A Novel and Efficient Method for the Preparation of α-Hydroxyimino Carbonyl Compounds from α,β-Unsaturated Carbonyl Compounds with Butyl Nitrite and Phenylsilane Catalyzed by a Cobalt(II) Complex

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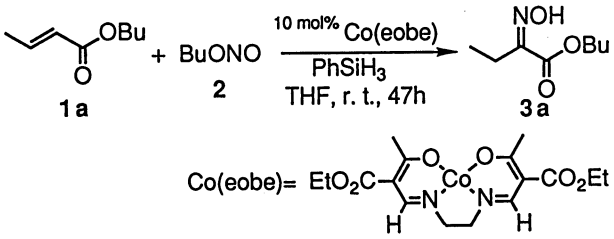
Various α,β-unsaturated carbonyl compounds, such as α,β-unsaturated esters, α,β-unsaturated ketones, α,β-unsaturated nitriles, and α,β-unsaturated amides, were directly converted to the corresponding α-hydroxyimino carbonyl compounds in high yields on treatment with butyl nitrite and phenylsilane in the presence of a catalytic amount of *N,N'*-bis(2-ethoxycarbonyl-3-oxobutylidene)ethylenediaminatocobalt(II) complex under mild conditions.

The introduction of a nitrogen atom into organic compounds is one of the most important reactions in organic synthesis, and several methods using various amines, nitrogen monoxide, azide, etc. with transition-metal complexes as a catalyst have been extensively investigated.[1] For example, concerning the introduction of a nitrogen atom into olefinic compounds, K. B. Sharpless and co-workers reported a method for the preparation of *cis*-2-aminocyclohexanol from cyclohexene with chloramine T (TsNClNa) catalyzed by osmium tetraoxide in *t*-butyl alcohol, followed by the reduction with sodium in liquid ammonia.[2] A method for the addition of *N*-chloro amines to olefins by using a redox catalyst, such as Cu(I)/Cu(II) or Fe(II)/Fe(III), was also presented.[3] We recently reported the α-nitrosation of α,β-unsaturated amides yielding the corresponding 2-nitroso amides with nitrogen monoxide and triethylsilane in the presence of a catalytic amount of *N,N'*-bis(2-ethoxycarbonyl-3-oxobutylidene)ethylenediaminatocobalt(II) (Co(eobe)) at room temperature.[4] However, the above-mentioned reaction is limited to α,β-unsaturated amides, and no practical methods for the direct introduction of a nitrogen atom at the α-position of α,β-unsaturated esters and α,β-unsaturated ketones catalyzed by transition-metal complexes have been reported at all.

We have considered the possibility of the employment of alkyl nitrites, which are commercially available reagents and are employed in various reactions, to introduce a nitrogen atom into organic compounds. For example, oximes of α-keto esters were prepared by the reaction of saturated esters with alkyl nitrite by a metal alkoxide.[5] Recently, the titanium chloride-promoted reaction of ketene alkyl silyl acetals with isopentyl nitrite affording oximes of α-keto esters was reported.[6]

In a previous communication,[7] we reported the α-oximation of various α,β-unsaturated esters with butyl nitrite and a silane affording the 2-hydroxyimino esters, the useful intermediates,[8] catalyzed by Co(eobe) under mild conditions. For example, when butyl crotonate (**1a**) was treated with butyl nitrite (**2**) and phenylsilane ($PhSiH_3$) in tetrahydrofuran (THF) in the presence of 10 mol% of Co(eobe) at room temperature, the corresponding oxime, butyl 2-(hydroxyimino)butyrate (**3a**), was obtained in an 89% yield (Scheme 1).



Scheme 1.

Here, we would like to discuss in detail the α-oximation of various α,β-unsaturated carbonyl compounds, such as α,β-unsaturated esters, α,β-unsaturated ketones, α,β-unsaturated nitriles, and α,β-unsaturated amides with butyl nitrite and a silane using a cobalt(II) complex as a catalyst.

Results and Discussion

α-Oximation of Butyl Crotonate (1a) with Butyl Nitrite (2). First, the reaction of butyl crotonate (**1a**) with butyl nitrite (**2**) and triethylsilane (Et_3SiH) in the presence of 10 mol% of Co(eobe) in 1,2-dichloroethane (DCE) was attempted at room temperature. It was found that butyl crotonate (**1a**) was consumed after 62 h, and butyl 2-(hydroxyimino)butyrate (**3a**) was obtained in a 28% yield (Entry 1 in Table 1). The effect of solvents on the yield of the oxime compound was studied by taking the reaction of butyl crotonate (**1a**) with butyl nitrite (**2**) and Et_3SiH catalyzed by Co(eobe) as a model. As shown in Table 1, a change in the

Table 1. α-Oximation of Butyl Crotonate (**1a**) in Various Solvents[a]

Entry	Solvent	Conversion[b]/%	Yield[c]/%
1	DCE	—	28
2	Benzene	85	39
3	AcOEt	100	55
4	THF	100	79

a) Reaction conditions; butyl crotonate (**1a**) 0.5 mmol, butyl nitrite (**2**) 1.5 mmol, Co(eobe) 0.05 mmol, Et_3SiH 1.5 mmol, solvent 2.5 ml, room temperature, under argon atmosphere. b) Determined by GC analysis. c) Isolated yield.

Table 2. α-Oximation of Butyl Crotonate (**1a**) Catalyzed by Various Cobalt(II) Complexes[a]

Entry	Co(II) complex	Conversion[b]/%	Yield[c]/%
1	Co(eobe)	100	79
2	Co(acacen)[d]	5	4
3	$Co(acac)_2$[e]	10	2
4	$Co(ecbo)_2$[f]	51	5

a) Reaction conditions; butyl crotonate (**1a**) 0.5 mmol, butyl nitrite (**2**) 1.5 mmol, Co(II) complex 0.05 mmol, Et_3SiH 1.5 mmol, THF 2.5 ml, room temperature, under argon atmosphere. b) Determined by GC analysis. c) Isolated yield. d) *N,N'*-Bis(1-methyl-3-oxobutylidene)ethylenediaminatocobalt(II). e) Bis(acetylacetonato)cobalt(II). f) Bis(2-ethoxycarbonyl-3-oxobutanalato)cobalt(II).

reaction medium from DCE to more polar solvents, such as ethyl acetate (EtOAc) and THF, improved the yield of oxime **3a**, especially in the case of THF, where oxime **3a** was obtained in a 79% yield (Entry 4).

Next, several cobalt(II) complexes were screened in the α-oximation of butyl crotonate (**1a**) in THF (See Table 2), and it was shown that Co(eobe) was the most effective catalyst for the present α-oximation of butyl crotonate (**1a**) (Entry 1). The catalytic activity of *N,N'*-bis(1-methyl-3-oxobutylidene)ethylenediaminatocobalt (II) (Co(acacen)) was very low (Entry 2), and in the cases of cobalt(II) complexes having 1,3-diketone-type ligands, the yields of oxime **3a** were low and reduction of **1a** to butyl butyrate with Et_3SiH proceeded exclusively (Entries 3 and 4).

Considering that a silane would be another important factor in the present reaction, the effect of various kinds of silanes on the α-oximation was examined by taking the reaction of butyl crotonate (**1a**) with butyl nitrite (**2**) in THF catalyzed by Co(eobe) as a model (See Table 3). Consequently, the yield of oxime **3a** increased in accordance with the reduction capability of the silane, and oxime **3a** was obtained in an 89% yield when $PhSiH_3$ was used (Entry 4). The influences of the amounts of butyl nitrite (**2**) and silane were also checked, and the oxime **3a** was produced in a 79% yield by using nearly one equivalent of $PhSiH_3$ to **1a** (Entry 5). On the other hand, the amount of butyl nitrite (**2**) influenced the reaction rate; that is, when one and a half equivalents of **2** to **1a** were used, the conversion of **1a** was reduced to 64% (Entry 6). This suggested that the step involving butyl nitrite (**2**) seemed to be the rate-determining step in the present reaction.

α-Oximation of Various α,β-Unsaturated Carbonyl Compounds with Butyl Nitrite and $PhSiH_3$ Catalyzed by Co(eobe). The above procedure was successfully applied to the α-oximation of various α,β-unsaturated carbonyl compounds such as α,β-unsaturated esters, α,β-unsaturated ketones, α,β-unsaturated nitriles, and α,β-unsaturated amides (See Table 4). First, the reactions of various α,β-unsaturated esters (**1b—i**) with butyl nitrite (**2**) and $PhSiH_3$ in the presence of 10 mol% of Co(eobe) in THF at room temperature were examined. As a result, acrylic esters (**1b** and **c**) and β-monosubstituted α,β-unsaturated esters (**1d—f**) were converted to the corresponding oximes (**3b—f**) in high yields (Entries 1—5). It was noted that the α-oximation of *p*-tolyl crotonate (**1g**) gave *p*-tolyl 2-(hydroxyimino)butyrate (**3g**) in a 78% yield accompanied without the decomposition of the *p*-tolyl ester moiety which was frequently observed when saturated esters were treated with alkyl nitrite in alcohol under basic conditions according to the conventional procedure[5] (Entry 6). The α-oximation of a functionalized α,β-unsaturated ester such as diethyl fumarate (**1h**) took place readily and the corresponding oxime **3h** was obtained in an 89% yield (Entry 7). In the case of a β,β-disubstituted α,β-unsaturated ester, such as benzyl 3-methylcrotonate (**1i**) hindered at the β-position, no reaction took place at all and the starting material was recovered (Entry 8).

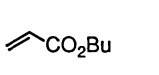
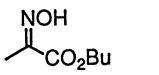
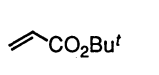
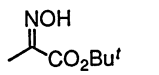
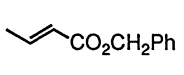
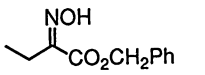
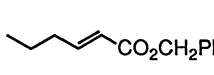
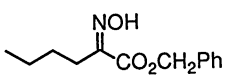
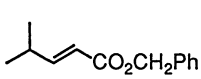
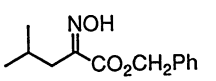
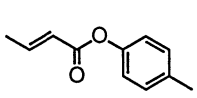
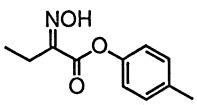
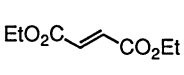
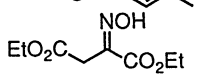
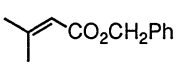
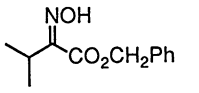
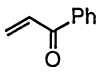
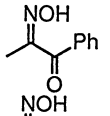
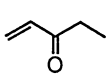
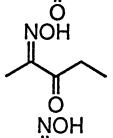
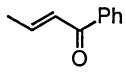
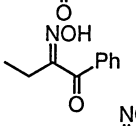
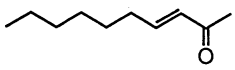
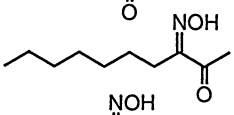
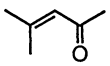
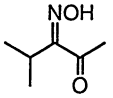
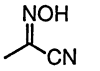
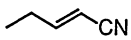
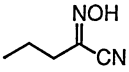
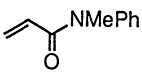
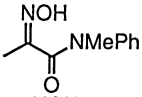
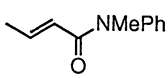
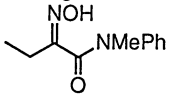
Next, the α-oximation of α,β-unsaturated ketones

Table 3. α-Oximation of Butyl Crotonate (**1a**) with Various Silanes and Butyl Nitrite (**2**)[a]

Entry	Silane	Amount of silane[b]	Amount of **2**[b]	Conversion[c]/%	Time/h	Yield[d]/%
1	Et_3SiH	3.0	3.0	100	62	79
2	Et_2SiH_2	3.0	3.0	100	47	84
3	Ph_2SiH_2	3.0	3.0	100	47	88
4	$PhSiH_3$	3.0	3.0	100	47	89
5	$PhSiH_3$	1.1	3.0	100	48	79
6	$PhSiH_3$	3.0	1.5	64	85	61

a) Reaction conditions; butyl crotonate (**1a**) 0.5 mmol, Co(eobe) 0.05 mmol, THF 2.5 ml, room temperature, under argon atmosphere. b) Equivalent per **1a**. c) Determined by GC analysis. d) Isolated yield.

Table 4. α-Oximation of Various α,β-Unsaturated Carbonyl Compounds

Entry	Substrate		Time/h	Product		Yield[b]/%
1		**1b**	41		**3b**	98
2		**1c**	48		**3c**	82
3		**1d**	41		**3d**	91
4		**1e**	48		**3e**	84
5		**1f**	48		**3f**	96
6		**1g**	21		**3g**	78
7		**1h**	21		**3h**	89
8[c]		**1i**	41		**3i**	0
9		**4a**	19		**5a**	93
10		**4b**	19		**5b**	89
11		**4c**	48		**5c**	95
12		**4d**	19		**5d**	70
13[c]		**4e**	15		**5e**	67
14		**6a**	21		**7a**	82
15		**6b**	37		**7b**	70
16		**8a**	48		**9a**	78
17		**8b**	60		**9b**	80

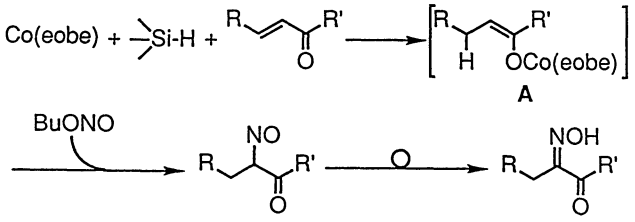
a) Reaction conditions; substrate 0.5 mmol, Co(eobe) 0.05 mmol, butyl nitrite (**2**) 1.5 mmol, $PhSiH_3$ 1.5 mmol, THF 2.5 ml, room temperature, under argon atmosphere. b) Isolated yield. c) Butyl nitrite (**2**) 3.0 mmol and $PhSiH_3$ 3.0 mmol were used at 60 °C.

under the above-mentioned conditions was investigated. It was found that vinyl ketones (**4a** and **b**) and β-monosubstituted α,β-unsaturated ketones (**4c** and **d**) also reacted with butyl nitrite (**2**) and $PhSiH_3$ to afford the monooximes (**5a**—**d**) of 1,2-diketones in high yields (Entries 9—12). The present method was effective for the selective preparation of monooximes of unsymmetrical 1,2-diketones, whereas the control of the chemoselectivity was difficult in the reaction of 1,2-diketones with hydroxylamine[9] or the α-oximation of saturated

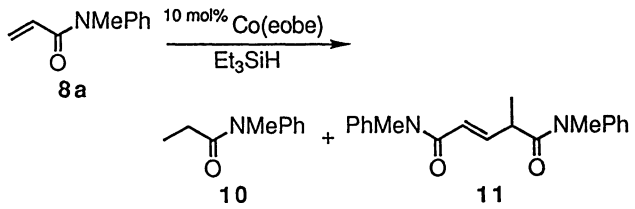
ketones having hydrogen atoms at both α-positions with alkyl nitrite under acidic conditions.[10] In the cases of α,β-unsaturated ketones, it should be pointed out that when a β,β-disubstituted α,β-unsaturated ketone such as mesityl oxide (**4e**) was treated with butyl nitrite (**2**) and $PhSiH_3$ in the presence of a catalytic amount of Co(eobe) at 60 °C, the corresponding oxime **5e** was obtained in a 67% yield, while in the case of benzyl 3-methylcrotonate (**1i**), no reaction took place at all under the same conditions (Entry 13).

The present procedure could also be applied to the α-oximation of α,β-unsaturated nitriles and α,β-unsaturated amides; for example, acrylonitrile (**6a**) and 2-pentenenitrile (**6b**) were converted to the corresponding oximes **7a** and **7b** in 82% and 70% yields, respectively (Entries 14 and 15), and acrylamide **8a** and crotonamide **8b**, respectively, afforded the 2-hydroxyimino amides **9a** and **9b** in good yields (Entries 16 and 17).

Even though the pathway of the present α-oximation has not yet been made clear, it can be assumed that the intermediate **A** shown in Scheme 2 is initially generated from α,β-unsaturated carbonyl compounds, Co(eobe), and a silane. The successive reaction of this intermediate **A** with butyl nitrite affords the corresponding oximes. This explanation is supported by the result that when acrylamide **8a** was treated with Et_3SiH and Co(eobe) in the absence of butyl nitrite (**2**), propionamide **10** (a reduced product) and a coupling product **11** of acrylamide were produced instead of the oxime as shown in Scheme 3. The difference in the reactivity



Scheme 2.



Scheme 3.

between β,β-disubstituted α,β-unsaturated ester **1i** and ketone **4e** suggests that a nucleophilic attack of the bulky active species, such as a cobalt hydride, on the β-position of α,β-unsaturated carbonyl compounds occurs first to generate the intermediate **A**.

It is concluded that butyl nitrite is an effective reagent for the α-oximation of α,β-unsaturated carbonyl compounds, such as α,β-unsaturated esters, α,β-unsaturated ketones, α,β-unsaturated nitriles, and α,β-unsaturated amides, in the presence of a silane and a catalytic amount of Co(eobe) to afford the corresponding oximes. The catalyst, Co(eobe), has the highest activity for α-oximation, and the combined use of phenylsilane in tetrahydrofuran improves the yield of the α-oximation of α,β-unsaturated carbonyl compounds. The present procedure thus provides a novel and useful method for the preparation of α-hydroxyimino carbonyl compounds directly from α,β-unsaturated carbonyl compounds under mild conditions.

Experimental

General: Melting points were measured on a Mettler FP62 apparatus and are uncorrected.

(a) Spectrometers: IR spectra were obtained by using a JASCO Model IR-700 infrared spectrometer on KBr pellets or liquid film on NaCl. ^1H NMR spectra were recorded with a JEOL Model FX270 spectrometer using $CDCl_3$ as the solvent and tetramethylsilane as an internal standard.

(b) Chromatography: Column chromatography was conducted using silica gel (Daiso gel IR-60). Preparative TLC was carried out on silica gel (E. Merck, 13895). GC-analyses were performed on a Shimadzu GC-15A chromatograph using a column packed with PEG 20M(20%) supporting Chromosorb W (3 mm×2 m), and the peak areas were obtained with a Shimadzu chromatopack CR-5A.

(c) Solvents and Reagents: 1,2-Dichloroethane and tetrahydrofuran were HPLC-grade and stored over molecular sieves. Toluene, benzene, and ethyl acetate were purified by distillation and stored over molecular sieves. Butyl nitrite (**2**) was purchased from TCI Co., Ltd. and stored in a cooled room after purification by distillation under reduced pressure. Triethylsilane, diethylsilane, diphenylsilane, and phenylsilane were purchased from Shin-Etsu Chemicals Co. and used without further purification.

(d) α,β-Unsaturated Carbonyl Compounds: Butyl acrylate (**1b**), *t*-butyl acrylate (**1c**), butyl crotonate (**1a**), *p*-tolyl crotonate (**1g**), and diethyl fumarate (**1h**) were purchased from TCI Co., Ltd. and purified by distillation. The other α,β-unsaturated esters were prepared from the corresponding acid chlorides and benzyl alcohol. Ethyl vinyl ketone (**4b**), 1-phenyl-2-buten-1-one (**4c**), 3-decen-2-one (**4d**), and mesityl oxide (**4e**) were purchased from Aldrich Chemical Company, Inc. or TCI Co., Ltd. and purified by distillation. 1-Phenyl-2-propen-1-one (**4a**) was prepared according to the reported method.[11] Acrylonitrile (**6a**) and 2-pentenenitrile (**6b**) were purchased from TCI Co., Ltd. and purified by distillation. *N*-Methylacrylanilide (**8a**) and *N*-methylcrotonanilide (**8b**) were prepared from the corresponding acid chlorides and *N*-methylaniline.

Preparation of Cobalt(II) Complexes. Bis(acetylacetonato)cobalt(II) ($Co(acac)_2$) was purchased from TCI Co., Ltd. and dried under reduced pressure (1 mmHg, 1 mmHg= 133.322 Pa) at 70 °C. *N,N'*-Bis(1-methyl-3-oxobutylidene)-ethylenediaminatocobalt(II) (Co(acacen))[12] and bis(2-ethoxycarbonyl-3-oxobutanalato)cobalt (II) ($Co(ecbo)_2$)[13] were prepared according to the reported methods, respectively. *N,N'*-Bis(2-ethoxycarbonyl-3-oxobutylidene)ethylenediaminato-

cobalt(II) (Co(eobe)) was prepared by a modified procedure of Kida's method:[14] An aqueous solution of sodium hydroxide (23.2 mmol, 11.6 ml) was added at 50 °C under an argon atmosphere to a solution of *N,N'*-bis(2-ethoxycarbonyl-3-oxobutylidene)ethylenediamine[15] (3.95 g, 11.6 mmol) in *N,N*-dimethylformamide (100 ml). After stirring for 0.5 h at 50 °C, a solution of cobalt(II) chloride hexahydrate (2.76 g, 11.6 mmol) in water (20 ml) was added, and the mixture was stirred for 0.5 h at 50 °C. After cooling at 0 °C, the orange precipitates were collected by filtration, washed with water (50 ml), and dried in vacuo at room temperature for 16 h. They were recrystallized from toluene to afford pure Co(eobe) (3.04 g, 66% yield). Mp 287—289 °C; IR(KBr) 1695 and 1585 cm^{-1} Found: C, 48.55; H, 5.71; N, 7.02%. Calcd for $C_{16}H_{22}N_2O_6Co$: C, 48.37; H, 5.58; N, 7.05%.

α-Oximation of Butyl Crotonate (1a) (*A Typical Procedure*, see Entry 4 in Table 3). Phenylsilane (162 mg, 1.5 mmol) and butyl nitrite (**2**) (159 mg, 1.5 mmol) were successively added to a solution of butyl crotonate (**1a**) (79 mg, 0.5 mmol) and Co(eobe) (20 mg, 0.05 mmol) in THF (2.5 ml). After stirring for 47 h at room temperature under an argon atmosphere, MeOH (1.5 ml) and concentrated HCl (3 drops) were added to the reaction mixture. After stirring for 30 min, water (20 ml) was added to the reaction mixture, which was then neutralized with a saturated aqueous $NaHCO_3$ solution. Organic materials were extracted with dichloromethane and the organic layer was washed with brine and dried over anhydrous magnesium sulfate. After evaporation of the solvent and purification by silica gel TLC (hexane–EtOAc, 3:1), butyl 2-(hydroxyimino)butyrate (**3a**)[16] was obtained (77 mg, 89% yield). ^1H NMR ($CDCl_3$) δ=0.95 (3H, t, *J*=7 Hz), 1.13 (3H, t, *J*=7 Hz), 1.43 (2H, sextet, *J*=7 Hz), 1.72 (2H, quintet, *J*=7 Hz), 2.64 (2H, q, *J*=7 Hz), and 4.26 (2H, t, *J*=7 Hz); IR ($CHCl_3$) 3278, 2962, and 1726 cm^{-1}.

Analytical Data of the Oximes (in Table 4). Butyl 2-(Hydroxyimino)propionate (3b): Mp 51—53 °C; ^1H NMR ($CDCl_3$) δ=0.95 (3H, t, *J*=7 Hz), 1.41 (2H, sextet, *J*=7 Hz), 1.70 (2H, quintet, *J*=7 Hz), and 4.23 (2H, t, *J*=7 Hz); IR ($CHCl_3$) 3284 and 1721 cm^{-1}. Found: C, 52.43; H, 8.26; N, 8.48%. Calcd for $C_7H_{13}NO_3$: C, 52.82; H, 8.23; N, 8.80%.

***t*-Butyl 2-(Hydroxyimino)propionate (3c):**[17] Mp 63—66 °C; ^1H NMR ($CDCl_3$) δ=1.53 (9H, s) and 2.06 (3H, s); IR ($CHCl_3$) 3280 and 1716 cm^{-1}. Found: C, 52.80; H, 8.14; N, 8.77%. Calcd for $C_7H_{13}NO_3$: C, 52.82; H, 8.23; N, 8.80%.

Benzyl 2-(Hydroxyimino)butyrate (3d): Mp 60—63 °C; ^1H NMR ($CDCl_3$) δ=1.08 (3H, t, *J*=7 Hz), 2.59 (2H, q, *J*=7 Hz), 5.25 (2H, s), and 7.37 (5H, m); IR ($CHCl_3$) 3280 and 1722 cm^{-1} Found: C, 64.02; H, 6.12; N, 6.45%. Calcd for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.32; N, 6.76%.

Benzyl 2-(Hydroxyimino)hexanoate (3e): Mp 75—78 °C; ^1H NMR ($CDCl_3$) δ=0.89 (3H, t, *J*=7 Hz), 1.33 (2H, sextet, *J*=7 Hz), 1.50 (2H, quintet, *J*=7 Hz), 2.59 (2H, t, *J*=7 Hz), 5.25 (2H, s), and 7.33 (5H, m); IR ($CHCl_3$) 3278 and 1722 cm^{-1}. Found: C, 65.84; H, 7.25; N, 6.05%. Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95%.

Benzyl 2-Hydroxyimino-4-methylpentanoate (3f): Mp 84—86 °C; ^1H NMR ($CDCl_3$) δ=0.89 (6H, d, *J*=7 Hz), 2.05 (2H, septet, *J*=7 Hz), 2.51 (2H, d, *J*=7 Hz), 5.27 (2H, s), and 7.35 (5H, m); IR ($CHCl_3$) 3286 and 1722 cm^{-1}. Found: C, 66.06; H, 7.45; N, 6.10%. Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95%.

***p*-Tolyl 2-(Hydroxyimino)butyrate (3g):** Mp 118—121 °C; ^1H NMR ($CDCl_3$) δ=1.16 (3H, t, *J*=7 Hz), 2.34 (3H, s), 2.70 (2H, q, *J*=7 Hz), 7.03 (2H, AB. d, *J*=6 Hz), and 7.19 (2H, AB. d, *J*=6 Hz); IR ($CHCl_3$) 3292 and 1738 cm^{-1}. Found: C, 63.33; H, 6.52; N, 6.80%. Calcd for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.32; N, 6.76%.

Diethyl 2-(Hydroxyimino)succinate (3h):[18] ^1H NMR ($CDCl_3$) δ=1.25 (3H, t, *J*=7 Hz), 1.33 (3H, t, *J*=7 Hz), 3.69 (2H, s), 4.18 (2H, q, *J*=7 Hz), and 4.32 (2H, q, *J*=7 Hz); IR ($CHCl_3$) 3150 and 1730 cm^{-1}.

2-Hydroxyimino-1-phenyl-1-propanone (5a): Mp 110—111 °C (lit,[10] mp 112—113 °C); ^1H NMR ($CDCl_3$) δ=2.18 (3H, s), 7.44 (2H, t, *J*=8 Hz), 7.57 (1H, t, *J*=8 Hz), and 7.89 (2H, d, *J*=8 Hz); IR ($CHCl_3$) 3315 and 1665 cm^{-1}.

2-Hydroxyimino-3-pentanone (5b): Mp 68—69 °C (lit,[19] mp 70—71 °C); ^1H NMR ($CDCl_3$) δ=1.10 (3H, t, *J*=7 Hz), 2.00 (3H, s), and 2.80 (2H, q, *J*=7 Hz); IR (KBr) 3328 and 1670 cm^{-1}.

2-Hydroxyimino-1-phenyl-1-butanone (5c):[20] Mp 116—119 °C; ^1H NMR ($CDCl_3$) δ=1.09 (3H, t, *J*=7 Hz), 2.69 (2H, q, *J*=7 Hz), 7.40 (2H, t, *J*=8 Hz), 7.53 (1H, dt, *J*=2 and 8 Hz), and 7.85 (2H, dd, *J*=2 and 8 Hz); IR ($CHCl_3$) 3316 and 1665 cm^{-1}.

3-Hydroxyimino-2-decanone (5d): Mp 52—54 °C (lit,[21] mp 51—52 °C); ^1H NMR ($CDCl_3$) δ=0.88 (3H, t, *J*=7 Hz), 1.29 (8H, m), 1.44 (2H, m), 2.38 (3H, s), and 2.55 (2H, t, *J*=7 Hz); IR ($CHCl_3$) 3298 and 1692 cm^{-1}.

3-Hydroxyimino-4-methyl-2-pentanone (5e): Mp 77—78 °C (lit,[22] 78—79 °C); ^1H NMR ($CDCl_3$) δ=1.21 (6H, d, *J*=7 Hz), 2.32 (3H, s), and 3.42 (1H, septet, *J*=7 Hz); IR ($CHCl_3$) 3294 and 1692 cm^{-1}.

2-(Hydroxyimino)propanenitrile (7a):[23] E-Form; ^1H NMR ($CDCl_3$) δ=2.20 (3H, s) and 9.53 (1H, br); IR (neat) 3308, 2234, and 1624 cm^{-1}: Z-Form; ^1H NMR ($CDCl_3$) δ=2.13 (3H, s) and 8.75 (1H, br); IR (neat) 3332, 2244, and 1624 cm^{-1}.

2-(Hydroxyimino)pentanenitrile (7b):[23] E-Form; ^1H NMR ($CDCl_3$) δ=1.01 (3H, t, *J*=7 Hz), 1.69 (2H, sextet, *J*=7 Hz), 2.51 (2H, t, *J*=7 Hz), and 9.25 (1H, br); IR (neat) 3344, 2230, and 1623 cm^{-1}: Z-Form; ^1H NMR ($CDCl_3$) δ=0.99 (3H, t, *J*=7 Hz), 1.68 (2H, sextet, *J*=7 Hz), 2.43 (2H, t, *J*=7 Hz), and 9.45 (1H, br); IR (neat) 3336, 2238, and 1625 cm^{-1}.

***N*-Methyl-2-(hydroxyimino)propionanilide (9a):** E-Form; mp 146—148 °C; ^1H NMR ($CDCl_3$) δ=1.87 (3H, s), 3.35 (3H, s), and 6.80—7.45 (5H); IR ($CHCl_3$) 3320 and 1648 cm^{-1}. Found: C, 62.75; H, 6.52; N, 14.44%. Calcd for $C_{10}H_{12}N_2O_2$: C, 62.49; H, 6.29; N, 14.57%. Z-Form; mp 115—118 °C; ^1H NMR ($CDCl_3$) δ=1.76 (3H, s), 3.35 (3H, s), 7.12 (1H, br), and 7.32 (5H, m); IR ($CHCl_3$) 3150 and 1651 cm^{-1}. Found: C, 62.62; H, 6.22; N, 14.44%. Calcd for $C_{10}H_{12}N_2O_2$: C, 62.49; H, 6.29; N, 14.57%.

***N*-Methyl-2-(hydroxyimino)butyranilide (9b):** E-Form; mp 83—84 °C; ^1H NMR ($CDCl_3$) δ=1.07 (3H, t, *J*=7 Hz), 2.38 (2H, q, *J*=7 Hz), 3.37 (3H, s), 7.20—7.50 (5H, m), and 8.70 (1H, br); IR ($CHCl_3$) 3320 and 1647 cm^{-1}. Found: C, 64.15; H, 6.76; N, 13.20%. Calcd for $C_{11}H_{14}N_2O_2$: C, 64.06; H, 6.84; N, 13.58%. Z-Form; ^1H NMR ($CDCl_3$) δ=0.93 (3H, t, *J*=7 Hz), 2.07 (2H, q, *J*=7 Hz), 3.37 (3H, s), 7.35 (5H, m), and 7.77 (1H, br); IR (neat) 3304 and 1640 cm^{-1}. Found: C, 64.45; H, 6.99; N, 13.30%. Calcd for $C_{11}H_{14}N_2O_2$: C, 64.06; H, 6.84; N, 13.58%.

Reaction of *N*-Methylacrylanilide (8a) with Triethylsilane in the Presence of Co(eobe) (Scheme 3). Triethylsilane (349 mg, 3.0 mmol) was added to a solution of *N*-methylacrylanilide (**8a**) (161 mg, 1.0 mmol) and Co(eobe) (20 mg, 0.05 mmol) in 1,2-dichloroethane (5 ml). After stirring for 48 h at room

temperature under an argon atmosphere, the solvent was removed under reduced pressure. After purification by silica gel TLC (hexane–EtOAc, 1 : 1), *N*-methylpropionanilide (**10**) and (E)-*N,N'*-dimethyl-1-butene-1,3-dicarboxanilide (**11**) were obtained in 5% and 24% yields, respectively. **10**: Mp 55—56 °C (lit,[24] mp 56 °C). ^{1}H NMR and retention time in GC analysis of this sample were identical with those of the authentic sample.

11: ^{1}H NMR ($CDCl_3$) δ=1.08 (3H, d, *J*=7 Hz), 3.10 (1H, quintet, *J*=7 Hz), 3.17 (3H, s), 3.32 (3H, s), 5.56 (1H, d, *J*=17 Hz), 6.81 (1H, dd, *J*=17 and 7 Hz), and 7.00—7.50 (10H); IR ($CHCl_3$) 1664, 1634, and 1596 cm^{-1}. Found: C, 74.93; H, 6.99; N, 8.30%. Calcd for $C_{20}H_{22}N_2O_2$: C, 74.51; H, 6.88; N, 8.69%.

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