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# Nickel-Catalyzed Dehydrogenation of Amines to Nitriles

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**Synopsis.** Aliphatic primary amines having α-methylene underwent oxidative dehydrogenation on treatment with $NiSO_4$ as a catalyst and $K_2S_2O_8$ as an oxidant to give the corresponding nitriles in good yields. Benzhydrylamine was converted to benzhydrylideneamine quantitatively under the same reaction conditions.

Selective transformation of functional groups of organic compounds is important in synthetic chemistry. Stoichiometric metal oxidants such as manganese dioxide, silver oxide, lead tetraacetate, nickel peroxide, and chromium compounds are generally the method of choice for this purpose. The stoichiometric use and disposal of these reagents is undesirable from economical and environmental viewpoints. As a result, there has been much recent interest in the catalytic system by these metal reagents.[1]

We previously reported that nickel catalyst with $K_2S_2O_8$ as an oxidant was efficient for the oxidative dehydrogenation of allylic alcohols to the corresponding unsaturated carbonyl compounds.[2] The catalytically active species in the system is nickel peroxide, and the method is considered as catalytic nickel peroxide oxidation. Here we report that this system has been found to be also effective for the catalytic dehydrogenation of primary amines to nitriles (Eq. 1).

$$RCH_2NH_2 \xrightarrow[H_2O\text{-}CH_2Cl_2,\ r.t.]{NiSO_4/K_2S_2O_8\text{-}NaOH} RCN \qquad (1)$$

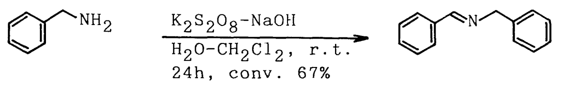
Several reagents have been reported on the oxidative method for the synthesis of nitriles from amines.[3,4] The metal oxidants such as silver oxide,[5] lead tetraacetate,[6] cobalt oxide,[7] and nickel peroxide[8] have been known as stoichiometric reagents for this purpose, but an efficient catalytic system has not yet been known. Though ruthenium-catalyzed oxidations of amines to nitriles with $O_2$,[9,10] PhIO,[11] and $K_2S_2O_8$[12] as the oxidants were reported, those methods could not be used for synthetic purposes because a considerable amount of by-products had been produced. The method described in this paper is the first practical method for the transformation of amines to nitriles by catalytic dehydrogenation reaction.

## Results and Discussion

The results of the nickel-catalyzed oxidation of aliphatic primary amines are summarized in Table 1. The reaction was performed by the addition of aqueous $NiSO_4$ to the vigorous stirring mixture of amine in $CH_2Cl_2$ and aqueous basic solution of $K_2S_2O_8$ at room temperature. $NiSO_4$ was converted to fine black precipitates of nickel peroxide immediately. This catalytic oxidation did not proceed under acidic or neutral conditions, because the catalytically active nickel peroxide formed only in the basic conditions. The amines were generally dehydrogenated to the corresponding nitriles at room temperature with 1—2 mol% of nickel catalyst over 90% yields.

The oxidation of benzylamine proceeded smoothly and 93% of benzonitrile was isolated in 6 h (Run 1). The olefinic double bond and ether bond were not affected under the reaction conditions and only the amine functional group was dehydrogenated to nitrile (Runs 8, 9). The diamines such as 1,3-benzenedimethanamine and 1,6-hexanediamine were also dehydrogenated to the corresponding dinitriles, isophthalonitrile and adiponitrile in 92% and 93% yield respectively (Runs 3, 10). The oxidation of 1,6-hexanediamine with stoichiometric amount of nickel peroxide was reported to result in the formation of adiponitrile only in 23% yield.[8]

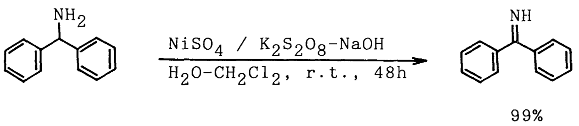
The nickel catalyst is essential for the dehydrogenation of amines to nitriles. When the oxidation of benzylamine was performed without the catalyst, the amine was slowly converted to *N*-benzylidenebenzylamine as the sole product, and benzonitrile was not detected (Eq. 2). *N*-Benzylidenebenzylamine was the condensation product of benzylamine and benzaldehyde which was produced primarily by uncatalyzed oxidation.



(2)

Nickel peroxide is generally prepared by the treatment of NaOCl with nickel sulfate.[8] The use of NaOCl as the oxidant in this nickel-catalyzed oxidation gave complex mixture of the products, because NaOCl itself reacted with amines without catalyst.

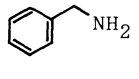
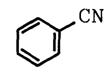
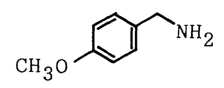
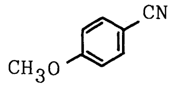
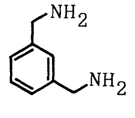
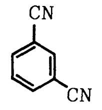
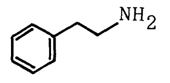
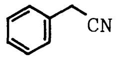
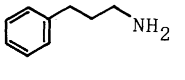
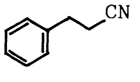
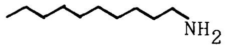
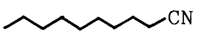
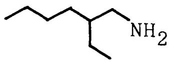
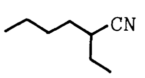
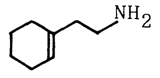
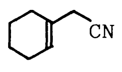
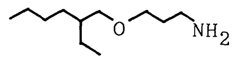
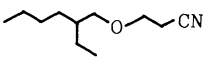
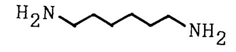
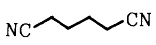
Benzhydrylamine was dehydrogenated slowly under the same catalytic conditions to benzhydrylideneamine quantitatively (Eq. 3). 1-Phenylethylamine was converted to acetophenone which was hydrolysis product of primarily formed imine in 90% yield in 6 h.



(3)

Though the oxidation of amines with stoichiometric amount of nickel peroxide was reported to give relatively good results for the formation of nitriles among the methods reported so far,[8] the use of stoichiometric amount of the reagent decrease its usability. This catalytic oxidation is able to replace the stoichiometric nickel peroxide oxidation because of the requirement of only 1—2 mol% of nickel sulfate

Table 1. Nickel-Catalyzed Oxidation of Aliphatic Primary Amines with $K_2S_2O_8$[a)]

| Run | Amine | $NiSO_4$<br>mol% | Time<br>h | Nitrile | Yield[b)]<br>% |
|---|---|---|---|---|---|
| 1 |  | 0.5 | 6 |  | 93 |
| 2 |  | 1 | 5 |  | 84 |
| 3 |  | 2 | 24 |  | 92 |
| 4 |  | 1 | 24 |  | 97 |
| 5 |  | 1 | 14 |  | 94 |
| 6 |  | 1.5 | 24 |  | 96 |
| 7 |  | 1 | 24 |  | 90 |
| 8 |  | 1 | 24 |  | 95 |
| 9 |  | 1 | 24 |  | 96 |
| 10 |  | 2 | 24 |  | 93 |

a) See experimental section for reaction conditions. b) Isolated yield.

and the higher yield of nitrile than that of the stoichiometric method.

## Experimental

$^1H$ NMR spectra were measured on JEOL JNM-PMX60Si spectrometer. IR spectra were measured using JASCO FT/IR-3 spectrometer. Elemental analyses were performed on a YANACO MT-5 elemental analyzer. The commercially available amines and $K_2S_2O_8$ were used without further purification. Column chromatography was carried out with silica gel (Wakogel C-200) at atmospheric pressure. $NiSO_4 \cdot 6H_2O$ was used as 0.040 mol dm$^{-3}$ aqueous stock solution.

**Nickel-Catalyzed Oxidation of Benzylamine with $K_2S_2O_8$.** Aqueous solution of 0.040 mol dm$^{-3}$ $NiSO_4$ (0.50 mL, 0.020 mmol) was added to the stirring mixture of benzylamine (0.429 g, 4.00 mmol) in $CH_2Cl_2$ (10 mL) and aqueous solution (50 mL) of $K_2S_2O_8$/NaOH (2.7 g, 10 mmol/0.80 g, 20 mmol). Fine black precipitates of nickel peroxide was formed immediately upon addition of $NiSO_4$. The resulted mixture was stirred vigorously at room temperature. After stirring for 6 h, the mixture was passed through a short Celite column to remove the black precipitates of nickel peroxide. The filtrate was extracted with $CH_2Cl_2$ (10 mL$\times$2). The combined extracts were dried over anhydrous $Na_2SO_4$ and evaporated under reduced pressure. The oily residue was purified by silica-gel column chromatography ($CH_2Cl_2$ as eluent) to give benzonitrile (0.384 g, 93%). The amines sited in Table 1 were oxidized in the same manner as mentioned above. These products were identified by comparison of physical data with those of commercial or reported samples.[4,5)]

**3-(2-Ethylhexyloxy)propionitrile.** Colorless oil. Bp 130—135 °C/18 mmHg (Kugelrohr; 1 mmHg≈133.322 Pa). IR (neat) 2255 cm$^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$=0.45—1.95 (m, 15H), 2.50 (t, 2H, $J$=6 Hz), 3.0—3.4 (m, 2H), 3.53 (t, 2H, $J$=6 Hz). Anal. ($C_{11}H_{21}NO$) C, H, N.

**Nickel-Catalyzed Oxidation of Benzhydrylamine with $K_2S_2O_8$.** Benzhydrylamine (0.733 g, 4.00 mmol) was oxidized with 1 mol% of $NiSO_4$ in the same way as described in nickel-catalyzed oxidation of benzylamine for 48 h at room temperature. Evaporation of $CH_2Cl_2$ extract gave almost pure benzhydrylideneamine (0.718 g, 99%).

**Oxidation of Benzylamine in the Absence of Nickel Catalyst.** Benzylamine was oxidized as described in nickel-catalyzed oxidation except the addition of $NiSO_4$. After stirring for 24 h at room temperature, the $CH_2Cl_2$ layer was separated and the aqueous layer was extracted once with $CH_2Cl_2$. The combined $CH_2Cl_2$ layer was dried over anhydrous $Na_2SO_4$ and the solvent was evaporated under a reduced pressure. $^1$H NMR analysis of the residue indicated that the residue contained *N*-benzylidenebenzylamine and benzylamine. The yields of the products were determined by $^1$H NMR. The imine was identified by comparison with the sample obtained by condensation of benzaldehyde with benzylamine.

## References

1) R. A. Sheldon and J. K. Kochi, "Metal-Catalyzed Oxidations of Organic Compounds," Academic Press, New York (1981).

2) S. Yamazaki and Y. Yamazaki, *Chem. Lett.*, **1989**, 1361.

3) A phase transfer catalyzed oxidation of amines to nitriles by NaOCl was reported: G. A. Lee and H. H. Freedman, *Tetrahedron Lett.*, **1976**, 1641.

4) Oxidation of amines to nitriles at the nickel hydroxide electrode in aqueous basic media was reported: U. Feldhues and H. J. Schäfer, *Synthesis*, **1982**, 145.

5) Silver oxide: T. G. Clarke, N. A. Hampson, J. B. Lee, J. R. Morley, and B. Scanlon, *Tetrahedron Lett.*, **1968**, 5685; Silver picolinate: J. B. Lee, C. Parkin, M. J. Shaw, N. A. Hampson, and K. I. MacDonald, *Tetrahedron*, **29**, 751 (1973).

6) A. Stojilikovic, V. Andrejevic, and M. Lj. Mihailovic, *Tetrahedron*, **23**, 721 (1967).

7) J. S. Belew, C. Garza, and J. W. Mathieson, *J. Chem. Soc. D*, **1970**, 634.

8) K. Nakagawa and T. Tsuji, *Chem. Pharm. Bull.*, **11**, 296 (1963); M. V. George and K. S. Balachandran, *Chem. Rev.*, **75**, 491 (1975).

9) R. Tang, S. E. Diamond, N. Neary, and F. Mares, *J. Chem. Soc., Chem. Commun.*, **1978**, 562.

10) S. Cenini, F. Porta, and M. Pizzottio, *J. Mol. Catal.*, **15**, 297 (1982).

11) F. Porta, C. Crotti, S. Cenini, and G. Palmisano, *J. Mol. Catal.*, **50**, 333 (1989).

12) G. Green, W. P. Griffith, D. M. Hollinshead, S. V. Ley, and M. Schröder, *J. Chem. Soc., Perkin Trans. 1*, **1984**, 681.