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A NOVEL SYNTHESIS OF 4,6-DIMETHYL-2-PYRONE FROM CARBON DIOXIDE AND MESITYL OXIDE IN THE PRESENCE OF AN ETHYLZINC CARBAMATE

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Abstract: The title synthesis, the first example of the CO₂ fixation by use of an α , β -unsaturated ketone, has been successfully carried out, most preferably in triethylamine or pyridine at 120-160°C in the presence of ethylzinc diphenylcarbamate.

Fixation of carbon dioxide in the atmosphere into organic compounds not only is an interesting approach to the development of efficient synthetic methods of organic chemicals, but also should reduce its green house effect on the earth. For the synthetic purpose, either CO_2 or the organic compound to react with CO_2 has to be activated by forming precursors.^{1,2} Thus, carbon dioxide has been fixed by the reactions with amines, alcohols, alkylene oxides, unsaturated hydrocarbons and so

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forth in the presence of organometallic compounds.³ Previous reports on the synthesis of 2-pyrones in this manner include such starting materials as mono-^{4a} and disubstituted alkynes,^{4b} diynes,⁵ and allene.⁶ Exceptionally, N,N-diethylaminophenylacetylene^{7a} and bis(N,N-diethylaminoethynyl)benzenes^{7b} have been reported to react spontaneously with CO₂ to yield a 4-pyrone derivative and poly(4-pyrone)s, respectively.

As reported in our previous paper,⁸ a *sec*-arylamine reacts with diethylzinc to afford ethylzinc N, N-diarylamide (1; eq. 1), and CO₂ can be readily inserted into the Zn-N bond of 1 to form ethylzinc arylcarbamate (2; eq. 2). Based on this fact, here we wish to report an unprecedented synthesis of a 2-pyrone derivative, i. e., 4,6dimethyl-2-pyrone (4,6-dimethyl-2*H*-pyran-2-one; 4), from mesityl oxide (4methyl-3-penten-2-one; 3) and CO₂ in the presence of 2 (eq. 3).



Screeninng of solvents for the synthesis revealed that triethylamine, pyridine and acetonitrile were almost equally excellent, whereas 1,4-dioxane and n-hexane were much less effective. Figure 1 depicts the effect of temperature on the reaction of

mesityl oxide with CO_2 in triethylamine in the presence of ethylzinc methylphenylcarbamate. The yield of **4** dramatically increased from ca. 70°C, reaching the highest yield at ca. 160°C.



FIG. 1 Dependence of the yield of 2-pyrone derivative 4 on the reaction temperature

Reaction conditions: diethylzinc, 20 mmol; N-methylaniline, 20 mmol; CO₂, 50 atm; triethylamine, 10 mL; mesityl oxide, 20 mmol; 20 h.

Table 1 summarizes the effect of the structures of *sec*-amines on the yield of **4**. When organozinc aromatic amides obtained by the reaction of diethylzinc and aromatic *sec*-amines such as diphenylamine and N-methylaniline were used, the yield of **4** was relatively high (Nos. 1 and 2).⁹ However, it was much lower when organozinc aliphatic amides obtained from diethylzinc and aliphatic *sec*-amines such as N,N-dibutylamine, N,N-methylbenzylamine and piperidine were employed (Nos. 4-6). Further, neither a *sec*-amine alone (No. 3) nor diethylzinc alone (No. 7) was effective for the formation of **4** from mesityl oxide and CO₂.

No.	\mathbb{R}^1	\mathbb{R}^2	Yield / %
1	Ph	Ph	39
2	Me	Ph	29
3 ^b	Me	Ph	0
4	n-Bu	<i>n</i> -Bu	13
5	Me	Bz	8
6		(NH	8
7 ^c			0

Table 1. Effect of the structures of *sec*-amines on the yield of 2-pyrone derivative 4^a

^a Reaction conditions: diethylzinc, 20 mmol; sec-amine, 20 mmol; CO₂, 50 atm; triethylamine, 10 mL; mesityl oxide, 20 mmol; 120°C, 72 h. ^b Reaction without diethylzinc.
^c Reaction without sec-amine.

The same 2-pyrone derivative has been synthesized by the reaction of allene with CO_2 in the presence of transition metal compounds.⁶ However, it should be noted that the highest yield of **4** in the present work, i. e. 45%, which was attained under the same reaction conditions as those for Run No. 1 but with a longer reaction time of 96 h, is remarkably much higher than those recorded in the earlier papers, i. e., $4.7\%^{6a}$ and 7%.^{6b}

In summary, we have found that mesityl oxide reacted with CO_2 at 120-160°C in the presence of an ethylzinc alkyl- or arylcarbamate to afford 4,6-dimethyl-2-pyrone (4) in a relatively good yield. This reaction is the first example to use an α , β unsaturated ketone as a starting material for the CO_2 fixation reaction. Further studies are in progress to reveal the scope and limitations of this type of CO_2 fixation reactions as well as to establish the reaction mechanism, using various α,β -unsaturated ketones.

EXPERIMENTAL SECTION

The general reaction procedure was as follows. A mixture of diethylzinc (20 mmol from a 2.67 M stock solution in dioxane) and sec-amine (20 mmol) in a solvent (10 mL),¹⁰ placed in a 100 mL stainless steel autoclave under a pressure (50 atm) of CO₂, was allowed to react at 120°C for 3 h to afford ethylzinc carbamate (eq. 2). After cooling to room temperature and purging off of CO₂, mesityl oxide (20 mmol) was added to the reaction mixture, and CO₂ gas was introduced again as before. After heating the autoclave at a given temperature for a given time, the reaction mixture was cooled to room temperature. The remaining CO₂ gas was discharged, and the yellow solid formed was dissolved in dil. HCl (50 mL). Then, the aqueous solution was extracted with chloroform (5 \times 50 mL). The organic layer was dried with anhydrous sodium sulfate and distilled to afford a practically pure product. After recrystallization from diethyl ether, it was unambiguously identified by spectroscopic analyses to be 4; IR (KBr): 1724 (C=O stretch), 1646 cm⁻¹ (C=C stretch). ¹H NMR (CDCl₃/ 400 MHz): δ 2.12, 2.22 (s, -CH₃); 5.86, 5.94 (s, =CH-). ¹³C NMR (CDCl₃/100 MHz): δ 19.7, 21.3 (-CH₃), 106.3, 110.4 (=CH-), 156.2, 161.1, 163.1 (qC); GC-MS (70 eV): 124 (M⁺). These spectroscopic data were identical with those of a commercial product (Aldrich). The yield of 4 given above is based on mesityl oxide.

Quantitative gas chromatography was performed on a Shimadzu GC-8A instrument with a $1.5 \text{ m} \times 4 \text{ mm}$ (i. d.) column packed with 10% PEG-20M on Shimalite W. ¹H and ¹³C NMR spectra were recorded on a JNM-EX400 FT-NMR spectrometer (JEOL Ltd.) using CDCl₃ and TMS as solvent and internal standard, respectively. IR spectra were measured using a JEOL JIR-7000 FT-IR spectrometer. GC-MS analysis was carried out with use of a Shimadzu spectrometer, Model GCMS-QP1000.

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9 'H NMR analysis of the reaction mixtures before the addition of 3 has revealed that zinc amides were formed nearly quantitatively in these two cases.

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