

# Magnesium(II) and other alkali and alkaline earth metals

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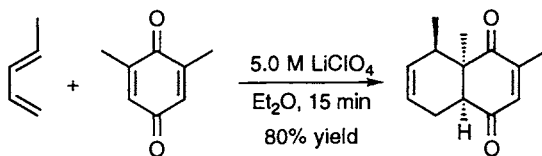
## 1. Introduction

Alkali and alkaline earth metal salts have mild Lewis acidities and have been utilized as a promoter or catalyst for organic reactions. Among the alkali metal salts,  $\text{LiClO}_4$ ,<sup>1-3</sup> usually used as a concentrated solution in diethyl ether, is the most popular reagent to induce various transformations, including Diels–Alder reactions,<sup>4,5</sup> 1,3-sigmatropic rearrangements,<sup>6</sup> Mukaiyama aldol additions,<sup>7,8</sup> and Michael additions.<sup>9</sup> A catalytic amount of the lithium compound has also been found effective to promote these reactions.<sup>7,8,10</sup> Additionally,  $\text{LiBF}_4$  and  $\text{LiNTf}_2$  have been used as lithium Lewis acid alternatives for Diels–Alder reactions.<sup>11,12</sup> The alkaline earth metal salt  $\text{MgBr}_2$ <sup>13</sup> is commonly used as a Lewis acid capable of forming strong bidentate chelates with  $\alpha$ -alkoxy carbonyl compounds. It has thus been successfully applied to diastereoselective hetero-Diels–Alder reactions,<sup>14,15</sup> Mukaiyama aldol additions,<sup>16,17</sup> and allylation reactions.<sup>18-21</sup> Chiral bis(oxazoline)-Mg(II) complexes have been developed and proven to be excellent chiral Lewis acid catalysts for enantioselective Diels–Alder reactions<sup>22,23</sup> and 1,3-dipolar cycloaddition reactions.<sup>24</sup> The moderate Lewis acidity and reactivity of the chiral magnesium reagents are useful in obtaining high enantioselectivity and designing new catalysts for asymmetric synthesis.

## 2. Cycloaddition reactions

In 1986 Braun and Sauer found the enhanced endo selectivity for the Diels–Alder reaction of methyl acrylate and cyclopentadiene in concentrated solutions of lithium perchlorate in diethyl ether, THF, and DME.<sup>4</sup> Four years later Grieco *et al.* described such a solvent system, a 5.0 M solution of  $\text{LiClO}_4$  in diethyl ether, which had a greater accelerating effect on the [4+2]-cycloaddition.<sup>5</sup> For example, the reaction of *trans*-piperylene with 2,6-dimethylbenzoquinone in a 5.0 M ether solution of  $\text{LiClO}_4$  at ambient temperature and pressure is complete within 15 min, affording an 80% yield of cycloadduct

(Scheme 4.1), whereas the same reaction in benzene requires a longer reaction time and higher reaction temperature for completion of the reaction. The observed rate acceleration, which has been believed to come from a high internal solvent pressure, is due to the Lewis acidity of the lithium salt.<sup>25</sup> In 1993 Reetz *et al.* found that a catalytic amount of  $\text{LiClO}_4$  (3–25 mol%) suspended in dichloromethane is effective in promoting Diels–Alder reactions<sup>10</sup> in addition to Mukaiyama aldol reactions,<sup>8</sup> Michael additions,<sup>8</sup> and 1,3-Claisen rearrangements.<sup>10</sup> An example is provided by the reaction of methyl acrylate with cyclopentadiene in the presence of 25 mol% of  $\text{LiClO}_4$  (Scheme 4.2 in Protocol 1).<sup>10</sup> The conversion is 87% at  $-15^\circ\text{C}$  after a reaction time of 24 h and the *endo:exo* ratio is shown to be 7.3:1.

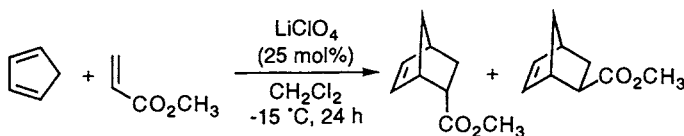


Scheme 4.1

## Protocol 1.

### Diels–Alder reaction of methyl acrylate with cyclopentadiene catalysed by $\text{LiClO}_4$ <sup>10</sup> (Scheme 4.2)

**Caution!** Carry out all procedures in a well-ventilated hood, and wear disposable vinyl or latex gloves and chemical-resistant safety goggles.



Scheme 4.2

## Equipment

- Magnetic stirrer
- Syringes
- Cooling bath with dry ice–acetone
- Schlenk flask (10 mL)
- Vacuum/inert gas source (argon)

## Materials

- Cyclopentadiene, 330 mg, 5 mmol
- Methyl acrylate, 86 mg, 1 mmol
- Lithium perchlorate, 25 mg, 0.25 mmol
- Dichloromethane, 16 mL
- Water
- Magnesium sulfate

flammable, toxic  
flammable, lachrymator  
oxidizer, irritant  
toxic, irritant  
hygroscopic

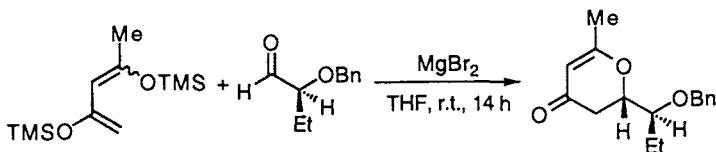
1. Ensure that the Schlenk flask and syringes have been dried and flushed with argon before use.
2. Dry dichloromethane by distillation over  $P_2O_5$  and then  $CaH_2$  prior to use.
3. Prepare a solution of methyl acrylate (86 mg, 1 mmol) and cyclopentadiene (330 mg, 5 mmol) in dry  $CH_2Cl_2$  (1 mL) under argon atmosphere.
4. After cooling the solution to  $-15^\circ C$ , add  $LiClO_4$  (25 mg, 0.25 mmol).
5. After stirring for 24 h, dilute the reaction mixture with  $CH_2Cl_2$  (15 mL).
6. Wash the dichloromethane solution with water twice (15 mL each). Dry the organic layer and then remove the organic solvent using a rotary evaporator to obtain the crude product (87% conversion, an *endo:exo* ratio of 7.3:1).
7. Determine the conversion based on methyl acrylate and the *endo:exo* ratio of the crude product by GC analysis.

Magnesium halides have been utilized as Lewis acids for [4+2]-cycloaddition reactions and shown to increase the regioselectivity, having an opposite effect to that of  $BF_3 \cdot OEt_2$ .<sup>14,15,26</sup> For example, the  $MgBr_2$ -promoted hetero-Diels–Alder reaction of a siloxy diene with  $\alpha$ -alkoxy aldehydes gives a single diastereomer (Scheme 4.3 in Protocol 2),<sup>15</sup> whereas under Lewis acid catalysis by either  $BF_3 \cdot OEt_2$  or  $ZnCl_2$ , another diastereomer is selectively obtained with a 1.4:1 ratio. The stereochemical outcome of the  $MgBr_2$ -promoted reaction reveals that the cycloaddition occurs from the less hindered face of a *syn* conformer of the aldehyde in which a chelation of the magnesium exists between the two oxygens.

## Protocol 2.

**Hetero-Diels–Alder reaction of 2,4-Bis(trimethylsiloxy)-1,3-pentadiene with 2-(benzyloxy)butyraldehyde promoted by magnesium bromide. synthesis of (2*S*\*,1'*S*\*)-2-[(1'-benzyloxy)propyl-6-methyl-2,3-dihydro-4*H*-pyran-4-one]<sup>15</sup> (Scheme 4.3)**

**Caution!** Carry out all procedures in a well-ventilated hood, and wear disposable vinyl or latex gloves and chemical-resistant safety goggles.



**Scheme 4.3**

## Equipment

- Magnetic stirrer
- Syringes
- Cooling bath with ice water
- Round-bottomed flask (200 mL)
- Vacuum/inert gas source (argon)

**Protocol 2. Continued****Materials**

• 2,4-Bis(trimethylsiloxy)-1,3-pentadiene, 9.10 g, 42.1 mmol	<b>flammable, moisture-sensitive</b>
• 2-(Benzyloxy)butyraldehyde, 3.00 g, 16.9 mmol	<b>irritant</b>
• Magnesium bromide (2.95 M solution in 10% benzene/ether), <sup>a</sup> 5.7 mL, 16.9 mmol	<b>irritant, hygroscopic</b>
• Dry tetrahydrofuran (THF), 80 mL	<b>flammable, irritant</b>
• Sodium bicarbonate	<b>moisture-sensitive</b>
• Ethyl ether	<b>flammable, irritant</b>
• Magnesium sulfate	<b>hygroscopic</b>
• Dichloromethane, 100 mL	<b>toxic, irritant</b>
• Trifluoroacetic acid, 4 mL	<b>corrosive, toxic</b>
• Sodium chloride	<b>hygroscopic, irritant</b>

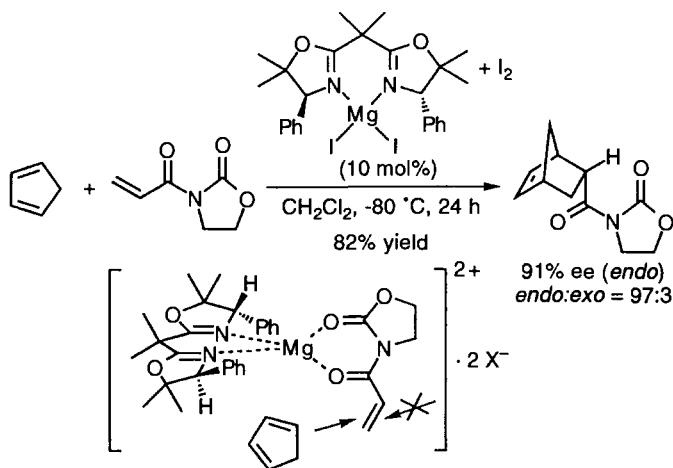
1. Ensure that all glass equipment has been dried in an oven before use.
2. Place 2-(benzyloxy)butyraldehyde (3.00 g, 16.9 mmol) in a 200 mL flask with a magnetic stirring bar under argon atmosphere and dissolve the aldehyde with dry THF (80 mL).
3. Cool the solution to 0°C and add a solution of magnesium bromide (2.95 M, 5.7 mL, 16.9 mmol) in 10% benzene/ether over 2 min.
4. After stirring for 10 min, add 2,4-bis(trimethylsiloxy)-1,3-pentadiene (9.10 g, 42.1 mmol) and warm the solution slowly to room temperature.
5. After stirring for 14 h, pour the solution into a saturated aqueous sodium bicarbonate solution and extract with ether. Dry the organic layer over anhydrous MgSO<sub>4</sub> and concentrate *in vacuo*.
6. Dissolve the resultant oil in 100 mL of CH<sub>2</sub>Cl<sub>2</sub> and add trifluoroacetic acid (4 mL). After stirring for 3 h, wash the solution with water, saturated aqueous sodium bicarbonate solution, and brine, then dry the organic layer over anhydrous MgSO<sub>4</sub> and concentrate *in vacuo*.
7. Purify the crude product by flash column chromatography on silica gel (40% ethyl acetate/hexane) to give 3.41 g (78%) of the title compound as a clear colourless oil and characterize by IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and elemental analysis.
8. Examine the crude and purified products by GLC (column: 4 ft, 3% OV-17, 210°C, 30 mL/min flow rate, *t<sub>R</sub>* = 10.1 min) and 500 MHz <sup>1</sup>H NMR experiments to confirm there is no detectable amount of the diastereomer.

<sup>a</sup> Magnesium bromide can be prepared from 1,2-dibromoethane and magnesium turnings in ether. Add benzene (c. 10%) to homogenize the two-phase mixture. Calculate the molarity by weighing the residual magnesium. The resultant solution can be stored for several months at room temperature.

In 1992 the first example of a chiral magnesium reagent as a catalyst for an asymmetric reaction was reported by Corey and Ishihara.<sup>22</sup> The chiral Mg catalyst is prepared by treatment of a chiral bis(oxazoline) ligand with MgI<sub>2</sub> and I<sub>2</sub> (co-catalyst) in CH<sub>2</sub>Cl<sub>2</sub>. When 3-acryloyloxazolidine-2-one is reacted with cyclopentadiene in the presence of the catalyst (10 mol%) at -80°C, the Diels–Alder product was obtained in 82% yield with 91% ee and an *endexo*

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ratio of 97/3 (Scheme 4.4).<sup>22</sup> A 1:1:1 complex of the chiral ligand,  $\text{Mg}^{2+}$ , and the dienophile is believed to be the reactive species in which the *s-cis* form of oxazolidinone co-ordinates to the metal. The diene approaches from the front side of the complex avoiding repulsion by the phenyl group (Scheme 4.4).



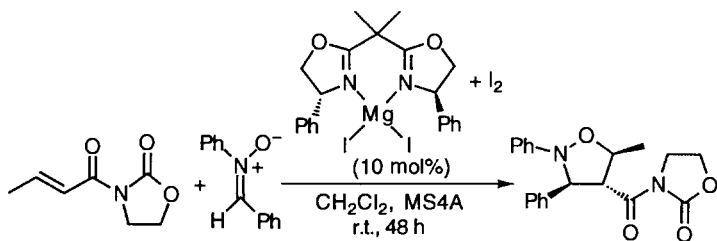
Scheme 4.4

This chiral bis(oxazoline)-magnesium catalyst has been successfully applied to the enantioselective 1,3-dipolar cycloaddition reaction of alkenes with nitrones to lead high *endo*-selectivity with up to 82% ee (Scheme 4.5 in Protocol 3).<sup>24</sup>

#### Protocol 3.

**Asymmetric 1,3-dipolar cycloaddition reaction of 3-((*E*)-2'-butenoyl)-1,3-oxazolidin-2-one with benzyldenephénylamine *N*-oxide catalysed by chiral Mg(II)-bisoxazoline complex<sup>24</sup> (Scheme 4.5)**

**Caution!** Carry out all procedures in a well-ventilated hood, and wear disposable vinyl or latex gloves and chemical-resistant safety goggles.



Scheme 4.5

**Protocol 3. Continued****Equipment**

- Magnetic stirrer
- Syringes
- Schlenk flask (10 mL, 5 mL)
- Vacuum/inert gas source (argon)

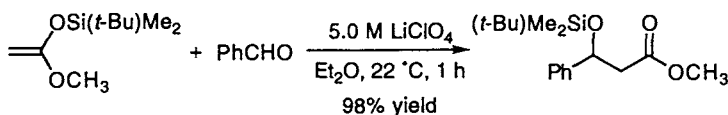
**Materials**

- 3-((*E*)-2'-butenoyl)-1,3-oxazolidin-2-one, 78 mg, 0.5 mmol **flammable, toxic**
- Benzyldenephénylamine *N*-oxide, 123 mg, 0.625 mmol
- (*R*)-2,2'-isopropylidenebis(4-phenyl-2-oxazoline), 410 mg, 1.25 mmol
- Magnesium, 48 mg, 2.0 mmol **moisture-sensitive**
- Iodine, 506 mg, 2.0 mmol **toxic, corrosive**
- Ethyl ether, 5 mL **flammable, irritant**
- Dichloromethane, 15 mL **toxic, irritant**
- 4Å powdered molecular sieves, 50–100 mg
- MeOH

1. Ensure that all glass equipment has been dried in an oven before use.
2. Activate the 4Å powdered molecular sieves by heating to 250°C for 3 h in high vacuum prior to use.
3. Place magnesium (48 mg, 2.0 mmol) and iodine (253 mg, 1.0 mmol) in a 10 mL flask with a magnetic stirring bar under N<sub>2</sub>. Add diethyl ether (5 mL) and stir the mixture at room temperature until the iodine colour disappears (2–3 h). Filter off the unreacted Mg and remove the solvent of the filtrate under reduced pressure at room temperature.
4. Dissolve the white MgI<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> and add (*R*)-2,2'-isopropylidenebis(4-phenyl-2-oxazoline) (410 mg, 1.25 mmol) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) to the resulting solution.
5. After stirring the milky suspension for 2 h, add I<sub>2</sub> (253 mg, 1.0 mmol) and stir the deep-red suspension for 2 h before use.
6. Add 3-((*E*)-2'-butenoyl)-1,3-oxazolidin-2-one (78 mg, 0.5 mmol) and benzyldenephénylamine *N*-oxide (123 mg, 0.625 mmol) to a suspension of 50–100 mg of 4Å powdered molecular sieves in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) in a 5 mL flask.
7. After stirring the mixture for 15 min, add the catalyst (0.05 mmol) with a glass pipette.
8. After stirring for 48 h, treat the reaction mixture with 5% MeOH in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) and filter the mixture through a 20 mm layer of silica gel.
9. Wash the silica gel layer with another 2 mL of 5% MeOH in CH<sub>2</sub>Cl<sub>2</sub> and remove the organic solvent using a rotary evaporator.
10. Purify the crude product by preparative TLC (silica gel, ether–petroleum ether (3:1)) to give a pure product in 81% yield (84% *endo*, 75% ee).
11. Determine the enantiomeric excess by HPLC analysis (Daicel Chiralcel OD, hexane/isopropanol = 9:1, flow rate = 1.0 mL/min), *t*<sub>R</sub> = 42 min (minor), *t*<sub>R</sub> = 58 min (major).

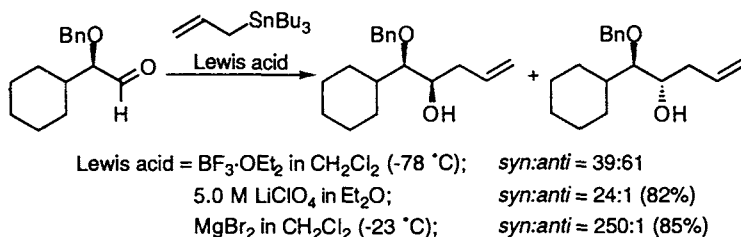
### 3. Aldol additions, allylations, and other reactions

Lithium and magnesium Lewis acid reagents are also effective promoters for nucleophilic carbon-carbon bond forming reactions. The Mukaiyama aldol reaction of ketene silyl acetals with aldehydes occurs at room temperature under the influence of a stoichiometric or catalytic amount of  $\text{LiClO}_4$ .<sup>7,8</sup> For example, the silyl ether derived from methyl acetate reacts with benzaldehyde in a 5.0 M ether solution of  $\text{LiClO}_4$  to provide the silylated aldol adduct in 98% yield (Scheme 4.6).<sup>7</sup> The use of a catalytic amount (3 mol%) of  $\text{LiClO}_4$  suspended in  $\text{CH}_2\text{Cl}_2$  results in complete conversion within 15 min.<sup>8</sup>



**Scheme 4.6**

The addition of allylstannanes to  $\alpha$ -alkoxy aldehydes has been shown to proceed with high diastereoselectivity under chelation control in the presence of  $\text{LiClO}_4$ <sup>27</sup> or  $\text{MgBr}_2$ .<sup>18–21</sup> When a mixture of  $\alpha$ -benzyloxy aldehyde and allyltributylstannane is treated with  $\text{MgBr}_2$  in  $\text{CH}_2\text{Cl}_2$ , the *syn*-product is obtained with >250:1 stereoselectivity.<sup>18</sup> In marked contrast, non-chelation-controlled stereochemistry is observed with  $\text{BF}_3 \cdot \text{OEt}_2$  (Scheme 4.7).<sup>18</sup> The high *syn*-selectivity provided by  $\text{MgBr}_2$  is due to the formation of a discrete bidentate chelate with the  $\alpha$ -alkoxy aldehyde.



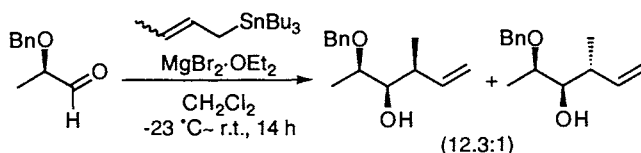
**Scheme 4.7**

The high levels of diastereofacial selectivity observed for the allylations are preserved for the case of crotylation where three contiguous chiral centres are defined during the reaction.<sup>19,20</sup> With  $\alpha$ -benzyloxy aldehyde, *syn,syn*-selectivity is observed regardless of the geometry of the crotyltin. However, higher diastereoselectivities are given with the *E*-stannane, for instance, a 12.3:1 ratio of *syn,syn/syn,anti* products is obtained with a 90:10 mixture of the *E*- and *Z*-stannanes (Scheme 4.8 in Protocol 4).<sup>21</sup>

**Protocol 4.**

**Addition of crotyltributylstannane to (*R*)-2-(benzyloxy)propionaldehyde promoted by magnesium bromide etherate. Preparation of (*2R,3R,4S*)-2-benzyloxy-4-methyl-5-hexen-3-ol<sup>21</sup> (Scheme 4.8)**

**Caution!** Carry out all procedures in a well-ventilated hood, and wear disposable vinyl or latex gloves and chemical-resistant safety goggles.



**Scheme 4.8**

**Equipment**

- Magnetic stirrer
- Syringes
- Cooling bath with dry ice/acetone
- Round-bottomed flask (100 mL)
- Vacuum/inert gas source (argon)

**Materials**

- |   |   |
|---|---|
| <ul style="list-style-type: none"> <li>• (<i>R</i>)-2-(Benzyloxy)propionaldehyde, 450 mg, 2.74 mmol</li> <li>• Crotyltributylstannane (<i>E:Z</i> = 90:10),<sup>a</sup> 1.42 g, 4.11 mmol</li> <li>• Magnesium bromide etherate, 1.14 g, 5.48 mmol</li> <li>• Dry dichloromethane, 30 mL</li> <li>• Sodium bicarbonate</li> <li>• Dichloromethane for extraction (80 mL)</li> <li>• Sodium sulfate</li> </ul> | <p>irritant</p> <p>irritant</p> <p>flammable, moisture-sensitive</p> <p>toxic, irritant</p> <p>moisture-sensitive</p> <p>toxic, irritant</p> <p>irritant, hygroscopic</p> |
|---|---|

1. Ensure that all glass equipment has been dried in an oven before use.
2. Place (*R*)-2-(benzyloxy)propionaldehyde (450 mg, 2.74 mmol) in an oven-dried 100 mL round bottom flask with a magnetic stirring bar under argon atmosphere and dilute the aldehyde with dry dichloromethane (30 mL).
3. After cooling the solution to  $-23^{\circ}\text{C}$  for 10 min, add magnesium bromide etherate (1.14 g, 5.48 mmol) all at once as a white powder. The mixture will become cloudy, and then over the next 10 min the solid material will partially dissolve and the solution will become slightly yellow.
4. After stirring for 15 min, add crotyltributylstannane (1.42 g, 4.11 mmol) dropwise via a syringe down the side of the flask to allow for ample cooling. Stir the mixture for an additional 2 h at  $-23^{\circ}\text{C}$  before the bath is allowed to expire.
5. After stirring for 12 h at room temperature, add saturated aqueous sodium bicarbonate solution (30 mL) and continue stirring for 25 min. Extract the mixture with  $\text{CH}_2\text{Cl}_2$  ( $4 \times 20$  mL) and dry the organic layer over anhydrous  $\text{Na}_2\text{SO}_4$ . Filter the organic layer through a plug of Celite<sup>®</sup> (1 cm) and silica gel (2 cm).



- Remove the solvent *in vacuo* and purify the crude product via radial plate liquid chromatography. Load the material onto a 4 mm plate with hexane (3 mL) and elute with 150 mL of hexane, 100 mL of 5% EtOAc/hexane, 100 mL of 10% EtOAc/hexane, and 150 mL of 15% EtOAc/hexane to give the title compound (509 mg, 84%, (2*R*,3*R*,4*S*)-isomer:(2*R*,3*R*,4*R*)-isomer = 12.3:1) as a clear colourless liquid.
- Determine the diastereomeric ratio by GLC analysis (GC DX-4 15 m column 120–180 °C at 3.5 °C/min, major, 13.72 min, minor, 14.00 min).

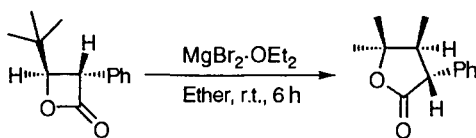
<sup>a</sup> Crotyltributylstannane can be obtained by tin anion displacement of the corresponding crotyl chloride.

The oxophilic nature of  $\text{MgBr}_2$  is valid for mediating numerous rearrangements of oxygen-containing compounds. A typical example of the stereospecific conversion of a  $\beta$ -lactone to a butyrolactone including methyl group migration is shown in Scheme 4.9 (Protocol 5).<sup>28</sup> Use of other conventional Lewis acids than  $\text{MgBr}_2 \cdot \text{OEt}_2$  results in recovery of the unreacted  $\beta$ -lactone or the occurrence of undesired side reactions. A stepwise mechanism involving a rate-determining ionization step is proposed for the rearrangement rather than a concerted mechanism.<sup>29</sup>

### Protocol 5.

**Rearrangement of a  $\beta$ -lactone to a butyrolactone promoted by magnesium bromide etherate. Preparation of *trans*-4,5-dihydro-3-phenyl-4,5,5-trimethyl-2(3*H*)-furanone<sup>29</sup> (Scheme 4.9)**

**Caution!** Carry out all procedures in a well-ventilated hood, and wear disposable vinyl or latex gloves and chemical-resistant safety goggles.



**Scheme 4.9**

### Equipment

- Magnetic stirrer
- Syringes
- Three-necked flask (25 mL)
- Vacuum/inert gas source (nitrogen)

### Materials

- *cis*-4-*tert*-Butyl-3-phenyloxetan-2-one,<sup>a</sup> 2.04 g, 10 mmol
- Magnesium bromide etherate, 2.58 g, 10 mmol
- Dry ether,<sup>b</sup> 10 mL
- Water, 10 mL
- Magnesium sulfate
- Hexane for recrystallization

irritant  
flammable, moisture-sensitive  
flammable, irritant

hygroscopic  
flammable, irritant

**Protocol 5. Continued**

1. Ensure that all glass equipment has been dried in an oven at 120°C for a minimum of 4 h and then assembled under a nitrogen stream before use.
2. Equip an oven-dried 25-mL three-necked flask with a nitrogen inlet and stirring bar and charge the flask with 10 mL of a 1.0 M solution of *cis*-4-*tert*-butyl-3-phenyloxetan-2-one (2.04 g, 10 mmol) in anhydrous ether.
3. Begin stirring and add magnesium bromide etherate (2.58 g, 10 mmol) in a single portion. Stir the light-yellow mixture under nitrogen for 6 h at room temperature, then terminate the reaction by the gradual addition of 10 mL of water.
4. Separate the layers and dry the ether layer over anhydrous MgSO<sub>4</sub>. After filtering the organic layer, remove the solvent under reduced pressure. Purify the crude product by recrystallization from hexane to afford the title compound (1.75 g, 86%) which displays the appropriate <sup>1</sup>H NMR (in CDCl<sub>3</sub>) and IR (KBr).

<sup>a</sup> *cis*-4-*tert*-Butyl-3-phenyloxetan-2-one can be conveniently prepared from phenylacetic acid by a two-step sequence: (1) deprotonation of the acid by 2 equiv of lithium di-isopropylamide in THF followed by treatment with 2,2-dimethylpropanal to afford the resulting β-hydroxy acid (74%), (2) cyclization of the acid with benzenesulfonyl chloride in pyridine at 0°C (94%).

<sup>b</sup> Dry ether is distilled from sodium benzophenone ketyl prior to use.

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