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The Ruthenium Catalyzed *N*-Alkylation of Amides with Alcohols

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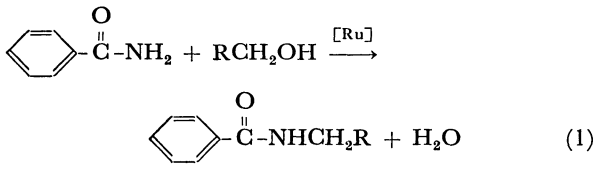
Amides reacted with primary alcohols in the presence of a catalytic amount of $RuCl_2(PPh_3)_3$ at 180 °C to give the corresponding *N*-monoalkyl amides in fairly good yields. Thus, benzamide reacted with 1-octanol to give *N*-octylbenzamide in 76% yield with excellent product selectivity. Little esterification of amides with alcohols occurred and selectivity to the *N*-alkylation was high. Most of the amides gave *N*-monoalkyl amides but no *N,N*-dialkyl amides. But formamide reacted with 1-butanol to give *N,N*-dibutylformamide, as well as *N*-butylformamide, in low yield. $RuCl_2(PPh_3)_3$ was the most effective catalyst for this reaction and $RuHCl(PPh_3)_3$ also had some catalytic activity.

N-Alkylation is important for selective synthesis of substituted amines; various methods have been developed. A conventional alkylating reagent is alkyl halide. On the other hand, *N*- and *C*-alkylation using alcohols as the alkylating reagent in the presence of Ni catalyst[1] have been reported and recently in the presence of Rh and Ru catalysts.[2-4]

We have previously demonstrated that ruthenium complexes were effective for the activation of alcohols and that they were excellent catalysts for *N*-alkylation and *N*-heterocyclization of aminoarenes and nitroarenes using alcohols.[3,4] This paper describes the alkylation



of amides with alcohols in the presence of ruthenium catalyst (Eq. 1).

Results and Discussion

Benzamide was *N*-alkylated with various alcohols in the presence of $RuCl_2(PPh_3)_3$. The results are summarized in Table 1. Ethanol, 1-propanol, 1-hexanol, 1-octanol, and 1-dodecanol are employed as alkylating reagents to give *N*-ethyl-, *N*-propyl-, *N*-hexyl-, *N*-octyl-, and *N*-dodecylbenzamide, respectively. The selectivities of the products were high. The conversions of benzamide increased with elongating a carbon chain of the alcohols; 1-octanol gave the best result. Benzyl alcohol gave *N*-benzylbenzamide with 94% selectivity(Run 8), but prolonging the reaction time induced a decrease in its selectivity. However, methanol and secondary alcohol, 2-propanol, gave almost no *N*-alkylbenzamides in this procedure. A similar tendency was observed in the ruthenium-catalyzed *N*-alkylation of aminoarenes using alcohols,[3] where methanol and secondary alcohols were much less reactive as alkylating reagents than primary alcohols were.

By the present procedure, benzamide was converted to *N*-alkylbenzamide selectively, *N,N*-dialkylbenzamide was not obtained as the product, even in the presence of excess alcohol. This result is in striking contrast to that of the *N*-alkylation of aniline,[3] where *N,N*-dialkylanilines were the major products under similar reaction conditions. The *N,N*-dialkylation of aniline appears to proceed stepwise *via* *N*-monoalkylation. The reaction is not controlled at the *N*-monoalkylation stage and proceed readily to the *N,N*-dialkylation step. Thus, these observations reveal that the amides are less reactive than aminoarenes in the *N*-alkylation by alcohols, presumably owing to a neighboring carbonyl group.

The results of the *N*-alkylation of other amides are listed in Table 2. *p*-Chlorobenzamide reacted with 1-butanol to give *N*-butyl-*p*-chlorobenzamide with high selectivity. The conversion of the amide slightly decreased as compared with that of benzamide. Furthermore, acetamide, phenylacetamide, and butanamide were also *N*-alkylated with alcohols. However,

TABLE 1. THE RUTHENIUM-CATALYZED *N*-ALKYLATION OF BENZAMIDE WITH ALCOHOL[a]

Run	Alcohol	Product	Benzamide[b] conversion/%	Product[c] selectivity/%
1[d]	Methanol	*N*-Methylbenzamide	4	—[e]
2	Ethanol	*N*-Ethylbenzamide	57	97
3	1-Propanol	*N*-Propylbenzamide	54	93
4[d]	2-Propanol	*N*-Isopropylbenzamide	14	—[e]
5	1-Hexanol	*N*-Hexylbenzamide	73	93
6	1-Octanol	*N*-Octylbenzamide	78	97
7[f]	1-Dodecanol	*N*-Dodecylbenzamide	61	96
8	Benzyl alcohol	*N*-Benzylbenzamide	34	94
9[g]	Benzyl alcohol	*N*-Benzylbenzamide	74	66

a) A mixture of benzamide(10 mmol), alcohol(5 ml), and $RuCl_2(PPh_3)_3$ (0.2 mmol) was heated at 180 °C for 4 h. b) Determined by GLC based on an amount of benzamide used. c) Determined by GLC based on the conversion of benzamide. d) $RuCl_2(PPh_3)_3$(0.1 mmol) was used. e) Product selectivities could not be estimated since the products gave only trace yields. f) The reaction time: 7 h. g) The reaction time: 12 h.

TABLE 2. *N*-ALKYLATION OF AMIDES BY $RuCl_2(PPh_3)_3$-ALCOHOL

Run	Amide	Alcohol	Product	Reaction time/h	Amide[b] conversion/%	Product[c] selectivity/%
10	*p*-Chlorobenzamide	1-Butanol	*N*-Butyl-*p*-chlorobenzamide	6	49	96
11	Acetamide	Ethanol	*N*-Ethylacetamide	4	9	100
12	Acetamide	Ethanol	*N*-Ethylacetamide	10	69	30
13	Acetamide	1-Octanol	*N*-Octylacetamide	4	30	80
14	Phenylacetamide	Ethanol	*N*-Ethylphenylacetamide	4	25	60
15	Butanamide	1-Butanol	*N*-Butylbutanamide	12	32	88
16	Butanamide	1-Octanol	*N*-Octylbutanamide	4	26	62
17	6-Hexanelactam	Ethanol		4	0	0
18	3-Pyridinecarboxamide	Ethanol		4	0	0
19	Acrylamide	Ethanol	(Propanamide)	4	58	64

a) A mixture of amide(10 mmol), alcohol(5 ml), and $RuCl_2(PPh_3)_3$ (0.2 mmol) was heated at 180 °C. b) Determined by GLC based on an amount of the amide used. c) Determined by GLC based on the conversion of amide.

TABLE 3. RUTHENIUM CATALYZED *N*-ALKYLATION OF BENZAMIDE. EFFECT OF CATALYST[a]

Run	Catalyst	Benzamide[b] conversion/%	*N*-Ethylbenzamide[c] selectivity/%
20	$RuCl_2(PPh_3)_3$	53	85
21	$RuHCl(PPh_3)_3$	33	67
22	$RuHCl(CO)(PPh_3)_3$	29	66
23	$Ru(CO)_3(PPh_3)_2$	8	Trace
24[d]	$RuH_2(PPh_3)_4$	4	Trace
25	$RuCl_3 \cdot nH_2O$	0	0
26[d]	$RhCl(PPh_3)_3$	0	0
27[d]	$RhH(PPh_3)_4$	9	Trace

a) A mixture of benzamide(10 mmol), ethanol(5 ml), and a catalyst(0.1 mmol) was heated at 180 °C for 4 h. b) Determined by GLC based on an amount of benzamide used. c) Determined by GLC based on the conversion of benzamide. d) Catalyst(0.2 mmol) was used.

in these cases the conversions of the amides decreased considerably and the selectivities were not high. 6-Hexanelactam and 3-pyridinecarboxamide were not converted at all. Secondary amides cannot be alkylated by the present systems as indicated by the result that no *N*,*N*-dialkyl amides were obtained while the *N*-alkyl amides formed. From the reaction solution of 3-pyridinecarboxamide, red crystals were obtained. These crystals had no catalytic activity in the *N*-alkylation of benzamide with ethanol.

Acrylamide reacted with ethanol in the presence of $RuCl_2(PPh_3)_3$ to give propanamide. Since $RuCl_2(PPh_3)_3$ is known as an effective catalyst for hydrogen transfer form alcohol,[5] propanamide was obtained by the transfer hydrogenation of acrylamide by ethanol.

Catalytic Activity. Several ruthenium and rhodium compounds were examined as catalysts for this reaction (Table 3). The catalytic activities decreased in the order of $RuCl_2(PPh_3)_3$, $RuHCl(PPh_3)_3$, and $RuHCl(CO)(PPh_3)_3$. $Ru(CO)_3(PPh_3)_2$ and $RuCl_3 \cdot nH_2O$ showed little catalytic activities. $RuH_2(PPh_3)_4$, $RuCl(PPh_3)_3$, and $RhH(PPh_3)_4$ also had no catalytic activities, though these complexes were reported to have the catalytic activities of the *N*-alkylation of aliphatic amines by alcohols.[2]

Reaction Conditions. The reaction of benzamide with ethanol was carried out at 150, 180, and 220 °C. The highest yield of *N*-ethylbenzamide was obtained at 180 °C. The conversion of benzamide was low at 150 °C. The selectivity of *N*-ethylbenzamide was low at 220 °C, although the conversion was high. Prolonging the reaction time and an increase in an amount of a catalyst did not improve the yield of *N*-ethylbenzamide appreciably.

In conventional *N*-alkylation of amides, alkyl halides or esters of sulfuric or sulfonic acids can be employed as the alkylating reagent.[6] Amides are very weak bases, far too weak to attack alkyl halides. Therefore, the amides must first be converted to their salts. There was no example of the transition-metal-catalyzed alkylation of amides using alcohols. Reid[7] reported

TABLE 4. *N*-ALKYLATION OF BENZAMIDE BY $RuCl_2(PPh_3)_3$-ALCOHOL. EFFECT OF REACTION CONDITIONS[a]

Run	Catalyst (mmol)	Reaction temp/°C	Reaction time/h	Benzamide[b] cnnversion/%	*N*-Ethylbenzamide[c] selectivity/%
28	0.1	150	4	24	58
20	0.1	180	4	53	85
29	0.1	220	4	88	51
30	0.1	180	5.5	57	90
31	0.1	180	6.5	62	80
2	0.2	180	4	57	97

a) A mixture of benzamide(10 mmol), ethanol(5 ml), and $RuCl_2(PPh_3)_3$ was heated. b) Determined by GLC based on the amount of benzamide used. c) Determined by GLC based on the conversion of benzamide.

that benzamide reacted with alcohols without catalyst at 220 °C for more than 60 h to give *N*-alkylbenzamides with low selectivities(30—70%) and a considerable amount of by-products by solvolysis.

This $RuCl_2(PPh_3)_3$–alcohol system has several advantages. The reaction proceeds under neutral conditions. The amides do not need to be activated to their salts. In comparison with the results of Reid, the ruthenium-catalyzed reaction is performed in shorter reaction time at lower reaction temperature. Furthermore the selectivities of the *N*-alkyl amides are high and no *N*,*N*-dialkyl amides are obtained except formamide(*vide infra*).

Two reaction paths, path A and path B, are possible for this reaction. In path A, alcohol is oxidized to aldehyde by a ruthenium complex and then the aldehyde reacts with amide to give *N*-acyl amino alcohol which undergoes dehydration; the dehydrated product is hydrogenated by hydride on the ruthenium complex or by ruthenium catalyzed transfer hydrogenation from alcohol.

Path A

$$R'CH_2OH \xrightarrow{[Ru]} R'CHO$$

$$R'CHO + RC(=O)-NH_2 \longrightarrow RC(=O)-N(H)-CH(OH)R' \quad \mathbf{1}$$

$$\xrightarrow[-H_2O]{} RC(=O)-N=CHR' \quad \mathbf{2} \xrightarrow{[Ru]} RC(=O)NHCH_2R'$$

The oxidation of alcohol by a ruthenium complex[8] has been reported by several authors and this step was assumed in the *N*-alkylation of aliphatic and aromatic amines with alcohols.[2,3] In the reaction of amide with aldehyde, the formation of *N*-acyl amino alcohol(**1**)[9] and its dehydrated product(**2**)[10] was ascertained.

Path B

$$RC(=O)NH_2 + R'CH_2OH \longrightarrow RC(=O)OCH_2R' + NH_3$$

$$NH_3 + R'CH_2OH \longrightarrow NH_2CH_2R' + H_2O$$

$$RC(=O)OCH_2R' + NH_2CH_2R' \longrightarrow RC(=O)NHCH_2R' + R'CH_2OH$$

In path B, alcoholysis of amide partially occurs, to give ester and ammonia. Then ammonia is alkylated with alcohol to alkylamine. The ester reacts with the alkylamine to produce *N*-alkyl amide.

The *N*-alkyl amides seem to be formed *via* path A, since ammonia, alkylamine, and ester were not produced substantially. Furthermore, addition of aldehyde gave a better yield of *N*-alkyl amides.[11] In a separate experiment ammonia reacted with alcohol to give trialkylamine, and monoalkylamine was not obtained.[12] These results indicate that path A is more plausible.

Formamide showed different results. Formamide reacted with 1-butanol for 24 h at 180 °C in the presence of $RuCl_2(PPh_3)_3$ to give *N*-butylformamide and *N*,*N*-dibutylformamide in 9 and 18% isolated yields, respectively (Eq. 2). Tributylamine was detected in 14% yield (based on formamide charged) in the reaction mixture after 8 h reaction time. *N*,*N*-Dialkyl amides were not obtained from other amides but only from formamide. Therefore, *N*,*N*-dibutylformamide seems to be produced from a different mechanism (path B′). Ammonia or alkylamine produced by Path B′

$$HC(=O)NH_2 + 1\text{-Butanol} \xrightarrow[180\,^\circ C,\ 24\,h]{RuCl_2(PPh_3)_3} \underset{18\%}{HC(=O)N(Bu)_2} + \underset{9\%}{HC(=O)NH(Bu)} \quad (2)$$

$$HC(=O)NH_2 + R'CH_2OH \xrightarrow{\text{path A}} HC(=O)NHCH_2R'$$

$$HC(=O)NHR + R'CH_2OH \longrightarrow HC(=O)OCH_2R' + NH_2R$$

$$NH_2R + R'CH_2OH \longrightarrow N(CH_2R')_2R$$

$$HC(=O)NHR + N(CH_2R')_2R \longrightarrow HC(=O)N(CH_2R')_2$$

R: H or CH_2R'

the alcoholysis of amide is alkylated to di- or trialkylamine. The di- or trialkylamine formed reacts with the amide, not with the ester, since butyl formate did not react with tributylamine (Eq. 3).[13] The exchange of amine was reported in the reaction of formamide with amine.[14] Path B′ is also supported by the result that formamide reacted with tributylamine in 1-butanol to give *N*,*N*-dibutylformamide and no *N*-butylformamide (Eq. 4).[15]

$$HC(=O)OBu + N(Bu)_3 \xrightarrow[n\text{-BuOH},\ 180\,^\circ C,\ 24\,h]{RuCl_2(PPh_3)_3} \text{no reaction} \quad (3)$$

$$HC(=O)NH_2 + N(Bu)_3 \xrightarrow[n\text{-BuOH},\ 180\,^\circ C,\ 24\,h]{RuCl_2(PPh_3)_3} \underset{48\%}{HC(=O)N(Bu)_2} + \underset{130\%}{N(Bu)_3} \quad (4)$$

Experimental

Analytical Procedure. GLC analysis was performed on a Shimadzu GC-3BT. The ^1H NMR spectra were obtained at 60 MHz with a JEOL JNM-60 NMR spectrometer or 100 MHz with a JEOL pulsed Fourier Transform spectrometer, model FX-100, and the ^{13}C NMR spectra were recorded at 25.05 MHz with a JEOL pulsed Fourier Transform spectrometer, model FX-100, using tetrametylsilane as an internal standard. IR spectra were measured on a Hitachi model 215 grating spectrophotometer. Elemental analysis were performed at the Microanalytical Center of Kyoto University. The mass spectra were recorded on a JMS 01SG mass spectrometer.

Materials. All substrates used were commercial products. The amides and alcohols were distilled or recrystallized before use. $RuCl_3 \cdot nH_2O$, $RhCl_3 \cdot nH_2O$, and PPh_3 were commercial products. $RuCl_2(PPh_3)_3$,[16] RuHCl-

$(PPh_3)_3$,[17] $RuHCl(CO)(PPh_3)_3$,[18] $Ru(CO)_3(PPh_3)_2$,[18] $RuH_2(PPh_3)_4$,[19] $RhCl(PPh_3)_3$,[20] and $RhH(PPh_3)_4$[18] were prepared according to the methods in the literature.

General Procedure. A stainless steel autoclave(50 ml) containing a glass liner was used in the reaction. Alcohol (5 ml), amide(10 mmol), and $RuCl_2(PPh_3)_3$ (0.2 mmol) were put into it with a magnetic stirring bar under argon flow. The reactor was sealed and degassed by three 15 atm pressurization-depressurization cycles with argon. The autoclave was heated at 180 °C in an oil bath for 4 h. The conversion of the amide and the selectivity of the product were determined with GLC(3 mmΦ×2.9 m column packed with 20% DEGA on Uniport B 80—100 mesh or with 10% Silicone SE-30 on Chromosorb W AW DMCS 80—100 mesh) by the internal standard method. The products were isolated by medium pressure column chromatography (silica gel 60, 40—64 μm, Merck). *N*-Ethylbenzamide,[21] *N*-propylbenzamide,[22] *N*-benzylbenzamide,[23] *N*-ethylacetamide,[24] *N*-butyl-*p*-chlorobenzamide,[25] *N*-butylformamide,[26] and *N*,*N*-dibutylformamide[27] were identified by comparison of their ^1H NMR spectral data with those in the literature. The identifications were confirmed with their ^{13}C NMR spectra. *N*-Ethylphenylacetamide was identified by comparison of ^{13}C and ^1H NMR spectra of authentic sample (mp 69 °C, lit, 69.5 °C) which was synthesized by the literature method.[28] The identities of other compounds were confirmed by IR, ^1H NMR, ^{13}C NMR, mass spectra, and elemental analysis.

The analytical data of the products are described below.

N-*Ethylbenzamide.* ^{13}C NMR($CDCl_3$) δ=14.7(q), 34.9 (t), 127.1(d,2C), 128.2(d,2C), 131.0(d), 134.7(s), 167.8(s). ^1H NMR (100 MHz)($CDCl_3$) δ=1.17(t, 3H), 3.41(d of q, 2H), 7.36(m, 4H), 7.80(m, 2H).

N-*Propylbenzamide.* ^{13}C NMR($CDCl_3$) δ=11.4(q), 22.9 (t), 41.7(t), 126.6(d,2C), 128.1(d,2C), 130.9(d), 134.5(s), 167.3(s). ^1H NMR (60 MHz) ($CDCl_3$) δ=0.95(t, 3H), 1.63 (Hex,2H), 3.38(q, 2H), 6.38(s, 1H), 7.18—7.88(m, 5H).

N-*Benzylbenzamide.* ^{13}C NMR($CDCl_3$) δ=43.7(t), 127.1(d,2C), 127.4(d,3C), 128.2(d,2C), 128.4(d,2C), 131.2 (d), 134.2(s), 138.4(s), 167.6(s). ^1H NMR(100 MHz) ($CDCl_3$) δ=4.44(d,2H), 7.18(s, 5H), 7.10—7.50(m, 3H), 7.71(m, 3H).

N-*Ethylacetamide.* ^{13}C NMR($CDCl_3$) δ=14.8(q), 23.2 (q), 34.4(t), 170.0(s). ^1H NMR(60 MHz)($CDCl_3$) δ=1.13 (t, 3H), 1.98(s, 3H), 3.27(d of q, 2H), 7.00(s, 1H).

N-*Butyl*-p-*chlorobenzamide.* ^{13}C NMR($CDCl_3$) δ=13.7 (q), 20.1(t), 31.6(t), 39.9(t), 128.4(d,2C), 128.5(d,2C), 133.2 (s), 137.3(3), 166.7(s). ^1H NMR(60 MHz)($CDCl_3$) δ=0.88 (t, 3H), 1.07—1.83(m, 4H), 3.49(q, 2H), 7.10—7.92(m, 5H).

N-*Butylformamide.* ^1H NMR(60 MHz)($CDCl_3$) δ=0.93 (t, 3H), 1.17—1.67(m, 4H), 3.26(q, 2H), 6.40(s, 1H), 8.12 (s, 1H).

N,N-*Dibutylformamide.* ^{13}C NMR($CDCl_3$) δ=13.6(q), 13.8(q), 19.6(t), 20.2(t), 29.4(t), 30.7(t), 41.9(t), 47.2(t), 162.6(d). ^1H NMR(60 MHz)($CDCl_3$) δ=0.93(t, 6H), 1.13—1.77(m, 8H), 3.22(q, 2H), 3.25(q, 2H), 8.00(s, 1H).

N-*Ethylphenylacetamide.* ^{13}C NMR($CDCl_3$) δ=14.4(q), 34.5(t), 43.4(t), 126.9(d), 128.8(d,2C), 129.3(d,2C), 135.6 (s), 171.8(s). ^1H NMR(60 MHz)($CDCl_3$) δ=1.03(t, 3H), 3.22(q, 2H), 3.51(s, 2H), 7.27(s, 6H).

N-*Hexylbenzamide.* ^{13}C NMR($CDCl_3$) δ=14.0(q), 22.5 (t), 26.7(t), 29.6(t), 31.5(t), 40.2(t), 127.0(d,2C), 128.2(d, 2C), 131.0(d), 134.8(s), 167.7(s). ^1H NMR(100 MHz) ($CDCl_3$) δ=0.86(t, 3H), 1.04—1.70(m, 8H), 3.37(q, 2H), 7.36(m, 4H), 7.82(m, 2H). IR(KBr disk) 3335(NH), 1625 (amide I), and 1525 cm^{-1}(amide II). MS, *m/e* 205(M^+). Calcd for $C_{13}H_{19}NO$: C, 76.06; H, 9.33; N, 6.82. Found: C, 76.31; H, 9.19; N, 6.62.

N-*Octylbenzamide.* ^{13}C NMR($CDCl_3$) δ=14.1(q), 22.7 (t), 27.1(t), 29.3(t), 29.4(t), 29.7(t), 31.8(t), 40.2(t), 127.1 (d,2C), 128.2(d,2C), 131.0(d), 134.8(s), 167.7(s). ^1H NMR (60 MHz)($CDCl_3$) δ=0.87(t, 3H), 1.08—1.87(m, 12H), 3.38 (q, 2H), 7.35(m, 4H), 7.85(m, 2H). IR(KBr disk) 3335 (NH), 1625(amide I), and 1525 cm^{-1}(amide II). MS, *m/e* 233(M^+). Calcd for $C_{15}H_{23}NO$: C, 77.21; H, 9.94; N, 6.00. Found: C, 77.08; H, 9.95; N, 5.96.

N-*Dodecylbenzamide.* ^{13}C NMR($CDCl_3$) δ=14.1(q), 22.7(t), 27.1(t), 29.4(t,2C), 29.7(t,5C), 31.9(t), 40.2(t), 127.1(d,2C), 128.2(d,2C), 131.0(d), 134.9(s), 167.7(s). ^1H NMR(60 MHz)($CDCl_3$) δ=0.89(t, 3H), 1.10—1.77(m, 20H), 3.37(q, 2H), 7.31(m, 4H), 7.80(m, 2H). IR(KBr disk) 3335(NH), 1625(amide I), and 1530 cm^{-1}(amide II). MS, *m/e* 289(M^+). Calcd for $C_{19}H_{31}NO$: C, 78.84; H, 10.80; N, 4.84. Found: C, 78.73; H, 10.95; N, 4.71.

N-*Octylacetamide.* ^{13}C NMR($CDCl_3$) δ=14.1(q), 22.8 (t and q, 2C), 27.2(t), 29.4(t), 29.5(t), 29.6(t), 32.0(t), 39.8(t), 170.8(s). ^1H NMR(100 MHz)($CDCl_3$) δ=0.88(t, 3H), 1.29(m, 12H), 1.96(s, 3H), 3.18(q, 2H), 8.04(t, 1H). IR(neat) 3290(NH), 1650(amide I), and 1560 cm^{-1}(amide II). MS, *m/e* 171(M^+). Calcd for $C_{10}H_{21}NO$: C, 70.12; H, 12.36; N, 8.18. Found: C, 70.41; H, 12.56; N, 8.48.

N-*Butylbutanamide.* ^{13}C NMR($CDCl_3$) δ=13.8(q, 2C), 19.4(t), 20.2(t), 31.8(t), 38.5(t), 39.3(t), 173.5(s). ^1H NMR (60 MHz)($CDCl_3$) δ=0.91(t, 3H), 0.93(t, 3H), 1.17—1.91 (m, 6H), 2.17(t, 2H), 3.18(q, 2H), 6.93(s, 1H). IR(neat) 3290(NH), 1640(amide I), and 1550 cm^{-1}(amide II). MS, *m/e* 143(M^+). Calcd for $C_8H_{17}NO$: C, 67.09; H, 11.96; N, 9.78. Found: C, 67.35; H, 12.25; N, 10.02.

N-*Octylbutanamide.* ^{13}C NMR($CDCl_3$) δ=13.8(q), 14.1 (q), 19.4(t), 22.7(t), 26.8(t), 27.1(t), 29.4(t, 2C), 29.8(t), 31.6(t), 31.9(t), 38.6(t), 39.6(t), 173.5(s). ^1H NMR(100 MHz)($CDCl_3$) δ=0.87(t, 3H), 0.94(t, 3H), 1.05—1.82(m, 14H), 2.18(t, 2H), 3.21(q, 2H), 7.12(t, 1H). IR(neat) 3275(NH), 1640(amide I), and 1550 cm^{-1} (amide II). MS, *m/e* 199(M^+). Calcd for $C_{12}H_{25}NO$: C, 72.31; H, 12.64; N, 7.03. Found: C, 72.55; H, 12.81; N, 7.08.

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11) Butanal(2.3 mmol) was added to the reaction of butanamide (10 mmol) with 1-butanol(5 ml) in the presence

of $RuCl_2(PPh_3)_3$ (0.2 mmol) at 180 °C for 4 h. The conversion of butanamide was 38% and the selectivity of *N*-butylbutanamide was 87%.

12) The mixture of ammonia(20 mmol), 1-butanol(5 ml), and $RuCl_2(PPh_3)_3$(0.2 mmol) was heated at 180 °C for 4 h in a 50 ml stainless steel autoclave. Tributylamine was produced in 16% yield(based on ammonia); dibutylamine was detected in only 1% yield and butylamine was not obtained.

13) The mixture of butyl formate(10 mmol), tributylamine (10 mmol), 1-butanol(5 ml), $RuCl_2(PPh_3)_3$(0.2 mmol), and H_2O(10 mmol) was heated at 180 °C for 24 h. The reaction did not proceed.

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15) The reaction of formamide(10 mmol), with tributylamine(10 mmol) in 1-butanol(5 ml) in the presence of $RuCl_2(PPh_3)_3$(0.2 mmol) was carried out at 180 °C for 24 h under argon in a 50 ml stainless steel autoclave. *N*,*N*-Dibutylformamide(4.0 mmol) and tributylamine(13 mmol) were detected after reaction.

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