An efficient synthesis of isoxepac and 2-ethylanthraquinone via intramolecular acylation catalyzed by chloroaluminate ionic liquids with P_2O_5

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Abstract

Acylation reaction directly using carboxylic acid as an acylation agent is the most ideal acylation method but demands rigorous reaction conditions. In this study, an efficient method was used in synthesizing isoxepac and 2-ethylanthraquinone from electron-poor substrates through intramolecular acylation catalyzed by chloroaluminate ionic liquids with P_2O_5. The condition optimization experiment was carried out, and the yield of isoxepac was improved to 82.7%. By studying the catalyzed intramolecular acylation of 2-(4-ethylbenzoyl) benzoic acid to obtain 2-ethylanthraquinone, the universality of chloroaluminate ionic liquids with P_2O_5 as catalysts for intramolecular acylation was confirmed. Compared with the original process, using ionic liquids catalysts in catalytic reactions can effectively reduce the amount of waste acid and water produced by post-treatment.

Introduction

In Friedel-Crafts acylation reactions, the acylation method directly using carboxylic acid as an acylation agent does not require the conversion of a carboxylic acid into acyl chloride, anhydride, or amide, is easy to operate, and is the most ideal acylation method, but the reaction conditions are demanding. Inorganic acids are used as catalysts in traditional processes [1]. In recent years, a variety of activator systems for the acylation of catalyzed carboxylic acids have been developed, including poly-phosphoric acid[2], hydrogen fluoride[3], trifluoromethanesulfonic acid[4], mesylate/phosphorus pentoxide[5], and Lewis acid[6].

Intramolecular acylation is a common reaction in organic synthesis, especially in the synthesis of heterocyclic compounds. In the study of Tran[7] et al., intramolecular Friedel–Crafts reaction between 3-arylpropionic acid and 4-arylbutyric acid was catalyzed by triflate anion ionic liquids under microwave irradiation. This environmentally friendly synthesis process allows the formation of cyclic ketones with good yields in a short reaction time. Zhang[8] et al. studied an efficient and straightforward synthesis method for indanone synthesis and prepared indanone fusion heterocyclic compound containing unique tetra-cyclic isoflavones. They used a one-pot method to obtain the product through a three-step tandem process (Riley oxidation/Friedel-Crafts reaction/SeO_2/$FeCl_3$ oxidation). Begum[9] et al. reported that the intramolecular acylation of 3-aryloxy propionic acid in the presence of acidified montmorillonite produced a high yield. The intramolecular acylation of benzene rings containing various substituents occurs at ortho and para positions and interposition. Catalysts treated with heterogeneous acids can be recycled and used for up to three cycles with little loss of activity.

Isoxepac is a key intermediate of olopatadine hydrochloride[10]. The main synthesis process of isoxepac generally uses benzene phthalide and p-hydroxyphenyl acetic acid to undergo intramolecular acylation reaction condensation reaction to get 4-[(2-carboxymethyl phenoxy) methyl] benzoic acid[11]. The benzene ring itself is passivated by the carboxyl group and has low reactivity. The preparation process is to use polyphosphoric acid (PPA) catalyzed intramolecular acylation reaction to get finished isoxepac[12, 13]. PPA is expensive and not recyclable. Moreover, PPA is an extremely viscous liquid at room temperature, which

can be completely removed only after a large amount of water washing[14]. This increases the cost of preparation, has a negative impact on the environment, and the process is in urgent need of improvement.

An important organic chemical intermediate, 2-ethylanthraquinone can be prepared by various processes. The most widely used process is the $AlCl_3$-catalyzed acylation reaction of phthalic anhydride with ethyl benzene for the synthesis of 2-(4-ethylbenzoyl) benzoic acid (BE acid), followed by fuming sulfuric acid-catalyzed cyclization dehydration to produce 2-ethylanthraquinone[15]. Fuming sulfuric acid, which is often used in the traditional process, is highly volatile and corrosive, and cannot be recovered after catalytic use, resulting in a large amount of waste acid wastewater and damaging production equipment. Liu[16] et al. studied H-β zeolite and dealumination H-β and compared the performance of e-BBA dehydration on zeolite with that of traditional industrial catalyst fuming sulfuric acid. After the 0.3 M HNO_3 treatment of the H-β zeolites, the catalytic performance improved greatly.

Ionic liquids have become potent substitutes for traditional organic reaction catalysts because of their high catalytic activity and recyclability[17–19], showing good development prospect in improving the original process, reducing production costs, and reducing environmental pollution. Chloroaluminate ionic liquids are sensitive to water, and thus their application, especially to Friedel-Crafts acylation reactions directly using carboxylic acid as an acylation agent, is greatly limited. Phosphorus pentoxide (P_2O_5) is cheap and can be used as a desiccant for gas and liquids and dehydration agent for organic synthesis[20]. In these study, triethylamine chloride aluminate ionic liquids were prepared and used as catalysts with P_2O_5 in isoxepac synthesis. In addition, the universality of chloroaluminate ionic liquids as catalysts of intramolecular acylation reaction was studied, and 2-(4-ethylbenzoyl) benzoic acid was catalyzed by chloroaluminate ionic liquids for 2-ethylanthraquinone synthesis. The reaction conditions were optimized, the yield was improved, and the reaction mechanism was explored. Chloroaluminate ionic liquids as replacements for PPA and fuming sulfuric acid can effectively reduce industrial waste acid waste water, reduce production cost, and meet the purpose of green chemistry.

Experiment

Chemicals

Anhydrous aluminum chloride ($AlCl_3$; 99%), triethylamine hydrochloride ($N(CH_3CH_2)_3HCl$; 98%) and phosphorus pentoxide (P_2O_5; 99%) were purchased from Damao Chemical Reagent Factory. 4-[(2-Carboxymethyl phenoxy) methyl] benzoic acid and 2-(4-ethylbenzoyl) benzoic acid were all provided by Jilin Sihuan Pharmaceutical Co., LTD. Deuterium chloroform (CCl_3D; 99.8%) was purchased from Cambridge Isotope Laboratory, Inc. (Andover, MA).

Synthesis of Chloride Aluminate Ionic liquids

The ILs $[Et_3NH]^+ [Al_2Cl_7]^-$ and $[Et_3NH]^+ [AlCl_4]^-$ were prepared by following the reported procedures.[21, 22] $[Et_3NH]^+ [Al_2Cl_7]^-$ and $[Et_3NH]^+ [AlCl_4]^-$ were prepared by stirring solid $[Et_3NH]^+ Cl^-$ (30mmol, 4.13g) and solid Anhydrous $AlCl_3$ (30 mmol (4.13g) or 60 mmol (8.26 g) at a 1:1 or 1:2 ratio under an N_2 atmosphere, The preparation process is shown in Scheme 1.

Intramolecular acylation of 2-[(4-carboxymethyl phenoxy) methyl] benzoic acid

2-[(4-carboxymethyl phenoxy) methyl] benzoic acid, chloroaluminate ionic liquids, P_2O_5, and solvent N-butyl acetate were added into a three-necked flask filled with N_2. The reaction was stopped after heating to 80℃ for 8 h. The preparation process is shown in Scheme 2. Purification method: the reaction solution is gradually added to ice water under agitation, and then the crude isoxepac is obtained by extraction of the solution. Adding 3 times the mass of crude isoxepac ethyl acetate and 5 wt.% activated carbon, heating reflux decolorization, the solution under the hot state of extraction and filtration to remove activated carbon, retained the filtrate recrystallization, extraction and filtration to obtain white solid isoxepac.

White solids, M.p. 130–132℃. ^{1}H NMR (400 MHz, Chloroform-d) δ 12.43 (s, 1H), 7.78 (d, *J* = 2.3 Hz, 1H), 7.94 (d, *J* = 9.2 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.35–7.46 (m, 3H), 7.24 (d, *J* = 8.4 Hz, 1H), 5.52 (s, 2H), 3.46 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 190.57, 137.54, 133.51, 132.42, 129.46, 129.22, 129.52, 128.57, 124.96, 121.05. IR (KBr): v 3264, 2906, 1665, 1610, 1150, 821 cm^{-1}.

Intramolecular acylation of 2-(4-ethylbenzoyl) benzoic acid

2-(4-Ethylbenzoyl) benzoic acid, chloroaluminate ionic liquids, P_2O_5, and solvent N-butyl acetate were added into a three-necked flask filled with N_2. The reaction was stopped after heating to120℃ for 8 h. The preparation process is shown in Scheme 3. Purification method: The reaction solution is poured into an ice bath, and pale yellow solids are separated. The filtrate, wash with alkali and deionized water three times respectively, measured pH to be neutral, collect the product and dry it on the surface dish. Add 1.5 times the weight of crude 2-ethylanthraquinone ethanol for recrystallization, pumping, and filtering to get light yellow solid product 2-ethylanthraquinone.

Pale yellow solids, M.p. 107–109℃. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.32 (dd, J = 5.5, 3.6 Hz, 2H), 8.25 (d, J = 8.0 Hz, 1H), 8.15 (d, J = 1.8 Hz, 1H), 7.86–7.74 (m, 2H), 7.64 (dd, J = 8.0, 1.9 Hz, 1H), 2.85 (q, J = 7.6 Hz, 2H), 1.35 (t, J = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 183.37, 182.91, 151.33, 133.99, 133.87, 133.80, 133.57, 133.50, 131.44, 127.51, 29.15, 14.97. IR (KBr): v 2968, 2933, 2874, 1673, 1593, 932,854 cm^{-1}.

Results And Discussion

Influence of acidity and dosage of ionic liquids on reaction

Aimed at identifying optimum reaction conditions for catalytic synthesis of isoxepac, a series of experiments was designed to investigate the influence of the acidity and dosage of ionic liquids on reactions. The results are presented in Table 1.

The catalytic activity of triethylamine ionic liquids with $[Al_2Cl_7]^-$ (N = 0.67) was higher than that of triethylamine ionic liquids with $[AlCl_4]^-$ (N = 0.5) anion. Catalytic activity increased with the concentration of $AlCl_3$ the in chloroaluminate ionic liquids. The acidity of polyphosphoric acid in the original process increased, indicating that the catalyst itself needs high acidity in the synthesis reaction of isoxepac and ionic liquids with high acidity $[Al_2Cl_7]^-$ are suitable for synthesizing isoxepac catalysts. The yield of isoxepac gradually increased with the increasing dosage of $[Et_3NH]^+$ $[Al_2Cl_7]^-$ in the system until the molar ratio of $[Et_3NH]^+$ $[Al_2Cl_7]^-$ to the reaction substrate was 2:1, at which the yield of isoxepac was the highest (82.6%). The reason was the gradual increase in the content of the catalytic active center $[Al_2Cl_7]^-$ in the system as the dosage of $[Et_3NH]^+$ $[Al_2Cl_7]^-$ catalysts gradually increased. When the content of $[Al_2Cl_7]^-$ was low, the substrate failed to make full contact with the catalytic active center. When the content of $[Al_2Cl_7]^-$ was high, the probability of the collision between the substrate and catalytic active center improved, and the optimal catalyst dosage condition was finally reached. The yield of isoxepac was unchanged despite the continuous increase in the content of the ionic liquids, and thus the best molar ratio of $[Et_3NH]^+$ $[Al_2Cl_7]^-$ ionic liquids and reaction substrate was 2:1, at which the yield of isoxepac was the highest.

Influence of P_2O_5 dosage on reaction

After determining the optimum acidity and dosage of isoxepac, the dosage of P_2O_5 as a water-absorbent should also be determined. As can be seen from Table 2, when the molar ratio of $[Et_3NH]^+$ $[Al_2Cl_7]^-$ to 4-[(2-carboxymethyl phenoxy) methyl] benzoic acid was 2:1, the reaction temperature was 80°C, the reaction time was 8 h, no water absorbent P_2O_5 was added, no subsequent reaction occurred, and no product remained after post-treatment. The results indicated that P_2O_5 is important to intramolecular acylation. Then, the yield of isoxepac gradually increased with increasing dosage of P_2O_5. The highest yield of isoxepac was obtained when the weight ratio of P_2O_5 to the reaction substrate was 0.5:1. The yield of isoxepac remained unchanged at increasing P_2O_5 content. Therefore, when the weight ratio of P_2O_5 to the reaction substrate was 0.5:1, the catalytic activity of the chloroaluminate ionic liquids in the reaction system was not obviously lost, and the yield of isoxepac was the highest.

Influence of reaction temperature on reaction

After the optimal acidity and dosage of ionic liquids and the dosage of water-absorbent P_2O_5 were determined, the effect of reaction temperature on the yield of isoxepac was further explored. As shown in Table 3, when the molar ratio of fixed $[Et_3NH]^+$ $[Al_2Cl_7]^-$ to substrate concentration was 2:1, the weight ratio of P_2O_5 to the substrate was 0.5:1, the reaction time was 8 h, and the yield of isoxepac increased to

a certain extent when the reaction temperature continued to increased gradually. After the temperature was increased to 90°C and 100°C, the yield of isoxepac decreased to a certain extent. TLC detection indicated newly generated impurity points, and high reaction temperature produced the byproducts of isoxepac, such as some ketones. Therefore, the optimum reaction temperature of intramolecular acylation to isoxepac is 80°C.

Influence of reaction time on reaction

After the optimal acidity and dosage of ionic liquid were determined, the dosage of P_2O_5, reaction temperature, and the effect of reaction time on the yield of isoxepac were explored. As shown in Table 4, when the molar ratio of fixed $[Et_3NH]^+$ $[Al_2Cl_7]^-$ to the substrate concentration was 2:1, the weight ratio of P_2O_5 to the substrate was 0.5:1, the reaction temperature was 80°C, the reaction time was 6 h, and the yield of isoxepac was low. The reaction substrate was not completely transformed. The yield of isoxepac increased gradually with increasing reaction time, and the highest yield of isoxepac was obtained at a reaction time of 8 h. As reaction time increased, the yield of isoxepac remained unchanged. Therefore, the optimal reaction time of isoxepac catalyzed by ionic liquid intramolecular acylation is 8 h.

Synthesis of 2-ethylanthraquinone by extended intramolecular acylation

The intramolecular acylation reaction of 2-[(4-carboxymethyl phenoxy) methyl] benzoic acid (BEA) catalyzed by chloroaluminate ionic liquids was carried out. As shown in Table 5, when the molar ratio of $[Et_3NH]^+$ $[Al_2Cl_7]^-$ ionic liquids to 2-(4-ethylbenzoyl) benzoic acid was 2:1, the weight ratio of P_2O_5 to the reaction substrate was 0.5:1, the reaction temperature was 120°C, and the reaction time was 8 h, the yield of finished 2-ethylanthraquinone obtained 56.1%. The cyclization dehydration of catalyzed intramolecular acylation reaction using chloroaluminate ionic liquid combined with P_2O_5 has certain universality. However, the carbonyl group in BEA greatly affected the reaction, and thus the yield was not as high as that of isoxepac.

Discussion on ionic liquid circulation and reaction mechanism

A possible mechanism for the catalytic synthesis of 2-ethylanthraquinone by $[Et_3NH]^+$ $[Al_2Cl_7]^-$ ionic liquids is proposed[23]. First, 2-[(4-carboxymethyl phenoxy) methyl] BEA reacts with P_2O_5 into BEA anhydride, which is more reactive than carboxylic acid in the acylation reaction[24]. Next, BEA anhydride reacts with $[Al_2Cl_7]^-$ to form carbonyl positive ions and carboxyl negative ions complex with $AlCl_3$. Then, the benzene ring of the other part of the reaction substrate attacks the carbonyl positive ion to generate products. Finally, the complex of 2-ethylanthraquinone and $AlCl_3$ is formed[25]. In addition, P_2O_5 generates H_3PO_4 for synergistic catalysis. The mechanism diagram is shown in Scheme 4.

P_2O_5 generates H_3PO_4, which promotes the partial decomplexation of carboxyl groups complexed with $AlCl_3$ together with cyclization of the H^+ of benzene, and returns to the raw material. However, owing to the complexation of Al and carbonyl O, $[AlCl_4]^-$ in the system cannot be returned to $[Al_2Cl_7]^-$ at the beginning of the reaction. Although excessive P_2O_5 has been added to remove the water generated in the reaction because the chloride aluminate ionic liquids are sensitive to acid, there is the destruction of part of the ionic liquids in the system and changes of the catalytic activity.

Although no cyclic catalysis of chloride aluminate ionic liquids in this reaction occurs, compared with the original process, the amount of wastewater produced by the reaction is still reduced to a certain extent. As shown in Table 6, compared with the original process, polyphosphoric acid with a higher cost is used for catalysis. Post-treatment requires a large amount of water washing to remove polyphosphoric acid, and the catalyst polyphosphoric acid cannot be recovered. Using $[Et_3NH]^+$ $[Al_2Cl_7]^-$ with a low preparation cost to catalyze the synthesis of isoxepac has obvious benefits, such as low post-treatment water waste and reduced production cost.

Table 6 Comparison of wastewater in two processes

Entry	Raw material Consumption (mol)	Wastewater Quantity (L)
Traditional process	1	5.3
New process	1	2.8

Conclusions

Isoxepac was synthesized by intramolecular acylation catalyzed by the chloroaluminate ionic liquids with P_2O_5, and the effects of different reaction conditions on the yield of isoxepac were investigated. By optimizing reaction conditions, in the selection of $[Et_3NH]^+$ $[Al_2Cl_7]^-$ ionic liquids as catalysts, the molar ratio of $[Et_3NH]^+$ $[Al_2Cl_7]^-$ and substrate concentration was 2:1, the weight ratio of P_2O_5 to the reaction substrate was 0.5:1, the reaction temperature was 80°C, the reaction was heated and stirred for 8 h, and isoxepac had the highest yield (82.6%). Compared with the original process, catalyzing the synthesis of isoxepac by using $[Et_3NH]^+$ $[Al_2Cl_7]^-$ ionic liquids had low preparation cost, which reduced the amount of post-treatment wastewater and low production cost. 2-ethylanthraquinone was obtained using the intramolecular acylation of 2-[(4-carboxymethylphenoxy) methyl] benzoic acid catalyzed by $[Et_3NH]^+$ $[Al_2Cl_7]^-$ ionic liquids with P_2O_5. The substitution of fuming sulfuric acid in the traditional process of catalyst was realized. The ionic liquids of chloroaluminate have certain general adaptability to catalyze intramolecular dehydration acylation.

Declarations

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Ethical Approval

Not applicable.

Competing interests

The authors have no relevant financial or non-financial interests to disclose.

Authors' contributions

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Qi Wang and Bin Zhang. The first draft of the manuscript was written by Qi Wang and Bin Zhang. All authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials

Supplementary data to this article can be found online at

The ^{1}H NMR、^{13}C NMR spectra of isoxepac (Figure S1 and Figure S2) and the ^{1}H NMR、^{13}C NMR spectra of 2-ethylanthraquinone (Figure S3 and Figure S4).

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Tables

Table 1-5 are available in the Supplemental Files section.

Scheme

Scheme 1-4 are available in supplementary section.

Supplementary Files

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