

- I. CATALYST SELECTIVITY IN THE DEUTERATION
OF ANTHRACENE AND NAPHTHALENE
- II. HYDROGENATION OF POLYNUCLEAR AROMATIC
HYDROCARBONS
- III. SYNTHESIS OF HIGH PURITY EICOSANE

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PART I

CATALYST SELECTIVITY IN THE DEUTERATION
OF ANTHRACENE AND NAPHTHALENE

CHAPTER I

INTRODUCTION

Synthesis of hydrocarbons related to constituents of petroleum and coal is a continuing effort at Oklahoma State University. The project as initially supported by the American Petroleum Institute (API)¹ synthesized high purity hydrocarbons for use as instrumental standards, and for thermodynamics studies by the Bureau of Mines Research Center, Bartlesville, Oklahoma.

With renewed emphasis on utilization of coal and heavy crude oils, the chemistry of aromatic hydrocarbons containing 2 to 6 fused rings, and their hydroaromatic homologs has received increased attention.² Under grants from the Environmental Protection Agency (EPA),¹ the Energy Research and Development Agency (ERDA)¹, and private industry,³ Polynuclear Aromatic (PNA) hydrocarbons are being synthesized for use in research on high energy fuels, pollution, cancer, and coal liquifaction and gasification.⁴

The synthesis of hydroaromatic hydrocarbons by selective catalytic hydrogenation offers an attractive one or two step alternative to a multi-step synthesis. The study of catalyst selectivity in the addition of hydrogen to aromatic molecules shows promise as a general technique for the synthesis of a spectrum of hydroaromatic compounds.

CHAPTER II

HISTORICAL

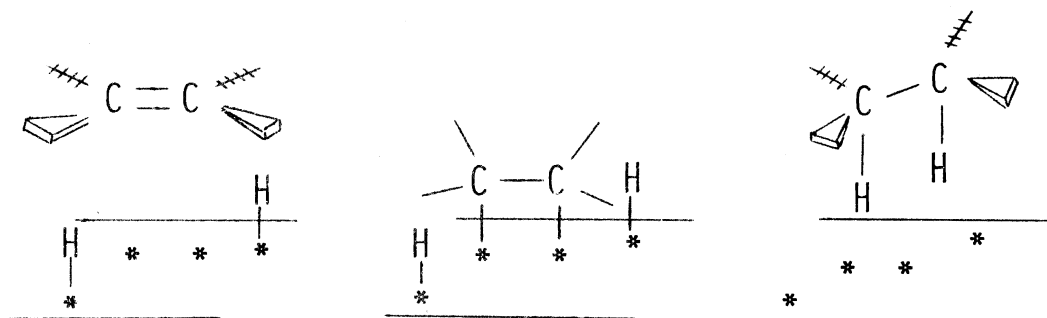
From the first studies of catalytic hydrogenation by Sabatier and Senderens in 1897,⁵ this process has evolved to an essential tool in both laboratory synthesis and industrial processes. This area has been studied intensely and volumes of empirical data and theory have accumulated.⁶ Kinetic theory is well developed from a macroscopic viewpoint,⁷ and technology is now available to study and to make calculations⁸ on the adsorption of simple molecules on catalyst surfaces. However for solution chemistry, which includes most catalytic systems, the problem is so complex that most studies are still approached from experimental kinetics, isolation of intermediates, or isotopic labeling.

Because of improvement in instrumentation and techniques of analysis, through use of nuclear magnetic resonance (NMR) and mass spectrometry, the use of deuterium has increased in mechanistic and structural studies.⁹

Evaluation of mechanistic theories of catalytic hydrogenation from the viewpoint of the organic molecule, has been based to a large extent upon deuterium exchange and hydrogenations of cyclic alkenes, alkanes, and substituted benzenes.¹⁰ These studies have resulted in the predominance of three theories, the first two of which were

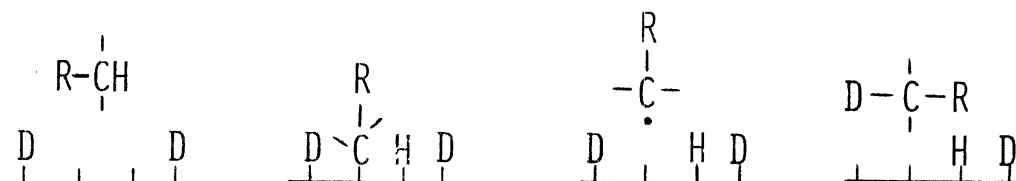
proposed in 1933 and 1934 by Horiuti and Polanyi,¹¹ and Farkas and Farkas.¹²

Horiuti and Polanyi proposed associative adsorption in which an unsaturated carbon carbon bond is opened and bonding with the catalyst surface is through the diasorbed molecule. Activated hydrogen on the catalyst adds to the molecule which simultaneously desorbs as the alkane.¹¹



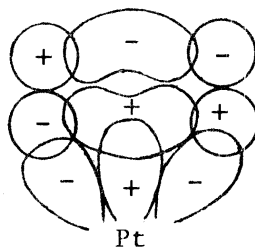
Associative Adsorption

Farkas and Farkas proposed the dissociative mechanism which occurs through initial cleavage of a σ , C-H bond resulting in linkage of the molecule to the catalyst through a single carbon. Upon desorption, the substrate radical combines with an activated hydrogen (or deuterium) to complete the exchange. These earlier mechanisms are reviewed in detail with other proposals, by Taylor,¹³ and the strong and weak points of each theory are discussed.



Dissociative Adsorption

The third mechanism proposed is the formation of π complex intermediate with the catalyst, as advocated by Rooney, Gault, and Kemball¹⁴ and Garnett and Sollich.¹⁵ This mechanism provides more description of the substrate catalyst bond. The theory encompasses the previous two and is extended to include π allyl or other more delocalized intermediates. Adsorption of saturated hydrocarbons proceeds by formation of a σ bonded alkyl, which by loss of hydrogen can form a π bonded olefinic



(Ethylene-Platinum)

π Complex

complex. This can be followed by formation of a π allyl complex or a delocalized complex which permits rationalization of isomerization during deuterium exchange. Aromatics and olefins are adsorbed directly as π complexes. Garnett and Sollich-Baumgardner¹⁶ have proposed a transition from the π complex to a σ bonded intermediate as in the dissociative mechanism. This transition in part explains the stepwise incorporation of deuterium, and the effects due to stereochemical hinderance in substituted compounds. The π complex mechanism explains the faster exchange on an aromatic molecule as compared to an alkane, which the previous theories failed to satisfactorily explain.

The mechanisms presented were proposed with no consideration of the surface geometry of the orbitals of the metal catalyst. Bond¹⁷ has discussed qualitatively the π complexes of mono and diolefins, and acetylenes from the viewpoint of the orbital geometry of the group VIII metals with face centered cubic crystal structures. Qualitative agreement with the π complex mechanism was observed. Evidence was presented for the presence of a σ diisorbed molecule although this state may not be relevant in hydrogenation. The argument for active or nonequivalent sites of hydrogen adsorption was rationalized, as was formation of an alkyl radical by cis addition of hydrogen to the π complex. Bond also showed parallels between heterogeneous and homogeneous catalysis.

Deuterium exchange in PNA hydrocarbons via heterogeneous and homogeneous catalysis has been investigated by Garnett.¹⁸ The active exchange sites of the molecule, in the presence of Pt, for polyphenyls and fused ring aromatics were determined. Homogeneous and heterogeneous catalysts were found to be similar, with greater selectivity by homogeneous catalysts and more complete exchange by heterogeneous catalysts.

The theory of active sites and bond multiplicity as proposed by Balandin,¹⁹ and favored by the Russians,²⁰ has been applied to kinetic studies in the hydrogenation of PNA hydrocarbons. This theory attempts to correlate hydrogenation rates of condensed ring systems to the position and number of shortened bonds in the molecule, relative to the active hydrogens on the catalyst.

Heterogeneous catalytic deuterations of unsaturated systems in general, is not the preferred method of selectively introducing deuterium into a molecule. Studies of the deuteration of methyl oleate by Dutton²¹ and similar studies by Smith and Roth,²² and Smith and

Deany²³ show that isomerization is prominent enough to exclude this method as a general technique for selective deuteration.

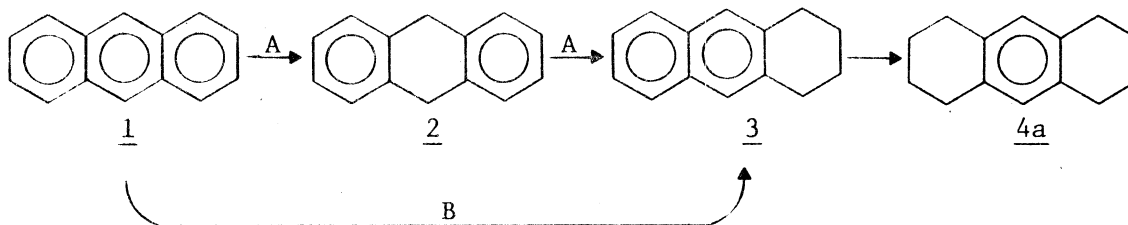
In some cases, however, selective incorporation of deuterium has been achieved. Burnham and Eisenbraun²⁴ have reported clean incorporation of deuterium at the benzylic position in deuteriumolysis of benzylic ketones. Friedman²⁵ has selectively introduced deuterium at the 9,10 position of anthracene and anthraquinone with $\text{Co}_2(\text{CO})_8$ and D_2 or D_2O and CO , to form 9,9,10,10-tetradeuterio-9,10-dihydroanthracene.

In work on catalysts modelled after enzyme systems, Efimov, Khidekel²⁶ and others have deuterated anthracene (1) with Rh-N-phenyl-anthranilic acid. Hydrogenation with this catalyst gave tetrahydroanthracene (3) and no 9,10-dihydroanthracene (2). In studies which led to the work to be presented, analogous observations were made in the hydrogenation of 1 to 3 with supported Rh. Results from hydrogenations with Pd and Pt catalysts indicate the presence of two hydrogenation processes. This result, as well as the stepwise process of converting 1 to 2 to 3, has been reported respectively, by Wiser²⁷ and Garlock²⁸ by observing hydrogen uptake and studying mixtures. However, further investigation of the processes was not pursued.

CHAPTER III

RESULTS AND DISCUSSION

Product formation curves (Figure 1) from hydrogenation of 1 with each of the three catalysts indicate the presence of two competing processes (shown as A and B below) which are catalyst dependent.



From Figure 1a, the predominant process in the presence of Pd/C is A, the reduction of 1 to 2, then isomerization and reduction of 2 to 3. Process B, the direct hydrogenation of the end ring is also represented to a significant extent as shown by rapid initial increase of 3. With the consumption of 1, only route A, (2 to 3), remains and the rate of formation of 3 then decreases. The curve for 3 becomes almost linear, and approximately equal to the decrease of 2 minus the increase of 4a.

Figure 1c, the hydrogenation of 1 with Rh/alumina, illustrates the predominance of process B in the formation of 3. The rate of formation of 3 is approximately equal to the rate of decrease of 1,

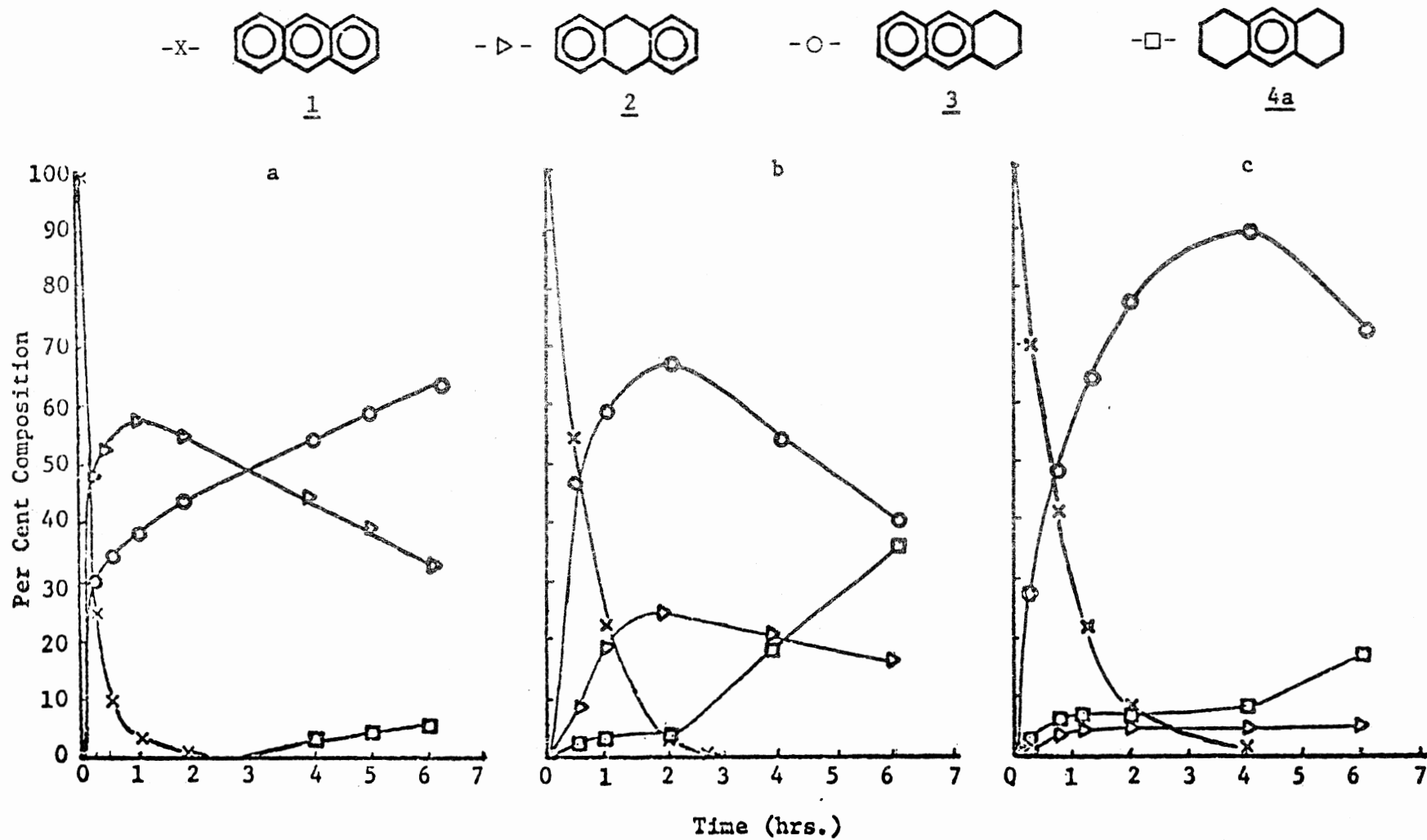


Figure 1. Product Formation in the Hydrogenation of 1 with a) 5% Pd/C, b) 5% Pt/C, and c) 5% Rh/Alumina in Refluxing Acetic Acid

with very little 2 formed. There is formation of 2 in the initial stages of the reaction, but the curve flattens out at approximately 5% 2 and either formation of 2 ceases or a steady state is reached. Both Pt and Rh are reported to be less efficient in promoting isomerization than Pd, which indicates 2 is not an intermediate in Rh catalyzed hydrogenation of 1 to 3.

The product formation curves from the Pt/C catalyzed hydrogenation of 1 (Figure 1b) show characteristics intermediate to the curves from Pd and Rh catalyzed reactions. Both 2 and 3 are produced in substantial amounts, indicating both processes A and B are operating. The rapid initial increase of 3 suggests the predominance of process B as long as 1 is available. Process B, (direct reduction of the end ring), is still in effect after 1 has been consumed, but the result is the reduction of 3 to 4a. This rate is greater than the rate of conversion of 2 to 3 (process A) as shown by the net decrease of 3.

Hydrogenation of 2 with each of the respective catalysts (Table I) shows the relative effectiveness in reducing 2 to 3 to be Pd > Pt > Rh.

TABLE I
HYDROGENATION OF 9,10-DIHYDROANTHRACENE (2) WITH
PLATINUM METAL CATALYSTS

Catalyst	Reaction Time hr	% Composition of Reaction Mixture			
		<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
5% Pd/C	5	59	32	7	2
5% Pt/C	7	79	6	10	5
5% Rh/alumina	9	85	3	7	5

Therefore, process A is only a minor route in Rh catalyzed hydrogenation of 1 to 3, but is more prominent with Pt catalyst.

Deuterium distribution in 3 produced with each of the three catalysts (Figure 2, Table II) supports the conclusions drawn from the product formation curves. Rh catalyzed deuteration of 1 gave 3 containing predominantly $C_{10}H_{10}D_4$ (61%). The curve is almost Gaussian, containing 16 percent $C_{10}H_{10}D_3$ and 11 percent $C_{10}H_9D_5$ as the second and third most abundant molecules in the distribution. The distribution curve of 3 from Pd/C shows a maximum at $C_{10}H_8D_6$ (31%) and is shifted to the right of the Rh curve by two deuteriums per molecule. The curve exhibits a wider distribution range than Rh or Pt, indicating more scrambling due to isomerization during reduction of 2 to 3.

Deuterium distribution in 3 from Pt/C catalyzed deuteration is dependent upon the extent of reaction (Figure 4). Two factors contribute to the differences in deuterium distributions in 3 with reaction time. As the reaction proceeds, the predominant process shifts from B to A. A sample of 3 isolated near the maximum yield has a distribution similar to that obtained with Rh as in Figure 2. A sample of 3, isolated later in the reaction shows that 3 formed when process A is the major route, has a distribution similar to 3 from the Pd/C reaction (Figure 4).

Increased deuterium exchange as the reaction proceeds appears to be the second factor contributing to an increased random distribution in 3. As deuterium exchange becomes more significant, the distribution curve shifts even farther to the right. The maximum for the Pt/C III curve is at $C_{10}H_7D_7$ (24.8%) which is one deuterium per molecule more than the maximum observed for Pd/C.

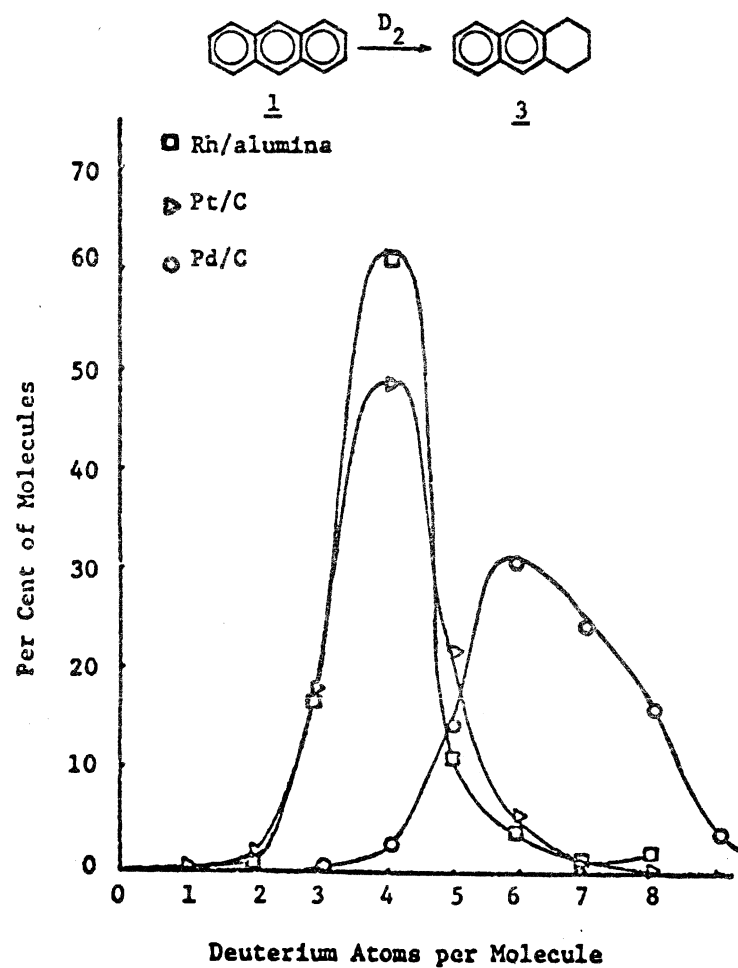


Figure 2. Deuterium Distribution from Pd/C, Pt/C, and Rh/Alumina Catalyzed Deuterations of 1

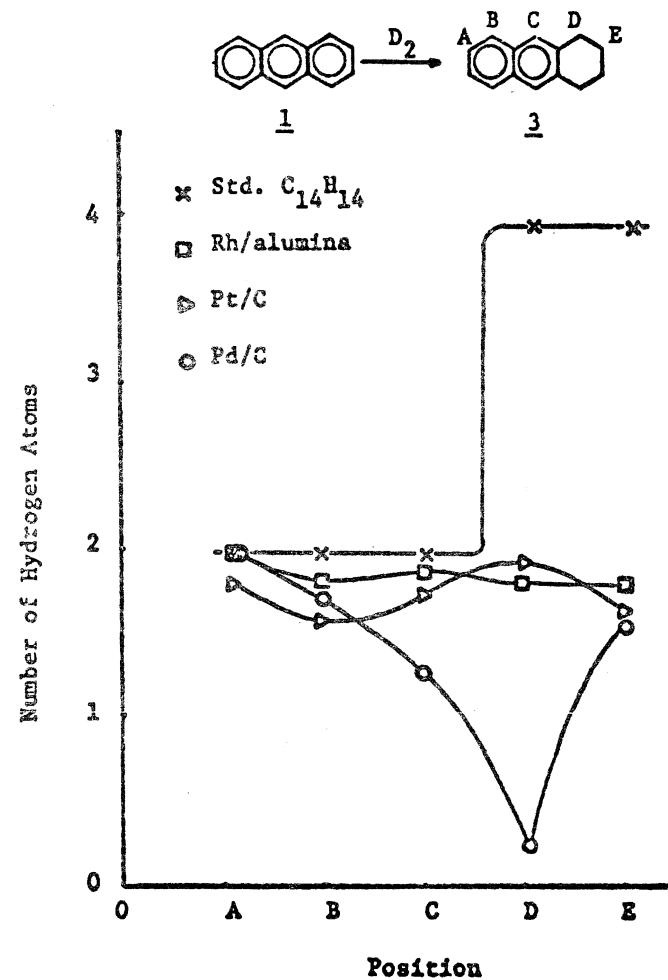


Figure 3. Deuterium Incorporation by Position from Pd/C, Pt/C, and Rh/Alumina Catalyzed Deuterations of 1

TABLE II
DEUTERIUM DISTRIBUTIONS OF TETRAHYDROANTHRACENE (3)

Catalyst	Percent of Molecules Containing D _(N) ^a										
	0 (182)	1 (183)	2 (184)	3 (185)	4 (186)	5 (187)	6 (188)	7 (189)	8 (190)	9 (191)	10 (192)
5% Pd/C	-	1	2.3	0.6	3.0	14.1	31.1	25.9	17.9	3.9	0.2
5% Pt/C I	0.2	0.3	2.8	17.7	49.4	23.5	5.1	0.9	0.2	-	-
5% Pt/C II	-	0.3	1.5	9.8	28.7	32.1	18.9	7.2	1.5	0.4	-
5% Pt/C III	-	-	-	0.8	5.6	14.0	23.0	24.8	18.4	8.9	4.0
5% Rh/alumina	0.2	0.3	2.1	16.2	61.1	11.3	4.9	1.2	2.2	-	-

^aN determined as m/e.

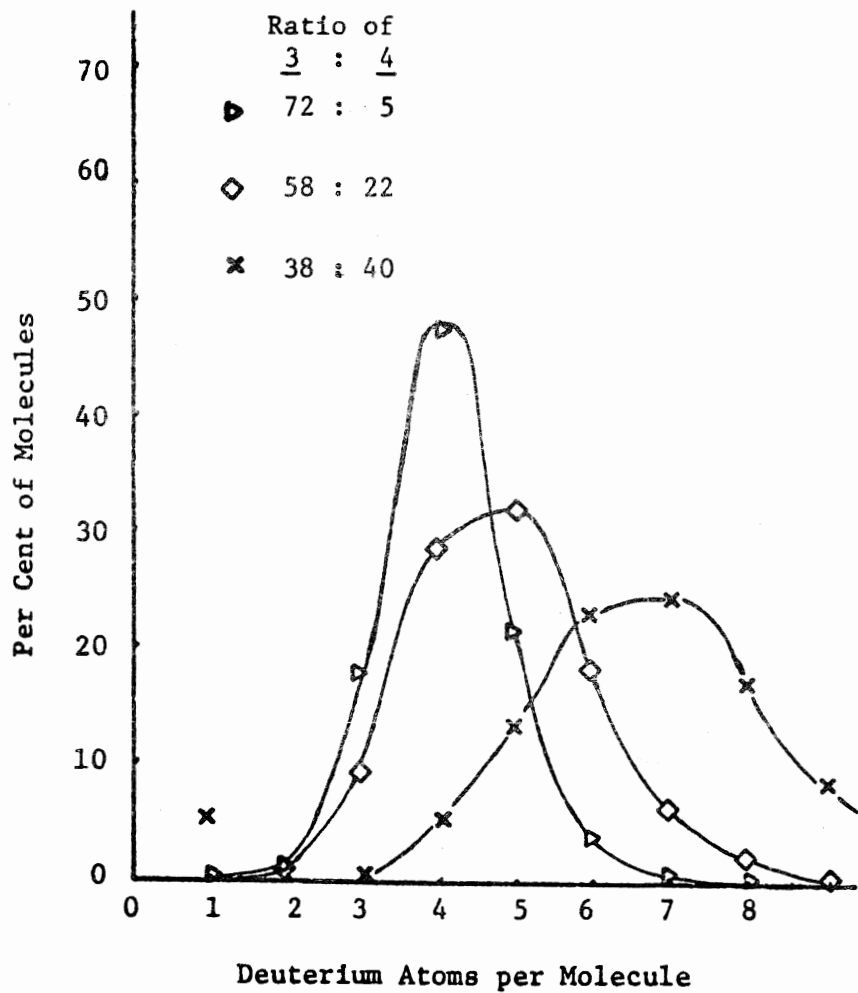


Figure 4. Deuteration of 1 Catalyzed with Pt/C. Dependence of Deuterium Distribution Upon Extent of Reaction

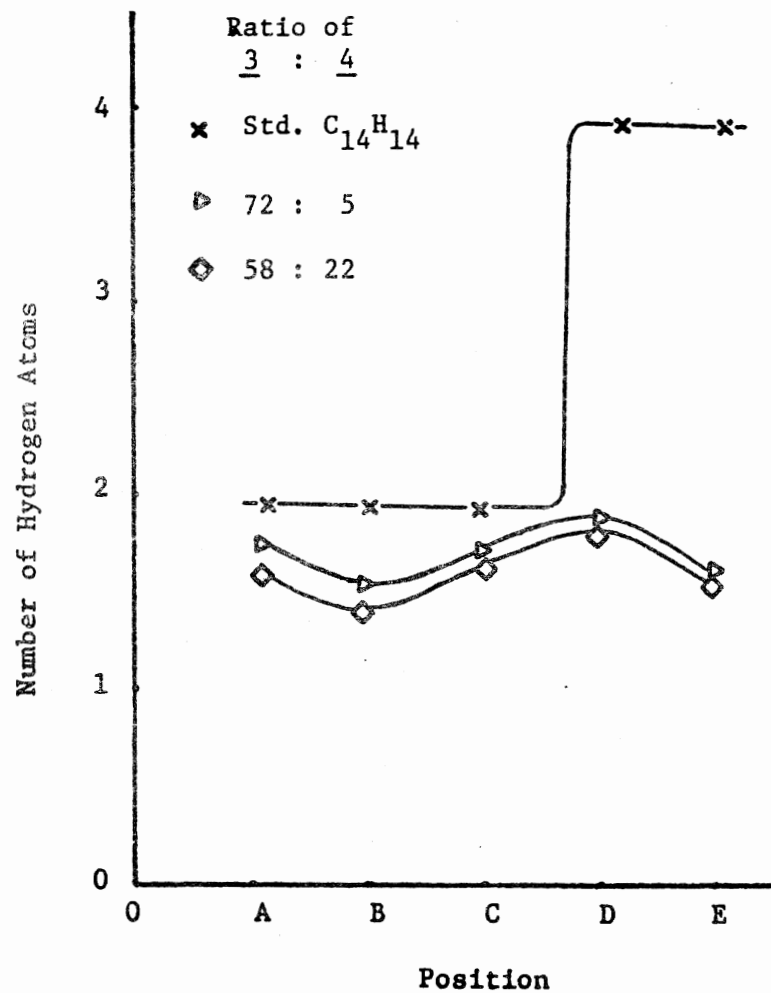


Figure 5. Deuteration of 1 Catalyzed with Pt/C. Dependence of Deuterium Incorporation Upon Extent of Reaction

Deuterium incorporation by position in 3 as determined by NMR (Figure 3, Table III) shows a clear difference between 3 from the Pd/C catalyzed reaction and 3 from Pt/C or Rh/alumina catalyzed runs. The number of hydrogens at each position (A, B, C, D, E) in deuterated 3 is compared to standard 3, ($C_{14}H_{14}$, denoted in Figure 3 by -x-), containing only the natural abundance of deuterium. Where process A is predominant (Pd/C) more deuterium is found at position C (9,10; 37.5%) and almost complete exchange at position D (1,4; 93%). The amount of deuterium added to the 2,3 position, (E) is similar for all three catalysts (Pd/C, 60%; Pt/C, 56%; Rh/alumina, 54%).

Rh and Pt catalyzed runs give 3 which show similar patterns of deuterium addition when 3 from Pt/C is isolated near the maximum yield. This similarity supports the predominance of process B for Pt and Rh cases. As shown in Figure 3, there is little incorporation of deuterium at positions A, B, or C with Rh or Pt. The amount of deuterium at C increases with extent of reaction with Pt/C. Positions D and E show similar incorporation for both Rh and Pt; containing respectively 55 and 54 percent with Rh and 51.5 and 56 percent with Pt.

Tetrahydroanthracene (3) from Pt/C-III showed deuterium exchange at positions A and B, causing band broadening in the NMR spectra. Accurate integration of the peaks was not possible, so an estimate was made of the overlapping areas by triangulation. The estimated numbers are presented in Table III, but are not plotted in Figure 5.

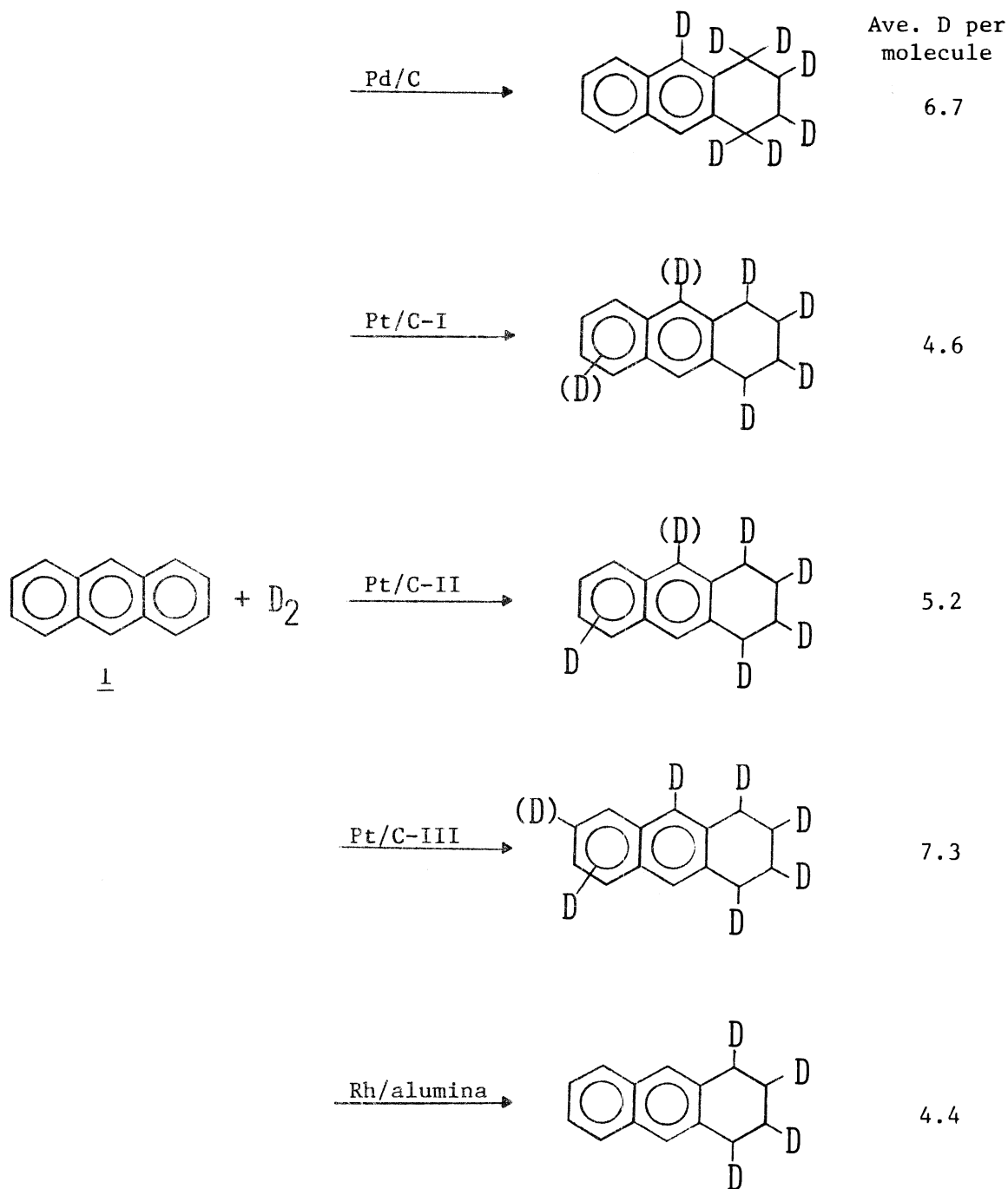
Calculation of the average number of deuterium atoms per molecule from mass spectrometry and NMR data, indicates that 3 from each of the five cases would contain deuterium as shown below. (D) represents less than one deuterium atom.

TABLE III
 DEUTERIUM DISTRIBUTION BY POSITION
 IN TETRAHYDROANTHRACENE (3)

Catalyst	Number of Hydrogens ^a at Position				
	A	B	C	D	E
Standard ^b C ₁₄ H ₁₄	2	2	2	4	4
5% Pd/C	2.0	1.7	1.3	0.3	1.6
5% Pt/C (I)	1.9	1.7	1.8	1.9	1.7
5% Pt/C (II)	1.7	1.5	1.7	1.9	1.7
5% Pt/C (III)	1.4	1.3	1.1	2.2	1.8
5% Rh/alumina	2.0	1.8	1.9	1.8	1.8

^aThe number of hydrogens at a given position is the average derived from 10 integrations each at two different amplitudes.

^bExternal standard of 60 mg of 1,2,3,4-tetrahydroanthracene in 0.6 g of CCl₄.



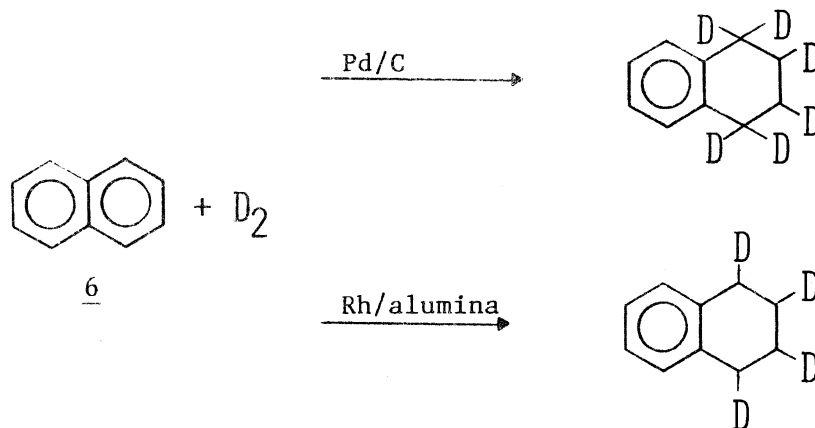
The study was extended to deuteration of naphthalene (6) and the dihydronaphthalenes to tetralin (9), to determine if the observed selectivity was a general characteristic of the catalyst or a property

unique to 1 and catalyst. Possible intermediates in the reduction, 1,2-dihydronaphthalene (7) and 1,4-dihydronaphthalene (8) were included to study the mechanism and intermediates involved.

Deuterium distributions in 9 formed from deuteration of 6 with Pd/C or Rh/alumina (Figure 6, Table IV) shows an even more distinctive catalyst effect than for 1. Exchange was extensive in 9 using Pd/C as shown by the high percentage of $C_{10}H_9D_5$ (31%) and $C_{10}H_8D_6$ (48%). In contrast, 9 from the Rh/alumina catalyzed deuteration contained a majority of $C_{10}H_8D_4$ (51%) which is analogous to 3 formed from 1 with Rh.

NMR spectra of 9 from the two catalysts (Figure 7, Table V) show incorporation of deuterium in the reduced ring with no deuterium detectable in the remaining aromatic ring. Deuterium incorporation in 9 with Rh/alumina is very close to 50 percent at each reduced position; position B, (1,4) contained 51.5% and C, (2,3); 50.5%. With Pd/C, deuterium incorporation in 9 is analogous to 3 with Pd/C; with 92% at position B and 56% at C.

The average number of deuterium atoms per molecule was calculated as 5.8 for 9 from Pd/C and 4.1 for 9 from Rh/alumina. Deuterium incorporation in 9 from 6 is shown below.



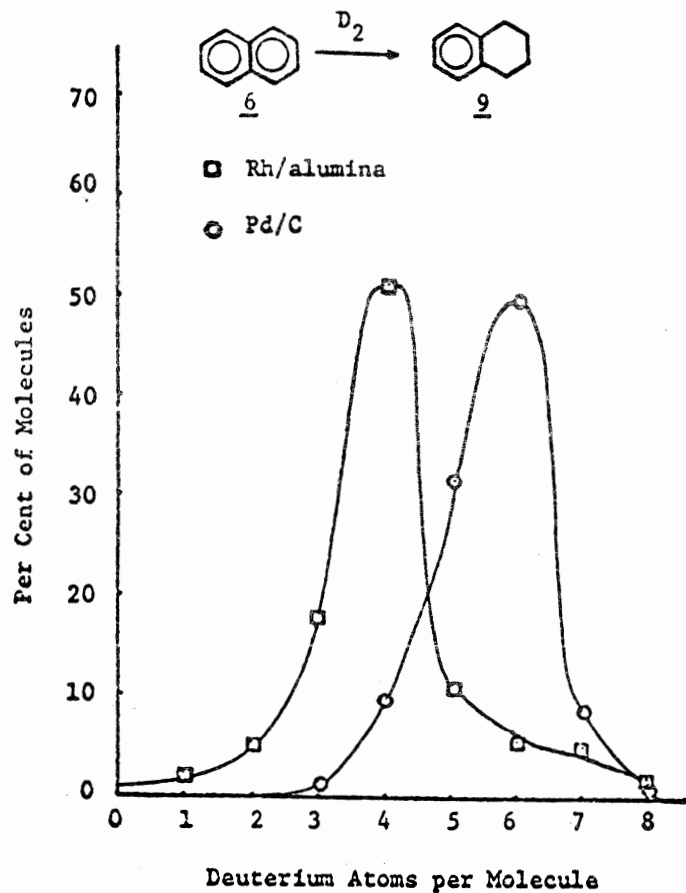


Figure 6. Deuterium Distribution From Deuteration of **6** in DOAc With Pd/C and Rh/Alumina

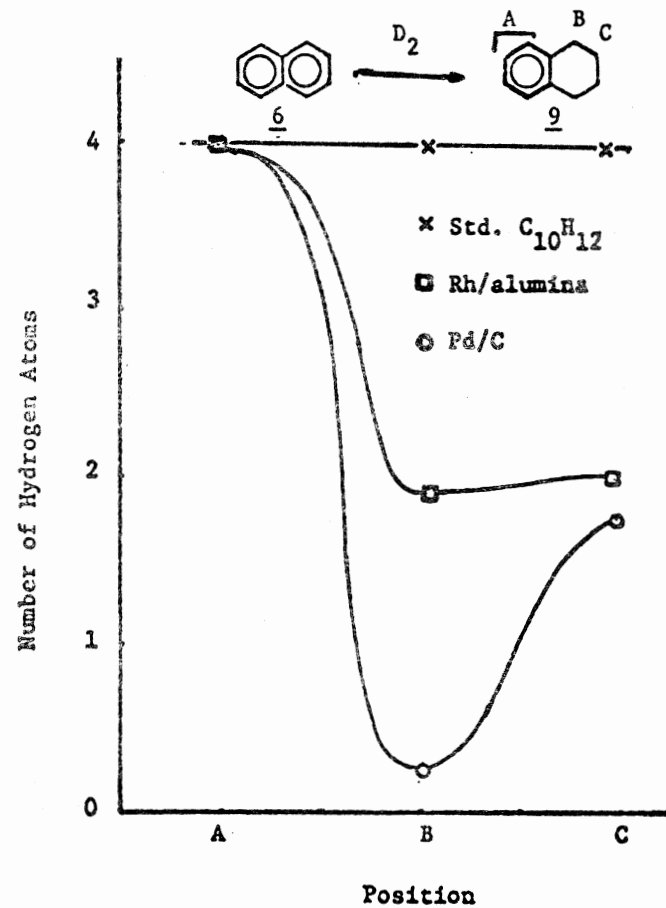
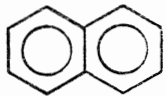
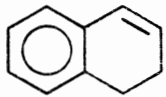
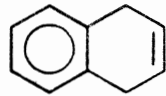
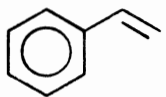


Figure 7. Deuterium Incorporation by Position, From Deuteration of **6** in DOAc With Pd/C and Rh/Alumina

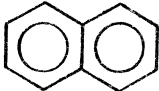
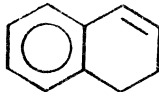
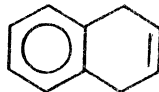
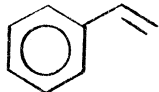
TABLE IV
 DEUTERIUM DISTRIBUTION OF TETRALIN (9) AND ETHYLBENZENE (12) FROM
 Pd/C AND Rh/ALUMINA CATALYZED DEUTERATIONS

Starting Material	Catalyst	Solvent	Percent of Molecules Containing D _(N) ^a								
			0 (132)	1 (133)	2 (134)	3 (135)	4 (136)	5 (137)	6 (138)	7 (139)	8 (140)
	Pd	DOAc	-	-	-	2.2	9.9	31.5	48.2	9.3	1.2
	Rh	DOAc	1.2	2.3	4.5	17.4	50.5	11.1	6.0	5.2	1.8
	Pd	DOAc	-	0.3	5.6	14.9	29.4	32.0	14.5	2.6	0.6
	Rh	DOAc	12.8	25.7	37.1	14.4	7.0	2.1	0.6	-	-
	Pd	DOAc	-	10.3	19.0	27.1	24.7	15.7	4.4	-	-
	Rh	DOAc	-	16.4	24.4	22.9	23.6	7.5	2.7	1.5	1.0
	Pd	EtOAc	-	27	42.5	23.7	6.0	0.7	-	-	-
	Rh	EtOAc	11.3	22.7	27.8	22.3	5.1	0.6	-	-	-
			(106)	(107)	(108)	(109)	(110)	(111)	(112)	(113)	(114)
	Pd	DOAc	1.8	7.4	22.9	29.4	26.0	12.1	0.2	-	-
	Rh	DOAc	9.1	17.5	27.0	30.8	14.4	1.0	-	-	-

^aN determined as m/e.

TABLE V

DEUTERIUM INCORPORATION BY POSITION IN TETRALIN AND ETHYLBENZENE
FROM Pd/C AND Rh/ALUMINA CATALYZED DEUTERATIONS

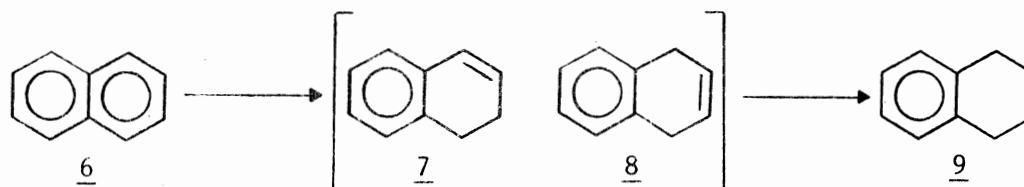
Starting Material	Catalyst	Solvent	Number of Hydrogens ^a at Position		
			A (ArH)	B (ArCH)	C (ArCHCH)
Standard ^b C ₁₀ H ₁₂			4	4	4
 <u>6</u>	Pd	DOAc	4	0.3	1.8
	Rh	DOAc	4	1.9	2.0
 <u>7</u>	Pd	DOAc	4	0.8	2.9
	Rh	DOAc	4	3.1	2.9
 <u>8</u>	Pd	DOAc	4	1.6	2.7
	Rh	DOAc	4	3.1	2.7
	Pd	EtOAc	4	3.2	2.5
	Rh	EtOAc	4	3.0	2.2
Standard ^c C ₈ H ₁₀			5	2	3
 <u>11</u>	Pd	DOAc	5	0.4	1.9
	Rh	DOAc	5	1.1	2.0

^aThe number of hydrogens at a given position is the average derived from integrations at two different amplitudes.

^bExternal standard of 30% by volume, of 9 in CCl₄.

^cExternal standard of 30% by volume, of 12 in CCl₄.

Although in the reduction of 6 to 9 an intermediate analogous to 2 is not possible, the existence of at least one of the dihydronaphthalenes 7 and 8 probable. Deuteration of 7 and 8 should give information as to the mechanism in the reduction of 6 to 9.



Deuteration of 7 to 9 resulted in distributions for both catalysts (Figure 8) in which there was approximately two deuterium atoms per molecule less than was observed for deuteration of 6 to 9. With Rh/alumina the maximum percent of molecules (37%) occurred at $C_{10}H_{10}D_2$. For Pd/C the maximum (32%) occurred at $C_{10}H_7D_5$ but the distribution was spread somewhat and $C_{10}H_8D_4$ made up 29% of the total molecules. Both curves had slightly wider ranges of distribution than the previous case.

The product from the Rh/alumina catalyzed deuteration contained 10% 6 indicating that some disproportionation occurred. The rate of reduction of 7 is much faster than 6 so it is believed that any 6 formed did not contribute significantly to 9.

Deuterium incorporation in 9 from 7 as shown by NMR analysis (Figure 9) differs from 9 produced from 6. Formation of 9 from 7 with Pd/C still shows a large amount of incorporation at the 1,4 position (81%) but this is 11% less than was observed in 9 from 6. Deuterium content at the 2,3 positions for 9 from 7 is approximately half (28.5%) that observed in 9 from 6. Incorporation appears to be concentrated at

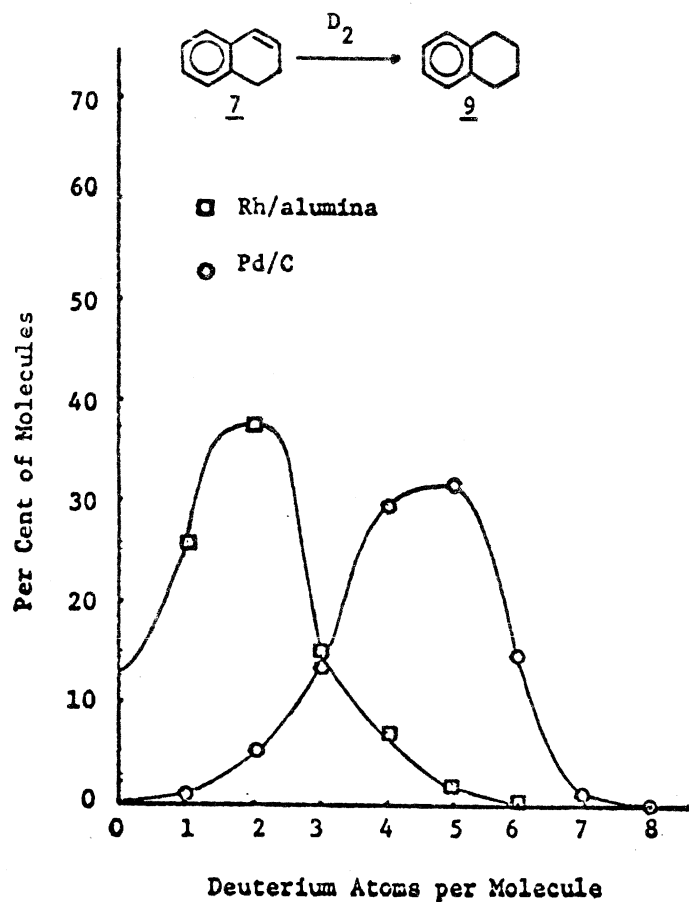


Figure 8. Deuterium Distribution From Deuteration of 7 in DOAc With Pd/C and Rh/Alumina

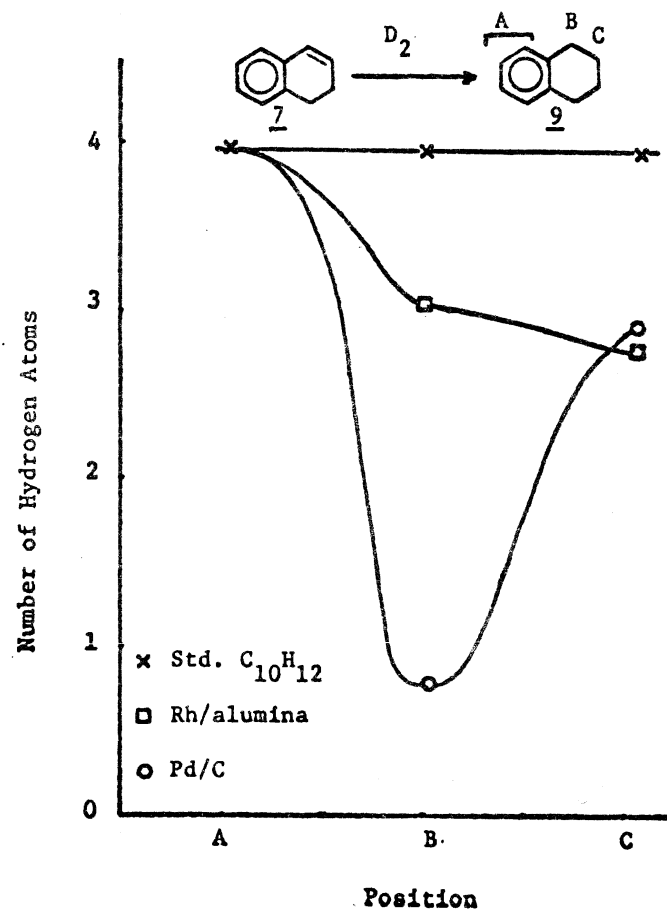
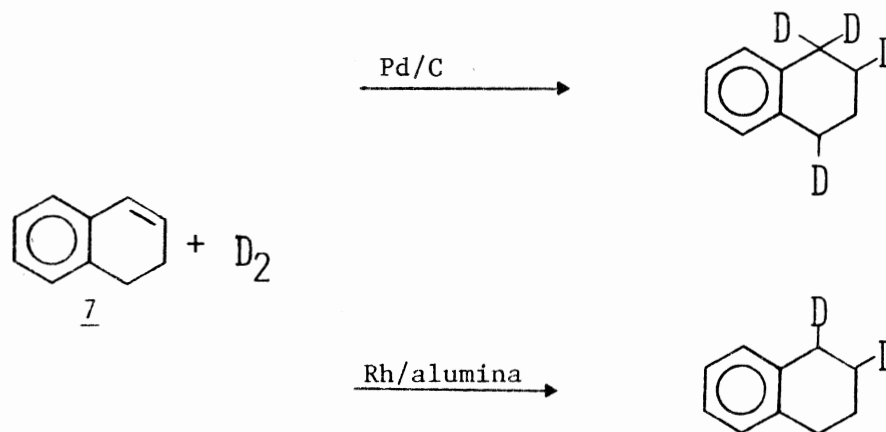


Figure 9. Deuterium Incorporation by Position, from Deuteration of 7 in DOAc With Pd/C and Rh/Alumina

the 1,2 position where the double bond existed, with some exchange at the 4 position and negligible incorporation at the 3 position.

Rh/alumina catalyzed deuteration of 7 yields 9 containing respectively 22.5 and 28.5 percent deuterium at the 1,4 (B) and 2,3 (C) positions. Such distribution suggests addition of deuterium at the double bond with little exchange at either the 3 or 4 position.

Average deuterium atoms per molecule for 9 from 7 was calculated as 4.3 with Pd/C and 2.0 with Rh/alumina. The respective deuterium incorporation is given below.



The other possible intermediate in hydrogenation of 6 to 9 is 8 in which the 1,4 positions are both allylic and benzylic and would appear to be highly reactive to D-H exchange. Deuteration of 8 to 9 in DOAc indicates however that 8 is not an intermediate when the reaction is performed in acetic acid under the conditions we used.

Deuterium distribution of 9 from 8 (Figure 10) has wider range than either of the two previous cases. The maxima are less prominent. Maxima for 9 from Pd/C occurs at $C_{10}H_9D_3$ (27.1%) but is followed

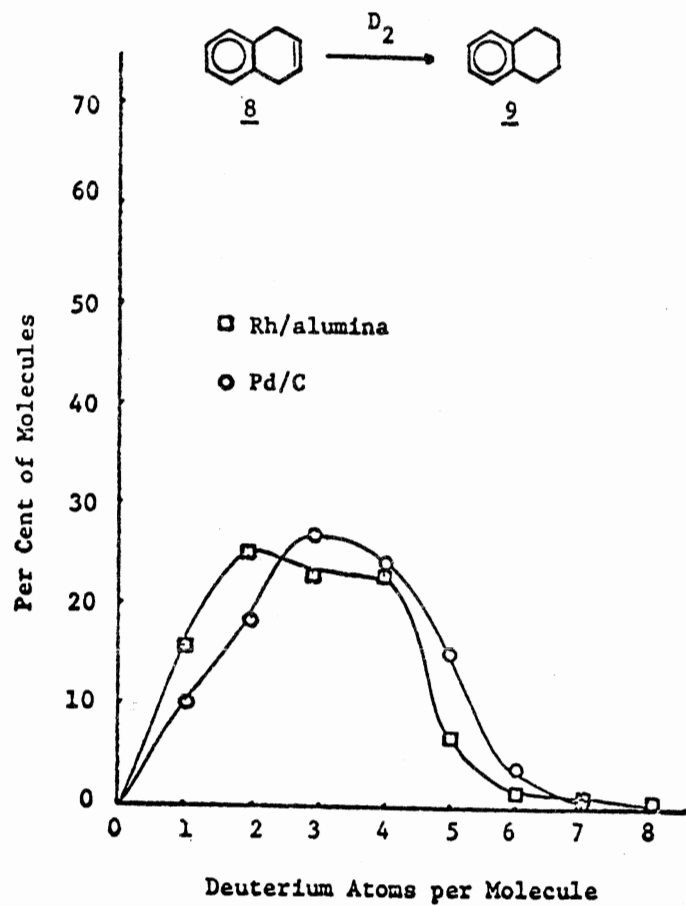


Figure 10. Deuterium Distribution From Deuteration of **8** in DOAc With Pd/C and Rh/Alumina

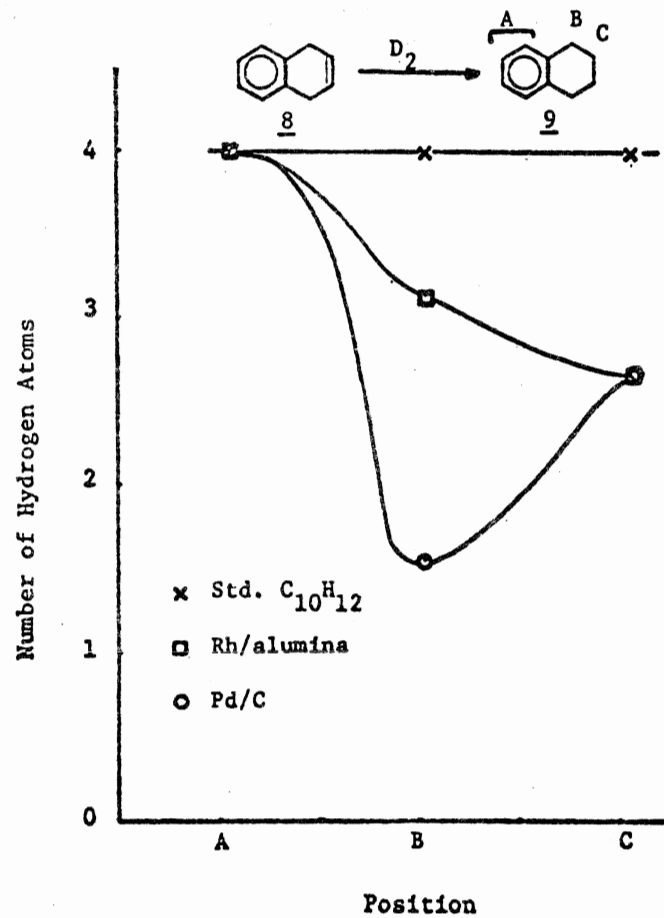
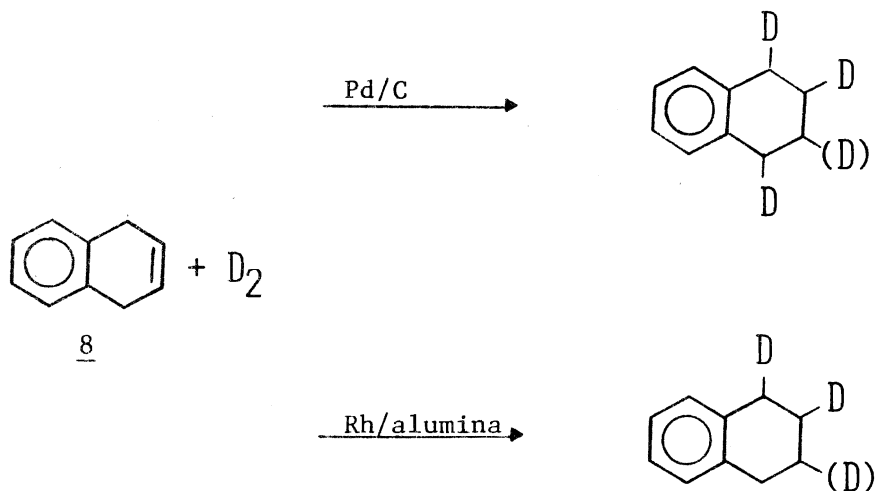


Figure 11. Deuterium Incorporation by Position, From Deuteration of **8** in DOAc With Pd/C and Rh/Alumina

closely by $C_{10}H_8D_4$ (24.7%). The distribution for the curve for 9 from Rh/alumina, has a maximum at $C_{10}H_{10}D_2$ (24.4%) but $C_{10}H_9D_3$ (22.9%) and $C_{10}H_8D_4$ (23.6%) occur very near the maximum, forming almost a plateau in the curve.

Distribution by position as determined by NMR (Figure 11) shows less incorporation of deuterium at the 1,4 positions (61.5%) with Pd/C; and slightly more at the 2,3 positions (32.8%) than was observed in 9 from 7. For 9 produced from 8 with Rh/alumina, there appears to be more deuterium incorporation than in 9 from 7, with increased random distribution in the reduced ring. The 1,4 positions contain 21.5% and the 2,3 position contains 32.8% deuterium.

The average deuterium atoms per molecule was calculated as 3.7 for Pd/C, and 2.6 with Rh/alumina. The incorporation of deuterium is represented below.



These effects are caused by isomerization of 8 to 7 during the reactions and apparently are due to a combined effect of solvent and catalyst. Solvent alone (HOAc) does not isomerize 8 under the

conditions which the deuterations were performed. In HOAc, 8 was not isomerized after 1 hour at 60°C nor after 1 hour at 80°C.

From the shape of the distribution curves and the patterns of deuterium incorporation in 9 from 8, it appears that the rate of isomerization is at least of the same order of magnitude as the rate of deuteration. If the rate of isomerization is >> that of deuteration then the results should be very similar to those seen for the preceding case (9 from 7). If the rate of isomerization is << that of deuteration the results should be very similar to those of the following case.

Deuteration of 8 in ethyl acetate gives 9 with deuterium distributions of much narrower range, and containing roughly two deuterium atoms per molecule less, than 9 from deuterations in DOAc. The distributions (Figure 12) for both catalysts are very similar, with maxima at $C_{10}H_{10}D_2$ (42.5%, Pd/C; 37.8%, Rh/alumina).

Deuterium incorporation by position in 9 (Figure 13) also shows close similarity between catalysts. The amount of deuterium at the 2,3-positions (37.3%, Pd/C; 45.5%, Rh/alumina) compared to the 1,4-position (20.3%, Pd/C; 24.8%, Rh/alumina) indicates that there is still some isomerization occurring. There is evidently some isomerization caused by catalyst but this contribution is small compared to that observed with acidic solvent and catalyst.

Average deuterium atoms per molecule was 2.2 for Pd/C and 2.4 for Rh/alumina and incorporation of deuterium is represented below.

In general, Rh does not seem to be subject to large solvent effects other than changing the reaction rates. Pd demonstrates sensitivity to the acidity of solvent in relation to its ability to promote isomerization and exchange. Sensitivity of Pd to acidity is

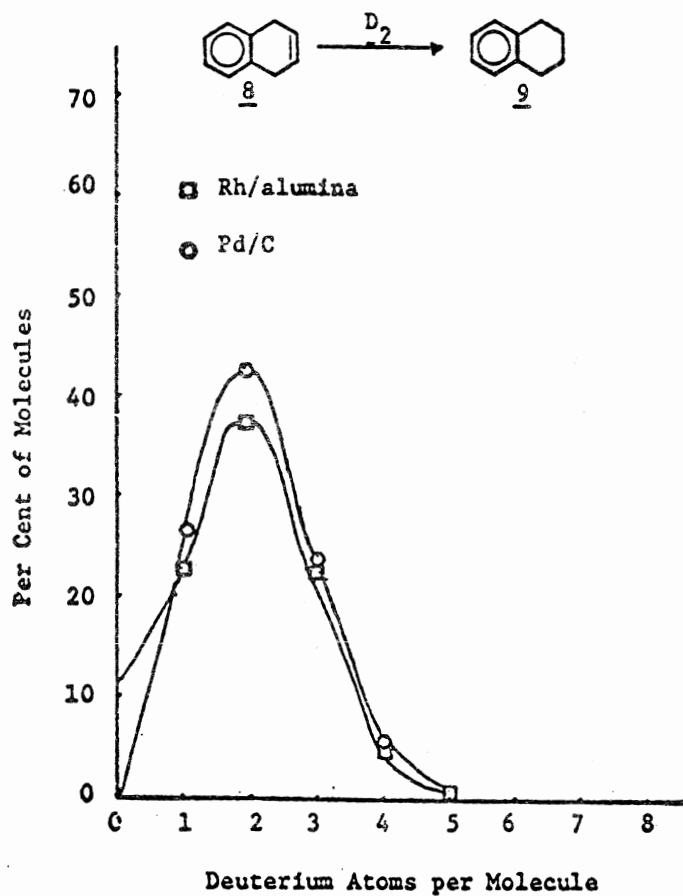


Figure 12. Deuterium Distribution From Deuteration of 8 in EtOAc With Pd/C and Rh/Alumina

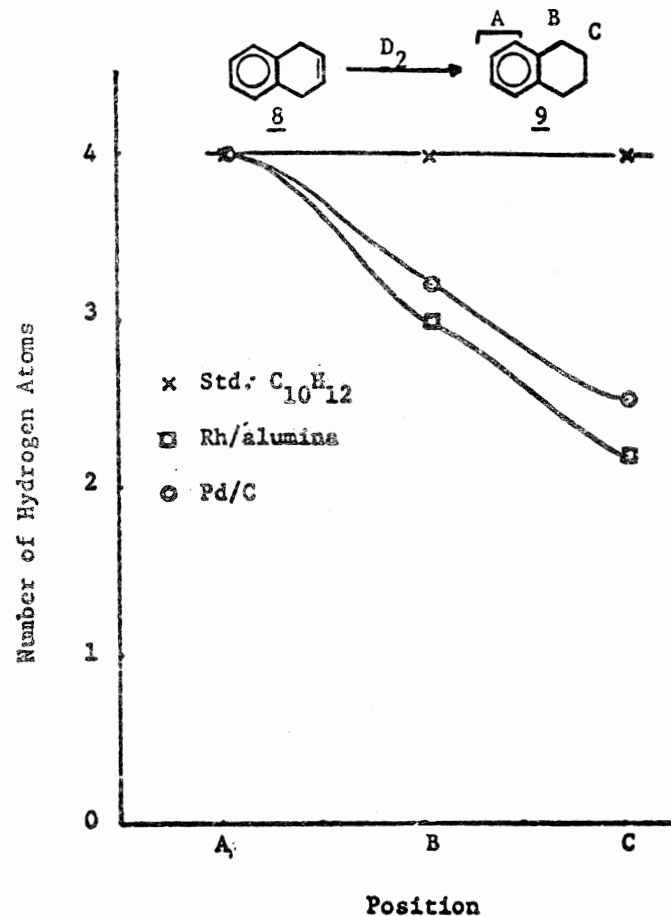
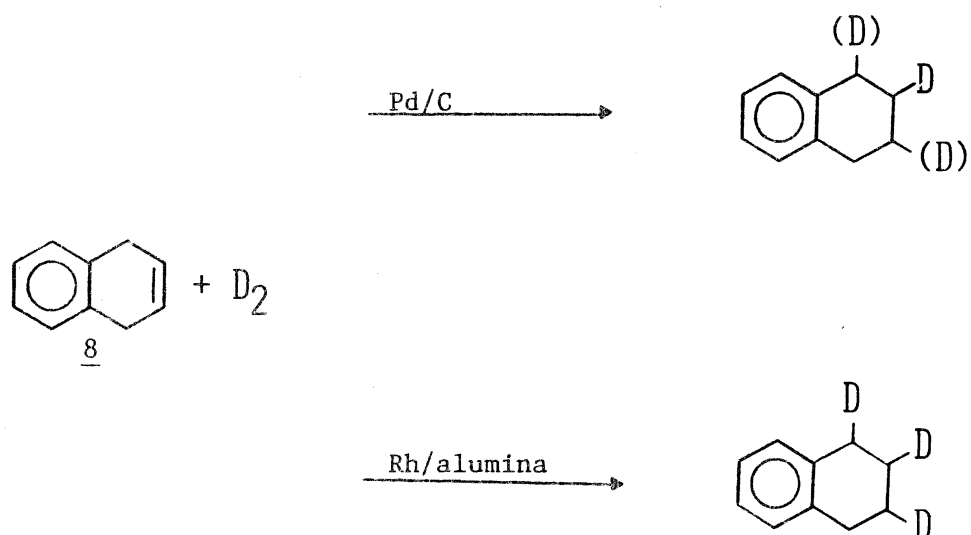


Figure 13. Deuterium Incorporation by Position, From Deuteration of 8 in EtOAc With Pd/C and Rh/Alumina



reported in the reduction of carbonyls, while Rh is reported to be inhibited by acidity in the reduction of benzene and acetophenone but unaffected in reduction of double bonds.²⁹

Styrene (11) was deuterated for comparison with results from 7, and the data were found to be analogous. The deuterium distributions for ethylbenzene (12) (Figure 14) show less difference between catalysts than was seen for 9 from 7. This is due in part to the fewer number of benzylic positions in 12 available for exchange. Maxima occurred at $C_8H_7D_3$ for both catalysts (29.4%, Pd/C; 30.8%, Rh/alumina). The curve produced with Pd/C is shifted slightly toward the right ($C_8H_6D_4$, 26%), while the curve produced with Rh/alumina is shifted noticeably toward $C_8H_8D_2$ (27%).

Deuterium incorporation by position in 12 (Figure 15) is very similar to that observed in 9 from 7. Deuteration of 11 with Pd/C gave

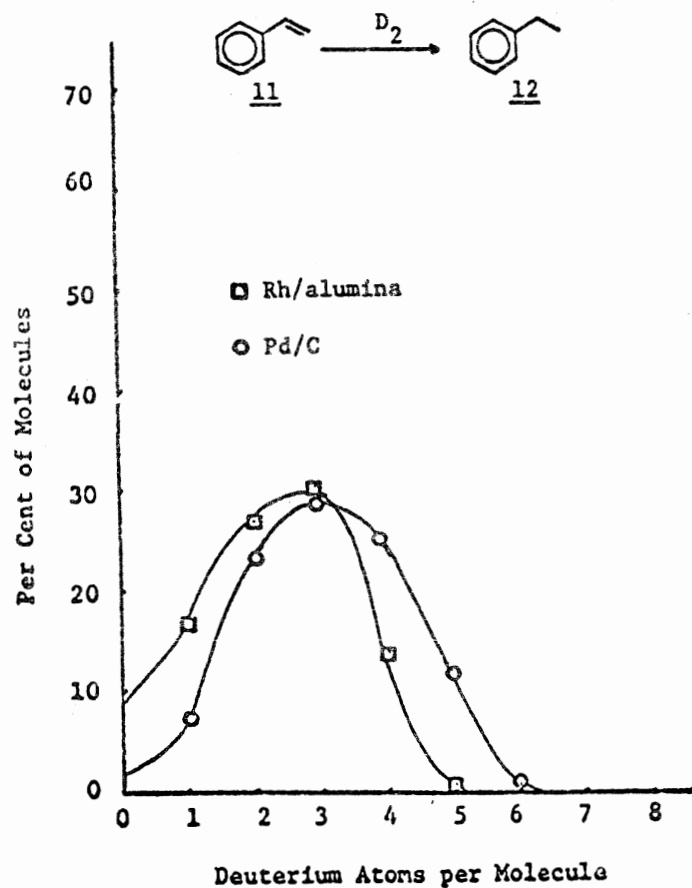


Figure 14. Deuterium Distribution From Deuteration of 11 in DOAc With Pd/C and Rh/Alumina

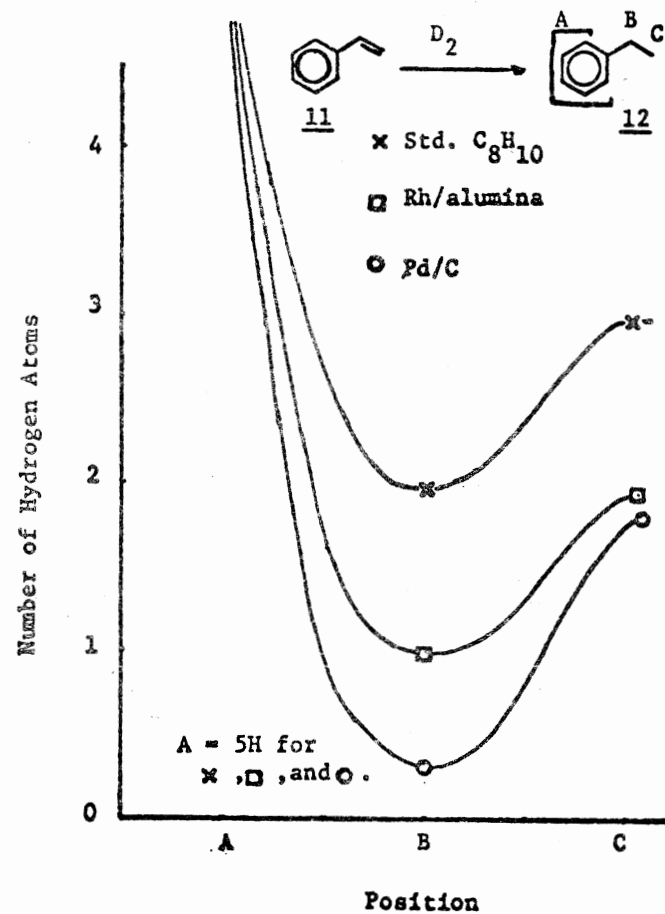
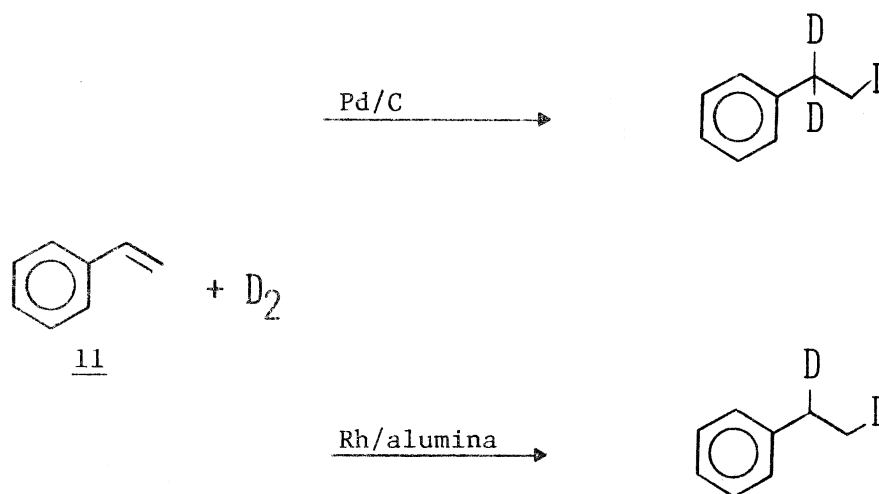


Figure 15. Deuterium Incorporation by Position From Deuteration of 11 in DOAc With Pd/C and Rh/Alumina

12 containing 81.5% deuterium at the benzylic position and 38.3% at position C. Incorporation of deuterium in 12 with Rh/alumina was almost totally from direct addition to the double bond with 46.5% deuterium at the benzylic position and 34.4% at C.

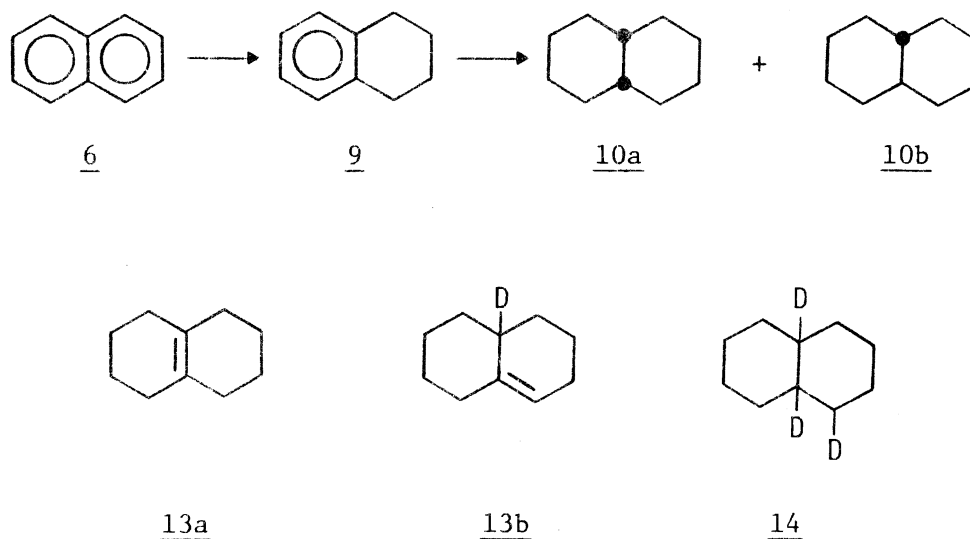
Average deuterium atoms per molecule was 2.9 for Pd/C and 2.1 for Rh/alumina as represented below.



Deuterium exchange on 9 in DOAc in the presence of either catalyst is much slower than incorporation by catalytic deuteration of 6, 7 or 8. Exchange on 9 in DOAc at room temperature with either catalyst was negligible after 18 hours. Exchange would occur faster at higher temperature but still not as fast as observed in the deuterations. Apparently the incorporation of deuterium observed in the reactions discussed occurs almost completely while the molecule is in a transition state on the catalyst.

Prolonged hydrogenation of 6 gives cis and trans decalin 10a and 10b in ratios dependent on catalyst. Pd/C gives a 1:1.3 (cis:trans) ratio while Rh/alumina gives a 9.5:1 (cis:trans) ratio. Platinum has

been reported to give a 1:1 ratio in the hydrogenation of symmetrical octalin (13a). Deuteration of octalin is reported to give decalin containing $C_{10}H_{15}D_3$ for most cis and trans, indicating isomerization of the hindered double bond to give 13b, which is reduced to 14.³⁰



In addition to the information obtained on catalytic selectivity, these studies resulted in the design and development of an improved glass hydrogenation apparatus.³¹ A conventional glass apparatus was modified as shown in Figure 16, (and as described in the Experimental) to carry out hydrogenation in refluxing solvents.

Traditionally, hydrogenations in glass apparatus are performed near ambient temperature and pressure.³² If a high boiling solvent such as HOAc or DMF is used, the reaction temperature can be raised somewhat. However, increased temperature decreases the solubility of hydrogen in the solvent. Unless the increase in reaction rate, due to temperature increase, is great enough to compensate, the reaction rate may be less than at room temperature.

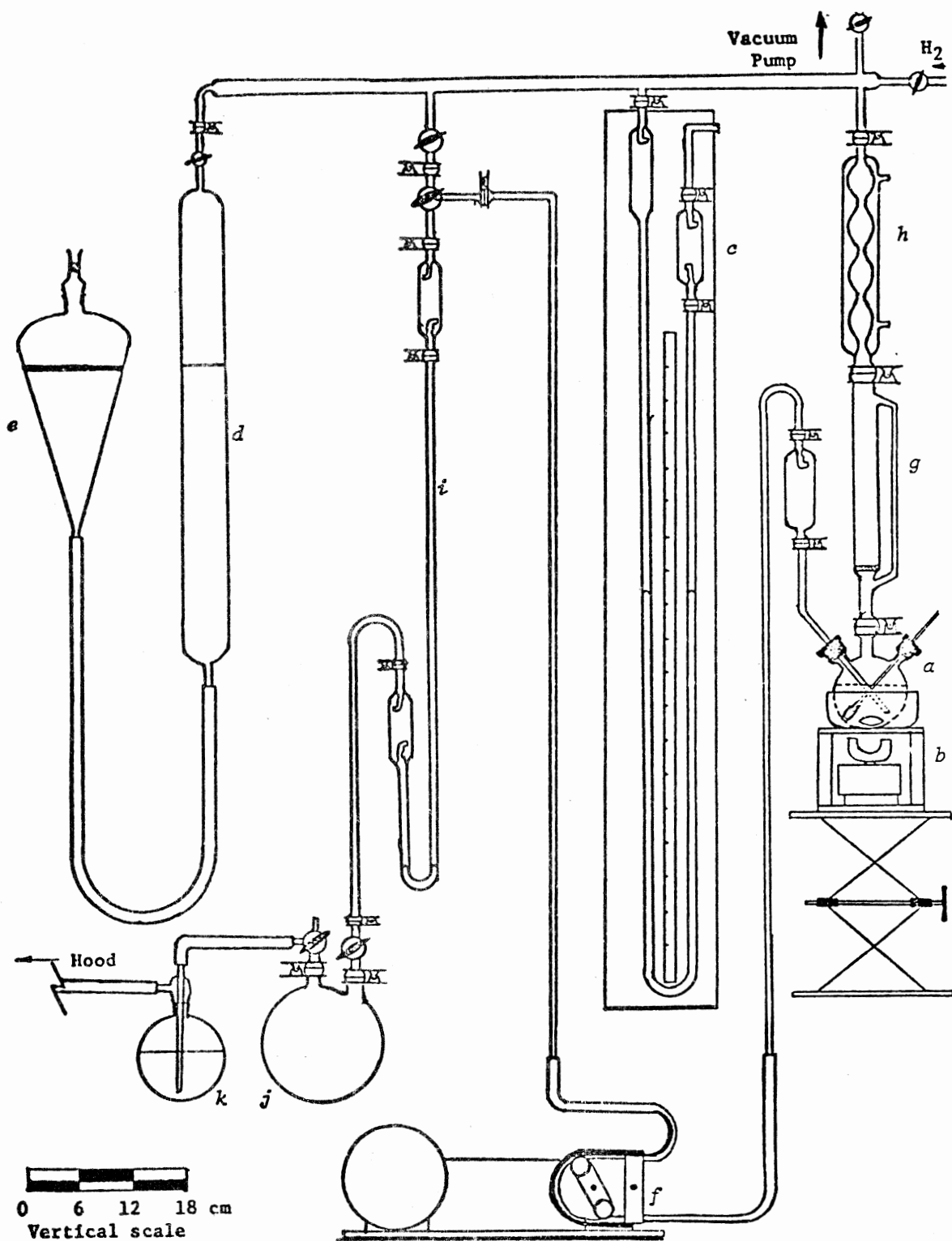


Figure 16. Hydrogenation Apparatus Fitted with Soxhlet Extractor and Modified for Hydrogen Recycle Capability

This point is illustrated in Table VI where increase in temperature decreases the reaction rate in the modified apparatus, but increases the rate in the conventional system, up to the boiling point of the solvent.

TABLE VI
HYDROGENATION OF CINNAMIC ACID IN 95% ETHANOL USING RECYCLING
AND CONVENTIONAL LOW PRESSURE SYSTEMS

Pressure mm Hg Above Ambient	Temperature °C	Minutes Required for 100% Hydrogenation	
		Recycling System	Conventional System
10	25	48	180
10	42	---	150
10	60	--	130
10	78	65	-- ^a
50	25	45	120

^aAt the boiling point of 95% EtOH (78°C) no uptake of H₂ was observed after 70 min. Temperature was allowed to fall below the boiling point of solvent and H₂ uptake was then observed immediately.

When the boiling point of the solvent is reached, hydrogenation ceases because of the inability of hydrogen to diffuse to the solvent through the vapor blanket.³³ An appreciation of the dramatic change in hydrogen uptake over the temperature range from ambient to boiling point of solvent using the conventional apparatus can be gained from reference to Figure 17 which shows the volume of hydrogen consumed plotted against time and the temperature of the reaction mixture.

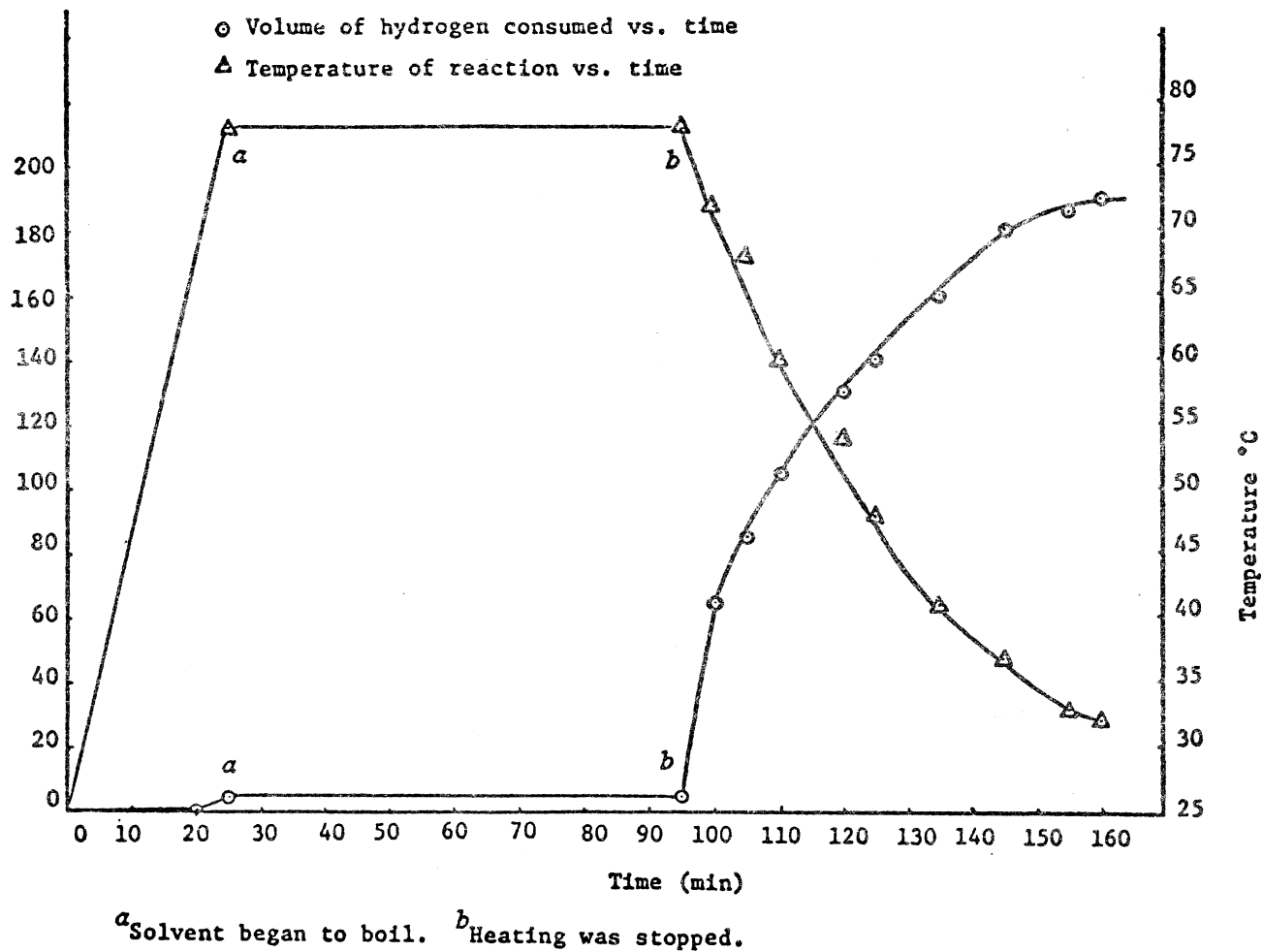
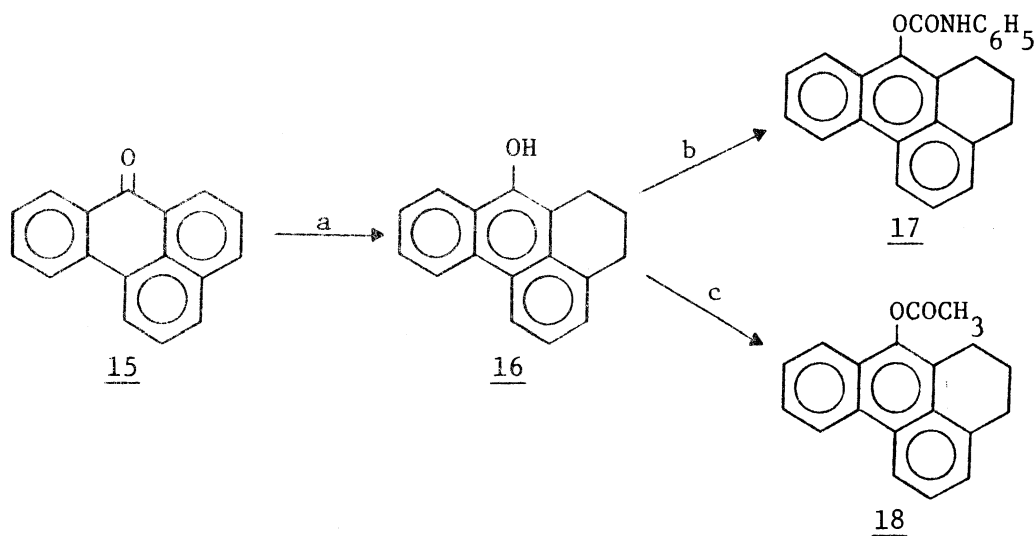


Figure 17. Hydrogenation of Cinnamic Acid in Refluxing 95% Ethanol Without Recycle of Hydrogen

A magnetically stirred mixture of 1 g of cinnamic acid, 50 ml of 95% ethanol, and 0.1 g of 5% Pd/C catalyst at 770 mm Hg did not appreciably absorb hydrogen during the time the solvent was refluxed. However, during cooling to ambient temperature, hydrogen was consumed (195 ml; 185 ml theoretical at 78°C).

The modified apparatus is more efficient than a conventional system as shown by the reduction of cinnamic acid in Table VI.

For another comparison, benzanthrone (15) was hydrogenated in acetic acid at 100°C and 810 mm both in the conventional manner and with the recycle apparatus. After 5 hr, the yield of the phenol 16 was 53% and 90%, respectively. The product yield was obtained by preparing and weighing the phenylurethane 17. The volumes of hydrogen consumed were 143 ml (stp) and 202 ml (stp) for the conventional and the recycle method, respectively. The theoretical hydrogen uptake was 196 ml (stp) and therefore the yields based on hydrogen were 73% and 103%, respectively. During recycle some hydrogen probably diffuses through the silicone rubber tubing. This loss varies with the duration of a run.



^aH₂, Pd/C. ^bPhenyl isocyanate, toluene, Δ. ^cAcetyl chloride

As shown in Table VI, pressure increase exerts a large effect on the conventional system, but has little effect on the hydrogen recycling system. Pressure increase from 10 mm Hg above ambient to 50 mm Hg increased the reaction rate by 33% for the conventional system but only 6% for the hydrogen recycling system.

The hydrogen recycling system apparently eliminates the limiting diffusion rate of hydrogen into the solution by delivering an excess of hydrogen to the catalyst and improving agitation. Linstead³⁴ has stated that an important role in dehydrogenation is the boiling of the solvent to aid the desorption of hydrogen from the catalyst. The agitation and boiling action caused by the recycling hydrogen may aid in desorption of the hydrogenated product, thereby increasing the rate of hydrogenation. These characteristics suggest the modified apparatus could be of value for kinetic studies in hydrogenation.

These modifications also allow the hydrogenation of insoluble substrates by Soxhlet addition. This technique gives a higher catalyst/substrate ratio for maximum efficiency and use of a minimum amount of solvent.

CHAPTER IV

EXPERIMENTAL

Product Formation Curves From the Hydrogenation of Anthracene (1).

One gram samples of 1 were hydrogenated at 810 mm Hg in refluxing acetic acid using 0.1 g of 5% Pd/C, 5% Pt/C, or 5% Rh/alumina³⁵ in an apparatus described in this section. Product formation curves were obtained by monitoring the reactions by GC³⁶ and are shown in Figure 1.

Hydrogenation of 9,10-Dihydroanthracene (2). One gram samples of 2 were hydrogenated under the conditions from which the product formation curves were obtained. Reaction times for 5% Pd/C, 5% Pt/C, 5% Rh/alumina catalyzed reactions were 5, 7, and 9 hours, respectively. Product ratios were determined by GC.³⁶

General Deuteration Procedure. All deuteration, unless otherwise noted, were performed in refluxing DOAc, under 810 mm Hg of 99% D₂ in the described apparatus. Catalyst to substrate ratios of 0.25 by weight were used and reactions were carried out until all starting material was consumed. Anthracene and naphthalene were desulfurized with Raney nickel³⁷ prior to deuteration. 1,4-Dihydronaphthalene was prepared as described later in this section from desulfurized naphthalene. 1,2-Dihydronaphthalene and styrene were not desulfurized.

Deuterated acetic acid was from two sources, 98% DOAc from Aldrich Chemical Co., Inc. and that prepared from 99% D₂O and reagent

grade acetic anhydride. These were reacted in dry glass apparatus under N_2 . The DOAc formed was distilled under dry N_2 and stored under N_2 in wax sealed bottles which had been dried at $600^\circ C$. The commercial DOAc was stored under argon in sealed bottles. No difference in results from these two reagents was observed.

The reaction apparatus (Soxhlet, condenser, and reaction flask) shown in Figure 16 was fired at $600^\circ C$, cooled, assembled, and evacuated to less than 4 mm Hg for several hours. The system was purged with dry N_2 for 15 minutes. The apparatus was then opened and catalyst, reactant, and solvent were quickly added. The system was evacuated and purged with N_2 three or four times. After the last evacuation, the system was pressured to 810 mm Hg with D_2 . During the reaction, D_2 was recycled into the reaction mixture at ca. 600 ml/min.³¹

Deuteration of Anthracene (1). Anthracene (2 g.) was deuterated using 5% Pd/C, 5% Pt/C, and 5% Rh/alumina. The results of the reactions are summarized in Table VII. Upon completion of the reaction, the mixture was filtered and the solvent was removed by evaporation. Isolation of 3 was achieved by column chromatography on a picric acid column³⁸ using isohexane as eluent. Further purification of 3 was attained by recrystallization from isohexane.

Deuterium distribution (Figure 2, Table II) was determined by field ionization mass spectrometry.³⁹ Distributions were determined from an average of 5 runs on 3 from each deuteration. Deuterium incorporation by position (Figure 3, Table III) was determined by nuclear magnetic resonance on a Varian XL-100 instrument. Ten integrations at two amplitudes were performed for each sample. All

TABLE VII

DEUTERATION OF ANTHRACENE (1) WITH SUPPORTED NOBLE METAL
CATALYSTS IN REFLUXING $\text{CH}_3\text{CO}_2\text{D}$

Catalyst	Reaction Time min	ml of D_2 Consumed	Composition of Reaction Mixture ^a					Purity ^a of <u>3</u> Isolated in %	Impurity ^a in <u>3</u>	Yield g (%)
			<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>			
5% Pd/C	250		-	18	37	36	9	99	<u>2</u>	0.5 (25)
5% Pt/C(I)	500		5	19	72	5	-	99	<u>1</u>	0.7 (35)
5% Pt/C(II)	180		-	18	58	22	2	97	<u>2</u>	0.3 (15)
5% Pt/C(III)			-	17	38	40	3	99	<u>2</u>	0.3 (15)
5% Rh/alumina	235		2	15	58	13	12	98	<u>2</u>	1.0 (50)

^aGC analysis.³⁶

solutions were 60 mg 3 in 0.6 g CCl₄ and were compared to an external standard of 3 of equal concentration.

Deuteration of Naphthalene (6). A 4 g sample of naphthalene (6) was deuterated in the presence of 1 g of 5% Pd/C for 5 hours at 80°C with a D₂ uptake of 1685 ml (1668 ml theoretical). The reaction mixture was filtered and slowly added to a saturated NaHCO₃ solution. The mixture was extracted with ether, dried (MgSO₄), filtered and concentrated by rotary evaporation to give 3.9 g (97%) of a colorless oil (GC analysis³⁶ 99% 9, 1% 10).

The reaction was repeated with 6 g of 6 and 1.5 g of 5% Rh/alumina. Deuterium consumption was 2445 ml (2500 ml theoretical) in 5 hours at 80°C. The workup as described yielded 5.8 g (97%) of product (GC analysis³⁶ 94.5% 9, 4.2% 6, 1% 10).

Deuterium distribution for tetralin(D) (Figures 6, 8, 10, 12, 14, Table IV) derived from 6, 7, and 8, and for ethylbenzene(D) derived from 11, was determined by low voltage (10 eV) electron impact mass spectra. Deuterium incorporation by position in 9 (Figures 7, 9, 11, 13, 15, Table V) was determined by NMR on a Varian XL-100 instrument using 30% by volume, 9 in CCl₄ with an external standard of 9 of equal concentration.

Deuteration of 1,2-Dihydronaphthalene (7). Six grams of 7 was deuterated for 4 hours at 80°C using 5% Pd/C. Deuterium uptake was 1160 ml (1200 ml theoretical). Workup as with 6 gave 4.3 g (70%) of product (GC analysis,³⁶ 98% 9, 2% 10).

With 5% Rh/alumina, 2 g of 7 consumed 320 ml (330 ml theoretical) D₂ in two hours. The yield was 1.5 g (75%) (GC analysis,³⁶ 90% 9, 10% 6).

Deuteration of 1,4-Dihydronaphthalene (8). 1,4-Dihydronaphthalene (2 g GC analysis,³⁶ 92% 8, 8% 6) deuterated at 60°C with 5% Pd/C, used

325 ml (330 ml theoretical) D_2 in 2.5 hours. The reaction mixture was filtered and DOAc was removed by rotary evaporation. An ether solution of the mixture was washed with water, dried ($MgSO_4$) and the ether was evaporated. Yield was 0.9 g (45%) (GC analysis, ³⁶ 98% 9, 2% 6).

The reaction was repeated with 5% Rh/alumina and 2 g starting material (GC analysis, ³⁶ 89% 8, 11% 6). Deuterium uptake was 455 ml (336 ml theoretical) in 2.25 hours. Workup as above yielded 0.9 g (45%) of product (GC analysis, ³⁶ 96% 9, 2.5% 6, 1.5% 10).

Deuteration of 8 (1 g samples) was repeated using ethyl acetate as solvent. With 5% Pd/C at 30°C starting material (GC analysis, ³⁶ 81% 8, 19% 6) consumed 115 ml (174 ml theoretical) D_2 in 1.5 hours. The reaction mixture was filtered and the solvent was evaporated to yield 0.95 g (95%) of product (GC analysis, ³⁶ 80% 9, 20% 6). With 5% Rh/alumina the starting material (GC analysis, ³⁶ 91% 8, 9% 6) took up 180 ml (174 ml theoretical) D_2 in 3 hours at 30°C. Product yield was 0.95 g (95%) (GC analysis, ³⁶ 91% 9, 9% 6).

Reduction of 6 in ethyl acetate was insignificant with both catalysts. The chemical shifts of the naphthyl hydrogens do not interfere with the analysis.

Preparation of 1,4-Dihydronaphthalene (8). To a solution of 5 g of 6 in 200 ml absolute ethanol at 0°C, 15 g of sodium spheres were added over a 12 hour period. The reaction was stirred until all sodium had reacted; approximately 2 hours after sodium addition was completed. Aqueous NH_4OAc was slowly added to the reaction mixture and the solution was extracted with ether. The ether layer was dried ($MgSO_4$), filtered, and concentrated by rotary evaporation. GC analysis ³⁶ of the product showed 8% 9, 61% 8, 6% 6, and 25% further

reduced products. The reaction mixture was passed through a 250 mm x 20 mm silica gel column with isohexane eluent and fractions were taken. Two grams of 8 (40%) was isolated (GC analysis,³⁶ 92% 8, 8% 6) mp 24-26°C (lit.⁴⁰ 26-27°C). ¹H NMR CCl₄ δ 3.22 (ArCH₂, 4), 5.78 (ArCH₂CH=CH, 2), 6.94 (ArH, 4).

Deuteration of Styrene (11). Styrene (4 g) was deuterated using 5% Pd/C at 60°C for 2 hours with a D₂ uptake of 950 ml (850 ml theoretical). The reaction workup as with 6 to give 0.9 g (22%) of 12 98% pure by GC analysis.³⁶

The reaction was repeated with 5% Rh/alumina to give 1.4 g (32%) of 12 95% pure by GC analysis.³⁶

Hydrogenation of Naphthalene (6) to (10a) and (10b). Naphthalene (0.4 g) was hydrogenated at 80°C for 9 hours with 0.46 g of 5% Pd/C with an H₂ uptake of 600 ml. Workup as for 6 gave ca. 0.35 g of product which contained 52% 9 and two isomers of decalin 26.8% trans (10a) and 20.5% cis (10b) by GC.³⁶ The reaction was repeated with 0.3 g 5% Rh/alumina and 0.3 g of 6. Reaction time was 7 hours with an H₂ uptake of 360 ml. The product obtained showed 53% 9 and 4.5% trans (10a) and 42.5% cis (10b). The isomers of decalin were identified with GC³⁶ by coinjection of pure standards with the reaction mixtures.

Exposure of Tetralin (9) to DOAc and Catalyst. Two 1 g samples of 9 were dissolved in DOAc (7 g) containing 0.1 g of 5% Pd/C or 5% Rh/alumina and agitated at room temperature (25°C) for 18 hours. The mixtures were filtered and 0.9 g of 6 was recovered from each reaction (90%). Low voltage (10 eV) mass spectra were taken to determine the extent of deuterium exchange. No exchange was observed for either sample under these reaction conditions.

Description of the Recycling Hydrogenation Apparatus Used for Deuteration Studies. Ambient-pressure catalytic hydrogenation is ordinarily carried out in a conventional glass system consisting of parts a-e in Figure 16. These parts are: hydrogenation flask (a), magnetic stirrer and Teflon-coated stirring bar (b), manometer (c), and gas burette (d) fitted with a mercury leveling bulb (e). This apparatus was modified to allow hydrogenations to be performed in refluxing solvent.

The first modification included the installation of a Soxhlet extractor⁴¹ and condenser (parts g and h) immediately above the hydrogenation flask. This extractor permits slow introduction of relatively insoluble material to the hydrogenation flask. With its use, there is an increase of catalyst/substrate ratio during addition and a decrease in the required volume of solvent. The slow introduction of sample also reduces the possibility that solution-precipitation of substrate will cause coating and deactivation of catalyst. To use the Soxhlet extractor (g), it is necessary to boil solvent, and thus a second modification (vent system, parts i, j, k) is required as a safety measure and to help maintain a constant working pressure during temperature changes.

A third modification was the addition of an explosion-proof peristaltic pump⁴² (part f) to enable recycle of hydrogen and introduce it directly to the liquid phase of the hydrogenation flask.

Hydrogenation of Benzanthrone (15) to 5,6-Dihydro-4H-9-oxybenz[de]-anthracene (16) and Isolation of 16 as (17) and (18). One g samples of 15 were hydrogenated in the recycling apparatus and in the conventional glass apparatus for 5 hours at 100°C in HOAc with 5% Pd/C (0.1 g). The

mixtures were filtered, dissolved in toluene and washed with water to remove the HOAc. Phenyl isocyanate was added to the toluene solutions and the mixtures were refluxed for 24 hours. The mixtures were concentrated to crystallize the urethanes as white crystals. Yields of 16 based on 17 isolated were: Conventional system, 0.8 g (53%) mp 190-194°C; Recycling system, 1.35 g (90%) mp 194-199°C. From a previous hydrogenation 14 was isolated, mp 147-149°C; lit.⁴³ 150-151°C.

16 (1 g) was reacted with acetyl chloride to give 18.

17 ¹H NMR (CDCl₃) δ 2.1 (m, ArCH₂CH₂-, 2H), 3.14 (m, ArCH₂CH₂, 4H), 7.1-7.7 (m, ArH, 9H), 7.86-8.05 (N-H, m, 1H), 8.45-8.75 (ArH, m, 2H).

18 ¹H NMR (CDCl₃) δ 2.05 (m, ArCH₂CH, 2H), 2.47 (s, CH₃C=O, 3H), 3.07 (ArCH₂, m, 2H), 7.2-7.9 (ArH, m, 5H), 8.45-8.75 (ArH, m, 2H), mass spectrum 70 eV, m/e (rel. intensity), 276 M⁺ (30), 234(100), 233(12), 215(24), 202(14), 188(9).

PART II

HYDROGENATION OF POLYNUCLEAR

AROMATIC HYDROCARBONS

CHAPTER V

INTRODUCTION AND HISTORICAL

The change in product ratios with variation in reaction conditions (catalyst, temperature, and pressure), during the hydrogenation of PNA hydrocarbons has been noted since the early work in this field. The hydrogenation of anthracene (1) with copper chromite is reported by Garlock²⁸ to give 2 in high yield during the stepwise process denoted as A in Part I. These results were supported by Sugino and Outi⁴⁴ in a detailed study of the hydrogenation of 1 with a copper catalyst. A gradual increase in pressure and temperature gave successively 2, 3, 4a, and 5. Schroeter⁴⁵ reduced 1 with nickel at 20 atm. and 180°C to 4a, and proposed 2 as an intermediate. Fries⁴⁶ and Hibino²⁷, however, have proposed the two simultaneous processes A and B, discussed in Part I, in the presence of nickel or platinum. Two processes have also been reported in the presence of nickel tungsten sulfide^{27b} and nickel chromium catalysts.⁴⁷ Hydrogenation of 1 with tungsten oxide at 360°C and 300 atm. gave 4a in 90% yield.⁴⁸

Synthesis of 3 by methods other than catalytic hydrogenation include reduction of 1 with LiAlH₄ at 230°C,⁴⁹ and reduction of the trisulfate ester of 2-hydroxy anthrahydroquinone with Raney nickel and NaOH.⁵⁰ Disproportionation of 2 to 1 and 3 and similarly formation of 3 from 1 and tetralin (9) in the presence of Pd/C has been reported.⁵¹

Hydrogenation of phenanthrene (19) has been shown to occur in a stepwise manner by Schroeter⁴⁵ and Burger and Mosettig,⁵² who reported a high yield (80%) of 9,10-dihydrophenanthrene (20) with copper chromite. Durland and Atkins⁵³ improved the yield to 87% with a decrease in temperature from 220°C to 150°C. They also reported a novel method of increasing the yield of 1,2,3,4-tetrahydrophenanthrene (21) from 6 to 40% through limitation of H₂.⁵⁴ The difference in pressure needed for the reaction was made up with N₂, and 19 was hydrogenated with Raney nickel catalyst. Symmetrical and unsymmetrical octahydrophenanthrene (22a and 22b) isomer ratios were changed by increasing the reaction temperature from 100°C to 130°C.⁵⁴ The higher temperature increased the yield of the unsymmetrical isomer (22b) to 33%. Reduction of 19 with molybdenum disulfide catalyst at 160-180° atm, 300-450°C gave 21, 22c, and perhydrophenanthrene (23) but no 20.⁵⁵ Schlegel⁴⁸ has reported that 19 hydrogenated in methanol, at 20°C with Raney nickel gave a greater yield of 21 than 20 but in boiling ether more 20 is obtained.

Extensive studies on the stereochemistry of phenanthrene hydrogenations with Adams catalyst at 60 psig in acetic acid or ethanol have been performed by Linstead and reviewed by H. A. Smith.⁵⁶ Of the six possible perhydrophenanthrene isomers Linstead found only cis and syn.

Kinetics of the hydrogenation of PNA hydrocarbons has been studied with numerous catalyst systems.^{56,57} Relative hydrogenation rates generally follow the order of linear and unsymmetrical systems > angular and symmetrical systems.^{20,57} The rate decreases due to steric hindrance as the number of substituents on the aromatic ring increases.⁵⁷

Homogeneous hydrogenation of PNA hydrocarbons has been investigated by Friedman using cobalt octacarbonyl.⁵⁸ Selectivity was shown, but the reactions were incomplete in many cases, in that starting material was not completely consumed. The mechanism of cobalt carbonyl catalyzed hydrogenations is believed to proceed by a free radical process.⁵⁹

Catalytic hydrocracking of anthracene and phenanthrene⁶⁰ has been shown to occur through the intermediates tetrahydroanthracene (3) and tetrahydrophenanthrene (21), respectively.

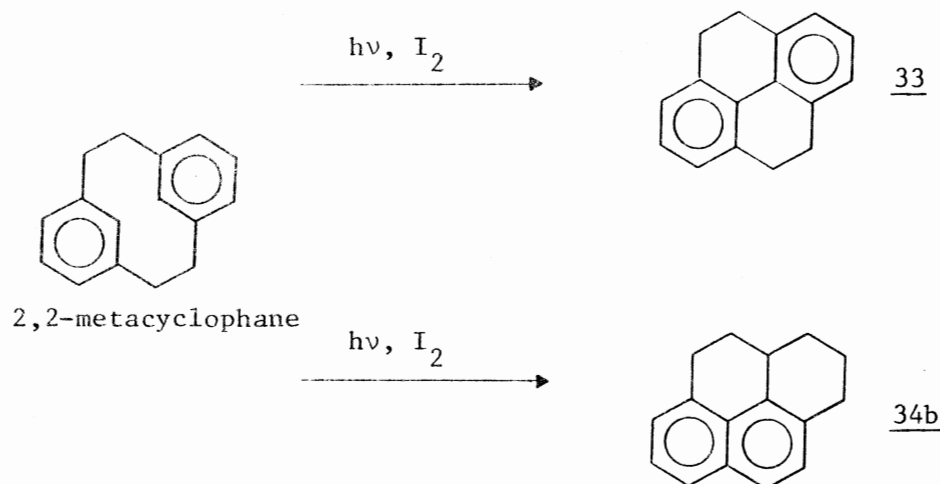
Hydrogenation of benz[a]anthracene (27) to 5,6-dihydrobenz[a]-anthracene (28a) with Pd/C has been done by Harvey.⁶¹ The synthesis of 7,12-dihydrobenz[a]anthracene (28b) is accomplished with dissolving metal reductions.^{62,63} Hydrogenation of (27) with Adams catalyst by Fieser and Hershberg⁶⁴ gave 8,9,10,11-tetrahydrobenz[a]anthracene. It was this work, combined with the hydrogenation of 7-methylbenz[a]-anthracene, that led to the first proposal of the selectivity of Pt for the terminal ring in linear hydrocarbons. The 5,6,8,9,10,11-hexahydroisomer (30a) has been synthesized by Burger and Mosettig,⁶⁵ while 1,2,3,4,7,12-hexahydrobenz[a]anthracene has been made by dissolving metal reduction.^{62,63}

In a recent publication, published just as this work was completed, Harvey⁶⁶ reports selective hydrogenation of several PNA hydrocarbons including 19, 27, and pyrene (31) with Pd and Pt. However, the studies as presented, were somewhat incomplete. The total hydrogenation of 27 to octadecahydrobenz[a]anthracene with excess Adams catalyst has been reported.⁶⁷

In earlier work, Coulson hydrogenated pyrene (31) to dihydropyrene (32) in an 80% yield using MoO₃/C catalyst at 100 atm., 400°C, for 4

hours in the presence of sulfur.⁶⁸ Longer reaction times resulted in lower yields, due to dehydrogenation or disproportionation to 31 and other products.

Hydrogenation of pyrene (31) with Raney nickel and copper chromite has produced two hexahydropyrene isomers, symmetrical (34a) and unsymmetrical (34b), as well as hexadecahydropyrene.⁶⁹ Hydrogenation of 31 to a mixture of dihydropyrene (32), tetrahydropyrene (33), hexahydropyrene (34a and 34b) and a small amount of hexadecahydropyrene in the presence of Pd/C, HCl, and AlCl₃ has been patented.⁷⁰ Tetrahydropyrene (33) has not been reported as a major hydrogenation product in high pressure hydrogenations. The synthesis of 33 and 34b by iodine catalyzed photolysis of 2,2-metacyclophane has been carried out as shown below.⁷¹



In addition to being a hydrogenation product of pyrene,⁷² one isomer of decahydropyrene (35a) has been prepared by the partial hydrogenation of 2,2-metacyclophane in the presence of Adams catalyst

and acetic acid.⁷³ Decahydropyrene (35b) is reported as a product in dehydrogenation of perhydropyrene with Cr_2O_3 /alumina at 450°C .⁷⁴

Chrysene has been hydrogenated to dodecahydro- and hexadecahydrochrysene with Raney nickel.⁷⁵ Hexahydrochrysene has been prepared by Lang and coworkers⁷⁶ by high pressure hydrogenation of chrysene.

Catalytic hydrogenations compliment dissolving metal reductions which often result in products containing isolated double bonds.⁶² This characteristic is due to the radical anion or dianion mechanism of dissolving metal reactions which results in maximum charge separation.⁷⁷ This effect is not generally present in catalytic hydrogenation and thus a different product is possible. A comprehensive review by Campbell⁷⁸ gives comparisons of the two reduction processes.

CHAPTER VI

RESULTS AND DISCUSSION

Selective hydrogenations of PNA hydrocarbons 1, 19, 27, 31, and 36 were carried out under mild conditions in the presence of noble metal catalysts Pd/C, Pt/C, and Rh/alumina.

The purity of the starting hydrocarbons with respect to catalyst poisons, particularly sulfur containing compounds, is critical with these catalysts. Treatment of commercial samples of 1, 19, 31, and 36 with Raney nickel catalyst for the removal of sulfur is essential. Attempts to hydrogenate the compounds, prior to treatment with Raney nickel catalyst, failed. In contrast, 27 was synthesized⁷⁹ and did not require desulfurization.

Hydrogenation of 1 with supported Rh catalysts gave 3 in yields of up to 90% by GC.³⁶ Prolonged hydrogenation resulted in 4a in 95% yield by GC.³⁶ Higher selectivity was obtained at lower pressures and the glass, hydrogen recycling apparatus was generally more selective than the Parr. The selectivity of Rh in reduction of the terminal ring in linearly annelated systems makes it the catalyst of choice as suggested by Freifelder,⁸⁰ for hydrogenation of 1 to 3 and 4a. Unsymmetrical octahydroanthracene (4b) was not isolated. However, an unknown product having the same relative GC retention time to 4a as did 22b to 22a,⁸¹ was believed to be 4b. The ratio by GC,³⁶ of 4a to this unknown was 2.2:1 with Pd/C and 21:1 with Rh/alumina.

Phenanthrene (19), pyrene (31), and chrysene (36) were more resistant to hydrogenation than 1 or 27 and higher pressures (30-75 psig) were required to obtain a reasonable reaction rate. The product formation curve for hydrogenation of 19 using Pd/C is shown in Figure 18. The predominant process is reduction of the 9,10 position to give 20, then isomerization and hydrogenation to 21. The rate of reduction of 21 is equal or greater than the preceding isomerization and 21 is not seen in high concentration; rather an increase of 22a and 22b in *ca.* 55:45 ratio is observed. The formation of 21 initially observed may be the result of direct hydrogenation of 19 at the 1,2,3,4 positions. The maxima for 20 and 21 are reached almost simultaneously and no 21 is seen after 19 is consumed. Subsequent reduction of 22a and 22b to 23 (six isomers) occurs, and 22b because of less steric hinderance reacts faster than 22a.

Relative efficiency of the three catalysts in hydrogenation of 19 is Pd > Rh > Pt. Hydrogenation of 19 in HOAc, 75 psig, 60°C, for 24 hours with each catalyst gave conversions to hydrogenated phenanthrenes of 100% with Pd (21% 20, 45% 22a, 34% 22b), 67% with Rh (33% 20, 13% 21, 6% 22a, 15% 22b), and 5% with Pt (3% 20, 2% 21). The selectivity of Rh for the terminal ring is still present as shown by the change in ratios of 22a:22b from the 55:45 ratio observed with Pd to 1:2.5 with Rh.

Hydrogenation of 21 in the presence of Pd/C gave the same 55:45 ratio of 22a:22b as observed from 19. Hydrogenation of 21 in the presence of Rh/alumina gave a 22a:22b ratio of 85:15 (Table VIII). Hydrogenation of 19 using Pd/C catalyst follows process C predominantly, with process D a possible minor route as shown. Process E does not appear to be significant with Pd/C. With Rh/alumina however, D and E

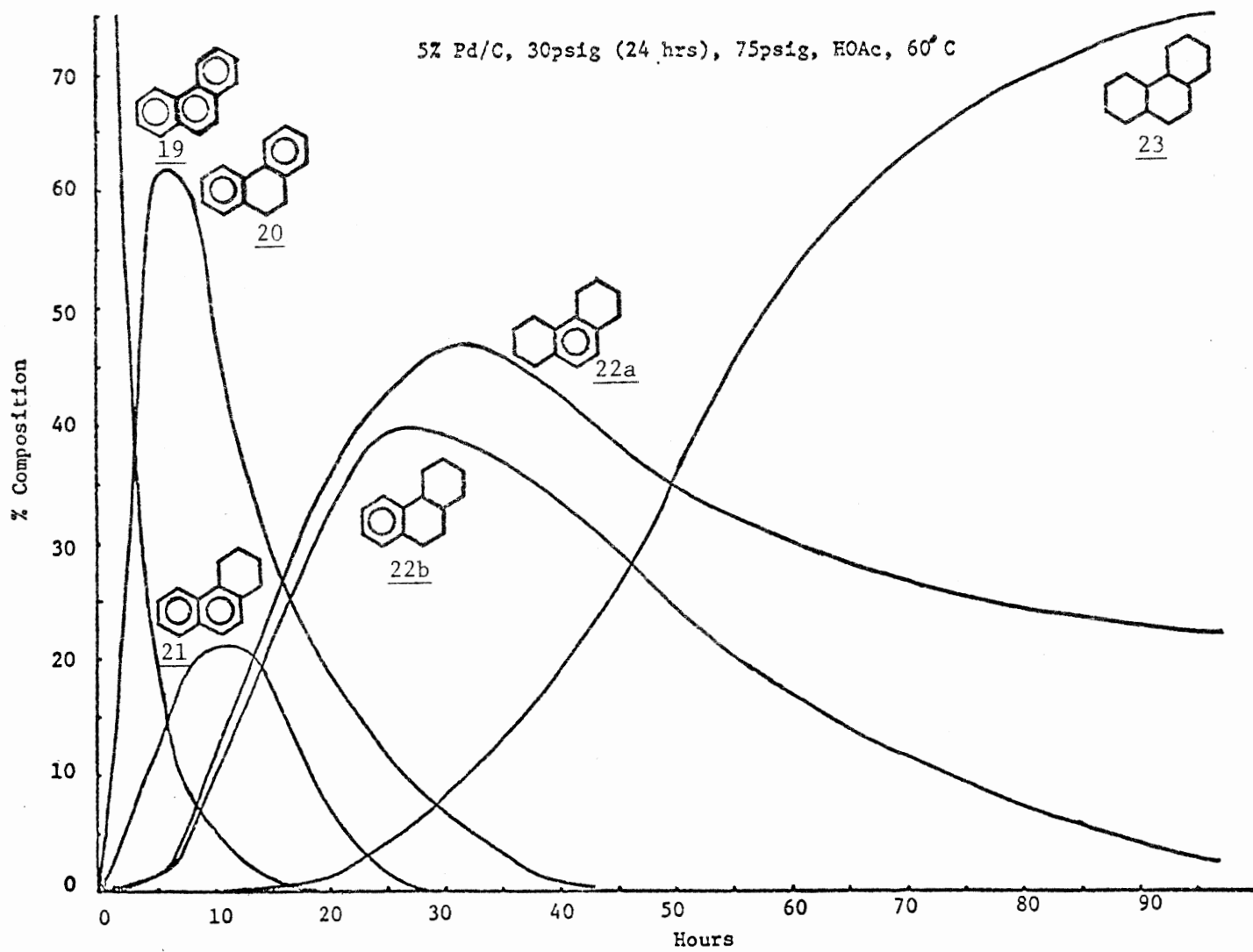
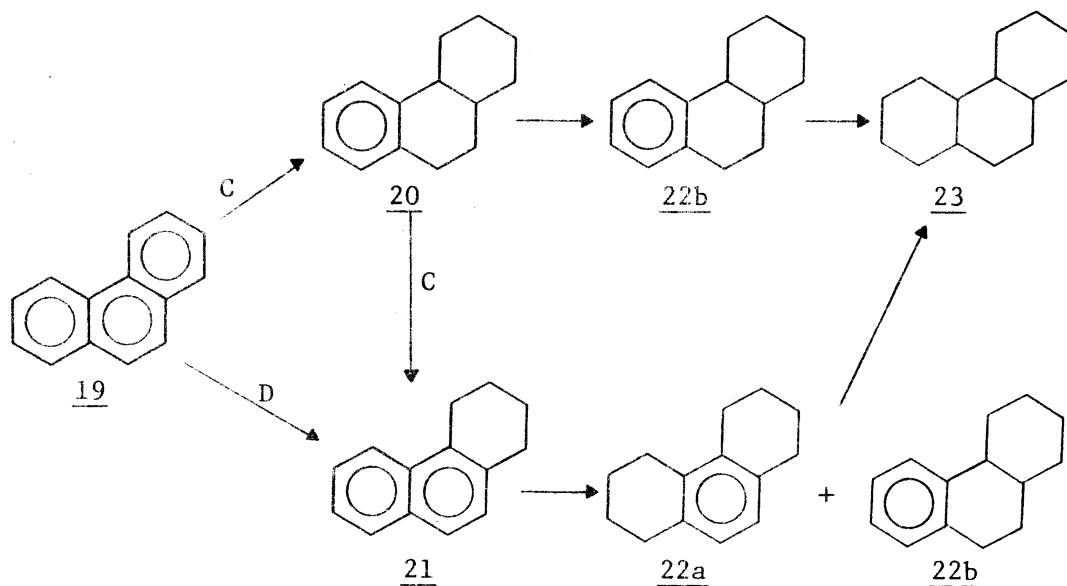


Figure 18. Product Formation in the Hydrogenation of Phenanthrene (19) Catalyzed by Pd/C

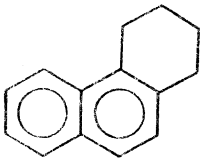
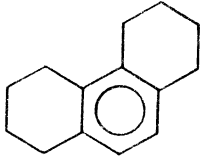
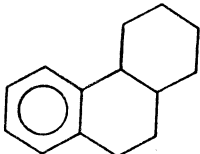
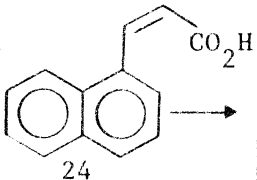
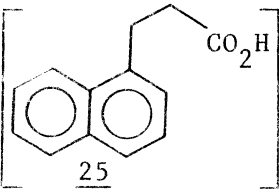
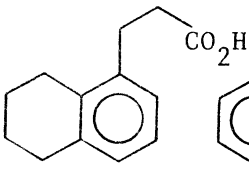
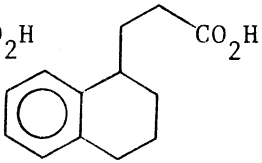


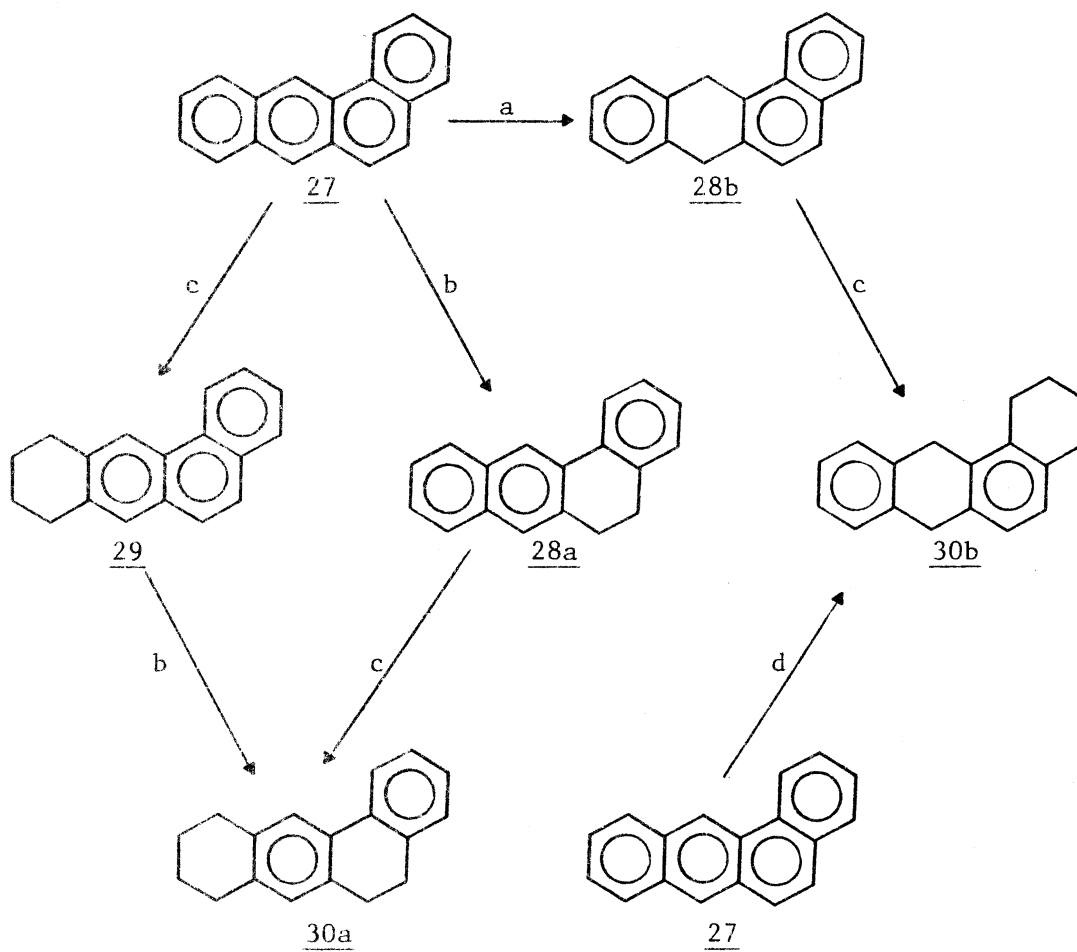
appear to be more competitive while C may be decreased because the inability of Rh to promote isomerization.

Rhodium is more sensitive to steric hinderance than Pd as shown in Table VIII. With Pd/C, hydrogenation of 24 gave the same ratio of 26a:26b as found for 22a:22b. In contrast, Rh/alumina gave a 72:28 ratio 26a:26b as compared to the 85:15, 22a:22b, ratio from 21.

The selectivity of Rh, Pt, and Pd has utility in synthesis of hydrogenated benz[a]anthracenes as shown in Figure 19. Hydrogenation of 27 in the presence of Pd/C gave 92% dihydrobenz[a]anthracene while with Pt and Rh, 29 was the major product in 85-90% yield.⁸² The 7.12-dihydrobenz[a]anthracene isomer (28b) is not a major hydrogenation product, but is synthesized in high yield by dissolving metal

TABLE VIII
EFFECTS OF STERIC HINDERANCE ON Pd AND Rh

Starting Compound	Catalyst	Product Ratio	
 <u>21</u>		 <u>22a</u>	 <u>22b</u>
	Pd	55	45
	Rh	85	15
 <u>24</u>		 <u>25</u>	
		 <u>26a</u>	 <u>26b</u>
	Pd	55	45
	Rh	72	28



- a) Li, NH₃, FeCl₃,⁶²
 Li, Et₂O (or Glyme)⁶³
- b) Pd/C, H₂

- c) Rh or Pt, H₂
- d) Na, isoamyl OH⁶⁴
 or isopropyl OH⁶³

Figure 19. Selective Hydrogenation Routes to Hydrogenated Benz[a]-anthracene Using Noble Metal Catalysts

reductions.^{62,63} This isomer is present as a byproduct in hydrogenation of 27 to 28a with Pd/C and 27 to 29 with Pt/C. Analysis of the reaction mixture by NMR showed 28b (ca. 5%) in the reaction of 27 to 29 with Pt, as reported by Harvey.⁶⁶ Analysis of the reaction mixture from the Rh catalyzed hydrogenation of 27 showed only a trace of 28b as compared to ca. 5% dihydro isomer shown by GC analysis. Therefore the dihydro isomer in the Rh/alumina catalyzed hydrogenation mixture is believed to be 23a. Hexahydrobenz[a]anthracenes are byproducts in the reaction of 27 to 29 from both Pt (6% by GC) and Rh (8% by GC) catalyzed hydrogenations.

The hexahydroisomers observed by GC in the Rh/alumina and Pt/C catalyzed hydrogenations of 27 to 29 are not necessarily the same. These isomers 30a and 30b were not resolved by GC.⁸² Harvey⁶⁶ has reported that 30a is not produced from 29 with Pt, and this study has shown Pt/C to be ineffective in reducing the 9,10 position of 19. Since 28b is present as a byproduct, reduction of 28b to 30b with Pt/C is likely. In the presence of 29, small amounts of 30a are difficult to detect by NMR since the distinguishing peaks are partially buried under those of 29. However the 7,12 hydrogens of 30b will be seen if present in sufficient concentration. An NMR of the reaction mixture of the hydrogenation of 27 to 29 showed a small amount of 30b along with ca. 5% 28b. This quantity of 30b does not appear to be enough to be the 6% hexahydro isomer shown by GC.⁸² Hydrogenation of 29 in the presence of Pt/C using HOAc solvent, 810 mm Hg hydrogen pressure 45°C for 2 hours gave a 10% conversion to a hexahydro isomer.⁸² Continuation of the reaction at room temperature for 24 hours gave ca. 20% conversion. Analysis of the reaction mixture by NMR showed no 30b but

the benzylic hydrogens at δ 2.7, indicative of 30a were observed. Therefore, it would appear that there is conversion of 29 to 30a in the presence of Pt. With Rhodium, 28a is the major dihydro isomer in reduction of 27 to 29. Rhodium will reduce the 9,10 position of 19 slowly, so 30a can result from reduction of 28a or 29 with Rh.

Hydrogenation of 28a in the presence of Rh or Pt gives 30a in 80 to 90% yield by GC, while hydrogenation of 29 using Pd gives 30a in *ca.* 72% by GC.⁸² Hydrogenation of 28b in the presence of Rh gave 30b in 75% yield by GC.⁸² Dissolving metal reduction of 27 also gives 30b in high yield⁶⁴ (90% by GC,⁸² 51% isolated) and appears to be the better method for synthesis of 30b at this time.

Hydrogenation of 27 to 28a in the presence of Pd/C also yielded 28b and 29 as minor products, as shown by NMR and GC. The major process is reduction of the 5,6 position of 27, but processes A and B described in Part I are also present. Ratios of 28a to 28b by NMR was *ca.* 6:1.

Hydrogenation of 31 with the respective noble metal catalysts showed the same relative efficiency as observed for 19, Pd > Rh > Pt. The product formation curve from Pd/C catalyzed hydrogenation of 31 is shown in Figure 20. The process is initially a straight forward reduction of the 4,5, then the 9,10 positions to give first 32, then 33 in high yield (*ca.* 80% by GC). Two competing processes then occur as depicted below. The major route as with 1 and 19 is isomerization and reduction to 34a and 34b, and eventually reduction to 35a and 35b (Process F).

Hydrogenation of 32 to 33 appears to be slightly faster than 31 to 32, since 32 is not observed as a major product during the reaction.

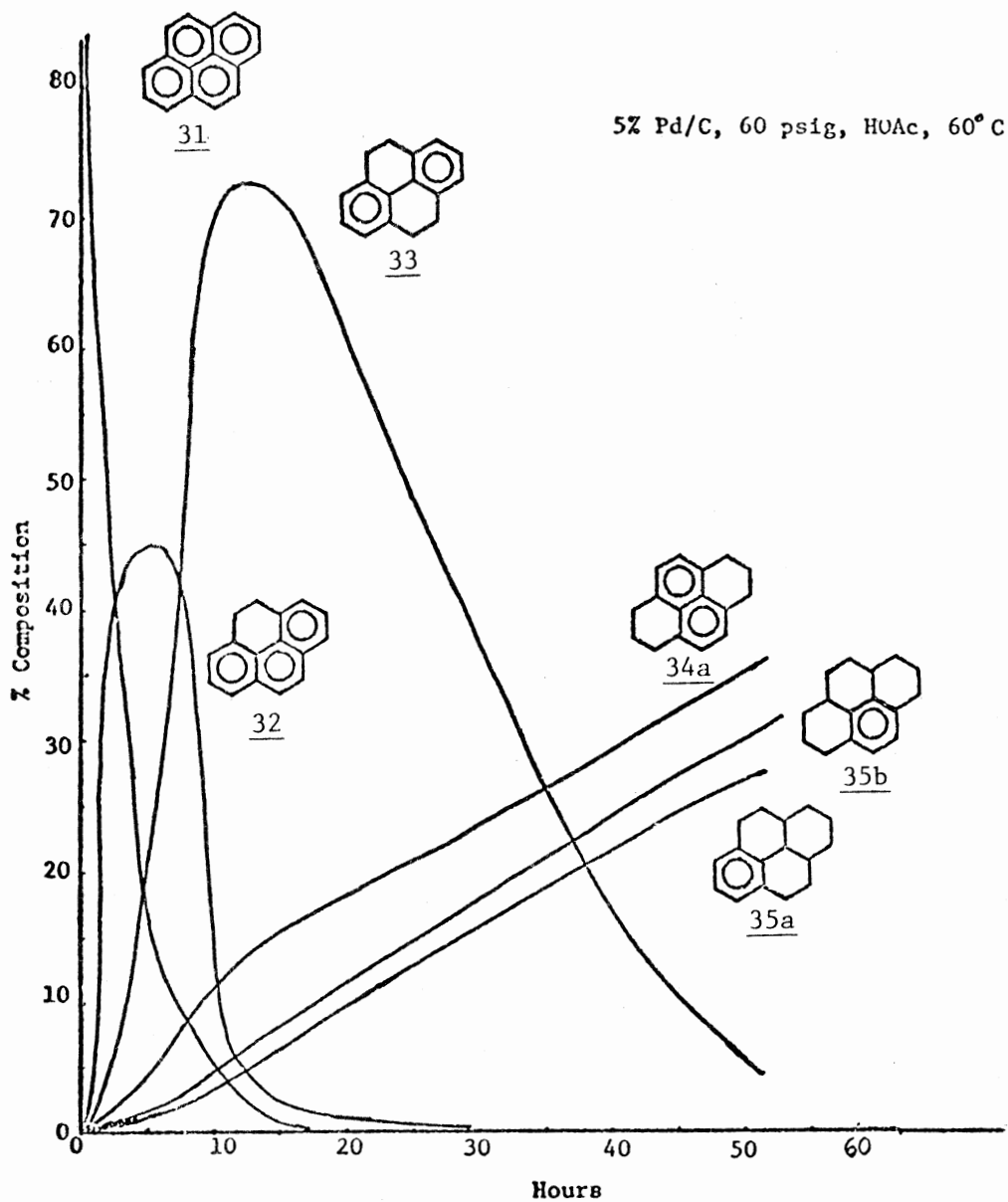
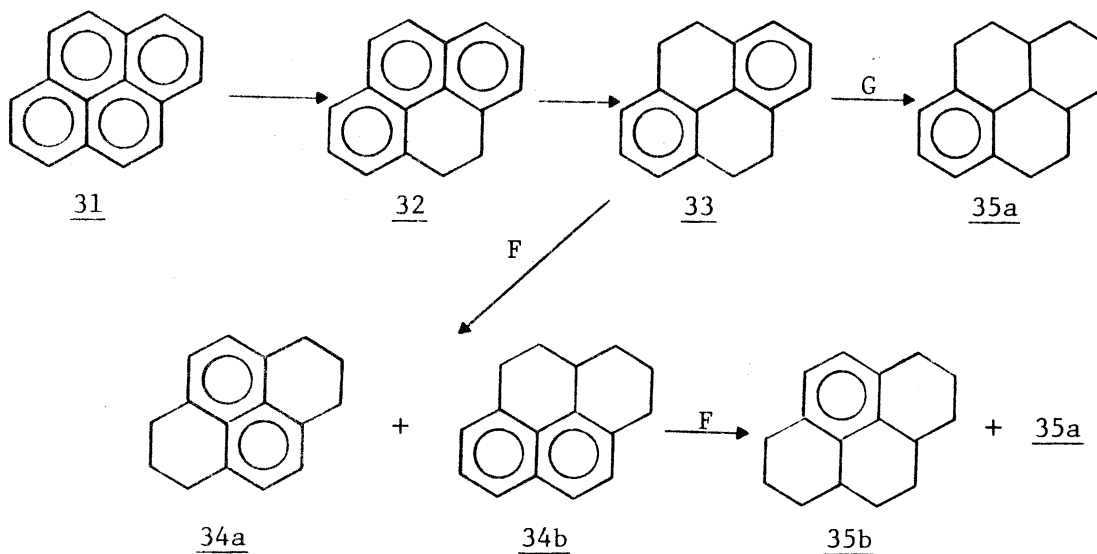


Figure 20. Product Formation in the Hydrogenation of Pyrene (31) Catalyzed by Pd/C

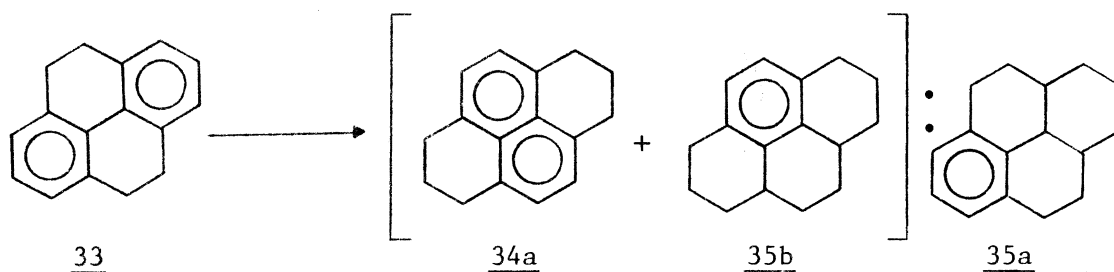


Processes F and G are influenced by temperature, catalysts, and solvent as shown in Table IX. Lowering the reaction temperature, use of a nonacidic solvent, or a catalyst which will not promote isomerization readily, decreases process F and increases process G.

In agreement with results in Part I, Pd/C shows a solvent effect in isomerization, whereas Rh/alumina shows little sensitivity to solvent.

Preliminary study of hydrogenation of chrysene (36) using Pd/C (Figure 21) shows the predominant process (H) to be analogous to that found for 19. Initial hydrogenation is at the 5,6 position to give dihydrochrysene (37), then isomerization and reduction to further hydrogenated products 38 and 39a as shown below.

TABLE IX
 TEMPERATURE, SOLVENT, AND CATALYST EFFECTS IN HYDROGENATION
 OF 4,5,9,10-TETRAHYDROPYRENE (33) USING
 NOBLE METAL CATALYSTS



Catalyst	Solvent	°C	Pressure (psig)	Product Ratio (34c + 35b):35a
Pd	HOAc	25	150	1.2
Pd	HOAc	60	60	4.0
Pd	F ₃ CO ₂ H	60	60	6.0
Pd	EtOAc	100	150	2.6
Rh	HOAc	100	150	1.6
Rh	EtOAc	100	150	1.5

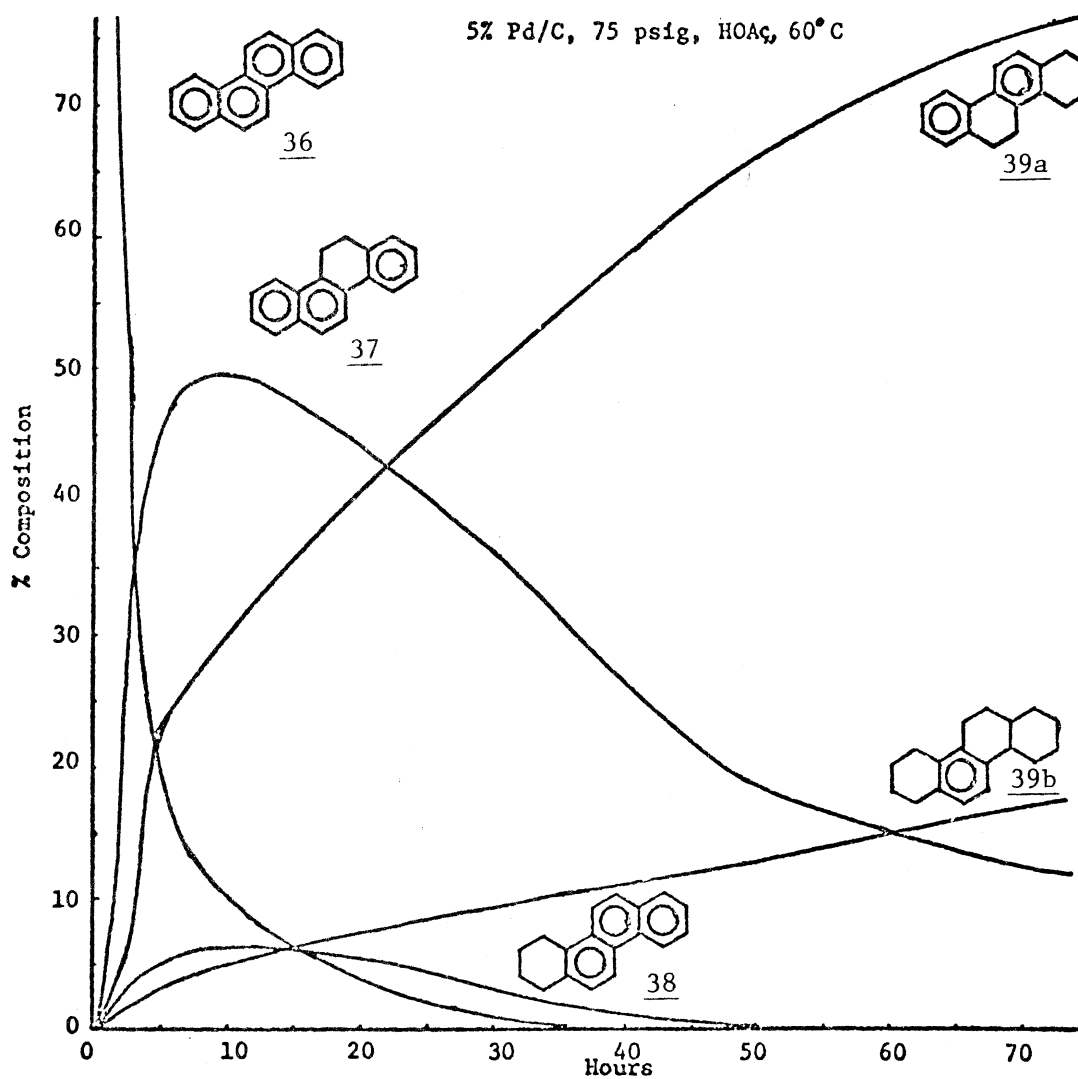
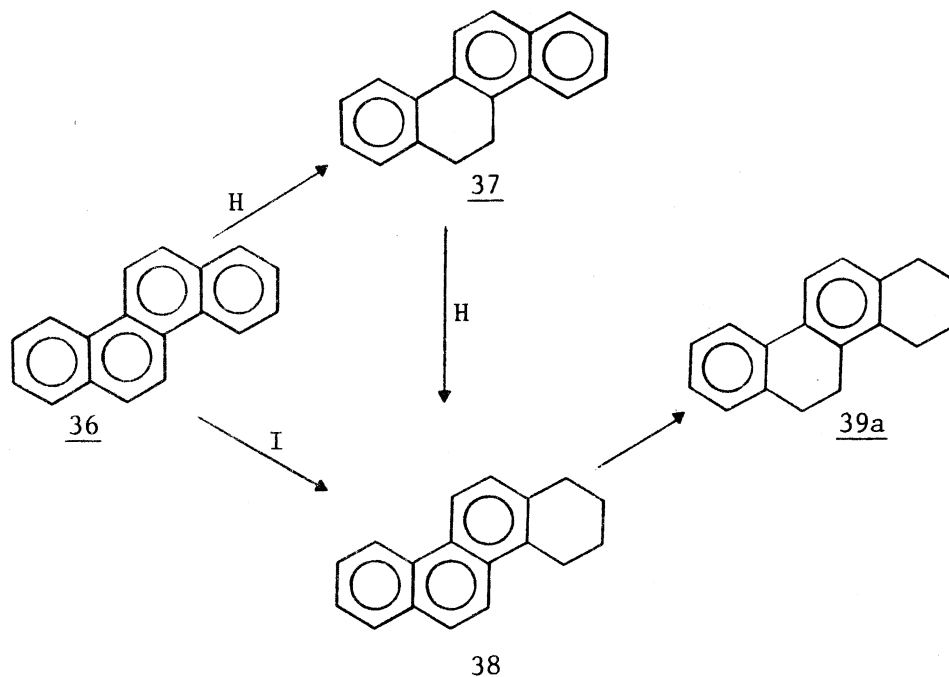


Figure 21. Product Formation in the Hydrogenation of Chrysene (36) Catalyzed by Pd/C



In all the systems studied, the isomerization step appeared to be the rate determining step in the process until steric hinderance became important. Steric hinderance did not become significant until multi-substituted rings such as those in 22a, 35a, and 35b were involved. The disubstituted compound 34a was readily hydrogenated to 35a in 57% yield by GC,³⁶ at 65 psig and 60°C.

With all systems studied, pressure has little effect on product ratios at any given point in the reaction. Ratios are controlled by temperature, catalyst, and solvent. Pressure and temperature will determine rate of reaction. Lowering the pressure slows the rate and allows intermediates to accumulate in higher concentrations than might be obtained at high pressures.

Efficient separation of the hydrogenated mixtures is a major problem in utilizing hydrogenation as a synthetic method. The use of

charge transfer complexes,⁸³ the most common of which are those of picric acid,^{83a} is a standard procedure in the separation and purification of aromatic hydrocarbons.⁸³ During this study an improved technique for separation of hydrocarbon mixtures by complexation was developed.³⁸ Conventionally, picrates are formed and isolated by crystallization from a solvent such as ethanol which has been saturated with picric acid and the hydrocarbon mixture.^{83a,b} The disadvantages of the conventional technique are that the recovery of compound is often low, and co-crystallization of other components in the mixture may contaminate the picrate.²⁸ A picrate cleavage technique by soxhlet extraction⁸⁴ was modified to allow the hydrocarbon mixtures to be chromatographed through a column of picric acid with isohexane. The picrate forming components in the mixture are retained on the column while the remainder are eluted. The recovery improvement in the purification of 3 compared to the conventional method is shown in Table X. Compared to recovery of ca. 40% by conventional methods, recovery of 3 by the picric acid column was 70 to 80% depending on the amount of 3 initially in the mixture.

The technique was extended to hydrogenation products of pyrene, benzanthracene, and chrysene which resulted in the isolation of 30a, 30b, 32, 34a, and 39a.

The method is most useful for separation of gross mixtures. It is not effective in removal of small impurities (<4-5%), although some improvement is seen. Usually impurities in low concentration can be removed by the conventional techniques of crystallization or conventional picrate formation.

TABLE X
SEPARATION OF ANTHRACENE HYDROGENATION PRODUCTS
BY PICRIC ACID COLUMN

Hydrocarbon Mixture ^a	g	Composition of Mixture					g of II Isolated	Percent Recovered II ^{a,b}	Molar Ratio of Picric Acid/II
		<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>			
A	75	2	30	57	11	0	17 ^c (24) ^d	39 ^c (58) ^d	1.5
B ^e	18	1	61	29	9	0	1 ^f	13 ^f	1.5
C ^g	34	0	4	82	13	1	11	40	1.5
D ^g	23	0	6	73	19	2	8(19) ^h	49(69) ^h	---
E	160	7	59	30	4	0	40 ⁱ	79 ⁱ	5.0
F	60	0	9	83	3	5	41 ^j	78 ^j	4.0

^aThe composition of mixtures and purity of recovered II were determined by GC studies using a Hewlett-Packard 5750 instrument fitted with a hydrogen-flame detector and a 0.25-in. x 6-ft. copper tube containing 1.5% OV-17 + 2% QF 1 coated on 80-100 mesh Gas-Chrom Q.

^bPurity of II was 99% except as noted.

^cPicrate formation, filtration and one recrystallization.

^dTotal of 3 obtained through processing mother liquor as well (cf. mixture B).

^eFiltrate of cropped picrate from A.

^fHydrocarbon 3 was contaminated with 15% of 2

^gMixture C was first processed with picric acid and the mother liquor provided mixture D, which in turn was freed of ethanol and passed through a picric acid column using isohexane solvent.

^hThe additional yield resulted from passing mixture D through a picric acid column.

ⁱMixture E was first processed with the picric acid column to separate 1 and 3 from 2, 4 and 5. Once 2, 4, and 5 had been eluted, 1 and 3 were removed from the column by continuous elution with isohexane. The solvent was removed and the picrate was reformed to allow removal of some 2.

^jMixture F yielded 78% of 3 in 99% through use of the column alone.

Improvement in the technology of preparative liquid chromatography shows potential in simplification of hydrocarbon separations.⁸⁵ The ability to perform large scale separations of these mixtures should make hydrogenation the preferred synthetic method for hydroaromatic hydrocarbons.

CHAPTER VII

EXPERIMENTAL

Desulfurization of Anthracene (1), Phenanthrene (19), Pyrene (31), and Chrysene (36). Hydrocarbons 1, 19, 31, and 36 were desulfurized with Raney nickel catalyst prepared by a simplified procedure,³⁷ and used within 24 to 48 hours after preparation. The hydrocarbon and Raney nickel catalyst were refluxed for 4 to 8 hours in an appropriate solvent,⁸⁶ (ethyl acetate, ethanol, or toluene), then allowed to cool overnight. The mixture was transferred under N₂ to a Soxhlet extractor,⁸⁷ and the hydrocarbon was extracted through a Dicalite⁸⁸ bed. Extraction often required several days. Upon completion the solution was cooled and the crystallized hydrocarbon was filtered. The filtrate was concentrated to obtain a second crop. The first two fractions were the only fractions hydrogenated.

General Hydrogenation Procedure. Hydrogenations at 810 mmHg (*ca.* 1 psig) were performed in a glass apparatus modified to allow hydrogenation in refluxing solvent and to provide for recycling of hydrogen into the reaction flask.³¹ Catalyst:substrate ratios of 1:10 were used for 1-30 g runs and 1:20 ratios were used for larger runs. The recycling hydrogen (*ca.* 600 ml/min) reduced the solvent boiling point to 90-115°. This effect was less in a larger flask and the reflux temperature rose accordingly. The increase in the reflux temperature did not influence the yield. Hydrogenations at 10 to 75 psig were done in a

Parr shaker⁸⁹ equipped with a sampling valve.⁹⁰ The shaker was heated to 60°C with three infrared heat lamps. In all cases the reactions were sampled periodically and the samples were analyzed by GC to determine when the maximum yield of the desired product was attained. The reaction mixture was filtered and solvent (HOAc) was removed by rotary evaporation. Remaining traces of HOAc were removed by washing an ether solution of the reaction mixture, first with a saturated NaHCO₃ solution, and then with water. The ether layer was dried (MgSO₄), filtered, and concentrated.

1,2,3,4-Tetrahydroanthracene (3). Anthracene (1), (34 g) was hydrogenated at 810 mm Hg and 115°C in refluxing HOAc with 1.5 g of 5% Rh/alumina for 36 hours. The reaction mixture was shown to contain 1% 1, 12% 2, 82% 3, and 4% 4a by GC analysis.³⁶ Isolation of 3 was attained by chromatography on a picric acid column,³⁸ as described in the following section to give 21g (60%) of 3.

Hydrogenation of 1 (180 g) at 50 psig, 60°C in 1.5 L HOAc in the presence of 9 g of 5% Rh/alumina for 9 hours gave 31% 3, 59% 4a, and 6.7% 5.³⁶ Isolation of 3 by picric acid column gave 40 g (22%) of 3. Additional runs at 15 to 30 psig, 60°C in HOAc typically gave 70-80% 3 by GC,³⁶ and separation by picric acid column gave *ca.* 60% overall yield of 3.

Preparation and Use of the Picric Acid Column. The column is prepared by packing picric acid into a previously described Soxhlet apparatus.⁸⁴ Packing consists of light tamping⁹¹ of the picric acid⁹² to avoid channeling. Optimum packing density has been found to be *ca.* 1 g/cc. The hydrocarbon mixture is then added to the column and elution with isohexane is begun. A molar ratio of picric acid to

picrate forming component of from 5 to 10:1 ordinarily gives good separation on one pass.

During migration of hydrocarbons through the column, picrate formation was observed by a color change of the column from yellow to orange or red. Fractions were taken when the orange band came to within 1 or 2 cm from the bottom of the column. Elution was then continued until the picrated compound was removed.

The hydrogenated anthracene mixture was placed in a Soxhlet apparatus containing a column of picric acid (15 cm) placed above basic alumina (4 cm), and the mixture was then eluted with isohexane. If removal of 2, 4, or 5 was incomplete as shown by GC,³⁶ the solution was again passed through the column. This process usually gave a fraction containing less than 1% of 2, 4, or 5. Yields from this process were from 68 to 84% (average *ca.* 80%), depending on column-packing density and amount of 3 to be removed. Isohexane was removed by rotary evaporation.

Analogous separation of the hydrogenated products of pyrene, benz-[a]anthracene, and chrysene was also achieved. Separation of 32 from 33, of 34a from 35a and 35b, 30a from 27, 28a, and 29, and 39a from 36, 37 and 38 was obtained using this technique.

Removal of Anthracene (1) with Maleic Anhydride and Final Purification of 1,2,3,4-Tetrahydroanthracene (3). The fraction containing 1 and 3 was refluxed for 2 hr with maleic anhydride in toluene using a 10:1 molar ratio of maleic anhydride:1. The toluene was removed by rotary evaporation and the reaction mixture was extracted through basic alumina with isohexane. The extracted product crystallized from the isohexane and was then filtered to give 3.

Mixtures containing more than 1% of 1 usually required two treatments with maleic anhydride to give 3 containing less than .01% of 1. Yields for this step usually exceeded 90%. (A 114-g sample of 3 containing 0.5% of 1 yielded 106 g of 3 containing less than 0.01% of 1. This purification scheme gave 3 in 99.95% purity in about 74% yield. Overall yield of 99.95% pure 3 was 59%.

A final recrystallization from isohexane yielded 3 at 99.99% purity as determined by GC analysis.³⁶ Kugelrohr distillation (102-108°C, 0.2 mm) of purified 3 to separate it from any particulate matter or trapped solvent gave 3, (mp 97.5-99° uncorrected), in 99.98% purity by GC³⁶ (lit.⁴⁹ 98-100°); picrate, mp 113-114°C uncorrected (lit.⁴⁹ 109-113°C). Distillation of 3 caused some conversion (trace) to 1.

Mass spectrum (70 eV) m/e (rel intensity) 182 (M^+ , 100), 181 (81), 165 (51), 154 (100), 153 (69), 152 (68), 141 (82), 115 (48); ¹H NMR (CCl₄) δ 7.59-7.48 (m, 2, ArH), 7.34 (s, 2, ArH), 7.26-7.15 (m, 2, ArH), 3.00-2.74 (m, 4, ArCH₂), 1.92-1.70 (m, 4, ArCH₂CH₂).

1,2,3,4,5,6,7,8-Octahydroanthracene (4a). The first fractions from the isolation of 3 by picric acid column³⁸ were combined to give 160 g of a 30:70 mixture of 3 and 4a.³⁶ This mixture was hydrogenated for 24 hours at 30 psig and 60°C in HOAc with 8 g of 5% Rh/alumina to give a 95% yield of 4a.³⁶ The crude product was recrystallized from 80:20 methanol:isopropyl alcohol and then from isohexane to give 80 g (50%) of 4a. mp 71-72°C (lit.⁹² 70.5-71°C); ¹H NMR (CCl₄) δ 6.60 (s, ArH, 2), 2.80-2.50 (m, ArCH₂, 8), 1.90-1.64 (m, ArCH₂CH₂, 8); mass spectrum (70 eV) m/e (rel intensity) 186 (M^+ , 100), 158 (74), 145 (34), 129 (29), 128 (28), 28 (38).

1,2,3,4,5,6,7,8-Octahydrophenanthrene (22a) and 1,2,3,4,4a,9,10,10a-Octahydrophenanthrene (22b). Two hundred grams of phenanthrene (19) was hydrogenated in the presence of 8 g of 5% Pd/C in 1.5 L HOAc, at 30 psig and 60°C for 24 hours. The crude product (195 g) contained³⁶ 56% 22a, 41% 22b, and 3% 23. Distillation (0.15 mm Hg) of the product mixture through a 160 mm x 18 mm diameter column packed with 1/4 in. perforated stainless steel saddles, yielded 63.4 g (30%) of 22b, (95% pure)³⁶ in the 72-78°C fraction. The third fraction (82°C) yielded 91 g (46%) 22a, (98% pure).³⁶ Further purification of 22a and 22b was attained by distillation on a Nestor Faust spinning band distillation unit to give 22a in 99.98% purity.³⁶ and 22b, (99% pure).³⁶ An authentic sample of 22b was coinjected with the hydrogenation sample for identification by GC.

22a bp 82°C at 0.15 mm Hg; ¹H NMR (CCl₄) δ 6.63 (s, ArH, 2) 2.63 (t, J = 2 Hz, ArCH₂, 4), 2.44 (t, J = 3 Hz, ArCH₂, 4) 1.90-1.52 (m, ArCH₂CH₂, 8); mass spectrum (70 eV) m/e (rel intensity) 186 (M⁺, 100), 158 (87), 145 (45), 143 (39), 128 (39), 127 (29), 44 (32), 28 (33).

22b bp 80°C at 0.65 mm Hg; ¹H NMR (CCl₄) δ 6.92 (s, ArH, 4), 2.90-2.50 (m, ArCH₂, 3), 2.14-1.78 (m, -CH₂, 2), 1.78-1.20 (m, -CH, 9), mass spectrum (70 eV), m/e (rel intensity) 186 (M⁺, 100), 143 (76), 129 (84), 128 (40), 43 (44), 29 (60).

Perhydrophenanthrene (23). Phenanthrene (250 g) was hydrogenated in the presence of 8 g of 5% Pd/C in 1.5 L HOAc at 30 psig for 24 hours. A sample showed the reaction mixture to contain,³⁶ 40% 22a, 35% 22b, 4% 21, and 3% 23. The hydrogen pressure was increased to 75 psig and the reaction mixture was continued for another 72 hours. The reaction mixture was worked up as previously described (GC analysis,³⁶ 75% 23,

23% 22a, 3% 22b). Distillation at 0.25 mm Hg, 60–90°C through the previously described column yielded 142 g (57%) 23, and 59 g (24%) (90–92°C) of 22a. Analysis of 23 by GC³⁶ showed 6 isomers present plus a small amount of 22b.

5,6,7,8-Tetrahydro-1-Naphthalenepropionic Acid (26a) and 1,2,3,4-Tetrahydro-1-Naphthalenepropionic Acid (26b). Hydrogenation of 2 g of 1-naphthyl acrylic acid (2 g) with 0.5 g of 5% Pd/C at 810 mm Hg in refluxing HOAc for 4 hours gave a 55:45 ratio³⁶ of 26a to 26b. The acids were treated with diazomethane and analyzed as the methylesters.⁸² Acids 26a and 26b were isolated by fractional recrystallization from isohexane to give 1.0 g of 26a (50%) and 0.4 g of 26b (25%). The reaction was repeated using 0.5 g of 5% Rh/alumina, and hydrogenation for 10 hours. The product mixture contained a 72:28 ratio of 26a to 26b.⁸² Crystallization from isohexane gave 1 g (50%) of 26a.

26a mp 133–136°C (lit.⁹⁴ 136); ¹H NMR (DCCl₃) δ 10.65 (broad s, CO₂H, 1), 8.2–7.9 (m, ArH, 3), 3.1–2.6 (m, ArCH₂, α to CO₂H), 2.0–1.7 (m, ArCH₂CH₂, 4); mass spectrum (70 eV) m/e (rel intensity) 204 (M⁺, 29), 144 (33), 131 (100), 129 (29), 125 (18), 91 (21).

26b mp 75–79°C (lit.⁹⁴ 71–72); ¹H NMR (CCl₄) δ 11.88 (broad s, CO₂H), 1) 7.2–6.8 (m, ArH, 4), 3.0–2.6 (m, ArCH₂, 3), 2.5–2.3 (t, J = 4 Hz, CH₂CO₂H, 2), 2.15–1.56 (m, -CH₂, 6); mass spectrum (70 eV) m/e (rel intensity) 204 (M⁺, 23), 144 (57), 13 (100), 129 (25), 115 (15), 91 (25).

5,6-Dihydrobenz[a]anthracene (28a). Benz[a]anthracene (27), (11.4 g) was hydrogenated in the presence of 1 g of 5% Pd/C in refluxing HOAc for 3 hours at 810 mm Hg. The crude product contained 92% 28a, 7% 29, and 1% hexahydrobenzanthracene 30a or 30b as

determined by GC⁸² and field ionization mass spectra (m/e M⁺ 230, 232, 234, respectively). Fractional recrystallization from isohexane gave 28a, 8.5 g (75%) 93% pure.⁸² Two more recrystallizations from isohexane gave 3.1 g (27%) of 28a in 99% purity.⁸² mp 97-99°C (lit.⁶¹ 96-96.5); ¹H NMR (CCl₄) δ 8.1 (s, ArH, 1), 7.96-7.56 (m, ArH, 4) 7.52-7.10 (m, ArH, 5), 3.2-2.8 (m, ArCH, 4); mass spectra (70 eV) m/e (rel intensity) 230 (M⁺, 100), 229 (69), 228 (40), 227 (10), 226 (14), 215 (12).

7,12-Dihydrobenz[a]anthracene (28b). Benz[a]anthracene (27), (10 g), was reacted with 1.5 g of Li metal in 300 ml glyme for 18 hours. Water (300 ml) was added to react the excess Li and the mixture was extracted with ether, and then was concentrated to give 10 g of viscous oil. The mixture contained 83% 28b, 3% 27, and 14% hexahydrobenz[a]anthracene (believed to be isomer 30b).⁸² The mixture was eluted through basic alumina with isohexane and two recrystallizations from isohexane yielded 1.5 g of 28b, 95% pure.⁸² mp 112.5-113°C (lit.⁶² 111-112); ¹H NMR (CCl₄) δ 8.12-7.02 (m, ArH, 10), 4.35 (t, J = 1 Hz, ArCH₂, 2), 4.08 (t, J = 2 Hz, ArCH₂, 2); mass spectrum (70 eV) m/e (rel intensity) 230 (M⁺, 93), 229 (100), 228 (87), 226 (32), 215 (16), 114 (24), 101 (15).

8,9,10,11-Tetrahydrobenz[a]anthracene (29). Benz[a]anthracene (27), (12 g) was hydrogenated in the presence of 1 g of 5% Rh/alumina, at a hydrogen pressure of 810 mm Hg in refluxing HOAc for 6 hours. The reaction mixture contained 85% 29, 8% hexahydrobenz[a]anthracene (30a or 30b), and 7% other products as determined by GC and field ionization mass spectrometry (m/e 232, 234, 230, 236, respectively). The reaction mixture was eluted through basic alumina with isohexane and fractionally recrystallized from isohexane to give 6.1 g (50%) of 29, 99% pure by

GC,⁹⁴ mp 88.5–90°C (lit.⁶⁴ 88.5–89.5); ¹H NMR (CCl₄) δ 8.56–8.42 (m, ArH, 1), 8.20 (s, ArH, 1) 7.80–7.64 (m, ArH, 1), 7.55–7.35 (m, ArH, 5), 2.96–2.90 (m, ArCH₂, 4), 2.0–1.75 (m, ArCH₂CH₂, 4); mass spectrum (70 eV) m/e (rel intensity) 232 (M⁺ 100), 231 (24), 215 (20), 205 (36), 191 (15), 101 (19).

5,6,8,9,10,11-Hexahydrobenz[a]anthracene (30a). Two grams of 28a were hydrogenated in the presence of .5 g of 5% Rh/alumina at a hydrogen pressure of 810 mm Hg in refluxing HOAc for 16 hours. The reaction mixture contained 81% hexahydro, 11% dihydro, 6% tetrahydro, and 3% octahydrobenz[a]anthracene as determined by GC and field ionization mass spectrometry (m/e 234, 230, 232, 236, respectively). The reaction mixture was passed through a picric acid column with isohexane to yield 0.5 g (25%) of a colorless oil,⁶⁵ 92% pure by GC.⁸² ¹H NMR (CCl₄) 7.6–7.5 (m, ArH, 1), 7.27 (s, ArH, 1), 7.2–7.0 (m, ArH, 3), 6.73 (s, ArH, 1), 2.9–2.5 (m, ArCH₂, 8), 1.9–1.6 (m, ArCH₂CH₂, 4); mass spectrum (70 eV) m/e (rel intensity) 234 (M⁺ 100), 233 (17), 232 (17), 228 (17), 206 (28), 191 (35).

The reaction was repeated using the same conditions with 1.3 g of 29 as the starting material and using 5% Pd/C. After 3 hours the reaction mixture contained 72% 30a, 12% 29 as determined by GC,⁸² and mass spectrometry. Coinjection of the two reaction mixtures gave only one major peak, corresponding to 30a.

1,2,3,4,7,12-Hexahydrobenz[a]anthracene (30b). One gram of 28b was hydrogenated for 16 hours at 810 mm Hg in refluxing HOAc with .50 g of 5% Rh/alumina. GC analysis showed the product mixture to contain 75% hexahydrobenz[a]anthracene, 14% 28b, 3% 29, and 10% further hydrogenated products. The reaction mixture was passed through a

picric acid column,³⁸ a silica gel column, and crystallized from iso-hexane-absolute ethanol to give 0.15 g of 30b mp 65-67 (lit.⁷⁴ 69-71). Hydrocarbon 30b was also prepared by the method of Fieser and Hershberg⁶⁴ in 51% yield (mp 67-68.5). The melting point of a mixture of 30b from these two reactions showed no depression and their NMR spectra were identical. ¹H NMR CCl₄ δ 7.4-6.7 (m, ArH, 6), 3.82 (s, ArCH₂, 2), 3.75 (s, ArCH₂, 2), 2.86-2.6 (m, ArCH₂, 4), 2.0-1.6 (m, -CH₂-, 4); mass spectrum (70 eV) m/e (rel intensity) 234 (M⁺, 100), 233 (33), 230 (26), 205 (27), 192 (28), 191 (66).

4,5-Dihydropyrene (32). Pyrene (31) (150 g) was hydrogenated in 1.5 L HOAc in the presence of 8 g of 5% Pd/C for 14 hours at 60 psig and 60°C. The crude product contained 4% 31, 42% 32, 28% 33, and 18% 34a.³⁶ Four passes through a picric acid column taking the second fraction each time yielded 29 g of 32 (19%), which was 94% pure by GC³⁶ analysis (mp 129.5-131°C). Further purification was obtained by picrate formation and recrystallization mp 131-132 (lit.⁶⁹ 132); ¹H NMR (CCl₄) δ 7.64-7.16 (m, ArH, 8), 3.17 (s, ArCH₂, 4); mass spectrum (70 eV) m/e (rel intensity) 204 (M⁺, 99), 203 (100), 202 (85), 101 (37), 99 (16), 88 (11).

4,5,9,10-Tetrahydropyrene (33). Pyrene (31) (220 g) was hydrogenated with 15 g 5% Pd/C in 1.5 L HOAc of 45 psig and 60°C for 24 hours. Two runs were performed giving a product mixture shown by GC³⁶ to contain 9% 32, 61% 33, 13% 34a, and 7% unknown (believed to be 34b). The crude product was recrystallized twice from isohexane and passed through a picric acid column to yield 110 g (49%) of 33, (95% pure).³⁶ Further purification was attained by hydrogenation of the mixture (100 g) using 8 g of 5% Pd/C in EtOAc at 60 psig and 60°C for

24 hours. Analysis of the product by GC³⁶ showed 1.3% 32, 74% 33, 13% 34a, and 1% 35b. Recrystallization from EtOAc gave 30 g of 33 in 99% purity³⁶ mp 135-136°C (lit.⁶⁸ 138); ¹H NMR (CCl₄) δ 6.92 (s, ArH, 6), 2.78 (s, ArCH₂, 8); mass spectrum (70 eV) m/e (rel intensity) 206 (M⁺, 100), 205 (59), 189 (12), 101 (16), 28 (15).

1,2,3,6,7,8-Hexahydropyrene (34a). Pyrene (31), (100 g) was hydrogenated using 8 g of 5% Pd/C in 1.5 L HOAc at 60 psig and 60°C for 45 hours. Two runs were carried out. The reaction mixtures contained³⁶ 27% 34a, 41% 35a, 24% 35b, and 6% 33. Separation of 34a was achieved via picric acid column³⁸ (250 g picric acid column, 15 cm x 4.5 cm diameter, 1 g/cc packing density) to yield 42 g (21%) of 34a which was found to be 98% pure by GC.³⁶ Further purification of 34a was obtained by recrystallization from isohexane and then sublimation. mp 132-133.5°C (lit.⁷³ 131-132); ¹H NMR (CCl₄) δ 6.83 (s, ArH, 4), 3.12-2.94 (t, J = 3 Hz, ArCH₂, 8), 2.16-1.84 (m, ArCH₂CH₂, 4); mass spectrum (70 eV) m/e (rel intensity) 208 (M⁺, 100), 207 (23), 202 (15), 179 (20), 165 (29), 89 (16).

1,2,3,3a,4,5,9,10,10a,10b-Decahydropyrene (35a) and 1,2,3,3a,4,5-5a,6,7,8-Decahydropyrene (35b). Pyrene (31) (60 g) was hydrogenated in the presence of 5 g of 5% Pd/C in 1 L HOAc at 75 psig and 60°C for 50 hours. The reaction mixture contained 67% 35b, 18% 35a, and 15% perhydropyrenes.³⁶ The mixture was filtered and solvent was removed. Upon standing white needles crystallized from the liquid product, the crystals were filtered and recrystallized from isohexane to give 5 g (12%) of 35a mp 124-126°C (lit.⁷³ 129) ¹H NMR (CCl₄) δ 6.92-6.64 (m, ArH, 3), 2.92-2.60 (m, ArCH₂, 5), 2.14-1.60 (m, -CH₂-, 7), 1.54-1.20 (m, -CH₂-, 5), mass spectrum (70 eV) m/e (rel intensity) 212 (M⁺, 100),

211 (30), 184 (92), 169 (18), 156 (15), 143 (15), 141 (31),
128 (18).

The remaining mixture was distilled at 0.15 mm Hg 120°C (lit.⁷³
60.2-123) through a 8.0 cm x 1.0 cm Vigereaux column to give 25 g
(40%) of 35b. GC analysis showed 35b to be 90% pure.³⁶

Hydrogenation of 34a (2.5 g) in the presence of 0.5 g of 5%
Pd/C in HOAc at 65 psig and 60°C for 24 hours gave 35a in 57% yield.³⁶
The ratio of 35a to 35b was 31:1. The reaction mixture was eluted
through a 20 cm x 1 cm silica gel column with isohexane to give 0.6 g
(24%) of 35b, a colorless oil. mp 6-9°C (lit.⁷³ 11°C); ¹H NMR (CCl₄)
δ 6.65 (s, ArH, 2), 2.80-2.20 (m, ArCH₂, 6), 2.10-0.80 (m, -CH₂, 7);
mass spectrum (70 eV) m/e (rel intensity) 212 (M⁺, 100) 184 (90),
141 (34), 128 (28), 115 (22).

1,2,3,4,5,6-Hexahydrochrysene (39a). Chrysene (36) (3 g x 3 runs)
was hydrogenated at 75 psig, 60°C in 300 ml HOAc for 72 hours with 0.3 g
of 5% Pd/C. The reaction was followed by GC⁹⁵ and mass spectrometry.³⁹
The final combined product mixtures (8 g) showed 76% 39, 12% 37, 1%
38, and 11% further hydrogenated products.⁹⁵ The mixture was eluted
through a picric acid column with isohexane.³⁸ Three crystallizations of
the first fraction from the column in isohexane gave 3.1 g (38%) of
39 in 94% purity.⁹⁵ mp 118-121°C (lit.⁷⁶ 110-110.5); ¹H NMR (CCl₄) δ
7.8-6.8 (m, ArH, 6), 2.9-2.5 (m, ArCH₂, 8), 2.0-1.6 (m, -CH₂-, 4); mass
spectrum (70 eV) m/e (rel intensity) 234 (M⁺, 100), 232 (10), 230 (16),
215 (7), 202 (10), 191 (34), 178 (11).

PART III

SYNTHESIS OF HIGH PURITY EICOSANE

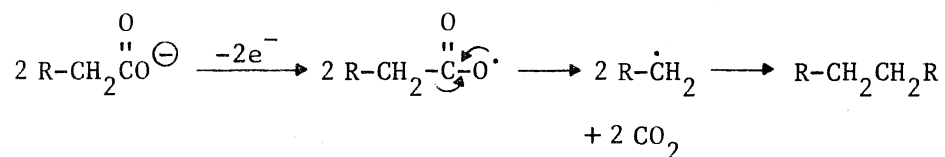
CHAPTER VIII

HISTORICAL AND INTRODUCTION

The anodic oxidation of acetate ions at smooth platinum electrodes described by Kolbe in 1849,⁹⁶ was the first study of an electrochemical process which has found general use in organic synthesis. The Kolbe electrolysis has been systematically studied for over a hundred years and many examples of the utility of the reaction and studies of the mechanisms are available. Two of the most recent and most complete reviews on the Kolbe and other electroorganic reactions have been published by Baizer⁹⁷ and Weinberg.⁹⁸

Initially the major use of the Kolbe reaction was the synthesis of long-chain hydrocarbons,⁹⁹ dicarboxylic acids,^{100a} (the Brown, Walker reaction),^{100b} and cross coupled products (fatty acid synthesis)¹⁰¹ of half esters and monocarboxylic acids.

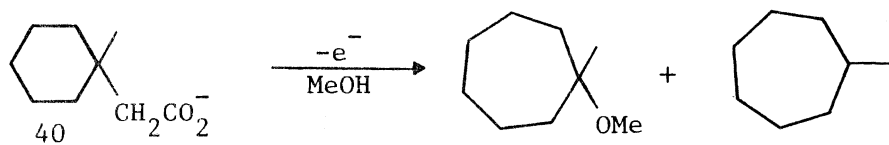
The mechanism of the Kolbe was initially believed to proceed by a one electron oxidation of the carboxylate ion to give the acyloxy radical; followed by decarboxylation to the alkyl radical which couples to give the dimer.



Side products such as alkenes and alkanes found in the reaction were consistent with a free radical mechanism. However, other side

products; ethers, alcohols, esters and rearrangement products were not satisfactorily explained. Changes in reaction parameters and reactants gave large changes in side products. In aqueous alkaline solutions the formation of alcohols predominates (the Hofer-Moest reaction).¹⁰²

These side products and changes in product ratios with different reaction conditions is explained by the presence of a competing process. Walling¹⁰³ proposed a competing two electron oxidation to give a carbonium ion intermediate which would explain the observed byproducts. This proposal was supported by Muhs¹⁰⁴ in the electrolysis of 1-methylcyclohexane acetic acid (40) which gave products matching those from reactions known to proceed by carbonium ion intermediates. The observed rearrangements were attributed to two electron oxidation.



Utley states⁹⁸ that "there are no examples of rearrangements by alkyl radicals and the observed rearrangements are diagnostic of the carbonium ion process." The two competing processes and the resulting products are outlined in Figure 22.⁹⁸

The predominance of the radical or carbonium ion process is dependent upon reaction conditions and the reactant. Compounds which form stable carbonium ions will follow that pathway and will not generally couple. These include α substituted carboxylic acids,

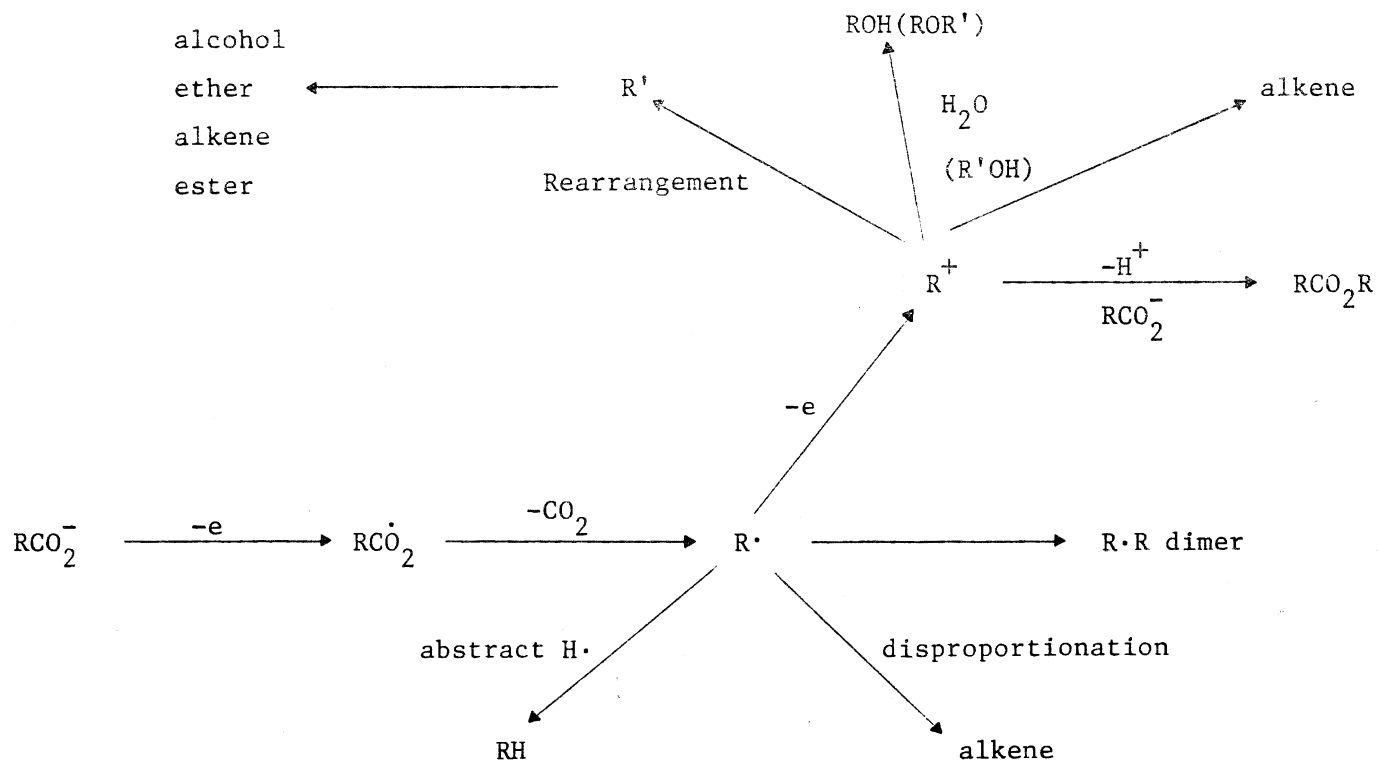


Figure 22. Anodic Oxidation of Carboxylates⁹⁸

α,β unsaturated carboxylates, aromatic acids, and dicarboxylic acids. Later work using nonaqueous solvents such as dimethyl formamide has modified earlier views somewhat. The yields of products from the radical process with α substituted acids such as phenyl and diphenyl acetic and propionic acids¹⁰⁵ has been enhanced through use of nonaqueous solvents such as dimethyl formamide. Dicarboxylic acids have been coupled by using the half ester as starting material.^{100a} The coupling of benzoate ion in pyridine to yield biphenyl has been reported.¹⁰⁶

The influence of experimental factors on the Kolbe has been summarized by Ebersson⁹⁷ and is presented in Table XI.

TABLE XI
INFLUENCE OF EXPERIMENTAL FACTORS ON THE MECHANISM
OF THE KOLBE REACTION⁹⁷

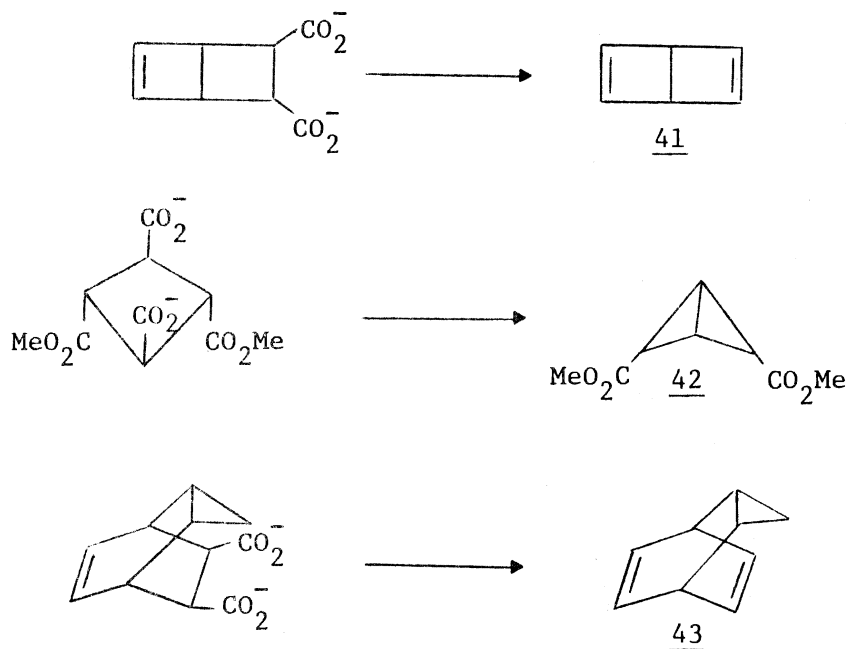
Formation of R· Favored by	Formation of R ⁺ Favored by
High current density	Low current density
Smooth Pt anode	C or PbO ₂ anode
Slightly acidic or neutral solution	alkaline solution
Nonaqueous solvent (methanol or DMF)	Water or water-pyridine
Low (room) temperature	Temperature effect not established
	Addition of anions ClO ₄ ⁻ , HCO ₃ ⁻ , SO ₄ ⁻ , F ⁻

Increase in temperature does not normally have a large effect in nonaqueous solvents. One well known exception in which large temperature effects were observed is in the electrolysis of 10-bromo undecanoic acid.¹⁰⁷ At 50°C in MeOH, 1,20-dibromo eicosane was the major product, but at 65°C the methyl ester predominated.

Certain practical limitations on the use of nonaqueous solvents exist. The solubility of inorganic salts is limited in these solvents and electrolytes such as the tetraalkyl ammonium salts may be required. The oxidation potential of nonaqueous solvents may limit their use. Dimethyl formamide for example is a widely used solvent but its oxidation potential limits its utility in anodic reactions.

The presence of divalent cations such as Pb^{+2} , Mn^{+2} , Fe^{+2} and Co^{+2} inhibit the radical process and promote the carbonium ion process. The interference from these ions is due to the competition with carboxylate ions for the electrode surface. The anode is eventually coated with metal oxides which will not support the radical process. Alkali and alkaline earth cations do not affect the Kolbe reaction.

The carbonium ion process, although undesirable in coupling reactions, has shown synthetic utility. The Kolbe electrolysis offers a mild method of bis-decarboxylation of 1,2 diacids. This method offers an alternative to decarboxylation with lead tetraacetate (the Grob degradation). Bis-decarboxylation has been used to synthesize Dewar benzene (41),^{108a} to make cyclopropane systems (42)^{108b} and to form double bonds in systems containing double bonds or strained rings (43).^{108c} Covey¹⁰⁹ has synthesized trans-stillene from meso and dl-2,3-diphenyl succinic acid.

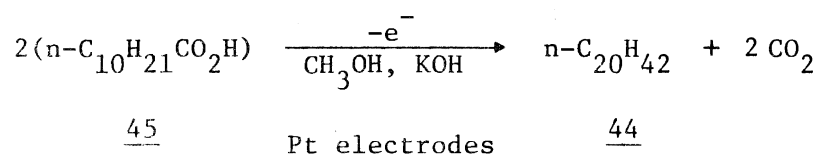


This laboratory was engaged by the Harry Diamond Laboratories¹¹⁰ to synthesize ultrapure eicosane ($n\text{-C}_{20}\text{H}_{42}$) (44) for crystallographic research. The Kolbe electrolysis, because of the lack of branched chain side products, was the method chosen for the synthesis.

CHAPTER IX

RESULTS AND DISCUSSION

The goal was to synthesize high purity (99.99⁺%) eicosane n-C₂₀H₄₂ (44) by electrolysis of the salt of undecanoic acid (45) as shown below.



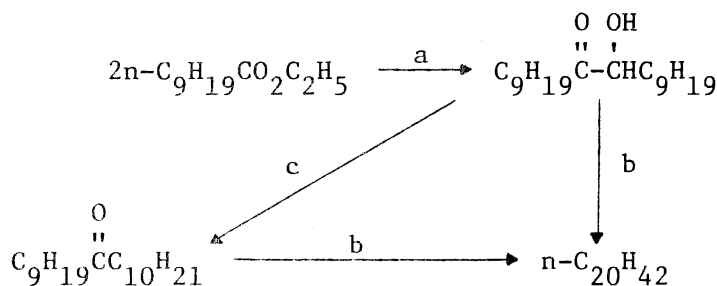
The critical part of this synthesis is obtaining rigorously pure 45.¹¹¹ Long chain fatty acids of odd carbon number were found to contain more impurities and to be much more difficult to purify than those acids containing even numbers of carbon atoms. The acids of even carbon number, (C₈, C₁₀, C₁₂, C_{2N}) are found in nature and appear to be much less branched than acids of odd carbon number which are synthesized. Impurities removed from the even carbon number acids appear to be acids of carbon numbers 2N-1 or 2N+1, whereas the odd carbon acids contain this type of impurity plus branched isomers.

Purification techniques tried on 45 were recrystallization, urea clathrate,¹¹² preparative gas chromatography and repeated fractional distillations.

Recrystallization removed some of the lower molecular weight impurities, but did not remove those which showed up by GC close to the

n-C₁₁ ethyl ester. These impurities were not removed by urea clathrate. This technique is supposed to remove branched chains by exclusion in the complex formation between urea and the linear acid. For this reason it is believed that the impurities encountered were isomers which contained methyl branches close (α or β) to the carboxyl group. The formation of urea clathrate with 3-methylundecanoic acid has been reported.^{112c} Preparative gas chromatography showed promise in trials with ethyl octanoate, but temperature limitations of the column packing prevented its use with longer chain esters. Repeated fractional distillation showed little promise until about the fourth distillation when decreases in impurities became significant. Although this method was tedious, it was the remaining alternative.

With the knowledge that the even carbon acids were more easily purified, n-ethyl decanoate (n(-C₉H₁₉CO₂C₂H₅)) was prepared and purified in an effort to make 44 through the acyloin condensation¹¹³ and reduction as shown below.



a) Na, toluene

b) NH₂NH₂, diethylene glycol

c) HOAc, Zn

The acyloin gave several side products which were not removed by recrystallization. Reduction gave an impure hydrocarbon, so the route was not investigated further.

The purification of 45 by distillation required a total 11 rounds of distillation. Two simple distillations were performed followed by 5 distillations through packed columns. The best fractions were forwarded to the next round while less satisfactory fractions were recycled to squeeze out more 45 of acceptable quality. The packed column distillations required 2 to 3 weeks each at 24 hours/day. Two spinning band distillations of the best fractions of the ethyl ester gave a product 99.9% pure by GC.¹¹⁶ The impurity was discovered upon making the methyl ester for GC analysis. This peak was hidden in the analysis of the ethyl ester. Two more distillations by spinning band on the methyl ester gave 45 99.99% pure by GC.¹¹⁶

Electrolysis of 45 gave 44 in 60% yield and GC analysis⁹⁴ showed no impurity.

CHAPTER X

EXPERIMENTAL

Description of the Kolbe Apparatus. The electrical circuit and the reaction chamber for the Kolbe electrolysis is shown in Figure 23. The circuit consists of a dc power source (P), variable resistor (R), volt meter (V), ammeter (A), two-way knife switch (D), simple knife switch (S) reactor cell (C) with platinum electrodes (E). The reactor cell consists of two parts held together by a flange (F). The top part has a sampling port (B) condenser (W) and vent to the hood (H). The lower part houses the electrodes (E) and the solution is stirred with a magnetic stirring bar (M). The reaction vessel was cooled with a water-ethylene glycol bath fed by a recirculating cooler (Blue M, Model PCC-4A).

Esterification of Undecanoic Acid (45). Undecanoic acid (6 M, 1114 g) was refluxed for 36 hours in 2 L of benzene with 18 g conc. H_2SO_4 and 600 ml 95% ethanol. Water was removed with a Dean-Stark azeotrope trap as described by Newman.¹¹⁴ The reaction was repeated and the reaction mixtures were combined. The mixture was neutralized with CaCO_3 , filtered, and the benzene was distilled off. The mixture was taken up in isohexane, washed with a saturated NaHCO_3 solution, washed with water, dried (MgSO_4), filtered, and the isohexane was removed. The mixture was distilled to give 2364 g (92%) of the ethyl ester. Ethyl undecanoate was purified by repeated distillations. Two

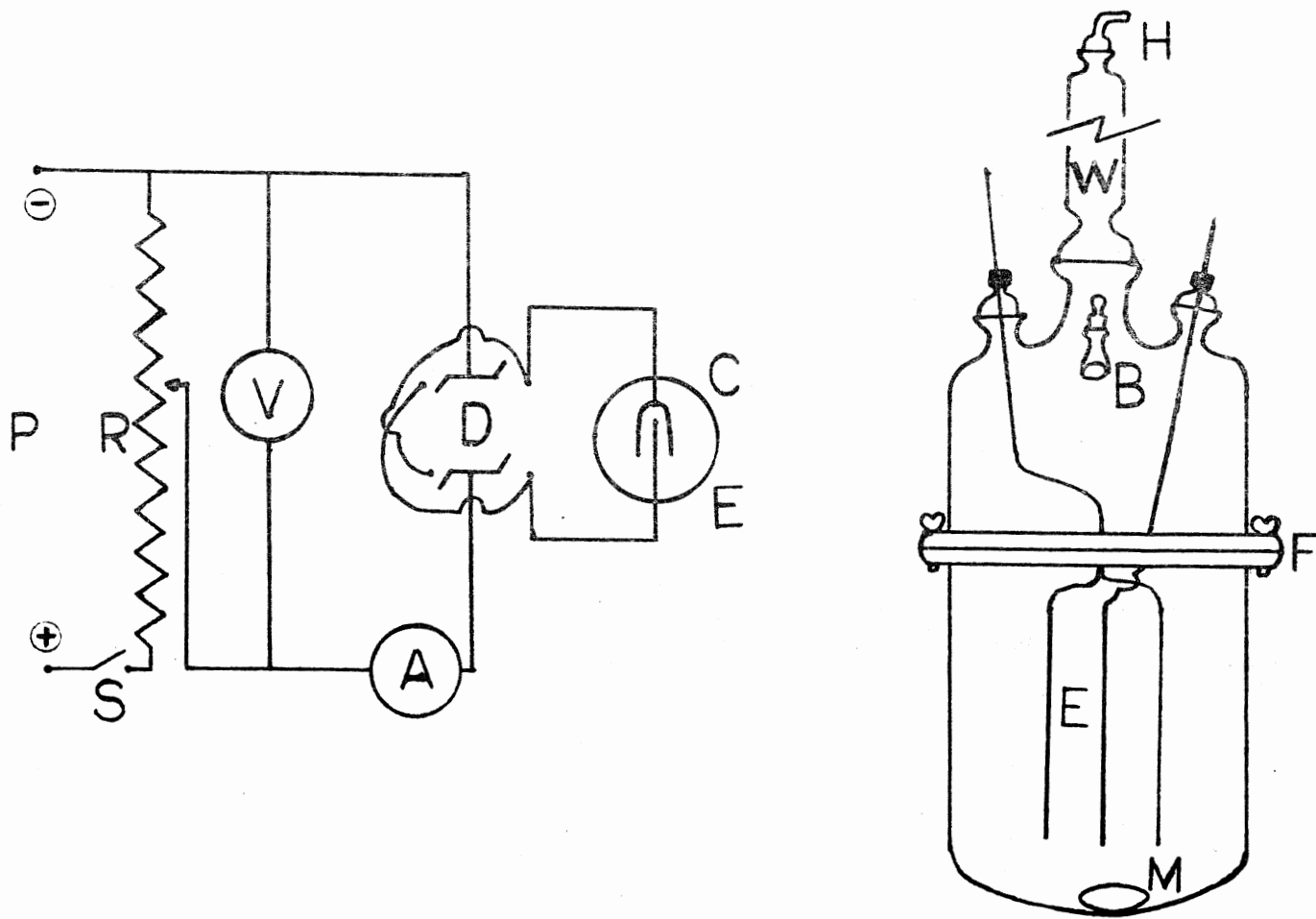


Figure 23. Electrical Circuit and Reaction Vessel for the Kolbe Electrolysis

distillations through columns packed with 1/4 in. x 1/4 in. stainless steel saddles (3 distillations through a 1 ft. x 1.5 in. diameter column, and 2 through a 3 ft. x 1.5 in. column) followed by two distillations through a Nester Faust spinning band unit were carried out.

Ethyl decanoate ($n\text{-C}_9\text{H}_{19}\text{CO}_2\text{C}_2\text{H}_5$) was similarly prepared in 86% yield.

Saponification of Ethyl Undecanoate. Ethyl undecanoate (163 g) was refluxed with 40 g NaOH in 1.2 L of water for 24 hours. The ethanol was distilled away from the reaction mixture. The remaining mixture was acidified with HCl, extracted with cyclohexane,¹¹⁵ dried (MgSO_4), filtered, and solvent was removed. Traces of solvent were removed under vacuum to give 142 g (100%) of undecanoic acid. Analysis by GC¹¹⁶ of the methyl ester showed an impurity of *ca.* 0.1%.

Methyl Undecanoate. Undecanoic acid (142 g) obtained as described above was refluxed for 30 hours with 3.6 g conc. H_2SO_4 in 500 ml MeOH. Adaptation of the procedure used for the ethyl ester gave 153 g (96.5%) of methyl undecanoate. This product was distilled twice using a Nester Faust spinning band distillation unit to give 99 g analyzed by GC as 99.99% pure. This ester was saponified as described for the ethyl ester to give 91 g of undecanoic acid.

Kolbe Electrolysis of Undecanoic Acid. Undecanoic acid (91 g) was dissolved in a solution of 500 ml absolute MeOH and 5.5 g KOH. The electrolysis was carried out at 35 volts and an average current of 6 amps for 18 hours. Temperature was held below 50°C and above 38°C. At a temperature of less than 38°C hydrocarbon precipitated and coated the electrodes. After 18 hours the reaction was stopped

and the mixture was allowed to cool. The hydrocarbon crystallized out and was filtered. The eicosane was dissolved in cyclohexane¹¹⁵ and washed alternately with conc. H_2SO_4 and distilled water until the H_2SO_4 layer did not become discolored when shaken with the cyclohexane solution. The cyclohexane layer was washed with water, bicarbonate solution and water, dried, filtered, and stripped of cyclohexane to give 43.5 g (63%) eicosane. The product showed a small impurity by GC,⁸² so it was distilled by Kugelrohr, recrystallized from absolute MeOH, and distilled again by Kugelrohr to give 40.9 g of eicosane which showed no impurity by GC.⁸² mp 37-38°C (lit.¹¹⁷ 36.8) mass spectrum (70 eV) m/e (rel intensity) 282 (M^+ , 100), 85 (42), 71 (64), 57 (100), 43 (84), 41 (38).

Acyloin Condensation of Ethyl Decanoate. In a dry system under N_2 , sodium metal (60 g) was added to 1.2 L of dry toluene and the mixture was refluxed. The sodium melted and was dispersed by a high speed stirrer. Ethyl decanoate (232 g) was added by dropping funnel over a period of 1 hour. The reaction was continued for 1/2 hour after the addition of the ester. Methanol was then added to destroy any remaining sodium. The reaction was cooled and water was added. The toluene layer was separated, washed twice with water, once with $NaHCO_3$ solution, and toluene was removed by rotary evaporation. The crude acyloin product (161 g, 89%) was recrystallized twice from isohexane to give 43 g which showed at least 7 other products by GC.⁸² Subsequent reduction by Wolf-Kishner reaction gave a hydrocarbon with several impurities.⁸²

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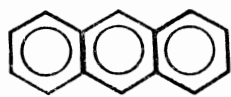
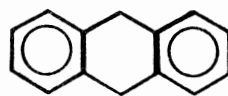
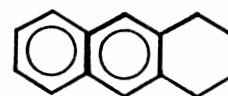
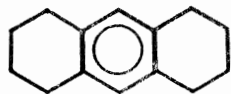
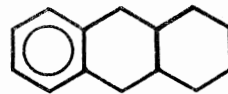
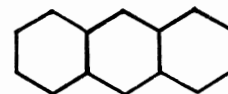
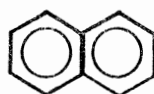
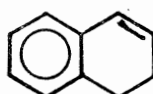
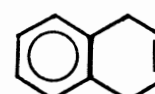
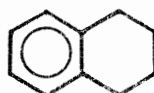
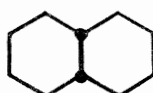
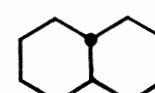
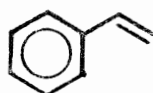
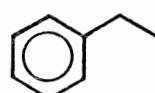
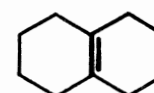
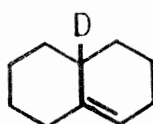
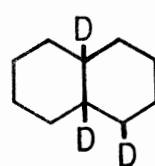
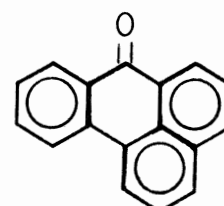
82. Analysis of the hydrogenation products of benz[a]anthracene, 1-naphthyl acrylic acid and analysis of Eicosane (44) were carried out on an 8 ft. x 1/4 in. copper tubing column containing 31 g 5% UCW 98/Chm. G. AW. DMSC treated at an oven temperature of 250°C.
83. (a) A. I. Vogel, "Practical Organic Chemistry", 3rd ed., John Wiley and Sons, New York, New York, 1966, p. 518; (b) Ref. 37a, p. 884; (c) H. Kessler and E. Mueller, J. Chrom., 24, 469 (1966); (d) D. M. Jewell, Anal. Chem., 47, 2048 (1975).
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85. A Waters Associates Prep LC System 500, preparative liquid chromatograph recently purchased, is presently being brought into use for purification of hydrocarbons.
86. Phenanthrene (19) was desulfurized in 95% ethanol, pyrene (31) in ethyl acetate as was 1, and chrysene (36) in toluene.
87. (a) C. E. Browne, W. L. Buchanan, and E. J. Eisenbraun, Chem. and Ind., 35, (1977); (b) This modification insures that a head of solvent will always be covering the Raney nickel. Dry, active Raney nickel is spontaneously combustible in air.
88. Dicalite is a tradename for a diatomaceous earth filter acid.
89. Parr hydrogenation apparatus Model 3921.
90. K. D. Cowan and E. J. Eisenbraun, Chem. and Ind., 415 (1976).
91. Excessive tamping will reduce flow to the point of blockage. Packing densities of from 0.9 to 1.1 g/cc were found to give efficient separations and acceptable flow rates.
92. A practical grade of picric acid containing 10-15% water was used. Lumps were broken to give a coarse grain but no effort was made to dry or grind the crystals, since anhydrous picric acid is explosive.
93. I. P. Tsukervanik and L. V. Bugrovia, Zhur. Obschchei Khim., 27, 889 (1957).
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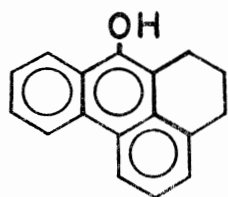
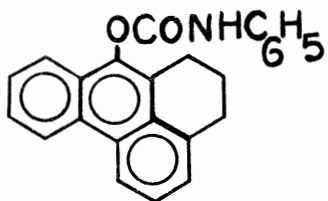
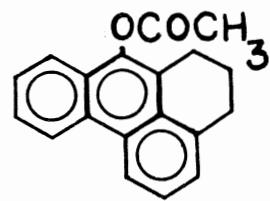
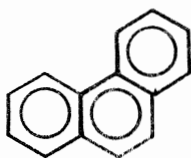
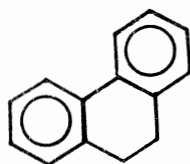
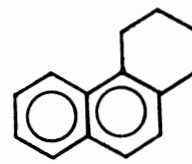
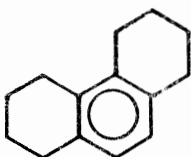
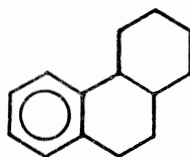
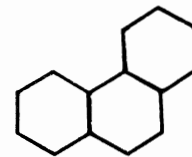
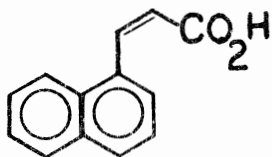
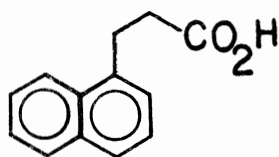
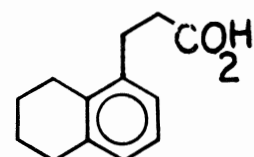
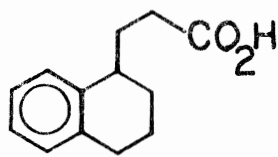
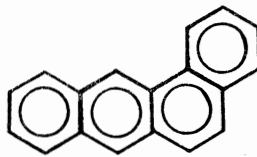
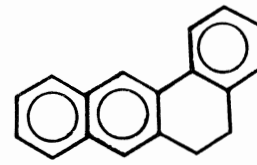
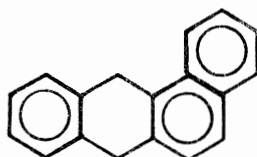
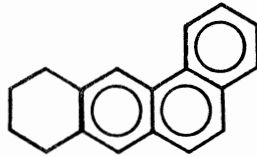
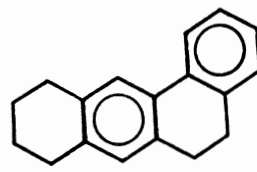
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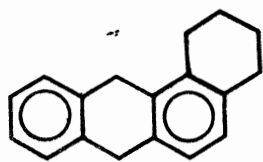
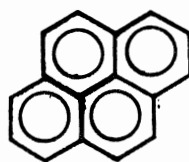
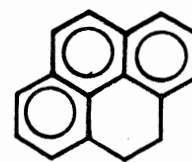
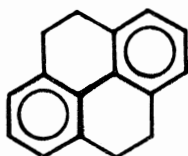
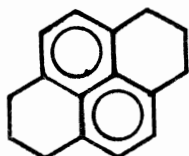
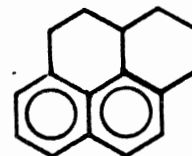
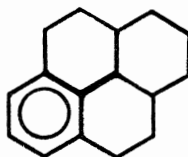
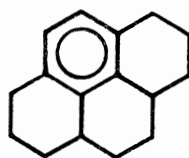
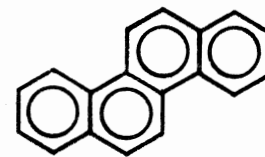
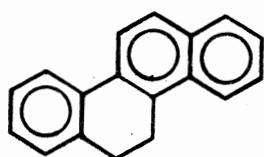
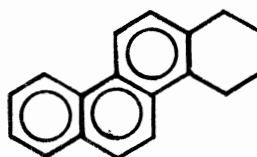
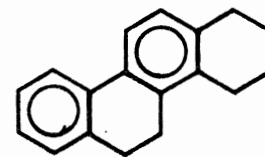
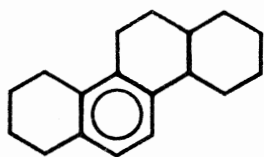
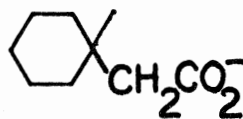
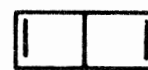
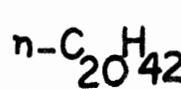
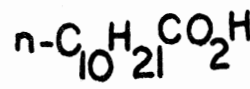
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MacMillan Company, New York, New York, 1972, p. 9-12.
115. Cyclohexane was treated by stirring with conc. H_2SO_4 for several
days to remove alkenes. The cyclohexane was then washed,
dried, and distilled.
116. Esters were analyzed on a 25% LAC 886/Chm.W column, 10 ft. x
1/4 in. copper tubing.
117. Chemical Rubber Co. Handbook of Chemistry and Physics, 52nd
Edition, 1971-1972.

APPENDIX

GLOSSARY OF STRUCTURES

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VITA

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Doctor of Philosophy

Thesis: I. CATALYST SELECTIVITY IN THE DEUTERATION OF ANTHRACENE
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II. HYDROGENATION OF POLYNUCLEAR AROMATIC HYDROCARBONS
III. SYNTHESIS OF HIGH PURITY EICOSANE

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