

Novel synthesis of enamines by iridium-catalyzed dehydrogenation of tertiary amines

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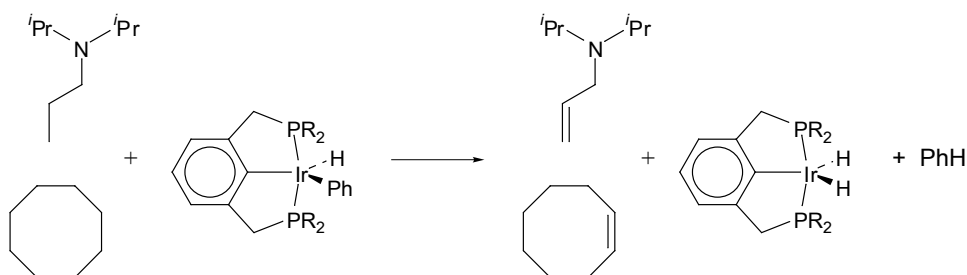
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General

¹H NMR (300 MHz, Varian Mercury 300), spectra were recorded in *p*-xylene-*d*₁₀. All dehydrogenations were conducted under argon using Schlenk techniques. Reagent grade solvents were used and dried according to established methods, then degassed with argon. NMR solvents were dried, vacuum-transferred, and stored in an argon-filled glovebox. (^t-BuPCP)IrH₂ (**1**) was prepared as reported by Kaska and Jensen.¹ Amines were purchased from Aldrich. N,N-diisopropylpropylamine was synthesized according to Kuffner and Koechlin.¹ All amines were dried according to established method and degassed with argon before use.³

Competition experiment with N,N-di(isopropyl)ethylamine and cyclooctane.

A solution of (^t-BuPCP)Ir(H)(Ph)⁴ (15 mM) was reacted with N,N-di(isopropyl)ethylamine (60 mM) and cyclooctane (COA; 600 mM). (^t-BuPCP)Ir(H)(Ph) is a source of (^t-BuPCP)Ir⁴, the presumed active species in the reactions catalyzed by **1**. In accord with that presumption, both N,N-di(isopropyl)ethylamine and COA were found to react with (^t-BuPCP)Ir(H)(Ph) to give **1** and the corresponding unsaturate (N,N-di(isopropyl)-vinylamine and cyclooctene respectively.



This competition experiment was conducted using (^{t-Bu}PCP)Ir(H)(Ph) (in the absence of TBE), rather than catalytically with **1** and TBE, in order to facilitate ¹H NMR characterization at the lowest possible concentrations of dehydrogenated substrate, and shortest possible times. The likelihood that the cyclooctene:vinylamine ratio would reflect thermodynamics rather than kinetics was therefore minimized.

As noted in the main body of this paper the ratio of cyclooctene to vinylamine remained roughly constant (1:2.0) in this experiment, even from the earliest reaction times, indicating that the observed product ratio reflects reaction kinetics, not thermodynamics. This indicates a kinetic selectivity, on a per mol basis, equal to:

$$[\text{N,N-di(isopropyl)vinylamine}][\text{COA}]/[\text{N,N-di(isopropyl)ethylamine}][\text{cyclooctene}] = 20$$

Note that since cyclooctane dehydrogenation is thermodynamically more favorable ($\Delta H = 24 \text{ kcal/mol}^5$) than dehydrogenation of an aminoethyl group (estimated $\Delta H = 26.1 \text{ kcal/mol}^6$), thermodynamics would only bias the ratio towards cyclooctene; therefore the observed selectivity must be kinetic.

Characterization and data for dehydrogenated products.

N, N-di(isopropyl)-vinylamine: Colorless oil, ^1H NMR (300 MHz, *p*-xylene- d_{10}) δ = 6.10 (dd, 15.6 Hz, 9.2 Hz, 1H), 3.83 (d, 9.2 Hz, 1 H), 3.82 (d, 15.6 Hz, 1 H), 3.41 (m, 6.5 Hz, 2 H), 1.03 (d, 6.5 Hz, 12 H). MS (EI) *m/z*: 127(parent), 112, 99, 70, 56.

N, N-dimethylvinylamine:⁷ Colorless oil, ^1H NMR (300 MHz, *p*-xylene- d_{10}) δ = 6.01 (dd, 15.2 Hz, 8.4 Hz, 1 H), 3.84 (d, 8.4 Hz, 1H), 3.74 (d, 15.2 Hz, 1H), 2.39 (s, 6H). MS (EI) *m/z*: 71(parent), 58, 56 44.

N, N-diethylvinylamine:⁷ Colorless oil, ^1H NMR (300 MHz, *p*-xylene- d_{10}) δ = 6.03 (dd, 15.2 Hz, 9.2 Hz, 1H), 3.78(d, 9.2 Hz, 1H), 3.75(d, 15.2 Hz, 1H), 2.81(q, 7.0 Hz, 4H), 1.05(t, 7.0 Hz, 6H). MS (EI) *m/z*: 99(parent), 84, 73, 71, 56.

N, N-divinyl-ethylamine: Colorless oil, ^1H NMR (300 MHz, *p*-xylene- d_{10}) δ = 6.00 (dd, 15.6 Hz, 9.0 Hz, 2 H), 3.93 (d, 15.6 Hz, 2 H), 3.86 (d, 9.0 Hz, 2 H), 3.14 (q, 7.0 Hz, 2H), 1.02 (t, 7.0 Hz, 3 H). MS (EI) *m/z*: 97(parent), 83, 70, 56.

N, N-dimethyl-2-propenylamine:⁸ colorless oil, ^1H NMR (300 MHz, *p*-xylene- d_{10}) δ = 3.84(s, 1 H), 3.70 (s, 1H), 2.49 (s, 6H), 1.75 (s, 3H).

N, N-diisopropyl-1-(E)-propenylamine: Colorless oil, ^1H NMR (300 MHz, *p*-xylene- d_{10}) δ = 6.04 (dq, 13.6 Hz, 1.3 Hz, 1 H), 4.25 (m, 13.6 Hz, 6.7 Hz, 1 H), 3.36 (m, 6.8 Hz, 2 H), 1.87 (dd, 6.7 Hz, 1.3 Hz, 3 H), 1.05 (d, 6.8 Hz, 12 H).

N, N-dipropyl-(E)-1-propenylamine:⁹ Colorless oil, ^1H NMR (300 MHz, *p*-xylene- d_{10}) δ = 5.89 (dd, 13.5 Hz, 1.5 Hz, 1H), 4.18 (qd, 6.3 Hz, 13.5 Hz, 1 H), 2.75 (t, 7.2 Hz, 4H), 1.85 (dd, 6.3 Hz, 1.5 Hz, 3H), 1.48 (tq, 7.2 Hz, 7.2 Hz, 4H), 0.98 (t, 7.2 Hz, 6H).

N, N-di-(E)-1-propenyl-propylamine: Colorless oil, ^1H NMR (300 MHz, *p*-xylene- d_{10}) δ = 5.91 (d, 13.6 Hz, 2 H), 5.38 (m, 13.6 Hz, 6.4 Hz, 2 H), 3.04 (t, 7.6 Hz, 2 H), 1.75 (d, 6.4 Hz, 6 H), 1.31 (m, 2H), 1.01 (t, 6.8 Hz, 3 H). MS (EI) *m/z*: 139(parent), 124, 110, 98, 70.

N-methylpyrrole:¹⁰ Colorless oil, ^1H NMR (300 MHz, *p*-xylene- d_{10}) δ = 6.58 (t, 2.1 Hz, 2H), 6.12 (t, 2.1 Hz, 2H), 3.63 (s, 3H).

N-vinylpyrrole:¹¹ Colorless oil, ¹H NMR (300 MHz, *p*-xylene-*d*₁₀) δ = 6.46 (t, 2.1 Hz, 2H), 6.33 (dd, 15.3 Hz, 8.7 Hz, 1H), 6.27 (t, 2.1 Hz, 2H), 3.85 (d, 8.7 Hz, 1H), 3.70 (d, 15.3 Hz, 1H).

N-vinylpiperidine:¹² Colorless oil, ¹H NMR (300 MHz, *p*-xylene-*d*₁₀) δ = 5.99 (dd, 15.3 Hz, 8.7 Hz, 1H), 3.90 (d, 15.3 Hz, 1H), 3.88(d, 8.7 Hz, 1H), 2.68 (t, 5.3 Hz, 4H), 1.65-1.50 (m, 6H).

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