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

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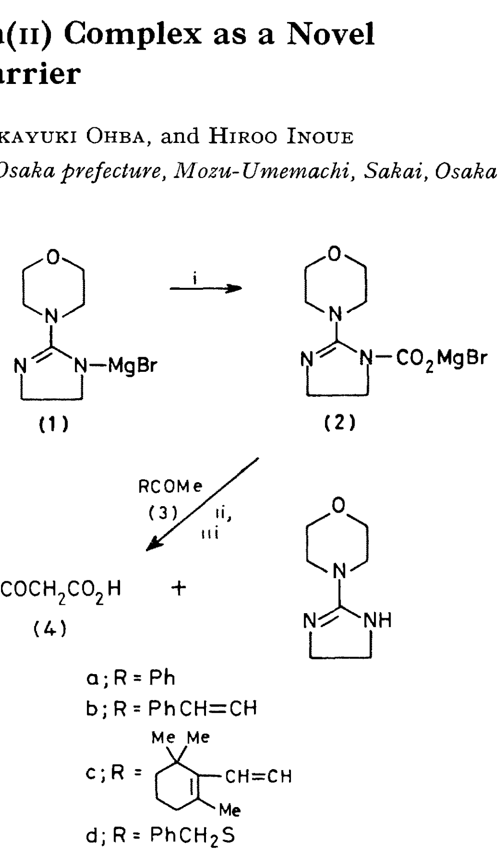
Summary The magnesium complex (**1**) has been found to undergo fixation of carbon dioxide and the resulting 1-carboxylato-complex (**2**) transfers the carboxylato group to active methylene compounds (**3**) including acetophenone, benzylideneacetone, β-ionone, and *S*-benzyl thioacetate, under mild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

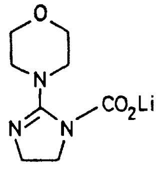
There has been considerable interest recently[1] in transcarboxylation using a carbon dioxide carrier which may be related to biotin enzymes in biological systems.[2] We now wish to report a novel type of carbon dioxide carrier, 2-morpholinoimidazolinomagnesium(II) complex (**1**), which is able to capture carbon dioxide and then transfer the captured CO_2 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[3] and phenylmagnesium bromide in tetrahydrofuran, was kept under argon dispersed in dry *NN*-dimethylformamide (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^{-1}. 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_2, 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**).



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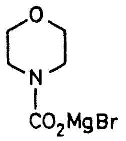

(6)

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^{II} 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)[b]	Time/h	% Yield of acid (4)[c]
(**3a**)	19	58
(**3b**)	19	76
(**3c**) (β-ionone)	19	77
(**3d**)	65	54

[a] $P(CO_2)$ = 3 kg/cm². [b] Molar ratio (**2**):(**3**) = 4:1. [c] 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/cm² 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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