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Michael Additions of Methylene Active Compounds to Chalcone in Ionic Liquids without any Catalyst: The Peculiar Properties of Ionic Liquids

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Abstract: Michael additions of malonodinitrile as well as several other reagents to chalcone have been found to proceed well in pure ionic liquids, without the addition of any catalyst. The catalytic effect of the residual acidity caused by hydrolysis of ionic liquids anions was excluded because HCl in dichloromethane did not catalyse the Michael addition of malonodinitrile. Piperidine was tested as the catalyst and was found to be a much better catalyst in ionic liquids than in dichloromethane. Therefore, the following question arose: what is the effect of ionic liquids on the dissociation constants of C–H acids?

Keywords: C–H activation · ionic liquids · methylene active compounds · Michael addition · organic synthesis

Introduction

The Michael addition is one of the most frequently used C–C bond-forming reactions in organic synthesis.[1–5] The catalysts used include different bases, such as the rubidium salt of L-proline.[6–8] Organocatalysts have also been used for Michael additions of aldehydes and ketones to unsaturated carbonyl derivatives or nitrostyrenes.[9–16] Reactions are usually carried out either in DMSO or by using an excess of one reagent as the solvent. High amounts of the catalyst (10–20 mol%) should be used and reaction times are very long 20–180 h). L-Proline alone was found to be a rather ineffective catalyst, but its catalytic efficiency raised considerably after the addition of up to 80 mol% of *trans*-2,5-dimethylpiperazine or piperazine as described by Hanessian.[12] McMillan's catalyst also gave just medium yields upon the Michael addition of different aldehydes to methyl vinyl ketone, but yields were raised after the addition of 4-ethoxycarbonylcatechol.[17] Ley et al. described the best catalyst for the Michael addition of ketones to nitrostyrene[18] and similarly of nitroalkanes to cyclohex-2-ene-1-one and benzylideneacetone[19] as well as dimethyl malonate[20] to 5-(pyrrolidin-2-yl)-1*H*-tetrazole. They screened a range of solvents and found that dichloromethane was the best; however, the reaction time is a rather long two to three days and the best enantiomeric excess (*ee*) and yields were achieved after the addition of an equivalent amount of base (piperidine or piperazine).

In recent years, ionic liquids have emerged as frequently used "green" solvents for many organic reactions, including transition-metal and biocatalysed reactions.[21–28] Dell'Anna found that [bmim]BF_4 is a good solvent for the addition of acetylacetone to methyl vinyl ketone when $Ni(acac)_2$ is used as the catalyst.[29] Yadav described [bmim]BF_4 as an excellent solvent for the Michael additions of β-ketoesters to methylvinyl ketone, cyclohexenone and cyclopentenone when copper(II) triflate was used as the catalyst.[30] We have found that L-proline in ionic liquids is a very good catalyst for the Michael addition of aliphatic aldehydes and ketones to β-nitrostyrenes.[31] Rasalkar very recently described the L-proline-catalysed Michael addition of ketones to nitrostyrene.[32] He tested several ionic liquids and 1-methoxyethyl-3-methylimidazolium methanesulfonate ([MOEMIM]OMs) was found to be the best. To achieve good yields, it was necessary to prolong the reaction time up to 60 h and catalyst loading had to be increased up to 40 mol% to achieve 75% *ee*. Very recently, Hagiwara described[33] the organocatalysed addition of aliphatic aldehydes to methyl vinyl ketone in ionic liquid [bmim]PF_6. 2-(*S*)-(1-Morpholinomethyl)piperidine was found to be the best organocatalyst, but the yields of the product were only medium with 11–51% *ee*.

In our recent work, we described the successful Michael additions of thiols to unsaturated ketones in ionic liquids without the addition of any base.[34] The main aim of this

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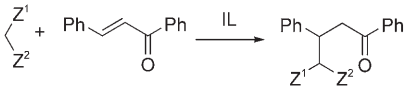
work was therefore to examine if the Michael addition of carbon nucleophiles can proceed in ionic liquids without any basic catalyst.

Results and Discussion

To start our research, we decided to study solvent effects on the reaction of malonodinitrile (**1a**) to chalcone (**2**). (Scheme 1). Reactions were performed in several ionic



1a-i 2 3a-i

Scheme 1. Michael addition of methylene active compounds to chalcone. IL = ionic liquid.

liquids. All the ionic liquids that we used were very pure (no UV absorbance from 200–400 nm) and neutral with the exception of IL**1** (pH 6.2; its hydrolysis was described in reference [35]), IL**5** (pH 4.2) and IL**7** (pH 2.3), which are acidic, and IL**8**, which is basic. The results are summarised in Table 1. Structures of ionic liquids are given in Figure 1.

Table 1. Study of the solvent effect on the addition of malonodinitrile (**1a**) to chalcone (**2**) (22 h, room temperature) without any catalyst.[a]

Entry	Solvent	Yield of **3a** [%]
1	IL**1**	76
2	IL**2**	53
3	IL**3**	95
4	IL**4**	15a
5	IL**5**	0[a]
6	IL**6**	10[a]
7	IL**7**	88[a]
8	IL**8**	95
9	CH_2Cl_2	0 (0[b])

[a] The same results were obtained when 5 mol% of L-proline as the catalysts was used. [b] 3–4 drops of HCl was added to the reaction mixture.

Reactions went smoothly in IL**1**, IL**2** and IL**3**, which are more or less neutral, but very good results were also achieved in acidic ionic liquid IL**7** and in basic ionic liquid IL**8**. The observation of the catalyst-free Michael addition in ionic liquids is very surprising, even though Michael addition in pure [bmim]BF_4 was briefly mentioned in a paper by Fan,[36] but without explanation. The observation of Ranu that Michael additions of carbon nucleophiles proceed well in [bmim]OH is not surprising, because this is in fact a basic solvent.[37] On the other hand, the product **3a** was isolated in very low yield (15 and 10%) in IL**4** and IL**6** and no addition reaction was observed in IL**5**. We do not have any explanation for this fact. Due to the fact that the Michael addition of malonodinitrile was also successful in acidic ionic liquids, we decided to test if the Michael addition of carbon

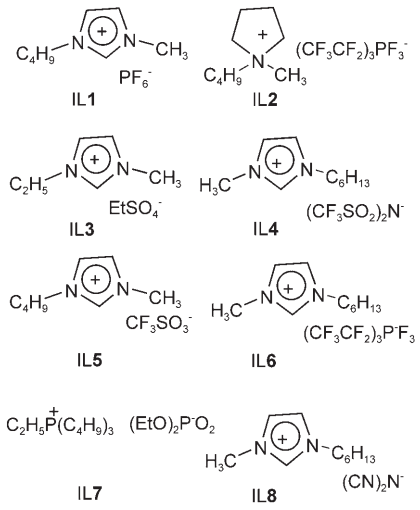


Figure 1. Structures of ionic liquids. IL**1** = 1-Butyl-3-methyl imidazolium hexafluorophosphate ([bmim]PF_6); IL**2** = 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate; IL**3** = 1-butyl-3-methylimidazolium ethylsulfate ([emim]SO_4Et, ECOENGTM212); IL**4** = 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; IL**5** = 1-butyl-3-methylimidazolium trifluoromethanesulfonate; IL**6** = 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate; IL**7** = tributyl(ethyl)phosphonium diethylphosphate; IL**8** = 1-butyl-3-methylimidazolium dicyanamide.

nucleophiles could be an acid-catalysed reaction, as we discovered in the additions of thiophenol to chalcone.[34] Attempts on the HCl-catalysed reaction in dichloromethane (Table 1, Entry 9) proved that the reaction cannot be catalysed by acids. From the results given in Table 1 it can be concluded that ionic liquids have a special effect on the Michael addition of malonodinitrile to chalcone.

We can speculate that malononitrile is acidic enough to be partially dissociated and ionic liquids are able to enhance the nucleophility of its anion. It is of interest to note that the higher nucleophilicity of halide anions in IL than in conventional solvents was described by Chi et al.,[38–40] and for water by Kim.[41] The higher nucleophilicity of halide anions in ionic liquids was made questionable in papers by Welton[42,43] and Landini.[44] Landini[44] proved that the nucleophilicities of halide ions and the azide ion in [hexmim]PF_6 are comparable with their nucleophility in methanol and is slightly lower than in DMSO. On the other hand, Welton[43] found that amines are more nucleophilic in 1-butyl-1-methylimidazolium trifluoromethylsulphonate and 1-butyl-1-methylpyrrolidinium trifluoromethylsulphonate than in dichloromethane and acetonitrile. Lancaster[45] also proved the higher nucleophilicity of amines in ionic liquids, but found that the nucleophilicity of halide anions is lower in ionic liquids than in dichloromethane and that the nucleophilicity order of different halides strongly depends on the structure of ionic liquids.

It was of interest to know if this peculiar property of ionic liquids would be apparent upon the Michael addition of other methylene active compounds and we decided, therefore, to extend the range of nucleophiles..

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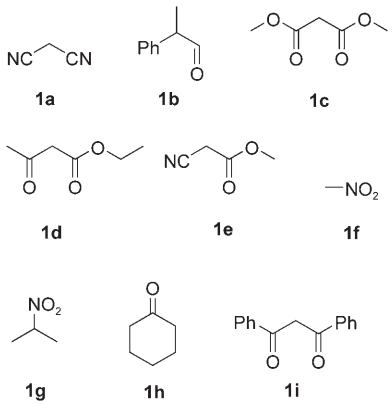


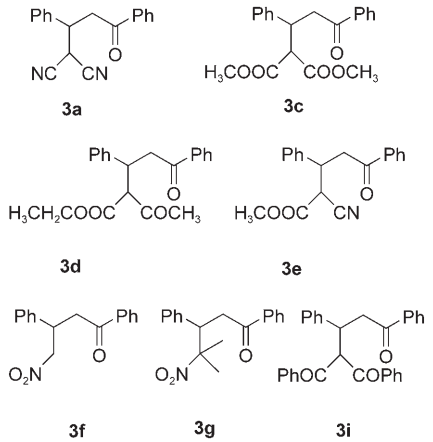
1a 1b 1c 1d 1e 1f 1g 1h 1i

The results of the additions without any catalyst are given in the Table 2. We checked the possibility of performing the addition of nine different methylene active compounds **1a–i** to chalcone (**2**) in different ionic liquids. The most reactive nucleophile **1a** gave the product **3a** in 76% yield in IL**1**, 53% yield in IL**2** and 95% yield in IL**3** and in IL**8**. Methyl cyanoacetate (**1e**) gave 34% of **3e** without any catalyst in IL**1** after 90 h at room temperature, while only traces of **3e** were detected (TLC) after 22 h. However, the product **3e** was isolated in 54% yield in IL**3** (22 h at room temperature). Similarly, nitromethane (**1f**) was unreactive in **IL2**, while the product **3f** was isolated in 71% yield when the reaction was performed in IL**3** under the same conditions. On the other hand, we do not have any explanation as to why acetylacetone (**1b**) did not undergo reaction, while dibenzoylmethane (**1i**) gave a reasonable yield (28%, 8 h, 80°C in IL**3**) of the product **3i**. It is of interest to note that Gryko[46] also described Michael additions with dibenzoylmethane and its analogues, but not with acetylacetone. 2-Phenylpropanal did not undergo Michael addition without the presence of any catalyst or in IL**3** (acidic IL) or IL**8** (basic IL). Prolonging the reaction time to 100 h did not affect the reaction course (Table 2, entries 5 and 6). The same results were obtained when the Michael addition of cyclohexanone (**1h**) on chalcone was performed (Table 2, entries 15 and 16).

Table 2. Michael additions of selected active methylene compounds to chalcone (**2**) in ionic liquids without any catalyst.

Entry	Nucleophile	Solvent	Reaction conditions	Product	Yield [%]
1	**1a**	IL**1**	22 h/RT	**3a**	76
2	**1a**	IL**2**	22 h/RT	**3a**	53
3	**1a**	IL**3**	22 h/RT	**3a**	95
4	**1a**	IL**8**	22 h/RT	**3a**	95
5	**1b**	IL**3**	22 h/RT	–	0[a]
6	**1b**	IL**8**	100 h/RT	–	0[a]
7	**1d**	IL**3**	100 h/RT	**3d**	39
8	**1d**	IL**5**	100 h/RT	**3d**	41
9	**1e**	IL**1**	90 h/RT	**3e**	34
10	**1e**	IL**3**	22 h/RT	**3e**	54
11	**1f**	IL**2**	16 h/80°C	–	0[a]
12	**1f**	IL**3**	8 h/80°C	**3f**	71
13	**1h**	IL**3**	22 h/RT	–	0[a]
14	**1h**	IL**8**	100 h/RT	–	0[a]
15	**1i**	IL**3**	22 h/RT	–	0[a]
16	**1i**	IL**3**	8 h/80°C	**3i**	28

[a] Only starting material was detected in the reaction mixture.



3a 3c 3d 3e 3f 3g 3i

From the results given in Table 2, it follows that ionic liquids are good media for catalyst-free Michael additions with a range of nucleophiles and we can speculate how they influence the reaction course. The explanation, which suggests the higher nucleophilicity of carbon nucleophiles in ionic liquids, analogously as was described for water,[41] amines[43,45] and thiols[34] is not sufficient because we have used methylene active compounds and not a real nucleophile, which would be formed from such a neutral reagent by addition of base. It is necessary to stress that we did not add any base to the reaction mixture by which a carbon nucleophile (anion) can be formed. It seems, therefore, reasonable to believe that dissociation constants of C–H acids are very different in ionic solvents than in conventional solvents, or that ionic liquids are shifting oxo–enol tautomeria of methylene active compounds towards the their enol forms. The other possible explanation for the observed behaviour is described by anion stabilization by ionic liquids.[47,48]

The fact that dimethyl malonate (**1c**) and 2-nitropropane (**1g**) did not undergo reaction with L-proline catalysis in dichloromethane was observed by Ley et al.[18–20] They reasoned that this is caused by their lower acidity and a stronger base should be added to the reaction mixture. Their reasoning was right, as after the addition of one equivalent of the stronger base (piperidine or *meso* 2,5-dimethylpiperazine) to the reaction mixture, they achieved high yields of the addition products, even though the reaction time was rather long (up to three days).

We decided, therefore, to examine the effect of L-proline or piperidine on the reaction course. Results are given in Table 3.

Michael addition of malonodinitrile (**1a**) was going well with both L-proline and piperidine as the catalysts. Piperidine was a much better catalyst, because just 2 h was enough to reach 91% yield of the product **3a**, whereas 22 h

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Table 3. Results of the Michael addition of carbon nucleophiles to chalcone (**2**) under catalysis in different solvents at room temperature.

Entry	Donor	Solvent	Catalyst[a]	t [h]	Product	Yield [%]
1	**1a**	IL**3**	L-proline	22	**3a**	95
2	**1a**	IL**3**	piperidine	2	**3a**	91
3	**1c**	IL**3**	L-proline	22	**3a**	0[c]
4	**1c**	IL**3**	piperidine	1	**3c**	59
5	**1c**	CH_2Cl_2	L-proline	22	**3c**	0[c]
6	**1c**	CH_2Cl_2	piperidine	22	**3c**	0[c]
7	**1g**	IL**1**	L-proline	12[b]	**3g**	31
8	**1g**	IL**1**	piperidine	3	**3g**	90
9	**1g**	IL**3**	L-proline	22	**3g**	25
10	**1g**	IL**3**	piperidine	3	**3g**	95
11	**1g**	CH_2Cl_2	L-proline	22	**3g**	0[c]
12	**1g**	CH_2Cl_2	piperidine	22	**3g**	0[c]

[a] 5 mol% of the catalysts were used. [b] Reaction at 80°C. [c] Only starting material only was detected in the reaction mixture.

were necessary to achieve 95% of **3a** when using L-proline as a catalyst.

It is not surprising that dimethyl malonate (**1c**) and 2-nitropropane (**1g**) did not react without any catalyst because they are less acidic than other reagents. The fact that dimethyl malonate (**1c**) and 2-nitropropane (**1g**) did not undergo reaction with L-proline catalysis in dichloromethane was observed by Ley et al.[18–20] They reasoned that it is due to their lower acidity and a stronger base should be added to the reaction mixture. Addition of dimethyl malonate (**1c**) also failed under L-proline catalysis both in IL**3** and in dichloromethane (Table 3, entries 3 and 5). Starting material was only detected in the reaction mixture after 22 h at room temperature. The reaction catalysed with 5 mol% of piperidine in IL**3** gave, after 1 h, 59% of **3c**, while after 22 h in dichloromethane only traces of **3c** were detected by TLC (Table 3, entries 4 and 6).

Reaction of 2-nitropropane (**1g**) with chalcone also proceeded very well under catalysis with 5 mol% of piperidine. We obtained 90% yield of the adduct **3g** after 3 h at room temperature when the reaction was performed in IL**1** and 95% of **3g** was obtained in IL**3** (Table 3, entries 8 and 10). L-Proline-catalysed addition of **1g** on chalcone in IL**1** after 22 h gave 31% of the adduct **3g** and 25% in IL**3** (Table 3, entries 7 and 9). Addition of 2-nitropropane (**1g**) on chalcone (**2**) in dichloromethane failed both under L-proline and piperidine catalysis (Table 3, entries 11 and 12).

Conclusion

We have demonstrated that the Michael addition of malononitrile and several other methylene active compounds proceeds successfully in pure ionic liquids, without any additional catalyst. This observation can be explained by the different dissociation constants of C–H acids in ionic liquids relative to classical solvents. It was also observed that piperidine-catalysed (5 mol%) reactions in ionic liquids proceed much faster than the same reactions in dichloromethane.

Experimental Section

General: NMR spectra were measured on a Varian Gemini 2000 spectrometer operating at 300 MHz (^{1}H NMR) and 75 MHz (^{13}C NMR); tetramethylsilane was used as an internal standard. MS spectra were measured at Micromass ZMD ESI (80 eV) system and substances were dissolved in acetonitrile/water (80:20). Elemental analysis were performed on a Carlo–Erba instrument. Enantioselectivity for the purified products was determined by HPLC (Krüss P3002RS instrument) on a chiral column Chiralcel OD-H by using *n*-hexane/2-propanol (90:10 v/v) as an eluent and cellulose tris(3,5-dimethylphenylcarbamate) coated on 5 μm silica-gel as a packing composition. MS data were obtained on a Hewlett–Packard, Agilent 1100 Series MSD HPLC-MS instrument. Organocatalysts and starting materials were purchased in reagent grade (Aldrich, Acros, Fluka, Merck) and used without further purification. Ionic liquids were purchased from Solvent Innovation and from Merck.

General experimental procedure: The ionic liquid (1 mL) was degassed by stirring under reduced pressure (oil pump), then catalyst (5 mol%) and chalcone **2** (0.208 g, 1.0 mmol) were added and the mixture was stirred for 15 min at room temperature. Nucleophile **1** (1.5 mmol) was then added and the resulting reaction mixture was stirred intensively for the specified time and temperature (see Tables 1, 2, and 3). The product was extracted by using several portions of diethyl ether and the combined extracts were evaporated in vacuo and purified by column chromatography on SiO_2 (hexane/ethyl acetate 4:1 or hexane/dichloromethane 2:1). Products were isolated as pure materials and their structure was proven by ^{1}H NMR spectra and new compounds were completely characterised. The spectroscopic characteristics of already known products, **3a**,[49] **3c**,[50] **3d**,[51] **3e**,[52] **3f**,[53] **3g**[54] and **3i**[55] were in agreement with published data.

Acknowledgements

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