Br]/BF_3; *3* – **4c**, [C_7Py][Br]/$SnCl_4$; *4* – **4c**, [bmim][Br]/$SnCl_4$.

The Beckmann rearrangement of the ketoximes in the presence of $TiCl_4$ and $AlCl_3$ catalysts also occurs readily and the conversion of the starting compound reaches almost 100% after 30 min. Ketoxime **4b** contains a methoxy group and also rearranges rapidly with $SnCl_4$ and BF_3 while reaction of these with ketoximes **4a,c** takes place more slowly, hence the effect of the structural features of the IL can be conveniently observed. Ketoximes rearrange somewhat more rapidly in the IL **2a** medium than in IL **1a** (Fig. 2).

The polarities of the IL [C_7Py][Br] and [bmim][Br] on the E_T^N scale are 0.840* and 0.614* respectively (here and subsequently the starred values of E_T^N were evaluated by us using method [12]). In agreement with the Hughes-Ingold law an increase in the polarity of the solvent raises the rate of the reaction in the case of formation of a bipolar transition state [13]. Because the Fries and Beckmann rearrangements correspond to just this requirement the results obtained are explained by the above difference in the overall polarity of the IL **1a** and **2a**. This is most likely since the highest rearrangement rate is observed in the IL **2a**.

For calculating the effect of a possible π-π interaction between the IL cation and the transition state for the Fries and Beckmann rearrangements the latter were also carried out in IL with the aliphatic tetrabutylammonium bromide cation [Bu_4N][Br] for which E_T^N = 0.389 [9]. For comparison of the course of the reaction in the IL medium and in general organic solvents the rearrangements were carried out in nitrobenzene (E_T^N = 0.324 [13]). It was found that the slowest of all of the Fries rearrangements occurs in the IL [Bu_4N][Br] (**1a**). By contrast, in this medium the Beckmann rearrangement occurs more rapidly than in other IL studied. The rate of both reactions in nitrobenzene was markedly greater than in IL (Fig. 3).

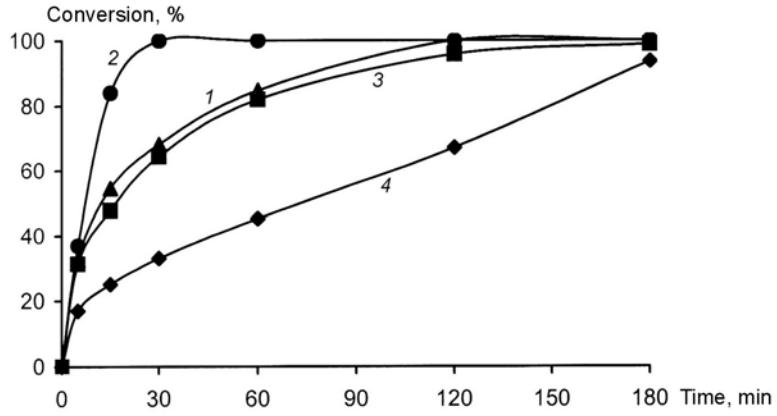


Fig. 3. $AlCl_3$-catalyzed Fries rearrangement of ester **3c** and $SnCl_4$-catalyzed Beckmann rearrangement of ketoxime **4c** in the ionic liquid [C_7Py][Br] and nitrobenzene at 120ºC: *1* – 4-chloroacetophenone oxime, [C_7Py][Br]/$SnCl_4$; *2* – 4-chloroacetophenone oxime, $PhNO_2$/$SnCl_4$; *3* – 4-chlorophenyl acetate, $PhNO_2$/$AlCl_3$; *4* – 4-chlorophenyl acetate, [C_7Py][Br]/$AlCl_3$.

Hence for an understanding of the results of the rearrangements there should be borne in mind not only the general polarity of the IL but also other possible interactions of the latter with the reaction substrates. For example this may relate to the π-π interaction between aromatic groups of the substrate and the cation of IL **1a** or **2a** which are also characteristic for nitrobenzene but not in the least typical of a [Bu_4N] cation. However, the nitrobenzene cannot take part in an ion-ion interaction with the transition state of the reaction which is possible for all IL. It follows from the results obtained that the π-π interaction is advantageous for the Fries rearrangement (increasing the reaction rate) but very undesirable for the Beckmann rearrangement (lowering the reaction rate), an ion-ion interaction between the IL and the reaction substrates lowering the rate of both rearrangements.

TABLE 2. Products Conversion and Content in the Reaction Mixture upon Claisen Rearrangement in Ionic Liquids and without Solvent*

Experiment No.	Ionic liquid	Ether	Conversion, %	**9**, %	**10**, %
1	[emim][OMs] (**1j**)	**5a**	93	95	5
2	[bmim][Br] (**1a**)	**5a**	100	71	11
3	[mPy][OTs] (**2d**)	**5a**	74	0	100
4	[C_7Py][Br] (**2a**)	**5a**	100	2	13
5	Without solvent	**5a**	68	99	1
6	[emim][OMs] (**1j**)	**5b**	100	61	39
7	[bmim][Br] (**1a**)	**5b**	58	90	10
8	[C_7Py][Br] (**2a**)	**5b**	100	44	56
9	Without solvent	**5b**	98	98	2
10	[emim][OMs] (**1j**)	**5c**	96	84	16
11	[bmim][Br] (**1a**)	**5c**	100	79	21
12	[C_7Py][Br] (**2a**)	**5c**	100	38	62
13	Without solvent	**5c**	49	41	57

* According to GLC data for the reaction mixture after 4 h at 200ºC.

Pericyclic reactions generally depend little on the nature of the solvent [13] hence in a Claisen rearrangement in different IL there is no marked difference in reaction rates, even though some difference is observed in the ratio of products (Table 2). Thus the allyl phenyl ethers **5a-c** in the 1-alkyl-3-methylimidazolium salts **1a,j** media are principally converted to the allylphenols **9a-c** but in the 1-alkylpyridinium salts **2a,d** they form more of the dihydrobenzo[*b*]furan derivatives **10a-c** which are the products of further cyclization of compounds **9a-c**. In all experiments with the ethers **5a-c** the phenol products of their hydrolysis are also observed.

In order to evaluate the effect of the hydrophobicity of the IL cation the Fries, Beckmann, and Claisen rearrangements were carried out in the 1-alkyl-3-methylimidazolium bromides **1** with alkyl substituents R of different lengths.

Increase in the length of R led to a small decrease in the polarity of the IL. On the E_T^N scale this was reflected in the following: [emim][Br] = 0.634*, [bmim][Br] = 0.614*, [hmim][Br] = 0.562*, and [omim][Br] = 0.549*. In IL hydrophobic alkyl groups there is possible a further hydrophobic interaction with the lipophilic groups of the reaction substrates and/or the transition states of the reaction. There is observed in the Fries rearrangement of 4-chlorophenyl acetate (**3c**) a lower yield of products with an increase in the length of R for the indicated dialkylimidazolium bromides (Table 3, experiments 1-3) with the exclusion of IL with R = octyl (Table 3, experiment 4). (Possibly in the latter case the octyl group is twisted into a shorter globular form). Thus the rate of rearrangement of the 4-chlorophenyl acetate (**3c**) decreases in the following IL order:

[emim][Br] > [omim][Br] > [bmim][Br] > [hmim][Br].

At the same time, the length of R in the IL does not significantly influence the ratio of reaction products.

A lowering of the conversion with increase in the length of R in the IL is also observed in the Beckmann rearrangement of the 4-chloroacetophenone oxime (**4c**) (Table 3, experiments 13-16) while, however, the conversions of this oxime after 3 h in the IL [omim][Br] and [hmim][Br] were almost identical. The curves characterizing the reaction rate graphically demonstrate its tendency to decrease in the IL series:

[emim][Br] > [bmim][Br] > [hmim][Br] ~ [omim][Br]

i.e. with an increase in the length of R in the IL cation (Fig. 4).

TABLE 3. Product Conversion and Content of the Reaction Mixture upon Fries, Beckmann, and Claisen Rearrangements in Ionic Liquids with different Alkyl Substituent Lengths

Ionic liquid	Fries rearrangement of ester **3c**			Beckmann rearrangement of oxime **4c**			Claisen rearrangement of ether **5a**			
	Experiment	Conversion, %*	**6c**, %*	Experiment	Conversion, %*[2]	**8c**, %*[2]	Experiment	Conversion, %*[3]	**9a**, %*[3]	**10a**, %*[3]
[emim][Br]	1	81	100	13	97	97	25	6	66	34
[bmim][Br]	2	59	97	14	96	98	26	100	71	11
[hmim][Br]	3	56	99	15	43	84	27	22	73	27
[omim]Br]	4	66	100	16	43	80	28	60	82	18
[bmmim][Br]	5	55	97	17	100	100	29	17	88	12
[bmim][Cl]	6	41	100	18	41	81	30	48	96	4
[bmim][I]	7	84	100	19	100	98	31	83	46	54
[bmim][BF_4]	8	0	0	20	85	98	32	2	50	50
[bmim][PF_6]	9	0	0	21	100	99	33	96	0	100
[C_7Py][Br]	10	94	98	22	96	96	34	100	2	13
[C_7Py][BF_4]	11	0	0	23	94	100	35	66	24	76
[C_7Py][PF_6]	12	0	0	24	100	100	36	55	0	100

* After 3 h with $AlCl_3$ at 120°C.
*[2] After 3 h with $SnCl_4$ at 120°C.
*[3] After 4 h at 200°C.

For the pericyclic Claisen rearrangement a clear effect of the length of the alkyl group on the conversion of the starting material **5a** in the alkylimidazolium salts was not observed (Table 3, experiments 25-28). A marked difference was also not observed in the ratio of products, the 2-allylphenol (**9a**) always being formed in excess.

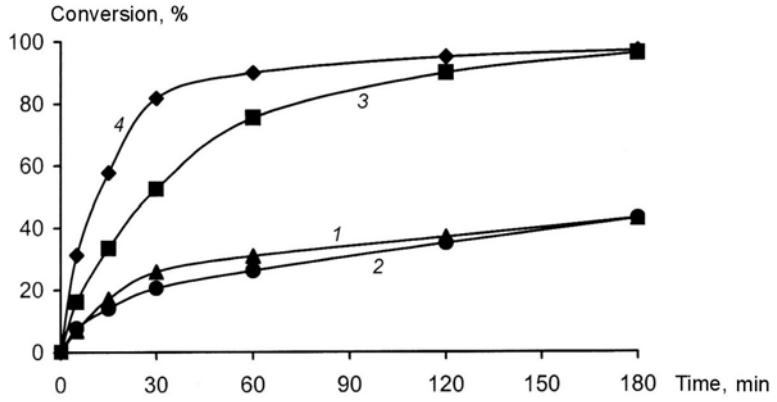


Fig. 4. $SnCl_4$-catalyzed Beckmann rearrangement of ketoxime **4c** at 120ºC in ionic liquids with different hydrophilicity: *1* – [hmim][Br]; *2* – [omim][Br]; *3* – [bmim][Br]; *4* – [emim][Br].

For reckoning the effect of the acid H-2 atom in the imidazolium ion on the rearrangements discussed they were carried out in the IL [bmim][Br] (**1a**), able to form a hydrogen bond with the reaction substrates (having H-2; E_T^N = 0.614*), and in the IL [bmmim][Br] (**1i**), having a methyl group in place of H-2 (with E_T^N = 0.486*) and so not possible in this case. The E_T^N values for the IL [bmim] series were significantly higher than for the [bmmim][Br]. This, *inter alia*, means that the acidity of the H-2 atom markedly augments the polarity of the IL.

For the Fries rearrangement, the conversion of the 4-chlorophenyl acetate (**3c**) in the IL [bmim][Br] is somewhat greater than in the IL [bmmim][Br] (Table 3, experiments 2, 5). An opposing tendency is seen in the Beckmann rearrangement of ketoxime **4c** in the [bmim][Br] and [bmmim][Br] media (Table 3, experiments 14, 17). This means that there is the undesirable formation in the Beckmann rearrangement of an additional hydrogen bond between the reaction substrates and the IL. Formation of such (an additional) bond in the pericyclic Claisen rearrangement of the allyl phenyl ether **5a** markedly increases the reaction rate (cf. experiments 26 and 29).

The type of anion in the IL markedly affects the rate of the Fries and Beckmann rearrangements but with the Claisen rearrangement this effect appears only in the product ratios. A less basic and/or more bulky anion binds more weakly with the IL cation thus increasing the possibility of a tighter interaction of this cation with the reaction substrates. The effect of halide anions on the Fries and Beckmann rearrangements corresponds to their nucleophilicity in polar protonic solvents: [bmim][I] > [bmim][Br] > [bmim][Cl] (Table 3). In the Fries rearrangement of ester **3c** and the Beckmann rearrangement of oxime **4c** the highest yield is seen in the [bmim][I] medium (Table 3, experiments 7, 19). In IL with the complex anions BF_4^- and PF_6^- the Fries rearrangement of ester **3c** does not occur at all (Table 3, experiments 8, 9, 11, 12). Independently of the nature of the cation the Beckmann rearrangement of ketoxime **4c** in IL was accompanied by a lowering of the rate in the series of anions: $PF_6^- > Br^- > BF_4^-$ (Table 3, experiments 22-24). It should be noted that ketoxime **4c** rearranges rapidly over the course of 5 min in the IL media [bmim][PF_6] and [C_7Py][PF_6] (Table 3, experiments 21 and 24). However, it has to be borne in mind that the literature reports the ready hydrolysis of the PF_6^- anion to form HF [7, 14] and the latter may be the real rearrangement catalyst. The results discussed confirm the opposing effects noted above for the nature of the IL anions on the rate of the Fries and Beckmann rearrangements.

In the Claisen rearrangement of the allyl phenyl ether **5a** the highest yields of 2-allylphenol (**9a**) are achieved in IL containing a halide anion (Table 3, experiments 25-30) with the exclusion of the IL [C_7Py][Br] and [bmim][I] (Table 3, experiments 31, 34). All of the allyl aryl ethers **5a-c** were readily converted to the corresponding 2-allylphenols in the IL with an alkanesulfonate anion [emim][OMs] (Table 2, experiments 1, 6, 10). In the IL [bmim][BF_4] the ether **5a** forms the allylphenol **9a** and dihydrobenzofuran **10a** (approximately 1:1 ratio) but in an IL containing the PF_6^- anion this ether is fully converted to product **10a** after 4 h (Table 3, experiments 33, 36).

Hence for the Fries and Beckmann rearrangements there is observed a small increase in the rate in the 1-heptylpyridinium bromide (**2a**) when compared with the 1-butyl-3-methylimidazolium bromide (**1a**). IL containing aromatic cations increase the rate of the Fries rearrangement but the rate of the Beckmann rearrangement increases with aliphatic cations. Both of these reactions take place more rapidly in the molecular liquid nitrobenzene than in IL. An increase in the hydrophobicity of the IL lowers the rate of the Fries and Beckmann rearrangements but the formation of a hydrogen bond between the H-2 atom of the imidazolium ion in the IL and electron donor groups of the reaction substrates affects their rates differently, increasing the former and slowing the latter. The rate of these rearrangements is greater in IL with the more nucleophilic anion **1c** than in IL with the less nucleophilic anion **1b**. The effect of complex anions on both reactions is opposed. IL with a PF_6^- anion lower the rate of the Fries rearrangement but speed up the Beckmann rearrangement. The products of the Claisen rearrangement of the allyl aryl ethers (2-allylphenols **9**) in IL frequently cyclize to dihydrobenzo[*b*]furans **10** and this cyclization is assisted by IL containing the more polar pyridinium cation and/or the PF_6^- anion.

EXPERIMENTAL

GLC analysis was carried out on a Hewlett Packard 5890 instrument with an A DB-5MS column (30 m×0.25 mm) and flame ionization detector (rates of H_2 30, air 300, and helium 25 ml/min). The evaporator temperature was 250ºC. GC/MS analysis was performed on a Shimadzu GC 2010 instrument with QP 2010 mass spectrometric detector (electron ionization energy 70 eV) and OAC 20i evaporator (ratio of separation of gas carried in the evaporator 1:30). The sample volume for analysis was 1μl.

^{1}H NMR spectra were taken on a Varian Mercury BB spectrometer (200 MHz) in $CDCl_3$ (compounds **6a-c, 7a, 8a-c, 9a-c, 10a-c**) or DMSO-d_6 (IL **1a-i, 2a-d**) with TMS as internal standard.

Ionic liquids: 1-butyl-3-methylimidazolium bromide, chloride, iodide, tetrafluoroborate, and hexafluorophosphate (**1a-e**), 1-alkyl(ethyl, hexyl, octyl)-3-methylimidazolium bromides (**1f-h**), 1-butyl-2,3-dimethylimidazolium bromide (**1i**), 1-heptylpyridinium bromide, tetrafluoroborate, and hexafluorophosphate (**2a-c**), and 1-methylpyridinium *p*-tolylsulfonate (**2d**) were prepared by a known methods [15-19]. The tetrabutylammonium bromide was obtained from the Aldrich company and the 3-ethyl-1-methylimidazolium methanesulfonate (**1j**) from Solvent-Innovation. The aryl acetates **3a-c**, ketoximes **4a-c**, and allyl aryl ethers **5a-c** were prepared by methods [20, 21].

Fries Rearrangement of 4-Chlorophenyl acetate (3c) in the medium [bmim][Br] in the Presence of $TiCl_4$ Catalyst. $TiCl_4$ (1.15 ml, 1.99 g, 10.5 mmol) was added to [bmim][Br] (1.15 g, 5.25 mmol). The mixture was held at 120ºC for 30 min under an argon atmosphere. Compound **1c** (0.75 g, 4.38 mmol) was added to the mixture and the product was held for 3 h at 120ºC. After 5, 15, 30, 60, 120, and 180 min samples (~ 1 mg) were removed for analysis. HCl (6M, 2 ml) was added to the sample which was thoroughly mixed and extracted with ether (2×3 ml). The combined extract was analyzed using GLC.

Fries rearrangement with other IL, aryl acetates, and Lewis acids was carried out similarly. The results obtained are correlated in Tables 1 and 3 and shown in Figs. 1 and 3.

Beckmann Rearrangement of 4-Chloroacetophenone Oxime (4c) in the Medium [Bu_4N][Br] in the Presence of $BF_3 \cdot OEt_2$ Catalyst. $BF_3 \cdot OEt_2$ (0.37 ml, 0.41 g, 2.92 mmol) was added to [Bu_4N][Br] (0.47 g, 1.46 mmol). The mixture obtained was held at 120ºC for 30 min under an argon atmosphere. Oxime **4c** (0.26 g, 1.46 mmol) was added and the reaction mixture was held for a further 3 h at 120ºC. After 5, 15, 30, 60, 120, and 180 min samples (~1 mg) were removed for analysis. Water (2 ml) was added to the sample which was thoroughly mixed and extracted with ether (2 x 3 ml). The combined extract was analyzed using GLC.

The Beckmann rearrangement with other IL, ketoximes, and Lewis acids was carried out similarly. The results obtained are correlated in Tables 1 and 3 and shown in Figures 2 and 4.

Claisen Rearrangement of Allyl Phenyl Ether (5a) in the Medium [bmim][Br]. Ether **5a** (0.30 g, 2.23 mmol) was added to [bmim][Br] (0.49 g, 2.23 mmol). The mixture obtained was held at 200ºC for 4 h under an argon atmosphere. After 5, 15, 30, 60, 120, 180, and 240 min samples (~1 mg) were removed for analysis. After treatment as reported above the samples were analyzed by GLC.

The Claisen rearrangements with other IL and with allylphenyl ethers were carried out similarly. The results obtained are collated in Tables 2 and 3.

Rearrangement Products 6-10. At the end of the rearrangement the reaction mixture was extracted three times with ether. The extract was evaporated and the residue was distilled under reduced pressure or recrystallized from dilute ethanol. In the case of a mixture (**6a** and **7a**, **9b** and **10b**, **9c** and **10c**) it was separated on a silica gel column using ethyl acetate and hexane (3:1) as eluent.

2-Hydroxyacetophenone (6a), colorless liquid, bp 76ºC (3 mm Hg) (bp 218ºC [22]). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 11.99 (1H, s, OH); 7.85 (1H, dd, *J* = 8.4 and 1.7, H-6); 7.49 (1H, dt, *J* = 8.4, *J* = 1.7, H-4); 6.90 (2H, m, H-3,5); 2.54 (3H, s, CH_3). Mass spectrum, *m/z* (I_{rel}, %): 136 $[M]^+$ (38).

4-Hydroxyacetophenone (7a), white crystals, mp 108ºC (dilute ethanol) (mp 108-109ºC [23]). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.26 (1H, s, OH); 7.86 (2H, d, *J* = 8.3, H-2,6); 6.9 (2H, d, *J* = 8.3, H-3,5); 2.54 (3H, s, CH_3). Mass spectrum, *m/z* (I_{rel}, %): 136 $[M]^+$ (30).

2-Hydroxy-5-methoxyacetophenone (6b), white crystals, mp 49ºC (dilute ethanol) (mp 52ºC [24]). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 11.45 (1H, s, OH); 7.29 (1H, d, *J* = 3.1, H-6); 7.16 (1H, dd, *J* = 8.9, *J* = 3.1, H-4); 6.88 (1H, d, *J* = 8.9, H-3); 4.25 (3H, s, CH_3); 3.08 (3H, s, CH_3). Mass spectrum, *m/z* (I_{rel}, %): 166 $[M]^+$ (87).

5-Chloro-2-hydroxyacetophenone (6c), white crystals, mp 53ºC (dilute ethanol). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 11.72 (1H, s, OH); 7.83 (1H, d, *J* = 2.7, H-6); 7.53 (1H, dd, *J* = 8.9, *J* = 2.7, H-4); 6.83 (1H, d, *J* = 8.9, H-3); 2.62 (3H, s, CH_3); Mass spectrum, *m/z* (I_{rel}, %): 170 $[M]^+$ (38).

N-Phenylethaneamide (8a), white crystals, mp 115ºC (dilute ethanol) (mp 113-115ºC [25, p. 1252]. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 9.90 (1H, s, NH); 7.50 (2H, d, *J* = 8.1, H-2,6); 7.31 (2H, t, *J* = 8.1, *J* = 7.7, H-3,5); 6.99 (1H, t, *J* = 8.1, *J* = 7.7, H-4); 2.02 (3H, s, CH_3). Mass spectrum, *m/z* (I_{rel}, %): 135 $[M]^+$ (24).

N-(4-Methoxyphenyl)ethaneamide (8b), white crystals, mp 127ºC (dilute ethanol) (mp 128-130ºC [25, p. 10]). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 9.76 (1H, s, NH); 7.45 (2H, d, *J* = 8.8, H-2,6); 6.83 (2H, d, *J* = 8.8, H-3,5); 3.69 (3H, s, OCH_3); 1.98 (3H, s, CH_3). Mass spectrum, *m/z* (I_{rel}, %): 165 $[M]^+$ (26).

N-(4-Chlorophenyl)ethaneamide (8c), white crystals, mp 173ºC (dilute ethanol) (mp 172-180ºC [25, p. 352]. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 10.04 (1H, s, NH); 7.58 (2H, d, *J* = 8.9, H-3,5); 7.30 (2H, d, *J* = 8.9, H-2,6); 2.02 (3H, s, CH_3). Mass spectrum, *m/z* (I_{rel}, %): 154 $[M]^+$ (100).

2-Allylphenol (9a), colorless liquid, bp 56ºC (3 mm Hg) (bp 103-106ºC (19 mm Hg) [20]). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 9.28 (1H, s, OH); 7.13-6.65 (4H, m, H-2,3,4,5); 5.93 (1H, ddt, *J* = 16.8, *J* = 9.9, *J* = 6.6, C<u>H</u>=CH_2); 5.01 (2H, m, CH=CH_2); 3.26 (2H, d, *J* = 6.6, ArCH_2). Mass spectrum, *m/z* (I_{rel}, %): 134 $[M]^+$ (100).

2-Methyl-2,3-dihydrobenzo[*b*]furan (10a), colorless liquid. ^{1}H NMR Spectrum, δ, ppm (*J*, Hz): 7.22-6.81 (4H, m, H-4 to H-7); 4.98 (1H, m, H-2); 3.36 (1H, dd, *J* = 15.5, *J* = 8.5, H-3); 2.86 (1H, dd, *J* = 15.5, *J* = 7.9, H-3); 1.52 (3H, d, *J* = 6.8, CH_3). The spectrum was identical to that reported in the literature [26]. Mass spectrum, *m/z* (I_{rel}, %): 134 $[M]^+$ (100).

2-Allyl-4-methoxyphenol (9b), colorless liquid, bp 74ºC (3 mm Hg) (bp 102ºC (10^{-1} mbar) [27]). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.82 (1H, s, OH); 6.74-6.54 (3H, m, H-2,4,5); 5.92 (1H, ddt, *J* = 17.0, *J* = 10.1, *J* = 6.6, CH=CH_2); 5.99 (2H, d, CH=CH_2); 3.62 (3H, s, OCH_3); 3.23 (2H, d, *J* = 6.7, ArCH_2). Mass spectrum, *m/z* (I_{rel}, %): 164 $[M]^+$ (100).

5-Methoxy-2-methyl-2,3-dihydrobenzo[*b*]furan (10b), colorless liquid. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.70-6.60 (3H, m, H-4,6,7); 4.84 (1H, m, H-2); 3.69 (3H, s, OCH_3); 3.20 (1H, dd, *J* = 15.9, *J* = 8.6, H-3); 2.75 (1H, dd, *J* = 15.9, *J* = 7.2, H-3); 1.40 (3H, d, *J* = 6.2, CH_3). The spectrum was identical to that reported in the literature [28]. Mass spectrum, *m/z* (I_{rel}, %): 164 $[M]^+$ (100).

2-Allyl-4-nitrophenol (9c), yellowish crystals, mp 75ºC (dilute ethanol) (mp 70-72ºC [29]). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 9.57 (1H, s, OH); 7.85-7.14 (3H, m, H-3,5,6); 5.95 (1H, ddt, *J* = 16.1, *J* = 10.1, *J* = 5.0, (C<u>H</u>=CH_2); 4.95 (2H, m, CH=C<u>H_2</u>); 3.70 (2H, d, *J* = 5.9, ArCH_2). Mass spectrum, *m/z* (I_{rel}, %): 179 $[M]^+$ (94).

2-Methyl-5-nitro-2,3-dihydrobenzo[*b*]furan (10c), yellowish liquid. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.85-7.07 (3H, m, H-4,6,7); 5.07 (1H, m, H-2); 3.55 (1H, dd, *J* = 15.6, *J* = 9.3, H-3); 3.18 (1H, dd, *J* = 15.6, *J* = 7.5, H-3); 1.82 (3H, d, *J* = 6.2, CH_3). Mass spectrum, *m/z* (I_{rel}, %): 179 $[M]^+$ (100).

The authors express their sincere thanks to the European Social Fund for financial support of this research.

REFERENCES

1. P. Wasserscheid and T. Welton, *Ionic Liquids in Synthesis*, 2nd ed., Wiley VCH, Weinheim (2008).
2. T. Welton, *Chem. Rev.*, **99**, 2071 (1999).
3. S. T. Handy, *Curr. Org. Chem.*, **9**, 959 (2005).
4. C. F. Poole, *J. Chromatogr., A*, **1037**, 49 (2004).
5. T. L. Greaves and C. Drummond, *Chem. Rev.*, **108**, 206 (2008).
6. V. I. Pârvulescu and C. Hardacre, *Chem. Rev.*, **107**, 2615 (2007).
7. S. Chowdhury, R. S. Mohan, and J. L. Scott, *Tetrahedron*, **63**, 2363 (2007).
8. J. R. Harjani, S. J. Nara, and M. M. Salunkhe, *Tetrahedron Lett.*, **42**, 1979 (2001).
9. C. Reichardt, *Green Chem.*, **7**, 339 (2005).
10. L. Crowhurst, N. L. Lancaster, J. M. Perez Arlandis, and T. Welton, *J. Am. Chem. Soc.*, **126**, 11549 (2004).
11. C. Reichardt, *Pure Appl. Chem.*, **76**, 1903 (2004).
12. M. J. Muldoon, C. M. Gordon, and I. R. Dunkin, *J. Chem. Soc., Perkin Trans. 2*, 433 (2001).
13. C. Reichardt, *Solvents and Solvent Effects in Organic* Chemistry [Russian translation], Mir, Moscow (1991).
14. N. Papaiconomou, N. Yakelis, J. Salminen, R. Bergman, and J.M. Prausnitz, *J. Chem. Eng. Data*, **51**, 1389 (2006).
15. J. Dupont, C. S. Consorti, P. A. Z. Suarez, and R. F. de Souza, *Org. Synth.*, **79**, 236 (2002).
16. J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker, and R. D. Rogers, *Green Chem.*, **3**, 156 (2001).
17. T. Nishida, Y. Tashiro, and M. Yamamoto, *J. Fluorine Chem.*, **120**, 135 (2003).
18. P. Nockemann, K. Binnemans, and K. Driesen, *Chem. Phys. Lett.*, **415**, 131 (2005).
19. F. F. C. Bazito, Y. Kawano, and R. M. Torresi, *Electrochim. Acta*, **52**, 6427 (2007).
20. B. S. Furniss, A. J. Hannaford, P. W. G. Smith, and A. R. Tatchell, *Vogel's Textbook of Practical Organic Chemistry*, 5th ed., Longman, Singapore (1999).

21. A. B. Fernandez, A. Marinas, T. Blasco, V. Fornes, and A. Corma, *J. Catal.*, **243**, 270 (2006).
22. K. V. Auwers, M. Lechner, and H. Bundesmann, *Chem. Ber.*, **58**, 36 (1925).
23. H. V. Krannichfeldt, *Chem. Ber.*, **47**, 156 (1914).
24. S. V. Konstanecki and V. Lampe, *Chem. Ber.*, **37**, 773 (1904).
25. *The Merck Index – An Encyclopedia of Chemicals, Drugs, and Biologicals*, 12th Ed., USA (1996).
26. F. Zulfigar and T. Kitazume, *Green Chem.*, **2**, 296 (2000).
27. R. Manetsch, Lei Zheng, M. T. Reymond, W.-D. Woggon, and J.-L. Reymond, *Chem. Eur. J.*, 2487 (2004).
28. Y. Ito, R. Kato, K. Hamashima, Y. Kataoka, Y. Oe, T. Ohta, and I. Furukawa, *J. Organometallic Chem.*, **692**, 691 (2007).
29. W. A. L. van Otterlo, G. L. Morgans, L. G. Madeley, S. Kuzvidza, S. S. Moleele, N. Thornton, and Ch. B. de Koning, *Tetrahedron*, **61**, 7746 (2005).