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LITHIUM 1,8-DIAZABICYCLO[5.4.0]UNDEC-7-EN-6-IDE AS A NOVEL CARBON DIOXIDE CARRIER

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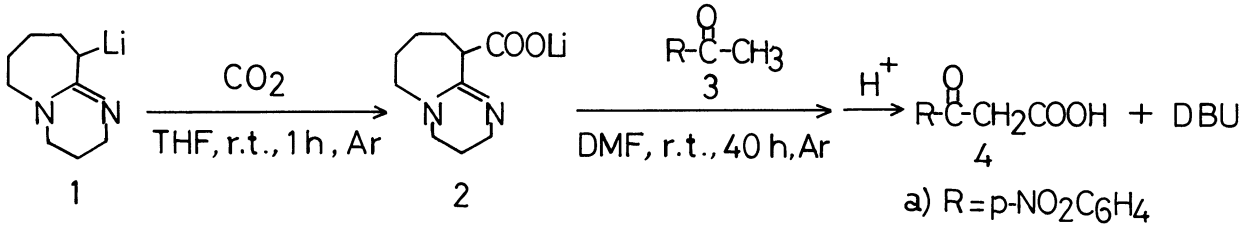
Lithium 1,8-diazabicyclo[5.4.0]undec-7-en-6-ide (1) has underwent the insertion of carbon dioxide and the resulting lithium 6-carboxylato complex (2) transfered the carboxylato moiety to active methylene compounds (3) such as p-nitroacetophenone, acetophenone, p-methoxyacetophenone, and s-benzylthioacetate under mild conditions.

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 reported[3] that 2-morpholino-4,5-dihydro-1-imidazolylmagnesium complex and magnesium(II) N,N'-dicyclohexylamidinide complex act effectively as carbon dioxide carrier, in which the fixation of CO_2 molecule would take place at the nitrogen atom followed by the N-CO_2 bond fission in the transcarboxylation reaction. In our continuing study on the carbon dioxide carrier, we have found the transcarboxylating function of lithium complex (1) which is readily derived from available 1,8-diazabicyclo[5.4.0]undec-7-ene(DBU). This transcarboxylation is particularly interesting, which involves the novel C-CO_2 bond cleavage under mild conditions.

To a solution of 1 prepared from DBU and butyllithium in tetrahydrofuran 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, which is isolable and stable at room temperature for several hours under argon, but on heating or on exposure to air it darkend with no well-defined melting (or decomposition) point. The IR spectrum(KBr) exhibited the carbonyl absorption at 1645 cm^{-1} and the C=N absorption at 1610 cm^{-1}. The ^{1}H-NMR spectrum($CDCl_3$) of 2 showed two multiplets around δ2.7-3.7(m, 6H) and 1.0-2.4(m, 9H), due to the protons of the C(2), C(9), C(11) positions and to those of the C(3), C(4), C(5), C(6), C(10) positions, respectively. Thus, the spectral data supported the structure of 2. The formation of the carboxylato-complex 2 was also supported by the quantitative evolution of CO_2 on treatment with a dilute aqueous sulfuric acid.

In order to examine the transcarboxylating ability, the complex 2 was reacted with active methylene compounds(3a-d). To a solution of 2(5.13 mmol) dissolved in dry DMF (10 ml), a solution of active methylene compound(1.28 mmol) in DMF(5 ml) was added with a syringe under argon atmosphere. After stirring under argon at room temperature for 40 h, the reaction was stopped by adding water and acidified with aqueous hydrochloric acid. The mixture was extracted several times with ether and the ethereal extracts were shaken three times with a 50 ml of aqueous sodium bicarbonate. The combined aqueous solution was again acidified slowly with aqueous hydrochloric acid and extracted

three times with 70 ml portions of ether. The ethereal layer was washed with water, dried over anhydrous $MgSO_4$, and evaporated. The residue was the carboxylated product, which was usually pure enough to give correct analysis. When 4 equiv of 2 was used in the reaction, p-nitrobenzoylacetic acid (4a), benzoylacetic acid (4b), p-methoxybenzoylacetic acid (4c), and (benzylthio)carbonylacetic acid (4d) were obtained in 63, 32, 12, and 10% yields, respectively, and 2 reverted to DBU. The reaction of acetophenone with magnesium(II)-carboxylato complex under similar conditions gave 4b in 22% yield, indicating that lithium complex is more effective than magnesium one. Scheme 1 outlines a pathway for the transcarboxylation reaction using the carbon dioxide carrier 1.



1 2

a) R = p-$NO_2C_6H_4$
b) R = C_6H_5
c) R = p-$CH_3OC_6H_4$
d) R = $C_6H_5CH_2S$

Scheme 1

In conclusion, we emphasize the unique feature of the new carbon dioxide carrier 1 in which the fixation and activation of CO_2, and its transfer to organic substances have occurred on the carbon atom at the 6 position. It is noteworthy that the electronic structure of the anionic moiety after releasing carbon dioxide (A) is quite similar to that (B) of biotin coenzyme as shown below. Work is in progress to investigate the structure-function correlation and the applicability of 1 to other organic syntheses.

A B

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