Preparation and Transcarboxylation of Magnesium(II) and Manganese(II) 2-Oxoimidazolidine-1-carboxylato-complexes

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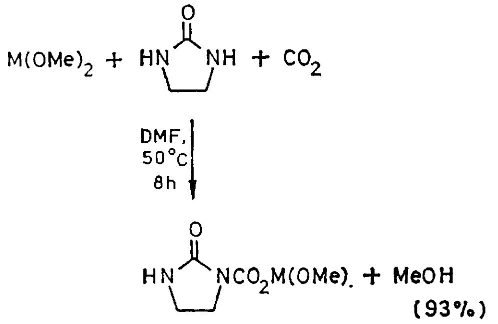
Summary Mg^{II} and Mn^{II} 2-oxoimidazolidine-1-carboxylato-complexes, $\overline{\text{C(:O)NHCH}_2\text{CH}_2\text{N}}\text{CO}_2\text{M(OMe)}$, which were isolated from the reaction of the metal dimethoxides, imidazolidin-2-one, and CO_2 act as CO_2 carriers in transferring the CO_2 unit to cyclohexanone; the ureido structure of the complexes plays an important role in this transfer.

Recently the preparation and characterization of transition-metal carbamato-complexes obtained from amines and CO_2 have been studied in relation to CO_2 co-ordination chemistry.[1] The use of ureas instead of amines would be expected to lead to potentially interesting new chemistry. In particular, 2-oxoimidazolidine-1-carboxylato-complexes may be related to the metallobiotin enzymes such as pyruvate carboxylase (Mn^{II}, Mg^{II})[2a,b] and transcarboxylase (Co^{II}, Zn^{II}, Cu^{II}).[2c] Here we report the preparation and reaction (decarboxylation and transcarboxylation) of the 2-oxoimidazolidine-1-carboxylato-complexes of Mg^{II} (**1**) and Mn^{II} (**2**).



(1) M = Mg^{II}
(2) M = Mn^{II}

Scheme 1

All operations were performed under nitrogen and in anhydrous solvents. The complexes (**1**)[3] and (**2**) were prepared as shown in Scheme 1, and the precipitates obtained were filtered off, washed with dimethylformamide (DMF) followed by tetrahydrofuran, and dried *in vacuo*.† Complexes (**1**) and (**2**) showed similar i.r. spectra except for a slight difference in the carbonyl region [(**1**): 1710 and 1650 cm^{-1}; (**2**): 1691 and 1620 cm^{-1}]. The fact that the carbonyl stretching absorption of the five-membered cyclic urea appears near 1720 cm^{-1} suggests the *N*-carboxylation of the imidazolidin-2-one in (**1**) and (**2**).[4,5] *O*-Carboxylation producing 2-oxy-2-imidazoline and carbonate groups is not probable because the cyclic imine band characteristic of 2-alkoxy-2-imidazoline appears in the 1655—1600 cm^{-1} region[5] and metal methylcarbonato complexes, $MeOCO_2$-M(OMe), show carbonyl bands at 1624 ($M = Mg^{II}$) and 1627 cm^{-1} ($M = Mn^{II}$ [6]).

Complexes (**1**) and (**2**) were thermally stable towards decarboxylation. However, their decarboxylations were greatly accelerated by the addition of MeI to give simultaneously *NN'*-dimethylimidazolidin-2-one in yields of 64% for (**1**) and 50% for (**2**) (Figure). The formation of *NN'*-dimethylimidazolidin-2-one suggests that methylation of the nitrogen atom of the ureido group with MeI creates a positively charged centre facilitating the release of CO_2. Acetic acid also effected the decarboxylation of (**1**) and (**2**) at ambient temperature. The decarboxylation of (**1**) and (**2**) caused by MeI or HOAc contrasts with the previous report that divalent metal ions, Mn^{II} or Cu^{II}, prevent the decarboxylation of *N*-carboxyimidazolidin-2-one in acidic aqueous solution forming an inactive metal chelate.[7]

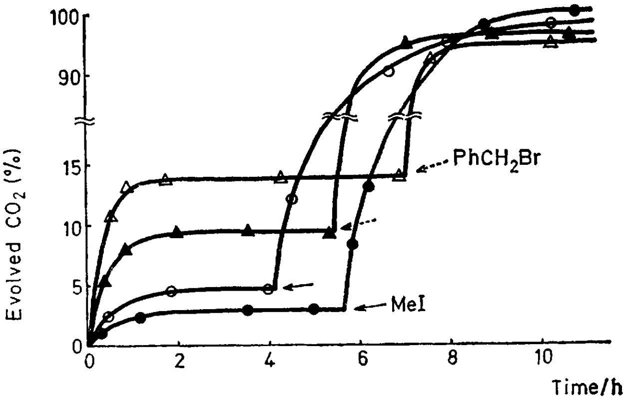


Figure. Decarboxylation of (**1**) (●, 90 °C), (**2**) (○, 120 °C), (**3**) (▲, 70 °C), and (**4**) (△, 70 °C). The arrows indicate the points at which MeI [for (**1**) and (**2**)] and $PhCH_2Br$ [for (**3**) and (**4**)] were added.

The transcarboxylating ability of (**1**) and (**2**) to an active hydrogen compound was examined using cyclohexanone. The reaction of (**1**) (3 equiv.) and cyclohexanone was carried out at 110 °C in DMF for 6 h under nitrogen. After hydrolysis, the mixture was treated with diazomethane to produce methyl 2-oxocyclohexanecarboxylate in 18% yield based on cyclohexanone. Use of a larger excess of (**1**) relative to cyclohexanone increased the yield to 28% for a 5:1 ratio and 43% for a 10:1 ratio. Under similar conditions, (**2**) gave the methyl ester in yields of 5·6% (3:1 ratio) and 10% (5:1 ratio). Thus, (**1**) and (**2**) acted as CO_2 carriers. To evaluate the role of the ureido structure of (**1**) and (**2**) in the transcarboxylation, the corresponding metal carbamato complexes (**3**) and (**4**) of a non-urea-type amine were prepared using morpholine (Scheme 2).† Complexes (**3**)

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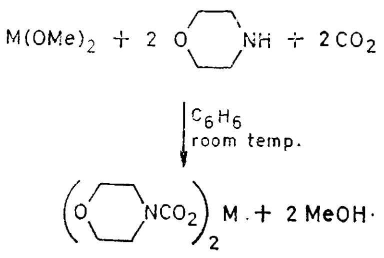
† Complexes (**1**) and (**2**) gave satisfactory analyses for the metal and for CO_2 and evolved MeOH on acidolysis. Complexes (**3**) and (**4**) were identified by their metal content, CO_2 evolution on acidolysis, and i.r. spectra.



(**3**) M = Mg^{II}
(**4**) M = Mn^{II}

Scheme 2

and (**4**) were soluble in polar solvents such as DMF and hexamethylphosphoric triamide (HMPA) and their decarboxylation behaviour‡ is illustrated in the Figure. However, neither complex transferred the CO$_2$ unit to cyclohexanone in DMF at temperatures in the range room temp. to 120 °C. This finding suggests the ureido structure in (**1**) and (**2**) is important for the transcarboxylation. The transcarboxylation from (**1**) or (**2**) to cyclohexanone may be assumed to proceed directly [2a] without participation of liberated CO$_2$,[8] in view of the insignificant thermal decarboxylation of (**1**) or (**2**) and the inability of (**3**) or (**4**) to transfer the CO$_2$ unit to cyclohexanone.

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‡ *N*-Benzylmorpholine was formed quantitatively in the decarboxylation of (**3**) or (**4**) caused by the addition of benzyl bromide (Figure).

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