Tetrahedron Letters,Vol.27,No.16,pp 1809-1810,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain

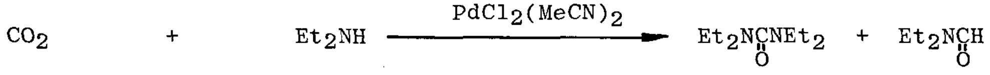
$PdCl_2(MeCN)_2$-CATALYZED CARBONYLATION OF DIETHYLAMINE WITH CARBON DIOXIDE: SELECTIVE SYNTHESIS OF TETRAETHYLUREA AND DIETHYLFORMAMIDE

Yoshiaki Morimoto, Yuzo Fujiwara,* Hiroshi Taniguchi,
Yuji Hori,† and Yoshiaki Nagano†
Department of Applied Chemistry, Faculty of Engineering,
Kyushu University, Hakozaki, Fukuoka 812, Japan
Department of Industrial Chemistry, Faculty of Science
and Technology, Saga University, Honjocho, Saga 840, Japan†

Abstract:The reaction of diethylamine with carbon dioxide (CO_2) with $PdCl_2(MeCN)_2$ as a catalyst gives tetraethylurea(1) or diethylformamide(2) selectively under mild reaction conditions by employing the $PPh_3/CCl_4/MeCN$ and the HCOONa/methyl cellosolve systems, respectively.

Effective synthetic utilization of carbon dioxide (CO_2) is of great importance. Relatively few reports, however, are available on the reactions of CO_2 with organic substrates in the presence of transition metal compounds.(1) We reported the fixation reaction of CO_2 with aromatic compounds such as benzene, anisole, furan, and thiophene by palladium catalysts to give aromatic acids.(2)

In order to further explore the synthetic reaction with CO_2, we have investigated the fixation reactions of CO_2 with a secondary amine like diethylamine under mild conditions. There are a few reports on the synthesis of formamides from amines, CO_2 and H_2 by transition metal catalysts.(3,4) However, these reactions employ high pressure of both CO_2 and H_2 gases. Now we find that N,N,N',N'-tetraethylurea(**1**) and N,N-diethylformamide(**2**) each can be prepared selectively by using the $PPh_3/MeCN/CCl_4$ and the HCOONa/methyl cellosolve systems, respectively from the reaction of atmospheric CO_2 with diethylamine with $PdCl_2(MeCN)_2$ as a catalyst under mild conditions without the use of H_2 gas:



$$CO_2 \qquad + \qquad Et_2NH \xrightarrow{\quad PdCl_2(MeCN)_2 \quad} Et_2N\underset{\underset{O}{\|}}{C}NEt_2 \; + \; Et_2N\underset{\underset{O}{\|}}{C}H$$

1 **2**

Typical experimental procedure is as follows. Diethylamine (20 mmol), $PdCl_2(MeCN)_2$ (0.5 mmol), an additive, a solvent (10 ml), and a magnetic stirring bar were placed in a 50-ml centrifuge tube and the tube was sealed with a cerum cap. After the tube had been bubbled with CO_2 for ten min, the mixture was stirred at room temperature under a balloon of CO_2 (1 atm) for 3 days. The reaction mixture was filtered and the starting amine was evaporated from the solution at room temperature. The yields of the urea and formamide were determined by GC (PEG 6000, 150 °C). The typical examples are shown in Table I.

Table I. Selective Carbonylation of Diethylamine with Carbon Dioxide to **1** or **2**[a]

Entry	Solvent (ml)	Additive (mmol)	Product and Yield, %[b]	
			1	**2**
1	MeCN + CCl_4(10+1)	PPh_3 (14)	710[c]	39
2	MeCN + CCl_4(10+1)	PPh_3 (14)[d]	564[c]	4
3	MeCN + CCl_4(10+1)	PPh_3 (4)	410[c]	2
4	MC[e](10)	HCOONa (0.5)	13	174[f]
5	MC[e](10)	HCOONa (0.5)[g]	46	163[f]

[a] $PdCl_2(MeCN)_2$ (0.5 mmol), room temperature, 72 h. [b] Yields are based on Pd. [c] Triphenylphosphine oxide was also formed. [d] $PdCl_2(MeCN)_2$ (0.2 mmol). [e] Methyl cellosolve. [f] Small amounts of $Et_2N\underset{\overset{\|}{O}}{C}OCH_2CH_2OCH_3$ were also formed. [g] $PdCl_2(PPh_3)_2$ was used as a catalyst.

One can see from Table I that **1** or **2** can be prepared with a common catalyst $PdCl_2(MeCN)_2$ by just changing the additive and the solvent from PPh_3/MeCN/CCl_4 (entries 1, 2 and 3) to HCOONa/Methyl cellosove (entries 4 and 5),respectively.[5)]

Substitution of other catalysts such as $PdCl_2$, $PdCl_2(PhCN)_2$, $PdCl_2(Et_2NH)_2$, $PdCl_2(dppe)_2$,$Pd(OAc)_2$, $Pd(OAc)_2(bpy)$, $Pd_2(dba)_3$, $Pd(acac)_2$, $Pd(NO_3)_2$, $PdPhI(PPh_3)_2$, $Pd(CO)(PPh_3)_3$, $Rh(CO)(PPh_3)_2Br$, $RuH_2(PPh_3)_4$, $RuCl_2(PPh_3)_2$ or other solvent systems resulted in inferior yields.

The selective formation of **1** and **2** from Et_2NH and CO_2 by the catalysis of Pd(II) complexes is new. The mechanism, especially for the formation of urea (**1**), is not yet clear, but probably involves an $HPdNEt_2$ intermediate derived via oxidative addition of Pd(0) species to $H\text{-}NEt_2$ which would be activated by the formation of a salt such as $HN^+Et_2(CCl_3)\cdot Cl^-$ with CCl_4, and coordination of CO_2 and its insertion into a Pd-N bond. Acetonitrile would serve as a good solvent for dissolving such a salt.

Reference and Note

1) (a) S. Inoue and N. Yamazaki (ed.), Organic and Bio-organic Chemistry of Carbon Dioxide, Kodansha Ltd.,and Wiley, Tokyo and New York, 1982. (b) W. Keim (Ed.), Catalysis in C_1 Chemistry, D. Reidel, Dordrecht, 1983.
2) H. Sugimoto, I. Kawata, H. Taniguchi, and Y. Fujiwara, J. Organomet. Chem., 266, C44 (1984).
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5) That CO_2 is the oxygen source of **1** and **2** formed, has been confirmed by blank tests using N_2 and CO instead of CO_2.

(Received in Japan 4 February 1986)