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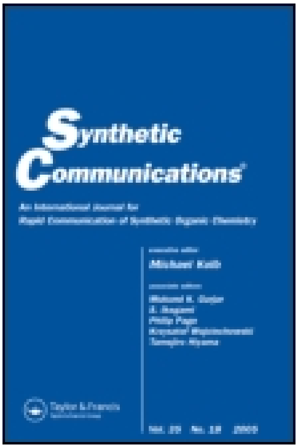

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
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Zinc-Catalyzed Reduction of Imines by Triethylsilane

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Available online: 19 Mar 2009

To cite this article: K. Anil Kumar, T. S. Sreelekha, K. N. Shivakumara, K. C. Prakasha & D. Channe Gowda (2009): Zinc-Catalyzed Reduction of Imines by Triethylsilane, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 39:8, 1332-1341

To link to this article: http://dx.doi.org/10.1080/00397910802521246

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Synthetic Communications®, 39: 1332–1341, 2009
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ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910802521246

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Zinc-Catalyzed Reduction of Imines by Triethylsilane

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Abstract: Low-cost zinc is employed as a catalyst along with triethylsilane (TES) in a simple, straightforward, chemoselective reduction of various aldimines and ketimines to the corresponding secondary amines at room temperature and pressure.

Keywords: Hydrogenation, imines, secondary amines, triethylsilane (TES), zinc dust

The conversion of carbonyl derivatives to secondary amines via imines is a very convenient and explicit route to the synthesis of substituted amines. However, difficulties may be encountered partly as a result of imine instability, which makes it cumbersome to easily access the imine in its pure form. Even though additions to the C=N bonds of imines, hydrazones, and oximes are well known, exploitation of these reactions is often limited by the poor electrophilicity of the C=N carbon.[1]

To date, several protocols have been utilized for the reduction of imines to secondary amines,[2–14] but some of them have limitations based on chemoselectivity, low yield, economic considerations, chemical efficiency, and waste disposal. Catalytic hydrogenation is also commonly used,[15] but the success of the reaction depends on the solvent, catalyst, and substrate. Catalytic hydrogenation employs highly diffusible, low-molecular-weight, flammable hydrogen gas, requires pressure equipment; and is often

Received June 18, 2008.

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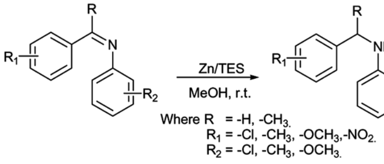
problematic because of harsh reaction conditions. Nowadays, silicon-based reducing agents are extensively used in organic synthesis.[16] Thus, triethylsilane (TES) has been the most popular of the silicon-based reducing agents, and Si-H containing system can provide the hydride for many or most of the reductions.

Recently metal-mediated reactions have wide scope in organic synthesis because of their simple workup and selectivity. Several methods have been developed based on the use of a variety of metals such as magnesium,[17] indium,[18] zinc,[19] and tin.[20] The utility of zinc for the synthesis of β,γ-unsaturated ketones by a reaction of an acid chloride with allyl bromide[21] and homoallylic alcohols has been demonstrated.[22] Further, the zinc-mediated preparation of triphenylphosphonium ylides,[23] amide bond formation,[24] Friedel–Crafts acylation,[24] carbamate formation,[24] and esterification of acid chloride[24] has been demonstrated. Zinc has also been employed as a catalyst along with different hydrogen donors in many functional group interconversions.[25] In this context, we report the zinc-catalyzed rapid and selective transfer hydrogenation of imines to corresponding secondary amines using TES at room temperature in methanol (Scheme 1).

The results given in Table 1 reveal the viability of using the Zn and TES system for the reduction of imines. The course of reaction was monitored by thin-layer chromatography (TLC) and infrared (IR) spectra. The workup and isolation of the products were easy. Thus all the compounds reduced by this system were obtained in moderate to good yields and most of the reactions were completed within 30 min. The products were characterized by comparison of their boiling or melting points, TLC, IR, and ^{1}H NMR spectra with authentic samples. The disappearance of strong absorption bands between 1690 and 1640 cm^{-1} due to C=N stretching and the appearance of a strong absorption bands between 3500 and 3200 cm^{-1} for the –NH group clearly show that the imines were reduced to corresponding secondary amines. In case of nitro imines, both nitro and imine undergo reduction to yield primary and secondary amines respectively.

To ensure the role of zinc, a controlled experiment was carried out using imines with TES without zinc dust, which failed to yield any



Where R = -H, $-CH_3$.
R_1 = -Cl, $-CH_3$, $-OCH_3$, $-NO_2$.
R_2 = -Cl, $-CH_3$, $-OCH_3$.

Scheme 1. Reduction of imines to secondary amines using triethylsilane.

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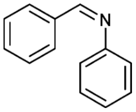
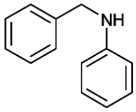
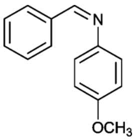
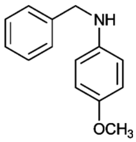
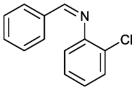
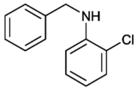
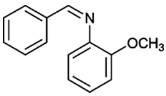
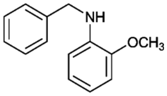
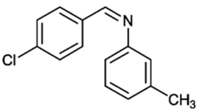
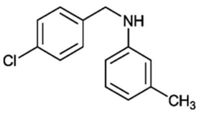
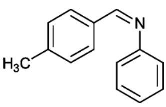
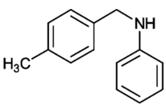
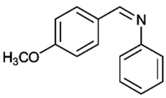
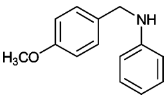
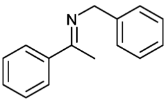
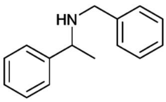
Table 1. Zinc-catalyzed reduction of imines to secondary amines using triethylsilane

					Melting point (°C)	
Entry	Substrate	Time (min)	Product[a,b]	Yield[c] (%)	Found	Lit.
1		20		85	36–37	35–38[29]
2		25		80	48–50	50–50.5[30]
3		20		82	38–39	39.5–40[31]
4		26		75	Oily	—
5		24		78	34–36	—
6		25		75	Oily	19–20[29]
7		26		76	45–46	46.5–47[30]
8		30		73	Oily	—

(*Continued*)

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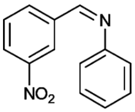
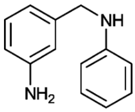
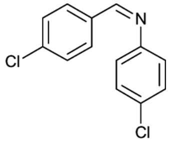
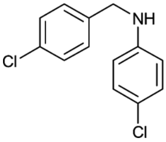
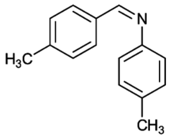
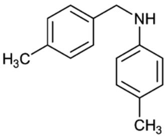
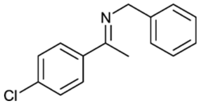
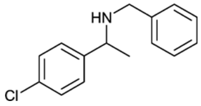
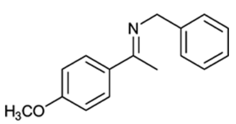
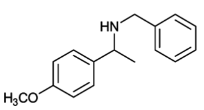
Table 1. Continued

					Melting point (°C)	
Entry	Substrate	Time (min)	Product[a,b]	Yield[c] (%)	Found	Lit.
9		23		75	83–84	84–85[32]
10		20		80	68–70	70–71[29]
11		28		75	55–56	60–61[30]
12		25		70	Oily	—
13		35		70	Oily	—

[a] ^{1}H NMR spectra were obtained on a 300-MHz Bruker FT-NMR spectrometer in $CDCl_3$ as the solvent and TMS as internal standard.

[b] Isolated products gave IR spectra in agreement with their structures.

[c] Isolated yields are based on a single experiment, and yields were not optimized.

reduced product. This clearly confirms that zinc catalyzes the reaction. In anticipating metal/alcohol reduction, experiments were performed in the absence of a hydrogen source (i.e., TES), by refluxing the substrate with methanol and zinc dust for 4–5 h. Even after a longer duration, the starting material was isolated in quantitative yield, which clearly shows the requirement of TES as a hydrogen source for the reduction. Here, methanol serves as a solvent. After the completion of reaction (Scheme 1), zinc

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was recycled almost quantitatively (>95%) after activation by treating it with acetic acid or 0.01 N HCl.

In summary, the TES/Zn method is useful for preparing a variety of secondary amines from suitable carbonyl compounds and amines. We have chosen TES as a reducing agent because of its ease of handling and high reactivity, which decomposes to an environmentally friendly by-product. The use of zinc dust instead of Pd/C,[26] $PdCl_2$,[27] ruthenium Grabbs, or Raney Ni not only reduces the cost and contains risk but also enhances the chemoselectivity, particularly with halogens, which are not compatible under Pd/C-, $PdCl_2$-, or Raney Ni–catalyzed transfer hydrogenation conditions. This procedure gave rise to the formation of secondary amines in moderate to good yields, had operational simplicity, had few by-products, used mild reaction condition, and offered an alternative to traditional synthetic procedures.

EXPERIMENTAL

The imines were either obtained from a commercial source or prepared from the corresponding carbonyl compound and amines as previously reported.[28] In cases where the imine was obtained as an E/Z mixture, no attempts were made to separate such imines, and they were used as such for the reduction. Zinc dust powder was purchased from Loba Chemie Pvt. Ltd. (Mumbai, India). TES and 60- to 120-mesh silica gel (for column chromatography) were purchased from E. Merck Ltd. (India). All the solvents used were analytical grade or were purified according to standard procedures. TLC was carried out on precoated silica-gel plates (Merck) using chloroform/methanol (90:10) as a solvent system. The melting points were determined by a open capillary apparatus and are uncorrected. IR spectra were recorded on a Jasco 4100 Fourier transform infrared (FTIR) spectrometer. ^1H NMR spectra were obtained on a 300-MHz Bruker FT-NMR spectrometer using $CDCl_3$ as a solvent and tetramethylsilane (TMS) as an internal standard.

Typical Procedure for the Reduction of Imines

Neat TES (20 mmol) was added dropwise from a dropping funnel to a stirred solution of substrate (5 mmol) and zinc dust (6 mmol) in methanol (10 ml) under a nitrogen atmosphere at room temperature. After the completion of reaction (monitored by TLC), the reaction mixture was filtered through celite, the organic layer was evaporated, and the residue was dissolved in dichloromethane or ether and washed with saturated $KHSO_4$ and brine solution. The organic layer was dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. The products were purified by column chromatography 60- to 120-mesh silica gel using a suitable eluting system (90:10 hexane–ethylacetate, 90:10 chloroform–hexane, 80:20 chloroform–methanol, 85:15 chloroform–methanol, 90:10 chloroform–methanol) at a flow rate of 20 drops per minute.

Analytical Data of Synthesized Compounds

Compound **1**, *N*-Phenylbenzylamine

IR (neat): $\nu = 3418, 2927, 1468, 1340, 1303\,\text{cm}^{-1}$; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) $\delta = 7.05$–7.15 (m, 7H, Ar-H), 6.56 (t, 1H, Ar-H), 6.42 (d, 2H, Ar-H), 4.33 (s, 2H, Ar-CH_2), 4.04 (s br, 1H, -NH).

Compound **2**, Benzyl-(4-methoxyphenyl)-amine

IR (neat): $\nu = 3398, 2930, 2852, 1463, 1341, 1255, 1041, 820\,\text{cm}^{-1}$; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) $\delta = 7.06$–7.15 (m, 5H, Ar-H), 6.55 (d, 2H, Ar-H), 6.30 (d, 2H, Ar-H), 4.32 (s, 2H, Ar-CH_2), 3.92 (s, 1H, -NH), 3.70 (s, 3H, Ar-OCH_3).

Compound **3**, Benzyl-(2-chlorophenyl)-amine

IR (neat): $\nu = 3406, 2925, 2850, 1470, 1334, 1291, 1255, 1041, 810\,\text{cm}^{-1}$; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) $\delta = 7.05$ (m, 6H, Ar-H), 6.92 (t, 1H, Ar-H), 6.52 (t, 1H, Ar-H), 6.37 (d, 1H, Ar-H), 4.32 (s, 2H, Ar-CH_2), 3.80 (s, 1H, -NH).

Compound **4**, Benzyl-(2-methoxyphenyl)-amine

IR (neat): $\nu = 3401, 2936, 2856, 1460, 1336, 1289, 1251, 1025, 841\,\text{cm}^{-1}$; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) $\delta = 7.06$–7.14 (m, 5H, Ar-H), 6.60 (t, 1H, Ar-H), 6.55 (d, 1H, Ar-H), 6.47 (t, 1H, Ar-H), 6.32 (d, 1H, Ar-H), 4.12 (s, 2H, Ar-CH_2), 3.85 (s, 1H, -NH) 3.75 (s, 3H, Ar-OCH_3).

Compound **5**, 4-chlorobenzyl-(3-methylphenyl)-amine

IR (neat): $\nu = 3408, 2930, 2916, 2870, 2863, 2856,1454, 1336, 720\,\text{cm}^{-1}$; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) $\delta = 7.14$ (d, 2H, Ar-H), 7.01 (d, 2H, Ar-H), 6.92 (t, 1H, Ar-H), 6.38 (d, 1H, Ar-H), 6.24 (s, 1H, Ar-H), 4.21 (s, 2H, Ar-CH_2), 3.78 (s, 1H, -NH), 2.42 (s, 3H, Ar-CH_3).

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Compound **6**, *N*-(4-Methylphenylmethyl)aniline

IR (neat): $\nu = 3408$, 2960, 2921, 2869, 2852, 1457, 1336, 1288 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) $\delta = 7.05$ (tt, 2H, Ar-H), 6.94 (d, 4H, Ar-H), 6.58 (t, 1H, Ar-H), 6.43 (dd, 2H, Ar-H), 4.28 (s, 2H, Ar-CH_2), 3.98 (s br, 1H, -NH), 2.35 (s, 3H, Ar-CH_3).

Compound **7**, *N*-(4-Methoxybenzyl)benzenamine

IR (neat): $\nu = 3398$, 2930, 2852, 1463, 1341, 1255, 1041, 820 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) $\delta = 7.05$ (t, 2H, Ar-H), 6.96 (d, 2H, Ar-H), 6.66 (d, 2H, Ar-H), 6.59 (t, 1H, Ar-H), 6.44 (d, 2H, Ar-H), 4.26 (s, 2H, Ar-CH_2), 3.90 (s, 1H, -NH), 3.81 (s, 3H, Ar-OCH_3).

Compound **8**, *N*-Benzyl-*N*-(1-phenylethyl)-amine

IR (neat): $\nu = 3400$, 2935, 2848, 1650, 1461, 1146, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) $\delta = 7.20$ (t, 2H, Ar-H), 7.14 (t, 2H, Ar-H), 7.12 (d, 2H, Ar-H), 7.08 (t, 1H, Ar-H), 7.07 (t, 1H, Ar-H), 7.06 (d, 2H, Ar-H), 3.77 (q, 1H, -CH), 3.58 (s, 2H, Ar-CH_2), 1.51 (s br, 1H, -NH), 1.32 (d, 3H, -CH_3).

Compound **9**, *N*-(3-Aminobenzyl)benzenamine

IR (neat): $\nu = 3401$, 3369, 1650, 1485, 1345 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) $\delta = 7.04$ (t, 2H, Ar-H), 6.89 (t, 1H, Ar-H), 6.58 (t, 1H, Ar-H), 6.43 (d, 2H, Ar-H), 6.42 (d, 1H, Ar-H), 6.27 (d, 1H, Ar-H), 6.26 (s, 1H, Ar-H), 4.35 (s, 2H, Ar-CH_2), 4.10 (s br, 1H, -NH), 3.32 (s, 2H, Ar-NH_2).

Compound **10**, *N*-(4-Chlorobenzyl)-4-chlorobenzenamine

IR (neat): $\nu = 3413$, 2918, 2860, 1475, 1334, 820, 723 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) $\delta = 7.15$ (d, 2H, Ar-H), 7.05 (d, 2H, Ar-H), 7.00 (d, 2H, Ar-H) 6.37 (d, 2H, Ar-H), 4.31 (s, 2H, Ar-CH_2), 4.09 (s, 1H, -NH).

Compound **11**, *N*-(4-Methylbenzyl)-4-methylbenzenamine

IR (neat): $\nu = 3405$, 2930, 2870, 2845, 1343, 1256, 1039 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) $\delta = 6.94$ (d, 4H, Ar-H), 6.84 (d, 2H, Ar-H), 6.31 (d, 2H, Ar-H), 4.29 (s, 2H, Ar-CH_2), 4.02 (s, 1H, -NH), 2.34 (s, 6H, Ar-2CH_3).

Compound **12**, *N*-Benzyl-1-(4-chlorophenyl)ethanamine

IR (neat): $\nu = 3408, 2935, 2848, 1650, 1461, 1146, 730\,\mathrm{cm}^{-1}$; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) $\delta = 7.22$ (d, 2H, Ar-H), 7.14 (t, 2H, Ar-H), 7.07 (t, 1H, Ar-H), 7.06 (d, 4H, Ar-H), 3.74 (q, 1H, -CH), 3.55 (s, 2H, Ar-CH_2), 1.51 (s br, 1H, -NH), 1.28 (d, 3H, -CH_3).

Compound **13**, *N*-Benzyl-1-(4-methoxyphenyl)ethanamine

IR (neat): $\nu = 3410, 2932, 2840, 1648, 1466, 1140, 735\,\mathrm{cm}^{-1}$; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) $\delta = 7.14$ (t, 2H, Ar-H), 7.07 (t, 1H, Ar-H), 7.06 (d, 2H, Ar-H), 7.01 (d, 2H, Ar-H), 6.72 (d, 2H, Ar-H), 3.76 (s, 3H, Ar-OCH_3), 3.72 (q, 1H, -CH), 3.56 (s, 2H, Ar-CH_2), 1.76 (s br, 1H, -NH), 1.30 (d, 3H, -CH_3).

ACKNOWLEDGMENT

The authors thank the Council of Scientific and Industrial Research (CSIR), New Delhi, India, for financial assistance.

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