Notes

Synthesis of Carbamates from Amine, Acetylenic Alcohol, and CO_2 using Lanthanide as Catalyst

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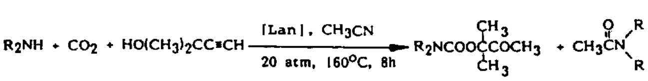
The combustion of fossile fuels generates a large quantity of carbon dioxide and, therefore, CO_2 is a very cheap carbon (C_1) source. But CO_2 is a very stable molecule. The reactivity of CO_2, however, can be greatly enhanced by the judicious use of metal catalyst. Therefore there has been a great deal of works devoted to CO_2 chemistry and are now available a number of books and review articles.[1-4]

The general methods available for the synthesis of carbamate are outlined in the reaction of isocyanates of alcohols,[5-6] the Curtius rearrangement of acylazide,[7] and formation of carbamates from N,N-disubstituted carbamoyl chloride.[8] However, the formation of these carbamates is not straight forward and always involves a multistep synthesis starting from toxic phosgene. Especially, catalytic synthesis of carbamates are rare. For example, Alper[9-10] or Fukuoka[11] synthesized carbamates from amines, alcohols, CO_2, and oxygen using Pd black or $PdCl_2$ as catalyst. As for reaction of CO_2 affording carbamates, Inoue *et al.*[12] synthesized carbamic ester from CO_2, epoxide, and amine. Vaska *et al.*[13] recently reported the reversible homogeneous catalysis of CO_2 hydrogenation/reduction at room temperature and low pressure. Dixneuf and coworkers[14] reported ruthenium catalyzed synthesis of vinylcarbamate from CO_2, terminal alkyne and secondary amine, and they also reported ruthenium catalyzed synthesis of O-β-oxoalkylcarbamates from CO_2, propagyl alcohol, and secondary amine.[15]

We have also been much interested in the activation of CO_2 by various metal complexes. As a results, we conceived formation of carbamates using CO_2. Secondary amines, acetylenic alcohols, and inner transition metal complexes. To our knowledge, we described as first example of the synthesis of carbamate by inner transition metal complexes. This related paper was published elsewhere.[16]

The catalytic formation of 1,1-dimethyl-2-oxopropyl-N, N-dialkylcarbamates can be effected by lanthanide metal chloride under reaction conditions described in eq. (1). Reactions invariably give a small amount of N,N-dialkylacetamide.

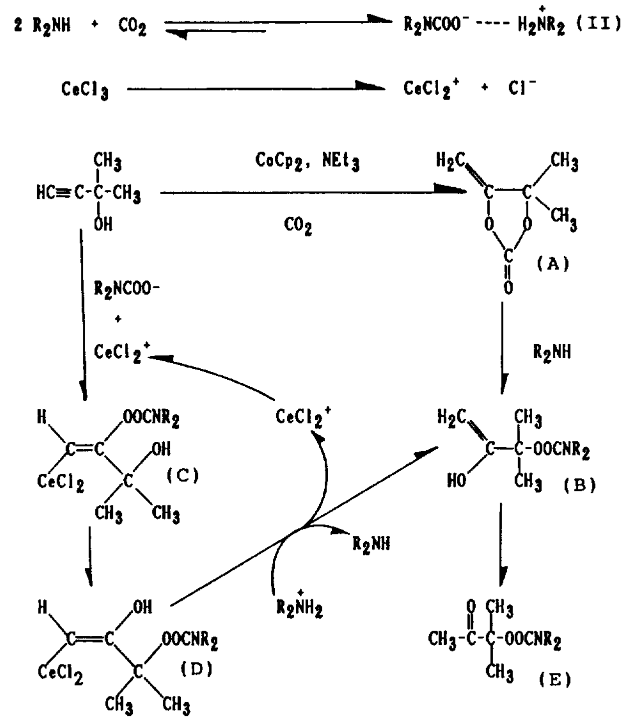


Equation (1)

Table 1. Reaction of CO_2, Amine, and 2-Methyl-3-butyn-2-ol[a]

No	Amine	Catalyst[b]	Product	Yield[c]
1	$(CH_2)_6NH$	A	$(CH_2)_6N-COOC(CH_3)_2COCH_3$	38
2		B	$(CH_2)_6N-COOC(CH_3)_2COCH_3$	27
3		C	$(CH_2)_6N-COOC(CH_3)_2COCH_3$	22
4		D	$(CH_2)_6N-COOC(CH_3)_2COCH_3$	20
5	$(CH_2)_5NH$	A	$(CH_2)_5N-COOC(CH_3)_2COCH_3$	21
6	$(CH_2)_4NH$	A	$(CH_2)_4N-COOC(CH_3)_2COCH_3$	31
7	O NH	A	O N-$COOC(CH_3)_2COCH_3$	8
8	$(C_2H_5)_2NH$	A	$(C_2H_5)_2$ N-$COOC(CH_3)_2COCH_3$	7
9	$(C_6H_5)_2NH$	A	—	0

[a] Reaction condition: alcohol; 10 mmol, amine: 20 mmol, catalyst; 0.2 mmol, CH_3CN; 10 m*l*, P_{CO_2}:20 atm, time: 8 hrs. [b] Catalyst: A; $CeCl_3$·Anhydrous, B; $PrCl_3·6H_2O$, C; $NdCl_3·6H_2O$, D; $GdCl_3$·anhydrous. [c] Isolated yield: Based on Alcohol.



Scheme 1.

The product yield are affected a little by the choice of different metals.

As shown in Table 1, $CeCl_3$ anhydrous was the best catalyst among them. Cyclic amines such as perhydroazepine, piperidine, and pyrrolidine give higher yields than open chain one, diethylamine. The unexpectedly poor yield from morpholine, however, seems to be connected its low basicity. The case of diphenylamine does not afford the corresponding product. This observation was more clearly represented from the comparative studies described in other paper.[16] Finally, in connection with the yields of carbamates, solvent also plays a role. For instance, these reactions employed various solvents such as diethylether, tetrahydrofuran, and acetonitrile. Of them, acetonitrile gives the highest yields.

Based on the known facts and reports by others[17-18], a possible mechanism for carbamate formation is proposed in Scheme 1. In this reaction, two equivalents of amine per alkyne are required in order to get the better yields in 1,1-dimethyl-2-oxopropyl-N,N-dialkylcarbamates. This is consistent with the in situ formation of ammonium carbamates, according to proposed mechanism of two possible reaction paths can account for the formation of 1,1-dimethyl-2-oxopropyl-N,N-dialkylcarbamates. (i) The intermediate (A) has been isolated from the reaction of 2-methyl-3-butyn-2-ol with CO_2 in the presence of NEt_3 and $CoCp_2$ at 80 °C, 50 atm, 5 hours.[17] Addition of a secondary amine to the carbonyl carbon of the carbonate (A) would then give the intermediate (B), the tautomeric form of (E).[18] (ii) First, $CeCl_2^+$ attacked terminal acethylene carbon and then carbamate ion [R_2NCOO^-] was added to the adjacent carbon. The transesterification of (C) into (D) would normally lead to (B), the precursor of (E).

The typical procedure of synthesis of 1,1-dimethyl-2-oxopropyl-N,N-dialkyl carbamates using lanthanide metal chloride as a catalyst; under the stream of nitrogen, secondary amine (20 mmol), 2-methyl-3-butyn-2-ol (10 mmol), acetonitrile (10 m*l*), and catalyst (0.2 mmol) were added with a magnetic stirring bar in a glass liner set in the reactor. After purging with CO_2 a few times, the reactor was pressurized to the desired pressure (P_{CO_2} = 20 atm). The system was heated to 160 °C in 30 min in a heating mantle and thermostated at this temperature with stirring for 8 hours. This reaction was terminated by rapid cooling and reactor was discharged. At the bottom of the resulting clear dark brown solution, lanthanide chloride residue was precipitated and it was discarded. The reaction mixture was reduced in volume to minimum amount. The reduced reaction mixture was chromatographed to give 1,1-dimethyl-2-oxopropyl-N,N-dialkyl carbamates as a pure product. The products were identified by IR, ^{1}H-NMR, and mass spectra, respectively. Spectral data of carbamates are as follows:

1,1-Dimethyl-2-oxopropyl-N,N-tetramethylene carbamate. IR(neat) 1700 cm^{-1} (C=O), 1690 cm^{-1} (NCOO), ^{1}H-NMR ($CDCl_3$) δ 1.42 (s, $2CH_3$), 1.90 (m, $2CH_2$), 2.09 (s, CH_3CO), 3.38 (m, $N(CH_2)_2$): MS (*m/e*) 199 (rel. int., 12, M^+), 98 (100), 70 (12), 43 (14).

1,1-Dimethyl-2-oxopropyl-N,N-pentamethylene carbamate. IR (neat) 1722 cm^{-1} (C=O), 1688 cm^{-1} (NCOO); ^{1}H-NMR ($CDCl_3$) δ 1.31 (s, $2CH_3$), 1.60 (m, $2CH_2$), 2.01 (s, CH_3CO), 3.40 (m, $N(CH_2)_2$); MS (*m/e*) 214 (rel. int., 3, M^+ + 1), 112 (45), 70 (100), 43 (30).

1,1-Dimethyl-2-oxopropyl-N,N-hexamethylene carbamate. IR (neat) 1720 cm^{-1} (C=O), 1685 cm^{-1} (NCOO); ^{1}H-NMR ($CDCl_3$) δ 1.42 (s, $2CH_3$), 1.62 (m, $4CH_2$), 2.02 (s, CH_3CO), 3.40 (m, $N(CH_2)_2$); MS (*m/e*) 228 (rel. int., 2, M^+ + 1), 126 (100), 98 (19), 43 (21).

1,1-Dimethyl-2-oxopropyl-N,N-(oxydiethyl)carbamate. IR (neat) 1726 cm^{-1} (C=O), 1700 cm^{-1} (NCOO); ^{1}H-NMR ($CDCl_3$) δ 1.40 (s, $2CH_3$), 2.03 (s, CH_3CO), 3.46 (m, $N(CH_2)$), 3.55 (m, $2CH_2$); MS (*m/e*) 216 (rel. int., 1, M^+ + 1), 114 (100), 43 (28).

1,1-Dimethyl-2-oxopropyl-N,N-dimethylcarbamate. IR (neat) 1720 cm^{-1} (C=O), 1690 cm^{-1} (NCOO); ^{1}H-NMR ($CDCl_3$) δ 1.61 (t, $2CH_3$), 1.46 (s, $2CH_3$), 2.14 (s, CH_3CO), 3.31 (q, $2CH_2$), MS (*m/e*), 202 (M^+ + 1).

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Syntheses of 5-Pentadecyl-10,15,20-Triphenylporphyrin, and Its Zn(II) and Mn(III) Complexes

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Solar energy storage systems, which mimic the plant photosynthesis system, are studied extensively[1,2]. We are in-