One-Pot Reductive Amination of Conjugated Aldehydes and Ketones with Silica Gel and Zinc Borohydride

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Reductive amination, which allows the conversion of carbonyl functionality to an amine, is an important process in organic synthesis. The reaction involves the initial formation of an imine from the reaction of a carbonyl compound with an amine and its subsequent reduction to an alkylated amine. The reductive amination reaction is termed as direct when a mixture of the carbonyl compound and the amine is treated with proper reducing agent in a single operation. A stepwise or indirect reaction involves the preformation of the intermediate imine followed by reduction in a separate step. A variety of reducing agents, such as hydrogen in the presence of metal catalysts,[1] sodium cyanoborohydride,[2] borane−pyridine,[3] borohydride exchange resin,[4] zinc−acetic acid,[5] sodium borohydride−magnesium chlorate,[6] zinc borohydride−zinc chloride,[7] and recently sodium triacetoxyborohydride,[8] have been developed for this conversion from time to time. Among these, the most general and commonly used methods include catalytic hydrogenation, reduction with sodium cyanoborohydride, and sodium triacetoxyborohydride. But, hydrogenation is not compatible with compounds containing a double or triple bond and several other reducible functional groups such as nitro or cyano. On the other hand, sodium cyanoborohydride may require up to a 5-fold excess of amine[9] and may result in the contamination of the product with cyanide.[10] Moreover, this reagent is highly toxic and generates toxic byproducts HCN and NaCN, upon workup. Sodium triacetoxyborohydride, although free from these drawbacks, has limitations with aromatic and unsaturated ketones. In fact, reductive amination of conjugated carbonyl compounds has not been addressed in details in any of the reported methods; only two examples, 1-acetylcyclohexene and cinnamaldehyde, have been included in sodium triacetoxyborohydride procedure.[8] Our recent endeavor of selective reduction of various important functionalities with zinc borohydride[11] prompted us to initiate a systematic study on this useful transformation. We have discovered that reductive amination of conjugated aldehyde and ketone is achieved by treatment of the corresponding carbonyl compound with an appropriate amine in the presence of silica gel followed by addition of zinc borohydride in a one-pot operation (Scheme 1). Although imines are, in general, prepared by the condensation of the carbonyl compound with an amine in the presence of a Lewis or protic acid,[12] our attempts to obtain the imines of conjugated carbonyl compounds, particularly ketones following reported procedures[12] using zinc chloride, boron trifluoride−etherate, *p*-toluenesulfonic acid, molecular sieves, failed. However, with our experience in surface-mediated solid-phase reactions[13] we solved this problem by carrying out the reaction on the surface of silica gel. Thus, when a mixture of the conjugated carbonyl compound and the amine being adsorbed on silica gel was stirred for 2−3 h, the corresponding imines are formed in good yields. So, a one-pot reductive amination procedure is designed as follows: a mixture of carbonyl compound and amine is adsorbed on the surface of silica gel, and a solution of zinc borohydride is added to it, after being stirred for 4 h. The reaction mixture is then stirred for another 30−60 min as required for completion (TLC). The product is isolated by simple extraction of the reaction mixture with ether.

Scheme 1

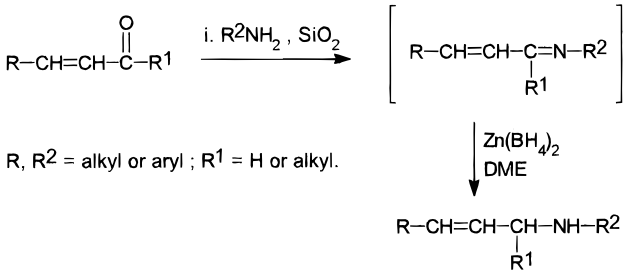

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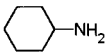
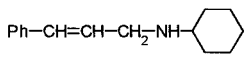
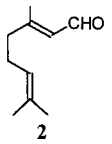
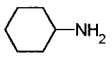
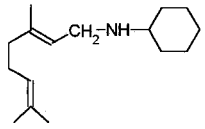
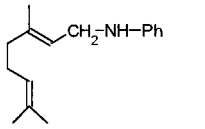
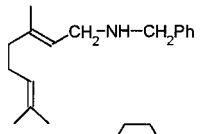
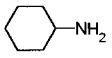
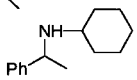
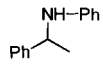
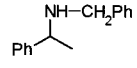
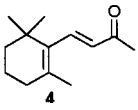
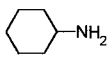
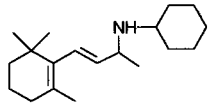
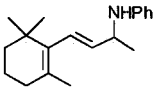
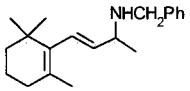
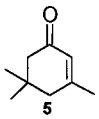
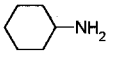
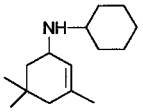
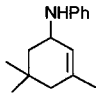
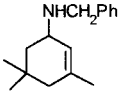
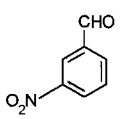
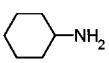
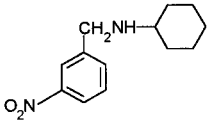
Table 1. Reductive Amination of Conjugated Aldehydes and Ketones

entry	carbonyl compound	amine	reduction time (min)	product	yield(%)[a]
1	Ph–CH=CH–CHO **1**		60	Ph–CH=CH–CH_2–NH– 	83
2	**1**	$PhNH_2$	60	Ph–CH=CH–CH_2–NHPh	84
3	**1**	$PhCH_2NH_2$	60	Ph–CH=CH–CH_2–$NHCH_2$Ph	85
4	 **2**		45[b]		80
5	**2**	$PhNH_2$	60		88
6	**2**	$PhCH_2NH_2$	55		85
7	 **3**		60[b]		75
8	**3**	$PhNH_2$	60		86
9	**3**	$PhCH_2NH_2$	60		90
10	 **4**		50[b]		85
11	**4**	$PhNH_2$	45		83
12	**4**	$PhCH_2NH_2$	40		80
13	 **5**		60[b]		80
14	**5**	$PhNH_2$	45		78
15	**5**	$PhCH_2NH_2$	60		90
16			240		89

[a]All yields refer to pure isolated products , fully characterized by spectral and analytical data
[b]The reduction step was run at 0°C (ice-water bath)

A variety of α,β-unsaturated aldehydes and ketones were subjected to reductive aminations by this procedure. The results are reported in Table 1. The acyclic, cyclic, and aromatic conjugated carbonyl compounds underwent successful reductive aminations with cyclohexylamine, aniline, and benzylamine to produce the corresponding amines in very good yields. In all the cases the reductions were very fast being complete within 60 min, although prior to addition of zinc borohydride the reaction was run for 4 h to ensure complete imine formation. The direct process using carbonyl compound, amine, and zinc borohydride all together also leads to reductive amination, but is always accompanied with reduction of carbonyl compounds to a varying degree. However, the stepwise process is free from any side reaction. The present procedure does not affect nitro (entry 16) and cyano[18] groups. The double bonds in conjugation do not undergo any isomerization or reduction during the process as well as in isolation. Moreover, zinc borohydride is neutral in nature and, in general, is compatible with many sensitive functionalities[11] like acetal[11d] and silyl ether.[14a]

When a secondary amine such as pyrrolidine was treated with cyclohexanone on the surface of silica gel followed by stirring with a solution of zinc borohydride in a similar way, the corresponding amine from the reduction of enamine was obtained without any difficulty.

In conclusion, the present procedure using silica gel and zinc borohydride provides a first general and efficient methodology for reductive amination of conjugated aldehydes and ketones. The notable advantages of this procedure are (a) operational simplicity, (b) use of no costly or toxic chemicals, (c) no environmental pollution from waste, (d) mild condition, (e) fast reaction, and (f) high yield.

Experimental Section

General Methods. General information regarding instruments and techniques used are the same as mentioned in our previous paper.[11m]

The conjugated carbonyl compounds and the amines are all commercial materials and were distilled before use. Silica gel (HF 254) was from SRL, India, and was activated by heating in a oven at 150 °C for 12 h before use. Zinc borohydride in DME was prepared from zinc chloride and sodium borohydride according to a reported procedure,[14b] and the crude solution was used without any purification.

General Procedure for Reductive Amination. Representative Procedure. A mixture of cinnamaldehyde (660 mg, 5 mmol) and benzylamine (535 mg, 5 mmol) was uniformly adsorbed on the surface of activated silica gel (5 g) by dropwise addition under stirring, and the mixture was then stirred at room temperature (30 °C) under nitrogen for 4 h to allow complete formation of the corresponding imine. A solution of zinc borohydride (5 mmol) in DME (5 mL) was added, and stirring was continued for 60 min to complete the reaction (TLC). The reaction mixture was then decomposed by careful dropwise addition of water (2 mL) and extracted with ether (3 × 20 mL). The extract was washed with brine, dried (Na_2SO_4), and evaporated to leave the crude product which was purified by column chromatography over silica gel to provide the pure product,[8] *N*-cinnamylbenzylamine (950 mg, 85%) as an oil: IR(neat) 1340, 1515, 1670, 3020 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.53 (2H, d, J = 6.9 Hz), 4.02 (2H, s), 6.38 (1H, dt, J = 15.9, 6.9 Hz), 6.58 (1H, d, J = 15.9 Hz), 7.22−7.56 (10H, m).

This procedure is followed for reductive amination of all conjugated aldehydes and ketones listed in Table 1. Although the results reported in Table 1 were based on mmol scale reactions, a few gram scale reactions were carried out to afford the corresponding products in analogously high yields. All the products have been characterized by their spectral (IR, ^1H and ^{13}C NMR) and analytical data. These data are presented below in order of the entries in Table 1.

1:[15] ***N*-Cinnamylcyclohexylamine**: mp 122 °C; IR(KBr) 1200, 1670, 3020, 3320 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.85−1.74 (6H, m), 1.62−1.92 (4H, m), 2.86−2.89 (1H, m), 3.2 (1H, broad), 3.53−3.64 (2H, m), 6.39 (1H, dt, J = 15, 6 Hz), 6.60 (1H, d, J =15 Hz), 7.3−7.42 (5H, m).

2:[15] ***N*-Cinnamylaniline**: IR(neat) 1340, 1515, 1670, 3020 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.74 (1H, broad), 3.85 (2H, d, J = 6 Hz), 6.27 (1H, dt, J = 12,6 Hz), 6.54−6.73 (4H, m), 7.13−7.34 (7H, m).

4: ***N*-(3,7-Dimethyl-2,6-octadienyl)cyclohexylamine**: IR-(neat) 1200, 1640, 1670, 3020, 3400 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.8−1.34 (6H, m), 1.59 (3H, s), 1.66 (6H, s), 1.76−1.83 (4H, m), 2.03−2.07 (4H, m), 2.74−2.82 (1H, m), 3.12 (1H, broad), 3.34−3.41 (2H, m), 5.04−5.06 (1H, m), 5.28−5.37 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.4 (CH_3), 17.6 (CH_3), 23.4 (CH_3), 25.4 (CH_2), 25.4 (CH_2), 25.7 (CH_2), 26.1 (CH_2), 27.3 (CH_2), 29.9 (CH_2), 32.1 (CH_2), 49.8 (CH), 60.4 (CH_2), 118.1 (CH), 119.0 (CH), 131.9 (C), 132.8 (C). Anal. Calcd for $C_{16}H_{29}N$: C, 81.63; H, 12.42; N, 5.95. Found: C, 81.70; H, 12.20; N, 5.72.

5: ***N*-(3,7-Dimethyl-2,6-octadienyl)aniline** IR(neat) 1340, 1515, 1670, 3020, 3400 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.62 (3H, s), 1.69 (3H, s), 1.71 (3H, s), 2.04−2.12 (4H, m), 3.59−3.71 (2H, m), 5.07−5.11 (1H, m), 5.31−5.35 (1H, m), 6.60−6.72 (3H, m), 7.15−7.24 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.3 (CH_3), 17.6 (CH_3), 25.7 (CH_3), 26.4 (CH_2), 39.4(CH_2), 41.9 (CH_2), 112.8 (2 CH), 117.2 (CH), 121.5 (CH), 122.2 (C), 123.9 (CH), 129.1 (2 CH), 138.9 (C), 148.9 (C). Anal. Calcd for $C_{16}H_{23}N$: C, 83.79; H, 10.11; N, 6.11. Found: C, 83.91; H, 10.21; N, 6.13.

6: ***N*-(3,7-Dimethyl-2,6-octadienyl)benzylamine** IR(neat) 1500, 1670, 3020, 3400 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.56 (6H, s), 1.61 (3H, s), 1.91−2.06 (4H, m), 3.15−3.20 (2H, m), 3.17 (2H, s), 5.04−5.06 (1H, m), 5.25−5.27 (1H, m), 7.16−7.28 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.2 (CH_3), 17.6 (CH_3), 25.7 (CH_3), 26.5 (CH_2), 39.6 (CH_2), 46.3 (CH_2), 53.4 (CH_2), 122.6 (CH), 123.5 (CH), 123.9 (CH), 124.1 (CH), 126.9 (CH), 128.1 (CH), 128.3 (CH), 128.3 (C), 137.9 (C), 140.2 (C). Anal. Calcd for $C_{17}H_{25}N$: C, 83.89; H, 10.35; N, 5.75. Found: C, 84.1; H, 10.40; N, 5.47.

7:[16] ***N*-(1-Phenylethyl)cyclohexylamine**: IR(neat) 1200, 1640 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.96−1.67 (10H, m), 1.32 (3H, d, J = 6.6 Hz), 1.97 (1H, broad), 2.27−2.50 (1H, m), 3.94 (1H, q, J = 6.6 Hz), 7.20−7.34 (5H, m).

8:[8] ***N*-(1-Phenylethyl)aniline**: IR(neat) 1500, 1670, 3020, 3420 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.42 (3H, d, J = 6.6 Hz), 1.69 (1H, broad), 4.00 (1H, q, J = 6.6 Hz), 7.06−7.36 (10H, m).

9:[17] ***N*-(1-Phenylethyl)benzylamine**: IR(neat) 1300, 1640 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.40 (3H, d, J = 6.6 Hz), 1.82 (1H, broad), 3.64 (2H, d, J = 5.5 Hz), 3.82 (1H, q, J = 6.6 Hz), 7.06−7.36 (10H, m).

10: ***N*-[1-Methyl-3-(2,6,6-trimethylcyclohex-1-enyl)prop-2-enyl]cyclohexylamine**: IR(neat) 1200, 1640, 1670 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.98 (6H, s), 1.02−1.24 (4H, m), 1.38 (3H, d, J = 6 Hz), 1.40−1.47 (2H, m), 1.62 (3H, s), 1.58−1.97 (10H, m), 2.91 (1H, broad), 3.03 (1H, m), 3.56−3.61 (1H, m), 5.38 (1H, dd, J = 15,9 Hz), 6.07 (1H, d, J = 15 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.1 (CH_3), 19.2 (CH_3), 19.8 (CH_2), 25.4 (2 CH_2), 25.6 (CH_2), 28.6 (CH_3), 28.8 (CH_3), 31.1 (CH_2), 32.5 (C), 39.1 (2 CH_2), 39.2 (CH_2), 59.9 (CH), 60.6 (CH), 129.4 (C), 131.4 (CH), 133.6 (CH), 136.2 (C). Anal. Calcd for $C_{19}H_{33}N$: C, 82.84; H, 12.07; N, 5.08. Found: C, 82.71; H, 12.10; N, 5.21.

11: ***N*-[1-Methyl-3-(2,6,6-trimethylcyclohex-1-enyl)prop-2-enyl]aniline**: IR(neat) 1300, 1640, 1670, 3020, 3400 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.89 (3H, s), 0.94 (3H, s), 1.35 (3H, d, J = 6 Hz), 1.39−1.60 (6H, m), 1.60 (3H, s), 3.92−4.10 (1H,

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m), 5.35 (1H, dd, J = 15,9 Hz), 6.07 (1H, d, J = 15 Hz), 6.63−6.66 (3H, m), 7.12−7.17 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.8 (CH_2), 21.3 (CH_3), 22.6 (CH_3), 28.5 (CH_3), 28.6 (CH_3), 32.5 (CH_2), 32.7 (C), 39.2 (CH_2), 51.3 (CH), 113.6 (2 CH), 117.1 (CH), 127.5 (CH), 128.1 (C), 129.0 (2 CH), 129.2 (C), 136.9 (CH), 147.5 (C). Anal. Calcd for $C_{19}H_{27}N$: C, 84.70; H, 10.10; N, 5.20. Found: C, 84.70; H, 10.32; N, 5.33.

12: ***N*-[1-Methyl-3-(2,6,6-trimethylcyclohex-1-enyl)prop-2-enyl]benzylamine**: IR(neat) 1640, 1670, 3020, 3400 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.00 (3H, s), 1.01 (3H, s), 1.22 (3H, d, J = 9 Hz), 1.42−1.99 (6H, m), 1.69 (3H, s), 3.28 (1H, quintet, J = 6 Hz), 3.67−3.87 (2H, AB q, J = 54, 12 Hz), 5.28 (1H, dd, J = 15, 9 Hz), 5.95 (1H, d, J = 15 Hz), 7.25−7.32 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.2 (CH_2), 21.7 (CH_3), 22.6 (CH_3), 28.9 (CH_3), 28.9 (CH_3), 32.6 (CH_2), 33.8 (C), 39.3 (CH_2), 51.5 (CH_2), 56.1 (CH), 126.8 (CH), 128.1 (CH), 128.2 (CH), 128.2 (CH), 128.3 (CH), 128.4 (CH), 128.4 (C), 137.0 (C), 137.7 (CH), 140.4 (C). Anal. Calcd for $C_{20}H_{29}N$: C, 84.75; H, 10.31; N, 4.94. Found: C, 84.60; H, 10.40; N, 5.20.

13: ***N*-(3,5,5-Trimethylcyclohex-2-enyl)cyclohexylamine**: IR(neat) 1200, 1670, 3020, 3400 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.96 (3H, s), 1.02 (3H, s), 1.02−1.85 (10H, m), 1.85 (3H, broad s), 1.90−2.33 (4H, m), 3.65−3.75 (1H, m), 3.84−3.90 (1H, m), 5.34 (1H, broad); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.0 (CH_2), 25.1 (CH_3), 25.1 (CH_2), 25.3 (CH_2), 25.4 (CH_2), 28.1 (CH_3), 28.4 (CH_3), 30.4 (CH_2), 32.5 (C), 40.9 (CH), 44.6 (CH_2), 45.2 (CH_2), 62.5 (CH), 115.7 (CH), 134.0 (C). Anal. Calcd for $C_{15}H_{27}N$: C, 81.38; H, 12.29; N, 6.33. Found: C, 81.52; H, 12.60; N, 6.53.

14: ***N*-(3,5,5-Trimethylcyclohex-2-enyl)aniline**: IR(neat) 1360, 1670, 3020, 3400 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (3H, s), 0.99 (3H, s), 1.58−1.88 (4H, m), 1.67 (3H, s), 4.1 (1H, broad), 5.42 (1H, broad s), 6.67−6.74 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.4 (CH_3), 26.1 (CH_3), 31.0 (C), 31.1 (CH_3), 44.0 (CH_2), 45.2 (CH_2), 66.8 (CH), 115.0 (2 CH), 118.5 (CH), 123.5 (2 CH), 129.2 (CH), 136.0 (C), 147.0 (C). Anal. Calcd for $C_{15}H_{21}N$: C, 83.67; H, 9.83; N, 6.50. Found: C, 83.63; H, 10.05; N, 6.23.

15: ***N*-(3,5,5-Trimethylcyclohex-2-enyl)benzylamine**: IR-(neat) 1360, 1600, 1670, 3020, 3400 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.86 (3H, s), 0.98 (3H, s), 1.55−1.86 (4H, m), 1.66 (3H, s), 3.18−3.28 (1H, broad), 3.81 (2H, d, J = 12 Hz), 4.17-4.22 (1H, broad), 5.40−5.43 (1H, m), 7.25−7.36 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.5 (CH_3), 26.1 (CH_3), 30.0 (C), 31.8 (CH_3), 44.2 (CH_2), 45.1 (CH_2), 53.0 (CH_2), 66.5 (CH), 122.5 (CH), 123.8 (2 CH), 126.9 (CH), 128.3 (2 CH), 134.7 (C), 140.4 (C). Anal. Calcd for $C_{16}H_{23}N$: C, 83.79; H, 10.11; N, 6.11. Found: C, 84.01; H, 10.21; N, 6.40.

16: ***N*-(3-Nitrobenzyl)cyclohexylamine**: mp 115−117 °C; IR (KBr) 1670, 3010, 3400 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.85−2.05 (10H, m), 2.79 (1H, t, J = 9 Hz), 3.77 (1H, broad, NH), 4.01 (2H, d, J = 6 Hz), 7.56 (1H, t, J = 6 Hz), 7.72 (1H, d, J = 6 Hz), 8.20 (1H, s), 8.22 (1H, d, J = 6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.1 (CH_2), 25.3 (CH_2), 25.4 (CH_2), 27.7 (CH_2), 29.4 (CH_2), 55.2 (CH_2), 61.9 (CH), 123.7 (CH), 124.4 (CH_2), 130.0 (CH), 135.9 (CH), 136.8 (C), 148.4 (C). Anal. Calcd for $C_{13}H_{18}N_2O_2$: C, 66.63; H, 7.75; N, 11.96. Found: C, 66.75; H, 7.86; N, 12.08.

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