



Silica supported-double metal cyanides (DMCs): A green and highly efficient catalytic protocol for isomerisation of 2'-hydroxychalcones to flavanones

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ARTICLE INFO

Article history:

Received 6 June 2012

Received in revised form 26 February 2013

Accepted 3 March 2013

Available online 19 March 2013

Keywords:

Silica supported-double metal cyanide

(DMC) catalyst

Isomerisation

2'-Hydroxychalcones

Flavanones

ABSTRACT

Four different double metal cyanides (NiHCFe, CrHCFe, MnHCFe and ZnHCFe) were synthesized, followed by adsorbed on silica gel and used as Lewis acid catalyst in the isomerisation of substituted 2'-hydroxychalcones to flavanones under solvent-free (dry) condition. Optimization of the reaction condition, temperature effects, DMC catalysts loading and re-useable catalytic activity were further studied during the reaction. Among these catalysts, NiHCFe at 35 mol% loading gave excellent yield (90%) at 100 °C temperature in 1.15 h. Catalyst (NiHCFe) easily recovered and re-used six times without much loss of its catalytic activity which gave 80–85% product yields each time. However, these DMCs were failed to give product in the solution phase even prolonging the reaction time at reflux temperature. Similarly, isomerization of substituted 2'-aminochalcones gave 2–5% yields either in solution phase or under solvent-free condition.

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1. Introduction

Flavanones (2,3-dihydroflavones) are central intermediate in the biogenesis of flavonoids and are present in plants as the largest single group conferring oxygen ring compounds [1]. They have no direct involvement in the growth and development of plants. However, they play an important role in protecting the plants from microbes and insects attack [2]. These polyphenolic molecules are the most fascinating and useful secondary metabolites which constitute an important component of human diet and known for their antioxidant activities [3,4]. They have further diverse spectrum of biological activities that include hepatoprotectors, hypotensive, antifungal, antibacterial and antitumor [5–8]. In the synthesis of pharmaceutical and biological significance molecules, they are widely used as synthons in the laboratory [9].

In the biogenesis, 2'-hydroxychalcones gave flavanones in the presence of enzyme chalcone isomerase [10]. Therefore, 2'-hydroxychalcones are commonly used in the flavanones synthesis under different acid and base [11,12] catalysts, thermolysis, electrolysis and photolysis [13] in the laboratories. These reactions gave variable yields (20–90%) depending upon the substituents on the aromatic rings. Flavanones have also been prepared using other methods like condensation of phenylpropionic acid with phenols [14,15]; solvent free synthesis using MW-irradiation of phloroglucinol and β -ketoesters [16]; using phase transfer catalysts

like tetrabutylammonium iodide, tetrabutylphosphonium bromide, hexadecyltrimethylammonium bromide; organocatalysts like glycine, L-proline, L-alanine, L-leucine and pyridine; ZnO supported-metal oxide (MgO, BaO, K₂O and Na₂O) catalysts under solvent free condition at high temperature [17–20] and MgO- and ZnO-impregnated with various other supports as HZSM-5, Al₂O₃ and SiO₂ [21–24]. Generally, it was observed that the yield of flavanone is less in solid-supported catalysts up to 100 °C might be due to less adsorption on the active sites and at high temperature (above 160 °C), the yield of flavanone is reduced due to prevention of adsorption [25]. To obviate such problems, recently several activators/promoters such as Lewis acids and metal salts, MW, ultrasound and solid support methods have been introduced [26–28]. However, some of these procedures have drawbacks such as long reaction time, decomposition, low yields, use of toxic reagents and tedious work up procedures [29–31] due to high temperature and deactivated and sterically hindered aromatic rings. Therefore, we have interest in new catalytic system for the synthesis of flavanones. Indeed, we need to develop an efficient and green protocol due to the growing awareness about environmental concerns. Therefore, the organic chemists are under increasing pressure to alter current working practices for the sustainable development in academia and industry research and to find environmentally benign and greener alternatives.

The solid support chemistry has been used for many syntheses [32]. Among the various advantages that solid-phase synthesis offers are the ability to use excess quantities of reagents to force reactions to completion and the easy of product isolation by simple filtration, thus affording the clean products with no further

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need for conventional work-up and purification. Therefore, homogeneous catalysts have been extensively investigated, but only few heterogeneous catalysts have been found. Heterogeneous catalysts in the organic synthesis have special interest from environmental and economical point of view. They have high turn-over numbers and easily separated from reaction mixtures. Similarly, it is found that the cyclization reaction of hydroxy group to a carbon–carbon unsaturated bond (like 2'-hydroxychalcones) is thermodynamically feasible but has high activation barriers.

The double metal cyanides (DMCs) are heterogeneous catalysts which have zeolite-type case structure and contain only Lewis acid sites [33]. These lowers the activation energy and so used as industrially applied solid Lewis catalysts for the ring opening and polymerization of epoxides producing polyether–polyols [34], transesterification of carbonates [35] and multi-component coupling reactions [36]. They were also reported as catalysts in hydroamination, copolymerization of CO₂ with propylene, cyclohexene and other epoxide ring opening reactions [37–39].

We report herein first time the use of NiHCFe, CrHCFe, MnHCFe, ZnHCFe catalysts for the isomerisation of 2'-hydroxychalcone to flavanone using silica gel support under solvent-free condition.

2. Experimental

2.1. Reagents and materials

The reagents (chemicals) were purchased from commercial sources and used without further purification. All reactions were monitored by TLC using pre-coated silica gel aluminum plates (contain ~13% CaSO₄ · ½ H₂O, silica gel/UV₂₅₄) purchased from Merck. Visualization of TLC plates was accomplished with UV lamp (short UV, 254 nm) and charring with 5% methanolic H₂SO₄ spray reagent. Metal hexacyanoferrate (MHCFe) was synthesized from potassium hexacyanoferrate (II), following Alam et al. method [40–42]. Chalcone derivatives were synthesized according a reported procedure [43,44].

2.2. Equipment

Melting points were recorded on perfit apparatus and are uncorrected. Elemental analysis was performed on a Vario EL–HNS analyzer. FT infrared (FTIR) spectra were recorded on a Nexus Thermo Nicolet FT-IR spectrometer using KBr pellets. ¹H and ¹³C NMR spectra were recorded in deuterated chloroform (CDCl₃) on a 500 MHz and 125 MHz (Bruker) respectively. Chemical shifts are given in parts per million (ppm) referenced to TMS.

2.3. Preparation of metal hexacyanoferrates (II)

A solution of potassium hexacyanoferrate (II) (167 mL, 0.1 M) was slowly added to an aqueous solution of the respective metal nitrate (500 mL, 0.1 M) with constant stirring at room temperature. A slight excess of metal salt was used for complete precipitation. A reaction mixture was then heated at 60 °C on a water bath for 2–3 h and kept as such for 24 h at ambient temperature. After 24 h, the precipitate was filtered on a Buckner funnel, washed thoroughly with Millipore water and dried in an oven at 60 °C. The dried product was powdered and sieved with 100 mesh size.

2.4. General procedure for the adsorption of double metal cyanide on silica

To a mixture of double metal cyanide (DMC, 35 mol%, CrHCFe – 12.5 mg; MnHCFe – 11.6 mg; NiHCFe – 12 mg; ZnHCFe – 13.3 mg) and silica gel (3 mmol, 180.24 mg) was added minimum amount of water. The slurry was stirred and grinded for 2 min, followed

by completely dried by heating under vacuum. DMCs–silica gel adsorbed catalysts were directly used in the reaction.

2.5. General procedure for the synthesis of flavanones

2'-Hydroxychalcone (1 mmol) in minimum CHCl₃ was added drop wise on a mixture of silica gel (3 mmol, 180.24 mg) and NiHCFe catalyst (35 mol%, 12 mg) or 2'-hydroxychalcone (1 mmol) in minimum CHCl₃ was added drop wise on DMCs–silica gel adsorbed catalysts (190–192 mg). Followed by evaporation of solvent, the reaction mixture was stirred and grinded at 100 °C temperature. Thin layer chromatography (TLC) monitoring, the reaction was completed in 1–1.15 h. The reaction mixture was cooled, dissolved in dichloromethane (CH₂Cl₂) and filtered DMC catalyst dried under vacuum for re-use. Dichloromethane solvent was evaporated in vacuo and recrystallized from methanol to obtain the pure product.

2.6. Characterization data for compounds 1b–20b

2-(4-Methoxyphenyl)-2,3-dihydrochromen-4-one (**1b**): Yield 80%; light yellow solid; mp: 95–96 °C (Lit. [45] 95–97 °C); IR ν_{\max} (KBr, cm⁻¹): 2956, 2923, 1680 (C=O), 1590, 1320, 1225; ¹H NMR (500 MHz, CDCl₃): δ 7.81 (dd, 1H, J=8.0 and 2 Hz), 7.52–7.48 (m, 1H), 7.41 (d, 2H, 8.5 Hz), 7.07–7.03 (m, 2H), 6.96 (dd, 2H, J=8.5 and 1.5 Hz), 5.43 (dd, 1H, J=13.5 and 2.5 Hz), 3.85 (s, 3H), 3.11 (dd, 1H, J=16.5 and 13.5), 2.86 (dd, 1H, J=17.0 and 3 Hz).

2-(4-Bromophenyl)-2,3-dihydrochromen-4-one (**2b**): Yield 90%; light yellow solid; mp: 119 °C (Lit. [46] 118–119 °C); IR ν_{\max} (KBr, cm⁻¹): 2965, 2930, 1685 (C=O), 1566, 1300, 1230; ¹H NMR (500 MHz, CDCl₃): δ 7.82 (dd, 1H, J=8.0 and 2 Hz), 7.48–7.59 (m, 3H), 7.34–7.49 (m, 2H), 7.03–7.10 (m, 2H), 5.47 (dd, 1H, J=13.0 and 3 Hz), 3.04 (dd, 1H, J=16 and 13.0 Hz), 2.88 (dd, 1H, J=16 and 3 Hz).

2-(3,4-Dimethoxyphenyl)-2,3-dihydrochromen-4-one (**3b**): Yield 78%; light yellow solid; mp: 148–149 °C; IR ν_{\max} (KBr, cm⁻¹): 2954, 2934, 1676 (C=O), 1545, 1322, 1221; ¹H NMR (500 MHz, CDCl₃): δ 8.20 (dd, 1H, J=1.5 Hz, J=7.8 Hz), 7.53 (d, 1H, J=7.5 Hz), 7.51 (dd, 1H, J=8 and 2 Hz), 7.40 (dd, 1H, J=8 and 6 Hz), 7.36 (d, 1H, J=2 Hz), 6.96 (d, 1H, J=8 Hz), 6.72 (s, 1H), 5.43 (dd, 1H, J=13.5 and 2.5 Hz), 3.98 (s, 3H), 3.95 (s, 3H), 3.11 (dd, 1H, J=16.5 and 13.5 Hz), 2.86 (dd, 1H, J=17.0 and 3 Hz). ¹³C NMR (125 MHz, CDCl₃): 178.3, 163.3, 156.1, 152.1, 149.3, 133.6, 125.6, 124.2, 123.9, 120.0, 118.0, 111.2, 108.8, 106.4, 56.1.

2-(3,4,5-Trimethoxyphenyl)-2,3-dihydrochromen-4-one (**4b**): Yield 75%; light yellow solid; mp=165–166 °C; IR ν_{\max} (KBr, cm⁻¹): 2956, 2923, 1680 (C=O), 1630, 1600, 1590, 1320, 1300, 1225, 964; ¹H NMR (500 MHz, CDCl₃): δ 8.06 (d, 2H, J=8 Hz), 6.95 (d, 2H, J=8 Hz), 6.66 (d, 1H, J=2.5 Hz), 6.78 (d, 1H, J=2.5 Hz), 5.32 (dd, 1H, J=13.5 and 2 Hz), 3.88 (s, 9H), 2.70 (dd, 1H, J=13.5 and 2.0 Hz), 2.98 (dd, 1H, J=16.8 and 13.0 Hz).

2-(3-Nitrophenyl)-2,3-dihydrochromen-4-one (**5b**): Yield 89%; light yellow solid; mp=173–174 °C (Lit. [47] 174–176 °C); IR ν_{\max} (KBr, cm⁻¹): 2956, 2923, 1698 (C=O), 1630, 1527 (CH=CH), 1490 (CNO₂), 1320, 1230, 965. ¹H NMR (500 MHz, CDCl₃): 8.2 (s, 1H), 8.12 (dd, 2H, J=14 and 3 Hz), 7.6 (d, 1H, 16 Hz), 7.52 (d, 2H, 14 Hz), 6.95 (d, 2H, J=8 Hz), 5.8 (dd, 1H, J=13.5 and 2 Hz), 3.11 (dd, 1H, J=16.5 and 13.5 Hz), 2.86 (dd, 1H, J=17.0 and 3 Hz).

7-Methoxy-2-(3-nitrophenyl)-2,3-dihydrochromen-4-one (**6b**): Yield=86%. light yellow solid; mp=89 °C; IR ν_{\max} (KBr, cm⁻¹): 2985, 1627 (C=O), 1630, 1527, 1486 (CNO₂), 1320, 1224. ¹H NMR (500 MHz, CDCl₃): 8.2 (s, 1H), 8.12 (dd, 1H, J=13 Hz), 7.6 (d, 1H, 16 Hz), 7.52 (d, 2H, 14 Hz), 6.95 (d, 2H, J=8 Hz), 5.8 (dd, 1H, J=13.5 and 2 Hz), 3.73 (s, 3H), 3.11 (dd, 1H, J=16.5 and 13.5 Hz), 2.86 (dd, 1H, J=17.0 and 3 Hz). ¹³C NMR (CDCl₃, 125 MHz): δ 196.9, 165.7, 157.9, 148.6, 141.6, 133.3, 130.4, 129.9, 122.4, 120, 112.7, 105.8, 100.4, 78, 55.9, 42.8.

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