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## 2-Morpholinoimidazolinomagnesium(11) Complex as a Novel Carbon Dioxide Carrier

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Summary The magnesium complex (1) has been found to undergo fixation of carbon dioxide and the resulting 1-carboxylato-complex (2) transfers the carboxylato group to active methylene compounds (3) including acetophenone, benzylideneacetone,  $\beta$ -ionone, and Sbenzyl thioacetate, under mild conditions.

THERE has been considerable interest recently<sup>1</sup> in transcarboxylation using a carbon dioxide carrier which may be related to biotin enzymes in biological systems.<sup>2</sup> We now wish to report a novel type of carbon dioxide carrier, 2-morpholinoimidazolinomagnesium(II) complex (1), which is able to capture carbon dioxide and then transfer the captured CO<sub>2</sub> unit to active methylene compounds under mild conditions, the carboxylato group being labilized by hydrogen abstraction from the active methylene compounds by a nitrogen atom in the 3-position.

Complex (1) prepared from 2-morpholinoimidazoline hydroiodide<sup>3</sup> and phenylmagnesium bromide in tetrahydrofuran, was kept under argon dispersed in dry NNdimethylformamide (DMF). Carbon dioxide was bubbled with stirring into the dispersed solution at room temperature for 1 h. The homogeneous solution obtained was evaporated and dried *in vacuo* at 40 °C to give complex (2) whose i.r. spectrum (2) exhibited carbonyl absorption at 1665 cm<sup>-1</sup>. In a separate experiment, we observed that complex (1) absorbs an equimolar amount of carbon dioxide and that complex (2) releases the fixed carbon dioxide quantitatively on treatment with dilute sulphuric acid solution.



i, CO<sub>2</sub>, room temp., 1 h, DMF, ii, DMF at room temp. under Ar; iii,  $H_3O^+$ .

To investigate the transcarboxylation process, complex (2) was allowed to react with the ketones (3a) and (3b) in dry DMF with bubbling argon at room temperature for 40 h. The reactions were stopped by adding water. When

the complex (2): substrate molar ratio was 4:1, benzoylacetic acid (4a) and 3-oxo-5-phenylpent-4-enoic acid (4b) were obtained in 50 and 51% yields, respectively, and (2) had been converted back into 2-morpholinoimidazoline, which indicated that the carboxylato group had been transferred to (3a) and (3b).



The transcarboxylating ability of (2) was compared with that of the lithium-carboxylato complex (5) and the magnesium(II) complex (6). The reactions were carried out using (3a) as the substrate under similar conditions to those used for (2) and it was found that (3a) was carboxylated by (5), in 9% yield, but not by (6). This also indicated that complex (2) is effective as a transcarboxylating reagent and in addition, the Mg<sup>II</sup> ion is considered to play an important role as a cofactor for the co-ordination of the substrate in the transcarboxylation process.

TABLE. Carboxylation of the ketones (3a-d) in DMF at room temperature with  $CO_2$  under pressure to give the acids (4a-d), respectively.ª

Ketone (3) <sup>b</sup>	Time/h	% Yield of acid (4)°
( <b>3a</b> )	19	58
(3b)	19	76
$(\mathbf{3c})$ ( $\beta$ -ionone)	19	77
(3d)	65	54

<sup>a</sup>  $P(CO_2) = 3 \text{ kg/cm}^2$ . <sup>b</sup> Molar ratio (2):(3) = 4:1. <sup>c</sup> Based on (3).

Finally, we carried out the reactions of complex (2)with the active methylene compounds (3a-d), in dry DMF under a pressure of carbon dioxide of 3 kg/cm<sup>2</sup> at room temperature. The results in the Table show that (2) is an effective carboxylation agent for the active methylene compounds investigated.

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