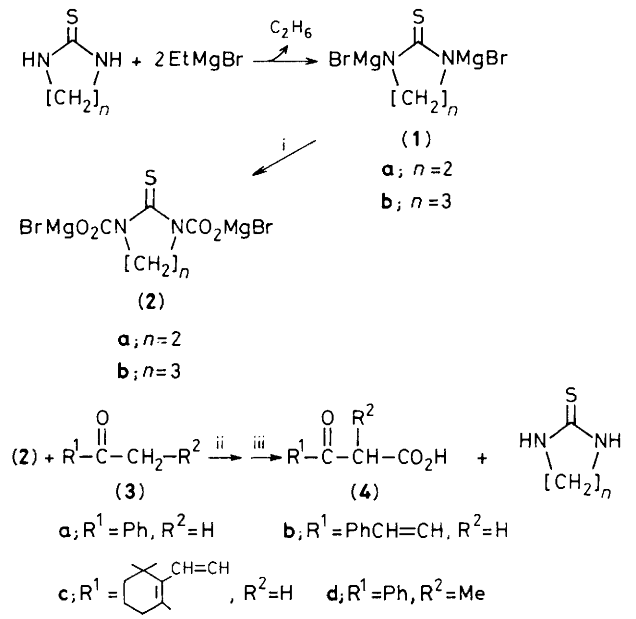
α-Carboxylation Reactions of Ketones with a Bromomagnesium Thioureide–Carbon Dioxide Complex

Noboru Matsumura,* Nobuyuki Asai, and Shigeo Yoneda*

Department of Applied Chemistry, University of Osaka Prefecture, Mozu-Umemachi, Sakai, Osaka 591, Japan

The magnesium complex (**1**) has been found to undergo fixation of carbon dioxide and the resulting carboxylato-complex (**2**) transfers the carboxylato group to several ketones with good yields.

The preparation and characterization of a new carbon dioxide carrier[1] are important in connection with biological biotin-dependent carboxylation[2] and in applications to organic synthesis using CO_2. Recently, we have reported[3] that the



Reagents and conditions: i, CO_2, room temp., 1 h, THF; ii, DMF at 15 °C under Ar; iii, H_3O^+.

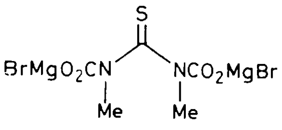
Table 1. Carboxylation of the ketones (**3a**—**d**) with (**2**), (**5**), (**6**), and (**7**).[a]

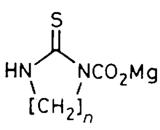
		% Yield of product (**4**)[b]					
Ketone	Time/h	(**2a**)	(**2b**)	(**5**)	(**6a**)	(**6b**)	(**7**)
(**3a**)	20	74	79	52	34	31	5
(**3b**)	20	78	78	71	25	11	5
(**3c**)	20	58	53	39	19	21	2
(**3d**)	20	49	80	12	2	2	3

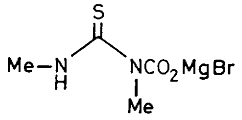
[a] Molar ratio (**2**):(**3**) = 4:1. [b] Based on (**3**).

2-morpholino-4,5-dihydroimidazol-1-ylmagnesium complex, the magnesium(II) *N,N'*-dicyclohexylamidinide complex, and lithium 1,8-diazabicyclo[5.4.0]undec-7-en-6-ide act effectively as carbon dioxide carriers. In our continuing studies on the structure–function correlation of CO_2 carriers, we have found that the magnesium(II) complex (**1**), which is readily derived from available cyclic thiourea derivatives, is an excellent transcarboxylating agent. This transcarboxylation is noteworthy, because it proceeds under mild reaction conditions (15 °C) compared with the conditions (110 °C) necessary for a ureide magnesium complex.[4]

To a solution of (**1**) prepared from a cyclic thiourea and ethylmagnesium bromide in tetrahydrofuran (THF) under argon, gaseous carbon dioxide was introduced with stirring at room temperature for 1 h. Evaporation of the solvent *in vacuo* afforded the complex (**2**) as a white solid. The i.r. spectrum (KBr) showed the carbonyl absorption at 1630 cm^{-1}. In order to examine the transcarboxylating ability, complex (**2**) was allowed to react with the ketones (**3a**—**d**). To a solution of (**2**) (5.66 mmol) dissolved in dry dimethylformamide (DMF) (10 ml), a ketone (1.42 mmol) was added by syringe under argon. After stirring under argon at room temperature for 20 h, the reaction was stopped by adding ice-water and acidified with aqueous hydrochloric acid. The mixture was extracted several times with diethyl ether and the extracts were shaken three times with 50 ml of aqueous sodium hydrogen carbonate. The combined aqueous solution was acidified slowly with aqueous hydrochloric acid with ice-cooling and extracted three times with 70 ml portions of diethyl ether. The diethyl ether layer was washed with water, dried over anhydrous $MgSO_4$, and evaporated in a rotary vacuum evaporator. The product, which was pure enough for analysis, was identified by comparison with an authentic sample. The results are shown in Table 1. The yields of α-carboxylated ketones shown in Table 1 indicate that complexes (**2a**), (**2b**), and (**5**) exhibit high activity for the transfer of their carbon dioxide moiety to ketones. Monocarboxylato complexes (**6a**), (**6b**), and (**7**), which were prepared from equimolar amounts of the thiourea [(**2a**), (**2b**), and (**5**)] and CO_2, are less active. Although the detailed mechanism of the reaction is not clear, the magnesium(II) metal ion seems to play a significant role in the carboxylation. Work is in progress to investigate the structure–function correlation and the use of (**1**) in other organic syntheses.


(**5**)


(**6**)
a; n = 2
b; n = 3


(**7**)

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References

1 H. Mori, H. Yamamoto, and T. Kwan, *Chem. Pharm. Bull.*, 1972, **20**, 2440; Y. Otsuji, M. Arakawa, N. Matsumura, and E. Haruki, *Chem. Lett.*, 1973, 1193; H. Mori, Y. Makino, H. Yamamoto, and T. Kwan, *Pharm. Bull.*, 1973, **21**, 915; T. Tsuda, Y. Chujo, and T. Saegusa, *J. Chem. Soc., Chem. Commun.*, 1976, 415; T. Tsuda, Y. Chujo, and T. Saegusa, *J. Am. Chem. Soc.*, 1978, **100**, 630; T. Tsuda, Y. Chujo, T. Hayasaki, and T. Saegusa, *J. Chem. Soc., Chem. Commun.*, 1979, 797; T. Tsuda, Y. Chujo, and T. Saegusa, *J. Am. Chem. Soc.*, 1980, **102**, 431.

2 J. Moss and M. D. Lane, *Adv. Enzymol.*, 1971, **35**, 321.

3 N. Matsumura, Y. Sakaguchi, T. Ohba, and H. Inoue, *J. Chem. Soc., Chem. Commun.*, 1980, 326; N. Matsumura, T. Ohba, Y. Sakaguchi, and H. Inoue, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 3949; N. Matsumura, T. Ohba, and S. Yoneda, *Chem. Lett.*, 1983, 317.

4 H. Sakurai, A. Shirahata, and A. Hosomi, *Tetrahedron Lett.*, 1980, 1967.