anhydrous ether in a nitrogen atmosphere was added dropwise 305.5 g. (1.03 moles) of diethyl (3,4-methylenedioxyphenyl)-malonate over a period of 5 hr. The solution was refluxed for 20 hr., cooled in an ice–salt bath, and decomposed with 770 g. of ammonium sulfate in 1500 ml. of water. The ether layer was removed, and the aqueous layer was extracted twice with ether. The ether extracts after drying and evaporation yielded 25.40 g. of an unidentified fraction, b.p. 160–165° (1.5 mm.). This contained some of the expected diol as shown by the formation of a dinaphthylurethane derivative, m.p. 297–298°. However, no diol could be crystallized by seeding the oil with pure diol. The diol was isolated by continuous extraction of the aqueous suspension from the reduction, with chloroform for 48 hr., evaporation of the chloroform, and recrystallization from benzene. The yield was 62 g. (30%), m.p. 79–81°.

Anal. Calcd. for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.11; H, 7.34.

2-(3,4-Dimethoxyphenyl)propane-1,3-diol Ditosylate.—A solution of 40 g. (0.188 mole) of 2-(3,4-dimethoxyphenyl)propane-1,3-diol in 200 ml. of dry pyridine was cooled to 0° and 80 g. (0.5 mole) of *p*-toluenesulfonyl chloride was added keeping the temperature below 10°. The solution was left overnight at 20° and then poured into an ice solution containing 300 ml. of concentrated hydrochloric acid. The solid which separated on scratching was recrystallized from absolute ethyl alcohol to give 72.5 g. (74%) of the ditosylate, m.p. 112.5–114.5°.

Anal. Calcd. for $C_{25}H_{28}O_6S_2$: C, 57.67; H, 5.42. Found: C, 57.69; H, 5.27.

Diethyl 3-(3,4-Dimethoxyphenyl)cyclobutanedicarboxylate.—To a solution of 88.3 g. (0.17 mole) of 2-(3,4-dimethoxyphenyl)-propane-1,3-diol ditosylate and 30.20 g. (0.19 mole) of diethyl malonate in 600 ml. of dioxane at 100° was added slowly (3 hr.) 7.65 g. (0.17 mole) of 53.3% sodium hydride in mineral oil. The mixture was refluxed for 3 hr., and then an additional 0.17 mole of sodium hydride was added. The mixture was refluxed an additional 15 hr., and the solvent was removed. The diester was extracted from the residue with ether, washed with water, and dried. It was purified partially before distillation by passing through an alumina column with ether. The diester (30.94 g., 54%) was a colorless oil, b.p. 178–181° (0.2 mm.), and was identified by its n.m.r. spectrum.

Acknowledgment.—We are grateful to Smith Kline and French Laboratories for support of this work.

Hydrogenation of Aniline to Cyclohexylamine with Platinum Metal Catalysts

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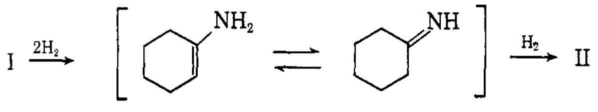
The platinum metals—rhodium, ruthenium, platinum, and palladium—have been investigated as catalysts for the liquid-phase hydrogenation of aniline (I) to cyclohexylamine (II). A major objective was to determine the extent and mechanism of formation of dicyclohexylamine (III). The effects of the addition of ammonia and of III were studied.

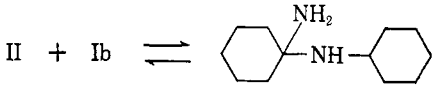
The literature indicates that ruthenium is the best of the platinum metal catalysts for the hydrogenation of aromatic amines to alicyclic amines.[1-4] Among the base metals, cobalt has been used with considerable success, although it requires rather high temperatures and pressures.[5-8]

The catalytic hydrogenation of I to II probably proceeds stepwise with the formation of enamine and imine intermediates (eq. 1).



Ia Ib (1)

The mechanism of formation of the major by-product (III) probably is the same as proposed for the production of secondary amines in the hydrogenation of nitriles.[9] This involves the addition of II to the imine Ib (eq. 2). IV then may undergo hydrogenolysis

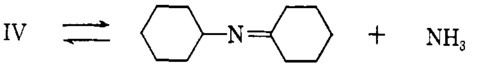


(2)

IV

directly to III (eq. 3) or lose ammonia to form a ketimine (V) (eq. 4), which then is reduced to III.

$$\mathrm{IV} \xrightarrow{H_2} \mathrm{III} + NH_3 \tag{3}$$



(4)

V

It also has been suggested[10] that, at sufficiently high temperatures (>160–170°), the nickel-catalyzed hydrogenation of I to II results in the formation of III by the following reaction.

$$2\mathrm{II} \longrightarrow \mathrm{III} + NH_3 \tag{5}$$

In addition to the formation of secondary amine, an important side reaction at very high temperatures is the production of cyclohexane. This reaction is

$$\mathrm{II} \xrightarrow{H_2} C_6H_{12} + NH_3 \tag{6}$$

noticeable below 300° but not important below 325° with nickel and cobalt catalysts.[5] Cyclohexane formation becomes excessive with the more active ruthenium catalyst at about 200° and is not diminished by the addition of III or ammonia.[11]

Experimental

Each experiment on the hydrogenation of I was run in a 1-l., stainless steel, rocking autoclave with 186 g. (2.0 moles) of I and, unless otherwise specified, 1.86 g. of a dry 5% metal-on-carbon catalyst (Engelhard Industries, Inc.) at 800–1000 p.s.i.g.

The effect of adding each of the following substances was studied: III (18.0 g., 0.10 mole, 5 mole % based on I), concentrated aqueous ammonia (14 ml., 0.2 mole, 10 mole % based on I), and ammonia (5 ml. as liquid ammonia, *ca.* 0.2 mole, 10 mole

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TABLE I

HYDROGENATION OF ANILINE[a]

Catalyst	Added	Temp., °C.	Time, hr.	Mole % yield[b] II	Mole % yield[b] III
Ru	. . .	120	11	71.5	15.5
	III[c]	120	11.5	69.5	15.5
	. . .	145	2	73	15.5
	III[c]	140	3	72	16.5
	concd. NH_4OH[d]	145	2.25	75[e]	3
[f]	NH_3[g]	145	18	82	6.5
Rh	. . .	120	5.75	63	25
	III[c]	120	12	65	25
	. . .	145	1.5	61	28
	NH_3[g]	145	4.5	[h]	
Pd	. . .	145	5	[i]	
Pt	. . .	145	5	[j]	

[a] Unless otherwise specified, each experiment was run in a 1-l. rocking autoclave with 186 g. (2.0 moles) of I and 1.86 g. of a 5% metal-on-carbon catalyst at 800–1000 p.s.i.g. until the reaction was completed. [b] Determined by gas–liquid chromatography. Reactions that went to completion resulted in about 0.5 mole % yields of cyclohexane and traces of benzene. [c] 18 g. (0.10 mole). [d] 14 ml. (0.2 mole). [e] 7% yield of cyclohexanol also was obtained. [f] Used 3.72 g. of catalyst. [g] Liquid NH_3, *ca.* 5 ml. (*ca.* 0.2 mole). [h] Little or no reaction at 1250 p.s.i.g. [i] *Ca.* one-third complete. [j] Little or no reaction at 1200 p.s.i.g.

% based on I). The liquid ammonia was added to the autoclave after the vessel, containing I and catalyst, had been cooled in a Dry Ice–acetone bath. The autoclave then was sealed and purged with nitrogen and then with hydrogen, and hydrogen was added while the vessel still was cold.

At the end of each reaction the autoclave was cooled and depressurized, and its contents were filtered to remove the catalyst. Methanol was used as a solvent to assist in removing the reaction mixture from the autoclave and for washing the filter cake. The filtered reaction mixture, now containing methanol, was separated by distillation into several fractions that then were analyzed by gas–liquid chromatography.

The results are summarized in Table I. Except for the experiments with added liquid ammonia, duplicate experiments gave excellent reproducibility both of reaction rates and product yields. Duplication of the experiment with the ruthenium catalyst and added liquid ammonia gave very good reproducibility of product yields; however, the reaction rates were variable due, no doubt, to variable losses of the volatile ammonia during loading and purging operations.

In one experiment, 198 g. (2.0 moles) of II was treated with 1.86 g. of 5% ruthenium on carbon and hydrogen for 5.75 hr. at 145° and 1075 p.s.i.g. After removal of the catalyst by filtration, the reaction mixture was analyzed by gas–liquid chromatography. About 3% of II had been converted into III. No other reaction was detected.

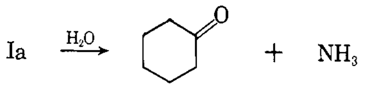
The material balances for the experiments described in Table I are significantly less than quantitative. It is likely that this is due to mechanical losses, since no other products were detected.

Results and Discussion

The palladium catalyst was severely inhibited and the platinum catalyst almost completely poisoned, presumably by the strongly adsorbed II initially formed. No further work was done with these catalysts. Similar inhibitions of platinum catalysts have been reported.[12] The use of an acid medium with platinum catalysts to convert toxic free bases to nontoxic ammonium ions is well known. Such techniques were not used in this study.

Ammonia suppresses the formation of secondary amines during the hydrogenation of nitriles,[13] and it has been postulated that this effect is due to the reverse of eq. 4.[13] The formation of an N-substituted imine and ammonia from an imine and a primary amine (eq. 2 and 4) proceeds at room temperature, is not catalyzed, and should be suppressed by ammonia.[10] Indeed, it has been demonstrated that the reaction sequence in eq. 2 and 4 is in fact reversible.[14]

The use of dry ammonia resulted in considerable inhibition with ruthenium and complete inhibition with rhodium. The experiment with ruthenium was carried to completion; although the reaction was impractically slow, the ammonia significantly decreased the formation of III. Water is known to eliminate the catalyst toxicity of ammonia by converting it to the nontoxic ammonium cation.[15,16] Predictably, the use of aqueous ammonia with the ruthenium catalyst did not cause any inhibition and still decreased the formation of III. However, there resulted the expected formation of cyclohexanone (and its subsequent reduction to cyclohexanol) by hydrolysis of enamine intermediates[17,18] (eq. 7). Thus, the use of either dry or aqueous ammonia to decrease the formation of III is not feasible.



(7)

The addition of III retards the formation of additional secondary amine in the nickel-,[5,6] cobalt-,[5,6] and ruthenium-catalyzed[11] hydrogenations of I at high temperatures (>200°). This effect of added III probably is due to the demonstrated reversibility[19] of the reaction shown in eq. 5. No such effect was observed in our experiments at lower temperatures with ruthenium and rhodium catalysts; results of the treatment of II with a ruthenium catalyst at 145° in the presence of hydrogen indicated that the reaction shown in eq. 5 is of minor importance under our experimental conditions. Furthermore, the added III retarded the rate of the rhodium-catalyzed hydrogenation, although the rate with the ruthenium catalyst was little affected. An inhibitory effect of alkyl amines on a rhodium catalyst previously has been reported.[20]

There was very little formation of cyclohexane (<1%) with ruthenium or rhodium catalysts at 145°.

In the range of 120–145°, temperature had little or no effect on the formation of III with either the rhodium or ruthenium catalyst (Table I). A 2–3% yield of III has been reported at mild temperatures (25–90°) with a rhodium catalyst at very high catalyst levels.[21]

In the absence of added III or ammonia, the rhodium catalyst was more active than ruthenium, as has been previously reported.[22] The rates of hydrogenation were quite temperature dependent with each catalyst (Table I).

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The ruthenium catalyst was significantly superior to rhodium with respect to the selective formation of II rather than III under all conditions studied.

Conformations of Bicyclo[3.3.1]nonanes. 3-Methyl-2,4-dioxabicyclo[3.3.1]nonane

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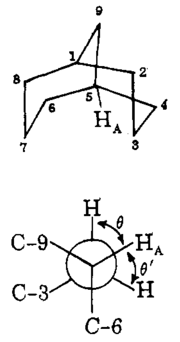
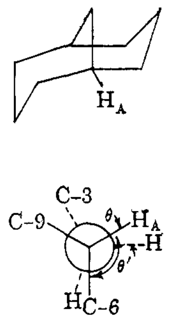
The bicyclo[3.3.1]nonane ring is interesting because the two "inside" hydrogens on C-3 and C-7 in the conformation (I) must have a considerable interaction. As a part of a program of study of the chemistry of the bridged medium rings it was important to ascertain the effect of this interaction on the preferred conformation of the ring. Until recently no information pertinent to this problem has been available, but it has been shown[1] *via* X-ray analysis that the hydrogen repulsion is relieved by flattening each ring *via* spreading the ring angles to 114°. The preferred conformation is the double chair (I) where the "inside" atoms at C-3 and C-7 are both hydrogen.

This paper describes an attempt to solve the conformational problem through the use of n.m.r. spectroscopy. Vicinal coupling constants are primarily dependent on the dihedral angle,[2] so that the bridgehead proton, H_A, should be nearly equivalently coupled to the two protons at C-4 in I ($\theta = \theta'$), but unequally coupled to the same pair in II ($\theta \neq \theta'$). For conformation I, H_A is expected to exhibit a triplet (AX_2) in the n.m.r. spectrum, whereas for II a quartet (doublets of a doublet, AXY with $J_{AX} \neq J_{AY}$) should appear. Thus the n.m.r. spectrum might be expected to differentiate between I and II in two ways: (a) the difference in the vicinal coupling constants and (b) the difference in the spectral patterns for the bridgehead proton, H_A.



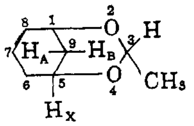
I



II

Actually the situation is considerably less favorable than this analysis would suggest. Unless the protons under consideration can be isolated from those in the remainder of the molecule, the spectrum would probably be too complex for analysis. Even then analysis would be troublesome unless the protons had a sufficiently large chemical shift difference. Distortion of the molecule from the symmetrical conformations I and II might tend toward a common spectrum intermediate between the extremes depicted above. Finally rapid interconversion of I and II would lead to a pair of coupling constants which are a weighted average of those characteristic of the protons in each environment.[4] Thus it is possible that an unambiguous conformational assignment might not be possible. Seeking a simple, readily accessible molecule to permit an experimental test of n.m.r. for conformational studies in this ring system we chose to study some 2,4-dioxabicyclo[3.3.1]nonanes.

All attempts to prepare a cyclic acetal from cyclohexane-1,3-diol (predominantly the *cis* isomer) and various aldehydes failed. Exchange methods utilizing commercially available acetals or ketals fared no better. Apparently the equilibrium concentration of cyclic acetal is negligibly small, the reduced stability of the acetal undoubtedly being an effect of the hydrogen repulsions mentioned earlier. Eventually we prepared a sample of 3-methyl-2,4-dioxabicyclo[3.3.1]nonane (III), albeit in low yield, by the method of Croxall, Glavis, and Neher.[5] III was clearly identified by (a) its molecular weight, which eliminates polymeric acetals, (b) its hydrolysis to give acetaldehyde, (c) its infrared spectrum which shows the absence of hydroxyl and carbonyl groups, and the presence of ether links, and (d) its n.m.r. spectrum which is discussed in detail below.



III

The n.m.r. spectrum of III exhibits peaks in three general groups, a sharp quartet at τ 4.74, a poorly resolved quintet at 5.79, some 16–20 peaks between 7.2 and 8.0 merging into a series of peaks between 8.0 and 9.0, and a sharp doublet at 8.8. Some of the bands are immediately and unequivocally assignable. The sharp quartet (1H) at τ 4.74 is due to the C-3 proton which is uniquely coupled (J = 5.0 c.p.s.) to the methyl protons as an AX_3 set. Accordingly the methyl group shows up as a clean doublet (3H) at τ 8.8 with the same coupling. The most important feature of the spectrum for our analysis is the incompletely resolved quintet (2H) at τ 5.79. A repetitive spacing of 2.5 c.p.s. and a width at half-height of 9.0 c.p.s. characterize the peak. It is certainly due to the bridgehead protons. The remainder of the spectrum is complex. It is pleasing to note that the τ 8–9 section of the spectrum bears a very strong resemblance to that of *cis*-1,3-

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