**Introduction**

*O-(2,4-Dinitrophenyl)hydroxylamine* (1) is an orange solid (mp = 112 °C)\(^1\) and fairly stable when exposed to air. It is commercially available and can be readily synthesized by Charette’s method on a large scale:\(^1\) Nucleophilic aromatic substitution of 2,4-dinitrochlorobenzene by \(N\)-hydroxyphthalimide followed by hydrazinolysis gives 1 in 94% yield over two steps (Scheme 1).

\[
\text{O}_2\text{N} \quad \text{NO}_2 \quad \text{Cl} \\
\text{1. } \text{N-hydroxyphthalimide} \\
\text{Et}_3\text{N, acetone} \\
\text{r.t., 2 h, 95%} \\
\text{O}_2\text{N} \quad \text{NO}_2 \\
\text{2. } \text{H}_2\text{NNH}_2 \cdot \text{H}_2\text{O, CH}_2\text{Cl}_2–\text{MeOH (8:1)} \\
\text{0 °C, 8 h, 99%} \\
\text{1}
\]

Scheme 1

Abstracts

(A) **Amination of C-Nucleophiles**

Following Sheradsky and co-worker’s report,\(^2\) the amination of different C-nucleophiles was assessed.\(^2\) The results reveal that the enolates derived from deprotonation of variously substituted ethyl acetates smoothly undergo amination with 1, affording ethyl amino acetates in moderate to good yields in most cases. However, the amination of the carbanion derived from phenylacetonitrile gives the desired product in only 7% yield. In addition, neither Reformatsky reagents nor silyl enolates are susceptible to this transformation, even under violent reflux conditions.

(B) **Amination of N-Nucleophiles with C=N Bonds**

Amination of pyridines with 1 followed by protection of the resultant free NH\(_3\) group and deprotonation with a base leads to N-iminopyridinium ylides in up to 99% yield.\(^3\) The yields are depended on the steric hindrance of the 2- and 6-positions and the electronic densities of the pyridine rings. The product N-iminopyridinium ylides are versatile building blocks for the preparation of pyridine derivatives.\(^3\) The amination is also applicable to other heterocycles such as imidazoles.\(^3\)

As an electrophilic amination reagent, 1 is used to donate a free NH\(_3\) group to a variety of C-, N-, and O-nucleophiles to give products of significant importance in both synthetic and medicinal chemistry. The byproduct is 2,4-dinitrophenol (Scheme 2). Amination with 1 features the advantages of mild reaction conditions, simple and safe operations, and wide substrate scope.
(C) Amination of N-Nucleophiles with N–H Bonds
Transfer of amino groups to N-nucleophiles with N–H bonds yields hydrazines which are important intermediates in medicinal chemistry. Amination of the acidic N–H bond in 1H-quinazoline-2,4-diones was readily achieved by Tran et al. with yields. Later, the same group extended the methodology to the synthesis of 3-amino-1H-quinazoline-2,4-dione motifs. Chen et al. achieved the amination of the less acidic N–H bonds of pyroles with O-nucleophiles. Amination of N-nucleophiles with N–H bonds yields diverse primary anilines in moderate to good yields. One of the key steps involved in the mechanism is an α-nitro-facilitated 1,2-aryl migration.

(D) Amination of O-Nucleophiles
Castellino and Rapoport studied the amine exchange reaction of 1 with phenols. Their results indicated that the process is sensitive to the pK_a of the phenol. The reactions of phenols without strong electron-donating groups gave the desired products in moderate to good yields. However, the reaction of 3,5-dimethoxyphenol gave the corresponding product in only 13% NMR yield. Transfer of amino groups to N-nucleophiles with N–H bonds yields diverse primary anilines in moderate to good yields. One of the key steps involved in the mechanism is an α-nitro-facilitated 1,2-aryl migration.

(E) Amination of Arylboronic Acids
Kürti and co-workers reported the first metal-free amination of aromatic boronic acids with 1 under mild reaction conditions, producing diverse primary anilines in moderate to good yields. One of the key steps involved in the mechanism is an α-nitro-facilitated 1,2-aryl migration.

(F) Aziridination of Olefins
Yan and co-workers reported that in the presence of the tertiary amine N-methylpyrrolidine (NMP), α,β-unsaturated ketones can be aziridinated with 1 to give N-unsubstituted aziridines. Recent studies by Kürti et al. reveal that electron-rich olefins can be smoothly converted into N-unsubstituted aziridines by 1 under the catalysis of Du Bois’ catalyst [Rh_{esp}] with broad substrate scope and functionalization tolerance. The key intermediate of the former reaction is a hydrazinium salt, while that of the latter is a triplet nitrene.

References