Rhenium(VII) Oxo Complexes as Extremely Active Catalysts in the Dehydration of Primary Amides and Aldoximes to Nitriles

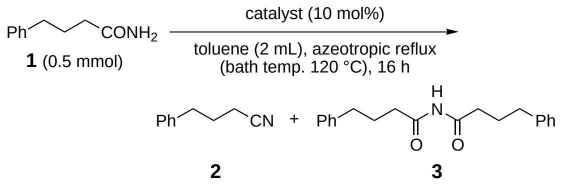
Kazuaki Ishihara, Yoshiro Furuya, and
Hisashi Yamamoto*

The synthetic importance of the dehydration of primary alkyl or aryl amides to their corresponding nitriles has been thoroughly documented in the literature.[1,2] Many of these reported methods, however, require the use of stoichiometric or excess amounts of highly reactive reagents or harsh conditions in acidic or basic media, or they involve tedious workup procedures. More recently, several methods for dehydration of primary amides under milder conditions have been developed.[3] In 1990, Watanabe et al.[3a] found that dichlorotris(triphenylphosphane)ruthenium (1 mol %) catalyzes the dehydration of primary amides in the presence of urea derivatives (1 equiv) in diglyme at 180 °C. In 1996, Mioskowski and co-workers[3b] developed the paraformaldehyde-catalyzed (490 mol %) water-transfer reaction of primary amides in a formic acid/acetonitrile mixture. In this reaction, acetamide is produced instead of water. In 1999, Bose et al.[3c,d] reported the first catalytic dehydration of primary amides in the absence of any additives except for catalyst. Unfortunately, this method requires a large amount of highly toxic dibutyltin oxide (25–35 mol[3c] or 37 mol %[3d]) as a catalyst.

In our continued studies on the development of various catalytic dehydration reactions in the absence of any additives except for catalyst, such as direct amide condensation,[4] direct ester condensation,[5] and dehydration of alcohols to alkenes,[6] we were interested in nitrile synthesis by catalytic dehydration reactions. We describe herein rhenium(VII) oxo complexes[78] as extremely active catalysts (1 mol %) for dehydration of not only primary amides but also of aldoximes to the corresponding nitriles.

We first investigated the catalytic activities (10 mol %) of various metal salts, metal alkoxides, metal oxides, and organometallic compounds that promote the model reaction of 4-phenylbutyramide in toluene at azeotropic reflux (120 °C) with removal of water (Dean–Stark apparatus) for 16 hours (Table 1). Commercially available trimethylsilylperrhenate[9] was the most effective catalyst for this reaction (Table 1, entry 1), and a 65–70 wt % aqueous solution of perrhenic acid[9] and rhenium(VII) oxide[9] exhibited higher catalytic activities than other metal compounds (Table 1, entries 2 and 4). When the temperature was raised from 120 °C to 125 °C, the perrhenic acid catalyzed conversion into the corresponding nitrile was increased from 38 % to 78 % (Table 1, entry 3), whereas rhenium(VI) and rhenium(IV) oxides were inert (Table 1, entries 12 and 13). As trimethylsilylperrhenate and rhenium(VII) oxide are very moisture-sensitive and highly expensive compounds, we chose aqueous perrhenic acid (which is easy to handle and less expensive than trimethylsilylperrhenate) as a practical dehydration catalyst. Interestingly, dibutyltin oxide was almost inert under the same conditions (Table 1, entry 10).[3c,d]

Table 1. Dehydration of 4-phenylbutyramide catalyzed by metal compounds.



Entry	Catalyst	**1/2/3**
1	$[(Me_3SiO)ReO_3]$	15:82:3
2	aqueous $[(HO)ReO_3]$[a]	60:38:2
3[b]	aqueous $[(HO)ReO_3]$[a]	19:78:3
4	$[(ReO_3)_2O]$	62:32:6
5[c]	$Zr(O\mathit{i}Pr)_4$	77:23:0
6[c]	$Hf(O\mathit{t}Bu)_4$	82:18:0
7	$[WOCl_3]$	81:14:5
8	$[MoO_2Cl_2]$	81:11:8
9	$Ti(O\mathit{i}Pr)_4$	89:11:0
10	Bu_2SnO	99:1:0
11	$[VO(O\mathit{i}Pr)_3]$	100:0:0
12	$[ReO_3]$	100:0:0
13	$[ReO_2]$	100:0:0
14	$[RuCl_2(\mathit{p}\text{-cymene})]_2$	100:0:0

[a] A 65–70 wt % solution of perrhenic acid (9–10 mol %) in water. [b] 125 °C (bath temperature). [c] 130 °C (bath temperature), 20 h.

We next investigated the solvent effect on the dehydration reaction of 4-phenylbutyramide catalyzed by aqueous perrhenic acid (9–10 mol %) under azeotropic reflux conditions (Table 2). The yield of the corresponding nitrile was increased in the order toluene < chlorobenzene < *o*-xylene (Table 2, entries 4, 3, and 2). Anisole was also a good solvent, but its polarity slightly lowered the catalytic activity of perrhenic acid (Table 2, entry 1). The dehydration of 4-phenylbutyramide occurs smoothly only at temperatures above 125 °C. The addition of molecular sieves to the reaction mixture disturbed the dehydration.

To explore the generality and scope of the above perrhenic acid catalyzed dehydration reaction, various structurally

Table 2. Solvent effect on the dehydration of 4-phenylbutyramide catalyzed by aqueous perrhenic acid.[a]

$$\mathbf{1}\ \text{(0.5 mmol)}\ \xrightarrow[\text{solvent (2 mL), azeotropic reflux, 5 h}]{\text{aqueous [(HO)ReO}_3\text{] (9–10 mol\%)}}\ \mathbf{2} + \mathbf{3}$$

Entry	Solvent	t [°C]	**1/2/3**
1	anisole	165	11:85:4
2	*o*-xylene	155	7:91:2
3	PhCl	140	9:89:2
4	toluene	125	62:36:2
5	heptane	110	98:2:0
6	EtCN	110	95:5:0
7	dioxane	110	91:9:0

[a] A 65–70 wt % solution of perrhenic acid (9–10 mol %) in water.

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[*] Prof. Dr. H. Yamamoto, Prof. Dr. K. Ishihara, Y. Furuya
Graduate School of Engineering, Nagoya University
SORST, Japan and Science Technology Corporation (JST)
Furo-cho, Chikusa, Nagoya 464-8603 (Japan)
Fax: (+81) 52-789-3222
E-mail: yamamoto@cc.nagoya-u.ac.jp

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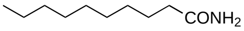
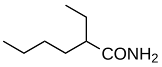
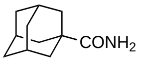
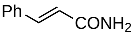
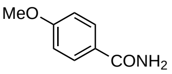
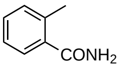
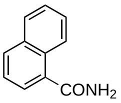
diverse primary amides were examined (Table 3). The use of perrhenic acid (1 mol%) under azeotropic reflux conditions in mesitylene was adequate for dehydrating not only aliphatic amides but also aromatic amides. The catalyst could be quantitatively recovered from the reaction mixture by distillation of products and solvents or extraction with water. For example, the catalyst was reused for the dehydration of *o*-toluamide more than three times with no loss of catalytic activity (Table 3, entry 7).[10] This result means that the turnover number (TON) is greater than 300. The reaction was successful for sterically congested amides such as 1-adamantanecarboxamide and *o*-toluamide (Table 3, entries 4 and 7). The reaction of 3-ethylhexanamide was carried out in toluene in the presence of trimethylsilylperrhenate (10 mol%) because the boiling point of the corresponding nitrile is close to that of mesitylene (Table 3, entry 3). The use of dibutyltin oxide instead of perrhenic acid under the same conditions gave poor results, even in mesitylene (Table 3, entry 6).[3c,d] Anisole was effective as a solvent for the reaction of a less soluble amide (1-naphthalenecarboxamide; Table 3, entry 8).

Table 3. Dehydration reaction of primary amides catalyzed by aqueous perrhenic acid.[a]

$$\underset{\text{(1 mmol)}}{\text{R–CONH}_2} \xrightarrow[\text{mesitylene (2 mL), azeotropic reflux (bath temp. 165–170 °C), 1 day}]{\text{aqueous [(HO)ReO}_3\text{] (0.9–1 mol\%)}} \text{R–CN}$$

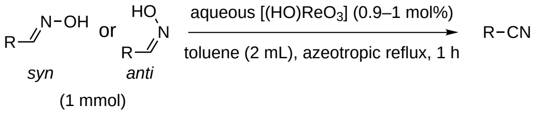
Entry	Primary amide	Yield [%]
1		54 (81[b])
2	$PhCH_2CH_2CH_2CONH_2$	91
3		79[c]
4		84
5		64
6		91 (25[d])
7[e]		> 99 (1st run) > 99 (2nd run) > 99 (3rd run)
8		93[f]

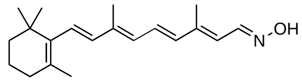
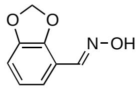
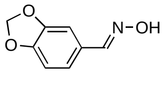
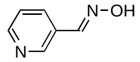
[a] A 65–70 wt% solution of perrhenic acid (9–10 mol%) in water. [b] $[(Me_3SiO)ReO_3]$ (1 mol%) for 2 days. [c] $[(Me_3SiO)ReO_3]$ (10 mol%), toluene. [d] Bu_2SnO (10 mol%). [e] Perrhenic acid (1 mol%) was reused. [f] Anisole.

Dehydration of aldoximes with an appropriate dehydrating agent is an alternative method for the synthesis of nitriles.[11] Very recently, Yang and Chang reported that catalytic dehydration of aldoximes can be performed efficiently with $[\{RuCl_2(p\text{-cymene})\}_2]$ (3 mol%).[11a] However, this reaction requires molecular sieves (2 wt equiv) to increase the reaction rate. According to our comparative experiment indicated in Table 1, entry 14, $[\{RuCl_2(p\text{-cymene})\}_2]$ was inert for the dehydration of primary amides. Thus, we took an interest in the catalytic activity of perrhenic acid for dehydration of aldoximes to nitriles.

The dehydration reaction was examined with various structurally diverse aldoximes in the presence of aqueous perrhenic acid (1 mol%) under azeotropic reflux conditions in toluene or mesitylene (Table 4). The reaction was complete in less than 1 h for all aliphatic and aromatic substrates, except nicotinaldoxime, and the corresponding nitriles were isolated in good to excellent yields. Sterically congested aldoximes such as cyclohexanecarboaldoxime (Table 4, entry 2), *o*-methoxybenzaldoxime (Table 4, entry 5), *α*-naphthalenecarboaldoxime (Table 4, entry 10), and mesitylenecarboaldoxime (Table 4, entry 11) were more reactive than less hindered aldoximes such as decanaldoxime (Table 4, entry 1), *m*- and *p*-methoxybenzaldoximes (Table 4, entries 6 and 7), and nicotinaldoxime (Table 4, entry 12): the former were dehydrated at reflux in toluene, whereas the latter were dehydrated at reflux in mesitylene. *trans*-2-Decenaldoxime and *all-trans*-retinaldoxime[11a] were readily converted into their corresponding nitriles in high yield with partial inversion of the double bond (Table 4, entries 3 and 4). The present method was useful for acid-sensitive substrates such as 2,3-(methylenedioxy)benzaldoxime (Table 4, entry 8) and 3,4-(methylenedioxy)benzaldoxime (Table 4, entry 9). Further-

Table 4. Catalytic dehydration of aldoximes to nitriles.

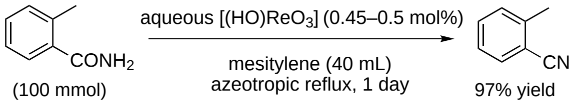


Entry	Aldoxime[a]	*syn*/*anti*	Yield [%]
1	$n\text{-}C_{10}H_{21}CH{=}NOH$	0:100	> 99[b]
2	$cyclo\text{-}C_6H_{11}CH{=}NOH$	63:37	91
3	$(2E)\text{-}n\text{-}C_8H_{17}CH{=}CHCH{=}NOH$	93:7	91
4		100:0	91[d,e]
5	$o\text{-}(MeO)C_6H_4CH{=}NOH$	100:0	94
6	$m\text{-}(MeO)C_6H_4CH{=}NOH$	100:0	86[b]
7	$p\text{-}(MeO)C_6H_4CH{=}NOH$	100:0	97[b]
8		100:0	95[b]
9		100:0	99[b]
10	1-NapCH=NOH	100:0	98
11	$2,4,6\text{-}Me_3C_6H_2CH{=}NOH$	100:0	> 99
12		100:0	84[b,e,f]

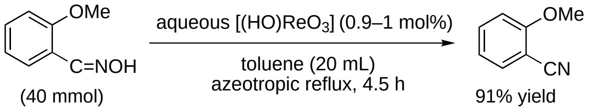
[a] Aldoximes were prepared in good yields by reaction of the corresponding aldehydes with $NH_2OH{\cdot}HCl$ (in pyridine/EtOH 1:1[11a] or in an aqueous solution of Na_2CO_3[12]). [b] Mesitylene. [c] The *E*/*Z* ratio of the product was 92:8. [d] *o*-Xylene, 2 h. [e] The isolated product was > 98% *all-trans*. [f] 3 h.

more, perrhenic acid could be used as a dehydration catalyst in the presence of basic nitrogen-containing compounds: nicotinaldoxime was smoothly dehydrated with the catalyst system to give 3-cyanopyridine in 84% yield (Table 4, entry 12).

The applicability of the present protocol to a large-scale process was then investigated. Complete dehydration of *o*-toluamide (100 mmol) and *o*-methoxybenzaldoxime (40 mmol) was observed in the presence of aqueous perrhenic acid (< 1 mol%), and the corresponding nitriles were isolated in high yields [Eqs. (1) and (2)].

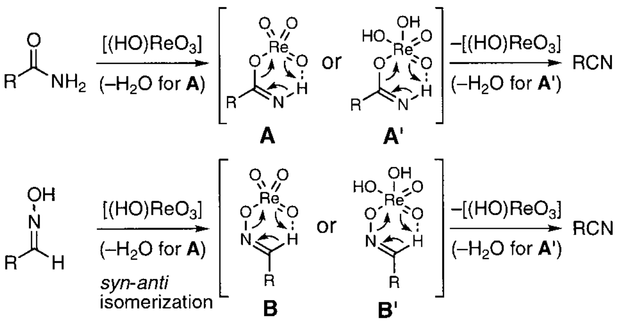


(1)



(2)

Based on the reactivities of primary amides and aldoximes in perrhenic acid catalyzed dehydrations, we propose the mechanism shown in Scheme 1. The reaction of the substrates and perrhenic acid leads to six-membered cyclic transition states **A** and **B** (upon dehydration) or to the analogous transition states **A**′ and **B**′ (without dehydration)[3c,d]. Dehydration of primary amides and aldoximes to produce nitriles should be promoted by selective coordination of rhenium(VII) oxo complexes with their oxygen atoms. On the contrary, the coordination of the catalyst with the nitrogen atom of primary amides should give the corresponding imides. Therefore, the oxophilicity of rhenium(VII) oxo complexes is a significant factor in obtaining nitriles as major products.[13,14] The high reactivity of sterically congested aldoximes and the low reactivity of less hindered aldoximes can be explained through **B** or **B**′, which is generated from a *syn* isomer of aldoximes. *Syn*/*anti* isomerization of aldoximes is known to occur under thermal or acidic conditions.[15] Therefore, the reactivity of aldoximes for dehydration may depend on their *syn*/*anti* equilibrium under the reaction conditions. It is not clear why trimethylsilylperrhenate is more active than perrhenic acid and rhenium(VII) oxide. Pure perrhenic acid has not been isolated because it exists preferentially as the dimeric anhydride [$O_3ReOReO_3$] under anhydrous conditions,[16] whereas trimethylsilylperrhenate is monomeric. Therefore, monomeric rhenium(VII) oxo species may be more active than dimeric or oligomeric complexes.



Scheme 1. Proposed mechanism for the dehydration of primary amides and aldoximes to form nitriles.

In conclusion, we have reported herein several noteworthy features of new catalysts for the dehydration of primary amides and aldoximes. The reaction proceeds under essentially neutral conditions, and the catalyst is recoverable and reusable. This protocol can be readily applied to large-scale processes with high efficiency and selectivity, making it an economical and environmentally benign process for the preparation of nitriles.

Experimental Section

General procedure (Tables 3 and 4):[10] A solution of primary amides (1 mmol) or aldoximes (1 mmol), perrhenic acid (65–70 wt% solution in water, 1.66 μL, 0.009–0.010 mmol, 0.9–1.0 mol%), and solvent (2 mL) was heated at azeotropic reflux with the removal of water. After several hours, the mixture was cooled to ambient temperature and saturated aqueous $NaHCO_3$ (100 μL) was added. After stirring for 10 min, the mixture was dried over $MgSO_4$, filtered, and concentrated under vacuum. The crude product was purified by flash column chromatography on silica gel.

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[10] The catalysts, aqueous [$(HO)ReO_3$] (colorless), and [$(Me_3SiO)ReO_3$] (white), were often recovered as a dark solid by partial reduction to lower valent rhenium oxides such as [$ReO_3 \cdot xH_2O$](black), [ReO_2] (brown), [ReO_3] (red), or [Re_2O_5] (blue). However, the recovered catalyst was still active for the dehydration. Lower valent rhenium oxides could be oxidized to perrhenic acid (colorless) or its anhydride (yellow) by treatment with hydrogen peroxide (35%) at 50 °C for 12 h and removal of excess hydrogen peroxide and water under vacuum at

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Lewis Acid Promoted, O-Selective, Nucleophilic Addition of Silyl Enol Ethers to N=O bonds**

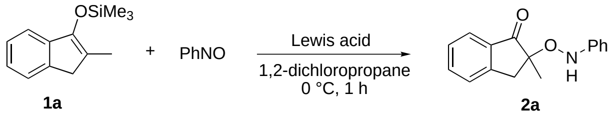
Norie Momiyama and Hisashi Yamamoto*

We report herein the first regioselective synthesis of α-aminooxy ketones from silyl enol ethers and nitrosobenzene [Eq. (1)]. The direct introduction of aminooxy or hydroxyamino groups at the α position of carbonyl compounds has not been part of synthetic practice, in sharp contrast to the very widespread addition of formyl electrophiles at the α position of ketone enolates or their equivalents, that is, aldol synthesis.[1] In fact, there are only a few reports on the use of nitrosobenzene[2] for nucleophilic addition with the silyl enol ethers of acetophenone and propiophenone to generate the corresponding α-hydroxyamino derivatives [Eq. (2)].[3] We were surprised to learn that treatment of silyl enol ethers with nitrosobenzene in the presence of various Lewis acid catalysts proceeds smoothly to generate previously unknown α-aminooxy ketones in high yields. The present procedure has important implications in the N–O–C-bond construction from these simple starting compounds and can open a new entry to useful building blocks for potentially important, biologically active compounds.[4]

Our initial design of a nucleophilic addition of silyl enol ethers to nitrosobenzene rested on finding a suitable catalyst that could facilitate N-alkylation with various silyl enol ethers. Trimethylsilyl triflate was chosen as a Lewis acid for this reaction based on its use in Mukaiyama-type aldol reactions.[5] However, nucleophilic addition catalyzed by trimethylsilyl triflate did *not* provide the N-adduct (hydroxyamino ketone). An X-ray crystallographic study or chemical transformation with acetyl chloride demonstrated that the N-adduct was not formed; instead the O-adduct (aminooxy ketone) was the product of the reaction [Eq. (1)].[6] We then focused on Lewis acid catalyzed O-selective nucleophilic addition as a new strategy for constructing N–O–C bonds.

A variety of Lewis acid catalysts were examined and are summarized in Table 1. Alkylsilyl triflates efficiently mediated the O-selective nucleophilic addition of silyl enol ether **1a** to nitrosobenzene (1,2-dichloropropane, 0 °C) to give the O-adduct **2a** in excellent yield (Table 1). The use of triethylsilyl triflate (10 mol %) led to the isolation of **2a** in 94 % yield (Table 1, entry 3); even a lower amount of the catalyst (1 mol %) still provided the product in 74 % yield (Table 1, entry 5). Titanium(IV) chloride, iron(III) chloride, and copper(II) triflate also led to the formation of **2a** in moderate to good yields (Table 1, entries 7, 8, 11).

Table 1. O-Alkylation of **1a** catalyzed by various Lewis acids.



Entry	Lewis acid	Equiv [mol %]	Yield [%][a]
1	none		< 1
2	Me_3SiOTf	5	86
3	Et_3SiOTf	10	94
4	Et_3SiOTf	5	88
5	Et_3SiOTf	1	74
6	*t*$BuMe_2SiOTf$	5	83
7	$TiCl_4$	5	71
8	$FeCl_3$	5	60
9	Me_3SiNTf_2	5	54
10	[AgOTf]	5	52
11	$[Cu(OTf)_2]$	5	58
12	$[Sn(OTf)_2]$	5	50

[a] Yield of isolated product.

Since aromatic C-nitroso compounds are known to exist as blue or green monomers and colorless dimers,[7] chemical models of the catalyst–nitrosobenzene complex predict the two coordination geometries **A** and **B** (Scheme 1). However, as Lewis acids promote the dimerization of the monomer nitrosobenzene,[8,9] O-alkylation may proceed via intermediacy of the Lewis acid coordinated nitroso dimer complex **A**. This process does not proceed through an aldol pathway in

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[*] Prof. H. Yamamoto, N. Momiyama
Graduate School of Engineering, Nagoya University, SORST
Japan Science and Technology Corporation (JST)
Chikusa, Nagoya 464-8603 (Japan)
Fax: (+81) 52-789-3222
E-mail: yamamoto@cc.nagoya-u.ac.jp

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