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Mild and convenient one pot synthesis of Schiff bases in the presence of P_2O_5/Al_2O_3 as new catalyst under solvent-free conditions

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Abstract

In this study P_2O_5/Al_2O_3 is found to catalyze the preparation of Schiff bases from the reaction of carbonyl compounds with primary amines efficiently under solvent-free conditions. The advantages of this friendly, environmentally and mild method are such as simplicity of the reaction procedure, the elimination of solvents, simple work-up, high product yields and short reaction times.

Keywords: Catalyst; Schiff base; P_2O_5; Solvent-free; Alumina

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1. Introduction

Organic reactions under solvent-free conditions have gained in popularity in recent years [1]. This is because solvent-free reactions usually need shorter reaction times and simpler reactors and resulting simple and efficient work up procedures. Furthermore, reactions, which performed under solvent-free conditions especially have been important and attracted much attention [2].

The development of cleaner technologies is a major in green chemistry. Among the several aspects of green chemistry, the reduction or replacement of volatile organic solvents from the reaction medium is of at most importance [3]. The solid-state reaction or solvent free reaction has many advantages: reduced pollution, low costs and simplicity in process and handling. These factors are especially important in industry [4]. For the increasing environmental and economical concerns in recent years, it is now essential for chemists to search environmentally reactions as many as possible.

Schiff base ligands, as variety of compounds with imine group, have gained importance because of physiological and pharmacological activities associated with them. They constitute an interesting class of chelating agents capable of coordination metal ions given complex, which serves as models for biological system [5–7]. A lot of investigations have been made concerning the synthesis of Schiff bases [8–13], but these procedures have some limitations such as low yield, long reaction times, highly environmental pollution regarding to solvent, hardness reaction work up. These are once again topical in connection with a diverse rang of application in organic synthesis, bioorganic and medicinal chemistry. Also these complexes find many important catalytic applications, such as catalysts for epoxidation of olefins [14], alkene cyclopropanation [15], trimethylsilylcyanation of aromatic aldehydes [16], borohydride reduction of aromatic ketones [17], asymmetric oxidation of methyl phenyl sulfide [18], enantioselective epoxidation of silyl enol [19], ring opening polymerization of lactide [20], application of ion-selective electrodes [21–25], determination of heavy metal ions in environment samples [26], extraction of metal ions [27], etc.

A solvent-free or solid state reaction may be carried out using the reactants alone or incorporating them in clays, zeolites, silica, alumina or other matrices [28]. In recent years, β-zeolite [29], montmorillonite clays [30], SiO_2 and Al_2O_3 were employed as catalysts for this purpose to obtain relatively better results.

Alumina is a particularly interesting metal oxide as it is widely used industrially as filler, adsorbent, drying agent, catalyst support and reagent. γ-Alumina is the transition alumina most commonly utilized to carry out surface organic chemistry [31]. In contrast to clays and zeolites, this material does not contain accessible channels or cavities and shows large surface area and highly porous exteriors available to substrates [32]. Although some of these methods represent a convenient proce-

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dure with good to high product yields, representation of a new, efficient and facile procedure for synthesis of these compounds can be very significant.

In continuation of our research, because of these economical and environmental reasons, here we hope to report a procedure using P_2O_5/Al_2O_3 as a catalyst for the synthesis of Schiff bases from carbonyl compounds and different amines in the absence of a solvent under mild reaction conditions.

2. Experimental

2.1. Materials

Chemicals were purchased from the Merck and Fluka Chemical Companies in high purity. All of the materials were of commercial reagent grade. The amines and carbonyl compounds were purified by standard procedures.

2.2. Apparatus

IR spectra were recorded as KBr pellet on a Perkin-Elmer 781 spectrophotometer and an Impact 400 Nicolet FT-IR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ and DMSO solvents on a Bruker DRX-400 spectrometer (400 MHz) using TMS as an internal reference. Melting points obtained with a Yanagimoto micro melting point apparatus are uncorrected. The purity determination of the substrates and reactions monitoring were accomplished by TLC on silica-gel polygram SILG/UV 254 plates.

2.3. General procedure

2.3.1. Procedure for preparation of P_2O_5/Al_2O_3 catalyst

A mixture of phosphorous pentoxide (1 g) and alumina (6 g) have been placed in a flask and stirred for 2 h at room temperature. The obtained homogeneous mixture, free flowing, white powder substance is sensitive towards moisture and thus should be stored in a dedicator.

2.3.2. General procedure and then a typical reaction for preparation of Schiff bases **3a–3k** and **6a–6e**

In a typical reaction, a mixture of benzaldehyde (0.21 g, 2 mmol), isopropyl amine (0.25 g, 2 mmol) and P_2O_5/Al_2O_3 mixture (0.6 g, 3 mol% of P_2O_5/benzaldehyde) was ground thoroughly in a mortar. The resulting mixture was placed in a flask and mechanically stirred for 30 min. The progress of the reaction was monitored by TLC. After completion of the reaction, methanol (15 ml) was added to the reaction mixture, filtered off the solid product and was washed with cold methanol. The crude product was purified by recrystallization from petroleum ether and the pure Schiff base **3a** was obtained as a yellow liquid in 80% yield. The Schiff base products were identified by spectroscopic data.

Benzylidene isopropylamine (**3a**): yellow liquid (lit) [33]; ^{1}H NMR ($CDCl_3$, 400 MHz)/δ ppm 1.20 (d, 6H, $J = 7.1$ Hz), 3.40–3.55 (m, 1H), 7.29–7.75 (m, 5H), 8.38 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz)/δ ppm 24.3, 62.1, 136.7, 158.7.

Benzylidene cyclohexylamine (**3b**): yellow liquid (lit) [34]; ^{1}H NMR ($CDCl_3$, 400 MHz)/δ ppm 1.10–1.80 (m, 10H), 3.21 (m, 1H), 7.39–7.67 (m, 5H), 8.38 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz)/δ ppm 24.8, 25.7, 34.5, 70.1, 136.7, 158.5.

Benzylidene allylamine (**3c**): yellow liquid (lit) [35]; ^{1}H NMR ($CDCl_3$, 400 MHz)/δ ppm 4.21 (dd, 2H, $J_1 = 2.2$ Hz, $J_2 = 6.1$ Hz), 5.08–5.25 (dd, 2H, $J_1 = 2.2$ Hz, $J_2 = 10.1$ Hz), 5.80–6.12 (m, 1H), 7.31–7.72 (m, 5H), 8.35 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz)/δ ppm 63.5, 116.1, 135.9, 136.2, 162.1.

N-phenyl-N-(1-phenylmethylidene) amine (**3d**): white solid; m.p. 65–67 °C; IR (KBr)/ν (cm^{-1}) 3052 (Ar, C–H), 1623 (s, C=N), 1405, 1560 (Ar, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz)/δ ppm 7.2–7.78 (m, 10H), 8.3 (s, 1H).

N-[1-(3-methyl-phenyl)-methylidene]-N-phenylamine (**3e**): brown oil; IR (KBr)/ν (cm^{-1}) 3027 (Ar, C–H), 1630 (s, C=N), 1435, 1500 (Ar, C=C), 2900 (C–H); ^{1}H NMR ($CDCl_3$, 400 MHz)/δ ppm 2.6 (s, 3H), 7.2–8.2 (m, 9H), 8.65 (s, 1H).

N-[1-(4-methyl-phenyl)-methylidene]-N-phenylamine (**3f**): brown oil; IR (KBr)/ν (cm^{-1}) 3027 (Ar, C–H), 1630 (s, C=N), 1435, 1500 (Ar, C=C), 2900 (C–H); ^{1}H NMR ($CDCl_3$, 400 MHz)/δ ppm 2.2(s, 3H), 6.8–7.7 (m, 9H), 8.25 (s, 1H).

N-[1-(3-chloro-phenyl)-methylidene]-N-phenylamine (**3g**): brown oil; IR (KBr)/ν (cm^{-1}) 3060 (Ar, C–H), 1623 (s, C=N), 1435, 1560 (Ar, C=C), 1050 (C–Cl); ^{1}H NMR ($CDCl_3$, 400 MHz)/δ ppm 6.8–7.8 (m, 9H), 8.3(s, 1H).

N-[1-(4-chloro-phenyl)-methylidene]-N-phenylamine (**3h**): white solid; m.p. 53–56 °C; IR (KBr)/ν (cm^{-1}) 3060 (Ar, C–H), 1618 (s, C=N), 1475, 1567 (Ar, C=C), 1086 (C–Cl); ^{1}H NMR ($CDCl_3$, 400 MHz)/δ ppm 7.2–8.4 (m, 9H), 8.6 (s, 1H).

N-[1-(4-bromo-phenyl)-methylidene]-N-phenylamine (**3i**): pale yellow solid; m.p. 61–63 °C; IR (KBr)/ν (cm^{-1}) 3056 (Ar, C–H), 1625 (s, C=N), 1445, 1535 (Ar, C=C), 1135 (C–Br); ^{1}H NMR ($CDCl_3$, 400 MHz)/δ ppm 7.2–8.4 (m, 9H), 8.6 (s, 1H).

N-[1-(3-nitro-phenyl)-methylidene]-N-phenylamine (**3j**): yellow solid; m.p. 66–68 °C; IR (KBr)/ν (cm^{-1}) 3010 (Ar, C–H), 1625 (s, C=N), 1470, 1582 (Ar, C=C), 1320, 1517 (N–O); ^{1}H NMR (DMSO, 400 MHz)/δ ppm 7.3–7.93 (m, 9H), 8.5 (s, 1H).

N-[1-(4-nitro-phenyl)-methylidene]-N-phenylamine (**3k**): yellow solid; m.p. 138–140 °C; IR (KBr)/ν (cm^{-1}) 3010 (Ar, C–H), 1625 (s, C=N), 1480, 1593 (Ar, C=C), 1310, 1500 (N–O); ^{1}H NMR (DMSO, 400 MHz)/δ ppm 7.3–7.93 (m, 9H), 8.5 (s, 1H).

N-[1-(4-methyl-phenyl)-methylidene]-N-phenylamine (**6a**): brown oil; IR (KBr)/ν (cm^{-1}) 3027 (Ar, C–H), 2900 (C–H), 1630 (s, C=N), 1435, 1500 (Ar, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz)/δ ppm 2.2 (s, 3H), 6.8–7.7 (m, 9H), 8.25 (s, 1H).

N-(4-nitrobenzylidene)-benzylamine (**6b**): m.p. 56–58 °C (lit) [36]; ^{1}H NMR ($CDCl_3$, 400 MHz)/δ ppm 4.84 (s, 2H), 7.30–8.07 (m, 9H), 8.42 (s, 1H).

Benzylidene benzylamine-1-methyl (**6c**): yellow solid; m.p. 56–58 °C (lit) [37]; ^{1}H NMR ($CDCl_3$, 400 MHz)/δ ppm 2.25 (s, 3H), 4.75 (s, 2H), 7.10–7.80 (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz)/δ ppm 15.9, 57.6, 140.6, 141.1, 165.1.

Benzylidene cyclohexylamine-1-methyl (**6d**): liquid (lit) [38]; ^{1}H NMR ($CDCl_3$, 400 MHz)/δ ppm 1.10–1.80 (m, 10H), 2.15 (s, 3H), 3.20 (m, 1H), 7.10–8.0 (m, 5H); ^{13}C NMR ($CDCl_3$,