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One-pot green synthesis of enamides and 1,3-diynes

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ABSTRACT

A green organic synthetic method combining reductive acylation of ketoximes and oxidative coupling of terminal alkynes was developed. This novel process enables enamides and 1,3-diynes to be synthesized simultaneously in high yields and under mild conditions without the use of terminal reductants/oxidants.

1. Introduction

Oxidation and reduction are fundamental reactions; however, these reactions produce reduced or oxidized wastes because of their intrinsic properties. In green chemistry, O_2 or H_2O_2 is used in many oxidations [1–5], and H_2 is used in many reductions [6–9]. These reactions, which produce no byproducts or only water as a byproduct, are ideal transformations. However, there are many organic transformations that require stoichiometric or super-stoichiometric terminal oxidants such as Cr(VI), Cu(II), periodate, and *m*-CPBA, or terminal reductants such as nitrites, Zn powder, Fe powder, stannous chloride, and Hantzsch dihydropyridines [10–13]. In accord with the principles of green chemistry [10–16], we hypothesized that if an oxidation was combined with a reduction in one pot, the use of oxidants and reductants could be avoided. This would be an ideal method for minimizing waste generation.

Enamides are versatile building blocks in organic synthesis [17–24]. However, the preparation of enamides involves reductive acylation of ketoximes in the presence of super-stoichiometric Fe powder, PEt_3, or $NaHSO_3$ [25–29]. 1,3-Diynes are useful structures in linearly π-conjugated acetylenic oligomers and nonlinear optical materials [30–32]. The conventional method for the synthesis of 1,3-diynes is oxidative homocoupling of terminal alkynes in the presence of Ag_2O, Me_3NO, Cu(II), or O_2 [33–38]. In this paper, we describe a promising example of green organic synthesis, which combines the oxidative coupling of terminal alkynes for 1,3-diyne formation with reductive acylation of ketoximes for enamide preparation in one pot (Scheme 1).

2. Experimental

2.1. General remarks

Unless otherwise stated, all reagents and solvents were

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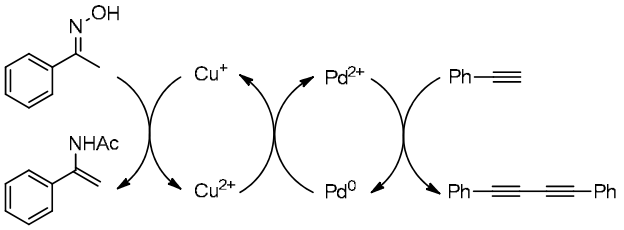

Scheme 1. [Pd/Cu]-catalyzed synthesis of enamides and 1,3-diynes.

purchased from commercial suppliers and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded using Varian instruments at 400 and 100 MHz, respectively, with tetramethylsilane as an internal standard. All products were isolated using short chromatography on a silica-gel (200–300 mesh) column, with petroleum ether (60–90 °C) and EtOAc as the eluent, unless otherwise stated. Compounds that had previously been described in the literature were characterized by comparison of their ^{1}H NMR and ^{13}C NMR spectra with the reported data template.

*2.2. General procedure for synthesis of enamide **3a** and 1,3-diyne **4a***

A 25 mL round-bottomed flask charged with ketoxime **1a** (67.5 mg, 0.5 mmol), phenylacetylene **2a** (102.0 mg, 1.0 mmol), acetic anhydride (102.0 mg, 1.0 mmol), pyridine (47.4 mg, 0.6 mmol), CuI (9.5 mg, 10 mol%), and $Pd(PPh_3)_2Cl_2$ (0.7 mg, 0.2 mol%) in 1,2-dichloroethane (5.0 mL) was stirred at 120 °C for 5 h under Ar. After completion of the reaction (detected using thin-layer chromatography), the reaction mixture was cooled to room temperature, diluted with EtOAc (10 mL), and washed with H_2O (10 mL), brine (10 mL), and $CuSO_4$ (2 mol/L, 5 mL). The organic layers were dried over anhydrous Na_2SO_4 and evaporated in vacuo. The residue was purified by chromatography on silica gel to afford enamide **3a** (77.3 mg, 96% yield) and 1,3-diyne **4a** (82.8 mg, 82% yield).

*2.3. Analytical data for enamides **3** and 1,3-diynes **4***

N-(1-Phenylvinyl)acetamide (**3a**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.34 (m, 6H), 5.78 (s, 1H), 5.07 (s, 1H), 2.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 140.5, 138.2, 128.5, 126.0, 102.6, 24.3.

N-[1-(*p*-Tolyl)vinyl]acetamide (**3b**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 7.2 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 7.10 (s, 1H), 5.77 (s, 1H), 5.04 (s, 1H), 2.35 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 140.4, 138.5, 135.5, 129.3, 125.9, 101.9, 24.4, 21.1.

N-[1-(4-Methoxyphenyl)vinyl]acetamide (**3c**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 8.0 Hz, 2H), 7.17 (s, 1H), 6.86 (d, J = 8.8 Hz, 2H), 5.69 (s, 1H), 4.99 (s, 1H), 3.79 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 159.8, 140.1, 130.8, 127.3, 113.9, 101.5, 55.3, 24.4.

N-[1-(4-Nitrophenyl)vinyl]acetamide (**3d**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.0 Hz, 2H), 7.15 (s, 1H), 5.79 (s, 1H), 5.25 (s, 1H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 147.6, 144.1, 139.2, 126.8, 123.8, 107.1, 24.1.

N-[1-(4-Fluorophenyl)vinyl]acetamide (**3e**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.33 (t, J = 7.2 Hz, 2H), 7.28 (s, 1H), 7.02–6.98 (t, J = 8.4 Hz, 2H), 5.67 (s, 1H), 4.99 (s, 1H), 2.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 162.8 (J_{CF} = 247.2 Hz), 139.7, 134.3, 127.9 (J_{CF} = 8.2 Hz), 115.4 (J_{CF} = 21.4 Hz), 103.1, 24.2.

N-[1-(4-Chlorophenyl)vinyl]acetamide (**3f**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 5H), 5.70 (s, 1H), 5.06 (s, 1H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 139.6, 136.5, 134.4, 128.7, 127.4, 103.7, 24.2.

N-[1-(4-Bromophenyl)vinyl]acetamide (**3g**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.11 (s, 1H), 5.73 (s, 1H), 5.07 (s, 1H), 2.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 139.6, 137.0, 131.7, 127.6, 122.6, 103.7, 24.3.

N-[1-(3,4-Dimethylphenyl)vinyl]acetamide (**3h**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18–7.10 (m, 4H), 5.77 (s, 1H), 5.04 (s, 1H), 2.27 (s, 3H), 2.26 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 140.5, 137.2, 136.8, 135.9, 129.8, 127.2, 123.4, 101.6, 24.4, 19.8, 19.5. HRMS Calcd (ESI) m/z for $C_{12}H_{15}NNaO$: $[M + Na]^+$ 212.1046, found: 212.1050.

N-[1-(5,6,7,8-Tetrahydronaphthalen-2-yl)vinyl]acetamide (**3i**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14–7.11 (m, 2H), 7.06 (d, J = 8.0 Hz, 1H), 6.87 (s, 1H), 5.82 (s, 1H), 5.03 (s, 1H), 2.77 (s, 4H), 2.12 (s, 3H), 1.80 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 140.5, 137.9, 137.4, 135.6, 129.4, 126.5, 123.1, 101.4, 29.4, 29.1, 24.6, 23.0. HRMS Calcd (ESI) m/z for $C_{14}H_{17}NNaO$: $[M + Na]^+$ 238.1202, found: 238.1207.

N-[1-(2,5-Dimethylphenyl)vinyl]acetamide (**3j**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (s, 1H), 7.09–7.06 (m, 3H), 5.97 (s, 1H), 4.65 (s, 1H), 2.32 (s, 3H), 2.29 (s, 3H), 1.93 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 140.7, 138.4, 135.3, 132.6, 130.3, 129.8, 129.1, 102.1, 24.2, 20.8, 19.1. HRMS Calcd (ESI) m/z for $C_{12}H_{16}NO$: $[M + H]^+$ 190.1226, found: 190.1227.

N-[1-(3-Methoxyphenyl)vinyl]acetamide (**3k**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.24 (m, 2H), 6.98 (d, J = 7.2 Hz, 1H), 6.93 (s, 1H), 6.86 (d, J = 8.0 Hz, 1H), 5.80 (s, 1H), 5.07 (s, 1H), 3.80 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 159.6, 140.4, 139.8, 129.6, 118.4, 113.8, 112.0, 102.6, 55.3, 24.4.

N-[1-(Naphthalen-2-yl)vinyl]acetamide (**3l**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.82 (m, 4H), 7.54–7.49 (m, 3H), 7.08 (s, 1H), 5.92 (s, 1H), 5.24 (s, 1H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 140.4, 135.5, 133.2, 133.0, 128.4, 128.1, 127.6, 126.5, 126.4, 124.7, 124.0, 103.4, 24.4.

(*E*)-*N*-(1-Phenylprop-1-en-1-yl)acetamide (**3m**). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.11 (s, 1H), 7.36–7.22 (m, 5H), 5.89–5.87 (m, 1H), 1.99 (s, 3H), 1.64 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.8, 138.4, 134.7, 128.2, 127.2, 125.1, 119.3, 22.7, 13.8.

N-(2-Methyl-1-phenylprop-1-en-1-yl)acetamide (**3n**). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.02 (s, 1H), 7.30–7.21 (m, 5H), 1.87 (s, 3H), 1.70 (s, 3H), 1.68 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.5, 139.1, 128.8, 127.7, 127.3, 126.7, 22.7, 20.7, 20.7.

N-(1-Phenylvinyl)propionamide (**3o**). ^{1}H NMR (400 MHz,