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A Novel Method for the Preparation of 2-Hydroxyiminocarboxylic Acid Esters . Cobalt(II) Catalyzed α-Oximation of α,β-Unsaturated Esters with Butyl Nitrite and Phenylsilane

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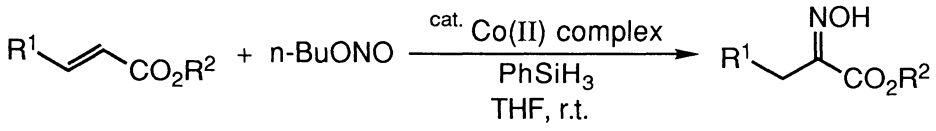
Various α,β-unsaturated esters are directly converted to the corresponding 2-hydroxyiminocarboxylic acid esters with butyl nitrite and phenylsilane in high yields by use of N,N'-bis(2-ethoxycarbonyl-3-oxobutylidene)ethylenediaminato cobalt(II) complex as catalyst under mild condition.

Introduction of nitrogen atom into organic compounds catalyzed by transition-metal complexes has been investigated extensively because of the usefulness in organic synthesis.[1] However, no practical method for the preparation of carboxylic acid esters substituted by nitrogen atom at α-posotion directly from α,β-unsaturated esters was reported at all. In the previous communication, we reported the nitrosation of α,β-unsaturated carboxamides with nitric oxide and triethylsilane in the presence of a catalytic amount of N,N'-bis(2-ethoxycarbonyl-3-oxobutylidene)-ethylenediaminatocobalt(II) complex to afford the corresponding 2-nitrosocarboxamides at room temperature.[2] Since the above mentioned reaction is limited to α,β-unsaturated carboxamides, we continued to study the introduction of nitrogen atom into α,β-unsaturated esters, and it was found that the desired products were obtained by use of butyl nitrite as nitrogen source in the presence of a silane and a catalytic amount of cobalt(II) complex.

In this communication, we would like to report a novel method for the preparation of 2-hydroxyiminocarboxylic acid esters, the interesting synthetic intermediates,[3] from α,β-unsaturated esters on treatment with butyl nitrite and phenylsilane catalyzed by N,N'-bis(2-ethoxycarbonyl-3-oxobutylidene)ethylene-diaminatocobalt(II) complex (Scheme 1).



Scheme 1.

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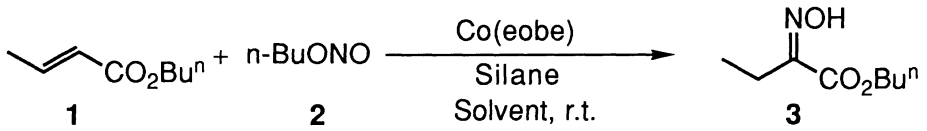
Table 1. Oximation of Butyl Crotonate with Butyl Nitrite Catalyzed by Co(eobe)[a)]

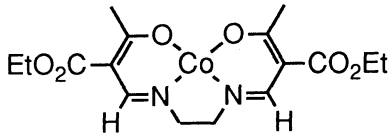


1 2 3

Entry	Solvent	Silane	Time / h	Yield of **3** / %[b)]
1	DCE	Et_3SiH	62	28
2	EtOAc	Et_3SiH	62	55
3	THF	Et_3SiH	62	79
4	THF	Et_2SiH_2	47	89
5	THF	$PhSiH_3$	47	84
6	THF	$(MeO)_3SiH$	68	0

a) Reaction condition; butyl crotonate (**1**) (0.5 mmol), butyl nitrite (**2**) (1.5 mmol), Co(eobe) (0.05 mmol), silane (1.5 mmol), solvent (2.5 ml), room temperature, under argon atmosphere.
b) Isolated yield.

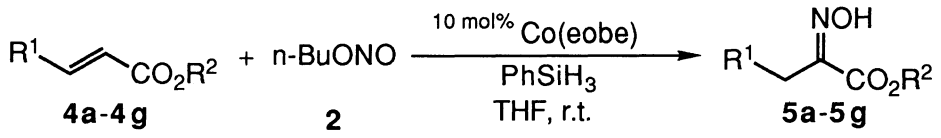
First, we tried the reaction of butyl crotonate (**1**) (71 mg, 0.5 mmol) with butyl nitrite (**2**) [4)] (159 mg, 1.5 mmol) in the presence of triethylsilane (174 mg, 1.5 mmol) and 10 mol% of N,N'-bis(2-ethoxycarbonyl-3-oxobutylidene)ethylenediaminatocobalt(II) complex [5)] (Co(eobe), 20 mg, 0.05 mmol) in 1,2-dichloroethane (DCE, 2.5 ml)at room temperature. And it was found that butyl 2-hydroxyiminobutyrate (**3**) was obtained in 28% yield after 62 h (Entry 1 in Table 1). Then, various solvents and silanes were screened in order to improve the yield of the α-oximation by taking the reaction of **1** and **2** in the presence of 10 mol% of Co(eobe) as a model. As shown in Table 1, a change in the reaction medium from DCE to more polar solvents such as ethyl acetate (EtOAc) and tetrahydrofuran (THF) gave better result (Entries 2 and 3). It is noted that **3** was obtained in 79% yield when THF was used as a solvent (Entry 3). Furthermore, when the polyhydrosilane such as diethylsilane or phenylsilane was used instead of triethylsilane, the α-oximation of **1** proceeded smoothly to afford **3** in good yields (Entries 4 and 5). In particular, the use of phenylsilane gave the best result and the yield of **3** was raised up to 89% (Entry 5).



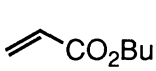
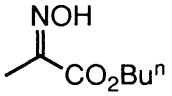
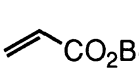
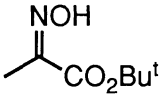
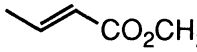
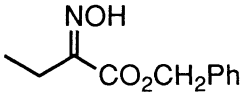
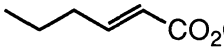
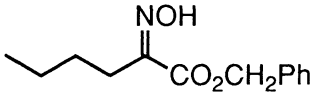
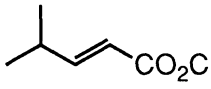
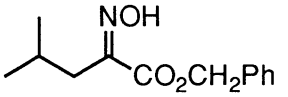
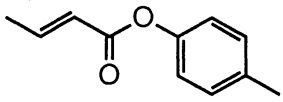
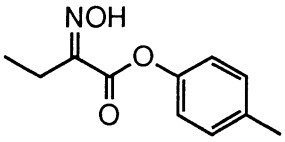
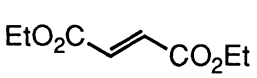
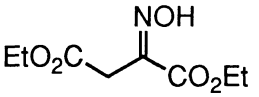
Co(eobe)

Next, the conversion of various α,β-unsaturated esters (**4a-4g**) to the corresponding 2-hydroxyiminocarboxylic acid esters (**5a-5g**) with **2** was examined by use of phenylsilane and 10 mol% of Co(eobe) in THF,[6)] and the results are summarized in Table 2. Acrylic acid esters (**4a** and **4b**) were converted to the corresponding 2-hydroxyiminocarboxylic acid esters (**5a** and **5b**) in high yields (Entries 1 and 2) and β-substituted α,β-unsaturated esters (**4c-4e**) also gave good results (Entries 3-5). The α-oximation of tolyl crotonate (**4f**) proceeded rapidly as compared with that of benzyl crotonate (**4c**) to afford tolyl 2-hydroxyimino-butyrate (**5f**) in 78% yield (Entry 6). Furthermore, in the case of α,β-unsaturated ester having electron-withdrawing substituent

Table 2. The Oximation of Various α,β-Unsaturated Carboxylic Acid with Butyl Nitrite and Phenylsilane Catalyzed by Co(eobe) [a)]



4a-4g 2 5a-5g

Entry	Substrate (4a-4g)		Time / h	Product (5a-5g)[b)]		Yield / %[c)]
1		4a	41		5a	98
2		4b	48		5b	82
3		4c	41		5c	91
4		4d	48		5d	84
5		4e	48		5e	96
6		4f	21		5f	78
7		4g	21		5g	89

a) Reaction condition; substrate (**4a-4g**) (0.5 mmol), butyl nitrite (**2**) (1.5 mmol), Co(eobe) (0.05 mmol), $PhSiH_3$ (1.5 mmol), THF (2.5 ml), room temperature, under argon atmosphere.
b) Satisfactory NMR and IR were obtained.
c) Isolated yield.

such as diethyl fumarate, the reaction took place readily and diethyl 2-hydroxyiminosuccinate was obtained in 89% yield (Entry 7).

A typical procedure is described for the oximation of butyl crotonate (**1**) : To a solution of butyl crotonate (**1**) (79 mg, 0.5 mmol) and N,N'-bis(2-ethoxycarbonyl-3-oxobutylidene)ethylenediaminatocobalt(II) (Co(eobe), 20 mg, 0.05 mmol) in THF (2.5 ml) were successively added phenylsilane (162 mg, 1.5 mmol) and butyl nitrite (**2**) [4)] (159 mg, 1.5 mmol). After stirring for 47 h at room temperature under 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, and then neutralized with 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 solvent and purification by silica gel TLC (hexane-EtOAc, 3:1), butyl 2-hydroxyiminobutyrate (**3**) was obtained (77 mg, 89%).

Thus, it is noted that the oximation of α,β-unsaturated esters with butyl nitrite and phenylsilane catalyzed by N,N'-bis(2-ethoxycarbonyl-3-oxobutylidene)ethylenediaminatocobalt(II) (Co(eobe)) provides a novel method for preparation of 2-hydroxyiminocarboxylic acid esters, useful synthetic intermediates, under mild conditions.

References

1) For example : J.Tsuji and M. Takahashi, *J. Mol. Cat.*, **10**, 107 (1981) ; A. O. Chong, K. Oshima, and K. B. Sharpless, *J. Am. Chem. Soc.*, **99** 3420 (1977) ; S. -I. Murahashi, T. Shimamura, and I. Moritani, *J. Chem. Soc., Chem. Commun.*, **1974**, 931; Y. Tanigawa, K.Nishimura, A. Kawasaki, and S. -I. Murahashi, *Tetrahedron Lett.*, **1982**, 5549 ; T. Okamoto, K. Kobayashi, S. Oka, and S. Tanimoto, *J. Org. Chem.*, **52**, 5089 (1987).

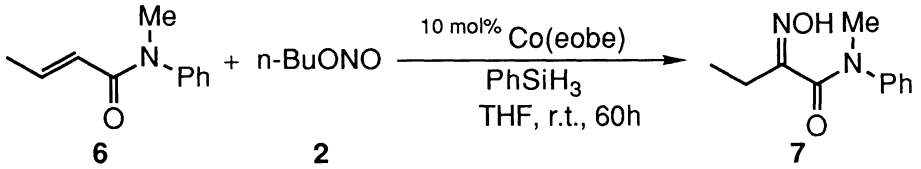
2) K. Kato and T. Mukaiyama, *Chem. Lett.*, in press.

3) D. Shemin and R. M. Herbst, *J. Am. Chem. Soc.*, **60**, 1951 (1938) ; M. W. Tijhuis, J. D. M. Herscheid, and H. C. J. Ottenheijm, *Synthesis*, **1980**, 890.

4) Butyl nitrite was distilled before use.

5) This complex was prepared by modified procedure of Nishida's method [7] : To a solution of N,N'-bis(2-ethoxy-carbonyl-3-oxobutylidene)ethylenediamine [8] (3.95 g, 11.6 mmol) in dimethylformamide (100 ml) was added an aqueous solution of sodium hydroxide (23.2 mmol, 11.6 ml) at 50 °C under argon atmosphere. 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 r. t. for 16 h. They were re-crystallized from toluene to afford the pure complex (3.04 g, 66% yield).

6) α,β-Unsaturated carboxamides were also converted directly to the corresponding 2-hydroxyimino-carboxamides in good yields. For example, in the case of N-methylcrotonanilide (**6**), N-methyl-2-hydroxy-iminobutananilide (**7**) was obtained in 80% yield (Scheme 2).



6 **2** **7**

Scheme 2.

7) Y. Nishida, K. Hayashida, N. Oishi, and S. Kida, *Inorg. Chim. Acta.*, **38**, 213 (1980).

8) E. G. Jager, *Z. Chem.*, **8** ,30, 392, and 475 (1968).

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