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Cobalt-Catalyzed Photochemical Carbonylation of Allylic Amines

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Allylic amines are carbonylated at room temperature in the presence of cobalt catalysts under UV irradiation. With allylamine, 2-pyrrolidone, N,N'-diallylurea, and N-allyl-3-butenamide were obtained. The photochemical cleavage of C-N bond of amines coordinated to cobalt metals was suggested.

Cobalt-catalyzed photochemical hydroformylation of olefins has been found to proceed at 80 °C and 80 atm of synthesis gas.[1] We have found that the reaction proceeds even at room temperature.[2] In our continuing effort to study the hydroformylation of substituted olefins, we have studied the carbonylation of allylic amines. Allylamine is thermally carbonylated to afford 2-pyrrolidone under highly severe conditions of 280 °C and 300 atm of carbon monoxide in the presence of $Co_2(CO)_8$.[3] With copper catalyst the carbonylation of allylamine gives N-allylformamide at 120 °C and 60-80 atm of carbon monoxide.[4] We wish to report that the cobalt-catalyzed carbonylation of allylic amines under UV irradiation gives 2-pyrrolidones, N-alkenyl β,γ-unsaturated amides, and N,N'-dialkenyl-ureas at room temperature as shown in Eq. 1.

(1)

1 2 3 4

A typical procedure for the photochemical carbonylation is as follows: In a home-made 10 cm^3 stainless-steel UV autoclave equipped with a quartz window (20 mm diameter, 15 mm thickness) and a magnetically driven up-and-down stirrer was added 5 cm^3 of a solution of allylamine (0.1 mol dm^{-3}), cobalt catalyst (0.005 mol dm^{-3}), and tributyl phosphine (0.05 mol dm^{-3}). The autoclave was flushed with synthesis gas or carbon monoxide three times and then pressurized to a desired pressure. Irradiation was achieved with a high-pressure Hg lamp (500 W) through a quartz lens.

First, we attempted the photochemical hydroformylation of allylamine

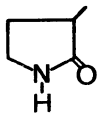
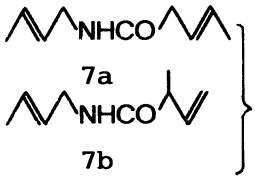
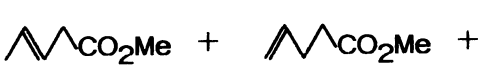
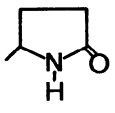
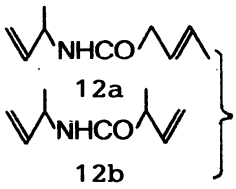
Table 1. Photochemical Carbonylation of Allylamine

Entry	P_{CO} /atm	P_{H_2} /atm	Catalyst	Phosphine	Solvent	Conv. of amine/%	Product yield[a]/%		
							2	**3**	**4**
1	20	20	$Co(OAc)_2$	PBu_3	MeOH	15.2	8.6	-	1.0
2	40	40	$Co(OAc)_2$	PBu_3	MeOH	15.5	9.7	-	1.0
3[b]	40	40	$Co(OAc)_2$	PBu_3	MeOH	30.8	20.4	-	1.8
4	60	60	$Co(OAc)_2$	PBu_3	MeOH	12.1	5.9	-	1.4
5	40	40	$Co_2(CO)_8$	PBu_3	MeOH	16.3	11.0	-	0.9
6	40	40	$Co_2(CO)_8$	-	MeOH	39.6	2.6	13.3	6.0
7	40	40	$Co_2(CO)_8$	-	C_6H_6	40.6	7.3	10.4	4.7
8	20	-	$Co_2(CO)_8$	-	MeOH	40.5	2.1	13.0	3.8
9	50	-	$Co_2(CO)_8$	-	MeOH	40.4	2.0	11.4	5.2
10	50	-	$Co_2(CO)_8$	-	C_6H_6	35.8	6.1	9.7	3.6
11[b]	50	-	$Co_2(CO)_8$	-	C_6H_6	61.3	10.7	17.2	4.8
12	100	-	$Co_2(CO)_8$	-	MeOH	39.8	1.4	8.9	8.0
13	50	-	$Co_2(CO)_8$	PBu_3	MeOH	3.4	1.7	-	0.2
14	50	-	$Co(OAc)_2$	PBu_3	MeOH	3.0	0.7	-	0.8

Conditions: Allylamine, 0.10 mol dm^{-3}; catalyst, 0.005 mol dm^{-3}; PBu_3, 0.05 mol dm^{-3}; temperature, 25 °C; reaction time, 18 h (Conditions are not optimized). a) Determined by GLC, and mol % based on allylamine. The isolated products by a preparative GLC gave satisfactory NMR and GC-MS spectral data. b) Reaction time was 42 h.

with synthesis gas to afford 3-aminobutanal. However, allylamine did not undergo hydroformylation, but carbonylation to give 2-pyrrolidone (**2**), and N,N'-diallylurea (**4**). The representative results are shown in Table 1. In the cobalt-phosphine catalyst system, lactam **2** was a main product, and urea **4** was a minor product. Non-carbonylated product such as diallylamine was also formed (1.0 % in Entry 2). The reaction was slow under the conditions employed. Higher pressure rather retarded the reaction (Entry 4). $Co(OAc)_2$ and $Co_2(CO)_8$ as precatalysts gave similar results (Entries 2 and 5). However, in the absence of phosphine, the reaction with $Co_2(CO)_8$ was about twice faster than that in the presence of phosphine, and N-allyl-3-butenamide (**3**) was newly produced as a main product (Entry 6). This is the first example in the carbonylation of allylamine, though its formation has been reported in the Rh-catalyzed azacarbonylation of allylphosphates.[5] In the absence of phosphine, the carbonylation reaction proceeded even by carbon monoxide alone (Entries 8-12), and hydrogen had no effect on both the reaction rate and the product distribution (Entries 6 and 9). However, in the presence of phosphine,

Table 2. Photochemical Carbonylation of Substituted Allylamines

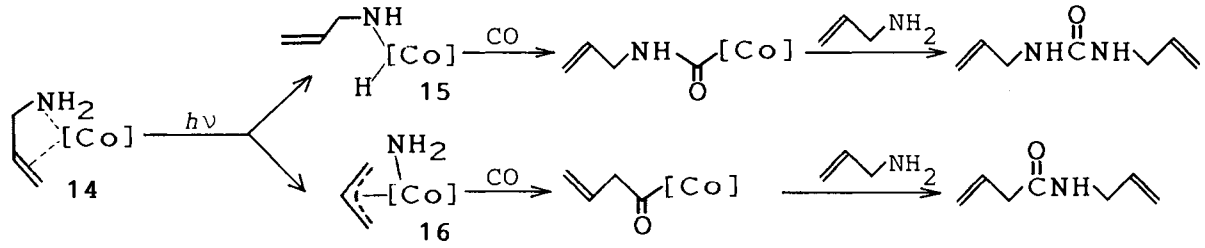
Amine (Conv./%)	Solvent	Product (yield/%)[a]			
 **5** (31.1)	MeOH	 (0.4) **6**	 **7a** + **7b** (4.5) (**7a** : **7b** = 95 : 5)	 **8** (7.3)	
		 **9a** + **9b** + **9c** (3.9) (**9a** : **9b** : **9c** = 73 : 8 : 19)			
5 (56.5)	C_6H_6	**6** (20.6)	**7a** + **7b** (7.7) (**7a** : **7b** = 95 : 5)	**8** (8.6)	
 **10** (25.8)	MeOH	 (4.0) **11**	 **12a** + **12b** (4.0) (**12a** : **12b** = 95 : 5)	 **13** (4.0)	
		Esters (**9a** + **9b** + **9c**) (4.7) (**9a** : **9b** : **9c** = 74 : 9 : 17)			
10 (54.0)	C_6H_6	**11** (22.1)	**12a** + **12b** (6.4) (**12a** : **12b** = 96 : 4)	**13** (7.8)	

Conditions were same as in Table 1, catalyst; $Co_2(CO)_8$ without phosphine, P_{CO}; 50 atm. a) See footnote a) in Table 1. For the compounds containing 2-butenyl group, stereochemistry (E or Z) could not be determined.

the addition of hydrogen was essential to the initiation of the reaction (Entries 13 and 14). Other metal carbonyls such as $Ru_3(CO)_{12}$ and $Rh_6(CO)_{16}$ were ineffective with synthesis gas or carbon monoxide alone under the conditions employed.

The formation of N-allyl-3-butenamide (**4**) suggests that the reaction proceeds via allylcobalt complex formed by the carbon-nitrogen bond cleavage of allylamine coordinated to metals. The photochemical carbonylation of substituted allylic amines was examined, and the representative results are shown in Table 2. Carbonylation of 3-butenamine (**5**) gave the corresponding lactam (**6**), urea (**8**) and two isomers of amide (**7a** and **7b**). In addition, three isomers of methyl ester of pentenoic acid (**9a**, **9b**, and **9c**) were also obtained in the reaction in MeOH solution. From 1-methylallylamine (**10**), the corresponding lactam (**11**), two isomers

of amide (**12a** and **12b**), and urea (**13**) were obtained. The reaction in methanol solution gave also the same esters (**9a-9c**). In the amides, the ratios of **7a** to **7b** and **12a** to **12b** were 95 ; 5 in both cases. The rearrangement takes place at the acyl group, and the amino group retains the original amine form. With different amines almost the same ratios in the isomers of ester were found. These results suggest the formation of π-allylcobalt intermediate. Saturated amine such as butylamine gave N,N'-dibutylurea predominantly. It has been suggested that unsaturated amines act as bidentate ligands such as olefinic phosphines.[6] Thus, the unsaturated amine-coordinated cobalt complexes will proceed to two courses of reaction upon irradiation; one is the oxidative addition by N-H bond cleavage followed by the urea formation, and another by C-N bond cleavage followed by the amide formation (Scheme 1).



Scheme 1.

There are two possible courses for the lactam formation; one is the reaction via a hydrocobalt complex similar to that in the photochemical hydroformylation of olefins.[1] At least, in the presence of phosphine, the formation of lactam **2** is presumably by a way of such hydrocobalt complex, because no reaction takes place when hydrogen is absent. Another is the course via the intermadiate **15** followed by the intramolecular hydrogen addition, CO insertion, and reductive elimination. In the absence of phosphine, the lactam may be formed via latter course, because hydrogen has no effect on the reaction. Further studies on the photochemically active species and reaction mechanism are in progress.

References

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