Regiospecific Hydrogenation of Quinolines and Indoles in the Heterocyclic Ring

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Quinolines, indoles, acridine, and carbazole were hydrogenated using a large variety of heterogeneous catalysts in hydrocarbon solvents in an effort to achieve selective hydrogenation of the heterocyclic ring. When quinolines were hydrogenated using supported platinum, palladium, rhodium, ruthenium, or nickel metal catalysts in the presence of hydrogen sulfide, carbon disulfide, or carbon monoxide, there was exclusive hydrogenation of the heterocyclic ring to give only 1,2,3,4-tetrahydroquinolines. Use of iridium, rhenium, molybdenum(VI) oxide, tungsten(VI) oxide, chromium(III) oxide, iron(III) oxide, cobalt(II) oxide-molybdenum(VI) oxide, or copper chromite catalysts also caused exclusive hydrogenation of the heterocyclic ring even without addition of sulfur compounds or carbon monoxide. Hydrogenation of indoles using platinum, rhenium, or, in some cases, nickel catalysts (with or without sulfur compounds) occurred exclusively in the heterocyclic ring to give indolines, but conversions were affected by indole-indoline equilibria.

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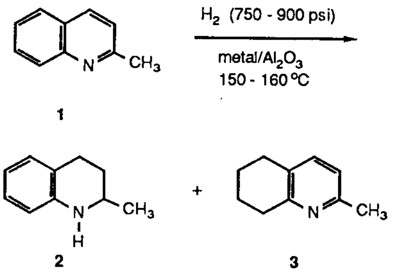
Heavy oil, shale oil, and coal-derived liquids contain considerable nitrogen which must be removed to prevent poisoning of many refining catalysts and to avoid having products which form gums and sediments or cause air pollution when burned [1]. The major nitrogen containing compounds are pyridines, pyrroles, quinolines, indoles, acridines, carbazoles, and other benzo derivatives of these compounds [1]. Current hydrodenitrogenation methods consume far more hydrogen than necessary to remove nitrogen because many simple aromatic rings are hydrogenated in the process. For example, quinoline is converted mainly to propylcyclohexane rather than propylbenzene [1,2].

To reduce hydrogen consumption we have searched for (1) catalysts to hydrogenate nitrogen containing aromatic rings while leaving simple aromatic rings untouched, and (2) methods to remove nitrogen from the products of the first step without hydrogenating simple aromatic rings. Ideally quinoline would be exclusively hydrogenated to 1,2,3,4-tetrahydroquinoline which would then be denitrogenated to give propylbenzene rather than propylcyclohexane. This paper deals with the first goal of selectively hydrogenating the nitrogen containing ring of quinolines, acridine, indoles, and carbazole. Most hydrogenation were carried out with quinolines and indoles substituted with alkyl groups in the nitrogen containing ring because they are commonly found [3] in crude oils and, based on previous studies [4], are more difficult to hydrogenate in the heterocyclic ring. Other workers have recently reported on the selective hydrogenation of the heterocyclic ring of quinolines, acridine, and indole using chlorotris(triphenylphosphine)rhodium(I) [5], transition metal carbonyl hydrides [6,7], and metallophthalocyanines [8].

Results and Discussion.

Hydrogenation of Quinolines.

When 2-methylquinoline (**1**) was hydrogenated using supported palladium, platinum, rhodium, ruthenium, or nickel metal catalysts with *n*-hexadecane as solvent, mixtures of 2-methyl-1,2,3,4-tetrahydroquinoline (**2**) and 2-methyl-5,6,7,8-tetrahydroquinoline (**3**) were obtained as shown in Table I. Hydrogenation of 4-methylquinoline, 2,4-dimethylquinoline, and 6-methylquinoline also gave mixtures of the 1,2,3,4- and 5,6,7,8-tetrahydro products. Decahydro products were not observed except when ruthenium on alumina was used as catalyst.



Ratios of the 1,2,3,4- and 5,6,7,8-tetrahydro products obtained using these catalysts have not been previously reported except in the case of nickel catalysts. The 64:36 product ratio obtained from 4-methylquinoline using nickel on silica-alumina (Table I) compares well with the 66:34 ratio previously reported using an unsupported nickel metal catalyst [4]. However, the 76:24 and 63:27 ratios obtained from 2-methylquinoline using nickel on silica-alumina and Raney nickel do not agree with the 96:4 ratio observed using the unsupported nickel catalyst. Our

Table I

Hydrogenation of Quinolines [a]

Quinoline	Catalyst [b]	Temp, °C	Time [c], h	Product Ratio [d] % 1,2,3,4-tetrahydro	 % 5,6,7,8-tetrahydro
2-methylquinoline	Pd/Al_2O_3	160	1.0	54	46
2-methylquinoline	Pt/Al_2O_3	150	1.0	92 [e]	8
2-methylquinoline	Pt/C	150	1.0	96 [e]	4
2-methylquinoline	Ru/Al_2O_3	160	1.6	74	26 [f]
2-methylquinoline	Rh/Al_2O_3	100	0.5	63	37
2-methylquinoline	Ni/SiO_2-Al_2O_3	160	1.5	74	26
2-methylquinoline	Raney Ni	160	2.2	63	37
2-methylquinoline	NiO-MoO_3/Al_2O_3	300	3.0	92 [h]	8 [i]
2-methylquinoline	NiO-MoO_3/Al_2O_3 [g] (sulfided)	300	1.5	98 [h]	2
4-methylquinoline	Pt/Al_2O_3	160	2.0	97	3
4-methylquinoline	Ni/SiO_2-Al_2O_3	160	1.5	64	36
6-methylquinoline	Pd/Al_2O_3	105	1.0	98.5	1.5
2,4-dimethylquinoline	Pt/Al_2O_3	160	1.5	88	12

[a] *Initial hydrogen pressure was 750 psi at room temperature.* [b] *All catalysts are 5% metal except for* Ni/SiO_2-Al_2O_3 *which is 60-65% Ni and* NiO-MoO_3/Al_2O_3 (Shell 324) which is 2.7% Ni (as NiO) and 13.2% Mo (as MoO_3). [c] An additional 0.5 hour was needed to reach the desired temperature. [d] Unless otherwise specified, no other products were observed except for 2-3% starting material. [e] Absolute yield of two products totaled 100% based on consumed starting material. [f] Decahydroquinolines were also produced (12% of products). [g] In this run only, the NiO-MoO_3/Al_2O_3 catalyst (Shell 324) was presulfided using 10% H_2S and 90% H_2 at 375°. [h] In these cases 6-7% starting material was unreacted. [i] At 250° the ratio of **2**:**3** was 99:1.

results for 2-methylquinoline are more consistent with the results previously reported for 3-methylquinoline and 4-methylquinoline [4]. Hydrogenation of 2,4-dimethylquinoline using platinum on alumina gave an 88:12 product ratio which is in marked contrast to an unfavorable 20:80 ratio previously observed using unsupported nickel as catalyst [4].

When trace amounts of sulfur compounds such as hydrogen sulfide or carbon disulfide were added to the reactions catalyzed by palladium, platinum, rhodium, ruthenium, or nickel, the quinolines were hydrogenated exclusively in the heterocyclic ring to give only the 1,2,3,4-tetrahydro product. The results with and without sulfur compounds present are compared in Table II. The absolute yields were 99-100% based on consumed starting material; only 2-3% of the quinoline was not hydrogenated. Carbon disulfide under the hydrogenation conditions was converted to hydrogen sulfide. The sulfur to metal atom ratio was 7:1 or higher for platinum, palladium, rhodium, and ruthenium catalysts. Sulfur appears to deactivate the catalysts for hydrogenation of the nonheterocyclic ring much more than for the heterocyclic ring. Slightly higher temperatures were used to obtain reaction rates similar to those when no sulfur was present. It was not determined if smaller amounts of sulfur compounds would cause exclusive production of the 1,2,3,4-tetrahydro product. Addition of much larger amounts of sulfur compound (Table II) still resulted in exclusive production of the desired product, but the catalysts were less active and required higher temperatures to get comparable reaction rates.

Hydrogenation of quinolines could also be carried out without hydrogenating simple aromatic rings in other molecules. When 2-methylquinoline was hydrogenated (platinum on alumina with carbon disulfide, 160°) using toluene as solvent, no methylcyclohexane was produced and **2** was the exclusive product. Also, hydrogenation of 2-methylquinoline in the presence of an equimolar amount of naphthalene in *n*-hexadecane gave only **2** and no hydrogenation products of naphthalene.

The exclusive formation of the 1,2,3,4-tetrahydro product was observed in all cases where sulfur compounds were added, and no exceptions to the examples in Table II were observed. However, lower temperatures are important in these reactions to assure kinetic control. If the 2-methylquinoline was hydrogenated at 160° using platinum on alumina with carbon disulfide present and then the temperature was raised to 350°C for 8 hours, the product composition changed from 97% **2** and 3% **1** to 44% **2**, 24% **3**, 22% **1**, and 10% other products.

Addition of carbon monoxide instead of sulfur com-

Table II

Comparison of Product Ratios from Hydrogenation of Quinolines in the Presence or Absence of Sulfur Compounds or Carbon Monoxide [a]

Quinoline	Catalyst [b]	Sulfur Compound or CO	Temp, °C	Time [c], h	Product Ratio [d] % 1,2,3,4-tetrahydro	Product Ratio [d] % 5,6,7,8-tetrahydro
2-methylquinoline	Pd/Al_2O_3	None	160	1.0	54	46
2-methylquinoline	Pd/Al_2O_3	CS_2	160	3.3	100 [e]	0
2-methylquinoline	Pd/Al_2O_3	CO	182	2.2	100	0
2-methylquinoline	Pt/Al_2O_3	None	150	1.0	92 [e]	8
2-methylquinoline	Pt/Al_2O_3	H_2S	160	1.5	100	0
2-methylquinoline	Pt/Al_2O_3	CS_2	160	1.2	100 [e]	0
2-methylquinoline	Pt/Al_2O_3	CS_2 [f]	200	2.2	100	0
2-methylquinoline	Ru/Al_2O_3	None	160	1.6	74 [g]	26
2-methylquinoline	Ru/Al_2O_3	CS_2	160	3.2	100 [h]	0
2-methylquinoline	Rh/Al_2O_3	None	100	0.5	63	37
2-methylquinoline	Rh/Al_2O_3	CS_2	150	4.2	100 [e]	0
2-methylquinoline	Ni/SiO_2-Al_2O_3	None	160	1.5	74	26
2-methylquinoline	Ni/SiO_2-Al_2O_3	CS_2	175	2.5	100 [e]	0
4-methylquinoline	Pt/Al_2O_3	None	160	2.0	97	3
4-methylquinoline	Pt/Al_2O_3	H_2S	160	2.5	100	0
2,4-dimethylquinoline	Pt/Al_2O_3	None	160	1.5	88	12
2,4-dimethylquinoline	Pt/Al_2O_3	CS_2	160	1.7	100	0

[a] Initial hydrogen pressure at room temperature was 750 psi. [b] All catalysts were 5% metal except for Ni/SiO_2-Al_2O_3 which was 60-65% Ni. [c] An additional 0.5 hour was needed to reach the desired temperature. [d] Unless otherwise noted, no other products were observed except for 2-3% starting material. [e] Absolute yield of product(s) was 99-100% based on consumed starting material. [f] Instead of usual 0.025 g of CS_2, 0.2 g was used. Also a run with 1.0 g of CS_2 gave the same results at 225°. [g] Decahydroquinolines (12% of products) were also present. [h] No decahydroquinolines were present.

Table III

Hydrogenation of Quinolines with Re, Ir, Mo, W, Cr, and Fe Catalysts [a]

Quinoline	Catalyst [b] (weight, g)	Temp, °C	Time [c], h	Product Ratio [d] % 1,2,3,4-tetrahydro	Product Ratio [d] % 5,6,7,8-tetrahydro
2-methylquinoline	Re/Al_2O_3 (0.2)	171	3.5	100 [e]	0
2-methylquinoline	Ir/C (0.2)	132	2.5	100 [e]	0
2-methylquinoline	IrO_2 (0.3)	150	7	100	0
2-methylquinoline	MoO_3/Al_2O_3 (0.7)	250	5	100 [e]	0
2-methylquinoline	WO_3/Al_2O_3 (0.7)	250	3.5	100 [e]	0
2-methylquinoline	Cr_2O_3/Al_2O_3 (0.7)	250	3.5	100 [e]	0
2-methylquinoline	Fe_2O_3/Al_2O_3 (1.0)	300	7	100 [f]	0
2-methylquinoline	CoO-MoO_3/Al_2O_3 (0.7)	250	3	100	0
2-methylquinoline	copper chromite (0.7)	200	3	100	0
2-methylquinoline	$Fe(CO)_5$ (0.9)	250	7.5	100 [f]	0
4-methylquinoline	Ir/Al_2O_3 (0.3)	160	4.5	100	0
2-isobutylquinoline	Re/Al_2O_3 (0.2)	200	7	100	0

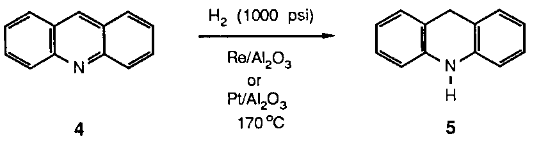
[a] Initial hydrogen pressure was 750 psi at room temperature. [b] The supported catalysts contained 5% Re, 5% Ir, 10% MoO_3, 10% WO_3, 15% Cr_2O_3, or 20% Fe_2O_3. The CoO-MoO_3/Al_2O_3 (Shell 344) contained 9.8% Mo (as MoO_3) and 2.4% Co (as CoO) and the copper chromite analyzed 51% CuO and 47% Cr_2O_3. [c] An additional 0.5 hour was needed to reach the desired temperature. [d] Unless otherwise noted, no other products were observed except for 2-3% starting material. [e] Absolute yield was 99-100% based on consumed starting material. [f] Unreacted starting material was 20-30%.

pounds also resulted in the 1,2,3,4-tetrahydro product being produced exclusively. Hydrogenation of 2-methylquinoline using palladium on alumina gave a 54:46 ratio of **2** to **3** without carbon monoxide present, but 100% **2** with carbon monoxide present (Table II).

Catalysts were also found that did not require the addition of carbon monoxide or sulfur compounds to produce 1,2,3,4-tetrahydroquinolines exclusively. These were iridium, rhenium, molybdenum(VI) oxide, tungsten(VI) oxide, chromium(III) oxide, iron(III) oxide, and cobalt(II) oxide-molybdenum(VI) oxide on alumina, iridium on carbon, iridium(IV) oxide, and copper chromite. The results are shown in Table III. The solvent was *n*-hexadecane, but cyclohexane gave the same results in the hydrogenation of 2-methylquinoline using rhenium on alumina. As shown in the case of iridium, the type of catalyst support or absence of support did not change the result except that iridium on carbon was a more active catalyst. The molybdenum(VI) oxide, tungsten(VI) oxide, chromium(III) oxide, iron(III) oxide, and cobalt(II) oxide-molybdenum(VI) oxide on alumina and copper chromite catalysts were less active and required higher reaction temperatures than the iridium and rhenium catalysts, but they have the advantage of being less expensive catalysts. As discussed previously, lower temperatures are necessary in these reactions to assure kinetic control. Use of the nickel(II) oxide-molybdenum(VI) oxide on alumina catalyst at 300° gave a 92:8 ratio of **2**:**3**, but at 250° **2** was almost produced exclusively with a 99:1 ratio (Table I). Exclusive production of **2** was also achieved using the homogeneous catalyst, iron pentacarbonyl.

Hydrogenation of quinolines using rhenium and iridium catalysts could also be carried out without hydrogenating simple aromatic rings in other molecules. Hydrogenation of 2-methylquinoline (rhenium on alumina, 171°) and 4-methylquinoline (iridium on alumina, 160°) in the presence of an equimolar amount of naphthalene in *n*-hexadecane, gave only **2** and no hydrogenation products of naphthalene.

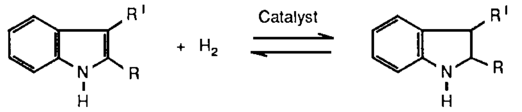
Acridine (**4**) a benzoquinoline, was also hydrogenated exclusively in the heterocyclic ring to give the dihydro product **5**. It was not necessary to use sulfur compounds with the platinum catalyst to obtain this result.



4 **5**

Hydrogenation of Indoles.

Indoles were hydrogenated using many of the same catalysts used for quinolines; however, higher temperatures and pressures and more catalyst were required to achieve suitable reaction rates and conversions. As will be discussed later, equilibria were established between the indole **6** and the indoline **7**.



6a, R = R^1 = H
6b, R = CH_3, R^1 = H
6c, R = R^1 = CH_3

7a, R = R^1 = H
7b, R = CH_3, R^1 = H
7c, R = R^1 = CH_3

The reaction conditions and products obtained in the hydrogenation of indole **6a** in *n*-hexadecane are shown in Table IV. Indoline **7a** was the only product in many cases, but with some catalysts 1-6% of other products were also observed (Table IV). Using platinum on alumina as catalyst, hydrogenation of indole in *n*-hexadecane at 1200 psi hydrogen and 227° led to 64% indoline and 36% indole while hydrogenation at 2200 psi at the same temperature led to 82% indoline and 18% indole. Use of longer reaction times or more catalyst did not increase the conversion indicating an equilibrium situation. No octahydroindole was observed. Other workers [9] have found that indole was hydrogenated under mild conditions using platinum in acetic acid, but octahydroindole was produced along with the indoline.

The nickel on silica-alumina catalyst which caused hydrogenation of indole at a lower temperature (160°, 1675 psi hydrogen) allowed a 93% conversion of indole to indoline. Although no octahydroindole was observed, higher pressures and temperatures and more catalyst caused production of considerable octahydroindole. Hydrogenation of 2-methylindole using nickel on silica-alumina under the more mild conditions described for indole gave some octahydro product in addition to the 2-methylindoline.

Indole could still be hydrogenated in the heterocyclic ring to give indoline if trace amounts of sulfur compounds such as carbon disulfide were added (Table IV). Reaction rates were much slower with the sulfur deactivated catalysts unless the temperature was increased. The higher temperatures caused less indoline to be present at equilibrium. For example, use of platinum on alumina at 300° gave 57% indoline at equilibrium while at 227° there was 82%.

Additional evidence for equilibria in these reactions was obtained by subjecting indoline to the same reaction conditions as indole. Using palladium on alumina in *n*-hexadecane at 300° and 2600 psi hydrogen with a trace of carbon disulfide present, indoline gave an equilibrium mixture containing 57% indoline and 42% indole which compares well with 55 and 44% values obtained when indole was hydrogenated under the same conditions.

Table IV

Hydrogenation of Indole

Catalyst [a] (weight, g)	Sulfur Compound	Temp, °C	Time [b], h	Pressure [c], psi	% Products [d]		
					Indoline	Indole	Other
Pt/Al_2O_3 (0.6)	None	227	10.5 [d]	2200	82 [e]	18	—
Pt/Al_2O_3 (0.6)	None	227	5.0	1200	65	35	—
Ni/SiO_2-Al_2O_3 (1.0)	None	160	0.7	1395	92 [e]	7	1 [f]
Pd/Al_2O_3 (0.5)	None	143	6.0	1725	76	21	3 [f]
Re/Al_2O_3 (0.6)	None	227	12.6 [g]	2510	82	18	—
Pd/Al_2O_3 (0.5)	CS2 [h]	300	6.0	2600	55	44	1 [i]
Ni/SiO_2-Al_2O_3 (1.0)	CS2 [h]	182	4.7	1575	88	12	—
Pt/Al_2O_3 (0.8)	CS2 [h]	300	5.5	2715	57	39	4 [i]
NiO-MoO_3/Al_2O_3 (1.0)	[j]	232	6.0	2160	56	37	7 [i]

[a] All catalyst were 5% metal except for Ni/SiO_2-Al_2O_3 which was 60-65% Ni and NiO-MoO_3/Al_2O_3 (Shell which is 2.7% Ni (as NiO) and 13.2% Mo (as MoO_3). [b] An additional 0.5 hour was needed to reach the desired temperature. [c] Pressure at end of run at temperature indicated. [e] Use of external standards showed that 99-100% of the starting material was accounted for by the products. [f] A tetrahydroindole based on ms only. [g] The product mixtures at 6.3 and 12.6 hours were the same. [h] In these runs 12, 45, and 50 mg of CS_2 was added to the Pd, Ni, and Pt catalyzed reactions, respectively. [i] 2-Ethylaniline. [j] The NiO-MoO_3/Al_2O_3 catalyst was presulfided using 10% H_2S-90% H_2 at 350°.

It was observed that alkyl substitution in the indole greatly affected the equilibrium between the indole and indoline. Hydrogenation of indole, 2-methylindole, and 2,3-dimethylindole in *n*-hexadecane using platinum on alumina as catalyst gave the equilibrium percentages of indole and indoline products shown in Table V. For 2,3-dimethylindole, the indole was favored at equilibrium. The effect of alkyl substitution on the equilibria of indoles and indolines has also been observed using a copper chromite catalyst [10].

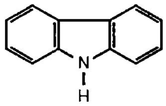
Table V

Hydrogenation of Indoles Using Pt/Al_2O_3 Catalyst (227°, 2200 psi) [a]

Indole	% Products at Equilibrium	
	Indoline	Indole
indole	82	18
2-methylindole	65	35
2,3-dimethylindole	28	72

[a] Catalyst was 5% Pt on alumina. Pressure was 2200 psi at 227° at end of runs.

Hydrogenation of carbazole (**8**) using platinum on alumina was more difficult than for indoles and resulted in a reaction product consisting of 53% carbazole, 36% 1,2,3,4-tetrahydrocarbazole (**9**), 5% *cis*-hexahydrocarbazole (**10**), and 6% dodecahydrocarbazoles. The equilibrium results observed for indoles is useful in explaining the 88:12 ratio of **9** to **10** since they are an alkyl substituted indole and indoline, respectively, where the indole should be greatly favored at equilibrium.



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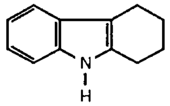

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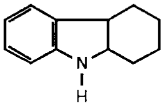

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EXPERIMENTAL

The catalysts were obtained from the following sources: platinum on alumina, rhodium on alumina, ruthenium on alumina, Aldrich Chemical; rhenium on alumina, palladium on carbon, Strem Chemical; iridium on carbon, iridium(IV) oxide, nickel on silica-alumina, molybdenum(VI) oxide on alumina, tungsten(VI) oxide on alumina, chromium(III) oxide on alumina, iron(III) oxide on alumina, copper chromite, Raney nickel (activated), Alfa Products. All were in powdered form. Metal contents are noted in the Tables. Reactions were carried out in a 300 ml stainless steel autoclave from Autoclave Engineers. Gas chromatographic analyses were performed on a Perkin-Elmer 3920B gas chromatograph equipped with a flame ionization detector using stainless steel columns on 10% Carbowax 20M on Chromosorb P. The column sizes were: Column A, 6 ft × 1/8 in.; Column B, 5 ft, × 1/4 in.; Column C, 1.0 ft × 1/8 in.; Column D, 1.5 ft × 1/8 in.; Column E, 1.5 ft × 1/4 in. Short columns were necessary for products obtained from indoles, acridine, and carbazole, so gc analyses could be carried out at lower temperatures where dehydrogenation would not occur. Response factors were used in determining the relative percentages of products. For some reactions which are noted in the Tables, absolute yields were determined using external standards.

Typical Procedure for Hydrogenation of Quinolines (Table I).

To a 300 ml autoclave was added 10.0 g (0.070 mole) of 2-methylquinoline, 90.0 g of *n*-hexadecane, and 0.20 g of 5% platinum on alumina. The autoclave was pressured with hydrogen to 700 psi, stirred briefly, and then the pressure was released. This was repeated three more times. The autoclave was pressured with hydrogen to 750 psi at room temperature and then heated with rapid stirring (1100 rpm) to 150° over 0.5 hour and maintained at 150° for 1.0 hour. The autoclave was cooled to room temperature, and the contents were suctioned filtered. To obtain complete recovery of the hexadecane solution, the autoclave and catalyst were washed with acetone which was evaporated separately before combining with the main filtrate. Gc (Column A, 200°) and gc-ms analysis of the hexadecane solution showed that the reaction product consisted of 90% 2-methyl-1,2,3,4-tetrahydroquinoline (**2**), 8% 2-methyl-5,6,7,8-tetrahydroquinoline (**3**), and 2% 2-methylquinoline (**1**) which gave a 92:8 ratio of **2** to **3**. Gc analysis using external standards showed that the absolute yields of **2** and **3** totaled 100% based on consumed starting material. Products were isolated by preparative gc (Column B, 200°). Compound **2** was identified by comparison (ir, nmr, ms retention time) with an authentic sample.

Compound **3** gave; ir (neat): 1594, 1573, 808 cm^{-1}; nmr (deuteriochloroform): δ 1.58-2.18 (m, 4H), 2.51 (s, 3H), 2.53-3.20 (m, 4H), 6.87, 7.27 (ABq, 2H, J = 8 Hz); ms: m/e 147 (M^+).

Anal. Calcd. for $C_{10}H_{13}N$: C, 81.58; H, 8.90; N, 9.52. Found: C, 81.32; H, 8.98; N, 9.43.

Other reactions in Table I were carried out in the same manner except that for the nickel on silica-alumina, Raney nickel, and nickel(II) oxide-molybdenum(VI) oxide on alumina catalyzed reactions, the amounts of catalyst were 0.70, 1.0, and 1.0 g, respectively, instead of the usual 0.20 g. Also changes in temperatures and times are noted in Table I. Products were isolated by preparative gc (Column B, 210°).

The 4-methyl-1,2,3,4-tetrahydroquinoline gave; ir (neat): 3395, 1607, 1584, 1308, 746 cm^{-1}; nmr (deuteriochloroform): δ 1.29 (d, 3H, J = 7 Hz), 1.43-2.33 (m, 2H), 2.53-3.18 (m, 1 H), 3.28 (t, 2H, J = 6 Hz), 3.78 (br s, 1H), 6.33-7.23 (m, 4H); ms: m/e 147 (M^+).

Anal. Calcd. for $C_{10}H_{13}N$: C, 81.58; H, 8.90; N, 9.52. Found: C, 81.31; H, 8.70; N, 9.51.

The 4-methyl-5,6,7,8-tetrahydroquinoline gave; ir (neat): 1587, 1568, 824 cm^{-1}; nmr (deuteriochloroform): δ 1.60-2.11 (m, 4H), 2.21 (s, 3H), 2.34-3.14 (m, 4H), 6.89, 8.22 (ABq, 2H, J = 5 Hz); ms: m/e 147 (M^+).

Anal. Calcd. for $C_{10}H_{13}N$: C, 81.58; H, 8.90; N, 9.52. Found: C, 81.31; H, 8.76; N, 9.42.

The 2,4-dimethyl-1,2,3,4-tetrahydroquinoline, which was an 83:17 mixture of isomers of similar retention time, gave; ir (neat): 3385, 1603, 1580, 1304, 743 cm^{-1}; nmr (deuteriochloroform): δ 1.18 (d, 3H, J = 7 Hz), 1.31 (d, 3H, J = 7 Hz), 1.50-2.17 (m, 2H), 2.60-3.20 (m, 1H), 3.20-3.85 (m, 2H), 6.33-7.27 (m, 4H); ms: m/e 161 (M^+).

Anal. Calcd. for $C_{11}H_{15}N$: C, 81.93; H, 9.38; N, 8.69. Found: C, 81.97; H, 9.38; N, 8.58.

The 2,4-dimethyl-5,6,7,8-tetrahydroquinoline gave; ir (neat): 1599, 1561, 742 cm^{-1}; nmr (deuteriochloroform): δ 1.66-2.01 (m, 4H), 2.18 (s, 3H), 2.46 (s, 3H), 2.46-3.16 (m, 4H), 6.77 (s, 1H); ms: m/e 161 (M^+).

Anal. Calcd. for $C_{11}H_{15}N$: C, 81.93; H, 9.38; N, 8.69. Found: C, 81.76; H, 9.39; N, 8.65.

The 2-isobutyl-1,2,3,4-tetrahydroquinoline gave; ir (neat): 3403, 1607, 1585, 1308, 741 cm^{-1}; nmr (deuteriochloroform): δ 0.94 (d, 6H, J = 7 Hz) 1.10-2.20 (m, 5H), 2.45-2.95 (m, 2H), 2.95-3.95 (m, 2H), 6.35-7.10 (m, 4H).

Anal. Calcd. for $C_{13}H_{19}N$: C, 82.48; H, 10.12; N, 7.40. Found: C, 82.63; H, 10.06; N, 7.30.

The 6-methyl-1,2,3,4-tetrahydroquinoline and 6-methyl-5,6,7,8-tetrahydroquinoline were identified by comparison with authentic samples.

Typical Procedure for Hydrogenation of Quinolines with Sulfur Compound Present (Table II).

To a 300 ml autoclave was added 10.0 g (0.070 mole) of 2-methylquinoline, 90 g of *n*-hexadecane, 0.20 g of 5% platinum on alumina, and 20 μl (0.025 g) of carbon disulfide. After mixing, the autoclave was pressured with hydrogen to 700 psi, stirred a few seconds, and the pressure was released. This was repeated three more times. The autoclave was pressured with hydrogen to 750 psi at room temperature and then heated with rapid stirring to 160° over 0.5 hour and maintained at 160° for 1.2 hours. After cooling and filtering as described above, gc analysis (Column A, 200°) of the hexadecane solution showed that the product consisted of 97% 2-methyl-1,2,3,4-tetrahydroquinoline (**2**) and 3% 2-methylquinoline (**1**). Gc analysis using an external standard showed that the absolute yield of **2** was 100% based on consumed starting material.

Other reactions where carbon disulfide was present were carried out in the same manner except when nickel on silica-alumina was used, the amount of catalyst was 0.70 g and carbon disulfide was 60 μl (0.075 g). When hydrogen sulfide was used instead of carbon disulfide, about 0.1 g of the gas was added after the autoclave was flushed with hydrogen and before it wsa pressured to 750 psi with hydrogen. Differences in reaction temperatures and times are noted in Table II.

Hydrogenation of 2-Methylquinoline in the Presence of Carbon Monoxide.

To a 300 ml autoclave was added 10.0 g (0.070 mole) of 2-methylquinoline, 90.0 g of *n*-hexadecane, and 0.20 g of 5% palladium on alumina. The autoclave was flushed with hydrogen four times as described previously. Carbon monoxide was then flowed through the autoclave to displace hydrogen, and the carbon monoxide pressure was brought to 50 psi gauge pressure. Then 800 psi hydrogen was also added. The autoclave was heated with rapid stirring to 200° over 0.5 hour and then maintained at 200° for 3.2 hours. After cooling and filtration as described previously, gc analyses (Column A, 200°) of the hexadecane solution showed that the product consisted of 94% 2-methyl-1,2,3,4-tetrahydroquinoline and 6% starting material. A second run with the carbon monoxide at 7 psi gauge pressure gave the same result. In this case the reaction temperature was 182° for 2.7 hours. A third run with the carbon monoxide pressure at atmospheric pressure gave a mixture of 99.4% 2-methyl-1,2,3,4-tetrahydroquinoline and 0.6% 2-methyl-5,6,7,8-tetrahydroquinoline. In this run the reaction temperature was 176° for 3 hours.

Typical Procedure for Hydrogenation of Quinolines Using Rhenium, Iridium, Molybdenum, Tungsten, Chromium, and Iron Catalysts (Table III).

To a 300 ml autoclave was added 10.0 g (0.070 mole) of 2-methylquinoline, 90.0 g of *n*-hexadecane, and 0.20 g of 5% rhenium on alumina. The autoclave was flushed with hydrogen four times as described previously and then pressured to 750 psi with hydrogen at room temperature. The autoclave was heated with rapid stirring to 171° over 0.5 hour and then maintained at 171° for 3.5 hours. After cooling and filtration as previously described, gc analysis (Column A, 200°) of the hexadecane solution showed that the product consisted of 97% 2-methyl-1,2,3,4-tetrahydroquinoline (**2**) and 3% starting material and that the absolute yield of **2** was 100% based ion consumed starting material. The same result was obtained when cyclohexane was used as solvent instead of *n*-hexadecane.

Other reactions in Table III were carried out the same way except that the amount of catalyst, reaction temperature, and time were sometimes different as shown in Table III. Also for reactions using molybdenum(VI) oxide, tungsten(VI) oxide, chromium(III) oxide, or cobalt(II) oxide-molybdenum(VI) oxide on alumina, the amount of hexadecane and 2-methylquinoline was 70% of that in the procedure above. For reactions involving iridium(IV) oxide, rhenium on alumina with 2-isobutylquinoline, and iridium on alumina with 4-methylquinoline, the amount of hexadecane and quinoline compound was 75% of that in the procedure above.

Hydrogenation of Acridine (4).

To a 300 ml autoclave was added 5.00 g (0.028 mole) of acridine, 95.0 g of *n*-hexadecane, and 0.50 g of 5% platinum on alumina. The autoclave was flushed with hydrogen as described previously and then filled to 800 psi at room temperature. The autoclave was heated with rapid stirring to 170° (1000 psi) over 1.0 hour and then maintained at this temperature for 7 hours. After cooling, 50 g of toluene was added to the reaction mixture which was stirred and filtered. A gray solid was filtered out which was dissolved in ether, and the ether solution was filtered and evaporated to give 3.9 g (77%) of 9,10-dihydroacridine as white crystals, mp 170-171° (lit [11] mp 169-171°). Gc analysis (Column C, 167°) of the filtrate showed that it contained only 9,10-dihydroacridine and starting material. The total absolute yield of 9,10-dihydroacridine was 96%. When 5% rhenium on alumina was used as catalyst under similar conditions, 9,10-dihydroacridine and starting material were also the only compounds observed.

Typical Procedure for Hydrogenation of Indoles (Tables IV and V).

To a 300 ml autoclave was added 10.0 g (0.085 mole) of indole, 90.0 g of *n*-hexadecane, and 0.60 g of 5% platinum on alumina. The autoclave was pressured with hydrogen to 700 psi, stirred briefly, and then the pressure was released. This was repeated three more times. The autoclave was pressured with hydrogen to 1890 psi at room temperature and then heated with rapid stirring to 227° over 0.5 hour and maintained at 227° for 10.5 hours. The final pressure at 227° was 2200 psi. The autoclave was cooled to room temperature, and the contents were suction filtered. To obtain complete recovery of the hexadecane solution, the autoclave and catalyst were washed with acetone which was evaporated separately before combining with the main filtrate. Gc and gc-ms (Column D, 147°) of the hexadecane solution showed that the reaction product consisted of 82% indoline and 18% indole. An identical reaction carried out for 4.5 hours at 227° gave the same percentages of indoline and indole. Gc analysis using external standards showed that these two compounds accounted for 99% of the starting material.

The indoline was isolated by extraction of the *n*-hexadecane solution with 5% aqueous hydrochloric acid. The hydrochloric acid extract was washed four times with methylene chloride, neutralized with 25% sodium hydroxide solution to *p*H 8-9, and then extracted with methylene chloride. The methylene chloride extract was washed with water, dried with anhydrous sodium sulfate, and evaporated under vacuum using rotary evaporator to give the indoline which was identical (ir, nmr, ms, retention time) to an authentic sample.

The other hydrogenations described in Tables IV and V were carried out the same way as described above except for some differences in pressures, temperatures, times, and/or amounts of catalyst which are noted in the tables.

The 2-methylindoline (**7b**) was isolated as described for indoline and gave; ir (neat): 3365, 1608, 1245, 742, 710 cm^{-1}; nmr (deuteriochloroform): δ 1.17 (d, 3H, J = 7 Hz), 2.23-3.34 (m, 2H), 3.40-4.15 (m, 2H), 6.34-7.18 (m, 4H); ms: m/e 133 (M^+).

Anal. Calcd. for $C_9H_{11}N$: C, 81.15; H, 8.33; N, 10.52. Found: C, 80.90; H, 8.50; N, 10.34.

The 2,3-dimethylindoline (**7c**) was an 82:18 mixture of the *trans* and *cis* isomers, respectively, with the *trans* isomer having slightly shorter retention (Column D, 147°). The nmr spectra were in agreement with those previously reported [12].

Hydrogenation of Carbazole (**8**).

To a 300 ml autoclave was added 5.00 g (0.030 mole) carbazole, 95.0 g of *n*-hexadecane, and 0.70 g of 5% platinum on alumina. The autoclave was flushed with hydrogen as previously described and then filled to 1690 psi at room temperature. The autoclave was heated with rapid stirring to 25.0° over 1.0 hour and then maintained at 250° for 3.2 hours. The final pressure was 2260 psi. After cooling, 100 g of toluene was added to the reaction mixture which was stirred and then filtered. A gray solid was filtered out which was dissolved in ether, and the ether solution was filtered and evaporated to give 1.9 g of unreacted carbazole as white crystals, mp 246-247° (lit [11] mp 247-248°). Gc (Column C, 200°) and gc-ms of the filtrate showed that it contained carbazole, 1,2,3,4-tetrahydrocarbazole (**9**), *cis*-2,3,4,4a,9,9a-hexahydrocarbazole (**10**), and dodecahydrocarbazoles. Taking into account the isolated carbazole, the relative percentages were 53% carbazole, 36%, 1,2,3,4-tetrahydrocarbazole, 5% *cis*-2,3,4,4a,9,9a-hexahydrocarbazole, and 6% dodecahydrocarbazoles.

The *cis*-2,3,4,4a,9,9a-hexahydrocarbazole was isolated by preparative gc (Column E, 160°) as a white solid, mp 94-96° (lit [13] mp 95-96°).

The 1,2,3,4-tetrahydrocarbazole was also isolated by preparative gc (Column E, 210°) as a white solid, mp 117-119° (lit [14] mp 118-119°).

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