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A novel one-pot reductive amination of aldehydes and ketones with lithium perchlorate and zirconium borohydride–piperazine complexes

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This paper is dedicated to Morteza Nilforoushan for his contribution in Iranian pharmaceutical industry

Abstract—A novel, one-pot reductive mono-alkylation method of amines (primary and secondary), 1,2-phenylenediamine, *O*-trimethylsilylhydroxylamine, and *N*,*N*-dimethylhydrazine was developed using $LiClO_4$ (5 mol %) as a source for in situ generation of imine, iminium ion, oxime, and hydrazone, and zirconium borohydride–piperazine complex as reducing agent. This condition is especially useful for situations in which it is not practical to use the amine in excess (as is typically the case under acid-catalyzed conditions) or for acid-sensitive compounds.

1. Introduction

The direct reductive amination,[1] which allows the conversion of carbonyl functionality to structurally diverse primary, secondary, and tertiary amines, is an important method in organic synthesis.[2] The overall process involves the formation of an imine or iminium ion intermediate upon reaction of a carbonyl compound with ammonia, primary or secondary amine, followed by in situ reduction to an alkylated amine of higher order in a single operation. This reaction offers compelling advantages over amine synthesis, including brevity, wide commercial availability of substrates, and generally mild reaction conditions. Several reagents, which effect reductive amination have been recently developed, including the following: catalytic hydrogenation,[3] Zn–AcOH,[4] Et_3SiH–CF_3CO_2H,[5] Bu_3SnH–DMF.[6] In addition, various modified borohydride derivatives, which effect direct and indirect reductive amination, have been developed including the following: $NaBH_3CN$,[7a] $NaBH(OAc)_3$,[7b] pyridine–BH_3,[7c] $ZnCl_2$–$NaBH_4$,[7d] silica gel–$Zn(BH_4)_2$,[7e] $Ti(O\text{-}i\text{-}Pr)_4$–$NaBH_4$,[7f] and $NiCl_2$–$NaBH_4$.[7g] However, in terms of functional group tolerance, side reactions and reaction conditions, most of these reagents may have one or more drawbacks. For example, catalytic hydrogenation is incompatible with compounds containing other reducible functional groups such as double and triple bonds, nitro, cyano, and furyl groups.[8] $NaBH_4$, which is used for reductive amination requires harsh reaction conditions.[9] Cyanoborohydride and tin hydride reagents are highly toxic and generate toxic by-products such as HCN, NaCN,[10] or upon workup, organotin compounds. $NaBH(OAc)_3$ is flammable, water-reactive, and poorly soluble in most of the commonly used organic solvents. Pyridine–BH_3 is unstable to heat and must be handled with extreme care. Other hydrides such as zinc borohydride and nickel boride are not suitable for use in chemoselective reduction of imines having ketone, ester, and amide groups.[11] However, since carbonyl compounds themselves are also reduced under the conditions used, many of these reactions require an excess amount of the amines to obtain good yields of products. In addition, in some cases, some correlations between reaction time and reactivity of the amine species have been observed. For example, secondary alkylamines give moderate yields, as compared to primary alkylamines.[12] Reductive amination of conjugated carbonyl compounds has been addressed in detail in many of the reported methods; only two examples use sodium triacetoxyborohydride[7a] and silica gel–zinc borohydride[7e] procedures. Furthermore, while the literature abounds with heterogenous reductive amination processes,[3,13] little attention has been paid to the use of homogenous catalysts.[14] Direct reductive amination is performed in anhydrous conditions in order to avoid the decomposition of the reducing agents or catalysts, and to enhance the generation of the intermediate imines or iminium ions. As a result, the selection of the reagent is crucial. If one

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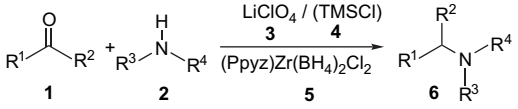
could perform the direct reductive amination of carbonyl compounds in air and in the presence of moisture, it should be of considerable interest. Thus, it is challenging to develop such an effective catalyst or reagent.

Our recent endeavor of selective reduction of various important functionalities with zirconium borohydride–piperazine complex[15] prompted us to initiate a systematic study of this useful air and thermally stable reducing agent. In this paper, we report our results on the development of a highly practical method for the synthesis of amine derivatives by the direct reductive amination of carbonyl compounds in the presence of lithium perchlorate (5 mol %) as a Lewis acid and zirconium borohydride–piperazine complex as a reducing agent in reagent grade dichloromethane (DCM). Varieties of aldehydes were subjected to direct reductive amination by this procedure. The results appear in Scheme 1. The acyclic and conjugated carbonyl compounds underwent successful reductive amination with diethylamine to produce the corresponding tertiary amines in good to excellent yields. Without $LiClO_4$, the process of using carbonyl compounds with amines, in the presence of zirconium borohydride–piperazine complex, does not smoothly lead to reductive amination, but is generally accompanied by reductive products of the carbonyl compounds.



	R^1	R^2	R^3	R^4	6%
a	*i*-Propyl	H	Et	Et	87
b	*n*-Propyl	H	Et	Et	90
c	4-Br-Phenyl	H	Et	Et	75
d	4-Pyridyl	H	Et	Et	80
e	*trans*-Cinnamyl	H	Et	Et	82
f	4-Cl-Phenyl	H	2-NH_2Phenyl	H	90
g	4-Cl-Phenyl	H	Phenyl	H	95
h	*trans*-Cinnamyl	H	Phenyl	H	92
i	4-NO_2-Phenyl	H	Phenyl	H	90
j	4-NC-Phenyl	H	Phenyl	H	90
k	Benzyl	Me	Phenyl	H	95
l	Phenyl	Me	Phenyl	H	84
m	4-Cl-Phenyl	H	O-TMSi	H	89
n	*trans*-Cinnamyl	H	H	NMe_2	80

Scheme 1.

Although many of the reported protocols for reductive aminations work well for the preparation of tertiary amines, in many cases the synthesis of secondary amines is compromised of overalkylation reactions.[16] However, because of their potential as robust pharmacophores and as useful synthetic intermediates, the synthesis of these amines has long been of interest.[17] To test the synthetic feasibility of our approach, we studied the direct reductive amination of an aldehyde with aniline. Thus, treatment of 4-chlorobenzaldehyde with aniline in DCM in the presence of $LiClO_4$ (5 mol %) and a stoichiometric amount of TMSCl as activator, afforded the corresponding iminium salt that was reduced with zirconium borohydride–piperazine complex to give *N*-(4-chlorophenyl) aniline in 90% isolated yield. To obtain good yields, the use of TMSCl was important in this reaction. In contrast, reaction with primary amines gave the corresponding imines, as determined by ^1H NMR of the crude reaction mixtures.

Next, we turned our attention to the direct mono-N-alkylation of a symmetrical primary diamine. In the presence of a catalytic amount of $LiClO_4$ (5 mol %) and TMSCl (stoichiometric), 1,2-diaminobenzene underwent mono-N-alkylation under the usual one-pot aminoreduction conditions in high yield. Di-alkylation was not detected. Under our standard conditions, direct reductive amination of *p*-nitro- and *p*-cyano benzaldehydes with primary amines proceeded smoothly with full conversion of aldehydes and good yields of the desired alkylated amines (Scheme 1, entries i and j). With these results in hand, we next studied the regioselective one-pot reductive amination of *trans*-cinnamaldehyde with aniline in the presence of $LiClO_4$ (5 mol %)/TMSCl (stoichiometric) and zirconium borohydride–piperazine complex as the reducing agent in DCM. It afforded the expected substituted cinnamyl amine in 92% isolated yields. The result is interesting since acetophenone has been shown to be an inert or difficult substrate in some reported reductive aminations,[18] the use of our procedure also enabled the reductive amination of ketones.

The substrate versatility of this direct reductive amination method was further demonstrated by the successful preparation of several *N*- and *O*-substituted primary amines. Thus, the reductive amination of 4-chlorobenzaldehyde and *trans*-cinnamaldehyde with *O*-trimethylsilylhydroxylamine and *N*,*N*-dimethylhydrazine resulted in the corresponding monoalkylated products as showed in Scheme 1. In both entries, no overalkylations were detected.

In summary, we have established a lithium perchlorate/zirconium borohydride–piperazine complex promoted direct reductive N-alkylation methodology, which is selective and efficient. High selectivity of the converting primary amine and symmetrical diamine, mono-N-alkylations has been clearly demonstrated, and use of protecting groups has been eliminated. This methodology proves to be a general protocol for the syntheses of the *N*-alkylated hydroxylamines and hydrazines, offering a wide variety of applications.

2. Experimental section

2.1. General procedure

2.1.1. Preparation of N-mono-alkylation of amines and amine derivatives. To a suspension containing $LiClO_4$ (11 mg, 5 mol %) in reagent grade DCM (8 mL), carbonyl compound (2 mmol) and diethylamine (2.2 mmol) were added and the mixture vigorously stirred for 15 min at 40 °C. After this time, zirconium borohydride–piperazine complex (104 mg, 3 mmol, 1.5 equiv) was added, the mixture was stirred for an additional 3 h. The reaction mixture was washed with water followed by brine solution and then extracted with CH_2Cl_2, dried over Na_2SO_4, concentrated under vacuum, and the crude mixture was purified by column chromatography on silica gel (hexane:ethylacetate, 2:1) to afford pure products. When aniline, *O*-trimethylsilylhydroxylamine, and *N*,*N*-dimethylhydrazine were used as the amine compound, the procedure was the same, but 2.0 mmol of trimethylsilyl chloride was used before reduction. All products were identified by comparing their NMR and IR values with those of authentic samples.[7b,11,19–21]

Compound **6a**.[19] Oil; IR: 2930, 2850, 2700, 1490 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): δ 0.87 (d, J=7.9 Hz, 6H), 1.4 (t, J=7.6 Hz, 6H), 1.8 (m, 1H), 2.3 (d, J=8.1 Hz, 2H), 2.6 (q, J=7.6 Hz, 4H); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 20.68 (CH_3), 25.02 (CH_3), 29.43 (CH), 53.33 (CH_2), 66.79 (CH_2).

Compound **6b**.[19] Oil; IR: 2930, 2840, 2700, 1490 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): δ 0.87–0.98 (t, J=8.3 Hz, 3H), 1.1–1.3 (m, 4H), 1.4–1.8 (t, J=7.8 Hz, 6H), 2.3 (q, J=7.8 Hz, 4H), 2.6 (t, 7.8 Hz, 2H); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 10.27 (CH_3), 13.79 (CH_3), 20.55 (CH_2), 28.82 (CH_2), 53.21 (CH_2), 58.41 (CH_2).

Compound **6c**.[19] Oil; IR: 2958, 2880, 2800, 1620, 1500, 740, 700 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): δ 1.3 (t, J=7.3 Hz, 6H), 2.7 (q, J=7.3 Hz, 4H), 3.5 (s, 2H), 7.4 (d, J=7.8 Hz, 2H), 7.5 (d, J=7.8 Hz, 2H); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 11.25 (CH_3), 46.42 (CH_2), 56.60 (CH_2), 119.24 (C), 128.41 (CH), 130.64 (CH), 139.23 (C).

Compound **6d**.[19] Oil; IR: 3055, 2926, 2850, 1602, 1503 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): δ 1.3 (t, J=7.8 Hz, 6H), 2.7 (q, J=7.8 Hz, 4H), 3.5 (s, 2H), 6.75 (d, J=7.8 Hz, 2H), 8.6 (d, J=7.8 Hz, 2H); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 11.24 (CH_3), 46.10 (CH_2), 56.60 (CH_2), 121.30 (CH), 149.24 (CH), 151.91 (C).

Compound **6e**.[19] Oil; IR: 3057, 3030, 2940, 2817, 1597, 1494, 967 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): δ 1.3 (t, J=7.8 Hz, 6H), 2.7 (q, J=7.8 Hz, 4H), 3.5 (d, J=6.3 Hz, 2H), 6.4 (m, 1H), 6.6 (d, J=6.3 Hz, 1H), 7.6 (m, 5H); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 11.24 (CH_3), 46.42 (CH_2), 55.20 (CH_2), 120.1 (CH), 124.1 (CH), 127.1 (CH), 128.2 (CH), 134.41 (CH), 135.64 (C).

Compound **6f**.[19] Oil; IR: 3415, 2920, 1593, 1494, 1319, 1265, 1086, 1008, 808, 743, 690 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): δ 4.3 (s, 2H), 3.6 (br s, 3H), 6.5–6.8 (m, 4H), 7.1–7.8 (m, 4H); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 47.36 (CH_2), 113.02 (CH), 117.95 (CH), 128.93 (CH), 129.31 (CH), 130.21 (CH), 131.11 (CH), 132.22 (C), 135.40 (C), 138.48 (C), 148.12 (C).

Compound **6g**.[20] Oil; IR: 3415, 2920, 1593, 1494, 1319, 1265, 1086, 1008, 808, 743, 690 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): δ 4.3 (s, 2H), 3.6 (br s, 1H), 6.5–6.8 (m, 5H), 7.1–7.8 (m, 4H); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 47.36 (CH_2), 113.02 (CH), 117.95 (CH), 128.93 (CH), 129.31 (CH), 130.21 (CH), 131.11 (C), 132.22 (C), 138.48 (C).

Compound **6h**.[21] Oil; IR: 3315, 3057, 3025, 2930, 2817, 1597, 1494, 1447, 967, 779, 692 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 3.9 (br s, 1H), 4.1 (d, J=6.4 Hz, 2H), 6.5–6.8 (m, 7H), 7.1–7.8 (m, 5H); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 47.36 (CH_2), 113.02 (CH), 117.95 (CH), 128.93 (CH), 129.31 (CH), 130.21 (CH), 131.11 (CH), 132.22 (CH), 138.48 (CH), 142.12 (C), 148 (C).

Compound **6i**.[11] IR: 3440, 3060, 2935, 1634, 1519, 1352, 1139 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 4.2 (s, 1H), 4.47 (s, 2H), 6.6 (m, 2H), 6.7–6.8 (m, 1H), 7.2 (d, J=8.1 Hz, 2H), 7.45 (m, 2H), 7.6 (d, J=8.1 Hz, 2H); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 47.204 (CH_2), 112.91 (CH), 118.27 (CH), 128.931 (CH), 129.43 (CH), 130.21 (CH), 140.62 (C), 143.00 (C), 157.44 (C).

Compound **6j**.[11] IR: 3330, 2940, 2850, 2210, 1610, 1530 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 4.2 (s, 1H), 4.47 (s, 2H), 6.6 (m, 2H), 6.7–6.8 (m, 1H), 7.2 (d, J=8.4 Hz, 2H), 7.45 (m, 2H), 7.6 (d, J=8.4 Hz, 2H); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 47.55 (CH_2), 110.99 (C), 113.02 (CH), 117.95 (CH), 118.27 (CN), 128.93 (CH), 129.54 (CH), 130.21 (CH), 145.62 (C), 147.60 (C).

Compound **6k**.[7b] Oil; IR: 3411, 3055, 2926, 1602, 1503 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): δ 1.1 (d, J=6.7 Hz, 3H), 2.7 (d, J=7.9 Hz, 2H), 3.4 (m, 1H), 3.7 (br s, 1H), 6.8 (m, 4H), 7.3 (m, 6H); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 22.10 (CH_3), 44.21 (CH_2), 48.29 (CH), 114.11 (CH), 116.10 (CH), 126.00 (CH), 128.90 (CH), 131.20 (CH), 132.00 (CH), 140.25 (C), 147.32 (C).

Compound **6l**.[11] Oil; IR: 3411, 3055, 2926, 1602, 1503 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.58 (d, J=6.8 Hz, 3H), 4.45 (q, J=6.8 Hz, 1H), 4.11 (br s, 1H), 6.6 (m, 2H), 6.7–6.8 (m, 2H), 7.2 (m, 2H), 7.45–7.6 (m, 4H); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 24.73 (CH_3), 53.26 (CH), 112.91 (CH), 118.27 (CH), 125.03 (CH), 126.01 (CH), 129.43 (CH), 130.21 (CH), 145.62 (C), 147.00 (C).

Compound **6m**.[19] The TMS group was removed after hydrolysis. Oil; IR: 3410, 2905, 1648, 1478, 1401, 1046, 1021, 818, 756, 621 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): δ 4.3 (s, 2H), 8.21 (s, 1H), 7.5–7.7 (m, 1H), 7.1 (d, J=7.36 Hz, 2H), 7.3 (d, J=7.36 Hz, 2H); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 51.10 (CH_2), 127.95 (CH), 128.93 (CH), 129.31 (CH), 138.48 (C).

Compound **6n**.[19] Oil; IR: 3410, 2945, 1685, 1662, 1577, 1472, 1085, 877, 818, 726, 623, 514 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): δ 2.3 (s, 6H), 3.6 (d, J=6.3 Hz, 2H), 3.3 (s, 1H), 6.0 (m, 1H), 6.7 (m, 2H), 7.4 (m, 5H); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 32.3 (CH_2), 42.47 (CH_3), 119.24 (CH), 125.40 (CH), 127.20 (CH), 128.41 (CH), 129.64 (C), 135.40 (CH).

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