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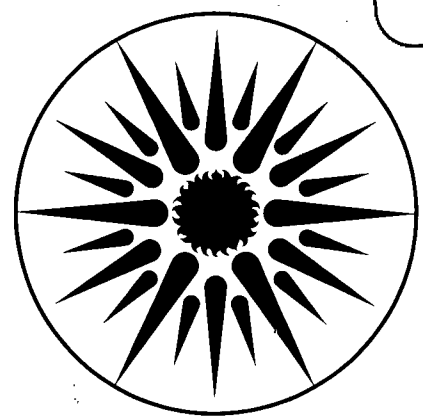
HOMOGENEOUS CATALYTIC HYDROGENATION. 2. SELECTIVE
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CATALYZED BY CHLORO(TRISTRIPHENYLPHOSPHINE)RHODIUM(I)

R.H. Fish and A.D. Thormodsen

July 1983

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Homogeneous Catalytic Hydrogenation. 2.
Selective Reductions of Polynuclear Heteroaromatic Compounds
Catalyzed by Chloro(Tris(triphenylphosphine)Rhodium(I))

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Abstract: The selective reductions of polynuclear heteroaromatic nitrogen compounds such as quinoline, 1, 5,6-benzoquinoline, 2, 7,8-benzoquinoline, 3, acridine, 4, phenanthridine, 5, and in one case, a sulfur heterocyclic compound, benzothiophene, 6, with Wilkinson's catalyst, $(\phi_3P)_3RhCl$, provided under rather mild hydrogenation conditions, the corresponding saturated nitrogen and sulfur heterocyclic analogs of the above-mentioned compounds in excellent yields.

In addition, compounds that inhibit the rate of hydrogenation of 1 in the conversion to 1,2,3,4-tetrahydroquinoline, 12, include pyridine, 8, 3-methylpyridine, 9, and 12 itself. These results are indicative of electronic effects in these competitive hydrogenation reactions, while 2-methylpyridine, 11, slightly reduces the rate of hydrogenation of 1 implicating a steric effect. It was also observed that indole, 10, increased the rate of hydrogenation of 1 to 12, while thiophene, 7, had no effect.

The substitution of deuterium gas for hydrogen gas in the reduction of 1 provided information on the reversibility of the hydrogenation step, stereoselectivity in the reduction of the 3,4-double bond and the implication of cyclometallation reactions which caused the exchange of H

for D at the 8 and possibly 2 positions. Similar deuteration data with compound 5 strengthened the concept of dehydrogenation in the hydrogenation step and in fact provided independent evidence for the facile dehydrogenation of 9,9'-dideutero-1-deuterophenanthridine catalyzed by $(\phi_3P)_3RhCl$.

Introduction

Recently, we discovered that the nitrogen heterocyclic ring incorporated in polynuclear heteroaromatic nitrogen compounds can be regioselectively reduced under a variety of homogeneous hydrogenation conditions.^{1a,b} These results are important, since they have practical implications for the future synthetic fuel industry with regard to coal liquefaction and the up-grading of coal liquids and shale oils as well as the ultimate removal of nitrogen from these synthetic fuels.

In our quest for catalysts that could perform these reductions under rather mild conditions, we have discovered that Wilkinson's catalyst, $(\phi_3P)_3RhCl$, can selectively reduce the heterocyclic ring in polynuclear heteroaromatic nitrogen and sulfur model synthetic fuel compounds.

Although Wilkinson's catalyst has been one of the most extensively studied homogeneous hydrogenation catalysts known,^{2a-d} to our knowledge, this is the first reported use of this catalyst for the selective hydrogenation of the types of model synthetic fuel compounds shown in the Chart under homogeneous conditions.³ Additionally, we will demonstrate the usefulness of deuterium gas, in place of hydrogen gas, for understanding the various mechanisms involved in the reduction of

polynuclear heteroaromatic compounds, including reversibility in the hydrogenation of the carbon-nitrogen double bond, i.e., dehydrogenation, as well as the implication of a cyclometallation reaction in the exchange of hydrogen for deuterium in the aromatic ring that is in proximity to the heterocyclic ring and the position alpha to the nitrogen atom. We have also attempted to define what potential inhibitory effects other model synthetic fuel constituents would have on the rate of hydrogenation using compound 1 for these studies.

Results and Discussion

Selective Hydrogenation

Table 1 contains the data for the selective reduction of compounds 1-5 for the nitrogen heterocyclic ring, and in one case, 6, a sulfur heterocyclic ring, catalyzed by $(\phi_3P)_3RhCl$ under a standard set of conditions. We made no effort to study the variation of substrate to metal ratio, but found that turnover numbers ranged from 5 to ~2 per hour with the 10:1 substrate/metal ratio used. Substrates 1, 2, 4, and 5 were highly reactive providing in nearly all cases quantitative conversions to the saturated nitrogen heterocyclic product, while substrates 3 and 6 were not as reactive, although they retained the regioselectivity observed with the other substrates mentioned.

Inhibition Studies

As stated, we wanted to learn about other potential synthetic fuel compounds that might inhibit these hydrogenation reactions. Quinoline, 1, was chosen as the model compound, and interestingly we found that the rate of hydrogenation was not affected by thiophene, 7, but was totally

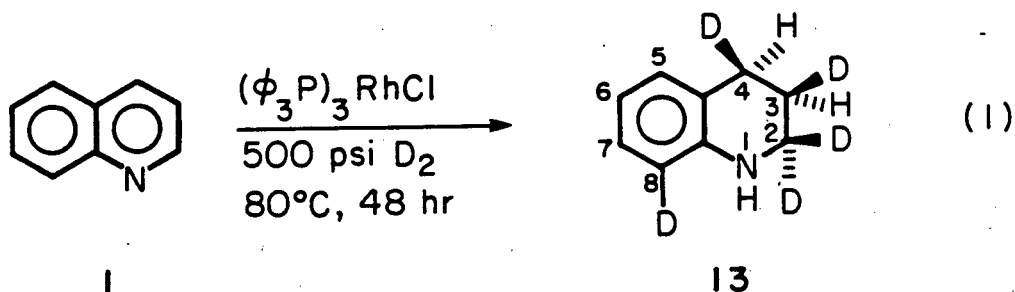
quenched by pyridine, 8 and 3-methylpyridine 9,⁴ (1:1 molar ratio of 7, 8 and 9 to 1). Moreover, the rate of hydrogenation of 1 was enhanced by indole, 10, by a factor of 1.4, while 10 itself was not hydrogenated. In addition, 2-methylpyridine, 11, slightly retarded the rate as did the product 1,2,3,4-tetrahydroquinoline, 12. (Table 2).

It appears that competitive binding of the substrates to the rhodium metal center is a highly critical parameter that encompasses both steric and electronic effects. For example, 8 (pK_b 8.42) and 12 (pK_b ~9.38) are stronger bases than 1 (pK_b 9.52) with 8 quenching and 12 retarding the rate of hydrogenation of 1, whereas thiophene an aromatic sulfur compound has no effect. It is interesting to note that 8 and 9 quench, but 2-methylpyridine, 11, (pK_b 8.03) slightly retards the hydrogenation rate of 1, and this clearly must be a consequence of a steric effect in binding at the rhodium metal center.^{5,2d} At this time, we have no definitive reason why indole (10) enhances the hydrogenation rate of 1, other than possibility assisting in the dissociation of triphenylphosphine from the rhodium metal center to a highly reactive 14 electron species, thus permitting a more facile pathway for quinoline coordination to rhodium.^{2a-d}

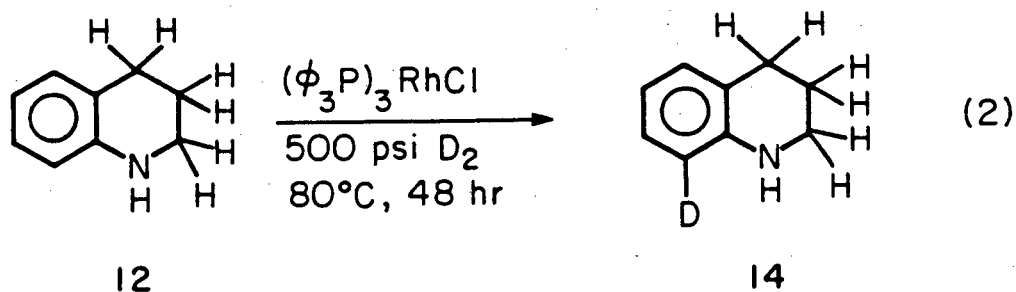
Deuterium Gas Experiments

The substitution of deuterium gas (D_2) for hydrogen gas (H_2) has been shown to be helpful in elucidating mechanisms and stereochemistry in homogeneous hydrogenation reactions.^{2c,d} The reaction of 1 with D_2 gas (500 psi) and $(\phi_3P)_3RhCl$ at 80°C for 48h (10:1 substrate to metal ratio) followed by analysis by gas chromatography - mass spectrometry (GC-MS) and 400 MHz 1H nuclear magnetic resonance spectroscopy (nmr)

provided the results depicted in Equation 1.



The reaction product, 13, had 1.6D at position 2, 1.0 D each at positions 3 and 4 and 0.7 D at position 8. The deuterium on the nitrogen atom (N-D) gets readily exchanged due to traces of water in the sample preparation procedures for both GC-EIMS and nmr analysis. The high field ^1H nmr spectrum at 400 MHz also provided information concerning the stereochemistry of deuteriums at positions 3 and 4. The line-width for multiplets at 1.90 ppm, assigned to H-3, and 2.73 ppm, assigned to H-4, were both 12.1 Hz; clearly, indicative of a cis configuration⁶ for the hydrogens on carbons 3 and 4^{2a,c,d} (Eq. 1), i.e., a 3,4-cis-deuteration of the 3,4-double bond. More importantly, when compound 12 was subjected to the same deuteration condition as shown in equation 1, no exchange of the saturated nitrogen ring hydrogens was observed by 250 MHz ^1H nmr spectroscopy. However, exchange of the aromatic hydrogen (position 8) that is beta to the nitrogen readily occurs with incorporation of 0.7 D as evidenced by the decrease in the area of the doublet at 6.42 ppm, assigned to the proton on C-8 of compound 14 (Eq. 2).



The experiment defined in equation 1 also showed by GC-EIMS that the remaining quinoline (~2%) was monodeuterated [$M^{+\bullet}$, m/e 130 (100% RA)]. Furthermore, if the reduction of 1 with deuterium gas (Eq. 1) was allowed to proceed to only a 50% conversion of the deuterated tetrahydroquinoline, the remaining isolated 1 had deuterium incorporation exclusively at C-2 as evidenced by its 250 MHz 1H nmr spectrum (8.9 ppm, doublet of doublets, 0.3D). A GC-EIMS analysis showed a m/e 130 ion for quinoline-2-d, but in approximately 10% relative abundance. This strongly implies that the second deuterium incorporation at C-2, (i.e., 13) comes predominately, but not exclusively, by deuteration of quinoline-2-d. This is substantiated by GC-EIMS and nmr analyses of the deuterated tetrahydroquinoline formed in the incomplete reduction (~50%), which indicates mainly 1,2,3,4-tetrahydroquinoline- d_3 rather than the d_4 compounds formed in the quantitative conversion, i.e., one deuterium at C-2 rather than 1.6D.

Plausible Mechanistic Pathways in the Hydrogenation of 1

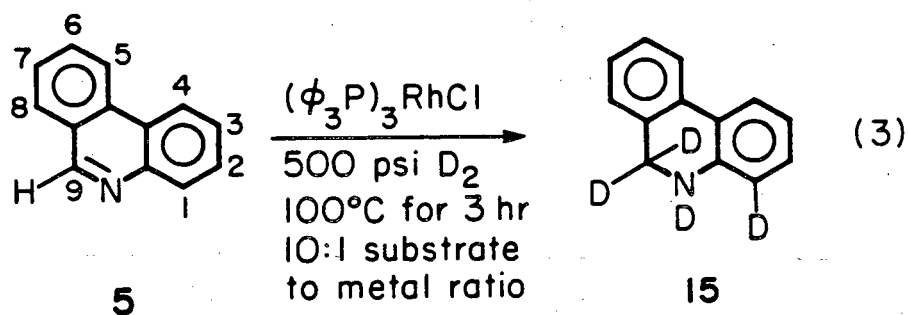
The above stated deuterium results can be accommodated by several plausible rhodium intermediates as shown in the Scheme. Intermediate B can occur via intramolecular addition of deuterium (or hydrogen) to the carbon-nitrogen double bond via Intermediate A. Exchange of the hydrogen on the carbon that is alpha to nitrogen and allylic to the 3,4-double bond can occur by two conceivable pathways: (1) oxidative addition (cyclometallation) to give C or the apparently more predominate mechanism (2) where intermediate B can exchange hydrogen for deuterium by being in equilibrium with A and quinoline-2-d. The latter compound can then recycle to B. Reduction of the 3,4-double bond may have a com-

parable rate to the dehydrogenation step, i.e., $B \xrightarrow{+} A \xrightarrow{+} 1$, but effectively eliminates any exchange at position 2. The cyclometallation reaction (oxidative addition) at position 8 (intermediate E) will allow exchange of that aromatic hydrogen.

Intermediates C and E (Scheme) have some precedents in the literature. For example, Stone et al.^{8a,b} reported on several ortho-metallation reactions with Os and Ru carbonyls and compound 3 (Chart) to provide the five-membered ring equivalent to intermediate E (Scheme) and Yin and Deeming⁹ have observed metallation of carbon atoms alpha to a nitrogen atom in several aromatic imine ($\phi-C=N-$) derivatives. Kaesz et al.^{10a,b} have reported on a cyclometallated product, which had a metalla-azacyclopropane structure, as established by single-crystal-x-ray crystallography and represents a model for Intermediate C (Scheme). Laine et al have also postulated these metalla-azacyclopropane intermediates in deuterium exchange reactions with trialkylamine compounds as substrates and rhodium cluster carbonyls as catalysts.¹¹ The homogeneous catalytic activation of C-H bonds for hydrogen-deuterium exchange has been reviewed extensively by Parshall¹² and Dehand and Pfeiffer¹³.

Dehydrogenation Step in Hydrogenation of 5

In further experiments to provide more support for the dehydrogenation sequence, $B \xrightarrow{+} A \xrightarrow{+} 1$ (Scheme), we studied the deuteration of compound 5 and found, by GC-EIMS (m/e 184 32% RA) and 250 MHz 1H nmr spectroscopy, two deuteriums at position 9 (absence of nmr signal at 4.4 ppm, singlet) and approximately 0.3 D at position 1 (7.66 ppm doublet) for compound 15. Again, as in the deuterium gas experiments with 1, the N-D group gets exchanged to some extent upon work-up. (Eq. 3).



This result supports the fact that activation of hydrogen on the carbon atom alpha to the nitrogen atom is a prerequisite for exchange, i.e., benzylic or allylic carbon positions. Furthermore, reaction of compound 15 with catalytic amounts of $(\phi_3P)_3RhCl$ readily provided the dehydrogenated product (25°C, 1 hr), phenanthridine- d_2 , with deuteriums at the 9 and 2 positions as determined by GC-EIMS and 250 MHz 1H nmr spectroscopy (absence of singlet at 9.3 ppm assigned to the proton on carbon 9).

Clearly, from the above-stated results, the dehydrogenation step by a plausible intermediate such as B (Scheme) to deuterated 1, possibly via intermediate A, definitely occurs under the hydrogenation conditions.¹⁴ Obviously, the isolation of complexes such as A-E (Scheme) would help to understand these rather complicated hydrogenation reactions and such studies are underway to clarify these points.

Conclusions

Our results show the mechanistic complexities in the hydrogenation of polynuclear heteroaromatic nitrogen compounds; but clearly, several plausible reaction pathways have been elucidated. Namely, the reduction of the carbon-nitrogen double bond, i.e., 1, 2, 3, and 5, is the initial product of hydrogen transfer from rhodium to the complexed substrate.

This is followed by a reversible dehydrogenation step, which was proven via deuterium experiments with 1 and 5, that must have a comparable rate to the stereospecific reduction of the 3,4 double bond in compounds such as 1-3. However in the hydrogenation of compounds such as 5 the metal catalyzed dehydrogenation step must be extremely facile due to the benzylic nature of the methylene group alpha to the nitrogen atom. In addition, cyclometallation reactions play a role in not only the exchange of aromatic hydrogens^{12,13} but conceivably also in the exchange of hydrogens on the carbon alpha to the nitrogen.

It was also observed that both steric and electronic effects control the hydrogenation rates of our substrates in the presence of compounds that can competitively bind to the rhodium metal center. This type of data will be highly useful in attempting to define the reactivity of these model coal compounds in very complex matrices such as coal liquids and shale oils.

Finally, we have also carried out similar hydrogenation experiments with substrates 1-6, using the heterogenized form of Wilkinson's catalyst, bonded to phosphinated polystyrene-divinylbenzene (2% or 20% crosslinked, 1-2% loading), and have found the same regioselectivity and excellent product conversions we observed in this present study.¹⁵ Subsequent manuscripts will also detail catalytic transfer hydrogenation results that exploit the above mentioned metal catalyzed dehydrogenation of 9,10-dihydrophenanthridine.¹⁶

Experimental

Materials and Instrumentation

The benzene (HPLC grade) was distilled from 4Å^o molecular seive and stored under Argon before use. Compound 1 (Aldrich) was distilled from 4Å^o molecular seive, while compound 3 (Aldrich) was purified by sublimation. compounds 2,4,5 and 6 were analyzed by capillary column gas chromatography and found to have > 99% purity (Aldrich). The Wilkinson's catalyst was either purchased from Alfa Inorganics or Strem Chemical or was provided as a gift from Englehard Industries. The capillary gas chromatography analyses were performed on a HP5880A instrument with a 15m x .035 mm DB-5 (J&W) capillary column, flame ionization detection with the following condition: 50^o to 200^oC with 1.5 min. initial hold at 50^o and 10^oC/min. to 200^oC with a 10 min. hold at 200^oC.

The GC-MS analyses were performed on a Finnigan 4023 quadropole mass spectrometer with a 30m x .031 mm DB-5 (J&W) capillary column and temperature programmed from 45^oC to 300^oC at 4^oC/min.

The nmr spectrometers used for ¹H nmr spectra were a 250 MHz instrument with a Nicolet computer located in the Department of Chemistry, University of California, Berkeley, CA and a 400 MHz Bruker nmr spectrometer located at the NBS-NML laboratory Gaithersburg, MD.

The kinetic apparatus (1991 ACK kinetic apparatus) was designed by us and built by Parr Instrument Co. to facilitate sampling of our reaction mixtures under the pressure and temperature conditions of the reaction. Figure 1 shows a schematic of the apparatus set-up used to follow

the rate of our hydrogenation reactions.

Procedure for Following Rates of Hydrogenation of Compounds 1-6
Using Wilkinson's Catalysts

The 1991 ACK kinetic apparatus in Figure 1 can be used as follows in a typical rate experiment. To the 45 ml reactor cup was added 0.1 mmole (92.5 mg) chloro(tris(triphenylphosphine)rhodium(I) and 1 mmole of compound 1-6, dissolved in 20 ml of benzene along with a stirring bar. The reactor cup, G, (Figure 1) was attached to the sample head. The hydrogen gas line was attached to valve D and with valves E and B open, the system was purged with hydrogen gas for 60 sec. The reactor was pressured with H₂ gas to 500 psi (valve B closed) and the cup (G) placed in a thermostated oil bath (80^o±1.0^o) and the temperature allowed to equilibrate for 5 min.. At regular intervals samples were removed for capillary gas chromatography analysis. For ease of sampling we followed a procedure in which valve E was opened and a sample was removed by previously inserting a syringe into the septum (C) with the barrel cut in half. Thus, approximately 100 μl of sample flowed into the cut off barrel to be readily sampled for GC analysis via a 10 μl syringe. After removal of the cut off syringe from the septum, valve D is opened along with valve E (cautiously) and the hydrogen gas forces the liquid back into the reactor. The pressure in the reactor can be readjusted to its initial reading by closing valve E and bleeding H₂ gas out of valve B. The entire sampling operation can be conveniently carried out in 1.5 min. and at intervals of 30 min. to 1 hr. depending on the rate of the reaction and GC analysis time. In this manner, five data points were obtained and analyzed graphically on an Apple II Plus computer using

plotting routines, while linear least squares analysis of the plots of percent conversion versus time provided slopes that gave pseudo zero order rates (%/min) at low conversions (linear for conversion up to 25%).

Inhibition Rate Studies

The inhibition rate studies were carried out in the above-mentioned reactor with 92.5 mg (0.1 mmole) Wilkinson's catalyst, 118 μ l, (1 mmole) quinoline, 1, and 1 mmole of the compound being studied as the inhibition or enhancer of the hydrogenation rate (Table 2) of 1 all dissolved in 20 ml of benzene. The reactor was pressurized to 310 psi H₂ and heated to 77°C ($\pm 2^\circ$). Five data points, as before, were plotted and analyzed by linear least square analysis (% conversion vs. time).

From the slope of the plots of % conversion vs time, we obtained a rate of hydrogenation (% conversion/min.), which was used to calculate the relative rates (compound 1 set to 1.0) by simply dividing the quinoline rate into the rates of the other substrates studied.

Deuteration of Compound 1

92 mg (0.1 mmole) of Wilkinson's catalyst and 129 mg (1 mmole) of compound 1 dissolved in 20 ml of benzene was placed in a Parr mini-reactor (45 ml). The mini-reactor was pressurized to 500 psi with deuterium gas and heated at 80° in a constant temperature oil for 10 hr. The reaction mixture was analyzed by capillary column gas chromatography and showed 100% conversion to deuterated tetrahydroquinoline. The reaction mixture was filtered through a 10 cm Florisil column to remove the catalyst and the solvent removed on a rotary evaporator. The capillary

column GC-EIMS results provided evidence for tetrahydroquinoline-d₄, m/e 137, while the 400 MHz ¹H nmr spectrum (benzene d₆) gave multiplets at 1.90 (H-3), 2.73 (H-4), 3.24 (H-2), 6.42 (H-8), 6.55 (H-5), and 6.93 (H-6, H-7) ppm with areas of 1:1:0.4:0.6:1:2 respectively, clearly defining the positions of deuteration.

A small amount (~ 2%) of compound 1 that remained after reduction was also analyzed by GC-EIMS to show m/e 130 (100% RA) indicative of deuterium incorporation in the starting material. To verify this result, we ran the deuteration of 1 to partial completion (~50% THQ) and after work-up by filtering through a 10 cm Florisil column and eluting with benzene-acetone (9:1), quinoline-2-d₁ was found by 250 MHz ¹H nmr (8.9 ppm d,d 0.3 D) and GC-EIMS (m/e 130 ~ 10% RA).

Deuteration of Compound 12

92.5 mg (0.1 mmole of Wilkinson's catalyst and 120 μ l (1 mmole) of 1,2,3,4-tetrahydroquinoline, 12, dissolved in 20 ml of benzene was placed in the 45 ml Parr mini-reactor. The reactor was pressurized to 500 psi with D₂ gas and heated at 80^o for 20 hr. The catalyst was removed by passing the reaction mixture through a 10 cm column of Florisil and removal of the benzene by rotary evaporation. The GC-EIMS analysis showed the m/e 134 ion (44% RA) indicative of 1,2,3,4-tetrahydroquinoline-d₁. The 250 MHz ¹H nmr spectrum (CDCl₃, TMS) provided clear evidence for deuterium exchange at C8 (6.42 ppm doublet, ~ 0.7D) and no deuterium incorporation at carbons C₁-C₄.

Deuteration of Compound 5

92.5 mg (0.1 mmole) of Wilkinson's catalyst and 100 mg (0.56 mmole) of 5 dissolved in 20 ml of purified benzene was placed in a Parr mini-

reactor (45 ml). The reactor was pressurized to 350 psi with deuterium gas and heated at 80°C for 2 hr. After reaction, the catalyst was removed by passing the reaction mixture through a column of Florisil (10 cm) and the benzene removed by rotary evaporation.

A ^1H 250 MHz nmr spectrum of the product, 15, provided unequivocal evidence for total deuteration at C-2 with the absence of the singlet for the methylene group alpha to the nitrogen atom at 4.4 ppm. The doublet (J_{ortho} 4.7 Hz; J_{meta} 2 Hz) at 7.66 ppm assigned to C-1 was reduced in area by about 30% (0.30). A GC-EIMS analysis of 15 indicated dihydrophenanthridine- d_3 with $\underline{m/e}$ 184 (32% RA).

Dehydrogenation of Dihydrophenanthridine- d_3 with Wilkinson's Catalyst

Dihydrophenanthridine- d_3 (1 mmole) and Wilkinson's catalyst (0.1 mmole) were dissolved in 20 ml of benzene and allowed to remain at room temperature (25°C) for 48 hr. The catalyst was removed via Florisil chromatography and a 250 MHz ^1H nmr spectrum revealed phenanthridine- d_2 with the pertinent absence of a signal at 9.3 ppm (singlet) for the proton at carbon 9. GC analysis also showed only phenanthridine and no dihydrophenanthridine and GC-EIMS analysis provided the $\underline{m/e}$ 181 (63% RA) and 182 (10%) indicative of d_1 and d_2 compounds.

Acknowledgements:

We wish to thank Dr. Heinz Heinemann of LBL for continued encouragement and support of our catalysis program. The 400 MHz ^1H NMR spectra were kindly recorded by Drs. R. Johannesen and Bruce Coxon at the NBS-NML High Field nmr facility located at NBS, Gaithersburg, MD.

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Chart

**Model Synthetic Fuel Compounds Used in
Hydrogenation Reactions with Wilkinson's Catalyst**

Scheme

Plausible Rhodium Complexes as Intermediates in the
Catalytic Hydrogenation of Quinoline, 1.

Figure 1

Schematic Diagram of the Parr Kinetic Apparatus for Use
in Hydrogenation Rate Studies.

- A. Rupture Disk
- B. Outlet Valve
- C. Septum Port
- D. Inlet Valve
- E. Dip Tube Valve
- F. Dip Tube
- G. Reactor Cup

Table 1

Reductions of Compounds, 1-6, Under
Hydrogenation Conditions with $(\phi_3P)_3RhCl$ as Catalyst

Substrate	H ₂ (psi)	Temp. (°C)	Time (Hr)	Product (%) ^{a,b}
<u>1</u>	500	80	2	1,2,3,4-Tetrahydroquinoline (100)
<u>2</u>	500	80	2	1,2,3,4-Tetrahydro-5,6-benzoquinoline (100)
<u>3</u>	500	80	2	1,2,3,4-Tetrahydro-7,8-benzoquinoline (17)
<u>4</u>	500	80	2	9,10-Dihydroacridine (87)
<u>5</u>	500	80	2	9,10-Dihydrophenanthridine (100)
<u>6</u>	500	80	2	2,3-Dihydrobenzothiophene (15.3)

- a. Percent conversion to product. The remaining substrate represents the percent difference in product conversion. The solvent used was benzene and the substrate to metal ratio was 10:1.
- b. Reactions were run in a Parr Kinetic Apparatus with a 45 ml capacity and the ability to remove samples under pressure and temperature (see Experimental Section and Figure 1).

Table 2

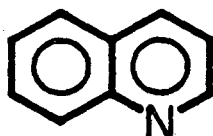
Relative Rates of Hydrogenation of Compound 1
in the Presence of Other Substrates

Added Substrate ^a	H ₂ (psi)	Relative Rates of Hydrogenation, 1
None	310	1.0
Pyridine	310	0.0
2-methylpyridine ^b	310	0.6
3-methylpyridine ^b	310	0.05
Thiophene	310	0.9
1,2,3,4-Tetrahydroquinoline	310	0.40
Indole	310	1.4

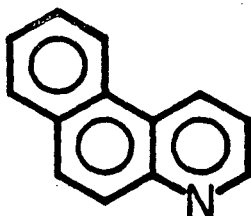
a. 1 mmole of 1 and 1 mmole of added substrate and 0.1 mmole of Wilkinson's catalyst at 77°C (±2°) (see Experimental Section for details regarding calculations of relative rates).

b. 85°C (±2°).

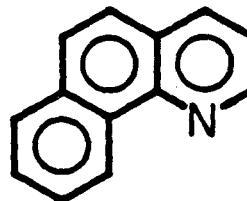
Chart



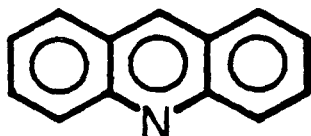
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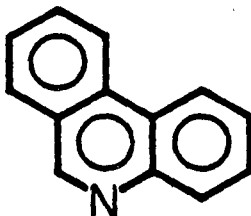
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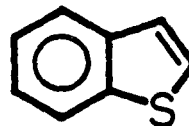
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4



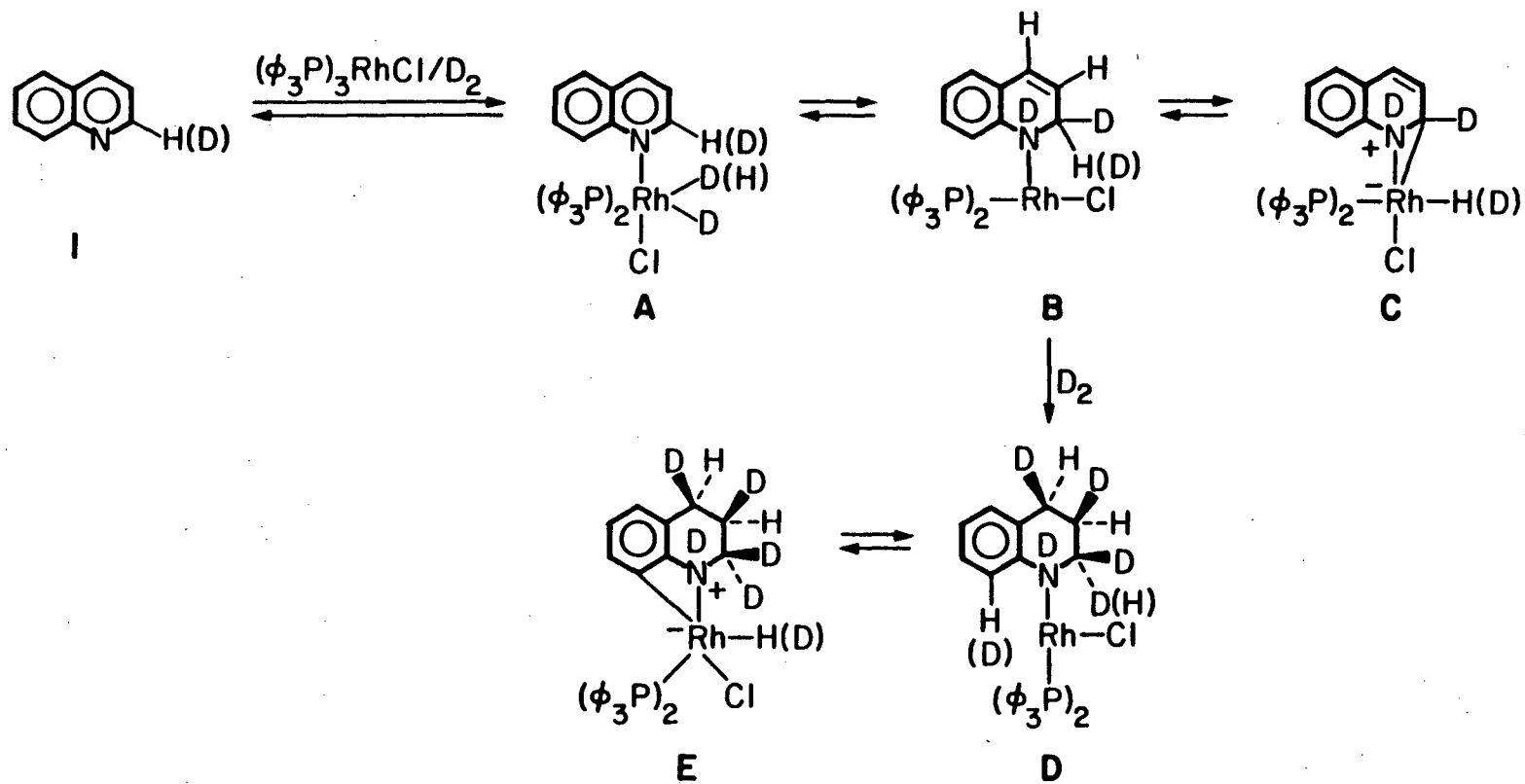
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6

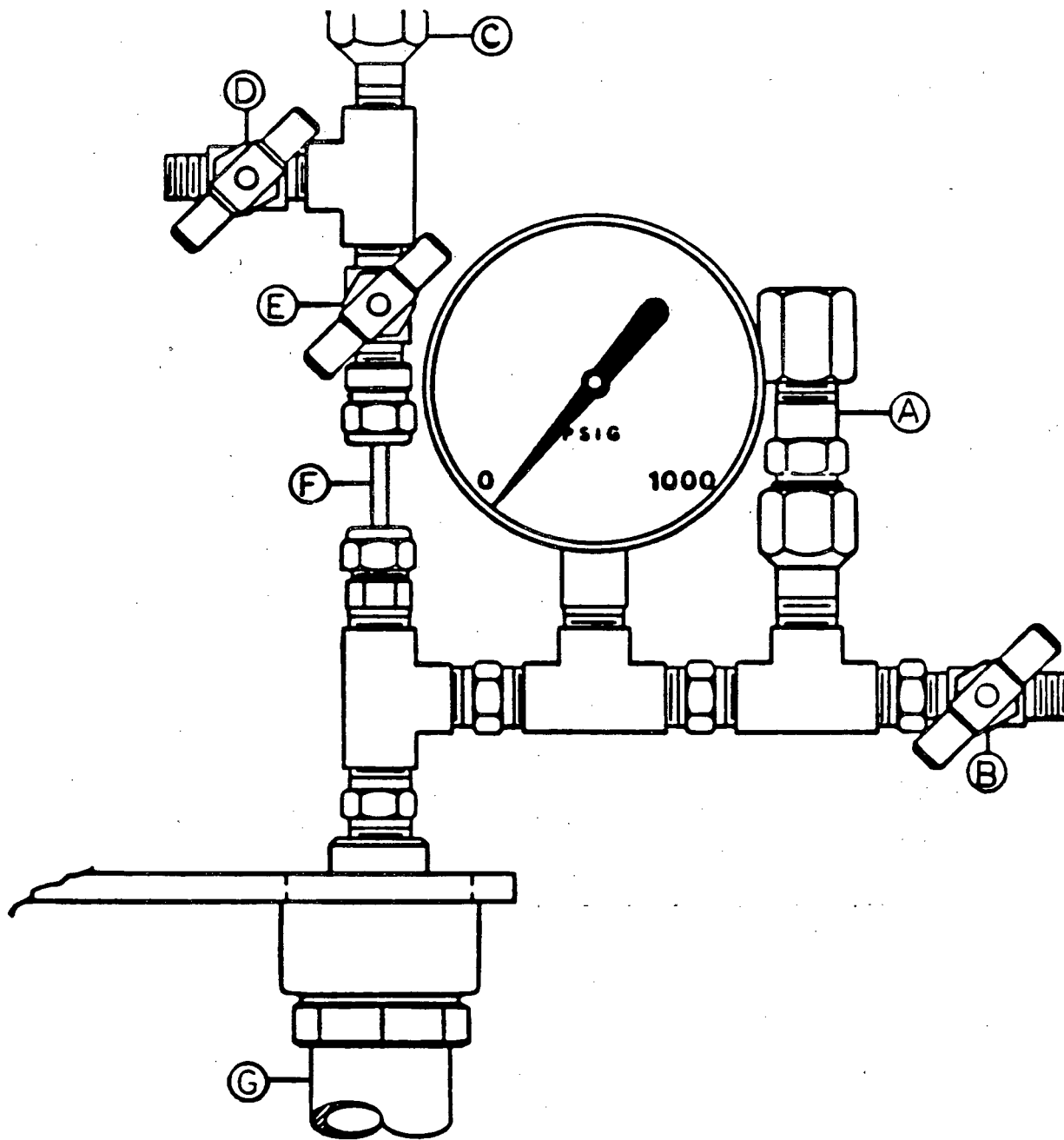
XBL 8211-3297

SCHEME



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FIGURE 1



XBL 836-10434

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