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The Reactions and Syntheses with Organometallic Compounds. II.[1] The Deallylation Reaction with Pd^{II} and a New Synthesis of Primary Amines

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The N-(allyl)C bond of N-acyl-alkyl-allylamines could be easily cleaved by a stoichiometric amount of Pd^{II} in AcOH at 80° to afford the acyl derivatives of the primary amines and π-allyl palladium complex, the latter of which was attacked by the nucleophiles to furnish the unsaturated carbonyl compounds and Pd(0). An above amount of Pd^{II} could be replaced by a catalytic amount of $PdCl_2$ combined with a sufficient amount of inexpensive reagents, that are $CuCl_2$ and AcONa. Thus, this method is applied to a new synthesis of primary amines from the corresponding alkyl halides.

A Favorskii type of rearrangement of N-alkyl-α-haloacetanilides with Grignard reagents was described in the previous paper,[1] which was initially operated in the presence of dichlorodiphosphine nickel complex and was extended to a new synthesis of indole-3-acetic acid finally modified with no use of transition metal complexes. Since the utilization of transition metal complexes for organic syntheses is still a very fascinating problem, further studies on the reaction of N-acyl-allyl-alkyl amines[for example, **1**] with Pd^{II} have been carried out to prove that the N-(allyl)C bond of these compounds is readily cleaved to afford the acyl derivative (**2**) of the primary amine with the simultaneous generation of π-allyl palladium complex (**3**). In the present paper, deallylation reaction of the above acylated amines (**1** and **5a**, *etc.*) with Pd^{II} are described, and developed to a new synthesis of primary amines.

It has been known that Pd^{II} is coordinated with the double bond to generate the olefin-$PdCl_2$, which can be attacked by the nucleophiles. Moreover, tetrakis(triphenylphosphine)-palladium (**0**) can afford the relatively stable σ-complexes[R-Pd-X$(PPh_3)_2$ *etc.*] on treatment with alkyl halides,[3a] acyl halides,[3a] and olefinic compounds.[3b] Therefore, the intramolecular cyclization reaction of the double bond with the halo-alkyl moiety in the molecule (**1**) in the presence of Pd^{II} could be expected, for which purpose the compound (**1**) was reacted with $PdCl_2$ (1.2 mol) and AcONa (2.4 mol) in AcOH at 80°. The cyclization reaction leading to **1'** possibly through **1a**, **1b** and **1c**, however, did not proceed at all,[4] and N-chloroacetylbenzylamine (**2**) was obtained as a major product in 55.2% yield, which was apparently generated by cleavage of N-(allyl)C bond. On this reaction, the C–N bond fission of the N-allyl group must have occurred to generate a π-allyl palladium complex (**3**), which might be assumed to undergo the attack of nucleophiles (AcO^- *etc.*) to give Pd(0) and the unsaturated carbonyl compounds[5] although they were not identified. Addition of Cu(II) salt to reoxidize Pd(0) was expected to render this reaction more effective like the well known Wacker process for the direct preparation

1) Part I: M. Mori, S. Nishimura, and Y. Ban, *Tetrahedron Letters*, **1973**, 4951.
2) Location: *Kita 12–jo, Nishi 6–chome, Kitaku, Sapporo, 060, Japan.*
3) *a*) P. Fitton, M. P. Johnson, and J.E. McKeon, *Chem. Commun.*, **1968**, 6; *b*) P. Fitton and J.E. McKeon, *Chem. Commun.*, **1968**, 4.
4) In the other particular cases of the basic tertiary amines involving the N-allyl and aralkyl groups, an intramolecular cyclization reaction occurred to afford the isoquinoline derivatives. These results will be published in the forthcoming paper.
5) *a*) P.M. Maitlis, "The Organic Chemistry of Palladium," Vol. I, ed by P.M. Maitlis, F.G.A. Stone and Robert West, Academic Press, New York, 1971, p. 175; *b*) *Idem, ibid.*, Vol. II, p. 78.

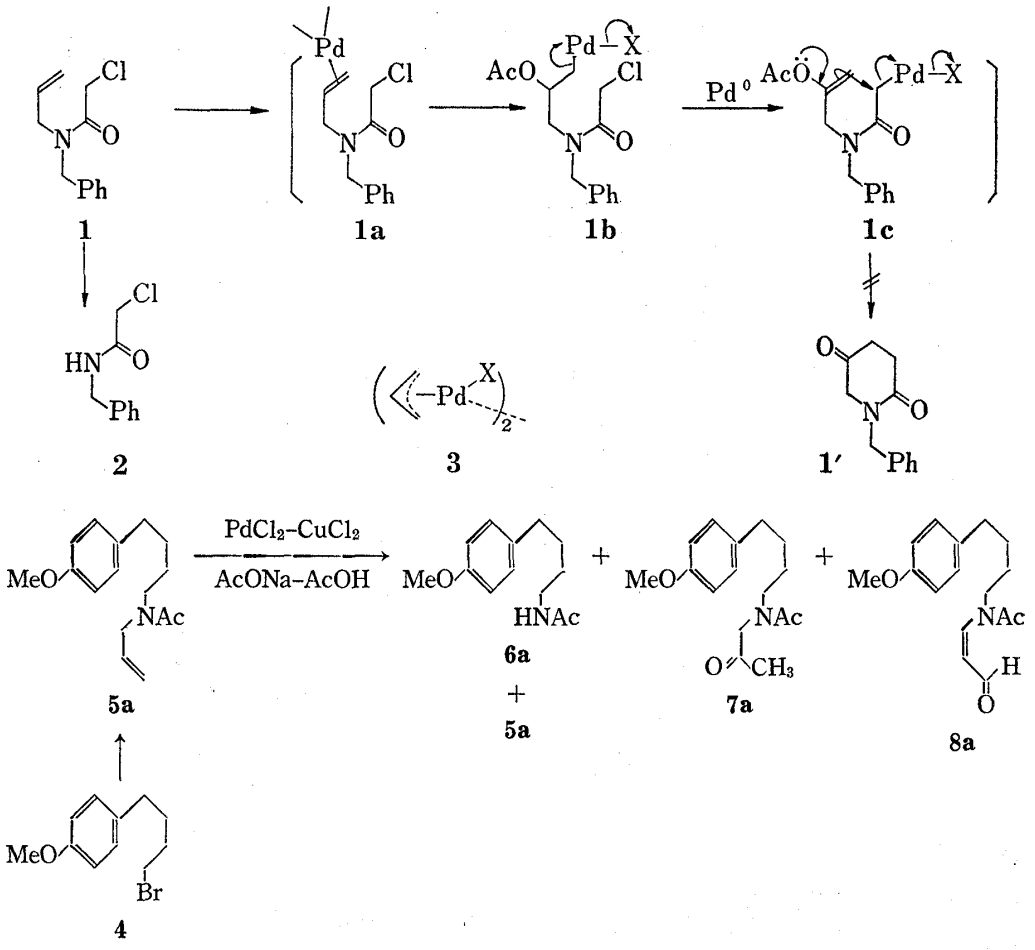


Chart 1

of acetaldehyde from ethylene.[5b] Thus, the deallylation reaction was proved to be more predominant in the presence of a catalytic amount of $PdCl_2$ associated with a stoichiometric amount of $CuCl_2$ and AcONa.

In general, π-allyl palladium complexes (**3** and **11**, *etc.*) are generated from the reaction of $PdCl_2$ with an allyl halide or allyl alcohol, in which the functional groups leave as a result of the bond fission between carbon and halogen atom or hydroxyl group.[5a] Although further examples of this type of reactions have been so far known with a variety of analogues,[6] there seemed not to have appeared any studies on the fission product borne with a hetero atom on a fragmentation reaction. Thus, attention was drawn to investigate the broken part bearing a nitrogen atom. With this aim in mind, the compound (**5a**, 1 mol) was heated in the presence of 0.2 mol of $PdCl_2$, 2.2 mol of $CuCl_2$ and AcONa in AcOH at 60° for 4 hr to give the product (**6a**) in 42.7% yield together with the ketonic product (**7a**, 9.6%), the enamide aldehyde (**8a**, 6.4%) and the recovered starting material (**5a**, 16.5%). It might be assumed that the initial step of this reaction involves an attack of Pd^{II} on the double bond furnishing the olefin $PdCl_2$ (**9**), followed by the coordination of the lone pair of amide nitrogen to give the secondary amide (**6**) and π-allyl palladium complex (**3**). The whole plausible processes are shown in Chart 2, and the N-(allyl)C bond fission substantially occurs in **9a** (See **5**→**9**→**10**→**6**+**3**). The ketonic product (**7**) must have been formed when AcO^- attacked the β-position of the nitrogen of **9** to provide the **6**-complex (**9a**), which was subject to depalladation and hydrolysis

6) *a*) J. Smidt and R. Siver, *Angew. Chem.*, **71**, 626 (1959); *b*) J.M. Kliegman, *J. Organometal. Chem.*, **1971**, 73; *c*) A.C. Cope, J.M. Kliegman, and E.C. Friedrich, *J. Am. Chem. Soc.*, **89**, 287(1967); *d*) Y. Takahashi, A. Tokuda, S. Sakai, and Y. Ishii, *J. Organometal. Chem.*, **1972**, 415.

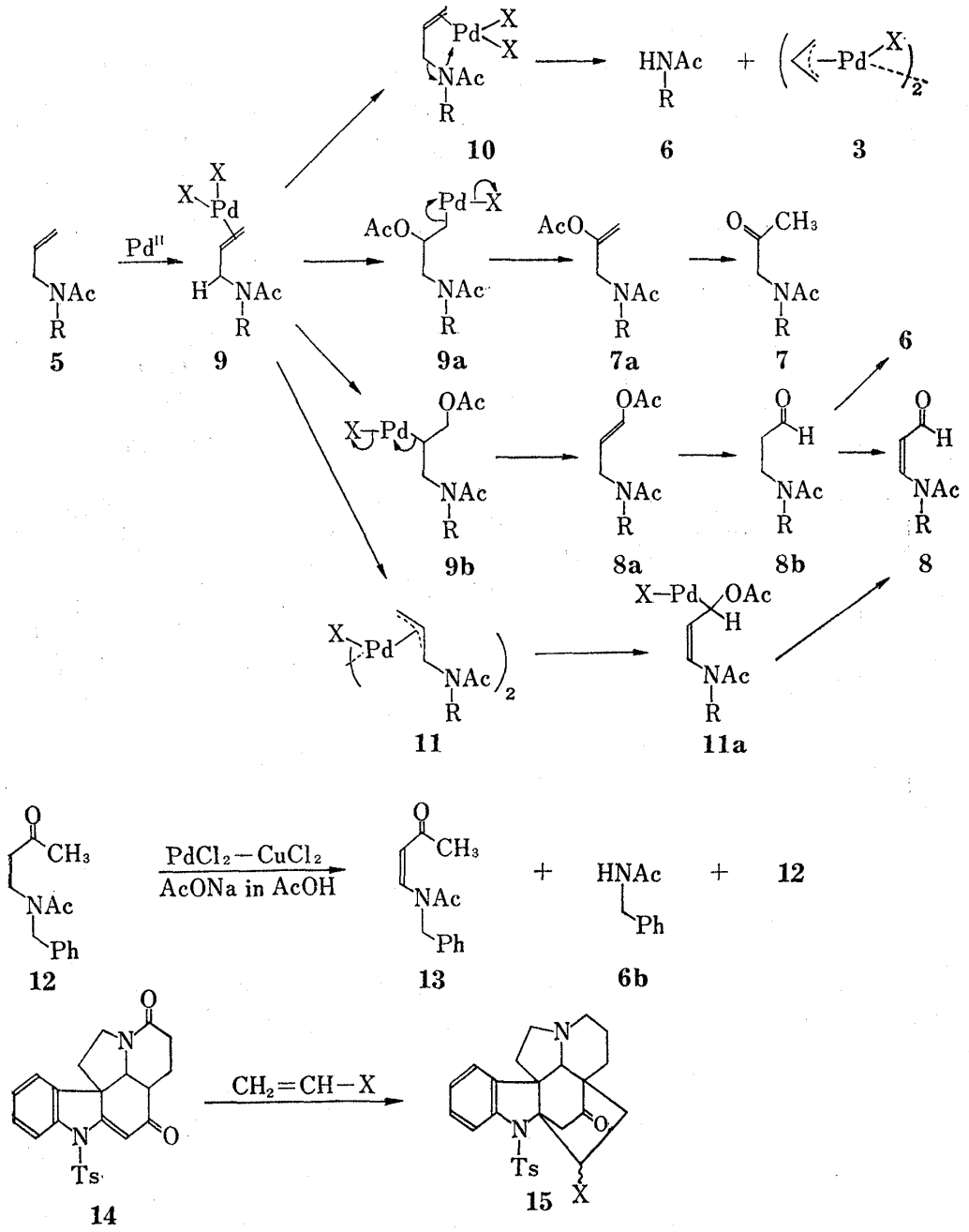
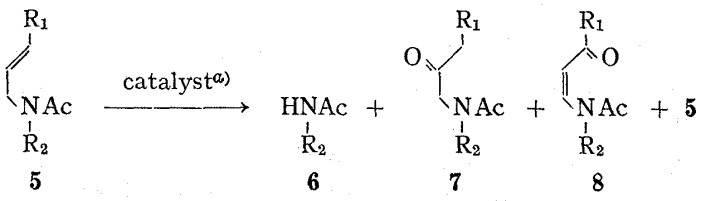


Chart 2

as are shown in the scheme (**9**→**9a**→**7a**→**7**). The reaction mechanism for generation of the enamide aldehyde (**8**) seems to be more complicated. The aldehyde (**8**) should be obtained when AcO^- attacked the γ-position of the nitrogen of **9** giving **9b**, which was subjected to depalladation, hydrolysis and oxidation in the scheme (**9**→**9b**→**8a**→**8b**→**8**). In the alternative pathway, the hydrogen at α-position of the nitrogen in **9** may be abstracted to give a π-allyl palladium complex (**11**) which can be attacked by AcO^- at γ-position to finally give the enamide aldehyde (**8**).[7] To confirm these assumptions, the ketoamide (**12**) possessing the carbonyl carbon in the γ-position of the nitrogen was reacted with $PdCl_2$ in the presence of $CuCl_2$ and AcONa to yield the enamide ketone (**13**) in 17.1% yield. The resulting enamide ketone such as **13**, could be available as the starting material for the two-fold Michael reaction, which has been developed in this laboratory with a similar enamide system (**14**) providing **15** on

7) R. Huttel and H. Christ, *Chem. Ber.*, **97**, 1439 (1964).

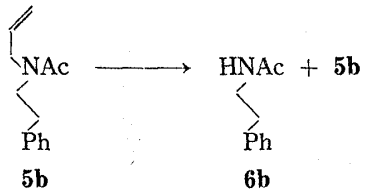
Table I. The Effect of Catalysts



R_1	R_2	Catalysts	Yield of 6(%)	7(%)	8(%)	5(%)
H	CH_2Ph	$PdCl_2$–$CuCl_2$–AcONa	59.2	8.6	5.2	25.2
H	CH_2CH_2Ph	$PdCl_2$–$Cu(OAc)_2$ b)–AcONa	60.2	0	0	28.8
H	CH_2CH_2Ph	$Pd(OAc)_2$–$Cu(OAc)_2$ b)	46.4	0	0	51.3
H	CH_2CH_2Ph	$Pd(OAc)_2$–$Cu(OAc)_2$ b)–NaCl	61.7		trace	20.0
H	CH_2CH_2Ph	$Pd(OAc)_2$	40.0	0	25.4	0
H	CH_2CH_2Ph	$PdCl_2$	33.9	0	0	35.0
H	CH_2CH_2Ph	Na_2PdCl_4	trace			
CH_3	CH_2CH_2Ph	$Pd(OAc)_2$–$Cu(OAc)_2$ b)–NaCl	57.1	0	0	9.7

a) The compound (3) was warmed at 60—80° for several hours in AcOH under the stream of nitrogen or argon.
b) mono hydrate

Table II. The Effect of the Amount of NaCl



NaCl	Yield of 6b	5b
0 mol	17.2%	68.6%
0.5	25.8	60.8
1	45.7	33.0
3	44.8	35.7
5	42.6	25.8

Reaction condition; N-acetyl-N-allyl-phenetyalmine (1 mol. eq.) was warmed at 80° for 1 hr in the presence of $Pd(OAc)_2$ (0.2 mol. eq.), $Cu(OAc)_2 \cdot H_2O$ (2 mol. eq.) and various amounts of NaCl.

condensation with vinyl methyl sulfone.[8] The validity of this type of enamide ketone for the above reaction is now being investigated.

Effects of combined metallic reagents on the present deallylation reactions are summarized in Table I. In the second run when $Cu(OAc)_2 \cdot H_2O$ was employed in place of $CuCl_2$, neither **7** nor **8** was obtained although the reaction rate of deallylation was rather decreased. When $Pd(OAc)_2$[9] and $Cu(OAc)_2 \cdot H_2O$ were used in lieu of $PdCl_2$ and $CuCl_2$, respectively, the reaction rate was more sluggish. As the rate of N-(allyl)C bond fission seemed to be increased by action of Cl^-, the reactions were carried out with various amounts of NaCl in the mixture of $Pd(OAc)_2$ and $Cu(OAc)_2$, the results of which are compiled in Table II. It is clearly indicated

8) T. Ohnuma, T. Oishi, and Y. Ban, *Chem. Commun.*, **1973**, 301.
9) T. Matsuda, T. Mitsuyasu, and Y. Nakamura, *Kogyo Kagaku Zasshi*, **72**, 1951 (1969).

that addition of NaCl gave a remarkable effect on the yields of reactions. It is noteworthy that an appreciable amount of the enamide aldehyde (**8**) was produced when 1 mol of $Pd(OAc)_2$ was used (Table I). The anion(AcO^-) was not necessary in this reaction, but without the AcO^- the yield of **8** was considerably low, and the presence of a ligand such as PPh_3[10] also prevented the progress of the reaction.

With the homoallyl derivative (**16**), the double bond could be expected to migrate to the allyl position of the nitrogen by an effect of Pd^{II}, thus being broken at the N-(allyl)C bond. The compound (**16**) was treated with $Pd(OAc)_2$ and $Cu(OAc)_2$ under the same condition as above to give the ester (**17**), while C–N bond fission did not occur. Probably, the reaction mechanism for the generation of this compound may be assumed that the double bond of the substrate (**16**) must have been attacked by Pd^{II} to generate the olefin-$PdCl_2$ (**18**), which in turn, was converted to the σ-complex (**19**) in the presence of AcO^-, and finally furnished the product (**17**).

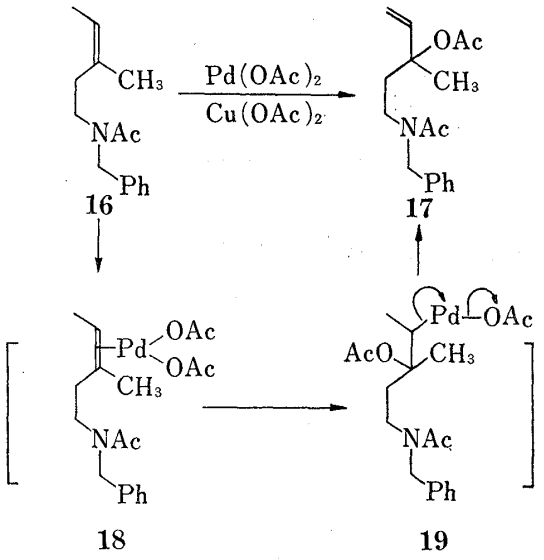
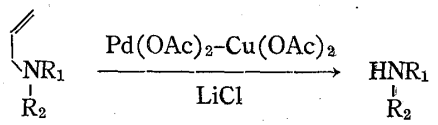


Chart 3

TABLE III. The Effects of N-Acyl Groups



5 **6**

R_1	R_2	Yield of 6
COPh	CH_2CH_2Ph	66.7%
$COCH_3$	CH_2CH_2Ph	61.7
$COOCH_3$	CH_2Ph	76.0
Ts	CH_2CH_2Ph	69.0

Reaction condition; N-acyl-N-allylphenethylamine (1 mol. eq.) was warmed at 50° for several hours in the presence of $Pd(OAc)_2$ (0.2 mol. eq.), $Cu(OAc)_2 \cdot H_2O$ (2mol. eq.) and LiCl (1 mol. eq.).

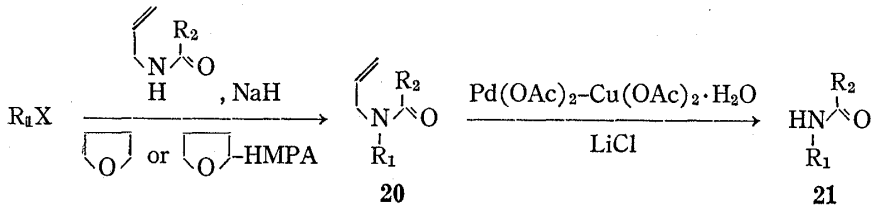
Subsequently, the effects of N-acyl groups on the yields of the deallylation reactions were studied (See Table III). The pronounced differences were not observed even with the tosyl group at nitrogen.

It is well known that the benzyl group attached to the nitrogen bearing an acyl group can not be released by hydrogenolysis with Pd–C which is effective for elimination of benzyl group from the basic nitrogen. The method using sodium metal dissolved in liquid ammonia developed by Sugasawa and Fujii is only effective for removal of benzyl group from the acyl amide.[11] The present data demonstrate that the fission of the N-(allyl)C bond is readily performed, in which case the N-benzyl group remains unchanged under the above conditions. Therefore, it may be suggested that the allyl group could be sometimes more useful than the benzyl substituent as the protecting group of nitrogen.

Although there have been known a number of synthetic methods of primary amines,[12] the present reaction could be extended to another new method for a synthesis of primary amines from alkyl halides in the following way. Alkyl halides are reacted with N-acyl-allylamine in the presence of NaH in THF or in THF–HMPA by heating the mixture at 50° for

10) G. Booth and J. Chatt, *J. Chem. Soc.* (*A*), **1966**, 634.
11) S. Sugasawa and T. Fujii, *Chem. Pharm. Bull.* (Tokyo), **6**, 587 (1958).
12) *a*) T. Mukaiyama and T. Taguchi, *Tetrahedron Letters*, **1970**, 3411; *b*) T. Okamoto, M. Hirobe, C. Mizushima, and A. Osawa, *Chem. Pharm. Bull.* (Tokyo), **11**, 780 (1963); *c*) S. Gabriel, *Chem. Ber.*, **20**, 2224 (1887); *cf.* M.S. Gibson and R.W. Bradshaw, *Angew. Chem.*, **80**, 986 (1968).

TABLE IV. The Synthesis of Primary Amines



R_1	R_2	Yield of 20	Yield of 21
p-MeO-Ph$(CH_2)_3CH_2Br$	CH_3	83.2%	64.0%
p-MeO-Ph$(CH_2)_3CH_2Br$	OCH_3	80.0	59.7
$CH_3(CH_2)_3CH_2Br$	CH_3	97.2	68.6
$CH_3(CH_2)_3CH_2Br$	Ph	76.5	65.0
$CH_3(CH_2)_3CH_2Br$	OCH_3	87.3	63.5
$PhCH_2Br$	CH_3	58.2	59.2
$PhCH_2Br$	OCH_3	—	76.0
$PhCH_2CH_2Br$	CH_3	—	61.7
$PhCH_2CH_2Br$	Ph	—	66.7

several hours to give the N-alkyl-acyl-allyl-amines, which are treated with $Pd(OAc)_2$, $Cu(OAc)_2 \cdot H_2O$ and LiCl in AcOH at 60° for several hours, providing the N-acyl derivatives of the desired primary amines. As the yields of these reactions have not yet been satisfactory as are shown in Table IV, it may be utilized as a new synthetic method of primary amines, since the starting material is easily recovered.

Further studies on an extention of these reactions are in progress.

Experimental[13,14]

N-Chloroacetyl-N-benzyl-allylamine (1)——To a solution of N-benzyl-allylamine (1.9 g) and anhydrous K_2CO_3 (1.35 g) in 30 ml of acetone was added chloroacetylchloride (1.75 g) under cooling with ice water and the mixture was stirred at room temperature for 3 hr. After evaporation of the acetone, the residue was extracted with water, 10% HCl solution, dried over Na_2SO_4, and the solvent was evaporated. The residual oil was distilled under reduced pressure to furnish 1.5 g of the colorless oil (**1**,[15]). bp.$_3$141—142°. NMR ($CDCl_3$) δ: (2H, m, $NC\underline{H}_2CH$), 4.10 (2H, s, $NCOC\underline{H}_2Cl$), 4.59 (2H, s, $NC\underline{H}_2Ph$), 4.9—6.1 (3H, m, vinyl protons), IR ν_{max}^{film} cm^{-1}: 1650 (C=O).

The Reaction of N-Chloroacetyl-benzyl-allylamine (1) with $PdCl_2$——A mixture of 221.5 mg of N-chloroacetyl-benzyl-allylamine (**1**), 212.9 mg of $PdCl_2$ and 236 mg of anhydrous AcONa in 3 ml of AcOH was heated at 80° with stirring for 5 hr under a stream of argon, during which time the solid deposited. The precipitates were filtered off and the filtrate was concentrated. Benzene was added and the benzene layer was washed with saturated $NaHSO_3$ solution, dried over Na_2SO_4, and the solvent was evaporated. The residue was submitted to chromatography on silica gel eluted with hexane–acetone (4: 1). The crystallized fraction was dissolved in benzene and the benzene solution was washed with saturated $NaHCO_3$ solution. The solvent was removed and the residue (117 mg) was recrystallized from benzene–hexane to give colorless plates, mp 93—93.5° (lit.[16] mp 93°). IR ν_{max}^{Nujol} cm^{-1}: 3260 (NH), 1650 (C=O). NMR ($CDCl_3$) δ: 4.10 (2H, s, $COC\underline{H}_2Cl$), 4.49 (2H, d, J=6, N-$C\underline{H}_2Ph$), 7.30 (5H, s, aromatic protons), 6.5—7.2 (1H, m, $N\underline{H}$). Mass Spectrum *m/e*: 185, 183 (M^+). *Anal.* Calcd. for $C_9H_{10}ONCl$: C, 58.86; H, 5.49; N, 7.63. Found: C, 58.77; H, 5.38; N, 7.70.

13) Melting points were measured with Yamato MP-1 and uncorrected. Spectra reported herein were measured on a 215 Hitach grating infrared spectrophotometers, Hitachi R-20B (NMR, 60 MHz), and a Hitachi RMU-7M double forcussing mass spectrometer. The authors are indebted to Mrs. H. Matsumoto, Misses A. Maeda, and C. Ohara for microanalyses, Mrs. M. Ohnuma for obtaining NMR spectra and Miss M. Takahashi for mass spectral measurements.

14) The following abbreviations are used: b=broad, d=doublet, m=multiplet, q=quartet, s=singlet, t=triplet, THF=tetrahydrofuran, HMPA=hexamethylphosphoroamide.

15) P.C. Hamm and A.J. Speziale, U.S. Patent 2863752 (1958) [*C. A.*, **54**, 20059*d* (1960)].

16) Z. Horii and T. Watanabe, *Yakugaku Zasshi*, **81**, 636 (1961).

4-(4-Methoxyphenyl)-butyl Bromide (4)——To a solution of 4-(4-methoxyphenyl)-butan-1-ol[17] (21.9 g) in CCl_4 (60 ml) was added PBr_3 (14.6 g) under ice cooling. The mixture was stirred at room temperature overnight, and refluxed for 30 min. On cooling, the whole mixture was poured on ice, extracted with CCl_4, and the extract was dried over $CaCl_2$. The solvent was evaporated and the residue was distilled to afford 20.6 g (64%) of colorless oil, $bp_{2.5}$ 135°. NMR ($CDCl_3$) δ: 2.53 (2H, broad triplet, $J=7$ Hz, $-C\underline{H}_2Ph$), 3.30 (2H, t, $J=6$ Hz, $-C\underline{H}_2Br$), 3.70 (3H, s, $OC\underline{H}_3$). Mass Spectrum *m/e*: 244, 242 (M^+).

N-[4-(4-Methoxyphenyl)butyl]-N-acetyl-N-allylamine (5a)——To a suspension of NaH (70%, 1 g) in 20 ml of THF was added a solution of N-acetyl-allylamine (1.98 g) in THF (5 ml) under ice cooling, during which time hydrogen was evolved simultaneously. After the mixture was stirred at room temperature for 45 min, the bromide (4, 4.8 g) in THF (30 ml) was added to the above solution, and the whole mixture was warmed at 50° for 6 hr. Benzene was added, and the benzene layer was washed with water, dried and the solvent was evaporated. The residual oil was purified by chromatography on silica gel eluted with benzene–acetone (4: 1) to afford 4.35 g (83.2%) of the product (**5a**). IR ν_{max}^{film} cm^{-1}: 1630 (C=O). NMR ($CDCl_3$) δ: 2.06 (3H, s, $-NCO-C\underline{H}_3$), 3.78 (3H, s, $-OC\underline{H}_3$), 4.7—6.7 (3H, m, vinyl protons). The starting material (827 mg) was recovered unchanged.

The Reaction of N-[4-(4-Methoxyphenyl)butyl]-N-acetyl-N-allylamine (5a) with $PdCl_2$ and $CuCl_2$——A mixture of the above amide (**5a**, 650 mg), $PdCl_2$ (50 mg), AcONa (500 mg) and $CuCl_2$ (404 mg) in acetic acid (3 ml) was warmed at 60° with stirring under a stream of argon for 4 hr. The solvent was removed *in vacuo*, benzene was added to the residue, and the insoluble material was filtered off. The filtrate was washed with water, saturated $NaHCO_3$ solution, dried over Na_2SO_4, and the solvent was evaporated. The residue was submitted to chromatography on silica gel, which was eluted with benzene–acetone (4: 1).

The first fraction furnished 44 mg (6.4%) of the enamide aldehyde (**8a**) as an oil. IR ν_{max}^{film} cm^{-1}: 1690 (C=O), 1660 (C=O), 1600 (C=C). NMR ($CDCl_3$) δ: 2.33 (3H, s, $NCOC\underline{H}_3$), 3.78 (3H, s, $-OC\underline{H}_3$), 5.63 (1H, q, $J=15$ and 8 Hz, $-CH=\underline{H}C-CHO$), 7.85 (1H, d, $J=15$ Hz, $-C\underline{H}=CH-CHO$), 9.43 (1H, d, $J=8$ Hz, $-C\underline{H}O$). Mass Spectrum *m/e*: 275 (M^+).

The second fraction gave 107 mg (16.5%) of the starting material (**5a**).

The third fraction provided 66 mg (9.6%) of the ketoamide (**7a**) as an oil. IR ν_{max}^{film} cm^{-1}: 1720 (ketone C=O), 1630 (amide C=O). NMR ($CDCl_3$) δ: 2.10 and 2.13 (6H, s and s, $-NCOC\underline{H}_3$ and $-CH_2COC\underline{H}_3$), 3.78 (3H, s, $OC\underline{H}_3$), 4.05 (2H, s, $NC\underline{H}_2COCH_3$). Mass Spectrum *m/e*: 277 (M^+).

The last fraction afforded 235 mg (42.7%) of N-4-(4-methoxyphenyl)butyl acetamide (**6a**) as an oil. IR ν_{max}^{film} cm^{-1}: 3300 (NH), 1630 (C=O), 1540 (NH). NMR ($CDCl_3$) δ: 1.9 (3H, s, $NCOC\underline{H}_3$), 3.76 (3H, s, $OC\underline{H}_3$), 6.10 (1H, broard singlet, N$\underline{H}$). Mass Spectrum *m/e*: 221 (M^+).

N-(3-Oxobutyl)-N-benzyl Acetamide (12)——A mixture of benzylamine (5.35 g) and methyl vinyl ketone (3.85 g) in 30 ml of absolute ether was kept to leave in a refrigerator. After standing overnight, a solution of acetyl chloride (5 g) in 10 ml of absolute ether was added dropwise to the above mixture in the presence of the excess K_2CO_3 (solid, 6 g) under ice cooling. The whole mixture was stirred at room temperature for 2 hr. After reaction, water was added and the ether phase was separated, washed with water, dried over Na_2SO_4, and the ether was evaporated. The residue was distilled under reduced pressure to give 2.9 g (32.8%) of the product (**12**), bp_4 166—168°. IR ν_{max}^{film} cm^{-1}: 1700 (C=O), 1620 (amide C=O).

N-(3-Oxo-butene-1-yl)-N-benzyl Acetamide (13)——A mixture of ketoamine (**12**, 550 mg), $PdCl_2$ (177.5 mg), AcONa (500 mg) and $CuCl_2$ (336 mg) in AcOH (4 ml) was heated at 100° with stirring under the stream of nitrogen. After 2.5 hr, the AcOH was removed and benzene was added to the residue. The precipitates were filtered, washed with benzene, and the combined benzene extract was washed with saturated $NaHCO_3$ solution, dried over Na_2SO_4 and the solvent was removed. The residue was purified by chromatography on silica gel, on which the elution with benzene–ether–acetone (2: 1: 1) yielded 93 mg (17.1%) of the enamideketone (**13**). IR ν_{max}^{film} cm^{-1}: 1670 (C=O), 1605 (C=C), 1570 (NH). NMR ($CDCl_3$) δ: 2.15 (3H, s, $COC\underline{H}_3$), 2.39 (3H, s, $COC\underline{H}_3$), 4.87 (2H, s, $-NC\underline{H}_2Ph$), 4.63 (1H, d, $J=15$ Hz, $-NCH=C\underline{H}-$), 8.16 (1H, d, $J=15$ Hz, $-NC\underline{H}=CH-$). Mass Spectrum: *m/e* 217 (M^+). The other fraction yielded a mixture (303 mg) of N-acetyl-N-benzylamine and the starting material (**12**).

The Reaction of N-Acetyl-N-phenethyl-allylamine (5b) with $Pd(OAc)_2$——A mixture of N-acetyl-N-phenethyl-allylamine (**5b**, 520 mg) and $Pd(OAc)_2$ (685 mg) in 3 ml of AcOH was warmed at 70° with stirring under the stream of nitrogen for 30 min. The solvent was removed, $CHCl_3$ was added to the residue, the precipitates were filtered off. The $CHCl_3$ layer was washed with saturated $NaHCO_3$ solution, dried over Na_2SO_4 and the solvent was removed. The residual oil was purified by chromatography on silica gel eluted with benzene–hexane-acetone (2: 1: 1). The first fraction furnished 142 mg (25.4%) of the enamide aldehyde (**8**, R_1=H, R_2=$PhCH_2CH_2$), which was recrystallized from hexane–benzene to give colorless crystals. IR ν_{max}^{Nujol} cm^{-1}: 1705 (C=O), 1600 (C=C). NMR ($CDCl_3$) δ: 2.22 (3H, s, $-NCOC\underline{H}_3$), 5.73 (1H, q, $J=8$ and 15 Hz, $-NCH=C\underline{H}-$), 7.26 (5H, aromatic protons), 7.94 (1H, d, $J=15$ Hz, $-NC\underline{H}=CH-$), 9.47 (1H, d, $J=8$ Hz, $-C\underline{H}O$). Mass Spectrum *m/e*: 217 (M^+). *Anal.* Calcd. for $C_{13}H_{15}O_2N$: C; 71.85, H; 6.97, N; 6.45. Found: C, 71.86, H, 6.95, N; 6.57. The second fraction was concentrated, and the residual oil was washed with saturated $NaHSO_3$ solution, dried

17) R. Baird and S. Winstein, *J. Am. Chem. Soc.*, **84**, 788 (1962).

over Na_2SO_4 and the solvent was evaporated to provide 170 mg (40%) of N-acetyl phenethylamine (**6b**) as crystalls, whose infrared spectrum was identical with that of an authentic sample.

The Reaction of N-Acetyl-N-benzyl-N-(3-methyl-penten-3-yl)amine (16)——The compound (**16**) was prepared from N-(3-oxobutyl)-N-benzyl acetamide (**12**) by utilization of the usual Wittig reaction in the following way. To the suspension of triphenyl ethylphosphonium bromide in abs. ether (20 ml) was added the solution of *n*-BuLi (3.52 ml, 20% hexane solution) under the stream of nitrogen. The amide (**12**) was added to the above solution and the mixture was stirred overnight. Water was added to the solution and the whole mixture was extracted with ether. The ether solution was dried over Na_2SO_4 and concentrated. The residual oil was purified by chromatography on silica gel, on which the elution with benzene–acetone (4: 1) yielded 238 mg (9.7%) of pentenyl amine (**16**). IR ν_{max}^{film} cm^{-1}: 1630 (C=O). NMR ($CDCl_3$) δ: 1.5—1.7 (6H, b.s, $-C\underline{H}_3C=CHC-H_3$), 5.3 (1H, b.s, $CH_3C\underline{H}=C$). A mixture of **16** (238 mg), $Pd(OAc)_2$ (55 mg), $Cu(OAc)_2\cdot H_2O$ (400 mg) and LiCl (50 mg) in 3 ml of AcOH was warmed at 50° with stirring for 24 hr. The residue obtained in the usual mannar was submitted to chromatography on silica gel. Elution with benzene–hexane–acetone (1: 3: 1) furnished 38 mg (13%) of the ester (**17**) as colorless oil. IR ν_{max}^{film} cm^{-1}: 1720 (ester C=O), 1630 (amide C=O). NMR ($CDCl_3$) δ: 4.50—5.8 (3H, m, $-C\underline{H}=C\underline{H}_2$), 7.25 (5H, aromatic protons). Mass Spectrum *m/e*: 303 (M^+). The starting material (**16**, 109 mg) was recovered unchanged.

The General Procedure for the Synthesis of Primary Amines——To a suspension of NaH (1.5 mol.eq.) in THF or THF-HMPA was added a solution of N-acyl allylamine (1.2 mol.eq.) in THF and the resulting mixture was stirred at room temperature for 45 min. A solution of alkyl halide (1 mol.eq.) in the same solvent was added to the above solution, and the whole mixture was warmed at 50° for several hours. After reaction, water was added, the whole mixture was extracted with benzene, and the solvent was evaporated. The crude product was submitted to the appropriate purifications which were usually chromatography on silica gel or distillation. A mixture of the foregoing N-acyl alkyl allylamine (1 mol. eq.), $Pd(OAc)_2$ (0.2 mol. eq.), $Cu(OAc)_2$–H_2O (2 mol. eq.) and LiCl (1 mol. eq.) in AcOH was warmed at 60—80° with stirring under the stream of nitrogen or argon. The AcOH was removed under reduced pressure to leave the residue containing the inorganic substances, to which benzene was added, and the insoluble material was filtered off. The benzene solution was washed with sat. $NaHCO_3$ solution, dried over Na_2SO_4 and concentrated to give the residue, which was purified by chromatography on silica gel. A typical example according to the general procedure is described.

N-Benzoyl-N-pentylamine (21, R_1-C_5H_{11}, R_2-Ph)——To a suspension of NaH (60%, 900 mg) in 4 ml of HMPA–THF (1: 1) was added a solution of N-benzoyl allylamine (3.5 g) in 3 ml of THF under the stream of nitrogen. After 45 min, a solution of *n*-pentylbromide (3.0 g) in 3 ml of THF was added to the foregoing solution, and the mixture was refluxed for one night. The solvent was removed to give the residue, which was extracted with benzene and the benzene extract was washed with water, dried over Na_2SO_4 and concentrated. The residual oil was purified by chromatography on silica gel, which was eluted with benzene–acetone (4: 1) to afford 3.28 g (76.5%) of N-allyl-N-benzoyl-pentylamine (**20**, $R_1=C_5H_{11}$, R_2=Ph) as an oil. IR ν_{max}^{film} cm^{-1}: 1630 (C=O). A mixture of N-allyl-N-benzoyl-pentylamine (578 mg), Pd $(OAc)_2$ (167 mg), $Cu(OAc)_2\cdot H_2O$ (1.0 g) and LiCl (105 mg) in 6 ml of benzene–AcOH (1: 2) was warmed at 50° with stirring under the stream of argon overnight. After the solvent was removed under reduced pressure, benzene was added and the resulting precipitates were filtered off. The filtrate was washed with saturated $NaHCO_3$ solution, and concentrated. After purification by chromatography on silica gel eluted with CH_2Cl_2–ether (4: 1), N-benzoyl-pentylamine (**20**, $R_1=C_5H_{11}$, R_2=Ph, 310 mg, 65%) was obtained as an oil. IR ν_{max}^{film} cm^{-1}: 3200 (NH), 1630 (C=O), 1540 (NH). NMR ($CDCl_3$) δ: 0.89 (3H, b.t, $-CH_2C\underline{H}_3$) 1.1—1.7 [6H, m, $-(C\underline{H}_2)_3CH_3$], 3.40 (2H, b.q, $NC\underline{H}_2CH_2$–), 6.90 (1H, b.s, NH), 7.3—7.9 (5H, aromatic protons).

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