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Catalytic Hydrogenolyses of Benzylidene Compounds Bound to Two Oxygens, Two Nitrogens and Both Oxygen and Nitrogen

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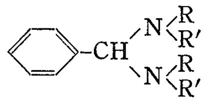
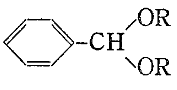
Catalytic hydrogenolyses of the benzylidene compounds, in which two oxygens, two nitrogens and both oxygen and nitrogen are bound to the α-carbon of the benzylidene, were investigated in order to know the condition of hydrogenolysis, which may affect one of the two bonds, if possible, and either one of the two when the two are different. Partial hydrogenolyses of the N,N′-benzylidenediamines and O,O′-benzylidenediethers and selective hydrogenolyses of the α-alkoxybenzylamines and N-(α-aminobenzyl)amides were realized by the method of using palladium-on-charcoal and Raney nickel catalyst. The catalytic hydrogenolyses of the latter two were influenced by solvent used and were selectively effected at the carbon-oxygen bond of the α-alkoxybenzylamines and at the carbon-amine nitrogen or carbon-amide nitrogen bond of the N-(α-aminobenzyl)amides.

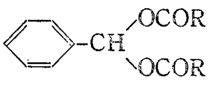
The benzylidene compounds, in which two oxygens, two nitrogens and both oxygen and nitrogen are bound to the α-carbon of the benzylidene, have been known as the following types. Our investigation on catalytic hydrogenolyses of these compounds is described in the present paper.



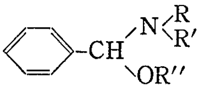
N,N′-benzylidenediamine



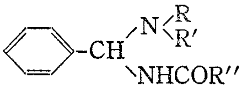
O,O′-benzylidenediether



O,O′-benzylidenediester



α-alkoxybenzylamine



N-(α-aminobenzyl)amide

Although the catalytic hydrogenolyses of N- and O-benzyl compounds to toluene have been well known in an abundance of papers, little is definitely known as for the hydrogenolyses of the above compounds other than O,O′-benzylidenediether[2,3] and O,O′-benzylidenediester.[4] The structures have the two α-carbon bonds bound to nitrogen and/or oxygen which might suffer catalytic hydrogenolysis. It appeared interesting to know the condition of hydrogenolysis under which one of these two bonds, if possible, is affected and also to know which bond is initially affected when the two are different.

For this investigation we adopted generally a catalytic reduction method using palladium-on-charcoal catalyst under ordinary pressure at room temperature. In addition, a method using Raney nickel catalyst under high hydrogen pressure at high temperature was also adopted for the hydrogenolyses of some α-alkoxybenzylamines and N-(α-aminobenzyl)-amides.

I. Catalytic Reductions of N,N′-Benzylidenediamines

Catalytic reduction of an ethanolic solution of N,N′-benzylidenebis(N-methylbenzylamine), as a representative, with palladium-on-charcoal catalyst under ordinary pressure at

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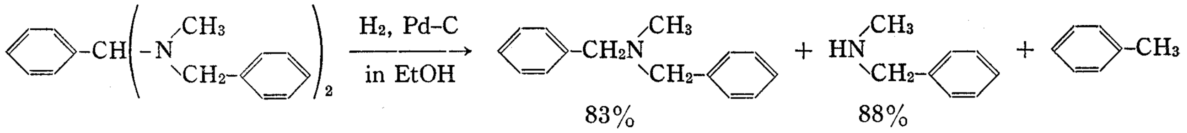
[1] Location: *2-2-1 Oshika, Shizuoka.*

[2] T. Kariyone and Y. Kimura, *Yakugaku Zasshi*, **43**, 746 (1923).

[3] T. Kariyone, T. Kajiura, A. Ueno and N. Suzuki, *Yakugaku Zasshi*, **73**, 493 (1953).

[4] A. Skita, *Ber.*, **48**, 1698 (1915).

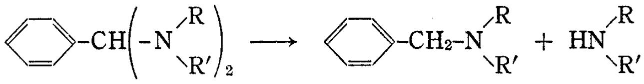
ordinary temperature resulted in formation of the products as shown in the following, when the reduction was interrupted after uptake of one molar equiv. of hydrogen. The yields shown are based on the products actually isolated.

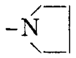
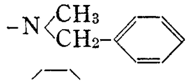
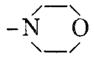


From this result, predominant hydrogenolysis of one of the two α-carbon-nitrogen bonds appeared possible, although the formation of a small amount of toluene through the secondary hydrogenolysis of the formed benzylamines could not be avoided.

Examinations with a number of N,N'-benzylidenediamines were carried out and the above mode of hydrogenolysis was generally realized. Results of the experiments are summarized in Table I. In these experiments only yields of the tertiary amine products were checked and the minor products, secondary amines and toluene, were not. As can be seen in Table I, the hydrogenolysis proceeded slower in benzene than in ethanol. With N,N'-benzylidenedipiperidine and N,N'-benzylidenedimorpholine almost no uptake of hydrogen was observed in benzene solution.

Table I. Catalytic Reductions[a] of N,N'-Benzylidenediamines over Palladium-on-charcoal



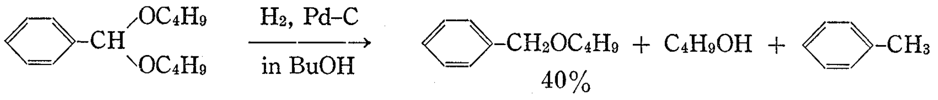
$-N\langle^{R}_{R'}$	Solvent	Hydrogenation time (hr)	Yield[b] of tert. amine (%)
	EtOH benzene	4.3 11.5	78 66
	EtOH	12.0	80
$-N\langle^{CH_3}_{CH_3}$	EtOH benzene	5.3 8.3	74 50
	EtOH benzene	5.3 7.7	83 69
	EtOH	13.5	90

[a] substrate; 0.02 mole, solvent; 40 ml, catalyst; 20% Pd-C 0.2 g, hydrogenation temp.; 11—12°, Hydrogenation was interrupted after uptake of one molar equiv. of hydrogen. The secondary amine product was not isolated.
[b] Yield is based on the product isolated.

II. Catalytic Reductions of O,O'-Benzylidenediethers and O,O'-Benzylidenediesters

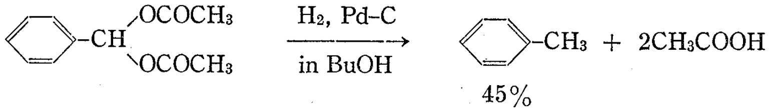
As for catalytic reductions of O,O'-benzylidenediether and O,O'-benzylidenediester there have been known several papers, in which catalytic reduction of benzaldehyde dibutylacetal over platinum-black in acetic acid was reported[2,3] to give methylcyclohexane, cyclohexylmethyl alcohol and that of benzylidene diacetate was reported[4] to result in the formation of toluene. In the present study, we examined catalytic reductions of benzaldehyde dibutylacetal and benzylidene diacetate under ordinary pressure at ordinary temperature using palladium-on-charcoal catalyst.

Catalytic reduction of benzaldehyde dibutylacetal under the condition proceeded in alcoholic medium, but not in dioxane and benzene. The reduction in butanol, when interrupted after uptake of one molar equiv. of hydrogen, resulted in the formation of benzylbutyl ether, but simultaneous formation of toluene could not be avoided, as shown in the following.



(recovery of the substrate; 27%)

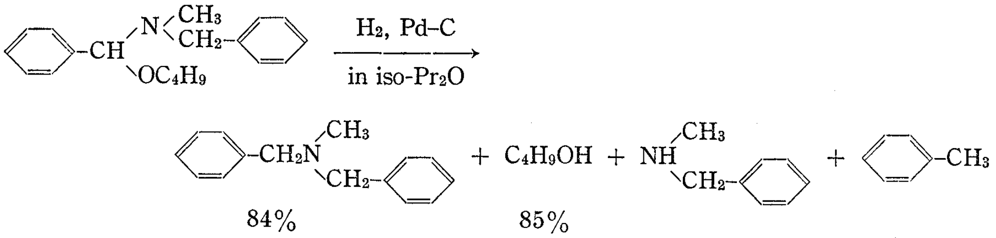
Catalytic reduction of benzylidene diacetate under the same condition proceeded very slowly (35 hr being required for uptake of one molar equiv. of hydrogen) in butanol and did not in dioxane. The former experiment in butanol resulted only in the formation of toluene (45%) with the 48% recovery of the substrate, but in no formation of benzyl acetate.



(recovery of the substrate; 48%)

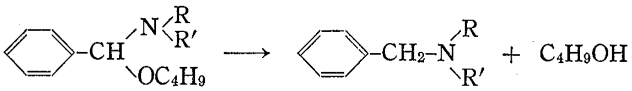
III. Catalytic Reductions of *α*-Alkoxybenzylamines

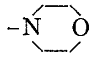
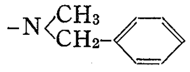
α-Alkoxybenzylamines have both the *α*-carbon-nitrogen and -oxygen bonds. It was our objective to see which bond would first suffer hydrogenolysis. N-(*α*-Butoxybenzyl)-N-methylbenzylamine, selected as a representative, was catalytically reduced in isopropyl ether using palladium-on-charcoal as catalyst. As is shown in the following, N-methyldibenzylamine and butyl alcohol were obtained as major products, which is an indication of predominant hydrogenolysis at the carbon-oxygen bond. N-Methylbenzylamine and toluene, detected only by gas chromatographic method as minor products, are supposedly formed through the secondary hydrogenolysis of major amine product, N-methyldibenzylamine.



Catalytic reductions of several *α*-butoxybenzylamines having various amine residues showed the same mode of hydrogenolysis. The conditions were the same as those for the above experiment except that as solvent were used dioxane and benzene, which were found to be more

Table II. Catalytc Reductions[a] of N-(*α*-Butoxybenzyl)amines over Palladium-on-charcoal



$-N{<}^{R}_{R'}$	Solvent	Hydrogenation time (min)	Yield[b] of tert. amine (%)
	benzene	75	83
	dioxane	85	79
$-N{<}^{CH_3}_{CH_3}$	benzene	25	82
	dioxane	35	68
	benzene	240	76
	dioxane	90	74
	benzene	65	78
	dioxane	95	71
	iso-Pr_2O	210	84

a) substrate; 0.04 mole, solvent; 100 ml, catalyst; 10% Pd-C 1 g, hydrogenation temp.; 25—30° Hydrogenation was interrupted after uptake of one molar equiv. of hydrogen.

b) Yield is based on the product isolated.

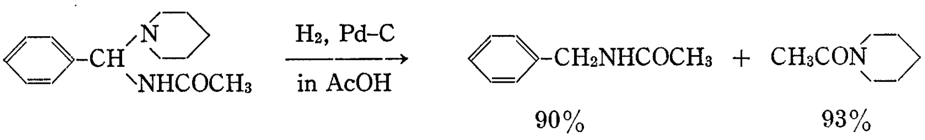
efficient toward hydrogenolysis than isopropyl ether. Results are summarized in Table II. In these experiments only the yields of tertiary amines isolated were checked.

Another reduction method using Raney nickel catalyst under high hydrogen pressure was also studied with N-(α-butoxybenzyl)piperidine as selected substrate. A reduction in dioxane at 65—70° under 80 kg/cm^2 of initial hydrogen pressure afforded N-benzylpiperidine in 89% yield, indicating the hydrogenolysis at the carbon-oxygen bond.

From the above data, the predominant hydrogenolysis at the carbon-oxygen bond of α-alkoxybenzylamines by catalytic reduction was generally realized.

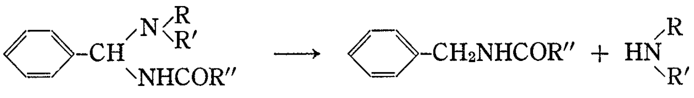
IV. Catalytic Reductions of N-(α-Aminobenzyl)amides

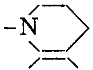
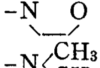
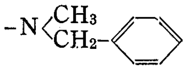
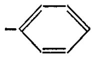
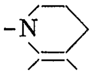
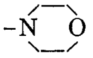
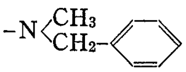
We investigated catalytic reductions of N-(α-aminobenzyl)amides possessing two α-carbon bonds bound to amine and amide nitrogens to see which bond would first suffer hydrogenolysis under varying conditions. With palladium-on-charcoal catalyst under ordinary pressure at ordinary temperature, N-(α-piperidinobenzyl)acetamide, selected as a representative, was subjected to catalytic reduction using benzene, dioxane, ethanol and acetic acid as solvents. Acetic acid was most efficient, while no hydrogenation occurred in benzene and dioxane. The reduction in acetic acid resulted in the formations of N-benzylacetamide and N-acetylpiperidine in over 90% yield.



Since the latter was considered to be formed from acetylation of the initial product, piperidine, with acetic acid solvent, hydrogenolysis at the α-carbon-amine nitrogen bond was shown

Table III. Catalytic Reductions[a] of N-(α-Aminobenzyl)amides over Palladium-on-charcoal



-R"	$-N{<}^{R}_{R'}$	Solvent	Hydrogenation time (hr)	Yild[b] of N-benzylamide (%)
$-CH_3$		AcOH EtOH	4.8 29.0	90 58[c]
		AcOH	3.3	88
	$-N{<}^{CH_3}_{CH_3}$	AcOH	1.4	88
		AcOH	3.0	79
		AcOH	26.0	88
		AcOH	5.5	90
	$-N{<}^{CH_3}_{CH_3}$	AcOH	20.5	76
		AcOH	7.0	84

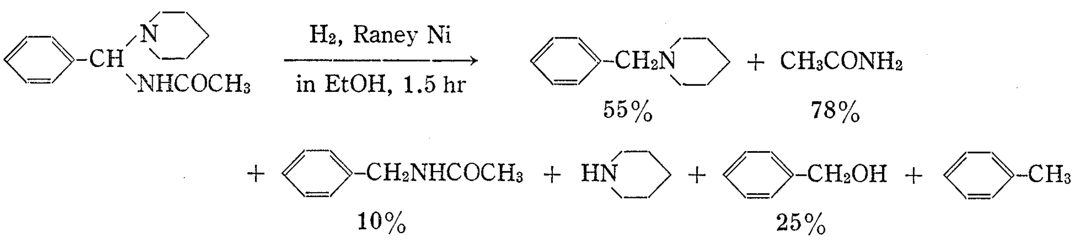
a) substrate; 0.04 mole, solvent; 100 ml, catalyst; 10% Pd-C 1 g, hydrogenation temp; 10—12° Hydrogenation was interrupted after uptake of one molar equiv. of hydrogen.

b) Yield is based on the product isolated.

c) In this run, hydrogenation was interrupted before uptake of one molar equiv. of hydrogen, and 38% recovery of the statring N-(α-piperidinobenzyl)acetamide was confirmed by gas chromatographic measurement.

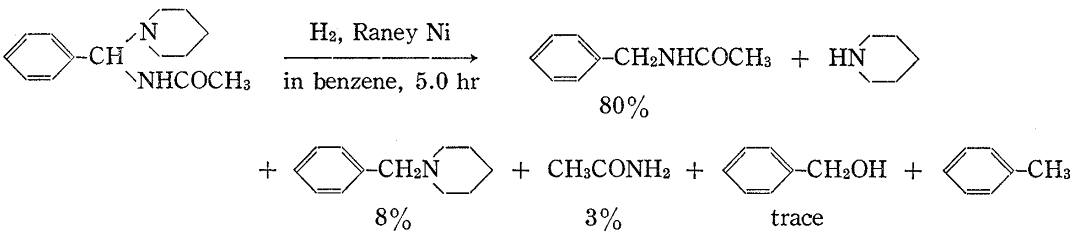
to occur exclusively. The reduction in ethanol also showed the same, but very slow hydrogenolysis (see Table III). Examined results of catalytic reductions of a number of N-(α-aminobenyl)acetamides and -benzamides with varying amine residues mostly in acetic acid, summarized in Table III, generally show that hydrogenolysis of the α-carbon-amine nitrogen bond occurred predominantly under the conditions adopted.

This hydrogenolysis mode of N-(α-aminobenzyl)amides was noticeable in contrast with that observed for the previously reported analogous methylene compounds, N-(aminomethyl)-amides,⁵⁾ where predominant hydrogenolysis takes place at the carbon-amide nitrogen bond under the condition using palladium-on-charcoal catalyst not only in acetic acid but also in ethanol and dioxane. This latter mode of hydrogenolysis has been also reported to occur with N-(aminomethyl)amides⁵⁾ and N-(α-aminobenzyl)amides⁶⁾ under the condition using Raney nickel catalyst under high hydrogen pressure at elevated temperature in ethanol, dioxane and pyridine for the former amides and in ethanol for the latter. In order to ascertain this report, N-(α-piperidinobenzyl)acetamide was then subjected to catalytic reduction over Raney nickel catalyst under high hydrogen pressure using ethanol as a solvent. Result is shown in the following.



Major products are seen from this result to be N-benzylpiperidine and acetamide. This indicates that in the mode similar to the previous report⁶⁾ the hydrogenolysis at the α-carbon-amide nitrogen bond is favorable under the condition, in contrast to the hydrogenolysis under ordinary hydrogen pressure over palladium-on-charcoal catalyst.

Further experiment with the same substrate under the same condition, but using benzene as a solvent in place of ethanol, gave the following result.



In this run the formation of N-benzylacetamide derived from the hydrogenolysis at the α-carbon-amine nitrogen bond seemed predominant, in contrast to the foresaid experiment in ethanolic medium. In both experiments described above, the products, N-benzylacetamide, N-benzylpiperidine, acetamide and benzyl alcohol were isolated by fractional distillation, and the other products, piperidine and toluene, were identified by gas chromatographic method. It is inferred that benzyl alcohol is a hydrogenation product from benzaldehyde formed by hydrolysis of the substrate and that toluene is a secondary hydrogenolysis product, possibly from benzyl alcohol, N-benzylpiperidine and/or N-benzylacetamide.

In order to obtain more accurate data on the selectivity of hydrogenolysis of the two carbon-nitrogen bonds in varying solvent, the catalytic reduction in various solvents under

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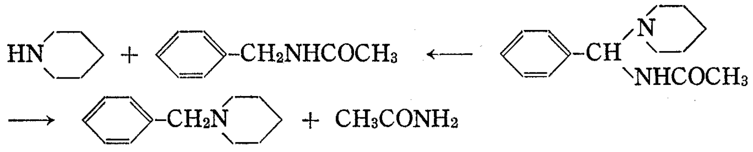
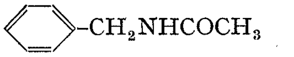
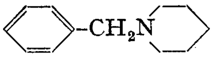
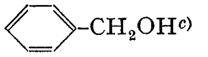
5) M. Sekiya and K. Ito, *Chem. Pharm. Bull.* (Tokyo), **14**, 996 (1966).
6) M. Sekiya and K. Ito, *Chem. Pharm. Bull.* (Tokyo), **11**, 892 (1963).

TABLE IV. Catalytic Reductions[a] of N-(α-Piperidinobenzyl)-acetamide over Raney Nickel



Solvent	Yield[b] (%)		
	A 	B 	C 
EtOH	17	31	17
BuOH	18	21	15
benzene	25	1	1.5
dioxane	18	0.5	0.1

Solvent	Recovery[d] of substrate	Proportion[e] of hydrogenolysis	Proportion[f] of hydrogenolysis site	
			>CH-N<	>CH-NHCO-
EtOH	31	48	36	64
BuOH	41	39	46	54
benzene	71	26	96	4
dioxane	77	18.5	97	3

a) substrate; 0.05 mole, solvent; 100 ml, catalyst; Raney nickel 4 g as 50% alloy, initial hydrogen pressure; 80 kg/cm², Hydrogenation temp.: 78—80° Hydrogenation was interrupted after 45 min.
b) Yield was calculated from peak area of their gas chromatogram.
c) Benzyl alcohol is presumed to be hydrogenation product of benzaldehyde formed through hydrolysis of the substrate.
d) Recovery of substrate was measured as benzaldehyde which was obtained by hydrolysis of a part of the reaction solution.
e) Percentage of proportion of direct hydrogenolysis of the substrate which was obtained by adding A and B.
f) Proportion of A:B which means proportion of hydrogenolysis occurred at both reaction sites.

standardized conditions were carried out at moderate temperature (78—80°) and interrupted after initial 45 minutes so as to avoid the secondary hydrogenolyses as far as possible. Data of the experiments are summarized in Table IV, where solvent effect on the hydrogenolyses is shown for ethanol, butanol, benzene and dioxane. As can be seen, the hydrogenolysis of the carbon-amide nitrogen bond occurs predominantly in alcoholic solvent, whereas predominant hydrogenolysis at the carbon-amine nitrogen bond occurs in aprotic solvent.

Other selected N-(α-aminobenzyl)acetamide, N-(α-morpholinobenzyl)acetamide and N-(α-N'-methylbenzylaminobenzyl)acetamide, were also subjected to catalytic reduction in butanol using Raney nickel catalyst under 70 kg/cm² of initial hydrogen pressure at 105—110°. Similar tendencies in hydrogenolysis were observed in these substrates. Observed proportion of the hydrogenolyses of the α-carbon bond bound to amine and amide nitrogen, based on the products isolated, were 58% for the former and 46% for the latter.

Experimental

Catalytic Reductions of N,N′-Benzylidenediamines over Palladium-on-charcoal——General Procedure: The following N,N′-benzylidendiamines shown with their melting points or boiling point were prepared according to the method reported by Sekiya, *et al.*[7] and used as substrates for the catalytic reduction: N,

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[7] M. Sekiya and H. Sakai, *Chem. Pharm. Bull.* (Tokyo), **17**, 32 (1969).

N′-benzylidenedipyrrolidine, mp 41—42°; N,N′-benzylidenedipiperidine, mp 81—82°; N,N′-benzylidenebisdimethylamine, bp 71—72° (5 mmHg); N,N′-benzylidenebis(N-methylbenzylamine), mp 44—45°; N,N′-benzylidenedimorphline, mp 105—106°.

To a solution of 0.02 mole of N,N′-benzylidenediamine dissolved in 40 ml of requisite solvent (ethanol and benzene) 0.2 g of 20% palladium-on-charcoal was suspended. The mixture was catalytically hydrogenated with constant stirring under ordinary pressure at room temperature (10—12°). After uptake of one molar equiv. of hydrogen, the catalyst was removed by filtration and the filtrate was concentrated under reduced pressure. Distillation of the residual liquid under reduced pressure gave tertiary amine product, which was identified by comparison of its IR spectrum with that of an authentic sample. In most runs, the distillate in the above concentration contained the secondary amine product, which was identified as picrate. In the run with N,N′-benzylidenebis(N-methylbenzylamine) separation of secondary and tertiary amine was made by fractional distillation. Existence of toluene in the reaction mixture was confirmed by gas chromatography using a column packed with 15% diethyleneglycol succinate on chromosorb P.

Data of the above catalytic reductions are listed in Table I. The following are physical and analytical data of the tertiary amines obtained. N-benzylpyrrolidine, bp 114—115° (20 mmHg). n_D^{25} 1.5267. *Anal.* Calcd. for $C_{11}H_{15}N$: C, 81.93; H, 9.38; N, 8.69. Found: C, 81.42; H, 9.18; N, 8.48. N-Benzylpiperidine, bp 119—120° (15 mmHg). n_D^{27} 1.5218. *Anal.* Calcd. for $C_{15}H_{17}N$: C, 85.26; H, 8.11; N, 6.63. Found: C, 85.34; H, 7.80; N, 6.49. N,N-Dimethylbenzylamine, bp 70—71° (15 mmHg). n_D^{25} 1.5005. *Anal.* Calcd. for $C_9H_{13}N$: C, 79.95; H, 9.61; N, 10.36. Found: C, 79.14; H, 9.51; N, 9.88. N-Methyldibenzylamine, bp 162—163° (15 mmHg). n_D^{27} 1.5548. *Anal.* Calcd. for $C_{15}H_{17}N$: C, 85.26; H, 8.11; N, 6.63. Found: C, 85.34; H, 7.80; N, 6.49. N-Benzylmorpholine, bp 130—131° (15 mmHg). n_D^{19} 1.5253. *Anal.* Calcd. for $C_{11}H_{15}ON$: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.05; H, 8.59; N, 7.83.

Catalytic Reductions of O,O′-Benzylidenediether over Palladium-on-charcoal——i) Catalytic Reduction of Benzaldehyde Dibutylacetal: To a solution of 23.6 g (0.1 mole) of benzaldehyde dibutylacetal (bp 113° (4 mmHg), n_D^{27} 1.4721) dissolved in 250 ml of butanol was added 1 g of 10% palladium-on-charcoal and the mixture was catalytically hydrogenated under ordinary hydrogen pressure at room temperature (28°). After uptake of one equiv. of hydrogen (*ca.* 1.2 hr), the catalyst was removed by filtration and the solution was concentrated. The residual liquid was fractionally distilled under reduced pressure to give 6.5 g (40%) of benzylbutyl ether, bp 110—111° (22 mmHg). n_D^{30} 1.4805. *Anal.* Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 79.65; H, 9.73. The starting benzaldehyde dibutylacetal (27%) was recovered as a successive distillate. Existence of toluene in the reaction solution was confirmed by the same manner as in the foregoing experiment.

ii) Catalytic Reduction of Benzylidene diacetate: To a solution of 20.8 g (0.1 mole) of benzylidene diacetate dissolved in 250 ml of butanol was added 1 g of 10% palladium-on-charcoal. The mixture was catalytically hydrogenated under ordinary hydrogen pressure at room temperature (17°). Uptake of one molar equiv. of hydrogen was completed after 35 hr. Concentration of the reaction solution gave 48% recovery of the starting benzylidene diacetate. Existence of toluene in the reaction mixture was analyzed quantitatively by gas chromatography using the same column as described above. Yield of toluene, 45%.

Catalytic Reductions of α-Butoxybenzylamines——i) Catalytic Reductions over Palladium-on-charcoal: The following α-butoxybenzylamines shown with their boiling points were prepared according to Stewart's method[8] and used as substrates for the catalytic reduction: N-(α-Butoxybenzyl)piperidine, bp 128° (0.2 mmHg). n_D^{26} 1.5051. N-(α-Butoxybenzyl)dimethylamine, bp 89—90° (0.2 mmHg), n_D^{26} 1.4880. N-(α-Butoxybenzyl)-N-methylbenzylamine, bp 137—139° (0.001 mmHg). n_D^{28} 1.5312; N-(α-butoxybenzyl)morpholine, bp 129—130° (0.5 mmHg). n_D^{19} 1.5011.

To a solution of 0.04 mole of α-butoxybenzylamine dissolved in 100 ml of requisite solvent (benzene and dioxane) was added 1 g of 10% palladium-on-charcoal. The mixture was catalytically hydrogenated under ordinary hydrogen pressure at room temperature (26—30°). After uptake of one molar equiv. of hydrogen the catalyst was filtered off and the solution was concentrated under reduced pressure. The tertiary amine product was obtained by distillation of the residual liquid under reduced pressure. The products obtained were identified by comparison of their IR spectra with those of authentic samples. In the run with N-(α-butoxybenzyl)-N-methylbenzylamine in isopropyl ether, butanol and toluene were analyzed quantitatively by gas chromatographic method using a column packed with 15% diethyleneglycol succinate on chromosorb P.

Conditions and the yields of the products are described in Table II. The tertiary amine products obtained in the above hydrogenation are the same as obtained in the foregoing catalytic reductions of N,N′-benzylidenediamines.

ii) Catalytic Reduction of N-(α-Butoxybenzyl)piperidine over Raney Nickel under High Hydrogen Pressure: In an autoclave 12.4 g (0.05 mole) of N-(α-butoxybenzyl)piperidine, 100 ml of dioxane and 1 g (as 50% alloy) of Raney nickel were placed. Under 80 kg/cm² (13°) of initial hydrogen pressure the mixture was heated and agitation was started at 65—70° and continued until uptake of hydrogen was al-

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[8] A.T. Stewart and C.R. Hauser, *J. Am. Chem. Soc.*, 77, 1098 (1955).

most ceased. Reaction time, 3.5 hr. After removal of the catalyst and concentration of the solution, the residual liquid was distilled under reduced pressure to give N-benzylpiperidine, bp 107—110° (12 mmHg), weighing 7.8 g (89%). Its IR spectrum was in good agreement with that of authentic sample.

Catalytic Reductions of N-(α-Aminobenzyl)amides——i) Catalytic Reductions over Palladium-on-charcoal: The following N-(α-aminobenzyl)amides shown with their melting points were prepared according to the method reported by Sekiya, *et al.*,[7] and were used as substrates for the catalytic reduction: N-(α-piperidinobenzyl)acetamide, mp 144—145°; N-(α-morpholinobenzyl)acetamide, mp 142—143°; N-(α-dimethylaminobenzyl)acetamide, mp 144—145°; N-(α-N′-methylbenzylaminobenzyl)acetamide, mp 145—146°; N-(α-piperidinobenzyl)benzamide, mp 158—159°; N-(α-morpholinobeznyl)benzamide, mp 145—146°; N-(α-dimethylaminobenzyl)benzamide, mp 90—92°; N-(α-N′-methylbenzylaminobenzyl)benzamide, mp 112—113°.

To a solution of 0.04 mole of N-(α-aminobenzyl)amide dissolved in 100 ml of acetic acid was added 1 g of 10% palladium-on-charcoal. The mixture was catalytically hydrogenated under ordinary hydrogen pressure at room temperature (13—16°). After uptake of one molar equiv. of hydrogen, the catalyst was removed by filtration and the filtrate was concentrated under reduced pressure. The residue was composed of N-benzylacetamide or N-benzylbenzamide, which were purified by distillation under reduced pressure or by recrystallization. Identities of these compounds were made by comparison of their IR spectra with those of authentic samples and by mixed melting point tests. The formation of the secondary amine product which should be formed was confirmed in the run with N-(α-piperidinobenzyl)acetamide as N-acetylpiperidine.

Selected N-(α-piperidinobenzyl)acetamide as representative, catalytic reduction under the condition similar to the above were examined using benzene, dioxane and ethanol in place of acetic acid. However, uptake of hydrogen was hardly observed when benzene and dioxane were used as solvent. In the run using ethanol, uptake of hydrogen proceeded gradually. After 29 hr treatment of the reaction mixture gave N-benzylacetamide in 58% yield which was confirmed and analyzed by gas chromatographic method using a column packed with 20% carbowax 20M on 10% KOH-chromosorb W. In addition to this product 38% recovery of the substrate was obtained as benzaldehyde from gas chromatogram (column; 15% diethyleneglycol on chromosorb P) of the hydrolytic solution obtained by heating the reaction mixture with 80% ethanol at 80° for 1 hr.

Data of the above catalytic reductions are recorded in Table III.

ii) Catalytic Reductions over Raney Nickel under High Hydrogen Pressure: In an autoclave 0.05 mole of N-(α-aminobenzyl)acetamide, 100 ml of requisite solvent and 2—4 g of Raney nickel (as 50% alloy) were placed under 70—80 kg/cm^2 of initial hydrogen pressure, and the mixture was heated. At limited range of temperature constant agitation was continued. After the hydrogenation the catalyst was removed by filtration.

In the run with N-(α-piperidinobenzyl)acetamide the yields of the products, N-benzylacetamide, N-benzylpiperidine and benzyl alcohol shown in Table IV, were determined by gas chromatographic measurement of the reaction solution using a column packed with 20% carbowax 20M on 10% KOH-Chromosorb W. Recovery of the substrate was confirmed as benzaldehyde by hydrolytic method.

In several runs, the following procedure was carried out for the product isolation. After removal of solvent from the reaction solution, the residual liquid was subjected to distillation under reduced pressure to give the following distillates. The first distillate, bp 60—130° (15 mmHg), was mainly composed of benzyl alcohol, acetamide and N,N-dialkylbenzylamine. From this mixture, acetamide was remained insoluble on extraction with petr. ether and fractional distillation of the solute of the extract under reduced pressure gave benzyl alcohol and N,N-dialkylbenzylamine, which were identified by comparison with IR spectra of authentic samples. The second distillate, bp 129—130° (0.1 mmHg), was shown to be N-benzylacetamide.

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