

## The Function of Magnesium(II) *N,N'*-Dicyclohexylamidinide Complexes as a Carbon Dioxide Carrier

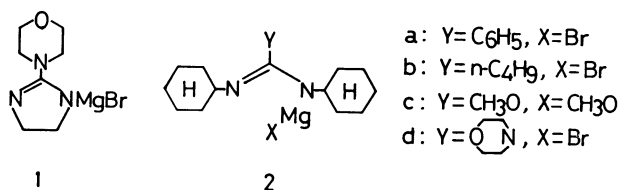
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**Synopsis.** It is found that magnesium(II) *N,N'*-dicyclohexylamidinide complexes are useful reagents for the fixation of carbon dioxide and the transfer of the captured carbon dioxide moiety to active methylene compounds.

A carbon dioxide carrier,<sup>1)</sup> which performs its function in the fixation of carbon dioxide and transcarboxylation, is of interest in connection with a biological biotin-dependent carboxylation<sup>2)</sup> and in applications to organic syntheses. Recently we have reported that 2-morpholino-4,5-dihydro-1-imidazolylmagnesium complex (**1**) acts effectively as a carbon dioxide carrier in the carboxylation of active methylene compounds under mild conditions.<sup>3)</sup> In our continuing investigation of carbon dioxide carrier, we have studied the transcarboxylating function of magnesium(II) complexes **2a–d** having an amidinide-type ligand which is derived readily from available dicyclohexylcarbodiimide (DCC). Herein, we wish to report that complexes **2a** and **2b** are the useful carbon dioxide carriers and that the C=N bond, the substituent Y of the amidinide type ligand and the magnesium(II) ion play an important role in the transcarboxylation process.



The transcarboxylating ability of complexes **3a–d**, prepared by the reactions of **2a–d** with carbon dioxide, was investigated using acetophenone as the substrate. The reaction afforded benzoylactic acid and **4a–d** as the products. The yield of benzoylactic acid shown in Table 1 indicated that complexes **3a** and **3b** exhibit activity for the transfer of their carbon dioxide moiety to acetophenone, but complexes **3c** and **3d** are much less active. Thus, contrary to complex **1**, the morpholino group of complex **3d** was undesirable for the activation of the carbon dioxide moiety.

Next, the transcarboxylating activity of complex **3b**

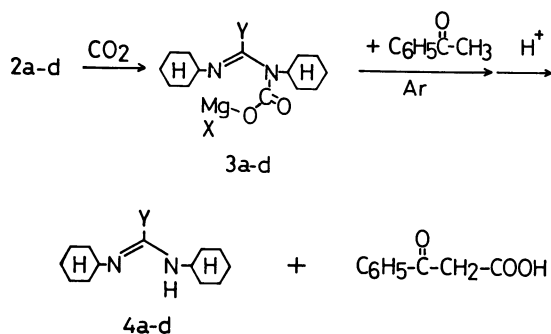


TABLE 1. THE YIELD OF BENZOYLACETIC ACID IN THE REACTION OF ACETOPHENONE WITH COMPLEXES **3a–d**

| Complex   | Yield/% <sup>b)</sup> |
|-----------|-----------------------|
| <b>3a</b> | 44                    |
| <b>3b</b> | 45                    |
| <b>3c</b> | Trace                 |
| <b>3d</b> | 8                     |

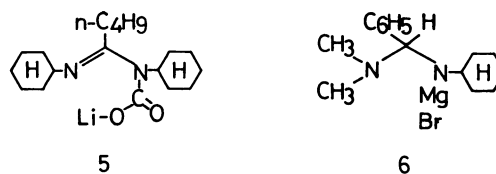
a) Solvent; DMF. Temperature; r. t. Reaction time; 40 h.

b) Based on acetophenone.

was compared with that of the lithium-carboxylato complex (**5**). It was observed that acetophenone is carboxylated by **5** in only 10% yield. The fact that the magnesium(II) complex is much more effective than the lithium complex was the same as that in the case of the imidazolinide complex **1** described previously.<sup>3)</sup>

In order to investigate whether the C=N bond of the *N,N'*-dicyclohexylamidinide ligand is required for the transcarboxylating function or not, we carried out the carboxylation of acetophenone using complex **6** under the similar conditions. The complex **6** absorbed an equimolar amount of carbon dioxide, but the resulting magnesium(II)-carboxylato complex was found not to transfer the carbon dioxide moiety to acetophenone at all. This fact demonstrates that the C=N bond is necessary for transcarboxylation.

Other active methylene compounds described in Table 2 also were carboxylated by the magnesium(II)-carboxylato complex **3a**. It is interesting that *S*-benzyl thioacetate is carboxylated though in a low yield, since it may be related to CH<sub>3</sub>CO-CoA in a biological system.



### Experimental

**Materials.** Active methylene compounds were distilled or recrystallized prior to use. Tetrahydrofuran (THF) was refluxed over LiAlH<sub>4</sub>, distilled and stored in argon atmosphere.

#### *Carboxylation of Active Methylene Compounds with 2a–d.*

A typical experiment was as follows: a solution of phenylmagnesium bromide, butylmagnesium bromide, magnesium dimethoxide, or morpholinomagnesium bromide (8.16 mmol) in THF (10 cm<sup>3</sup>) was under argon added to a solution of DCC (6.81 mmol) in THF (10 cm<sup>3</sup>) and the solution was stirred for 1 h. After removal of the solvent, the residue was dissolved in 25 cm<sup>3</sup> of *N,N*-dimethylformamide (DMF) by bubbling

TABLE 2. CARBOXYLATIONS OF ACTIVE METHYLENE COMPOUNDS WITH COMPLEX **3a** UNDER ARGON<sup>a)</sup>

| $\begin{array}{c} \text{R}_1-\text{CO}-\text{CH}_2-\text{R}_2 \\ \text{R}_1 \qquad \qquad \text{R}_2 \end{array}$ |                                               | Yield <sup>b)</sup> of<br>$\text{R}_1-\text{CO}-\text{CH}(\text{R}_2)-\text{COOH}$ |
|-------------------------------------------------------------------------------------------------------------------|-----------------------------------------------|------------------------------------------------------------------------------------|
| <i>p</i> -NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>                                                          | H                                             | 74                                                                                 |
| <i>p</i> -CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub>                                                         | H                                             | 14                                                                                 |
| C <sub>6</sub> H <sub>5</sub> -CH=CH                                                                              | H                                             | 50                                                                                 |
|  -CH=CH                          | H                                             | 68                                                                                 |
| C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> S                                                                   | H                                             | 24                                                                                 |
| C <sub>6</sub> H <sub>5</sub>                                                                                     | CH <sub>3</sub>                               | 32                                                                                 |
| <i>n</i> -C <sub>4</sub> H <sub>9</sub>                                                                           | H                                             | 8                                                                                  |
| -(CH <sub>2</sub> ) <sub>4</sub> -                                                                                |                                               | 25                                                                                 |
| H                                                                                                                 | C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> | 35                                                                                 |

a) Solvent; DMF. Temperature; r. t. Reaction time; 40

h. b) Based on the substrate.

carbon dioxide and the solution was stirred at room temperature for 1 h. The solvent was evaporated *in vacuo* at room temperature and the residue was dried *in vacuo* at 40 °C. The resulting white solid, which contains complex **3**, was allowed immediately to react under argon with active methylene compounds (1.7 mmol) in dry DMF (35 cm<sup>3</sup>) at room temperature for 40 h. The formation of complex **3** was confirmed by the method described previously:<sup>3)</sup> complex **3a** was confirmed by the facts that the IR spectrum of the solid has the carbonyl absorption at 1665 cm<sup>-1</sup> and that complex **2a** absorbs an equimolar amount of carbon dioxide and the fixed carbon dioxide is released quantitatively by treatment with a dilute sulfuric acid solution. The reaction was stopped by adding water. The carboxylation products and **4a—d** were isolated in the usual manner and were identified by a comparison of their melting points, IR, <sup>1</sup>H NMR, and mass spectra, and elemental analyses with those of the respective authentic specimens.

**Compounds 4a—d:** HCl salt of **4a**: mp 264—265 °C (decomp); IR (KBr) 3420 (NH), 1630 cm<sup>-1</sup> (C=N); <sup>1</sup>H NMR (CDCl<sub>3</sub>) 0.5—3.0 (m, 24H, NH+aliphatic) 6.9—7.7 (m, 5H, aromatic). Found: C, 71.11; H, 9.11; N, 8.73%. Calcd for C<sub>19</sub>H<sub>29</sub>N<sub>2</sub>Cl: C, 70.98; H, 8.91; N, 8.54%. **4b**: bp 161—162 °C/7 mmHg; IR (film) 3350 (NH), 1640 cm<sup>-1</sup> (C=N); <sup>1</sup>H

NMR (CDCl<sub>3</sub>) 0.5—2.5 (m, 29H, aliphatic), 2.5—3.2 (m, 3H, NH+NCH<sub>2</sub>); MS *m/e* 264 (M<sup>+</sup>), 235, 222, 153, 140, 101, 84, 83. Found: C, 76.95; H, 12.38; N, 10.53%. Calcd for C<sub>17</sub>H<sub>32</sub>N<sub>2</sub>: C, 77.21; H, 12.20; N, 10.59%. **4c**: bp 118—120 °C/2 mmHg; IR (film) 3440 (NH), 1660 cm<sup>-1</sup> (C=N); <sup>1</sup>H NMR (CDCl<sub>3</sub>) 0.7—3.4 (m, 23H, aliphatic), 3.5 (s, 3H, OCH<sub>3</sub>); MS *m/e* 238 (M<sup>+</sup>), 206, 165, 164, 83, 82, 81. Found: C, 70.53; H, 11.24; N, 11.60%. Calcd for C<sub>14</sub>H<sub>26</sub>N<sub>2</sub>O: C, 70.54; H, 10.99; N, 11.75%. **4d**: mp 99—101 °C; IR (KBr) 3380 (NH), 1630 cm<sup>-1</sup> (C=N); <sup>1</sup>H NMR (CDCl<sub>3</sub>) 1.0—2.2 (m, 22H, aliphatic), 2.2—3.9 (m, 9H, NH+morpholino). Found: C, 69.58; H, 10.65; N, 14.32%. Calcd for C<sub>17</sub>H<sub>31</sub>N<sub>3</sub>O: C, 69.86; H, 10.92; N, 14.34%.

**The Reaction of Acetophenone with Complex 6.** A solution of phenylmagnesium bromide (6.81 mmol) in 10 cm<sup>3</sup> of THF was added under argon, drop by drop, to a solution of *N*<sup>2</sup>-cyclohexyl-*N*<sup>1</sup>,*N*<sup>1</sup>-dimethylformamidinium (6.81 mmol), which was prepared by the method described in the literature,<sup>4)</sup> in 10 cm<sup>3</sup> of THF at room temperature. The mixture was magnetically stirred at this temperature for 1 h. After removal of the solvent *in vacuo*, the residue was dissolved in 25 cm<sup>3</sup> of DMF under bubbling carbon dioxide and the solution was stirred under bubbling carbon dioxide at room temperature for 1 h. The solvent was evaporated *in vacuo* at room temperature and the residue was dried *in vacuo* at 40 °C. The resulting white solid, which contains complex **6**, was allowed immediately to react under argon with acetophenone. The reaction mixture was treated by the method being similar to that in the cases of **2a—d**. Acetophenone and benzaldehyde were obtained in good yields, but benzoylacetic acid was not detected at all.

## References

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