The Platinum Complex Catalyzed Reductive *N*-Carbonylation of Nitroarenes to the Carbamates

Yoshihisa WATANABE,* Yasushi TSUJI, Ryo TAKEUCHI, and Naoki SUZUKI
Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606
(Received April 25, 1983)

The platium catalyst combined with triphenylphosphine, tin(IV) chloride, and triethylamine showed high activity for the reductive *N*-carbonylation of nitroarene in ethanol at 180 °C under carbon monoxide of 60 kg cm^{-2}. From nitrobenzene, ethyl phenylcarbamate was obtained in 83% yield. Iron(III) chloride, aluminum chloride and titanium(IV) chloride could be used as Lewis acids in place of tin(IV) chloride. Various nitroarenes were transformed into corresponding carbamate in moderate to excellent yields with the platinum catalyst.

Organic syntheses with carbon monoxide and synthesis gas are of current interest.[1,2] Many fundamental chemical feedstocks are derived by reaction with the gases. Among those chemicals, isocyanates are often employed for the production of urethane rubber, fiber, and synthetic leather. The conventional commercial methods for production of isocyanates consist of the catalytic hydrogenation of nitroarenes to aminoarenes and phosgenation of amines (Eq. 1).[3] However, this

$$ArNO_2 + 3H_2 \xrightarrow[-2H_2O]{} ArNH_2 \xrightarrow[-2HCl]{COCl_2} ArNCO \quad (1)$$

conventional process has several disadvantages: use of poisonous phosgen, formation of a lot of hydrogen chloride as a by-product, and consumption of a lot of electricity for production of phosgen. In place of this method, increasing attention has been paid to the reductive *N*-carbonylation of nitroarenes(Eq. 2). Intensive stud-

$$ArNO_2 + 3CO \longrightarrow ArNCO + 2CO_2 \quad (2)$$

ies have been focused on the catalyst for this reaction: several catalysts including palladium,[4] rhodium,[5] and selenium[6] compounds show high activities. When the reaction carried out in an alcohol medium, the carbonylation proceeds under milder conditions(Eq. 3).

$$ArNO_2 + 3CO + ROH \longrightarrow ArNHCOOEt + 2CO_2 \quad (3)$$

The products are arylcarbamates, which can be easily converted to the corresponding isocyanates by pyrolysis.[7]

Only a few studies have been reported on platinum complex catalyzed carbonylation with carbon monoxide. Ogata *et al.*[8] and Knifton[9] have reported that a platinum–tin(II) chloride catalyst system is effective for hydroformylation and hydroesterification of 1-alkene.

We recently reported the preliminary results of platinum complex catalyzed reductive *N*-carbonylation of nitrobenzene to ethyl phenylcarbamate.[10] To our knowledge, this is the first example of a platinum catalyst having a high activity for the reductive *N*-carbonylation nitrobenzene to the carbamate. In this paper, we describe the full details of our results(Eq. 4)

$$ArNO_2 + 3CO + EtOH \xrightarrow[Et_3N]{PtCl_2(PPh_3)_2\text{-}SnCl_4} ArNHCOOEt + 2CO_2 \quad (4)$$

Results and Discussion

The catalytic activity of dichlorobis(benzonitrile)-platinum ($Pt(PhCN)_2Cl_2$)–tin(II or IV) chloride system for reductive *N*-carbonylation of nitrobenzene was examined in the presence of different phosphorus(III) ligands. The results are listed in Table 1. Ethyl phenylcarbamate and aniline were obtained as the reaction products. In all cases, yields of the carbamate

TABLE 1. THE REDUCTIVE *N*-CARBONYLATION OF NITROBENZENE IN THE ABSENCE OF AMINE[a]

Run	Phosphorus(III) ligand	Tin halide	Conversion[b] %	Yield of products/%[b]	
				Carbamate[c]	Aniline
1	PPh_3	$SnCl_4$	97	22	34
2	$P(OPh)_3$	$SnCl_4$	52	13	26
3	$P(n\text{-}Bu)_3$	$SnCl_4$	20	0	15
4	—	$SnCl_4$	93	13	14
5	$Ph_2P(CH_2)_2PPh_2$	$SnCl_4$	27	10	11
6	$Ph_2P(CH_2)_3PPh_2$	$SnCl_4$	64	3	48
7	$Ph_2P(CH_2)_4PPh_2$	$SnCl_4$	78	1	61
8	PPh_3	$SnCl_2$	43	8	14
9	$P(OPh)_3$	$SnCl_2$	29	2	21
10	$P(n\text{-}Bu)_3$	$SnCl_2$	42	0	14

a) A mixture of nitrobenzene(40 mmol), $PtCl_2(PhCN)_2$(0.4 mmol; 1.0 mol% based on nitrobenzene), $SnCl_4$(2.0 mmol), phosphorus(III) ligand(1.6 mmol; 0.8 mmol for the bidentate ligands), and EtOH(20 ml) was reacted at 180 °C for 4 h under the initial pressure of 60 kg cm^{-2} carbon monoxide. b) Determined by GLC based on the amount of nitrobenzene charged. c) Ethyl phenylcarbamate.

TABLE 2. THE REDUCTIVE *N*-CARBONYLATION OF NITROBENZENE IN THE PRESENCE OF AMINE[a]

Run	Platinum complex	Phosphorus(III) ligand	Tin halide	Amine	Conversion[b] %	Yields of products/%[b] Carbamate[c]	Aniline
11	$PtCl_2(PPh_3)_2$	—	$SnCl_4$	Et_3N	97	83	8
12	$PtCl_2(PhCN)_2$	PPh_3[d]	$SnCl_4$	Et_3N	98	78	12
13	—	PPh_3[d]	$SnCl_4$	Et_3N	54	0	17
14	$PtCl_2(PhCN)_2$	—	$SnCl_4$	Et_3N	90	8	32
15	$PtCl_2(PPh_3)_2$	—	—	Et_3N	29	0	17
16	$PtCl_2(PPh_3)_2$	—	$SnCl_4$	—	96	19	42
17	$PtCl_2(PPh_3)_2$	—	$SnCl_2$	Et_3N	97	5	60

a) Nitrobenzene(40 mmol), platinum complex(0.2 mmol), $SnCl_4$(2.0 mmol), triethylamine(1.0 ml), EtOH(20 ml) at 180 °C for 4 h under the initial pressure of 60 kg cm^{-2} carbon monoxide. b) Determined by GLC based on the amount of nitrobenzene charged. c) Ethyl phenylcarbamate. d) 0.4 mmol.

were low. Among the phosphorus (III) ligands, triphenylphosphine, which is an effective ligand for the platinum catalyzed hydroformylation,[9a] gave the best yield(22%) of the carbamate, when combined with tin(IV) chloride(Run 1). However, tributylphosphine, a more basic ligand, gave no *N*-carbonylated product. Ogata and co-workers reported that diphosphorus(III) ligands ($Ph_2P(CH_2)_nPPh_2$), especially n=4, are highly effective for platinum catalyzed hydroformylation.[8] The diphosphorus(III) ligands such as 1,2-ethanediylbisdiphenylphosphine, 1,3-propanediylbisdiphenylphosphine, 1,4-butanediylbisdiphenylphosphine in this *N*-carbonylation, gave only low yields of the carbamate. But aniline was formed in large amounts with an increase in the methylene length of the ligands indicating that these ligands were not effective for *N*-carbonylation (Runs 5—7). These bidentate ligands were effective for transformation of nitrobenzene to aniline.

The catalytic activity of platinum–tin(IV) chloride for *N*-carbonylation was dramatically improved by the addition of a tertiary amine, such as triethylamine. The results are listed in Table 2. Some references indicated that in the transformation of nitroarenes to the corresponding isocyanates, activities of the palladium and rhodium catalysts are highly enhanced by adding a Lewis acid and an amine.[4-6] The platinum–tin(IV) chloride combined with triethylamine drastically enhanced the yield and selectivity of the carbamate(Runs 11 and 12). The triphenylphosphine–$PtCl_2(PhCN)_2$ pair showed a comparable catalytic activity with dichlorobis(triphenylphosphine)platinum ($PtCl_2(PPh_3)_2$).

The platinum catalyst showed the highest activity only when combined with triphenylphosphine, tin(IV) chloride, and triethylamine. If one of these components was removed from the reaction system, yield of the carbamate was reduced drastically(Runs 13—16). The carbamate was not obtained in the absence of the platinum complex or tin halide(Runs 13—15). It is well known that tin(II) chloride is effective as co-catalyst for platinum catalyzed hydroformylation[8,9a] and hydroesterification.[9b] When tin(II) chloride was used in place of tin(IV) chloride for this reaction, the yield of the carbamate was only 5%(Run 17), indicating that tin(IV) chloride is much more favorable for this reaction. Thus, the present platinum catalyst system was distinct from the previously reported platinum catalyst system.

TABLE 3. THE EFFECT OF AMINE ADDITIVES ON THE REDUCTIVE *N*-CARBONYLATION OF NITROBENZENE[a]

Run	Amine	Conversion %	Yield of products/%[b] Carbamate[c]	Aniline
18	*N*-Methyl piperidine	100	76	10
19	DBU[d]	98	62	16
20	Piperidine	96	46	26
21	Pyridine	97	23	35
22	Butylamine	90	13	31
23	Aniline	71	1	5

a) Nitrobenzene(40 mmol), $PtCl_2(PPh_3)_2$(0.2 mmol), $SnCl_4$(2.0 mmol), amine(1.0 ml), EtOH(20 ml) at 180 °C for 4 h under the initial pressure of 60 kg cm^{-2} carbon monoxide. b) Determined by GLC based on the amount of nitrobenzene charged. c) Ethyl phenylcarbamate. d) 1,8-Diazabicyclo[5.4.0.]undec-7-ene.

The carbamate was also produced in the presence of other tertiary amines(Table 3). There was no linear relationship between the pk_a value of the conjugated acid of amine and the yield of the carbamate. However, generally tertiary amines with high basicity were effective for the *N*-carbonylation. Secondary and primary amines were less favorable.

In Table 4, effects of different Lewis acids on the reaction were examined fixing a molar ratio of Lewis acid to Pt was 20. Tin(IV) chloride was the most effective among the Lewis acid examined. With tin(IV) halide, the yield of the carbamate was reduced in the following order; $SnCl_4 > SnBr_4 \gg SnI_4$. This is the order in which Lewis acidity decreased. In the precedent platinum catalyzed reactions(hydroformylation and hydroesterification),[8,9] only the combination of platinum complex with tin(II) chloride exhibits the high catalytic activity. It is noticeable that iron(III) chloride, aluminum chloride, and titanium(IV) chloride had comparable effectiveness to tin(IV) chloride as co-catalysts(Runs 28—30).

The reaction was remarkably affected by the nature of the diphosphorus(III) ligands. The results are listed

in Table 5. Triphenylphosphine was most effective. Chelating diphosphorus(III) ligands reduced the catalytic activity. Those bidentate ligands would form thermodynamically stable complexes and these rigid complexes would be unfavorable as catalysts. Tributylphosphine and triphenyl phosphite were less effective as ligands.

The optimum reaction temperature was 180 °C under the initial pressure of 60 kg cm^{-1} carbon monoxide. The results are listed in Table 6. Under the initial pressure of 40 kg cm^{-2} carbon monoxide, the yield of the carbamate decreased(Run 38, *cf.* Run 11). The carbamate was not obtained under lower pressure of carbon monoxide. The reaction at 200 °C reduced the selectivity of the carbamate and the reaction at 160 °C reduced both the conversion of nitrobenzene and the selectivity.

Various nitroarenes were also *N*-carbonylated by this procedure(Table 7). From nitroarenes with a methyl substituents, the corresponding carbamates were obtained in good to excellent isolated yields(Runs 42, 45, and 46). On the other hand, nitroarenes with a methoxyl substituent gave the corresponding

Table 4. The effect of Lewis acid on the reductive *N*-carbonylation of nitrobenzene[a]

Run	Lewis acid	Conversion[b] %	Yield of products/%[b]	
			Carbamate[c]	Aniline
24	$SnCl_4$	97	70	6
25	$SnCl_2$	98	40	25
26	$SnBr_4$	96	30	11
27	SnI_4	86	Trace	18
28	$FeCl_3$	98	64	15
29	$AlCl_3$	97	63	14
30	$TiCl_4$	95	61	12
31	$ZnCl_2$	28	0	14

a) Nitrobenzene (40 mmol), $PtCl_2(PPh_3)_2$ (0.2 mmol), Lewis acid(4.0 mmol), triethylamine(1.0 ml), EtOH(20 ml) at 180 °C for under the initial pressure of 60 kg cm^{-2} carbon monoxide. b) Determined by GLC based on the amount of nitrobenzene charged. c) Ethyl phenylcarbamate.

Table 5. The effect of phosphorus(III) ligand on the reductive *N*-carbonylation of nitrobenzene[a]

Run	Phosphorus(III) ligand	Conversion[b] %	Yield of products/%[b]	
			Carbamate[c]	Aniline
32	PPh_3	98	56	10
33	$Ph_2P(CH_2)_2PPh_2$	11	0	6
34	$Ph_2P(CH_2)_3PPh_2$	23	4	9
35	$Ph_2P(CH_2)_4PPh_2$	33	6	15
36	$P(n\text{-}Bu)_3$	97	29	31
37	$P(OPh)_3$	87	25	31

a) Nitrobenzene(40 mmol), $PtCl_2(PhCN)_2$(0.2 mmol), $SnCl_4$(2.0 mmol), phosphorus(III) ligand(0.8 mmol; 0.4 mmol for the bidentate ligands), triethylamine(1.0 ml), EtOH(20 ml) at 180 °C for 4 h under the initial pressure of 60 kg cm^{-2} carbon monoxide. b) Determined by GLC based on the amount of nitrobenzene charged. c) Ethyl phenylcarbamate.

Table 6. The effect of reaction temperature and carbon monoxide pressure on the reductive *N*-carbonylation of nitrobenzene[a]

Run	Initial carbon monoxide Pressure/kg cm^{-2}	Temp °C	Conversion[b] %	Yield of products/%[b]	
				Carbamate[c]	Aniline
11	60	180	97	83	8
38	40	180	97	68	7
39	20	180	87	0	14
40	60	200	93	69	5
41	60	160	62	30	5

a) Nitrobenzene(40 mmol), $PtCl_2(PPh_3)_2$(0.2 mmol), $SnCl_4$(2.0 mmol), triethylamine(1.0 ml), EtOH(20 ml) for 4 h. b) Determined by GLC based on the amount of nitrobenzene charged. c) Ethyl phenylcarbamate.

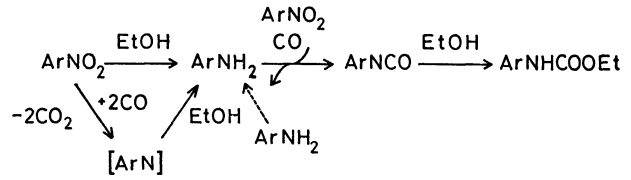
Table 7. The reductive *N*-carbonylation of various nitroarenes[a]

Run	Substrate	Product	Yield[b] %
42	*p*-Methylnitrobenzene	Ethyl 4-methylphenylcarbamate	87
43	*p*-Methoxynitrobenzene	Ethyl 4-methoxyphenylcarbamate	46
44	*p*-Chloronitrobenzene	Ethyl 4-chlorophenylcarbamate	59
45	*m*-Methylnitrobenzene	Ethyl 3-methylphenylcarbamate	64
46	*o*-Methylnitrobenzene	Ethyl 2-methylphenylcarbamte	74
47	*o*-Methoxynitrobenzene	Ethyl 2-methoxyphenylcarbamate	38
48	*o*-Chloronitrobenzene	Ethyl 2-chlorophenylcarbamate	42
49	1,4-Dimethyl-2-nitrobenzene	Ethyl 2,5-dimethylphenylcarbamate	71

a) Nitroarene(40 mmol), $PtCl_2(PPh_3)_2$(0.2 mmol), $SnCl_4$(4.0 mmol), triethylamine(1.0 ml), EtOH(20 ml) at 180 °C for 4 h under the initial pressure of 60 kg cm^{-2} carbon monoxide. b) Isolated yields.

carbamate in only moderate isolated yields and the reaction was accompanied by a considerable amount of tarry material (Runs 43 and 47). Under the same reaction conditions, *p*- or *o*- chloronitrobenzene gave moderate yields of the corresponding carbamates(Runs 44 and 48). 1-Nitronaphthalene gave only 1-naphthylamine as the product in 26% yield. From *p*-nitroaniline and *N,N*-dimethyl-3-nitroaniline, the corresponding *N*-carbonylated products were not obtained.

Two routes are possible for the reaction. One is the path in which aminoarene is carbonylated with carbon monoxide (Path A). Small amounts of aminoarenes were always detected as by-products. These would be formed by hydrogen transfer from ethanol to nitroarene or hydrogen abstraction by nitrene intermediate from ethanol. It is well known that the carbamates are obtained by transition metal catalyzed *N*-carbonylation of aminoarenes in the presence of an oxidant, such as nitroarenes or molecular oxygen.[11]



Path A.

In the present reaction, nitroarene may function as the oxidant for the carbonylation of aminoarene to the carbamate(Path A). However, an equimolar mixture of nitrobenzene and aniline under the same conditions as Run 11 gave low conversion of aniline, the yield of the carbamate was reduced to 38%, based on the total amount of nitrobenzene and aniline. This result indicated that Path A is unfavorable.

The other path is the route involving the carbonylation of a nitrene intermediate(Path B). Bennett *et al.* have reported formation of phenyl isocyanates from phenyl azide under carbon monoxide pressure.[12]

$$ArNO_2 \xrightarrow[-CO_2]{2CO} (ArN)[Pt] \xrightarrow{CO} (ArNCO)[Pt] \xrightarrow{EtOH} ArNHCOOEt + [Pt]$$

Path B.

They have proposed that phenylnitrene is the reaction intermediate. Collman *et al.* have also reported similar phenyl isocyanate formation from phenyl azide in the presence of a transition metal.[13] In our reaction, a nitrene intermediate would be generated by deoxygenation of nitroarene with carbon monoxide and the carbonylation of the nitrene intermediate would be followed, as shown in Path B. Iqbal also proposed the nitrene intermediate in the reaction of nitrobenzene with carbon monoxide.[14]

In this reaction, characterization of the active species could not be done. Several studies have indicated that a Lewis acid promotes migratory insertion of coordinated carbon monoxide to a carbon-metal bond.[15] In our reaction, a Lewis acid would be operative in promoted the insertion of carbon monoxide into a nitrogen-metal bond, which consequently generates an aryl isocyanate complex(Path B). Several transition metal nitrene complex[16] and isocyanate organometallic complex were isolated.[17] Schwetlick *et al.* isolated an isocyanate complex in the course of rhodium-catalyzed reductive *N*-carbonylation of nitromesitylene.[18] In the absence of amine, the yield of the carbamate was quite low and a considerable amount of tarry material was obtained. In the presence of amine, the reaction proceeded smoothly. The amine may function to weaken the Lewis acidity and to suppress side reaction promoted by Lewis acid.

Experimental

Material. The reagents employed in this study were purified before use. Carbon monoxide (>99.9%) was used without further purification. Ethanol(99.5%) was dried by reflux over freshly ignited and crushed CaO for 9 h and distilled carefully under Ar atmosphere. Platinum complexes were prepared by the literature methods.[19]

General Procedure. A 100 ml stainless steel autoclave (Nitto Koatsu) equipped with a magnetically driven stirrer was used. A glass liner was set in the autoclave and the inside of it was heated by a heat gun (400 W) for 2 min. After cooling in Ar steam, the reagents were charged in the following order: ethanol(20 ml), nitroarene(40 mmol), triethylamine(1.0 ml, 7.2 mmol), $PtCl_2(PPh_3)_2$ (158 mg, 0.2 mmol; 0.5 mol% based on nitroarene), and $SnCl_4$(0.47 ml, 4.0 mmol). After sealing and flushing with carbon monoxide, the reactor was pressured with carbon monoxide to 60 kg cm^{-2}. The autoclave was heated to 180 °C(20 min required) and then held at this temperature for 4 h. The reaction was terminated by rapid cooling and the autoclave was discharged. The resulting brown solution was analyzed with GLC. The products were isolated by vacuum distillation. The identification of the products was confirmed by elemental analysis, IR, ^{1}H-NMR, ^{13}C-NMR, and mass spectra. The boiling points and melting points are uncorrected. The GLC analysis was made with a column (3 mm $\phi \times 3$ m) packed with Silicone OV-17(2%) on Uniport HP 60—80 mesh. The oven temperature was programmed from 100 °C to 200 °C at a rate of 5 °C min^{-1}. The IR spectra were measured on a Hitachi model 215 grating spectrophotometer. The ^{13}C-NMR and ^{1}H-NMR spectra were recorded at 25.05 and 100 MHz respectively with a JEOL JNM FX 100 spectrometer. Samples were dissolved in $CDCl_3$, and the chemical shift values were expressed in relative to Me_4Si as an internal standard. Elemental analyses were performed at Microanalytical Center of Kyoto University. The mass spectra were recorded on a JMS OISG mass spectrometer.

The analytical data of the products are described below. The phenyl carbon resonances in the ^{13}C-NMR spectra were tentatively assigned by calculating their chemical shifts with additive parameters.[20]

Ethyl Phenylcarbamate. Yellow oil 117—119 °C/4 mmHg (1 mmHg≈133.322 Pa). All the spectral data (^{1}H-NMR, ^{13}C-NMR, and IR spectra) were consistent with those of an authentic sample.

Ethyl 4-Methylphenylcarbamate. Yellow oil, Kugelrohr distillation(65 °C/0.12 mmHg) ^{1}H-NMR (100 MHz)($CDCl_3$); δ 1.20 (t, 3H, $-OCH_2\underline{CH_3}$), 2.21 (s, 3H, $-\underline{CH_3}$), 4.41 (q, 2H, $-OC\underline{H_2}CH_3$), 6.98 (d, 2H, phenyl) 7.34 (d, 2H, phenyl). ^{13}C-NMR (25.05 MHz)($CDCl_3$); 14.6(q, $-OCH_2\underline{CH_3}$), 20.7 (q, $-\underline{CH_3}$), 60.9(t, $-O\underline{CH_2}CH_3$), 119.1 (d, phenyl 2, 6), 129.3 (d, phenyl 3, 5), 132.5(s, phenyl 4), 135.7(s, phenyl 1), 154.2

(s, C=O). IR(KBr): 3300 cm^{-1} (ν_{N-H}), 1710 cm^{-1} ($\nu_{C=O}$). MS(*m/e*): 179(M^+), 106(M^+—COOEt). Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82%. Found: C, 67.06; H, 7.42; N, 7.91%.

Ethyl 4-Chlorophenylcarbamate. Yellow crystals, bp 114—120 °C/0.18 mmHg. ^{1}H-NMR (100 MHz)($CDCl_3$); δ 1.28(t, 3H, $-OCH_2C\underline{H}_3$), 4.21(q, 2H, $-OC\underline{H}_2CH_3$), 7.20 (d, 2H, phenyl), 7.35(d, 2H, phenyl). ^{13}C-NMR (25.05 MHz)($CDCl_3$); 14.5(q, $-OCH_2\underline{C}H_3$), 61.4(t, $-O\underline{C}H_2CH_3$), 120.0(d, phenyl 2, 6), 128.2(s, phenyl 4), 128.9(d, phenyl 3, 5), 136.7(s, phenyl 1), 153.7(s, C=O). IR(KBr): 3300 cm^{-1} (ν_{N-H}), 1690 cm^{-1} ($\nu_{C=O}$). MS(*m/e*): 199(M^+), 126 (M^+—COOEt). Calcd for $C_9H_{10}NO_2Cl$: C, 54.15; H, 5.05; N, 7.02; Cl, 17.76%. Found: C, 54.17; H, 5.09; N, 7.02; Cl, 17.91%.

Ethyl 3-Methylphenylcarbamate. Yellow oil, bp 93 °C/0.08 mmHg. ^{1}H-NMR (100 MHz)($CDCl_3$); δ 1.25(t, 3H, $-OCH_2C\underline{H}_3$), 2.25(s, 3H, $-C\underline{H}_3$), 4.18(q, 2H, $-OC\underline{H}_2CH_3$), 6.79—7.17(m, 5H, phenyl and NH). ^{13}C-NMR(25.05 MHz) ($CDCl_3$); 14.5 (q, $-OCH_2\underline{C}H_3$), 21.4 (s, $-\underline{C}H_3$), 61.0 (t, $-O\underline{C}H_2CH_3$), 115.9(d, phenyl 6), 119.4(d, phenyl 2), 124.0 (d, phenyl 4), 128.7(d, phenyl 5), 138.1(s, phenyl 3), 138.7 (s, phenyl 1), 153.9(s, C=O). IR(neat): 3320 cm^{-1} (ν_{N-H}), 1705 cm^{-1} ($\nu_{C=O}$). MS(*m/e*): 179(M^+), 106(M^+—COOEt). Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82%. Found: C, 67.20; H, 7.22; N, 7.81%.

Ethyl 4-Methoxyphenylcarbamate. Yellow crystals, bp 126 °C/0.08 mmHg. ^{1}H-NMR (100 MHz) ($CDCl_3$); δ 1.27 (t, 3H, $-OCH_2C\underline{H}_3$), 3.74 (s, 3H, $-OC\underline{H}_3$), 4.19(q, 2H, $-OC\underline{H}_2CH_3$), 6.81(d, 2H, phenyl), 6.94(br, 1H, N$\underline{H}$), 7.29 (d, 2H, phenyl). ^{13}C-NMR (25.05 MHz)($CDCl_3$); 14.6(q, $-OCH_2\underline{C}H_3$), 55.5(q, $-O\underline{C}H_3$), 61.6(t, $-O\underline{C}H_2CH_3$), 114.1 (d, phenyl 3,5), 120.9(d, phenyl 2,6), 131.1(s, phenyl 1), 154.2(s, phenyl 4), 155.8(s, C=O). IR(KBr): 3310 cm^{-1} (ν_{N-H}), 1690 cm^{-1} ($\nu_{C=O}$). MS(*m/e*): 195(M^+), 122(M^+—COOEt). Calcd for $C_{10}H_{13}NO_3$: C, 61.53; H, 6.71; N, 7.18%. Found: C, 61.62; H, 6.63; N, 7.02%.

1-Naphthylamine. Red oil, bp 126 °C/0.12 mmHg. Spectra data of the isolated product were consistent with those of the authentic sample.

Ethyl 2-Methylphenylcarbamate. Colorless oil, bp 78—80 °C/0.06 mmHg. ^{1}H-NMR (100 MHz) ($CDCl_3$); δ 1.25 (t, 3H, $-OCH_2C\underline{H}_3$), 2.16 (s, 3H, $-C\underline{H}_3$), 4.16 (q, 2H, $-OC\underline{H}_2CH_3$), 6.65(br, 1H, N$\underline{H}$), 6.95—7.71(m, 4H, phenyl). ^{13}C-NMR(25.05 MHz)($CDCl_3$): 14.6(t, $-OCH_2\underline{C}H_3$), 17.6 (t, $-CH_3$), 61.6(t, $-O\underline{C}H_2CH_3$), 121.5(d, phenyl 6), 124.1 (d, phenyl 4), 126.6(d, phenyl 5), 128.0(s, phenyl 2), 130.3 (d, phenyl 3), 135.9(s, phenyl 1), 154.0(s, C=O). IR(neat): 3300 cm^{-1} (ν_{N-H}), 1730 cm^{-1} ($\nu_{C=O}$). MS(*m/e*): 179(M^+), 106(M^+—COOEt). Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82%. Found: C, 67.45; H, 7.27; N, 7.84%.

Ethyl 2-Methoxyphenylcarbamate. Colorless oil, bp 95—97 °C/0.13 mmHg. ^{1}H-NMR (100 MHz) ($CDCl_3$): δ 1.28 (t, 3H, $-OCH_2C\underline{H}_3$), 3.78 (s, 3H, $-OC\underline{H}_3$), 4.20 (q, 2H, $-OC\underline{H}_2CH_3$), 7.23(br, 1H, N$\underline{H}$), 6.70—7.23(m, 3H, phenyl), 7.97—8.12(m, 1H, phenyl). ^{13}C-NMR(25.05 MHz)($CDCl_3$): 14.6(q, $-OCH_2\underline{C}H_3$), 55.8(q, $-O\underline{C}H_3$), 61.6(t, $-O\underline{C}H_2CH_3$), 110.0(d, phenyl 3), 118.2(d, phenyl 6), 121.0 (d, phenyl 5), 122.7(d, phenyl 4), 127.7(s, phenyl 1), 147.6 (s, phenyl 2), 153.5(s, C=O). IR (neat): 3420 cm^{-1} (ν_{N-H}), 1730 cm^{-1} ($\nu_{C=O}$). MS (*m/e*): 195 (M^+). Calcd for $C_{10}H_{13}NO_3$: C, 61.53; H, 6.71; N, 7.18. Found: C, 60.42; H, 6.51; N, 6.94.

Ethyl 2,5-Dimethylphenylcarbamate. Ethanol was removed from the reaction mixture *in vacuo* at 50 °C. Then, petroleum ether was added to the residue. A soluble part was separated by filtration, and then the solvent was removed *in vacuo*. The product was afforded as crystals: brown crystals, mp 94—95 °C. ^{1}H-NMR (100 MHz) ($CDCl_3$): δ 1.31(t, 3H, $-OCH_2C\underline{H}_3$), 2.19(s, 3H, $-C\underline{H}_3$), 2.31(s, 3H, $-C\underline{H}_3$), 4.22(q, 2H, $-OC\underline{H}_2CH_3$), 6.36(br, 1H, $-N\underline{H}$), 6.83 (d, 1H, phenyl), 7.02(d, 1H, phenyl), 7.61(s, 1H, phenyl). ^{13}C-NMR(25.05 MHz)($CDCl_3$): δ 14.6(q, $-OCH_2\underline{C}H_3$), 17.2 (q, $-\underline{C}H_3$), 21.1(q, $-\underline{C}H_3$), 61.2(t, $-O\underline{C}H_2CH_3$), 121.8(d, phenyl 6), 124.5(s, phenyl 2), 124.8(d, phenyl 4), 130.1(d, phenyl 3), 135.6(s, phenyl 5), 136.5(s, phenyl 1), 153.9(s, C=O). IR(KBr): 3290 cm^{-1} (ν_{N-H}), 1685 cm^{-1} ($\nu_{C=O}$). MS (*m/e*): 193(M^+), 120(M^+—COOEt). Calcd for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25%. Found: C, 68.53; H, 7.92; N, 7.18%.

Ethyl 2-Chlorophenylcarbamate. Colorless oil, bp 70—72 °C/0.07 mmHg. ^{1}H-NMR(100 MHz)($CDCl_3$): δ 1.30(t, 3H, $-OCH_2C\underline{H}_3$), 4.22(q, 2H, $-OC\underline{H}_2CH_3$), 6.93(t of d, 1H, phenyl), 7.22 (t of d, 1H, phenyl), 7.29 (d of d, 1H, phenyl), 8.15(d of d, 1H, phenyl). ^{13}C-NMR(25.05 MHz) ($CDCl_3$): δ 14.5(t, $-OCH_2\underline{C}H_3$), 61.5(t, $-O\underline{C}H_2CH_3$), 119.9 (d, phenyl 6), 122.0 (s, phenyl 2), 123.6 (d, phenyl 4), 127.7 (d, phenyl 5), 129.0(d, phenyl 3), 134.8(s, phenyl 1), 153.2 (s, C=O). IR(neat): 3410 cm^{-1} (ν_{N-H}), 1730 cm^{-1} ($\nu_{C=O}$). MS(*m/e*): 199(M^+), 126(M^+—COOEt). Calcd for $C_9H_{10}NO_2Cl$: C, 54.15; H, 5.05; N, 7.02; Cl, 17.76%. Found: C, 54.97; H, 5.07; N, 7.36; Cl, 17.89%.

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