



Friedel–Crafts acylation of anthracene with oxalyl chloride catalyzed by ionic liquid of [bmim]Cl/AlCl₃

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ABSTRACT

The acylation reaction of anthracene with oxalyl chloride was investigated in the presence of [bmim]Cl/AlCl₃ ([bmim]⁺ = 1-butyl-3-methylimidazolium cation) ionic liquid. Pure 1,2-aceanthrylenedione was obtained by extraction and recrystallization of the reaction mixture. The structure of 1,2-aceanthrylenedione was identified by GC/MS, FTIR and ¹H NMR spectra. The effects of various reaction parameters were investigated. The optimum synthesis conditions of the acylation reaction were given as follows: reacting at 45 °C for 6 h, the molar ratio of AlCl₃ in [bmim]Cl/AlCl₃ to [bmim]Cl/AlCl₃ and [bmim]Cl/AlCl₃ to anthracene equal to 0.67 and 2, respectively, and the molar ratio of oxalyl chloride to anthracene equals to 2. At the optimum conditions, the yield of 1,2-aceanthrylenedione is 88.2% and the selectivity is 98.2%. The reusing experiment shows that [bmim]Cl/AlCl₃ can be used as both catalyst and solvent, and it is reusable and environmentally friendly for the preparation of 1,2-aceanthrylenedione.

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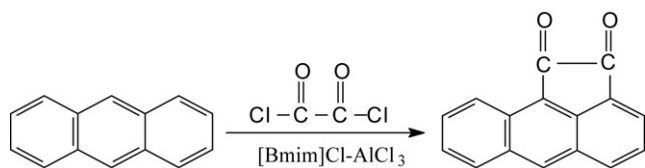
1. Introduction

Aromatic ketone is one of the most important fine chemicals, and has been widely used as pharmaceuticals, cosmetics, agrochemicals, dyes and special chemicals [1]. Friedel–Crafts acylation reactions are of great importance in both laboratory work and industry processes to synthesize aromatic ketones. AlCl₃, H₂SO₄, HF or other Lewis acid can be used as catalyst in conventional Friedel–Crafts reactions. However, these catalysts can cause a serious environmental problem during purification, and are very difficult to be reused. Therefore, it is important to replace these highly corrosive and hazardous acid catalysts with environmentally friendly catalysts which are active under mild conditions and can be easily regenerated after reaction.

In recent years, ionic liquids have shown great promise as an attractive alternative to conventional catalysts and solvents for synthesizing organic chemicals [2–5]. The increased interest for their investigations is mainly due to their green characteristics, such as chemical and thermal stability, no measurable vapor pressure, non-flammability, non-coordinating yet solvation properties [6]. They can be readily recycled, have profound effect on the activity and selectivity in reactions and in some cases, facilitate the isolation of products. Therefore, ionic liquids are considered

viable substitute for volatile organic solvents. Wikes firstly reported the acylation of benzene with the ionic liquid of [emim]Cl/AlCl₃ ([emim]⁺ = 1-methyl-3-ethylimidazolium cation) to produce acetophenone [7]. There is only mono-substitution when benzene and acetyl chloride were reacted in acidic [emim]Cl/AlCl₃ ionic liquid. Ionic liquid provided an excellent medium for this simple Friedel–Crafts reaction. At present, acylations of toluene and anisole catalyzed by ionic liquids have been widely and thoroughly investigated [7–10]. However, there are a few literatures about the acylation of polyaromatics in ionic liquids. Adams firstly investigated the acylations of some polyaromatics in [emim]Cl/AlCl₃ ionic liquids, such as naphthalene, pyrene, phenanthrene and anthracene [9]. These reactions efficiently gave the stereoelectronically favoured product. In the acetylation reaction of naphthalene, the major product was the thermodynamically unfavoured 1-isomer, with a 2% yield of the 2-isomer. The acetylation reactions of anthracene were found to behave in a different manner to those of simpler aromatic compounds. 9-Acetylanthracene is the initial product in the reaction, formed rapidly under 5 min, but this subsequently undergoes a slow disproportionation to anthracene and the two isomers of diacetylanthracene. Also, small amounts of 1- and 2-acetylanthracene are formed transiently. This implies that the monoacetylation of anthracene is reversible. The major products of the reaction of pyrene were the 1,6- and 1,8-isomers of diacetylpyrene. In the acetylation of phenanthrene, the monoacetyl derivatives are the major products, with very little of the diacetyl products formed.

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Scheme 1.

In the present paper, we report an efficient preparation method of 1,2-aceanthrylenedione through acylation of anthracene with oxalyl chloride in the presence of [bmim]Cl/AlCl₃ ionic liquid, which was demonstrated to be efficient and reusable catalyst and can be used as solvent for the acylation. The reaction process is displayed in Scheme 1.

2. Experiments

2.1. Synthesis of ionic liquid

[Bmim]Cl was prepared as follows: dried and redistilled *N*-methylimidazolium and a slight molar excess of 1-chlorobutane were placed into a stainless-steel autoclave. The autoclave was sealed, pressurized to 0.51 MPa with nitrogen and then heated to 90 °C for 18 h. After it was cooled to room temperature, the reaction mixture was transferred to a rotary evaporator where unreacted 1-chlorobutane and 1-methylimidazole were removed at 95 °C for several hours with nitrogen stripping. Then, the product was washed with the solvent of acetonitrile. The washed product was dried in a vacuum oven to remove the residual solvent and water.

[Bmim]Cl/AlCl₃ was prepared by slowly adding the weighed waterless AlCl₃ to imidazolium salt. The reaction mixture was left stirring overnight at room temperature in order to obtain a perfect homogenization of [bmim]Cl/AlCl₃. The whole reaction system was kept under dry nitrogen atmosphere to avoid hydrolysis of AlCl₃. [Bmim]Cl/AlCl₃ can be stored for a long time in dry inert atmosphere.

2.2. Acylation of anthracene and analysis of reaction product

Anthracene was recrystallized with ethanol. AlCl₃ was sublimated before used. All other chemicals used in the study were commercially available and used without further purification. Anthracene and oxalyl chloride were put into a 100-mL three-neck flask equipped with a stirrer, a reflux condenser with drying pipe and a thermometer, then certain amount of [bmim]Cl/AlCl₃ was added dropwise to the flask in 10 min with continuous stirring. The acylation reaction was conducted for certain time with continuous stirring under atmospheric pressure at 45 °C. Then the reaction mixture was cooled to room temperature, and induced into two liquid phases (organic phase and ionic liquid phase) by extracting with chloroform. Ionic liquid could be reused after the organic phase was extracted out with trichloromethane. Quantitative analysis was conducted according to the GC spectrum of organic phase accompanying with a correction factor. The organic phase was rinsed with acetonitrile and toluene after vacuum distillation, then red acicular 1,2-aceanthrylenedione was obtained after recrystallizing with ethanol. Melting point was determined in capillaries on a domestic melting point apparatus and was uncorrected. GC/MS analysis was carried out on HP 6890/5973 GC/MS. FTIR spectrum was obtained on a Nexus 470 FT-IR spectrometer. ¹H NMR analysis was recorded on a BRVKER2AR300 instrument with TMS as internal standard in CDCl₃. Chemical shifts are expressed in parts per million (δ , ppm). The concentration of reactants and products were directly given by

GC/MS software according to the area of each spectral peak accompanying with a correction factor.

3. Results and discussion

3.1. Spectra of product

The target crystal of red acicular 1,2-aceanthrylenedione was obtained with high purity of 98.3% and m.p. of 270–271 °C (literature value 270–273 °C [11]). GC/MS (*m/z* (%): 232 (M⁺, 59.0), 204 (100), 176 (88.1), 150 (16.2), 88 (22.5)); ¹H NMR (600 MHz, CDCl₃, δ _H: 9.20 (1H, d), 8.91 (1H, s), 8.38 (1H, d), 8.23 (1H, d), 8.09 (1H, d), 7.73–7.85 (3H, m)); FTIR (KBr film, 3045 cm⁻¹ (Ar-H), 1705–1735 cm⁻¹ (C=O), 1573 cm⁻¹ (C=C)). The result indicated that 1,2-aceanthrylenedione was successfully synthesized through acylation reaction of anthracene with oxalyl chloride catalyzed by [bmim]Cl/AlCl₃ ionic liquid.

3.2. Comparison of [bmim]Cl/AlCl₃ ionic liquid with AlCl₃

Friedel–Crafts acylation can be catalyzed by some other inorganic Lewis acidic catalysts, of which AlCl₃ has the highest catalytic activity. In order to compare, the acylation of anthracene with oxalyl chloride was also carried out with equivalent AlCl₃ as catalyst, and CS₂ was used as solvent. The results show that [bmim]Cl/AlCl₃ is an environmentally friendly catalyst, and the catalytic efficiency of [bmim]Cl/AlCl₃ is better than that of AlCl₃. The yields of 1,2-aceanthrylenedione when using [bmim]Cl/AlCl₃ and AlCl₃ were 88.2% and 83.8%, respectively, and the selectivity of 1,2-aceanthrylenedione were 98.2% and 92.3%, respectively. Furthermore, in the presence of [bmim]Cl/AlCl₃ ionic liquid, the isolation and purification for the target products was more easy and the acylation is free of any volatile organic solvent since the ionic liquid plays dual roles of Lewis acid catalyst and solvent. However, for AlCl₃ catalyst system, some problems were caused, such as heavy environmental pollution, troublesome recovery and purification of product, and difficult recovering of catalyst.

3.3. Effect of synthesis conditions on the preparation of 1,2-aceanthrylenedione

3.3.1. Effect of molar fraction of AlCl₃ in ionic liquid

The effect of molar fraction of AlCl₃ ($x(\text{AlCl}_3)$) in [bmim]Cl/AlCl₃ ionic liquid on the acylation reaction of anthracene with oxalyl chloride is given in Table 1. The molar fraction of AlCl₃ in [bmim]Cl/AlCl₃ imposes marked influence on the acylation reaction. The yield and selectivity of 1,2-aceanthrylenedione reach maximum and then decrease with the molar fraction of AlCl₃ variation from 0.33 to 0.75. The yield and selectivity of 1,2-aceanthrylenedione is highest when the molar fraction of AlCl₃ is 0.67 (i.e., $x(\text{AlCl}_3) = 0.67$ or $n(\text{AlCl}_3):n([\text{bmim}]\text{Cl}) = 2:1$), while the yield and selectivity decrease when $x(\text{AlCl}_3) > 0.67$. Depending on the proportions of [bmim]Cl to Lewis acid of AlCl₃, the acidity of

Table 1

Effect of molar fraction of AlCl₃ in ionic liquid on the acylation reaction.

$x(\text{AlCl}_3)$	$n(\text{AlCl}_3):n([\text{bmim}]\text{Cl})$	Yield (%)	Selectivity (%)
0.33	0.5:1.0	0	0
0.50	1.0:1.0	0	0
0.60	1.5:1.0	58.6	98.2
0.67	2.0:1.0	88.2	98.2
0.71	2.5:1.0	72.5	96.6
0.75	3.0:1.0	63.6	91.0

$n([\text{bmim}]\text{Cl}/\text{AlCl}_3):n(\text{anthracene}) = 2:1$, $n(\text{anthracene}):n(\text{oxalyl chloride}) = 1:2$, react for 6 h at 45 °C.

ionic liquid system can vary in wide range. However, Friedel–Crafts acylation was more easily catalyzed by acidic catalyst than by basic catalyst. With increasing of the molar percentage of AlCl_3 , chloroaluminates may be denoted as from Cl^- , AlCl_4^- , Al_2Cl_7^- to $\text{Al}_3\text{Cl}_{10}^-$ in $[\text{bmim}][\text{Cl}]/\text{AlCl}_3$ [12,13]. Hence, the ionic liquid is basic when the mole fraction of AlCl_3 in ionic liquid is less than 0.5, while over than 0.5, the ionic liquid would be acidic [14]. The increasing of yield and selectivity of 1,2-aceanthrylenedione can be explained by the variation of acidity of ionic liquid system. However, the decreasing may be due to the polymerization of anthracene because the polymerization becomes easy with the increasing of the ionic liquid's acidity.

3.3.2. Effect of molar ratio of ionic liquid to anthracene on the acylation reaction

The effects of molar ratio of $[\text{bmim}]\text{Cl}/\text{AlCl}_3$ to anthracene on the yield and selectivity of 1,2-aceanthrylenedione is shown in Fig. 1. The yield and selectivity of 1,2-aceanthrylenedione pass through a maximum and then decrease with the increasing of molar ratio. The maximum value of 88.2% of yield and 98.2% of selectivity are observed, respectively, when molar ratio of ionic liquid to anthracene is 2:1.

3.3.3. Effect of molar ratio of oxalyl chloride to anthracene on the acylation reaction

The effect of molar ratio of oxalyl chloride to anthracene on the yield and selectivity of 1,2-aceanthrylenedione is given in Fig. 2. As oxalyl chloride increases, the yield of target product reaches a maximum and then decreases. The yield maximum of 88.2% was obtained when molar ratio of oxalyl chloride to anthracene is 2:1.

3.3.4. Effect of reaction temperature on the acylation reaction

The effect of reaction temperature on the acylation reaction is shown in Fig. 3. Reaction temperature can markedly affect the yield and slightly affect the selectivity of target product. The yield of 1,2-aceanthrylenedione reaches 88.2% at 45 °C. An obvious decrease of yield and selectivity are observed when the reaction temperature is further raised. Since acylation is exothermic reaction, the equilibrium conversion decreases with further increasing reaction temperature. Therefore, 45 °C is the optimal reaction temperature.

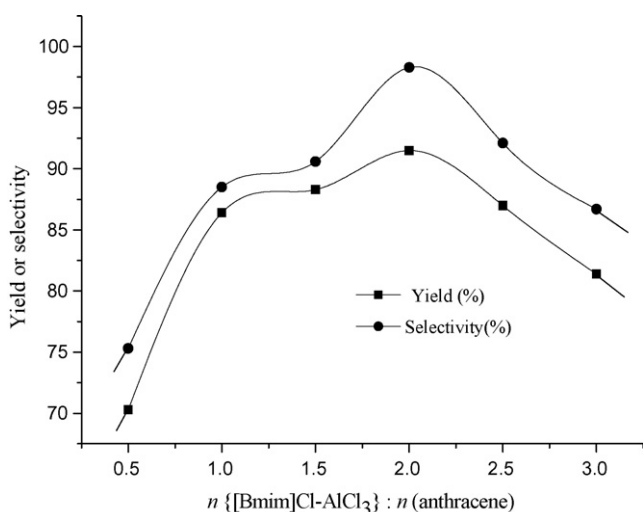


Fig. 1. Effect of molar ratio of ionic liquid to anthracene on the acylation reaction: $n(\text{anthracene}):n(\text{oxalyl chloride})=1:2$, $x(\text{AlCl}_3)=0.67$, react for 6 h at 45 °C.

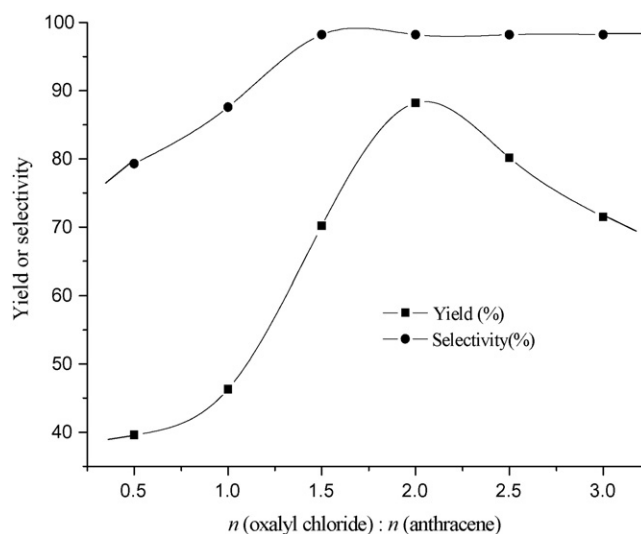


Fig. 2. Effect of molar ratio of oxalyl chloride to anthracene on the acylation reaction: $x(\text{AlCl}_3)=0.67$, $n([\text{bmim}]\text{Cl}/\text{AlCl}_3):n(\text{anthracene})=2:1$, react for 6 h at 45 °C.

3.3.5. Effect of reaction time on the acylation reaction

The influence of reaction time on the acylation reaction in $[\text{bmim}]\text{Cl}/\text{AlCl}_3$ ionic liquid system is given in Fig. 4. The yield increases with reaction time. The highest yield of 88.2% is achieved after 6 h and then reaches equilibrium reaction. However, reaction time has little influence on the selectivity of 1,2-aceanthrylenedione. As we know, most acylation reactions are performed with the aromatic-to-acyl ratio more than 1, typically 5 or 10. Hence, the influence of reaction time in the graph looks unusual. However, the reaction for polyaromatic of anthracene is very complex. According to GC/MS analyses, there are many other by-products, such as 1-chloro-2-(9-anthryl), 1-chloro-2-(1-anthryl), and 1-chloro-2-(2-anthryl) ethanedione, 1,2-(9,9-dianthryl), 1,2-(1,9-dianthryl), 1,2-(2,9-dianthryl), 1,2-(1,1-dianthryl), 1,2-(1,2-dianthryl), and 1,2-(2,2-dianthryl) ethanedione. Besides above by-products, there are some other small amounts of products which cannot be explained by conventional Friedel–Crafts reaction path, such as chloroanthracene, 9-anthric acid, 9-carbonyl chloride-10-anthric acid, 9-carbonyl acid-9,10-dihydro-

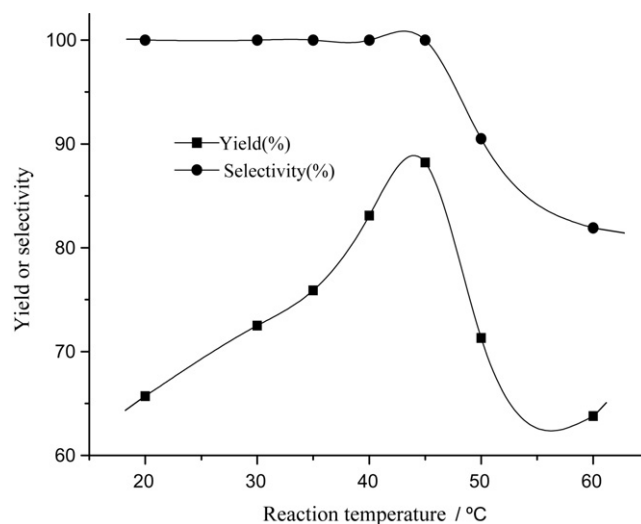


Fig. 3. Effect of reaction temperature on the acylation reaction: $x(\text{AlCl}_3)=0.67$, $n(\text{oxalyl chloride}):n(\text{anthracene})=2:1$, $n([\text{bmim}]\text{Cl}/\text{AlCl}_3):n(\text{anthracene})=2:1$, react for 6 h.

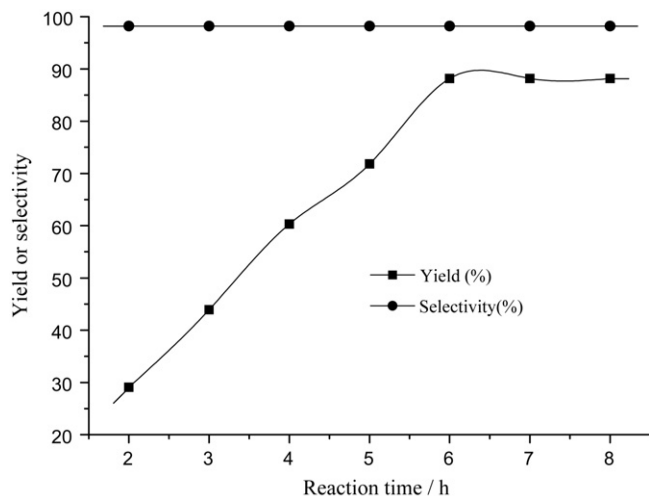


Fig. 4. Effects of reaction time on acylation reaction: $x(\text{AlCl}_3)=0.67$, $n(\text{oxalyl chloride}):n(\text{anthracene})=2:1$, $n([\text{bmim}]\text{Cl}/\text{AlCl}_3):n(\text{anthracene})=2:1$, react at 45°C .

Table 2

Reusing performance of $[\text{bmim}]\text{Cl}/\text{AlCl}_3$.

Reusing times	Yield (%)	Selectivity (%)
1	88.2	98.2
2	88.0	98.2
3	88.1	97.5
4	87.9	96.4
5	87.3	96.1

10-anthracenemethanol, 9-chloroethyl-10-chlorovinylanthracene and 9,10-dihydro-9,9'-dianthracene. The unusual graph may be caused by these unusual by-products. It should be noted that carbocyclic aromatics of anthracene, form highly coloured compounds in acidic $[\text{bmim}]\text{Cl}/\text{AlCl}_3$, probably π -complexes as they are paramagnetic. The fact that paramagnetic species are present, and that protons play a significant part in these reactions, suggests that the classical mechanisms proposed for the Friedel–Crafts reaction should be modified [9]. The unusual graph for the influence of reaction time was also appeared in the alkylation of anthracene and 2-chloropropane with $[\text{bmim}]\text{Cl}/\text{AlCl}_3$ ionic liquid.

3.4. Reusing performance of $[\text{bmim}]\text{Cl}/\text{AlCl}_3$ in the acylation reaction

In order to investigate the reusing performance of $[\text{bmim}]\text{Cl}/\text{AlCl}_3$, the recycle experiment was conducted. After extracting the reaction mixture with chloroform, the reaction mixture became two liquid phases, organic phase (unreaction reactants and products phase) and $[\text{bmim}]\text{Cl}/\text{AlCl}_3$ ionic liquid phase. $[\text{bmim}]\text{Cl}/\text{AlCl}_3$ was reused as catalyst after extracting out the organic phase with aether and vacuum drying (0.01 Torr) at $80\text{--}100^\circ\text{C}$ for 30 min. The acylation results which catalyzed by the recycled $[\text{bmim}]\text{Cl}/\text{AlCl}_3$ are summarized in Table 2.

The catalytic activity of $[\text{bmim}]\text{Cl}/\text{AlCl}_3$ decreases in some sort after being reused for five times. This indicates that $[\text{bmim}]\text{Cl}/\text{AlCl}_3$ is a reusable and environmentally friendly catalyst when it is used as catalyst and solvent for the synthesis of 1,2-aceanthryenedione.

4. Conclusion

Pure 1,2-aceanthryenedione was successfully prepared by acylation reaction of anthracene with oxalyl chloride in the presence of $[\text{bmim}]\text{Cl}/\text{AlCl}_3$ ionic liquid. The optimum reaction conditions for the acylation reactions are as follows: react for 6 h at 45°C with 2 mmol oxalyl chloride per mmol anthracene, 2 mmol AlCl_3 per mmol $[\text{bmim}]\text{Cl}$, 2 mmol ionic liquid per mmol anthracene. Under the optimal reaction conditions, 88.2% of yield and 98.2% of selectivity of 1,2-aceanthryenedione were obtained. Although the mechanism of acylation reaction, which catalyzed by $[\text{bmim}]\text{Cl}/\text{AlCl}_3$ ionic liquids, is not clear now, this research indicates that $[\text{bmim}]\text{Cl}/\text{AlCl}_3$ can be used as a novel environmentally friendly catalyst and solvent for anthracene's acylation reaction.

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