International Journal of Advanced Chemical Research
Vol. 1, No. 1, PP. 022-023 November 2012
http://www.wrpjournals.com/journal/V/IJMSC

RESEARCH ARTICLE

Study of Friedel-Crafts Acylation Process In Different Ionic Liquids

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Ionic liquids are Non-flammable, Negligible vapor pressure (High boiling point) High thermal, chemical, electrochemical stability and having high solvating ability. They are having tunable miscibility with water and Organic solvents, High electrical conductivity and Low viscosity in the liquid state. In present study we have synthesized acetates by Friedel crafts acylation. Mechanistic study of synthesis of different acetates in different Ionic Liquids has been reported here. In the presents study we have used triethylammonium sulphate [TEA][HSO_4], triethylammonium hydrogen chloride [TEA][HCl], choline bromide [ChBr], tetrabutylammonium bromide [TBAB], 1–butyl-3-methylimidazolium hexafluorophosphate [bmim][PF_6]. In the conventional method the yield is low and required more time. Optimization of reaction condition in synthesis of acetates investigated that 1–butyl-3-methylimidazolium hexafluorophosphate was the appropriate solvent with maximum yield and time factor.

Key words: Friedel-Crafts acylation, solvent-free.

INTRODUCTION

Friedel-Crafts acylation are a well-known class of reactions with a great industrial importance for the preparation of aryl ketones by acylation of arenes.[1] Reagents used are not only acyl halides but also carboxylic acids, esters, anhydrides, and ketenes [2] Friedel-Crafts acylation are generally performed using a Lewis acid catalyst, commonly $AlCl_3$. However, there are several drawbacks associated with this type of reactions. Friedel-Crafts acylation are not truly catalytic reactions, as they actually consume one molar equivalent of $AlCl_3$ per mole of reactant. The net result is massive usage of $AlCl_3$ and problems associated with disposal of salts and oxide by-products. In fact, the isolation of the product typically is carried out by quenching the reaction mixture with water. The hydrolysis process generates a large amount of aqueous solutions and suspensions containing aluminum salts, which requires additional treatment steps for eventual disposal of those solutions and suspensions, and which significantly increases the cost of the process.

Another drawback derived from the industrial application of Friedel-Crafts reactions relates to the solvents used. Common solvents for the reaction include chlorine-containing solvents such as methylene chloride or 1, 2-dichloroethylene, and volatile hydrocarbon solvents. In today's society the introduction of cleaner technologies in industry (the so-called "Green Chemistry") has become a major concern. Thus, the search for alternatives to environmentally damaging solvents has become a topic of highest priority. In the past few years, ionic liquids have received an upsurge of interest as green solvents, mainly as replacements for conventional media in chemical processes. Ionic liquids are organic salts with melting points under 300° C., often under room temperature. The most common cations in ionic liquids are imidazolium and pyridinium derivatives, although phosphonium and tetraalkylammonium derivatives often can also be used. Some suitable anions for ionic liquids are Cl^-, Br^-, I^-, PF_6^-, $CF_3CO_2^-$, $CH_3CO_2^-$, $CF_3CO_2^-$, SO_4^{2-}, NO_3^-, and $AlCl_4^-$. Ionic liquids have several properties that make them suitable as potential solvents for synthesis. They are liquids in a wide temperature range. They do not have measurable vapor pressure, therefore reactions can be carried out in closed reactors without any vapor release to the atmosphere. They show very good dissolution properties for most organic and inorganic compounds. They act as Brönsted acids, Lewis acids and/or superacids. Usually they have a high thermal stability up to 200° C. They are non-flammable, not expensive and easy to prepare.

The use of some ionic liquids in Friedel-Crafts acylations carried out with conventional Friedel-Crafts catalyst is known in the art and some patent applications on the subject have been published. Patent application WO 99/19288 describes a somewhat special Friedel-Crafts acylation, carried out in the presence of a complex catalytic ionic liquid system consisting of a Lewis acid (e.g. $FeCl_3$) and a compound of formula QCl, Q being an organic cation. Several alternative materials to Lewis acids have been proposed as catalysts for conventional Friedel-Crafts acylations, including zeolites, superacids, the lithium perchlorate/lanthanum triflate system, etc. But these catalysts are generally effective only under restrictive circumstances.[3] Zeolites have also been proposed as catalyst for Friedel-Crafts acylations in ionic liquids (cf. WO 03/028882). Thus, from what is known in the art it is derived that the provision of a reaction system for Friedel-Crafts acylations which use neither toxic solvents nor conventional Friedel-Crafts catalysts would be of great interest in industry.

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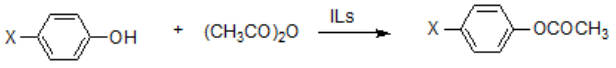
RESULT AND DISCUSSION

According to an aspect of the present invention, there is provided a preparation process of aromatic ketones by a Friedel-Crafts acylation reaction in an ionic liquid, between a Friedel-Crafts aromatic substrate and a Friedel-Crafts acylating agent, characterized in that the ionic liquid has the formula (I) and it is used in the absence of any other catalyst and/or solvent; where $[Q]^+$ is selected from the group consisting of substituted-imidazolium cations, substituted-pyridinium cations, ammonium cations, and phosponium cations. Preferably, $[Q]^+$ is a substituted imidazolium cation.

(I) $[Q]^+[CF_3SO_3]^-$

By Friedel-Crafts aromatic substrate and Friedel-Crafts aromatic acylating agent it is respectively meant any substrate and any reagent which are able to give an aromatic ketone by the acyl-de-hydrogenation classically known as Friedel-Crafts acylation, a textbook reaction that is assumed to occurs via an aromatic electrophilic substitution and that usually needs a Lewis acid catalyst. Preferred ionic liquids of formula (I) are 1-ethyl-3-methylimidazolium trifluoromethanesulfonate, 1,3-diethylimidazolium trifluoromethanesulfonate, and 1,3-dimethylimidazolium trifluoromethanesulfonate, 1-3butylmethyl immidazolium hexafloro phosphate, TBAB etc. In performing the Friedel-Crafts acylation, an aromatic substrate and an acylating agent are reacted together in the presence of the above-mentioned ionic liquids under suitable conditions to produce an aromatic ketone. Apparently, the ionic liquid simultaneously functions both as solvent and as catalyst. The reaction is useful with many types of substrates. Preferably, the Friedel-Crafts acylation agent is selected from carboxylic acid halides, carboxylic acid anhydrides, carboxylic acid esters and carboxylic acids. More preferably, the Friedel-Crafts acylating agent is a carboxylic acid anhydride. In a preferred embodiment of the present invention the Friedel-Crafts acylating agent is acetic acid anhydride, propionoic acid anhydride, butanoic acid anhydride, isobutanoic acid anhydride, pentanoic acid anhydride, benzoic acid anhydride, chloroacetic acid anhydride, acetyl chloride, propanoyl chloride, butanoyl chloride, benzoyl chloride, or chloroacetyl chloride.



Friedel craft Acylation

Table 2. Optimization of reaction conditions in the synthesis of O-acylated product

Entry	Catalyst	T(^{0}C)	Time (min)	Yields(%)
1	[TEA][HSO_4].2$AlCl_3$	Reflux	8	90
2	[bmim]PF_6. 2$AlCl_3$	Reflux	8	95
3	ChBr.2$AlCl_3$	Reflux	20	80
4	[TEA][HCl].2$AlCl_3$	Reflux	15	90
5	TBAB.2$AlCl_3$	Reflux	5	95

Friedel-Crafts aromatic substrate is selected from aromatic benzenoid compounds, aromatic benzenoid-fused compounds, and heteroaromatic compounds resulting from substitution of CH groups by N atoms in the previous ones; all these substrates being optionally substituted by substituents which are stable under Friedel-Crafts reaction conditions, or which have been suitably protected to be stable, according to the general common knowledge of a person skilled in the art.[4]Compounds containing ortho-para directing groups, including alkyl, hydroxy, alcoxy, halogen, and acetamido groups, are easily acylated and give mainly or exclusively the para products. Preferably, the Friedel-Crafts aromatic substrate is benzene, toluene or anisole. More preferably, the aromatic substrate is anisole. In a particular embodiment, the Friedel-Crafts acylating agent is attached to the Friedel-Crafts aromatic substrate, being the carbonyl group of the Friedel-Crafts acylating agent separated from the Friedel-Crafts aromatic substrate by a aliphatic chain from 2 to 4 carbon atoms, so an intramolecular ring closure is done, yielding a (5-7)-membered ring.

The term "Friedel-Crafts acylating agent" include compounds of the general formulae R_1COX, $R_1COOCOR_2$, R_1COOH, and R_1COOR_2; where X is a leaving group selected from Cl and Br; R_1 and R_2 are radicals, same or different, selected from the group consisting of H, (C_1-C_{40})-alkyl, (C_1-C_{40})-alkenyl, (C_1-C_{40})-alkynyl, or any of those groups substituted with (C_1-C_6)-alkyl, (C_1-C_6)-alcoxy, CN, OH or NO_2; R_1 and R_2 can also be selected from β-naphtyl, phenyl, Ph-(CH_2)n- with n=1-3, aliphatic heterocycles and aromatic heterocycles, and a radical derived from those through a mono- or a di-substitution on their rings, the substituents being a radical independently selected from the group consisting of halogen, (C_1-C_4)-alkyl, (C_1-C_4)-alcoxy, CN, OH or NO_2.

Conclusion

The present invention allows to carry out Friedel-Crafts acylation with good yields and high selectivity in para position of the Friedel-Crafts aromatic substrate. It is advantageous with regard to conventional Friedel-Crafts acylation reactions, since chlorine-containing solvents and conventional Friedel-Crafts catalysts are not used. Besides, aqueous work-up is not required to isolate the product of the reaction. Thus, the product can be easily separated from the ionic liquid by a physical process such as for example by solvent extraction with an inert solvent. Furthermore, the ionic liquid can be reused for further reactions once the previous products/reactants have been removed.

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