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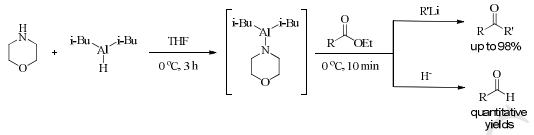

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Mild and direct conversion of esters to morpholine amides using diisobutyl(morpholino)aluminum: Application to efficient one-pot synthesis of ketones and aldehydes from esters

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ABSTRACT

Morpholine amide intermediates, which are easily prepared by aminolysis of various esters with diisobutyl(morpholino)aluminum, react with organolithium and reducing agents (DIBALH or LDBMA) without isolation of the aminolysis intermediates to give ketones in 83-95% yields and aldehydes quantitatively.

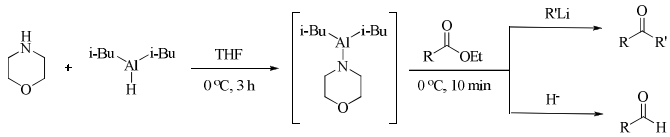
1. Introduction

Weinreb amides[1] are versatile building blocks that act as useful intermediates for the preparation of aldehydes and ketones from various carboxylic acid derivatives. These aldehydes/ketones, in turn, can be used for the synthesis of complex natural products showing significant biological activity and other useful materials. However, reaction involving Weinreb amides are not always suited for large-scale practical applications because of the high cost factor involved. Recently, morpholine and pyrrolidine amides[2] have been identified as possible inexpensive alternatives to Weinreb amides.

Among the numerous reported synthetic routes to Weinreb amides from carboxylic acid derivatives aminolysis of acid chlorides is considered the method of choice. On the other hand, the direct synthesis of tertiary amides, including Weinreb amides and morpholine amides from esters is a potentially attractive process in modern organic synthesis, but it requires harsh conditions generally.[3]

We very recently reported new one-pot synthetic method of aldehydes and ketones from acid chlorides via morpholine amide intermediates with proposed mechanism.[4] With this results in hand, we tried to synthesize of aldehydes and ketones from esters that are more valuable and difficult substrates than acid chlorides.

Herein, we report a new method for the direct conversion of esters to morpholine amides under mild conditions. This method involves a convenient one-pot synthesis of ketones and aldehydes via the reaction of organolithium reagents and reducing agents with morpholine amide intermediates, respectively (Scheme 1).



Scheme 1. New synthetic method of morpholine amides and ketones and aldehydes from esters

2. Results and discussion

2.1 Synthesis of morpholine amides from esters using diisobutyl(morpholino)aluminum

To demonstrate the feasibility of performing the desired reaction under a variety of conditions, we first synthesized tertiary amides from ethyl benzoate using various diisobutyl(amino)aluminum derivatives, which were easily prepared from secondary amines and diisobutylaluminum hydride (DIBALH). The corresponding tertiary amides could be obtained by reaction with ethyl benzoate only in the presence of diisobutyl(morpholino)aluminum because the oxygen atom of the morpholine amide intermediate coordinated with the aluminium metal to form a stable seven-membered ring.[5] The results are summarized in Table 1.

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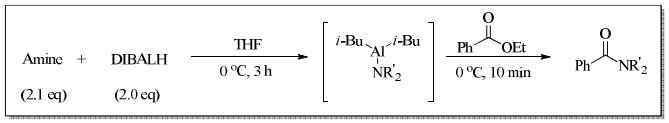
Table 1. Reaction of ethyl benzoate with diisobutyl(amino)aluminum for synthesizing tertiary amides[a]

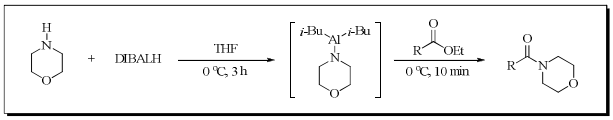


Entry	Ester	Amine	Yields of Amide (%)[a]
1	ethyl benzoate	morpholine	96
2		piperidine	0
3		pyrrolidine	0
4		pyrrole	0
5		diethylamine	0
6		dicyclohexylamine	0

[a]Yields were determined by GC.

We next synthesized morpholine amides from other esters under the optimal conditions deduced from previous experimental results. The results obtained for representative esters are summarized in Table 2.

Table 2. Synthesis of morpholine amides from representative esters[a,]



Entry	Ester	Product	Yield (%)[b]
1			96
2			93
3			92
4			98
5			98
6			94
7			97
8			95
9			90
10			96
11			92
12			96
13			91
14			92
15			92

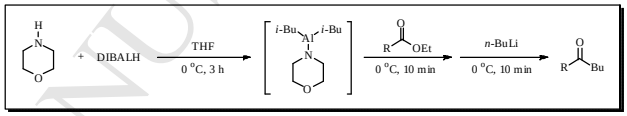
[a]Ester:Morpholine:DIBALH=1.0:2.1:2.0. [b]Isolated yield after silica column chromatography.

As shown in Table 2, various aromatic esters with electron-withdrawing and electron-donating substituents smoothly underwent the conversion to the corresponding morpholine amides in 90-98% yields (entries 2–11). A polyaromatic ester such as ethyl 2-naphthoate and a heterocyclic aromatic ester such as ethyl 2-furoate gave the corresponding morpholine amides in 96% and 91% yields, respectively, via the same methodology (entries 12 and 13). Furthermore, aliphatic esters smoothly afforded the corresponding morpholine amides in very high yield (92%) under the same reaction conditions (entries 14 and 15).

2.2 One-pot synthesis of ketones from esters without isolation of morpholine amide intermediates

We next anticipated that treatment of morpholine amide intermediates with *n*-BuLi or PhLi would be effective for the one-pot synthesis of ketones from representative esters. As expected, the corresponding ketones were isolated in 83-95% yields. However, with bromo-substituted esters, metal-halogen exchange products were obtained instead of the desired ketones. Table 3 summarizes the results of the one-pot synthesis of ketones from various esters.

Table 3. Synthesis of ketones from representative esters in a one-pot reaction[a]



Entry	Ester	Product	Yield (%)[b]
1			92
2[c]			91
3			92
4			93
5			92
6			80
7			86
8			91
9			91
10			89
11			91
12			83
13			91
14			91
15			92

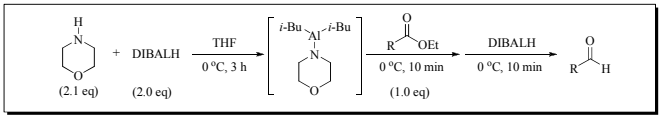
[a]Ester:Morpholine:DIBALH: RLi=1.0:2.1:2.0:2.0. [b]Isolated yield after silica column chromatography. [c]Used PhLi as nucleophile instead of *n*-BuLi.

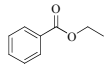
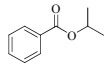
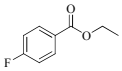
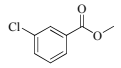
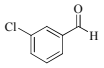
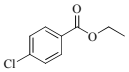
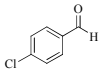
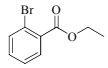
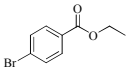
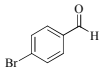
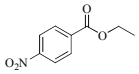
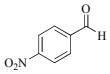
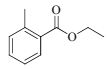
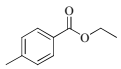
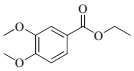
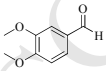
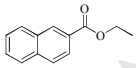
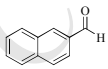
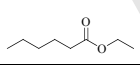
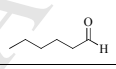
2.3 Quantitative one-pot synthesis of aldehydes from esters

With these results in hand, we tried to develop an efficient one-pot synthesis of aldehydes from representative aromatic and aliphatic esters via the reaction of morpholine amide intermediates with DIBALH. The results for representative esters are summarized in Table 4.

As shown in Table 4, various aromatic esters with electron-withdrawing, electron-donating substituents, and polyaromatic ester reacted perfectly to form the corresponding aldehydes in quantitative yields (entries 1–12). However, we were unfortunately unable to synthesize the corresponding aldehydes from aliphatic esters quantitatively (entry 13).

Table 4. Synthesis of aldehydes from representative esters in the one-pot reaction at 0 ℃

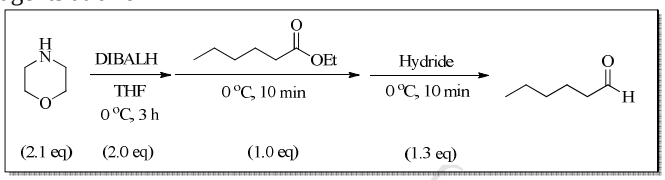


Entry	Ester	Product	DIBALH (eq)	Yield (%)[a]
1			1.1	>99 (99)
2			1.2	>99
3			1.1	>99
4			1.1	>99
5			1.1	>99 (99)
6			1.1	>99
7			1.1	>99 (99)
8			1.1	>99
9			1.1	>99
10			1.1	>99 (99)
11			1.1	>99
12			1.1	>99
13			1.3	84

[a]Yields were determined by GC. The values in parentheses are isolated yields.

Therefore, we decided to use the alkoxy derivatives of DIBALH[6] such as lithium diisobutyl-*t*-butoxyaluminum hydride (LDBBA), sodium diisobutyl-*t*-butoxyaluminum hydride (SDBBA), potassium diisobutyl-*t*-butoxyaluminum hydride (PDBBA), lithium diisobutyl-*i*-propoxyaluminum hydride (LDBIPA), lithium diisobutylethoxyaluminum hydride (LDBEA), and lithium diisobutylmethoxyaluminum hydride (LDBMA) instead of DIBALH for the quantitative synthesis of corresponding aldehydes from aliphatic esters. Among these partial reducing agents, we found that LDBMA is the most effective and quantitative partial reducing agent for the reduction of aliphatic esters to the corresponding aldehydes. The results are summarized in Table 5.

Table 5. Partial reduction of ethyl caproate with several reducing agents at 0 ℃

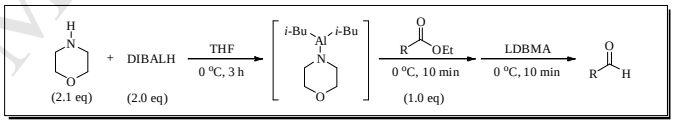


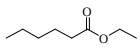
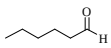
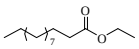
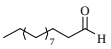
Entry	Hydride	Yields of Aldehyde (%)[a]
1	DIBALH	84
2	LDBBA	88
3	SDBBA	97
4	PDBBA	98
5	LDBIPA	97
6	LDBEA	98
7	LDBMA	99

[a]Yields were determined by GC.

Based on these results, we carried out the partial reduction of aliphatic esters to aldehydes using the optimized reaction conditions and LDBMA (entry 7). In result, the corresponding aldehydes were obtained quantitatively, as expected (Table 6).

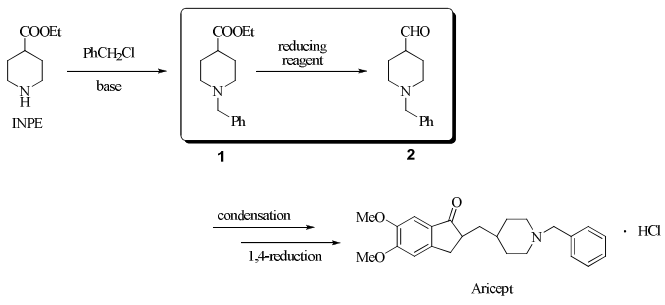
Table 6. Yields of corresponding aldehydes from aliphatic esters in the one-pot reaction at 0 ℃



Entry	Ester	Product	LDBMA (eq)	Yield (%)[a]
1			1.3	99
2			1.3	99 (99)

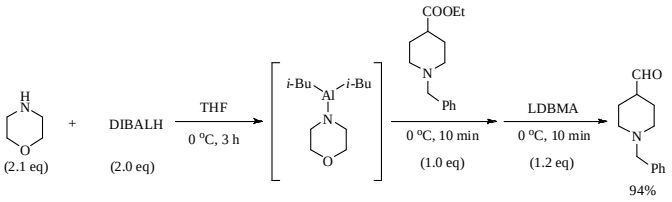
[a]Yields were determined by GC. The value in parenthesis is isolated yield.

In an extension of our methodology for quantitative partial reduction of esters to aldehydes, we carried out the synthesis of intermediate of donepezil hydrochloride (Aricept)[7] that is the popular agent for the treatment of mild to moderate dementia of the Alzheimer's type from *N*-benzyl ester **1** compound of ethyl isonipecotate (INPE) (Scheme 2).



Scheme 2. Common synthetic method of Aricept

We easily obtained the morpholine amide intermediate by reacting diisobutyl(morpholino)aluminum with *N*-benzyl ester **1** and treated it with LDBMA without isolating it to give *N*-benzyl-4-formylpiperidine **2** in 94% yield (Scheme 3). This result suggests that our new partial reduction method can be an alternative method for synthesis of Aricept



Scheme 3. Synthesis of an important intermediate in the synthesis of Aricept using the new partial reduction method

3. Conclusion

In summary, we have developed a new method for the direct synthesis of morpholine amides from esters in up to 98% yield. This method allows for the one-pot formation of ketones in 80-95% yield and aldehydes quantitatively by the partial alkylation and reduction of esters without isolation of the morpholine amide intermediates. The advantages of the present method include high product yields, mild reaction conditions (0 ℃), and process simplicity. Therefore, the methodology is believed to be broadly useful for the synthesis of ketones and aldehydes from esters in organic synthetic fields.

4. Experimental

4.1 General methods

All glassware used was dried thoroughly in an oven, assembled hot, and cooled under a stream of dry nitrogen prior to use. All reactions and manipulations of air- and moisturesensitive materials were carried out using standard techniques for the handling of air-sensitive materials. All chemicals were commercial products of the highest purity which were further purified before use by using standard methods before use. THF was dried over sodium-benzophenone and distilled. *n*-Butyllithium, DIBALH, esters, aldehydes, and morpholine were purchased from Aldrich Chemical Company, Alfa Aesar and Tokyo Chemical Industry Company (TCI). ^{1}H-NMR spectra were measured at 300 or 400 MHz with $CDCl_3$ as a solvent at ambient temperature unless otherwise indicated and the chemical shifts were recorded in parts per million downfield from tetramethylsilane (δ = 0 ppm) or based on residual $CHCl_3$ (δ = 7.26 ppm) as an internal standard. ^{13}C NMR spectra were recorded at 75 or 100 MHz with $CDCl_3$ as a solvent and referenced to the central line of the solvent (δ = 77.0 ppm). The coupling constants (*J*) are reported in hertz. Analytical thin-layer chromatography (TLC) was performed on glass precoated with silica gel (Merck, silica gel 60 F254). Column chromatography was carried out using 70 - 230 mesh silica gel (Merck) at normal pressure. GC analyses were performed on a Younglin Acme 6000M and 6100GC FID chromatography, using an HP-5 capillary column (30m). All GC yields were determined with the use of naphthalene as internal standard and authentic mixture.

4.2 Synthesis of morpholine amides from representative esters (Table 2)

The following experimental procedure for the synthesis of morpholino(phenyl)-methanone is representative. A dry and argon-flushed flask, equipped with a magnetic stirring bar and a septum, was charged with morpholine (0.18 mL, 2.1 mmol) and 10 mL THF. After cooling to 0 ℃, DIBALH (2.0 mL, 1.0 M in hexane, 2.0 mmol) was added dropwise and stirred for 3 h at same temperature. To a reaction mixture was slowly added ethyl benzoate (0.14 g, 1.0 mmol) and stirred for 10 min. The reaction was stopped by the aqueous 1 N HCl (10 mL) and extracted with diethyl ether (2 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the residue by column chromatography on silica gel yielded morpholino(phenyl)methanone (184 mg, 96%). All products in Table 2 were confirmed by comparison with ^{1}H NMR data reported in the literature.[8]

4.3 Synthesis of ketones from representative esters in a one-pot reaction (Table 3)

The following experimental procedure for the synthesis of 1-phenylpentanone is representative. A dry and argon-flushed flask, equipped with a magnetic stirring bar and a septum, was charged with morpholine (0.18 mL, 2.1 mmol) and 10 mL THF. After cooling to 0 ℃, DIBALH (2.0 mL, 1.0 M in hexane, 2.0 mmol) was added dropwise and stirred for 3 h at same temperature. To a reaction mixture was slowly added ethyl benzoate (0.14 g, 1.0 mmol) and stirred for 10 min. Then, *n*-BuLi (1.25 mL, 1.6 M in hexane, 2.0 mmol) was added and the mixture was stirred for 10 min again. The reaction was stopped by the aqueous 1 N HCl (10 mL) and extracted with diethyl ether (2 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the residue by column chromatography on silica gel yielded 1-phenylpentanone (150 mg, 92%). All products in Table 3 were confirmed by comparison with ^{1}H NMR data reported in the literature.[9]

4.4 Partial reduction of aromatic esters to corresponding aldehydes (Table 4)

The following experimental procedure for the partial reduction of ethyl benzoate to benzaldehyde is representative. A dry and argon-flushed flask, equipped with a magnetic stirring bar and a septum, was charged with morpholine (0.18 mL, 2.1 mmol) and THF (10 mL). After cooling to 0 ℃, DIBALH (2.0 mL, 1.0 M in hexane, 2.0 mmol) was added dropwise and the mixture was stirred for 3 h at the same temperature. Ethyl benzoate (0.14 g, 1.0 mmol) was added slowly to the reaction mixture, which was stirred for 10 min. Then, DIBALH (1.1 mL, 1.0 M in hexane, 1.1 mmol) was added and the mixture was stirred for 10 min again. The reaction was stopped aqueous 1 N HCl (10 mL) and extracted with diethyl ether (2 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the residue by short column chromatography on silica gel using Et_2O yielded benzaldehyde (106 mg, 99%). All products in Table 4 were confirmed through comparison with ^{1}H NMR and GC data of authentic sample.

4.5 Partial reduction of aliphatic esters to corresponding aldehydes (Table 6)

The following experimental procedure for the partial reduction of ethyl dodecanoate to benzaldehyde is representative. A dry and argon-flushed flask, equipped with a magnetic stirring bar and a septum, was charged with morpholine (0.18 mL, 2.1 mmol) and 10 mL THF. After cooling to 0 ℃, DIBALH (2.0 mL, 1.0 M in hexane, 2.0 mmol) was added dropwise and stirred for 3 h at same temperature. To a reaction mixture was slowly added ethyl dodecanoate (0.23 g, 1.0 mmol) and stirred for 10 min. Then, LDBMA (2.8 mL, 0.46 M in hexane-THF, 1.3 mmol) was added and the mixture was stirred for 10 min again. The reaction was stopped by the aqueous 1 N HCl (10 mL) and extracted with diethyl ether (2 x 10 mL). The combined organic layers were

dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the residue by short column chromatography on silica gel using Et_2O yielded dodecanal (183 mg, 99%). All products in Table 6 were confirmed by comparison with ^{1}H NMR and GC data of authentic sample.

4.6 Preparation of LDBMA

A dry and argon-flushed flask, equipped with a magnetic stirring bar and a septum, was charged with methanol (2.23 mL, 55 mmol) and 25 mL THF. After cooling to 0 ℃, *n*-butyllithium (20 mL, 2.5 M in hexane, 50 mmol) was added dropwise and stirred for 1 hr at room temperature. To a reaction mixture was slowly added DIBALH (50 mL, 1.0 M in hexane, 50 mmol) and stirred for 2 h at same temperature to give a colorless homogeneous solution. The concentration of LDBMA solution in THF-hexane was measured gasometrically by hydrolysis of an aliquot of the solution with a hydrolyzing mixture of *t*-butyl alcohol-THF (1:1) at 0 ℃.

4.7 Synthesis of *N*-benzyl-4-formylpiperidine (2)

A dry and argon-flushed flask, equipped with a magnetic stirring bar and a septum, was charged with morpholine (0.18 mL, 2.1 mmol) and 10 mL THF. After cooling to 0 ℃, DIBALH (2.0 mL, 1.0 M in hexane, 2.0 mmol) was added dropwise and stirred for 3 h at same temperature. To a reaction mixture was slowly added ethyl *N*-benzylpiperidine-4-carboxylate (0.247 g, 1.0 mmol) and stirred for 10 min. Then, LDBMA (2.8 mL, 0.46 M in hexane-THF, 1.3 mmol) was added and the mixture was stirred for 10 min again. The reaction was stopped by the aqueous 1 N HCl (10 mL) and extracted with diethyl ether (2 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the residue by column chromatography on silica gel yielded *N*-benzyl-4-formylpiperidine (191 mg, 94%). The product was confirmed by comparison with ^{1}H NMR data reported in the literature.[10]

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