Convenient Method for One-pot Preparation of 1,2-Diamines from Nitroolefins

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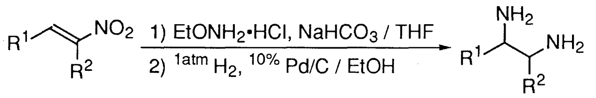
Convenient method for preparation of 1,2-diamine from the corresponding nitroolefin was established by successive reactions of Michael addition of *O*-ethylhydroxylamine to nitroolefin and reduction with hydrogen. The present preparative method was applicable to various nitroolefins by one-pot procedure.

Vicinal diamines are reliable building blocks for syntheses of various useful compounds such as natural products, medicinal compounds, or ligands of metal complexes,[1] and much effort has been made to develop a methodology for preparation of vicinal diamine. These compounds, 1,2-ethylenediamine for example, are industrially produced by reacting ammonia with the corresponding alkyl halide or alcohol. However, there still remain problems concerning the formation of polyamines as by-products which reduce yield of the desired vicinal diamines. It has been reported that olefins are also converted into the corresponding vicinal diamines in moderate to good yields via diols and diazides[2] or aziridines.[3] Some interesting results have been obtained in preparing vicinal diamines by the coupling reactions.[4,5] But many steps are needed to convert the starting materials into the corresponding vicinal diamines, and expensive reagents are employed to complete the reactions in the above-mentioned methods. Therefore, it has been desired to develop a simple method for preparation of vicinal diamines.

Recently, we have reported a convenient method for preparation of nitroolefins simply by treating olefins with nitric oxide.[6] Various olefins are effectively converted into the corresponding nitroolefins in high yields under an atmospheric pressure of nitric oxide in 1,2-dichloroethane and by successive treatment with acidic alumina. In this communication, we would like to report a convenient preparative method of 1,2-diamines from the corresponding nitroolefins, prepared by the above reaction, via Michael addition of *O*-ethylhydroxylamine to nitroolefin and subsequent reduction of the adduct (2-ethylhydroxylamino-1-nitroalkane) in one-pot procedure.[7]

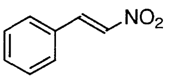
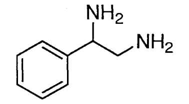
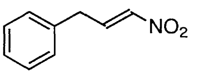
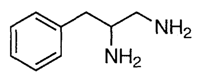
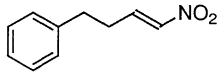
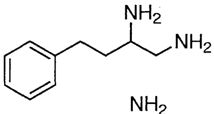
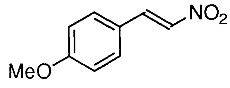
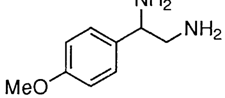
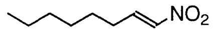
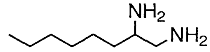
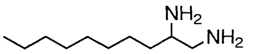
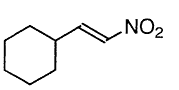
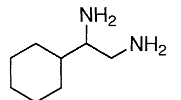
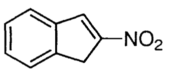
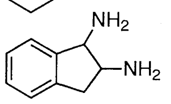
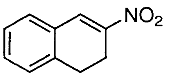
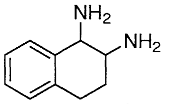
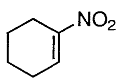
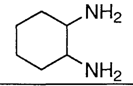


Scheme 1.

In the first place, Michael addition of ammonia, an amino group equivalent, was tried, and 2-amino-1-nitroalkane was afforded in quantitative yield. Successive reduction with hydrogen gave the corresponding 1,2-diamine in only 30% yield.[8] In the case of hydrogenative treatment of 2-benzylamino-1-nitroalkane, prepared by Michael addition of benzylamine, 2-benzylamino-1-aminoalkane alone resulted in 81% yield but the desired 1,2-diamine was not obtained.[9]

After examining various amino group equivalents, it was found that *O*-ethylhydroxylamine was quite effective to produce the corresponding 1,2-diamine: Namely, the corresponding nitroamine derivative was formed in quantitative yield by Michael addition of *O*-ethylhydroxylamine to nitrostyrene. The intermediate was successfully reduced into the corresponding 1,2-diamine in 83% yield under an atmospheric pressure of hydrogen in the presence of palladium on activated carbon (Pd 10%). The 1,2-diamine was identified by ^1H NMR, IR, and MS.[10] The results from these measurements supported that nitrogen-oxygen bond of *O*-ethylhydroxylamine moiety was

Table 1. Examples of syntheses of 1,2-diamines from the corresponding nitroolefins

Entry[a]	Nitroolefin	1,2-Diamine	Yield / %[d]
1			88
2			76
3			88
4[b]			64[e]
5			54
6			65[e]
7			69[e]
8[b]			77[f]
9[b]			90[g]
10[c]			48[h]

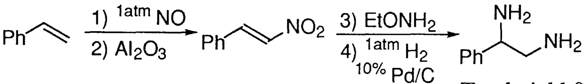
[a] Reaction conditions; nitroolefin 1.0 mmol, *O*-ehtylhydroxylamine 1.1 mmol, sodium hydrogen carbonate 1.1 mmol in THF 5 cm^3, RT. After Michael addition completed, $^{10\%}$Pd/C 100 mg in ethanol 5 cm^3, 1 atm H_2, RT. [b] *O*-ehtylhydroxylamine 5.0 mmol and sodium hydrogen carbonate 5.0 mmol were used. [c] After Michael addition completed, THF was removed by evaporation and hydrogenation was carried out with $^{10\%}$Pd/C 100 mg in ethanol 10 cm^3. [d] Isolated yields. Satisfactory spectra were obtained in measurements of ^1H NMR, IR, and MS. [e] Purified as oxalate salts. [f] Mixture of *cis*-form and *trans*-form. Ratio was not determined. [g] Mixture of *cis*-form and *trans*-form. Ratio was 88:12 and relative stereochemistry was not identified. [h] Mixture of *meso*-form and *dl*-form. Ratio of *meso*-form : *dl*-form was 81:19.

smoothly cleaved to afford free animo group along with ethanol.[11]

The present procedure for preparing 1,2-diamine was carried out simply in one-pot reaction; that is, Michael addition of *O*-ethylhydroxylamine to nitroolefin rapidly proceeded just by treating THF solution of nitrostyrene with *O*-ethylhydroxylamine hydrochloride and sodium hydrogen carbonate. After the addition reaction was completed, palladium on activated carbon (Pd 10%) and ethanol were added to the reaction mixture, and it was stirred under an atmospheric pressure of hydrogen at room temperature to give the desired 1,2-diamine in 88% yield.

The convenient one-pot procedure for preparation of 1,2-diamine was successfully applied to various nitroolefins (Table 1). In cases of nitroolefins derived from styrene or terminal olefins, the corresponding 1,2-diamines were obtained in good to high yields (Entries 1-4). Aliphatic nitroolefins were converted to the corresponding 1,2-diamines in moderate yields (Entries 5-7). Cyclic nitroolefins conjugated with aromatic ring also afforded the corresponding 1,2-diamines in 77% and 90% yields (Entries 8 and 9).

Since various nitroolefins are obtained by the aforementioned nitration of olefins, combination of the present procedure provides a simple method for synthesis of 1,2-diamines from olefins via only two step reactions. When styrene was employed, for example, the corresponding 1,2-diamine was obtained in 84% total yield based on styrene (Scheme 2).



Total yield 84%

Scheme 2.

A typical procedure is described for the synthesis of 1,2-diamino-1-phenylethane (Entry 1 in Table 1); to a solution of 1-nitro-2-phenylethene (149 mg, 1.0 mmol) in THF (5.0 cm^3) were added *O*-ethylhydroxylamine hydrochloride (107 mg, 1.1 mmol) and sodium hydrogen carbonate (92 mg, 1.1 mmol), and the reaction mixture was stirred at room temperature and monitored by TLC and/or GC analysis. After Michael addition was completed, palladium on activated carbon (Pd 10%, 100 mg) and ethanol (5.0 cm^3) were added to the reaction mixture, and stirring was continued overnight at room temperature under an atmospheric pressure of hydrogen. After filtration of catalyst through Celite pad, the solvent was removed under reduced pressure, and the crude product was purified by vacuum distillation to afford the corresponding 1,2-diamine in 88% yield (120 mg).

It is noted that convenient preparative method of 1,2-diamines from the corresponding nitroolefins by one-pot procedure was established by treating nitroolefin with *O*-ethylhydroxylamine, followed by hydrogenation.

References and Notes

1 M. T. Reetz, R. Jaeger, R. Drewlies, and M. Hübel, *Angew. Chem., Int. Ed. Engl.,* **30**, 103 (1991) and references are cited therein.

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7 Preparations from the corresponding nitroolefins were reported in literatures, but these methods were limited to some kinds of nitroolefins. P. Bitha and Yang-i Lin, *J. Heterocyclic Chem.*, **25**, 1035 (1988); M. S. Akhtar, V. L. Sharma, M. Seth, and A. P. Bhaduri, *Indian J. Chem.*, **27B**, 448 (1988); O. D. Strizhakov, E. P. Strizhakova, G. A. Ivko, and A. A. Akhrem, *Zh. Org. Khim.*, **25**, 653 (1989).

8 Reaction conditions were as follows; 2-amino-1-nitroalkane 1.0 mmol, Pd/C(10%) 100 mg in ethanol 5 cm^3, 1 atm H_2, RT.

9 Reaction conditions were as follows; 2-benzylamino-1-nitroalkane 1.0 mmol, PtO_2 30 mg in acetic acid 5 cm^3, 20 atm H_2, RT.

10 ^{1}H NMR ($CDCl_3$) δ=1.50 (4H, br s), 2.81 (1H, dd, J_1=6.92 Hz, J_2=12.86 Hz), 2.91 (1H, dd, J_1=5.28 Hz, J_2=12.86 Hz), 3.90 (1H, dd, J_1=6.92 Hz, J_2=5.28 Hz), 7.23-7.35 (5H, m); IR (neat) 3362, 3284, 2916, 2858, 1604, 1453, 887 cm^{-1}; MS *m/z* 30 ($CH_2NH_2^+$), 106 (M-$CH_2NH_2^+$).

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