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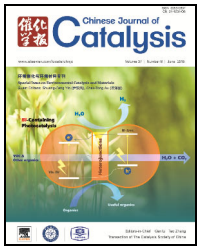

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Lewis base-assisted Lewis acid-catalyzed selective alkene formation *via* alcohol dehydration and synthesis of 2-cinnamyl-1,3-dicarbonyl compounds from 2-aryl-3,4-dihydropyrans

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ABSTRACT

Acid-catalyzed dehydration of alcohols has been widely employed for the synthesis of alkenes. However, activated alcohols when employed as substrates in dehydration reactions are often plagued by the lack of alkene selectivity. In this work, the reaction system can be significantly improved through enhancing the performance of Lewis acid catalysts in the dehydration of activated alcohols by combining with a Lewis base. Observations of the reaction mechanism revealed that the Lewis base component might have changed the reaction rate order. Although both the principal and side reaction rates decreased, the effect was markedly more observed on the latter reaction. Therefore, the selectivity of the dehydration reaction was improved. On the basis of this observation, a new route to synthesize 2-cinnamyl-1,3-dicarbonyl compounds was developed by using 2-aryl-3,4-dihydropyran as a starting substrate in the presence of a Lewis acid/Lewis base combined catalyst system.

1. Introduction

Dehydration of alcohols has been widely studied and employed in the manufacture of olefins together with other valuable intermediates [1]. In the chemical industry, 15% of the global styrene production is obtained through the dehydration of 1-phenylethanol—the byproduct in the propylene oxide synthesis from ethylbenzene hydroperoxide [2]. Therefore, this reaction has been extensively studied [3–8]. Organic chemists often use 1-arylethanol as a substrate to synthesize 1-arylethylene, which is a useful synthon [9–13]. One reason why 1-arylethylene is an attractive compound is because of the abundant accessibility of its starting substrate, making the 1-arylethanol dehydration reaction of significant industrial importance [14]. Although acid catalysts are well-known to be effective for promoting such reactions, when activated alcohols are used, there is a degree of difficulty—because of selectivity to form undesirable by-products—to find a suitable catalyst system that forms 1-arylethylene in a satisfactory yield [15]. To date, there is no current established catalyst system regarding the dehydration of 1-phenylethanol to yield 1-arylethylene. The reasons are two-fold: (1) typical industrial practices prefer the use of solid catalysts; the reported solid acids for the dehydration of 1-phenylethanol are generally associated sophisticated

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operational procedures [16,17]; however, synthetic chemists are not typically familiar with heterogeneous catalysis chemistry and therefore are unable to influence this reaction; (2) to facilitate industrial production, most reported systems for the dehydration of 1-phenylethanol operate in a fixed-bed reactor at high temperatures (> 250 °C) [18]; however, organic compounds with functional substituent groups may not be tolerable at such high temperatures. Although liquid-phase dehydration of 1-phenylethanol has also been investigated using either homogeneous acids [19] or heterogeneous solid acids [20,21], to concomitantly extend the knowledge of this relatively simple reaction to the dehydration of complex alcohol substrates requires a separate model reaction. Therefore, the requirement remains to develop an efficient liquid-phase system for 1-arylethylene production through the dehydration of 1-arylethanol.

Additionally, designing catalysts to achieve tailored properties is currently an area of significant investigation in both catalysis and organic synthesis [22–25]. Various catalyst combinations, such as Lewis acid/Brönsted base [26–28], Lewis acid/Lewis base [29], Lewis acid/Brönsted acid [30–32], Lewis acid/Lewis acid [33], and transition metal/Lewis acid [34,35] have been developed to provide unique catalytic activities. Such combinations not only offer new routes to synthesize bi-functional catalysts [36–41], but also allow newly designed bi-functional catalysts to circumvent technical difficulties encountered in such applications [42–45]. Herein, we introduce a Lewis base-assisted Lewis acid-catalyzed selective alkene formation through alcohol dehydration. This combined acid/base system is particularly effective for the synthesis of 1-arylethylene from activated 1-arylethanol. On the basis of this observation, a new method for the synthesis of 2-cinnarmyl-1,3-dicarbonyl compounds from 2-aryl-3,4-dihydropyrans was also developed by using an analogous acid/base combined catalyst system.

2. Experimental

2.1. General

Infrared spectra were recorded on a Bruker EQUINOX 55 spectrometer using KBr pellets or neat liquid technology. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV-400 or 600. Chemical shifts were expressed in ppm relative to solvated Me_4Si. All chemicals used were of reagent grade and were used as received without further purification. All reactions were conducted in a 10 mL V-type flask equipped with triangle magnetic stirring.

2.2. A typical alcohol dehydration procedure

In a typical reaction, alcohol (0.4 mmol) was mixed with $AlCl_3$ (0.02 mmol, 5 mol%) and triphenylphosphine (PPh_3, 0.02 mmol, 5 mol%) in nitromethane (1.0 mL). Thereafter the mixture was stirred at 80 °C for 2 h. After the reaction, the mixture was cooled to room temperature, and the product was isolated using preparative thin layer chromatography (TLC, eluting solution: petroleum ether/ethyl acetate, 5/1 (v/v)). Tests for substrate scope were all performed with an analogous procedure.

2.3. A typical ring-opening reaction procedure for 2-aryl-3,4-dihydropyrans

In a typical reaction, dihydropyran (0.20 mmol) was mixed with I_2 (0.01 mmol, 5 mol%) and PPh_3 (0.01 mmol, 5 mol%) in nitromethane (1.0 mL). The mixture was then stirred at 80 °C for 1 h. After the reaction, the mixture was cooled to room temperature, and the product isolated using preparative TLC (eluting solution: petroleum ether/ethyl acetate, 5/1 or 3/1 (v/v)). Tests for substrate scope were all performed with an analogous procedure.

(*E*)-3-(3-(*p*-Tolyl)allyl)pentane-2,4-dione (a mixture of enol and ketone form) (**6a**): colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 16.78 (s, 0.36H), 7.29–7.18 (m, 2H), 7.15–7.05 (m, 2H), 6.36 (dd, J = 42.9, 15.9 Hz, 1H), 6.21–5.94 (m, 1H), 3.79 (t, J = 7.3 Hz, 0.5H), 3.14 (d, J = 5.3 Hz, 0.96H), 2.73 (t, J = 7.2 Hz, 1.08H), 2.32 (s, 3H), 2.20 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 203.7, 191.6, 137.4, 137.2, 134.3, 134.0, 132.6, 129.9, 129.3, 129.2, 126.6, 126.1, 126.0, 124.4, 107.6, 68.4, 31.6, 30.9, 30.5, 29.4, 23.1, 21.1. IR (KBr) v: 2956, 2923, 1725, 1702, 1607, 1513, 1420, 1358, 1282, 1151, 970, 797, 505 cm^{-1}. HRMS m/z (ESI) calculated for $C_{15}H_{18}NaO_2$ $[M + Na]^+$ 253.1204 found 253.1224.

(*E*)-Methyl 2-acetyl-5-(4-fluorophenyl)hex-4-enoate (**6e**): colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.33 (dd, J = 8.7, 5.4 Hz, 2H), 6.99 (t, J = 8.7 Hz, 2H), 6.03 (d, J = 1.6 Hz, 1H), 3.76 (s, 3H), 3.44 (s, 1H), 2.65 (ddd, J = 25.1, 15.7, 12.7 Hz, 3H), 2.51–2.40 (m, 2H), 1.37 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C) δ = 176.5, 162.9, 161.2, 137.2, 133.7, 126.7, 126.7, 121.0, 115.1, 115.0, 68.8, 51.9, 47.5, 40.7, 28.4, 27.1. ^{19}F NMR (565 MHz, $CDCl_3$, 25 °C) δ = −115.8. IR (KBr) v: 3523, 2957, 2925, 1720, 1511, 1438, 1381, 1229, 1168, 1027, 819, 540 cm^{-1}. HRMS m/z (ESI) calculated for $C_{15}H_{17}FNaO_3$ $[M + Na]^+$ 287.1059 found 287.1067.

(*E*)-Methyl 2-acetyl-5-(4-chlorophenyl)hex-4-enoate (**6f**) [5]: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.32–7.24 (m, 4H), 6.08 (dd, J = 2.9, 1.6 Hz, 1H), 3.76 (s, 3H), 3.42 (s, 1H), 2.74–2.56 (m, 3H), 2.52–2.38 (m, 2H), 1.37 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C) δ = 207.0, 176.4, 139.5, 133.6, 132.8, 128.4, 126.4, 121.7, 68.8, 52.0, 47.5, 40.4, 28.4, 27.2.

(*E*)-2-Pivaloyl-5-(p-tolyl)pent-4-enenitrile (**6g**): colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.26–7.20 (m, 3H), 7.12 (d, J = 7.6 Hz, 2H), 6.50 (d, J = 15.7 Hz, 1H), 6.12–5.99 (m, 1H), 3.91 (t, J = 7.4 Hz, 1H), 2.75 (dd, J = 11.5, 7.1 Hz, 2H), 2.33 (s, 3H), 1.25–1.22 (m, 9H). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C) δ = 204.9, 137.8, 134.5, 133.6, 129.3, 126.2, 125.5, 122.3, 117.0, 45.6, 37.2, 33.4, 26.0, 21.2. IR (KBr) v: 2968, 2928, 2242, 2206, 1784, 1721, 1513, 1475, 1370, 1282, 1175, 1056, 968, 795, 507 cm^{-1}. HRMS m/z (ESI) calculated for $C_{17}H_{21}NNaO$ $[M + Na]^+$ 278.1521 found 278.1531.

(*E*)-Ethyl 2-(4-methoxybenzoyl)-5-(4-methoxyphenyl)pent-4-enoate (**6h**): colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$, TMS, 25 °C) δ = 8.00 (d, J = 8.9 Hz, 2H), 7.23 (d, J = 8.6 Hz, 2H), 6.94 (d, J