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# NaOEt: An Effective Reagent for the Direct Reductive Amination of Aldehydes and Ketones under Microwave Irradiation

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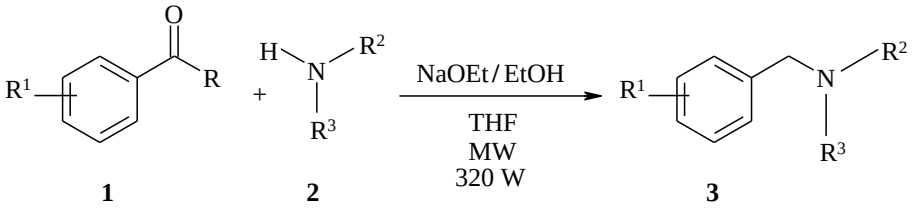
ABSTRACT

A simple, efficient, rapid and direct method of reductive amination of aldehydes and ketones into secondary and tertiary amines is developed. The reaction requires catalytic amount of sodium ethoxide (NaOEt, prepared *in situ* by the reaction of atomized sodium with EtOH) and works well in a mixture of EtOH-THF as a solvent. The yields are very high and the reactions go to completion within 2–5 min under microwave irradiation.




**1** **2** **3**

**Key words**: Aldehydes; ketones; reductive amination; NaOEt; EtOH-THF; microwave irradiation.

## 1. Introduction

Direct reductive amination of aldehydes and ketones to get secondary and tertiary amines is a synthetically important organic transformation, and is useful in the synthesis of a variety of pharmaceutically relevant organic compounds. In the reductive amination of carbonyl compounds with suitable reducing agents and aromatic amines, highly unstable imines are generally formed and there is no need to isolate these intermediates, which is the major advantage of this reaction. The choice of the reductant is very critical because the undesirable reduction of carbonyl group must be suppressed. Several reagents which effect direct reductive amination have been developed, including: $NaBH(OAc)_3$,[1] $ZnCl_2$-$NaBH_4$,[2] $NiCl_2$-$NaBH_4$,[3] $Ti(O^iPr)_4$-polymethylhydrosiloxane,[4] $Ti(O^iPr)_4$-$NaBH_4$,[5] *n*-$Bu_3SnH$,[6] *n*-$Bu_2SnClH$ and *n*-$Bu_2SnIH$ complexes,[7] decaborane,[8] $SiO_2$-$Zn(BH_4)_2$,[9] $Et_3SiH$-trifluoroacetic acid,[10] pyridine-$BH_3$,[11] $Et_3SiH$-$CF_3COOH$,[12] *n*-$Bu_2SnCl_2$/phenylsilane,[13] triethylsilane/iridium complex,[14] deep eutectic solvent-NaBH4,[15] $Au/TiO_2$-HCOOH,[16] $BH_3$·THF/AcOH/$CH_2Cl_2$ or $BH_3$·THF/TMSCl/DMF,[17] and use of $NaBH_4$-1-butyl-3-methylimidazolium tetrafluroborate ($BMIMBF_4$)[18] is reported.

Microwave assisted chemistry has attracted a considerable amount of attention and has been successfully applied in various fields of synthetic organic chemistry,[19–23] including the synthesis of heterocyclic compounds;[20] the rapid preparation of radio-labeled materials,[21] solvent-free

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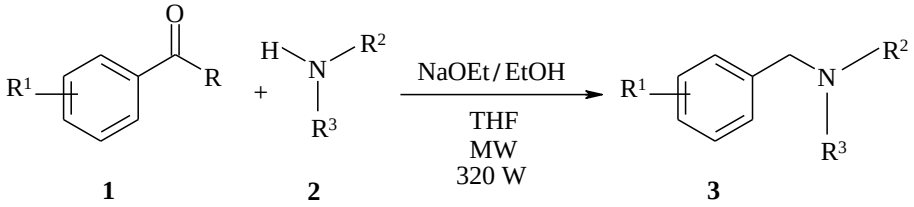
reactions [22] and phase-transfer catalysis [23]. It is evident that, microwave approaches can be developed for most chemical transformations which requiring heating. Microwave assisted formation of imines and their reduction into respective amines using either $PhSiH_3/Bu_2SnCl_2$ [24]; use of $NaBH_4$/Cation exchange resin [25] in the reductive amination of aldehydes and use of water-soluble transition metal catalysts [26] in the direct reductive amination of aldehydes with primary and secondary amines have been previously accomplished.

The advantages of performing reactions under controlled microwave irradiation are: significant rate enhancements and high product yields. We, therefore, were interested in developing a rapid and energy efficient protocol for the reductive amination of aldehydes and ketones; and herein, present an efficient and simple reductive amination of aldehydes and ketones to get secondary and tertiary amines respectively using NaOEt (prepared *in situ* by the reaction of atomized sodium in a mixture of EtOH-THF) under microwave irradiation within 2−5 min as shown in the **Scheme-1**.



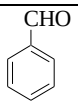
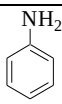
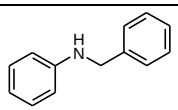
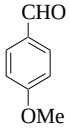
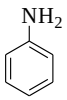
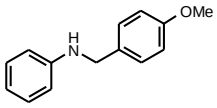

**1** **2** **3**

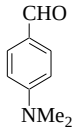
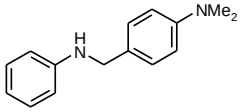
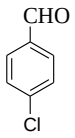
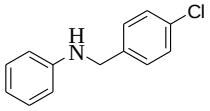
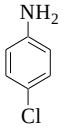
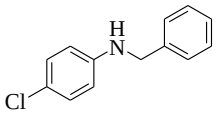
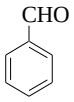
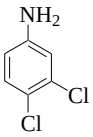
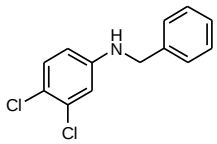
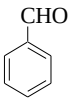
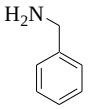
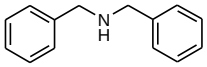
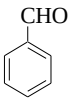
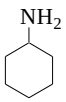
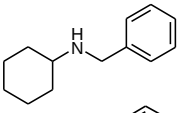
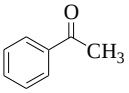
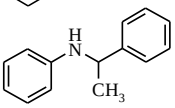
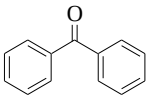
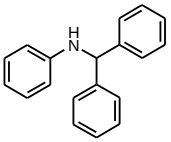
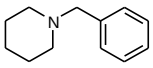
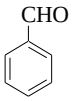
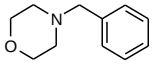
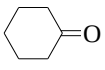
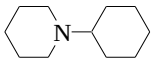
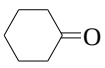
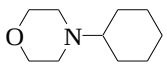
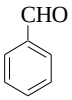
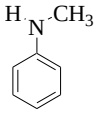
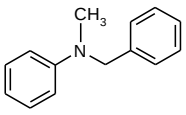
**Scheme-1:** Microwave-assisted reductive amination of aldehydes and ketones

## 2. Results and Discussion

In order to develop a new catalytic system for the reductive amination of aldehydes and ketones, atomized sodium in dry THF was selected for the purpose. It was seen that, this method did not require excess amount of amines compared to other methods and gave the intermediate imines instantaneously. Under this condition, carbonyl group was not reduced and the imine intermediates were converted easily to the corresponding amines. The absence of hydroxy byproducts indicated that, the above reaction condition was able to discriminate between the reduction of the imine intermediate and the carbonyl compound present in the reaction mixture. In order to show the general applicability of this method, we have applied this system for the reductive amination of structurally different carbonyl compounds and different amines. Under the said conditions, carbonyl compounds or amines carrying both electron donating and electron-withdrawing groups produced the corresponding amines with high selectivity. As indicated in **Table 1**, a variety of aldehydes and ketones when treated with primary and secondary amines in the presence of NaOEt in a mixture of EtOH-THF as a solvent, to afford the corresponding amines in very high to excellent yields under microwave irradiation. From the data present in this Table, it is clear that, the reductive amination of aldehydes and ketones using NaOEt in EtOH-THF under microwave irradiation at 320 W is very efficient and gives the products in short duration.

**Table 1**: NaOEt catalyzed reductive amination of aldehydes and ketones in EtOH-THF under microwave irradiation.

| Entry | Aldehyde (1) | Amine (2) | Product (3)[a] | Time (min) | Yield (%)[b] | M. P ( °C) Observed |
|---|---|---|---|---|---|---|
| **a** |   |   |   | 3 | 88 | 36−38 |
| **b** |   |   |   | 3 | 85 | 30−33 |

| | | | | | | |
|---|---|---|---|---|---|---|
| **c** |  |  |  | 4 | 80 | oily liq |
| **d** |  |  |  | 5 | 80 | oily liq |
| **e** |  |  |  | 4 | 79 | oily liq |
| **f** |  |  |  | 4 | 75 | oily liq |
| **g** |  |  |  | 4 | 90 | oily liq |
| **h** |  |  |  | 2 | 95 | oily liq |
| **i** |  |  |  | 5 | 80 | oily liq |
| **j** |  |  |  | 5 | 70 | oily liq |
| **k** |  |  |  | 2 | 97 | oily liq |
| **l** |  |  |  | 2 | 97 | oily liq |
| **m** |  |  |  | 2 | 98 | oily liq |
| **n** |  |  |  | 2 | 98 | oily liq |
| **o** |  |  |  | 3 | 96 | oily liq |

[a] Characterized by IR and GC-mass spectral analysis and by comparison with authentic samples.
[b] Isolated yields.

## 3. Experimental

### 3.1 Materials and instruments

All the reagents used were commercially available, all the liquid reagents and solvents were distilled before use. THF was distilled and dried over sodium. All the reactions were carried out in a MILESTONE microwave reactor at 320 W. The completion of the reaction was monitored on silica gel TLC plates by comparison with the authentic samples. GC-Mass spectra were obtained using a Shimadzu GC-MS QP 5050A instrument equipped with a 30 m length and 0.32 mm dia BP-5 column with the column temperature 80–15–250 °C.

### 3.2 General procedure for the reductive amination of aldehydes and ketones:

A mixture of the aldehyde/ketone (5 mmol), amine/aniline (7.5 mmol), NaOEt [Prepared *in situ* from 0.115 g of atomized sodium metal in a mixture of EtOH (1 mL) -THF (2 mL)] was taken in a Pyrex glass tube and placed in a microwave reactor at 320 W for 2 min (at intervals of 10 s). After the completion of the reaction (monitored by TLC using 8−10 % ethyl acetate in pentane or by GC), the product was extracted with diethyl ether (25 mL). The organic matter was filtered, washed with water (5 mL × 3), dried over anhydrous $Na_2SO_4$ and the product was obtained after the removal of solvent under vacuum. All the synthesized compounds are characterized by GC-Mass spectral analysis.

### 3.3. Spectral data

#### 3.3.1 *N*-Benzylaniline (3a):

FT-IR (neat): ν 3419, 3026, 2924, 2853, 1949, 1602, 1505, 1324, 11267, 989, 749 $cm^{-1}$;
$^1$HNMR (300 MHz, $CDCl_3$): δ 7.39−7.31 (m, 5H), 7.21 (t, 2H), 6.75 (t, 1H), 6.67 (d, 2H), 4.36 (s, 2H), 4.02 (br, 1H) ppm.
$^{13}$CNMR (75 MHz, $CDCl_3$): δ 148.2, 139.5, 129.3, 128.7, 127.6, 127.3, 117.6, 113.0, 48.3 ppm.

#### 3.3.2 *N*-(4′-Methoxybenzyl)-aniline (3b):

FT-IR (neat): ν 3416, 3019, 2930, 2835, 1922, 1603, 1508, 1321, 1247, 1177, 1034, 824, 750, 692 $cm^{-1}$;
$^1$HNMR (300 MHz, $CDCl_3$): δ 7.33 (d, 2H), 7.22 (t, 2H), 7.01−6.98 (m, 2H), 6.92 (d, 2H), 6.76 (t, 1H), 6.67 (d, 2H), 4.28 (s, 2H), 3.98 (br, 1H), 3.84 (s, 3H) ppm;
$^{13}$CNMR (75 MHz, $CDCl_3$): δ 158.8, 148.2, 131.4, 129.3, 128.8, 117.5, 114.0, 112.8, 55.2, 47.7 ppm.

#### 3.3.3 *N*-(4′-*N*,*N*-Dimethylbenzyl)-aniline (3c):

**FT**-IR (neat): ν 3413, 3019, 2931, 2834, 1922, 1600, 1500, 1325, 1239, 1170, 1024, 823, 752, 690 $cm^{-1}$;
$^1$HNMR (400 MHz, $CDCl_3$): δ 7.04 (t, 2H), 6.88 (d, 2H), 6.58 (m, 1H), 6.43−6.47 (m, 4H), 4.32 (s, 2H), 4.0 (br, 1H), 2.85 (s, 6H) ppm;
$^{13}$CNMR ($CDCl_3$, 75 MHz): δ 147.6, 131.2, 129.6, 127.9, 117.2, 113.5, 46.2, 40.3.

#### 3.3.4 *N*-(4-chlorobenzyl)-aniline (3d):

FT-IR (neat) ν: 3671, 3418, 2922, 2851, 1898, 1603, 1508, 1430, 1324, 1271, 1092, 1014, 814,750, 692 $cm^{-1}$.
$^1$HNMR (300 MHz, $CDCl_3$): δ 7.32 (s, 4H), 7.19 (t, 2H), 6.75 (t, 1H), 6.64 (d, 2H), 4.32 (s, 2H), 4.04 (br, 1H) ppm;
$^{13}$CNMR (75 MHz, $CDCl_3$): δ 147.8, 138.0, 132.8, 129.3, 128.7, 117.8, 112.9, 47.6 ppm.

#### 3.3.5 *N*-Benzyl-4-chloroaniline (3e):

FT-IR (neat): ν 3427, 3028, 2924, 2853, 1952, 1864, 1600, 1502, 1453, 1401, 1321, 1177, 1094, 915, 815, 733, 698, 505 $cm^{-1}$;
$^1$HNMR (300 MHz, $CDCl_3$): δ 7.37−7.31 (m, 5H), 6.14 (d, 2H), 6.56 (d, 2H), 4.32 (s, 2H), 4.1 (br, 1H) ppm;
$^{13}$CNMR (75 MHz, $CDCl_3$): δ 146.7, 139.0, 129.0, 128.7, 127.4, 127.3, 122.0, 114.0, 48.3 ppm.

#### 3.3.6 Dibenzylamine (3g):

FT-IR (neat): ν 3426, 3423, 3023, 2914, 2852, 1952, 1861, 1598, 1500, 1453, 1404, 1322, 1170, 1094, 915, 815, 733, 688, 507 $cm^{-1}$;

$^{1}$HNMR (400 MHz, $CDCl_3$): δ 7.34−7.21 (m, 10H), 3.80 (s, 4H), 1.71 (brs, 1H) ppm;
$^{13}$CNMR ($CDC1_3$, 100 MHz): δ 140.4, 128.5, 128.3, 127.1, 53.2 ppm.

**3.3.7 *N*-Cyclohexylbenzylamine (3h)**:
FT-IR (neat): ν 3420, 3023, 2917, 2852, 1952, 1861, 1598, 1500, 1453, 1404, 1322, 1170, 1093, 905, 816, 732, 668, 508 $cm^{-1}$;
$^{1}$HNMR (400 MHz, $CDCl_3$): δ 7.33−7.19 (m, 5H), 3.80 (s, 2H, $CH_2$), 2.53−2.43 (m, 1H, CH), 1.93−1.89 (m, 2H, $CH_2$), 1.75−1.70 (m, 2H, $CH_2$), 1.63−1.59 (m, 1H, NH), 1.35−1.04 (m, 6H, $CH_2$) ppm.
$^{13}$CNMR ($CDCl_3$, 75 MHz): δ 140.8, 128.2, 128.0, 126.6, 56.2, 51.0, 33.6, 26.2, 25.0 ppm.

**3.3.8 1-Benzylpiperidine (3k)**:
FT-IR (neat): ν 3033, 2983, 2630, 1727, 1379, 1240, 930, 752, 716, 700, 606 $cm^{-1}$;
$^{1}$HNMR (400 MHz, $CDCl_3$): δ 7.33−7.20 (m, 5H), 3.47−3.43(m, 4H), 2.37 (brs, 4H), 1.59−1.54 (m, 2H) ppm;
$^{13}$CNMR ($CDCl_3$, 100 MHz): δ 138.7, 129.3,128.1, 126.8, 63.9, 54.5, 26.2, 26.0, 24.4 ppm;

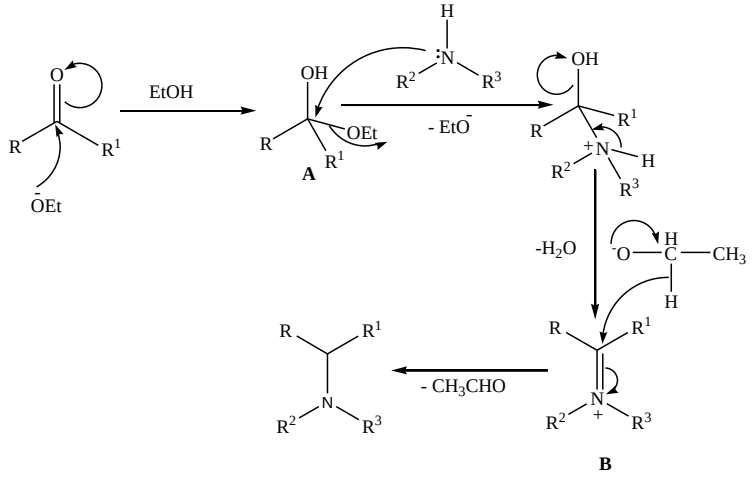
**3.3.9 4-Benzylmorpholine (3l)**:
FT-IR (neat): ν 3034, 2986, 2631, 1717, 1377, 1245, 1045, 939, 750, 716, 699, 609 $cm^{-1}$;
$^{1}$HNMR (400 MHz, $CDCl_3$): δ 7.45−7.28 (m, 5H), 4.68 (s, 2H), 2.10−2.00 (m, 8H) ppm;
$^{13}$CNMR ($CDCl_3$, 75 MHz): δ 140.5, 129.4, 128.1, 126.9, 66.3, 64.9, 60.4 ppm.

**3.3.10 4-Cyclohexylmorpholine (3n)**:
FT-IR (neat) ν: 3422, 3021, 2917, 2852, 1952, 1858, 1596, 1502, 1451, 1400, 1322, 1170, 1084, 900, 809, 731, 648, 500 $cm^{-1}$;
$^{1}$HNMR (400 MHz, $CDCl_3$) δ: 3.77−3.75 (m, 4H), 2.61−2.58 (m, 4H), 2.25−2.18 (m, 1H), 1.94−1.09 (m, 10H) ppm;
$^{13}$C NMR ($CDCl_3$, 100 MHz) δ: 67.5, 63.8, 49.7, 28.9, 26.3, 25.8 ppm.

**3.3.11 *N*-Benzyl-*N*-methylaniline (3o)**:
FT-IR (neat): ν 3430, 3029, 2926, 2874, 1952, 1850, 1599, 1502, 1451, 1443, 1322, 1178, 1089, 910, 809, 731, 653, 523 $cm^{-1}$;
$^{1}$HNMR (400 MHz, $CDCl_3$): δ 7.32−7.19 (m, 7H), 6.75−6.68 (m, 3H), 4.51 (s, 2H), 2.99 (s, 3H) ppm;
$^{13}$CNMR ($CDCl_3$, 100 MHz): δ 138.9, 133.2, 129.7, 128.4, 127.9, 127.1, 121.8, 114.2, 58.1, 41.8 ppm.

## 4. A Plausible Mechanism

A plausible mechanism for the direct reductive amination of carbonyl compounds with amines is envisaged. Ethoxide ion is expected to attack the carbonyl carbon to give an intermediate **A**, which on reaction with an amine in the subsequent step may give the iminium ion intermediate **B**. **B** in the presence of ethoxide ion is expected to get reduced to give the corresponding amine as shown in the **Scheme-2**.




**Scheme-2**: A plausible mechanism for the reductive amination of aldehydes and ketones

## 5. Conclusions

In conclusion, we have developed an easy approach to the direct reductive amination of aldehydes and ketones using NaOEt (prepared *in situ* by the reaction of atomized sodium in a mixture of EtOH-THF) under microwave irradiation at 320 W. The developed method is rapid, facile and energy efficient; involves simple workup, uses readily available chemicals and gives very high to excellent yield of the products in short durations. Hence, this procedure could be useful as an alternative to the existing methods of direct reductive amination of carbonyl compounds.

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## 7. Conflict of interest

There is no conflict of interest in publishing this work.

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