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Synthesis of chalcones via Claisen–Schmidt condensation reaction catalyzed by acyclic acidic ionic liquids

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ABSTRACT

Some recyclable acyclic SO_3H-functionalized ionic liquids have been used as catalysts for the synthesis of chalcones by Claisen–Schmidt condensation. The chalcones could simply be separated from the catalyst by decantation. After removal of the water from the reaction mixture the catalysts could be recycled and reused for several times without noticeably decreasing the catalytic activity.

1. Introduction

Chalcones and its derivatives are attracted increasing attention due to numerous pharmacological applications. They are main precursors for the biosynthesis of flavonoids and exhibit various biological activities such as anti-cancer [1], anti-inflammatory [2], nitric oxide regulation [3] and anti-hyperglycemic agents [4]. Traditionally, chalcones could be obtained via the Claisen–Schmidt condensation carried out in basic or acidic media under homogeneous conditions [5]. The heterogeneous catalysts have also been used for the Claisen–Schmidt condensation, including Lewis acids [6–9], Brønsted acids [10], solid acids [11–14], solid bases [15–17] and other catalysts with more or less success [18,19].

With the increasing public concern over environmental degradation and future resources, it is of great importance for chemists to come up with new approaches that are less hazardous to human health and environment. Being employed in large amounts and are usually volatile liquids, the solvents used in organic synthesis are high on the list of environmental pollutants. For overcoming these problems one approach is to use the water as the green medium [20], another approach is to develop new processes involving the solvent-free conditions. In recent years, ionic liquids have been emerged as a powerful alternative to conventional molecular organic solvents due to their particular properties, such as undetectable vapor pressure, wide liquid range, as well as ease of recovery and reuse, and making them a greener alternative to volatile organic solvents [21,22]. Combining the useful characteristics of solid acids and mineral acids, Brønsted-acidic task-specific ionic liquids (TSILs) are designed to replace traditional mineral liquid acids, such as sulfuric acid and hydrochloric acid in chemical processes [23]. Such acidic TSILs have dual role (solvent and catalyst) in organic reactions [24–27]. In fact, the use of Brønsted-acidic TSILs as catalysts is an area of ongoing activity; however, development and exploration of acidic TSILs are currently in the preliminary stage.

We are especially interested in developing the potential use of efficient, simple and inexpensive TSILs catalysts. In our previous work some novel and relatively cheap SO_3H-functional halogen-free acidic ionic liquids that bear an alkane sulfonic acid group in an acyclic trialkylammonium cation have been synthesized and their catalytic activity for acid-catalyzed reactions have also been investigated [28–31]. In continuation of our work in studying acid-catalyzed reactions in ionic liquids, we report here the synthesis of chalcones via the Claisen–Schmidt condensation in acidic ionic liquids.

2. Experimental

2.1. Materials and methods

Melting points were determined on Xd–6 microscope melting apparatus and reported uncorrected. ^1H NMR spectra were recorded on Bruker DRX300 (300 or 500 MHz) and ^{13}C NMR spectra

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on Bruker DRX300 (75.5 MHz) spectrometer. Mass spectra were obtained with automated FININIGAN Trace Ultra-Trace DSQ GC/MS spectrometer. All chemicals (AR grade) were commercially available and used directly without further purification.

2.2. Synthesis of SO_3H-functional halogen-free acidic ionic liquid (TSILs)

All acyclic SO_3H-functionalized halogen-free acids such as [TMPSA][HSO_4], [TEPSA][HSO_4] were synthesized according to our previous methods [31], the pyridine, imidazole-based SO_3H-functionalized ionic liquids for comparison were obtained according to reported methods [25,30]. The structures of TSILs were analyzed by ^{1}H NMR, ^{13}C NMR and MS spectral data (Scheme 1).

The selected spectral data for SO_3H-functionalized halogen-free TSILs:

N,*N*,*N*-trimethyl-*N*-propanesulfonic acid ammonium hydrogen sulfate [TMPSA][HSO_4] ^{1}H NMR (300 MHz, D_2O): δ 3.22 (t, J = 7.2 Hz, 2H, N–CH_2–C–C–SO_3), 2.90 (s, 9H, N–CH_3), 2.73 (t, J = 7.8 Hz, 2H, N–C–C–CH_2–SO_3), 1.99 (m, 2H, N–C–CH_2–C–SO_3). ^{13}C NMR (75.5 MHz, D_2O): δ 65.00, 52.51, 47.89, 18.85. MS (*m*/*z*): 279.05 (M^+), 182.14(100).

N,*N*,*N*-triethyl-*N*-propanesulfonic acid ammonium hydrogen sulfate [TEPSA][HSO_4] ^{1}H NMR (300 MHz, D_2O): δ 3.22–3.05 (m, 8H, (6H + 2H), N–CH_2–CH_3, N–CH_2–C–C–SO_3), 2.85 (t, J = 7.2 Hz 2H, N–C–C–CH_2–SO_3), 1.97 (m, 2H, N–C–CH_2–C–SO_3), 1.12 (t, 9H, N–C–CH_3). ^{13}C NMR (75.5 MHz, D_2O): δ 56.00, 52.95, 48.34, 18.93, 8.04. MS (*m*/*z*): 321.05 (M^+), 322.05, 320.15, 194.05(100).

N,*N*,*N*-tributyl-*N*-propanesulfonic acid ammonium hydrogen sulfate [TBPSA][HSO_4] ^{1}H NMR (500 MHz, D_2O): δ 3.28 (t, 2H, J = 4.0 Hz, N–CH_2–C–C–SO_3), 3.13 (t, 6H, J = 8.5 Hz, N–CH_2–C–C–CH_3), 2.85 (t, 2H, J = 7.0 Hz, N–C–C–CH_2–SO_3), 2.03 (m, 2H, N–C–CH_2–C–SO_3), 1.56 (m, 6H, N–C–CH_2–C–CH_3), 1.27 (m, 6H, N–C–C–CH_2–CH_3), 0.84 (t, 9H, J = 7.5 Hz, N–C–C–C–CH_3). ^{13}C NMR (75.5 MHz, D_2O): δ 58.49, 50.66, 48.42, 23.93, 20.36, 19.16, 14.46. MS (*m*/*z*): 405.29 (M^+), 406.28, 404.28(100).

N,*N*,*N*-trimethyl-*N*-butanesulfonic acid ammonium hydrogen sulfate [TMBSA][HSO_4] ^{1}H NMR (300 MHz, D_2O): δ 3.24 (t, J = 8.4 Hz, 2H, N–CH_2–C–C–C–SO_3), 2.99 (s, 9H, N–CH_3), 2.85 (t, J = 7.5 Hz, 2H, N–C–C–C–CH_2–SO_3), 1.82 (m, 2H, N–C–CH_2–C–C–SO_3), 1.70 (m, 2H, N–C–C–CH_2–C–SO_3). ^{13}C NMR (75.5 MHz, D_2O): δ 66.15, 53.16, 50.31, 21.46, 19.93. MS (*m*/*z*): 293.36 (M^+), 196.39(100).

N,*N*,*N*-triethyl-*N*-butanesulfonic acid ammonium hydrogen sulfate [TEBSA][HSO_4] ^{1***}H NMR (300 MHz, D_2O): δ 3.15 (q, J = 7.2 Hz, 6H, N–CH_2–CH_3), 3.07 (t, J = 8.4 Hz, 2H, N–CH_2–C–C–C–SO_3), 2.82 (t, J = 7.2 Hz, 2H, N–C–C–C–CH_2–SO_3), 1.68 (m, 4H, N–C–C_2H_4–C–SO_3), 1.11 (m, J = 7.2 Hz, 9H, N–CH_2–CH_3). ^{13}C NMR (75.5 MHz, D_2O): δ 56.21, 52.85, 50.32, 21.50, 20.20, 6.90. MS (*m*/*z*): 335.35 (M^+), 208.36(100).

N-propanesulfonic acid pyridinium hydrogen sulfate [PyPSA][HSO_4] ^{1}H NMR (300 MHz, D_2O): δ 8.62 (d, J = 6.0 Hz, 2H, H-2, H-6), 8.30 (t, J = 7.8 Hz, 1H, H-4), 7.84 (t, J = 6.9 Hz, 2H, H-3, H-5), 4.51 (t, J = 7.5 Hz, 2H, N–CH_2–C–C–SO_3), 2.73 (t, J = 7.2 Hz, 2H, N–C–C–C–CH_2–SO_3), 2.18–2.23 (m, 2H, N–C–CH_2–C–SO_3). ^{13}C NMR (75.5 MHz, D_2O): δ 146.35, 144.70, 128.82, 60.28, 47.48, 26.47.

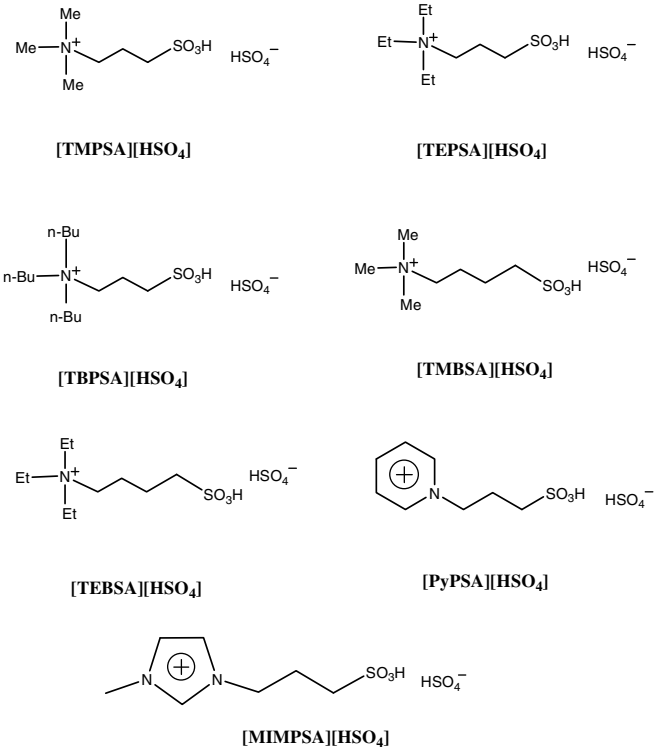
1-methyl-3-propanesulfonic acid imidazolium hydrogen sulfate [MIMPSA][HSO_4] ^{1}H NMR (300 MHz, D_2O): δ 8.47(s, 1H, CH), 7.24(d, J = 1.5 Hz, 1H, CH), 7.17(d, J = 1.5 Hz, 1H, CH), 4.08 (t, J = 6.9 Hz, 2H, N–CH_2–C–C–SO_3), 3.62 (s, 3H, N–CH_3), 2.64 (t, 2H, J = 7.5 Hz, 2H, N–C–C–CH_2–SO_3), 2.03 (m, 2H, N–C–CH_2–C–SO_3). ^{13}C NMR (75.5 MHz, D_2O): δ 136.53, 124.32, 122.57, 48.13, 47.66, 36.46, 25.48. MS (*m*/*z*): 302.0 (M^+), 300.93(100).

2.3. General procedure for the Claisen–Schmidt condensation catalyzed by TSILs

In a typical experiment, weighed 10 mmol benzaldehyde, 10 mmol acetophenone, and 2.0 mmol ionic liquid TSILs were mixed in a 25 mL round-bottom flask equipped with a distillation condenser. The reaction was typically allowed to proceed for a length of time at desired temperature with the vigorous stirring under N_2 atmosphere (Scheme 2), the resulting mixture became biphasic system when stilled for several minutes, and the upper product phase was separated from the catalyst by decantation (for 3a–i) or extracting by CH_2Cl_2 (for 3j). The catalyst was extracted with CH_2Cl_2 and dried in a vacuum for 2 h before reusing. The product was purified by recrystallization from ethanol and identified by ^{1}H NMR, and physical data (m.p) with those reported in literature.

The selected data for chalcone 3a:

1,3-Diphenypropenone (3a, $C_{15}H_{12}O$). Yellow crystals; m.p. 55–56 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.02 (dd, J = 1.5 Hz, J = 6.9 Hz, 2H), 7.82 (d, J = 15.9 Hz, 1H), 7.41–7.67 (m, 9H). MS (*m*/*z*): 209.07 (M^+ + 1, 100).



Scheme 1. Structures of the TSILs used in Claisen–Schmidt condensation.

3. Results and discussion

For the beginning of this study, benzaldehyde and acetophenone were employed as the model reactants at 140 °C under N_2 atmosphere in TSILs for a length of time to compare the catalytic performance of the TSILs.

As shown in Table 1, <5% yields of chalcone could be detected by GC in the absence of ionic liquids (entry 1), which indicated that the catalyst should be absolutely necessary for the Claisen–Schmidt reaction. All the seven TSILs proved to be very active, leading to 90–95% yield of chalcone in the presence of 20% TSILs (entries 2–16). In addition, ionic liquids containing the shorter length of alkyl chain are relatively cheaper. Further, the better