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RUTHENIUM CATALYZED SELECTIVE SYNTHESIS OF ENOL CARBAMATES BY FIXATION OF CARBON DIOXIDE

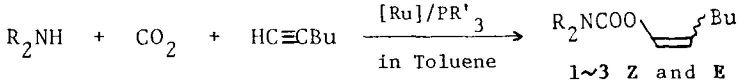
Take-aki Mitsudo,* Yoji Hori, Yasushi Yamakawa, and Yoshihisa Watanabe*
Department of Hydrocarbon Chemistry, Faculty of Engineering,
Kyoto University, Sakyo-ku, Kyoto 606, Japan

Summary: Secondary amines react with carbon dioxide and terminal alkynes in the presence of a catalytic amount of (η^4-1,5-cyclooctadiene)(η^6-1,3,5-cyclooctatriene)ruthenium [Ru(COD)(COT)] and tertiary phosphine in toluene to give enol carbamates in good yields with high regio- and stereoselectivity. Cyclic enol carbamates, 5-methylene-2-oxazolidinones are obtained from N-substituted propargylamines and carbon dioxide in high yields.

During the last decade considerable attentions have been paid to use carbon dioxide as a raw material in organic syntheses catalyzed by transition metal complexes.1) We recently reported a useful method for preparing enol carboxylates by addition of carboxylic acids to terminal alkynes catalyzed by a bis(η^5-cyclooctadienyl)ruthenium-tertiary phosphine-maleic anhydride system.2)

On the other hand, Dixneuf et al. have recently shown that enol carbamates can be prepared by addition of carbamic acids to terminal alkynes catalyzed by $Ru_3(CO)_{12}$3) or $RuCl_3$4), where yields and selectivities of carbamates are low for aliphatic acetylenes.

We now report that a bis(η^5-cyclooctadienyl)ruthenium or Ru(COD)(COT)-tertiary phosphine system catalyzes the reaction of secondary amines with carbon dioxide and terminal alkynes to give enol carbamates in good yields with high regio- and stereoselectivity (eq. 1).

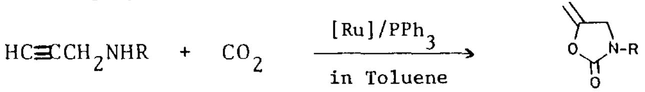


(1)

1~3 Z and E

R' = Cy or Ph R_2 **= Et$_2$,(1Z)/(1E): $-(CH_2)_4-$,(2Z)/(2E): n-Pr$_2$,(3Z)/(3E)**

Furthermore, the reaction of N-substituted propargylamines with carbon dioxide gives cyclic enol carbamates in high yields (eq. 2).



(2)

4~6

R = n-Pr,(4): PhCH$_2$,(5): i-Pr,(6)

In a typical procedure, diethylamine (1.46 g, 20 mmol), 1-hexyne (0.82 g, 10 mmol), Ru(COD)(COT) (0.063 g, 0.2 mmol), tricyclohexylphosphine (0.112 g, 0.4 mmol) and toluene (10 ml) were placed in a 100 ml autoclave and 50 atm of carbon dioxide was charged. The mixture was heated at 100°C for 8 h with stirring at 1000 rpm. Careful vacuum distillation of the

Table 1 Preparation of Enol Carbamates Catalyzed by $Ru(COD)(COT)/PR'_3$ [a)]

run	PR'_3	product	yield(%)[b)]	Z/E	run	PR'_3	product	yield(%)[b)]
1[c)]	PCy_3	(1Z),(1E)	62	92/8	5[d)]	PPh_3	(4)	(80)
2	PCy_3	(1Z),(1E)	(56)	90/10	6[d)]	PPh_3	(5)	(63)
3	PCy_3	(2Z),(2E)	57	86/14	7[d)]	PPh_3	(6)	73
4	PPh_3	(3Z),(3E)	37	90/10				

a) Amine: 20 mmol, 1-Hexyne: 10 mmol, Ru(COD)(COT): 0.2 mmol, Phosphine: 0.4 mmol, Toluene: 10 ml, CO_2: 50 atm, 100°C, 8 h. b) GLC yield (Isolated yield). c) 48 h.
d) N-Substituted propargylamine: 10 mmol.

reaction mixture afforded 1.12 g (yield 56 %) of 1-hexenyl N,N-diethylcarbamate (Z/E = 90/10) (Table 1, run 2). All products were characterized by spectroscopic and analytical data.

In the presence of a catalytic amount of Ru(COD)(COT) and a phosphine, the corresponding enol carbamates were obtained in good yields with high regio- and stereoselectivity for the Z isomer (eq. 1). The results are summarized in Table 1 (runs 1-4). The catalytic activity of bis(η^5-cyclooctadienyl)ruthenium is the same as that of Ru(COD)(COT). No maleic anhydride was required for this reaction. Carbon dioxide may play a similar role of a π-acid ligand as maleic anhydride. The most suitable phosphine ligand depended or the substrate. Oligomerization of the alkynes was limited under this reaction condition.

The reaction of N-substituted propargylamines with carbon dioxide catalyzed by Ru(COD)(COT) and triphenylphosphine selectively gave cyclic enol carbamates, 5-methylene-2-oxazolidinones,[5)] by the intramolcular addition reaction in high yields (eq. 2) (Table 1, runs 5-7). 5-Methylene-2-oxazolidinone can be utilized for the preparation of copolymers, as fungicides and as rust inhibitors.

One of the possible reaction routes is the nucleophilic attack of the carbamate anion on the coordinated alkyne and the subsequent reductive elimination of the enol carbamate, which was proposed in the addition reaction of carboxylic acid to terminal acetylene on the basis of the kinetic study and the results of the reaction with AcOD.[2b)] Studies on the scope and mechanism of the present reaction are now in progress.

References

1) A. Behr, "Catalysis in C_1 Chemistry", ed. by W. Keim, D. Reidel Publishing Co., Dordrecht, 1983, pp. 169-217.

2) a) T. Mitsudo, Y. Hori, Y. Yamakawa, and Y. Watanabe, Tetrahedron Lett., 1986, 27, 2125, and references cited therein. b) idem., J. Org. Chem., 1987, 52, 2230.

3) Y. Sasaki and P. H. Dixneuf, J. Chem. Soc. Chem. Commun., 1986, 790.

4) R. Mahé, P. H. Dixneuf, and S. Lécolier, Tetrahedron Lett., 1986, 27, 6333; Y. Sasaki and P. H. Dixneuf, J. Org. Chem., 1987, 52, 314.

5) It has been reported that 5-methylene-2-oxazolidinones are obtained from propargylamine and CO_2 by use of Cu catalysis in yields up to 65 %; P. Dimroth and H. Pasedach, Ger. Pat., 1164411; Chem. Abs., 1964, 60, 14510d.

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