Hydrogenation of *N*-Aryl Carbamates to *N*-Alicyclic Carbamates

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An economical, high-yield process is developed for the preparation of pure *N*-alicyclic carbamates by the rhodium-catalyzed hydrogenation of the corresponding *N*-aryl carbamates. The *N*-aryl carbamates are obtained by the simple reaction of low-cost aromatic isocyanates with an alcohol, preferably methanol.

Introduction

The preparative and commercial utility for the nuclear hydrogenation of *N*-aryl carbamates, particularly dicarbamates, to the corresponding *N*-alicyclic carbamates (Malz and Greenfield, 1978) is described.

We are unaware of any report of the nuclear hydrogenation of *N*-aryl carbamates. The palladium-catalyzed hydrogenation of an olefinic bond in aliphatic dicarbamates (Miyake et al., 1969), the platinum-catalyzed hydrogenation of the 3,4-olefinic bond in ring-substituted ethyl 1,2-dihydroquinoline-1-carboxylates (Scopes and Joule, 1972), and the palladium-catalyzed hydrogenolyses of the carbon–oxygen bond in *N*-phenyl carbamates formed from substituted phenols (Weaver et al., 1973) and formed from hydroxymethyl heterocyclic compounds (Kametani et al., 1958) have been described.

The *N*-alicyclic dicarbamates are of interest in the production of nondiscoloring *N*-alicyclic polyurethanes. One attractive route is the transesterification of the dicarbamates with polyols (Hubert et al., 1939; I. G. Farben, 1940; Caldwell, 1957; Haggis and Lambert, 1963; Miyake et al., 1969). A second route involves the conversion of the dicarbamates to the alicyclic isocyanates ordinarily used to produce such polyurethanes. This reaction has been extensively studied (Saunders and Frisch, 1962). High yields of diisocyanate have been obtained by pyrolysis of the corresponding carbamate when both reaction conditions and product isolation techniques minimize recombination of the isocyanate and alcohol products (De La Mater et al., 1975).

The most direct route to alicyclic isocyanates is the nuclear hydrogenation of the corresponding aromatic isocyanates. This requires an unlikely selective reduction of the aromatic ring in the presence of isocyanate groups. Attempted hydrogenations of phenyl isocyanate with nickel (Sabatier and Mailke, 1907) and palladium (Knopf, 1970) catalysts have been reported. No nuclear hydrogenation was detected in either case. Aniline, diphenylurea, and methane were obtained with the nickel catalyst. The palladium rapidly became poisoned, presumably from the products of the reduction of the isocyanate group. It has been suggested that the initial product is a formamide, with further hydrogenation to materials that poison the catalyst (Knopf, 1970). The hydrogenations of formanilide to *N*-cyclohexylformamide gave very low conversions with rhodium and ruthenium catalysts, probably because of similar poisoning (Malz and Greenfield, 1976). Our attempted nuclear hydrogenations of phenyl isocyanate were unsuccessful (Malz and Greenfield, 1972). Gas absorption indicated unsatisfactory conversions with platinum, palladium, rhodium, cobalt, and nickel catalysts. The results indicated that these catalysts became poisoned in each case. A ruthenium catalyst was unique in its resistance to poisoning, but gave *N*,*N*-dicyclohexylurea as the major product and no detectable cyclohexyl isocyanate.

Experimental Section and Results

Temperatures are in degrees Celsius; melting points are uncorrected. Raw materials were obtained from the following sources: phenyl isocyanate (practical) and 1-naphthyl isocyanate from Eastman Kodak; methylenedi-*p*-phenyl diisocyanate from Eastman Kodak (practical) and from Upjohn (Isonate 125MF); toluene diisocyanate (80:20 mixture of 2,4 and 2,6 isomers) from Rubicon; 1,5-naphthalene diisocyanate from Chemicals Procurement Laboratories; cyclohexyl isocyanate from Eastern Chemical Corp.; and *N*-methylaniline from Aldrich Chemical.

Most of the carbamates were prepared in approximately quantitative yield by the addition of the appropriate isocyanate to a stirred flask containing more than a sixfold excess of the appropriate anhydrous alcohol. The mixture was kept below reflux temperature until all the isocyanate had been added and then brought to and maintained at reflux for 1 h. The following carbamates were prepared in this manner: methyl carbanilate, mp 45.5–47 °C, lit. value 47 °C (Hofman, 1850); cyclohexyl carbanilate, mp 82–83 °C after recrystallization from hexane, lit. value 82.5 °C (Bouveault, 1904); and methyl 1-naphthylcarbamate, mp 121–122 °C, lit. value 124 °C (Bickel and French, 1926).

The following carbamates were prepared by addition of an anhydrous toluene slurry of the isocyanate to a mixture of anhydrous toluene and alcohol, both the toluene and alcohols having been dried by passage through a column of Linde 4-A Molecular Sieves: dimethyl 4,4′-methylenedicarbanilate, mp 185.5–186 °C, lit. value 183–183.5 °C (Siefken, 1949); diisopropyl 4,4′-methylenedicarbanilate (Dixon et al., 1972), mp 148.5–150 °C (not clear at 200 °C); a mixture of the dimethyl esters of 2,4- and 2,6-toluenedicarbamic acids (Siefken, 1949); and dimethyl 1,5-naphthalenedicarbamate, mp 249.5 °C (dec) after recrystallization from methanol, lit. value 245–246 °C (Siefken, 1949).

Ethyl *N*-methylcarbanilate, bp 85–90 °C (4–5 mm Hg) was prepared in 88% yield by the addition of ethyl chloroformate and dilute sodium hydroxide to a mixture of *N*-methylaniline (distilled before use), benzene, and water, following the general procedure of Dannley et al., 1954.

The 4,4′-methylenebis(*N*-methylaniline) was prepared by the reaction of *N*-methylaniline with aqueous formaldehyde and hydrochloric acid and melted at 54–55 °C after several recrystallizations from benzene–hexane, lit. value 54.4–56.2 °C (Sorenson and Campbell, 1968); 52.5–53.5 °C (Tomono et al., 1974).

Diethyl 4,4′-methylenedi(*N*-methylcarbanilate) was prepared by the addition of a solution of 31.0 g (0.287 mol) of distilled ethyl chloroformate in 100 mL of benzene to a stirred mixture of 31.0 g (0.137 mol) of 4,4′-methylenebis(*N*-methylaniline), 70 g (0.70 mol) of calcium carbonate, and 200 mL of benzene in 0.5 h at 20–40 °C. The reaction mixture was stirred at 45–50 °C for an ad-

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Table I. Hydrogenation of Methyl Carbanilate[a]

catalyst[b]						mol % yield	
metal	wt, g	concn, g/L	temp, °C	press., psig	time, h[c]	methyl carbanilate	methyl cyclohexylcarbamate
Rh	0.60	5	25-75	500-800	0.3[d]	--	96[e]
Ru	2.4	20	75	500-800	0.8[f]	--	95[e]
Pd	2.4	20	100	620-680	2.8	77[g]	22[g]
Pd	2.4	20	125	500-800	13	51[g]	47[g]
Pt	2.4	20	160	850	1.8	[h]	0[h]
Ni	2.4	20	150	660-880	12.5	63[g]	30[g]
Co	2.4	20	150	500-900	14.5	39[g]	45[g]

[a] Each experiment was run with 15.1 g (0.10 mol) of methyl carbanilate and 105 mL of 2-propanol. [b] The Rh, Ru, Pd, and Pt catalysts were 5% metal on carbon. The Ni and Co catalysts were 50% metal on kieselguhr. [c] Time at specified reaction temperature during gas absorption. [d] Little or no gas absorption in additional 0.8 h at 75 °C. [e] Isolated product, mp 73-74 °C. [f] Little or no gas absorption in additional 1.0 h. [g] Determined by IR analysis. [h] No detectable gas absorption indicated lack of reaction.

ditional 7 h. After filtering off the solids, concentrating the filtrate on a rotary evaporator under reduced pressure, and drying overnight over Drierite in a vacuum desiccator, there was obtained 31.5 g (61% yield) of diethyl 4,4′-methylenedi(*N*-methylcarbanilate) as a viscous yellow oil. Thin-layer chromatography on silica gel with 3% methanol in toluene showed only one spot both with UV and with iodine vapor detection. IR analysis indicated only traces of N-H absorption. Anal. Calcd for $C_{21}H_{26}N_2O_4$: C, 68.09; H, 7.07; N, 7.56. Found: C, 66.76; H, 6.83; N, 7.41.

The 5% platinum, palladium, rhodium, and ruthenium on carbon catalysts were obtained from Engelhard Industries. The 50% nickel on kieselguhr (Girdler G-49B), and 50% cobalt on kieselguhr (Girdler G-67RS) were obtained from Chemetron Corp. Only one batch of each catalyst was used.

Unless otherwise specified, each hydrogenation experiment was run in a 300-mL, stainless-steel, Magne Drive autoclave, and the reaction times are the times for complete conversion at the specified temperature, as indicated by gas absorption.

Hydrogenation of Methyl Carbanilate. A detailed description of one experiment is given to illustrate the procedure.

A mixture of 15.1 g (0.10 mol) of methyl carbanilate, 105 mL of 2-propanol, and 0.60 g of 5% rhodium on carbon was added to a 300-mL Magne Drive autoclave. The vessel was sealed, purged first with nitrogen and then with hydrogen, and pressured with hydrogen to 600 psig. The autoclave was heated with agitation for 0.3 h at 25–75 °C and 500–800 psig, followed by an additional 0.8 h at 75 °C with little or no gas absorption. The autoclave was cooled and depressurized. The reaction product was removed and filtered through Celite filter-aid to remove the catalyst. The solvent was removed in a rotary evaporator under vacuum. The white solid residue, after drying in a vacuum desiccator over Drierite, consisted of 15.1 g (96% yield) of methyl cyclohexylcarbamate, mp 73–74 °C, lit. value 75 °C (Chaleil, 1934). An authentic sample prepared from cyclohexyl isocyanate and methanol melted at 73.5–74 °C.

A comparison of several catalysts for the hydrogenation of methyl carbanilate is given in Table I.

Hydrogenation of Cyclohexyl Carbanilate. A mixture of 21.9 g (0.10 mol) of cyclohexyl carbanilate, 77 mL of 2-propanol, and 3.0 g of 5% rhodium on carbon was added to a 0.5 L, glass, low-pressure, Parr shaker bottle. The apparatus was purged first with nitrogen and then hydrogen, and pressured with hydrogen to 50 psig. The reaction mixture was agitated at room temperature and 50 to 25 psig for 3.0 h, followed by an additional 0.8 h with little or no gas absorption. The reaction product was filtered through Celite filter aid to remove the catalyst. The solvent was removed in a rotary evaporator under vacuum. The solid residue consisted of 23.3 g (99% yield) of cyclohexyl cyclohexylcarbamate, mp 77–78 °C. Anal. Calcd for $C_{13}H_{23}NO_2$: C, 69.29; H, 10.30; N, 6.21. Found: C, 69.43; H, 10.10; N, 6.20.

The above experiment was repeated in a 300-mL Magne Drive autoclave with 21.9 g (0.10 mol) of cyclohexyl carbanilate, 100 mL of 2-propanol, and 2.4 g of 5% rhodium on carbon for 0.4 h at 25 °C and 500–800 psig, followed by an additional 0.9 h with little or no gas absorption. The same isolation procedure as above yielded 21.9 g (97% yield) of cyclohexyl cyclohexylcarbamate, mp 77–78 °C.

Hydrogenation of Methyl 1-Naphthylcarbamate. A mixture of 20.1 g (0.10 mol) of methyl 1-naphthylcarbamate, 100 mL of 2-propanol, and 2.4 g of 5% rhodium on carbon was agitated at 22–31 °C and 500–800 psig for 3.7 h, followed by an additional 0.8 h with little or no gas absorption. Removal of catalyst and solvent in the usual manner yielded a residue of 21.0 g (99.5% yield) of a mixture of isomeric methyl 1-decahydronaphthylcarbamates, mp 104–114 °C. Anal. Calcd for $C_{12}H_{21}NO_2$: C, 68.20; H, 10.03; N, 6.63. Found: C, 68.61; H, 9.71; N, 6.69.

Hydrogenation of Diisopropyl 4,4′-Methylenedicarbanilate. A mixture of 23.6 g (0.064 mol) of diisopropyl 4,4′-methylenedicarbanilate, 97 mL of 2-propanol, and 2.4 g of 5% rhodium on carbon was agitated at 40 °C and 500–800 psig for 7.6 h, followed by an additional 1.1 h with little or no gas absorption. Removal of catalyst and solvent in the usual manner yielded a residue of 20.2 g (83% yield) of a mixture of isomeric diisopropyl 4,4′-methylenedicyclohexylcarbamates, mp 182–206 °C. Anal. Calcd for $C_{21}H_{38}N_2O_4$: C, 65.93; H, 10.01; N, 7.32. Found: C, 66.39; H, 10.24; N, 7.48.

Hydrogenation of Dimethyl Toluenedicarbamate. A mixture of 23.8 g (0.10 mol) of dimethyl toluenedicarbamates (prepared from the 80:20 mixture of 2,4- and 2,6-toluene diisocyanates), 100 mL of 2-propanol, and 2.4 g of 5% rhodium on carbon was agitated at room temperature and 500–800 psig for 2.8 h, with little or no gas absorption in an additional 0.8 h. Removal of catalyst and solvent in the usual manner yielded a white residue of 24.9 g (102% yield) of a mixture of isomeric dimethyl methylcyclohexyldicarbamates, mp 165–189 °C. Anal. Calcd for $C_{11}H_{20}N_2O_4$: C, 54.07; H, 8.27; N, 11.46. Found: C, 54.24; H, 8.23; N, 11.44.

Hydrogenation of Dimethyl 1,5-Naphthalenedicarbamate. A mixture of 15.1 g (0.055 mol) of dimethyl 1,5-naphthalenedicarbamate, 105 mL of 2-propanol, and 2.4 g of 5% rhodium on carbon was agitated at 45 °C and 500–800 psig for 3.8 h, with little or no gas absorption in

Table II. Effect of Purity of Dimethyl 4,4′-Methylenedicarbanilate on Rate of Rh-Catalyzed Hydrogenation to Dimethyl 4,4′-Methylenedicyclohexylcarbamate[a]

source of starting material[b]	cat. wt, g	cat. concn, g/L	temp, °C	time, h
I	2.4	20	50	6.5
II	2.4	20	50	1.3
I	0.8	6.7	100	5.3 (69% conversion)
II	0.8	6.7	100	0.7
II	0.6	5	75	6.0
III	0.6	5	75	3.0

[a] Each experiment was run with 20.0 g (0.064 mol) of dimethyl 4,4′-methylenedicarbanilate, 100 mL of 2-propanol, and a 5% Rh on carbon catalyst at 500–800 psig. [b] I prepared from Eastman Kodak practical grade methylenedi-*p*-phenyl diisocyanate. II prepared from Upjohn high purity methylenedi-*p*-phenyl diisocyanate (Isonate 125 MF). III prepared by recrystallization of II from methanol.

Table III. Relationship of Catalyst Level and Temperature in Rh-Catalyzed Hydrogenation of Dimethyl 4,4′-Methylenedicarbanilate[a]

cat. wt, g	cat. concn, g/L	temp, °C	time, h
0.4	3.3	75	13
0.4	3.3	100	6.0 (65% conversion)[b]
0.4	3.3	150	0.3 (50% conversion)[c]
0.8	6.7	50	12
0.8	6.7	75	3.0
0.8	6.7	100	0.7

[a] Each experiment was run with 20.0 g (0.064 mol) of dimethyl 4,4′-methylenedicarbanilate, 100 mL of 2-propanol, and a 5% Rh on carbon catalyst at 500–800 psig. [b] Reaction rate slow when shut down. [c] Reaction had stopped.

an additional 1.3 h. Removal of catalyst and solvent in the usual manner yielded a white residue of 14.2 g (91% yield) of a mixture of isomeric dimethyl 1,5-decahydronaphthalenedicarbamates, mp 211–233 °C. Anal. Calcd for $C_{14}H_{24}N_2O_4$: C, 59.14; H, 8.51; N, 9.85. Found: C, 59.20; H, 8.57; N, 9.79.

Hydrogenation of Ethyl *N*-Methylcarbanilate. A mixture of 17.9 g (0.10 mol) of ethyl *N*-methylcarbanilate, 100 mL of 2-propanol, and 2.4 g of 5% rhodium on carbon was agitated at 30–40 °C and 500–800 psig for 0.3 h, when gas absorption stopped. The catalyst and solvent were removed in the usual manner. Distillation of the residue gave a quantitative yield of ethyl *N*-methylcyclohexylcarbamate, bp 78–82 °C (mostly 81–82 °C) at 2 mm. An elemental analysis was obtained on a middle cut from the distillation. Anal. Calcd for $C_{10}H_{19}NO_2$: C, 64.83; H, 10.34; N, 7.56. Found: C, 64.73; H, 10.32; N, 7.44.

Hydrogenation of Diethyl 4,4′-Methylenedi(*N*-methylcarbanilate). A mixture of 29.5 g (0.0796 mol) of diethyl 4,4′-methylenedi(*N*-methylcarbanilate), 90 mL of 2-propanol, and 2.4 g of 5% rhodium on carbon was agitated at 425–800 psig for 7 h at 50 °C followed by 13 h at 75 °C with little or no gas absorption in the last 2 h. Removal of catalyst and solvent in the usual manner yielded 29.5 g (97% yield) of a viscous liquid residue of a mixture of isomers of diethyl 4,4′-methylenedi(*N*-methylcyclohexylcarbamate). Analysis by UV indicated the presence of about 1% of aromatic starting material. Anal. Calcd for $C_{21}H_{38}N_2O_4$: C, 65.94; H, 10.01; N, 7.32. Found: C, 66.26; H, 10.06; N, 7.41.

Rhodium-Catalyzed Hydrogenation of Dimethyl 4,4′-Methylenedicarbanilate. A detailed description of one experiment follows. A mixture of 20.0 g (0.064 mol) of dimethyl 4,4′-methylenedicarbanilate, 100 mL of 2-propanol, and 0.8 g of 5% rhodium on carbon was agitated at 75 °C and 500–800 psig for 3.0 h, followed by an additional 0.8 h with little or no gas absorption. The gas absorption was approximately quantitative. The catalyst was separated from the reaction mixture by centrifugation and then washed successively with three 600-mL portions of methanol, one 300-mL portion of 2-propanol, and one 150-mL portion of 2-propanol. The solvent was removed from the reaction product in a rotary evaporator under vacuum. The white solid residue was dried in a vacuum desiccator and consisted of 20.4 g (98% yield) of a mixture of isomers of dimethyl 4,4′-methylenedicyclohexylcarbamate, mp 128–135 °C. Anal. Calcd for $C_{17}H_{30}N_2O_4$: C, 62.56; H, 9.25; N, 8.58. Found: C, 63.10; H, 9.26; N, 8.35.

The results in Table II illustrate the effect of the purity of the dimethyl 4,4′-methylenedicarbanilate on its rate of hydrogenation.

Table III illustrates the interrelated effects of catalyst level and temperature on reaction rate.

Effect of Acid. Tables IV and V illustrate the effect of added acid in the hydrogenation of methyl carbanilate

Table IV. Effect of Acid in Hydrogenation of Methyl Carbanilate[a]

	catalyst					
metal	wt, g	concn, g/L	acid present[b]	temp, °C	press., psig	time, h
Rh	0.20	1.7	no	45	500-800	4.0
Rh	0.20	1.7	yes	45	500-800	3.5
Rh	0.10	0.83	no	100	500-800	2.2
Rh	0.10	0.83	yes	100	500-800	0.9
Rh	0.10	0.83	yes[c]	100	500-800	1.7
Ru	2.4	20	no	80	500-800	0.7
Ru	2.4	20	yes	80	500-800	2.7
Ru	0.60	5	no	90	500-800	9.0
Ru	0.60	5	yes	90	500-800	9.5
Pd	2.4	20	no	100	620-680	2.8 (22% conversion)
Pd	2.4	20	yes	100	500-800	2.2
Pt	2.4	20	no	160	850	no conversion
Pt	2.4	20	yes	45	500-800	4.0
Pt	0.8	6.7	yes	75	500-800	5.0
Pt	*d*	*d*	yes	75	500-800	8.8

[a] Each experiment was run with 15.1 g (0.10 mol) of methyl carbanilate, 105 mL of 2-propanol, and a 5% metal on carbon catalyst. [b] 0.10 mL (ca. 6 × 10^{-4} equiv.) of 6 N sulfuric acid. [c] 0.10 mL (ca. 6 × 10^{-4} equiv) of 6 N acetic acid. [d] Used catalyst recovered from preceding experiment.

Table V. Effect of Acid in the Hydrogenation of Dimethyl 4,4′-Methylenedicarbanilate[a]

source of starting material[b]	catalyst			acid present[c]	temp, °C	press., psig	time, h
	metal	wt, g	concn, g/L				
II	Rh	0.8	6.7	none	75	500–800	3.0
II	Rh	0.8	6.7	sulfuric	75	500–800	0.8
II	Rh	0.8	6.7	hydrochloric	75	500–800	1.8
II	Rh	0.8	6.7	phosphoric	75	500–800	1.4
III	Rh	0.6	5	none	75	500–800	3.0
III	Rh	0.6	5	sulfuric	75	500–800	1.0
III	Rh	0.6	5	sulfuric[d]	75	500–800	0.8
III	Pd	2.4	20	none	100	1120–1155	5.0 (16% conversion)
III	Pd	2.4	20	sulfuric	100	900–1200	5.0 (34% conversion)
III	Pt	2.4	20	none	125	725	no conversion
III	Pt	2.4	20	sulfuric	85	500–800	5.6 (82% conversion)

[a] Each experiment was run with 20.0 g (0.064 mol) of dimethyl 4,4′-methylenedicarbanilate, 100 mL of 2-propanol, and a 5% metal on carbon catalyst. [b] See Table II, footnote *b*. [c] 0.10 mL (ca. 6×10^{-4} equiv) of acid used. [d] 0.50 mL (ca. 30×10^{-4} equiv) of acid used.

Table VI. Catalyst Reuse in Rh-Catalyzed Hydrogenation of Dimethyl 4,4′-Methylenedicarbanilate[a]

expt. no.	catalyst	cat. treatment	time, h
1	0.8 g (6.7 g/L) fresh	none	3.0
2	recovered from expt. 1	*b*	4.0
3	recovered from expt. 2	*b*	5.0
4	recovered from expt. 3	*b*	8.4
5	0.6 g (5.0 g/L) fresh	none	6.0
6	recovered from expt. 5	*b*	9.0
7	recovered from expt. 6	*c*	4.3
8	recovered from expt. 7	*c*	6.0

[a] Each experiment was run with 20.0 g (0.064 mol) of dimethyl 4,4′-methylenedicarbanilate, 100 mL of 2-propanol, and a 5% Rh on carbon catalyst at 75 °C and 500–800 psig. [b] Washed successively with methanol and 2-propanol. [c] Washed successively with methanol, 6 N sulfuric acid, and 2-propanol.

Table VII. Catalyst Reuse in Acid-Promoted Rh-Catalyzed Hydrogenation of Dimethyl 4,4′-Methylenedicarbanilate

expt. no.	catalyst	cat. treatment	promoting acid	time, h
1	0.8 g (6.7 g/L) fresh	none	sulfuric	0.8
2	recovered from expt. 1	*b*	sulfuric	1.8
3	0.8 g (6.7 g/L) fresh	none	phosphoric	1.4
4	recovered from expt. 3	*c*	phosphoric	1.8

[a] Each experiment was run with 20.0 g (0.064 mol) of dimethyl 4,4′-methylenedicarbanilate, 100 mL of 2-propanol, a 5% Rh on carbon catalyst, and 0.10 mL (ca. 6×10^{-4} equiv) of either 6 N sulfuric acid or 6 N phosphoric acid at 75 °C and 500–800 psig. [b] Washed successively with methanol and 2-propanol. [c] Washed successively with methanol, 6 N sulfuric acid, and 2-propanol.

and of dimethyl 4,4′-methylenedicarbanilate, respectively.

Catalyst Reuse and Reactivation. Tables VI and VII illustrate catalyst reuse and reactivation in the rhodium-catalyzed hydrogenation of dimethyl 4,4′-methylenedicarbanilate.

Discussion

The carbamate group in *N*-aryl carbamates might influence the nuclear hydrogenation of the aromatic ring due to its electronic and steric effects on the adsorption of the aromatic nucleus on the catalyst and the rate of hydrogenation of the adsorbed species, the competitive adsorption of the carbamate group on the catalyst, and by the competitive adsorption of by-products formed from side reactions involving the carbamate group.

The electronic effect of substituents on the hydrogenation of a benzene ring (Mochida and Yoneda, 1968) and of olefinic bonds (Kieboom and Van Bekkum, 1972) appears to be small. The electronic effect of the carbamate substituent on the hydrogenation behavior of the aromatic ring probably is also of minor importance.

A steric interference of the carbamate group with adsorption of the aromatic ring can be expected by analogy with the effect of alkyl groups on the rates of hydrogenation of the benzene ring (Smith, 1967; Greenfield, 1973). It can also be anticipated that the carbamate group will compete with the aromatic ring for adsorption on the active sites of the catalyst.

Certain products, such as amines, isocyanates, and carbon monoxide, that may be formed from carbamates by thermal decomposition (Saunders and Frisch, 1962; Matusyak and Frisch, 1973), reactions with amines (Abbate et al., 1972), and hydrogenolysis reactions (Kametani et al., 1958; Weaver et al., 1973) might compete so strongly with aromatic ring adsorption as to be catalyst poisons.

The results in Table I show the relative order of catalyst activities for the nuclear hydrogenation of methyl carbanilate to methyl cyclohexylcarbamate is: Rh $\gg$ Ru $\gg$ Pd > Ni, Co, with platinum having little or no activity. Rhodium is much more active than the other catalysts. Similar results were obtained in the nuclear hydrogenation of *N*-aryl amides (Malz and Greenfield, 1976). It is difficult to interpret this order of activity simply in terms of intrinsic activities because of the possibility of varying catalyst surface areas, steric requirements, and resistance to inhibitors. Indeed, even in the comparatively simple hydrogenation of aromatic hydrocarbons, relative activities depend upon the physical form of the metal and the nature of the support of supported metals (Bond, 1962), and upon the solvent used (Rylander, 1967). The relative strengths of adsorption of sterically hindered compared to nonhindered aromatic hydrocarbons also depends on the metal (Smith, 1967).

The rhodium-catalyzed hydrogenation of the aromatic ring in *N*-aryl carbamates is of very general synthetic applicability. Excellent yields were obtained from both *N*-phenyl and *N*-naphthyl compounds, from bis carbamates such as methylenedicarbanilates, from dicarbamates such as toluene and 1,5-naphthalene dicarbamates, and from *N*-alkyl carbanilates and bis carbanilates such as an *N*-methylcarbanilate and a 4,4′-methylenedi(*N*-methylcarbanilate). Table II illustrates the importance of the purity of the *N*-aryl carbamate, in this case a 4,4′-methylenedicarbanilate, on its rate of rhodium-catalyzed hydrogenation. This would be an extremely important consideration in a commercial process. It appears that a practical process would require the carbamate preparation from the reaction of high quality isocyanate with alcohol under anhydrous conditions. Attempted hydrogenations of dimethyl 4,4′-methylenedicarbanilate that had been prepared under nonanhydrous conditions always resulted in catalyst poisoning and poor conversions (Malz and Greenfield, 1972). Table III illustrates the interrelated effects of catalyst level and temperature on reaction rate and catalyst inhibition in the rhodium-catalyzed hydrogenation of dimethyl 4,4′-methylenedicarbanilate. Catalyst poisoning at the lower catalyst level produces a decrease in conversion in going from 75 to 100 °C and, in spite of a very rapid initial rate of hydrogenation, even more severe poisoning and lower conversion at 150 °C. The catalyst poisoning at the higher catalyst level is less pronounced because of the larger number of active sites, and the hydrogenation rate increases with increasing temperature in the lower range of 50 to 100 °C.

The obvious explanation is that higher temperatures result in greater rates of nuclear hydrogenation but also produce increasing quantities of by-products that poison the catalyst. The severity of poisoning will be inversely related to the amount of catalyst present. Rhodium is known to be very susceptible to poisoning by amines (Freifelder, 1961; Greenfield, 1964) and by isocyanates (Malz and Greenfield, 1972), major products of carbamate decompositions (Saunders and Frisch, 1962).

The effect of acid on the rate of hydrogenation of methyl carbanilate is shown in Table IV. Traces of acid promote the rhodium, palladium, and platinum catalysts, but inhibit the ruthenium catalyst. A similar acid promotion of rhodium was found in the nuclear hydrogenation of *N*-aryl amides (Malz and Greenfield, 1976), and also in the hydrogenation of benzene (Greenfield, 1973). The acid promotion is presumably due to the neutralization of traces of bases initially present and/or formed from the carbamate. The effect with rhodium is more pronounced at lower catalyst levels, when the catalyst is more susceptible to poisoning, and at higher temperatures, when the formation of a larger amount of amine impurities would be expected.

The effect of acid on platinum is dramatic and even permits reuse of the platinum catalyst.

The effect of acid on ruthenium seems to be the result of two opposing factors, an acid inhibition of the catalyst and the neutralization of basic inhibitors. The latter effect appears to increase in importance when lower catalyst levels produce longer reaction times that permit greater amine formation. A similar lack of acid promotion was observed in the ruthenium-catalyzed hydrogenation of acetanilide, an *N*-aryl amide (Malz and Greenfield, 1976).

The promotion by acid of the rhodium-, palladium-, and platinum-catalyzed hydrogenation of dimethyl 4,4′-methylenedicarbanilate is shown in Table V. The results are similar to those obtained in the hydrogenation of methyl carbanilate. Rhodium remains by far the most active catalyst for the nuclear hydrogenation of *N*-aryl carbamates both with and without acid promotion.

Table VI illustrates how the rhodium catalyst recovered from the hydrogenation of dimethyl 4,4′-methylenedicarbanilate retains sufficient activity to permit several reuses. This is, of course, of major commercial importance. Furthermore, experiments 7 and 8 illustrate how extremely efficient an acid wash is in restoring the activity of the used catalyst. Part of the enhanced activity in these experiments may be the result of acid promotion by traces of acid remaining on the catalyst from the acid wash.

Table VII shows the feasibility of catalyst reuse in the rhodium-catalyzed hydrogenation of dimethyl 4,4′-methylenedicarbanilate with acid promotion both with and without an acid wash of the recovered catalyst.

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