Hydrogenation and Hydrogenolysis. XV.[1] Hydrogenation of Isomeric Anisidines with Platinum Metal Catalysts in Acetic Acid

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m-Anisidine was hydrogenolyzed to an extent of 92.5% in hydrogenation with a palladium catalyst in acetic acid at 60 °C and 90 kg/cm². The amount of hydrogenolysis in *o*- and *p*-anisidine was only 2.1 and 2.5%, respectively. This great difference in hydrogenolysis between the isomers was not observed with rhodium and platinum catalysts. With *m*- and *p*-anisidines, selectivity at the initiation of hydrogenation was studied for the formation of *N*-cyclohexylanisidine intermediates and for other products by an extrapolation method. Extensive hydrogenolysis of *m*-anisidine and slight hydrogenolysis of *o*- and *p*-anisidines over palladium result from a high selectivity in the formation of the enamine or imine intermediates. The hydrogenation pathways leading to hydrogenolysis and secondary amine formation over the three platinum metals are discussed.

In a previous paper,[2] it was shown that *m*-anisidine and *m*-phenetidine are hydrogenolyzed with a ruthenium catalyst to greater extents than the corresponding *ortho* and *para* isomers. With a rhodium catalyst, however, no appreciable difference in the amount of hydrogenolysis was observed among the isomers.[3] The ease of hydrogenolysis in the *meta* isomer over the *ortho* and *para* isomers was also observed in the hydrogenation of isomeric dimethoxybenzenes with platinum metal catalysts.[4] It has been suggested that the ready hydrogenolysis of methoxyl group in the *meta* isomers is due to the presence of electron releasing methoxy or amino group located *meta* to the methoxyl group to be hydrogenolyzed. The allyl-type ethers, formed as intermediates, have been assumed to hydrogenolyze readily, since the electron releasing groups would stabilize the transition states of carbonium ion character when the allyl ether intermediates are hydrogenolyzed. On the other hand, the electron releasing groups such as methoxy and amino might influence the distribution of various dihydro and tetrahydro intermediates in hydrogenation of aromatic compounds and thus cause differences in the amount of hydrogenolysis among the isomers.

In view of the pronounced effects of some electron releasing groups on the distribution of intermediates, as observed in the palladium-catalyzed hydrogenation of isomeric cresols[5] and ethyl tolyl ethers,[1,6] we have been interested in the hydrogenation of isomeric anisidines with a palladium catalyst. The presence of the amino group might lead to preferential formation of enamine or imine intermediate, which is expected to cause a great difference in the extent of hydrogenolysis among the isomers. In this investigation, acetic acid was chosen as the solvent, since anilines are hydrogenated most readily with palladium in this solvent,[7,8] and extensive formation of *N*-cyclohexylaniline as an intermediate allows to estimate the amount of the enamine or imine intermediate.[8] Anisidines were also hydrogenated using rhodium and platinum as catalysts under the same conditions in order to compare their selectivities with those of palladium.

The hydrogenation of anisidines with platinum metal catalysts was previously studied by Freifelder, Ng, and Helgren,[7] using ethanol–acetic acid and acetic acid as solvents. However, neither detailed analyses of high boiling products nor investigation of intermediates were made.

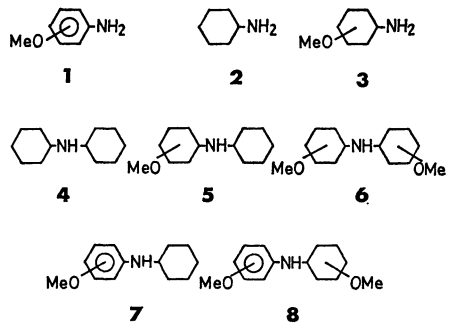
Results

Products of the hydrogenation of isomeric anisidines with 5% palladium-carbon, rhodium and 5% platinum-carbon catalysts in acetic acid at 60 °C under a hydro-

Table 1. Hydrogenation of anisidines with palladium, rhodium and platinum catalysts in acetic acid[a]

Anisidine	Catalyst	Composition of reac. mixture (%)[b]							
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Ortho	Pd/C	0.0	0.9	46.2	0.1	2.2	50.6	0.0	0.0
Meta	Pd/C	0.0	50.8	2.4	36.5	10.3	0.0	0.0	0.0
Para	Pd/C	0.0	1.0	34.8	0.3	2.4	61.5	0.0	0.0
Ortho	Rh[c]	0.0	4.4	62.7	0.8	5.0	22.3	0.0	0.0
Meta	Rh	0.0	10.1	72.4	5.3	12.2	0.0	0.0	0.0
Para	Rh	0.0	11.4	71.0	0.2	4.6	12.8	0.0	0.0
Meta	Pt/C	33.4	12.8	14.2	12.2	14.2	0.0	13.2	0.0
Para	Pt/C	16.8	8.7	8.1	17.1	27.2	7.5	9.1	5.5

a) The anisidine (0.03 mol) was hydrogenated in 15 ml acetic acid at 60 °C under 90±10 kg/cm² hydrogen pressure. b) Values are based on mol% of anisidine consumed for the formation of each compound. **1**: anisidine; **2**: cyclohexylamine; **3**: methoxycyclohexylamine; **4**: dicyclohexylamine; **5**: methoxydicyclohexylamine; **6**: dimethoxydicyclohexylamine; **7**: *N*-cyclohexylanisidine; **8**: *N*-(methoxycyclohexyl)anisidine. Trace amounts of cyclohexane, cyclohexanol, methoxycyclohexane and methoxycyclohexanol were formed besides the compounds given in the table. c) 4.8% of 2-methoxycyclohexanol was found in the products.



[The letters **a**, **b** and **c** attached to the compound numbers refer to the products from *o*-, *m*- and *p*-anisidine, respectively]

gen pressure of 90±10 kg/cm² are summarized in Table 1. Acetylation of anisidines always occurs to 2—23% extent under these conditions, the hydrogenation of the acetylation products being very slow. It was confirmed that neither the acetylation of saturated amines nor the transformation of 2 mol of saturated primary amine into secondary amine occurs under these conditions. The acetylation products are excluded from the composition of the reaction mixture in Table 1.

The proportion of hydrogenolysis was calculated according to

$$\frac{\%\ \text{yield}\ (\mathbf{2}+\mathbf{4}+(1/2)\times\mathbf{5}+(1/2)\times\mathbf{7})}{\%\ \text{of}\ \mathbf{1}\ \text{hydrogenated}}\times 100 \qquad (1)$$

using the data in Table 1. The results are given in Table 2.

The proportion of secondary amines in the product was calculated according to:

Table 2. Proportion of hydrogenolysis in hydrogenation of isomeric anisidines (%)

Catalyst	Anisidine		
	Ortho	*Meta*	*Para*
Pd/C	2.1	92.5	2.5
Rh	7.7	21.5	13.9
Pt/C	—	64.5[a)]	57.9[b)]

a) At 60.0% ring hydrogenation. b) At 75.9% ring hydrogenation.

Table 3. Proportion of secondary amines in the product from hydrogenation of isomeric anisidines (%)[a)].

Catalyst	Anisidine		
	Ortho	*Meta*	*Para*
Pd/C	52.9(36.0)	46.8(30.5)	64.2(47.3)
Rh	28.1(16.3)	17.5(9.60)	17.6(9.65)
Pt/C	—	59.5(42.3)[b)]	79.8(66.4)[c)]

a) Calculated according to Formula (2). Selectivity in mol% calculated according to Formula (3) is given in parentheses. b) At 66.6% conversion of *m*-anisidine. c) At 83.2% conversion of *p*-anisidine.

$$\frac{\%\ \text{yield}\ (\mathbf{4}+\mathbf{5}+\mathbf{6}+\mathbf{7}+\mathbf{8})}{\%\ \text{of}\ \mathbf{1}\ \text{converted}}\times 100 \qquad (2)$$

using the data in Table 1. The results are given in Table 3. The selectivity for secondary amine formation in mol% is given by

$$\frac{\%\ \text{yield}\ [(1/2)(\mathbf{4}+\mathbf{5}+\mathbf{6}+\mathbf{7}+\mathbf{8})]}{\%\ \text{yield}\ [\mathbf{2}+\mathbf{3}+(1/2)(\mathbf{4}+\mathbf{5}+\mathbf{6}+\mathbf{7}+\mathbf{8})]}\times 100 \qquad (3)$$

The effects of hydrogen pressure on hydrogenolysis and secondary amine formation in the hydrogenation with palladium and rhodium catalysts are shown in Figs. 1 and 2. In accord with the results obtained previously,[9] the amount of hydrogenolysis always decreased with increasing hydrogen pressure. The effect of hydrogen pressure on secondary amine formation is not so straightforward. Formation of secondary amines increases with increasing pressure with a palladium catalyst, whereas a reverse trend was observed with a rhodium catalyst.

In order to obtain information on intermediates, the variation in the composition of reaction mixture with hydrogenation was studied with *m*- and *p*-anisidines. The results are shown in Figs. 3—8. By extrapolating the selectivity for saturated primary

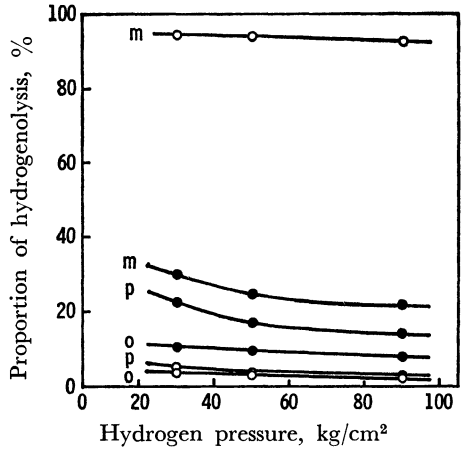


Fig. 1. Effect of hydrogen pressure on hydrogenolysis in hydrogenation of anisidines with Pd-C and Rh catalysts (AcOH, 60 °C). ○ Pd-C; ● Rh.

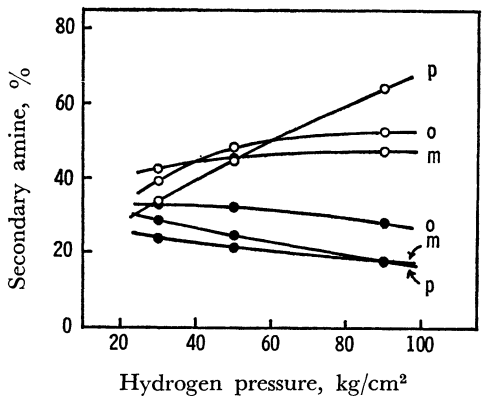


Fig. 2. Effect of hydrogen pressure on secondary amine formation in hydrogenation of anisidines with Pd-C and Rh catalysts (AcOH, 60 °C). ○ Pd-C; ● Rh.

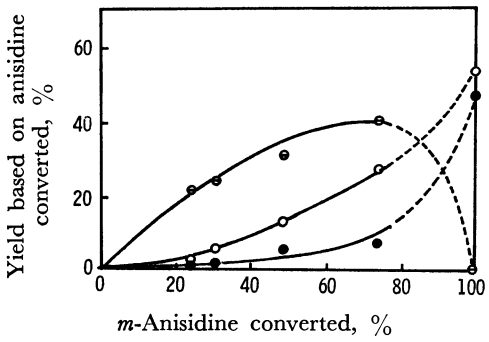


Fig. 3. Hydrogenation of *m*-anisidine with Pd-C catalyst in acetic acid. ⊖ *N*-Cyclohexyl-*m*-anisidine; ○ saturated primary amines; ● saturated secondary amines.

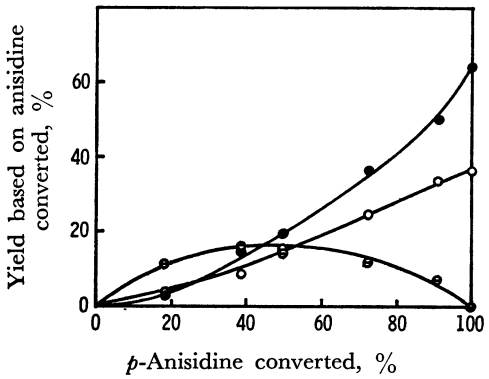


Fig. 4. Hydrogenation of *p*-anisidine with Pd-C catalyst in acetic acid. ⊖ *N*-(4-Methoxycyclohexyl)-*p*-anisidine. For other indications, see Fig. 3.

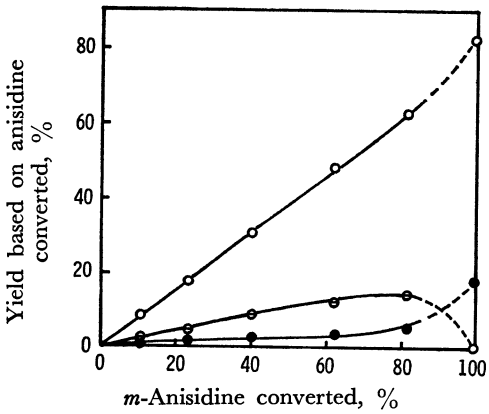


Fig. 5. Hydrogenation of *m*-anisidine with Rh catalyst in acetic acid. For indications, see Fig. 3.

amines, saturated secondary amines, and *N*-cyclohexylanisidines, together with the composition of reaction mixtures, the selectivity for individual products at the initiation of hydrogenation was obtained. The results are summarized in Table 4.

In order to know the behavior of *N*-cyclohexylanisidines, *N*-cyclohexyl-*m*-anisidine (**7b**) and *N*-(4-methoxycyclohexyl)-*p*-anisidine (**8c**) were hydrogenated in the presence of an equimolar amount of ammonium acetate (Table 5). Ammonia is formed together with *N*-cyclohexylanisidines in the hydrogenation of

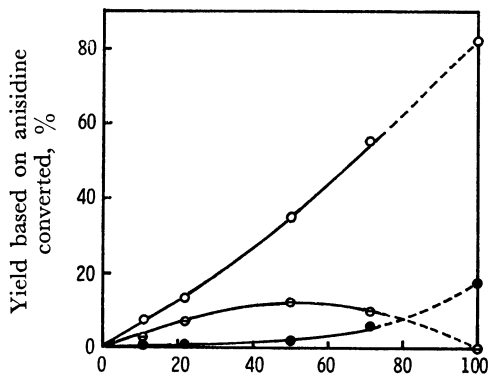


Fig. 6. Hydrogenation of *p*-anisidine with Rh catalyst in acetic acid. ⊖ *N*-Cyclohexyl- and *N*-(4-methoxycyclohexyl)-*p*-anisidine. For other indications see Fig. 3.

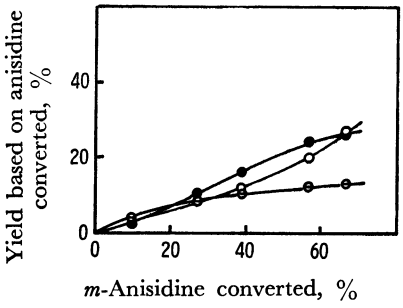


Fig. 7. Hydrogenation of *m*-anisidine with Pt-C catalyst in acetic acid. For indications, see Fig. 3.

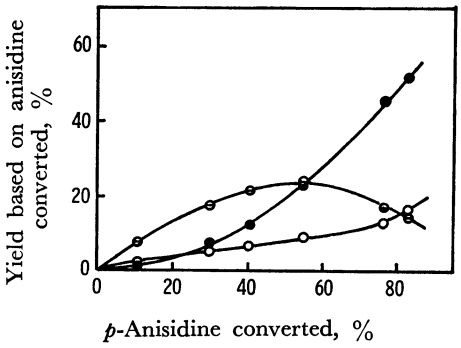


Fig. 8. Hydrogenation of *p*-anisidine with Pt-C catalyst in acetic acid. For indications, see Fig. 6.

anisidines. Its presence may have considerable influence on the course of the hydrogenation of the *N*-cyclohexylanisidines.[8]

Discussion

We see from Table 2 that the ease of hydrogenolysis in the *meta* isomer over the *ortho* and *para* isomers is most pronounced in the palladium-catalyzed hydrogenation. The amount of hydrogenolysis is as large as 92.5% in the *meta* isomer, whereas in the *ortho* and *para* isomers it is only 2.1 and 2.5%, respectively. The same trend is also seen over rhodium and platinum catalysts, although the difference in the amount of hydrogenolysis between the isomers is much smaller.

Table 4. Selectivity for formation of individual products at the initiation of hydrogenation as obtained by extrapolation (%)[a]

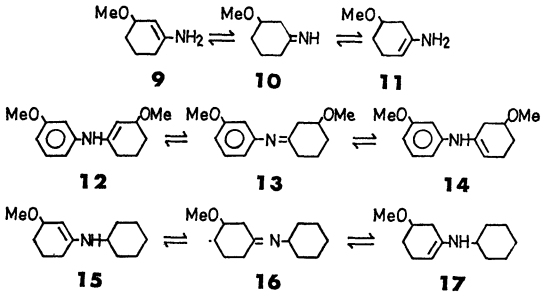
Anisidine	Catalyst	Selectivity for					Selectivity for secondary amines (mol%)[b]
		2	3	4+5+6	7	8	
Meta	Pd/C	2.1	0.5	0.0	97.4	0.0	94.9
Para	Pd/C	0.6	17.0	0.0	0.0	82.4	70.1
Meta	Rh	7.1	66.9	3.0	23.0	0.0	14.9
Para	Rh	9.3	52.7	5.0	7.3	25.7	23.5
Meta	Pt/C	23.8	9.2	5.0	62.0	0.0	50.4
Para	Pt/C	12.4	7.6	4.0	57.7	18.3	66.7

a) See footnote b, Table 1. b) Calculated according to Formula (3).

Table 5. Hydrogenation of *N*-cyclohexylanisidines in the presence of ammonium acetate[a]

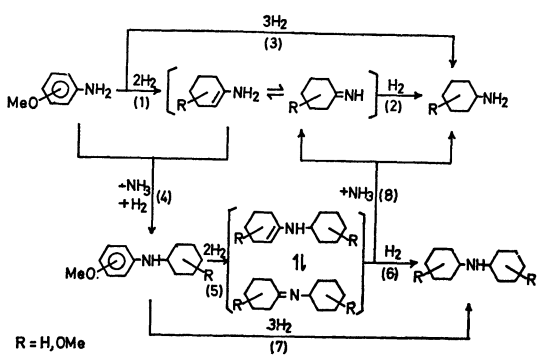
Compound[b]	Catalyst	Composition of reaction mixture (%)[c]					
		2	3	4	5	6	7b or 8c
7b	Pd/C	50.2	0.0	39.6	10.2	—	0.0
8c	Pd/C	0.2	26.3	—	2.4	71.1	0.0
7b	Rh	7.6	0.4	36.3	55.7	—	0.0
8c	Rh	0.0	0.5	—	18.5	81.0	0.0
7b	Pt/C	0.6	0.0	64.1	35.3	—	0.0

a) The compound (0.015 mol) was hydrogenated in 15 ml acetic acid at 60 °C under 90±10 kg/cm² with addition of 0.015 mol of ammonium acetate. b) **7b**: *N*-cyclohexyl-*m*-anisidine; **8c**: *N*-(4-methoxycyclohexyl)-*p*-anisidine. c) See footnote b, Table 1.



A noteworthy feature of the hydrogenation of *m*-anisidine is that complete loss of the methoxyl group was observed in *N*-cyclohexyl-*m*-anisidine intermediate with any of the catalysts investigated (Table 4). The result strongly suggests that the extensive hydrogenolysis in *m*-anisidine is related to the formation of allyl ether type enamines **9**, **12** or the corresponding imines **10**, **13**.[10] Enamines **11** and **14** are expected to isomerize readily to **9**, **10** and **12**, **13**, respectively, over the catalyst and their formation would also contribute to the extensive hydrogenolysis. The extremely high degree of hydrogenolysis of *m*-anisidine with a palladium catalyst may be explained by a high selectivity for formation of these enamines or imines, as indicated by the formation of **7b** in a selectivity of 94.9 mol%. Hydrogenolysis also occurred extensively in hydrogenation of **7b** with the palladium catalyst, which amounted to 89.8% (Table 5). It is probable that, as in the case of *m*-anisidine, **7b** is hydrogenated mostly through enamines **15**, **17** or imine **16** which are also expected to be readily susceptible to hydrogenolysis.

In accord with the finding by Ikedate *et al.*,[8] hydrogenation of **7b** and **8c** in the presence of ammonium acetate led to the formation of considerable amounts of primary amines with palladium (Table 5). This course of primary amine formation also occurred with the rhodium catalyst but to a much lesser extent, and practically not occurring at all with platinum (Table 5). The effect of increasing hydrogen pressure to increase the secondary amine formation with palladium (Fig. 2) can be explained by assuming that the hydrogenation of the enamines or imines from *N*-cyclohexylanisidines [step (6), Scheme 1] is more promoted by the increase of hydrogen pressure than the primary amine formation through the addition of ammonia [Step (8), Scheme 1]. In contrast to the palladium-catalyzed hydrogenation, this course of primary amine formation is not important with rhodium catalyst. Increase of hydrogen pressure would be favorable for the hydrogenation of the enamines or imines from anisidines [step (2), Scheme 1]. This may lead to



Scheme 1. Hydrogenation pathways of anisidines.

an increase in primary amine formation as seen in Fig. 2.

Very slight hydrogenolyses in *o*- and *p*-anisidines over palladium are noteworthy and could be understood in terms of high selectivity for enamine or imine formation over this metal. As in the case of *m*-anisidine, the selectivity for formation of *N*-cyclohexyl-*p*-anisidine intermediate is very high (70.1 mol%) (Table 4). However, in sharp contrast to the hydrogenation of *m*-anisidine, no loss of the methoxyl group was observed in the formation of this intermediate. Hydrogenation of the intermediate **8c** also gave only a small amount of hydrogenolysis (2.6%) (Table 5). The hydrogenation of *o*-anisidine appears very similar to that of *p*-anisidine. The results indicate that hydrogenolysis scarcely occurs at all in the course of the formation of enamine or imine intermediates as well as in their further hydrogenation in the cases of *o*- and *p*-anisidines. A probable course of hydrogenation leading to selective formation of the enamine or imine intermediate over palladium is suggested to be as shown in Scheme 2 for the hydrogenation of *p*-anisidine.

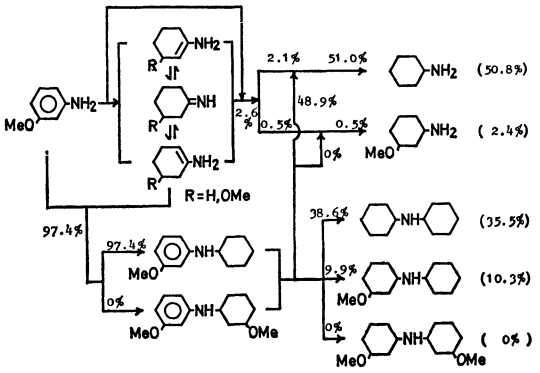
Scheme 2. Hydrogenation pathways leading to selective formation of the enamine or imine intermediate in *p*-anisidine.

The characteristic feature of the palladium-catalyzed hydrogenation of anisidines probably results from the selective hydrogenation of the enol ether moiety over the enamine moiety. This would lead to readily hydrogenolyzable enamines **9**, **11** or imine **10** in a high selectivity in the case of the *meta* isomer. Very poor tendency of palladium toward the hydrogenolysis of an enol ether,[1,11] might explain the occurrence of only slight hydrogenolysis in the course of the formation of enamines or imines in the case of *o*- and *p*-anisidines.

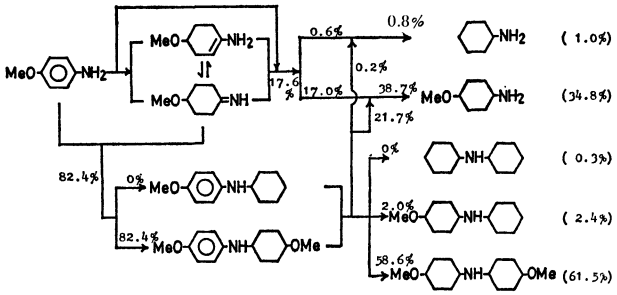
The primary amines formed at an initial stage of hydrogenation (Table 4) might arise through enamine or imine or through other unsaturated amines as intermediates. However, extensive hydrogenolysis at the primary amines from *m*-anisidine and slight hydrogenolysis at those from *p*-anisidine (Table 4) suggest that most of the primary amines is also formed through enamine or imine as an intermediate in the palladium-catalyzed hydrogenation.

On the basis of the results shown in Tables 4 and 5, the hydrogenation pathways of *m*- and *p*-anisidines over palladium are estimated to be those shown in Schemes 3 and 4. It is seen that the compositions of the products thus obtained are in good agreement with those in Table 1. They are also shown in parentheses theses in the Schemes.

In the rhodium-catalyzed hydrogenation, the formation of secondary amines is at low level and the formation of *N*-cyclohexylanisidines is not conspicuous. The selectivity for formation of secondary amines, however,



Scheme 3. Hydrogenation pathways of *m*-anisidine over a Pd-C catalyst in acetic acid (60 °C, 90±10 kg/cm² H_2).



Scheme 4. Hydrogenation pathways of *p*-anisidine over a Pd-C catalyst in acetic acid (60 °C, 90±10 kg/cm² H_2).

is larger at initiation than at complete hydrogenation, particularly in the case of *p*-anisidine. Since *N*-cyclohexylanisidines are mostly hydrogenated over rhodium catalyst to saturated secondary amines even in the presence of ammonium acetate (Table 5),[12] the result suggests that the selectivity for formation of *N*-cyclohexylanisidines decreases with decreasing concentration of anisidine in the course of hydrogenation. Accordingly the proportion of enamine or imine, formed from anisidine and hydrogenated directly to primary amine, might increase at a later stage of hydrogenation. This course of primary amine formation [step (2), Scheme 1] was suggested by Ikedate and Suzuki to be significant in the rhodium-catalyzed hydrogenation of aniline.[13] However, a great difference in the proportion of hydrogenolysis between the primary amines (9.6%) and *N*-cyclohexyl-*m*-anisidine (100%) found in the hydrogenation of *m*-anisidine (Table 4) suggests that most of the primary amines is formed in the rhodium-catalyzed hydrogenation through unsaturated amines as intermediates rather than through enamines or imines. A high degree of hydrogenolysis in the primary amines formed from the hydrogenation of **7b** (90%) (Table 5) might support the view, since it suggests that the formation of primary amines through enamines **9**, **11** or imine **10** would also result in extensive hydrogenolysis. It is of interest to note that, in line with the results with anisidines, 45—48% of cresol is hydrogenated to methylcyclohexanol through other intermediates

than methylcyclohexanone over a rhodium catalyst.[5] With palladium as a catalyst, however, all cresol is hydrogenated through the ketone as the intermediate.[5]

In the hydrogenation of anisidines with platinum, hydrogenolysis of the methoxy group as well as the formation of secondary amines occurred extensively. However, unlike the palladium-catalyzed hydrogenation, no great difference in the extent of hydrogenolysis was observed between *meta* and *para* isomers. An extensive loss of methoxyl group in *N*-cyclohexyl-*p*-anisidines (76%) (Table 4) indicates that hydrogenolysis has occurred extensively during the course of formation of enamine or imine intermediate. This result is plausible if we consider that platinum shows very high activity toward the hydrogenolysis of an enol ether.[1,11] The selectivity for formation of secondary amines does not differ much between the initiation and later stage of hydrogenation. With platinum considerable amounts of saturated secondary amines are formed together with *N*-cyclohexylanisidines (Figs. 7 and 8). However, when the selectivity for the formation of the saturated secondary amines is extrapolated to initiation, it is reduced to only a few percent (Table 4). Thus most of the secondary amines seems to be formed through *N*-cyclohexylanisidines as intermediates. Probably, in this case hydrogenation of the intermediates is fast as compared with that of anisidine. The same conclusion was also reached by Ikedate and Suzuki in the platinum-catalyzed hydrogenation of aniline.[13] Fairly large amounts of secondary amines formed over platinum indicate that the selectivity for the formation of enamine or imine intermediates is rather high over this metal.

Experimental

Materials. *o*-, *m*- and *p*-Anisidines (G. R. grade, Tokyo Kasei Kogyo) were used after distillation before use. *N*-cyclohexyl-*m*-anisidine (**7b**) and *N*-(4-methoxycyclohexyl)-*p*-anisidine (**8c**) were prepared by reductive condensation of the corresponding anisidine and cyclohexanone in isopropyl alcohol with 5% palladium–carbon at 35 °C and 3—7 kg/cm² pressure. **7b**: bp 175 °C/9 mmHg; **8c**: bp 175 °C/4 mmHg. The structures of **7b** and **8c** were confirmed by their NMR spectra (Table 6).

Catalysts. 5% Palladium-carbon and 5% platinum-carbon were obtained from Nippon Engelhard Co. Rhodium oxide was prepared by heating the rhodium hydroxide, precipitated from a hot rhodium chloride solution with an aqueous lithium hydroxide,[14] at 350 °C for 8 hr.

Solvent. The S. S. G. acetic acid (Wako Pure Chemical Ind.) was used without further purification.

Hydrogenations. All hydrogenations were carried out in a 40 ml stainless steel autoclave with a stirrer driven magnetically. The catalyst (0.2—3.2 g of the supported catalyst or 0.01—0.12 g of the oxide catalyst), the substrate (0.03 mol anisidine or 0.015 mol *N*-cyclohexylanisidine) and 15 ml acetic acid were put into the autoclave. After the air had been replaced by hydrogen, the autoclave was charged with hydrogen to the required pressure. The autoclave was then immersed in an oil bath maintained at 60±0.5 °C, hydrogenation being allowed to start after 20 min. The hydrogen pressure was kept constant within±10 kg/cm² during hydrogenation. The amount of catalyst used was adjusted to complete hydrogenation within a reasonable time (2—6 hr). Hydrogenation with the platinum catalyst became very

Table 6. Methoxy- and dimethoxydicyclohexylamines and *N*-cyclohexylanisidines

Compound	Bp (°C/mmHg)	n_D	NMR spectral data, δ[a]						
			Benzene ring protons	CH_3O (Benzene ring)	CH_3O (Cyclohexane ring)	$\diagdown CHO-$	$\diagdown CHNH-$	-NH-	Cyclohexane ring protons
5a	143.5/17	1.4811	—	—	3.24, 3H, s	3.1—3.4, 1H, m	2.2—2.8, 2H, m	0.7—2.1, 19H, bm	
6a	150/16	1.4808	—	—	3.24, 6H, s	3.1—3.4, 2H, m	2.6—2.9, 2H, m	0.8—2.2, 17H, bm	
5b	164/28	1.4833	—	—	3.30, 3H, s	3.2—3.4, 1H, m	2.2—2.8, 2H, m	0.8—2.2, 19H, bm	
5c	114—6/2	1.4824[b]	—	—	3.20, 3H, s	3.1—3.4, 1H, m	2.2—2.8, 2H, m	0.8—2.1, 19H, bm	
6c	181/17	1.4834[b]	—	—	3.20, 6H, s	3.1—3.4, 2H, m	2.4—2.9, 2H, m	0.8—2.2, 17H, bm	
7b	175/9	1.5568	6.8—7.2, 1H, t[$H_{(5)}$] 6.0—6.3, 3H, m[$H_{(3)}$,$H_{(4)}$,$H_{(6)}$]	3.67, 3H, s	—	—	2.8—3.3, 1H, m	3.33, 1H, s	0.8—2.3, 10H, bm
7c[c]	185/17[d]	—	6.7, 2H, d[$H_{(3)}$, $H_{(5)}$] 6.5, 2H, d[$H_{(2)}$, $H_{(6)}$]	3.53, 3H, s	—	—	2.8—3.3, 1H, m	3.20, 1H, s	0.7—2.2, 10H, bm
8c[c]	175/4[e]	—	6.7, 2H, d[$H_{(3)}$, $H_{(5)}$] 6.5, 2H, d[$H_{(2)}$, $H_{(6)}$]	3.50, 3H, s	3.10 3H, s	2.7—3.2, 2H, m		3.37, 1H, s	0.7—2.1, 8H, bm

a) Unless otherwise noted, the NMR spectra were obtained on a JEOL C-60HL spectrometer at 60 MHz using TMS as an internal standard at 25 °C in CCl_4 solution. b) n_D^{25}. c) The NMR spectra obtained at 50 °C in neat. d) Mp 42—43 °C. e) Solid at room temperature.

slow during the course of reaction and could not be completed by prolonging the reaction time (over 20 hr).

Analysis of Product. The reaction mixture was analyzed directly by gas chromatography. For low boiling products, a 3 mm×2.25 m column containing 10% PEG 6000—10% KOH on Chromosorb W was used in the temperature range 170—200 °C programmed at 4 °C/min. For high boiling products, a 3 mm×0.75 m column containing 30% PEG 20 M on Celite 545 was used at a temperature initially kept at 200 °C for 6 min and then programmed at 6 °C/min to 250 °C. For the separation of *N*-acetylanisidines and *N*-(methoxycyclohexyl)anisidines a combined column containing PEG 20M (3 mm×0.75 m) and OV-17 (3 mm×3 m) was used at 250 °C.

The secondary amines required for identification of the product peaks on gas chromatography were synthesized by the reductive condensation of the corresponding amines and cyclohexanones under the conditions described above for the preparation of **7b** and **8c**. Methoxycyclohexlamines for this condensation were prepared by hydrogenating the corresponding anisidines with ruthenium hydroxide as a catalyst in the presence of lithium hydroxide in isopropyl alcohol at 80 °C under 80—100 kg/cm².[2] The characteristics of the compounds synthesized are summarized in Table 6. The synthesis of 3,3′-dimethoxydicyclohexylamine (**6b**) and *N*-(3-methoxycyclohexyl)-*m*-anisidine (**8b**) was unsuccessful because of complete loss of the methoxyl group of the cyclohexanone component during the course of reductive condensation. Probable peaks of **6b** and **8b**, as inferred from the peaks of **6a**, **6c** and **8a**, **8c**, respectively, could not be found in the gas chromatograms of the products from hydrogenation of *m*-anisidine. A peak located around a probable peak region of **8b** was proved to be that of *N*-acetyl-*m*-anisidine by isolation with a gas chromatograph and measurement of its NMR spectrum. The gas chromatograms of the products at intermediate stages of hydrogenation often showed small peaks of *N*-cyclohexylideneanisidines in amounts less than 1%. They were added to the corresponding *N*-cyclohexylanisidines. *N*-Cyclohexylidenecyclohexylamines seem to undergo decomposition when subjected to gas chromatography in acetic acid solution. Their behavior on gas chromatography was not investigated further, but they can be neglected when we obtain the results in Table 4 by an extrapolation method. The peak areas were standardized by the mixtures of known compositions. This was done with *p*-anisidine and its hydrogenation products. The standardization for *o*- and *m*-anisidines and their hydrogenation products was approximated by applying that obtained with the *p*-anisidine series compounds.

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