

- I. DISSOLVING METAL REDUCTION OF PYRENE
WITH SODIUM IN HIGH BOILING ALCOHOL
AND AMINE SOLVENTS
- II. SYNTHESIS OF 1-¹³C-NAPHTHALENE AND
4-¹³C-2,6-DIMETHYLNAPHTHALENE

By

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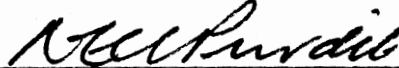


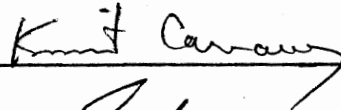
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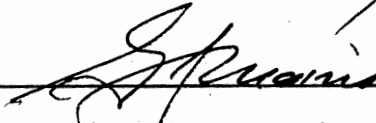
Thesis Approved:




Thesis Adviser









Dean of the Graduate College

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PART I

**DISSOLVING METAL REDUCTION OF PYRENE
WITH SODIUM IN HIGH BOILING ALCOHOL
AND AMINE SOLVENTS**

CHAPTER I

INTRODUCTION

Polynuclear aromatic (PNA) hydrocarbons have received considerable attention in recent years due to their natural occurrence in coal^{1a} and petroleum^{1b}, formation in coal liquification^{2a} and in petroleum refining,^{2b} as well as their presence as environmental pollutants from a variety of sources.³ Partially reduced PNA hydrocarbons are of equal interest because they commonly exist if the parent molecules are present. They are, however, less well characterized and thus less easily isolated and identified. Such partially reduced compounds are generally valuable as synthetic intermediates in the preparation of larger condensed ring systems.⁴

Clearly, if PNA hydrocarbons can be selectively reduced to specific hydroaromatics, the synthesis of larger PNA hydrocarbons might be greatly simplified. PNA hydrocarbons can generally be reduced by catalytic hydrogenation and/or by dissolving metal reactions. These reduction methods often complement each other in selectivity.

Although the catalytic hydrogenation of many PNA molecules is well documented,⁵ the investigation of dissolving metal reductions is minimal. The discovery that coal is more easily reduced with lithium in ethylenediamine than by catalytic hydrogenation⁶ has created an even greater demand to investigate the dissolving metal reduction of PNA molecules.

This study involves the reduction of pyrene (1) by dissolving metal

reactions. Selected reduced pyrene products obtained from these reductions were used in the preparation of other hydrocarbons as part of a hydrocarbon synthesis program at Oklahoma State University, Stillwater, Oklahoma.

CHAPTER II

HISTORICAL

The reduction of pyrene (1)⁷ and numerous other polynuclear aromatic PNA hydrocarbons via catalytic hydrogenation has been extensively investigated.^{5a-d} Reduction products are dependent upon substrate, solvent, temperature, pressure, time, and catalyst. The catalytic hydrogenation of pyrene appears to follow the sequence of steps shown in Figure 1.^{5a} The first molecule of H₂ adds to 1 to give 4,5-dihydropyrene (2a) which produces 4,5,9,10-tetrahydropyrene (3a) upon addition of a second molecule of H₂. Further reduction followed by isomerization leads to the formation of 1,2,3,3a,4,5-hexahydropyrene (4a) and 1,2,3,6,7,8-hexahydropyrene (4b). These reduce to give 1,2,3,3a,4,5,9,10,10a,10b-decahydropyrene (5a) and 1,2,3,3a,4,5,5a,6,7,8-decahydropyrene (5b) respectively. The product formation in the hydrogenation of pyrene has been plotted by Cowan^{5a} as shown in Figure 2.

Pyrene has also been reduced by dissolving metal reactions,⁸ however little emphasis has been given to detailed product formation and identification of these products. Birch reduction of pyrene is reported to give olefinic products whereas catalytic hydrogenation of 1 does not. Reduction of 1 with Li/NH₃⁹ and Na/NH₃^{10a,b} leads to the formation of unstable dihydropyrene isomers 2b and 2c as shown in part a of Figure 3. These hydrocarbons undergo facile isomerization to the stable 4,5-dihydropyrene (2a) during column chromatography (silica gel) and gas

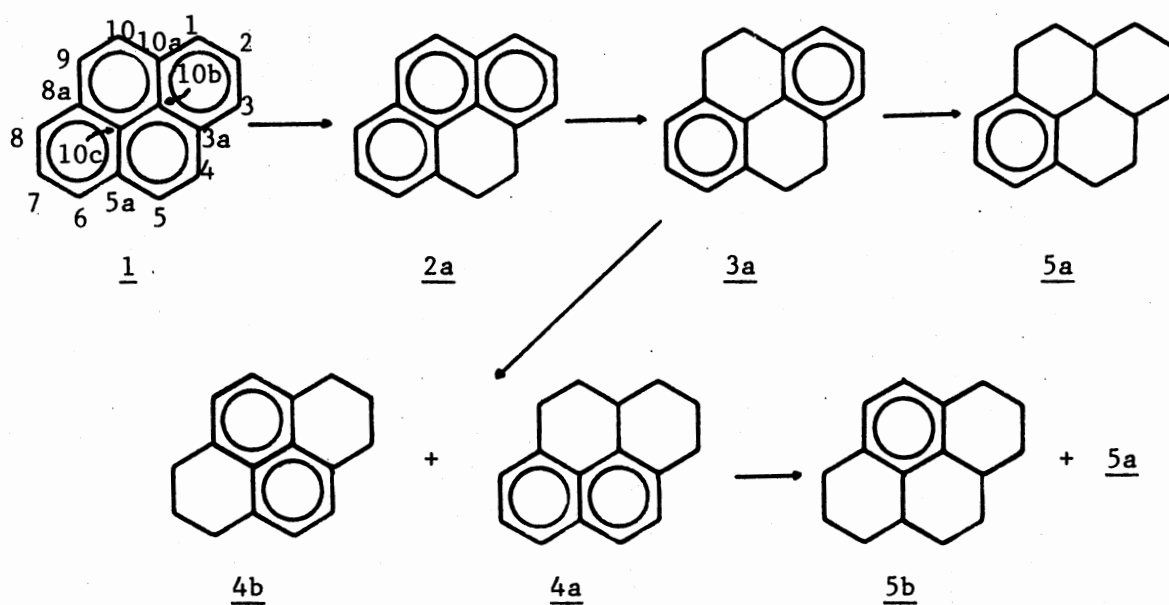


Figure 1. Pd/C Catalyzed Hydrogenation of Pyrene (1) - Reduction Sequence.

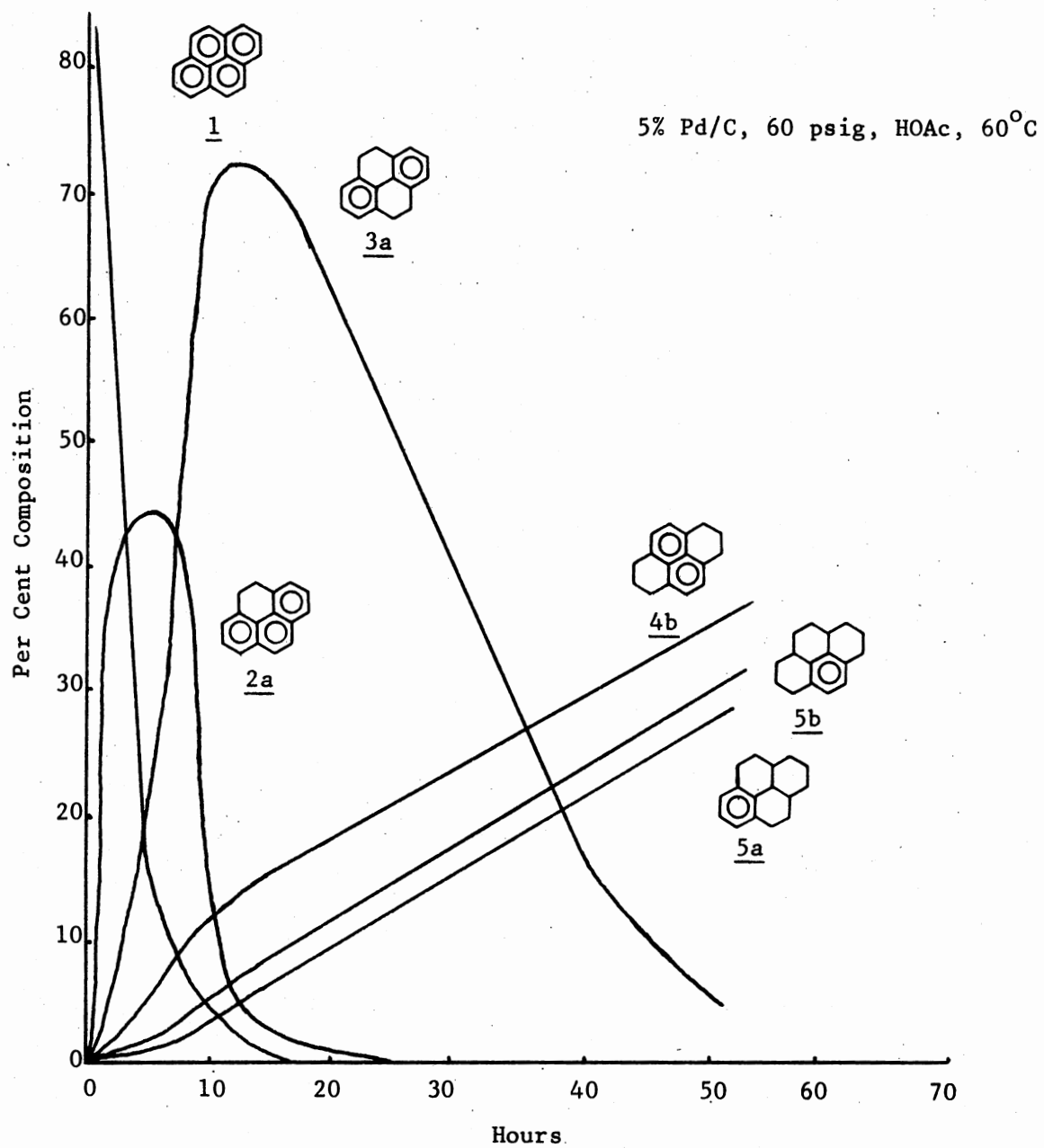


Figure 2. Pd/C Catalyzed Hydrogenation of Pyrene (1) - Product Formation.

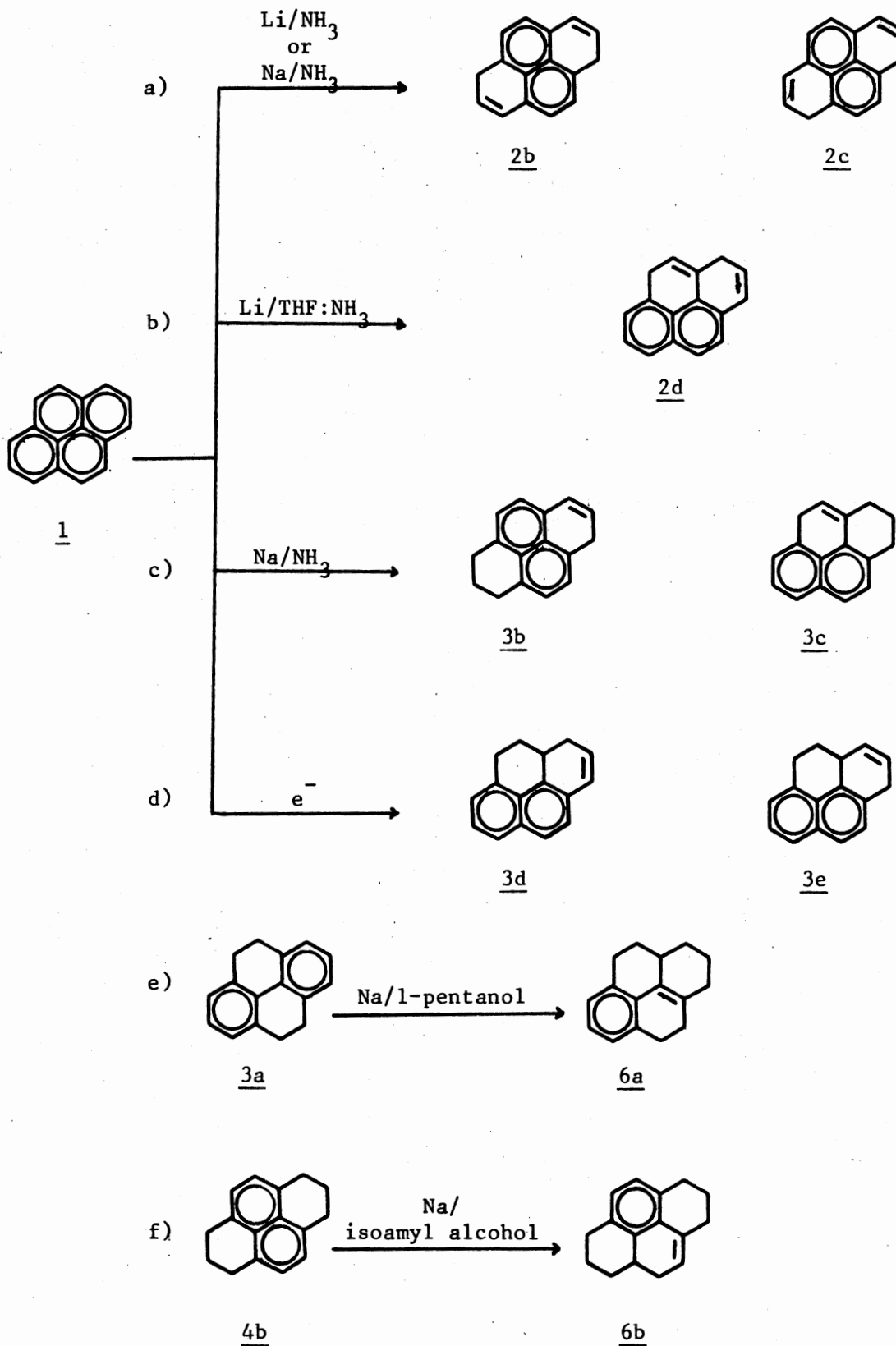


Figure 3. Olefin Containing Products from Dissolving Metal Reductions of 1, 3a, and 4b.

chromatography (150-170°C).⁹ 1,9-Dihydropyrene (2d) has been obtained by reducing pyrene (1) with lithium in THF:NH₃ (1:2)¹¹ as shown in part b of Figure 3. The unstable tetrahydropyrene isomers 3b (60%) and 3c (30%) are obtained from 1 with sodium in ammonia¹² (part c of Figure 3), while electrolytic reduction of 1¹³ affords tetrahydropyrenes 3d and 3e (part d of Figure 3). Octahydropyrenes 6a and 6b are obtained by reducing 3a^{13,14a,b} and 4b¹³ respectively with sodium in isoamyl alcohol (parts e and f of Figure 3). Coulson¹⁵ previously obtained 3a and 4b with sodium in 1-pentanol but incorrectly assigned their structures.

The mechanism for one-electron reduction of pyrene has not been examined due to the complexity of the aromatic system. The mechanism for reducing less complex PNA systems is well documented^{16a-f} and should be similar for the pyrene system. Figure 4 illustrates the mechanism for dissolving metal reduction of naphthalene (7). The addition of an electron to form the radical anion 8 is considered to be a reversible process.¹⁷ Evidence for the existence of such radical anion intermediates has been reported.^{18a-j} Addition of another electron to form dianion 9 is more difficult because of the negative charge of 8. In ether solvents, one atom of sodium reacts reversibly to produce the green salt of a radical anion, and in ammonia two atoms react reversibly to give the red dianion salt.^{16a} Solvent effects are therefore critical for most dissolving metal reductions.

Dihydronaphthalenes 12a and 12b, like the olefin containing reduced pyrenes, are not obtained by catalytic hydrogenation. In addition to reduction, 7 has been shown to undergo reductive amination^{16a,19a-d} and/or reductive dimerization^{16a,19a-d} with sodium and selected amine solvents to give products such as 14^{19a,b} and 15.^{19e} Observations of similar pro-

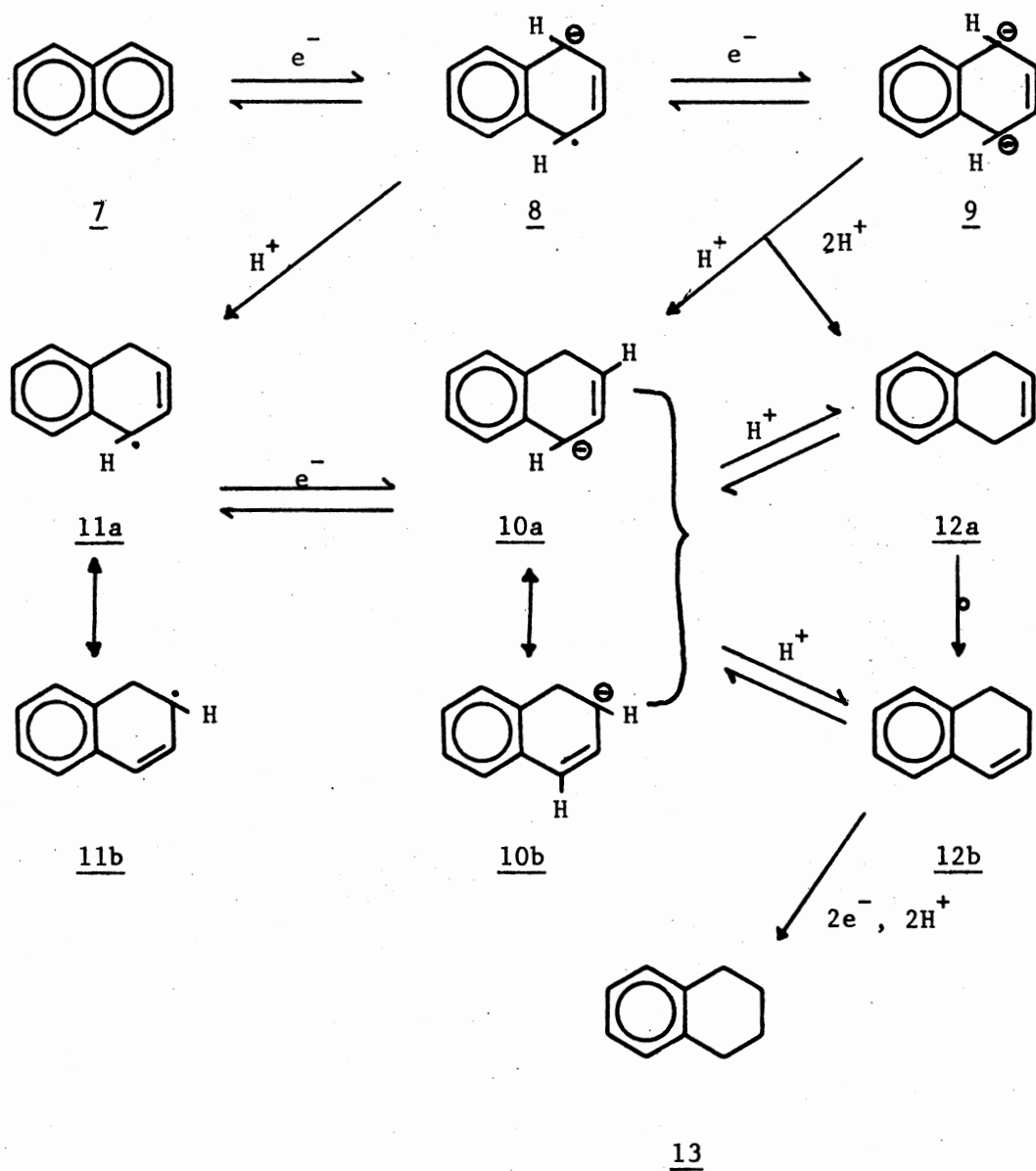
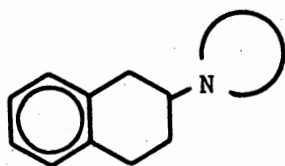
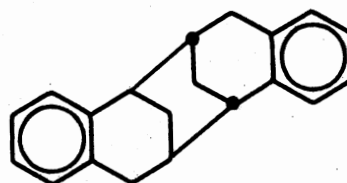


Figure 4. Mechanism for Reduction of Naphthalene with Sodium.

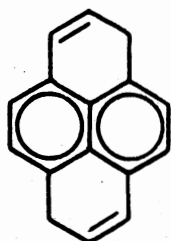
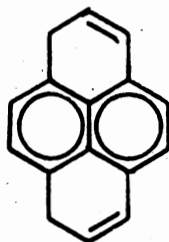
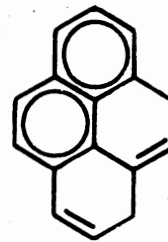
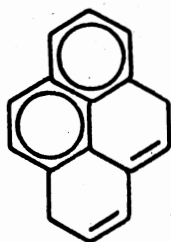
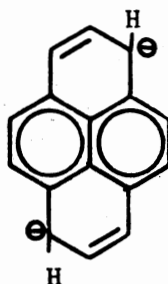
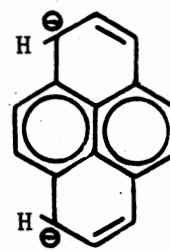
ducts from pyrene (1) have not been reported.

1415

Various workers have provided information (sometimes conflicting) which suggests the possible radical anion or dianion salts formed in the initial reduction of pyrene (1). Reduction of 1 with sodium in ammonia/ether/ethanol (10:6:1) has been shown to give a dihydropyrene which is relatively unstable and autoxidizes to 1.^{10b} This can not be the stable product 2a which is obtained from catalytic hydrogenation. The dihydropyrene obtained had a UV spectrum characteristic of a vinyl naphthalene system, suggesting 2b-2e as possible isomers. Catalytic hydrogenation of the unstable dihydropyrene isomer(s) gave only 4b, therefore, isomers 2b and 2c are the preferred structures and have been postulated to exist in equilibrium.^{10b} Treatment of 2b and 2c with KOH/alcohol or phenyllithium affords the red salts 16a and 16b¹³ which are analogous to 9, the red dianion salt of naphthalene.

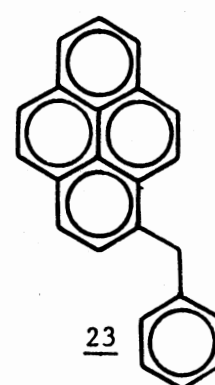
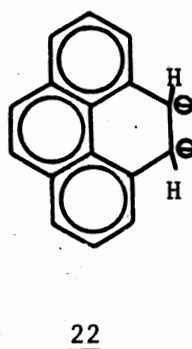
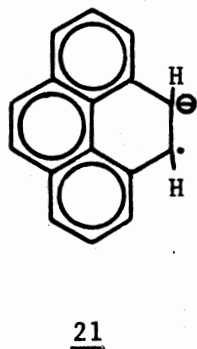
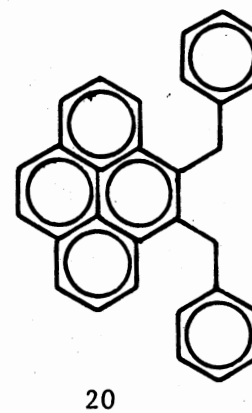
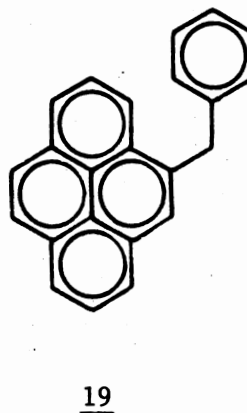
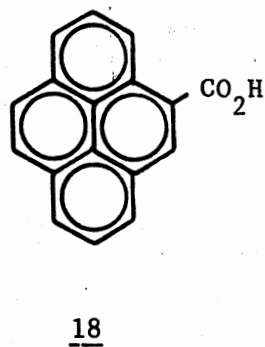
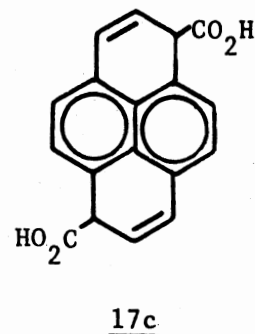
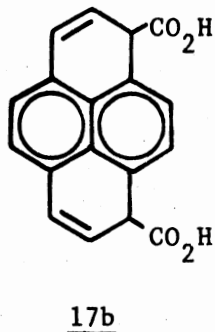
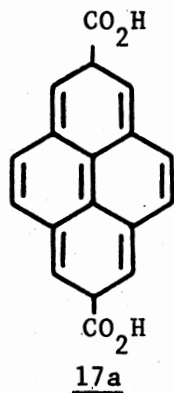
Under similar reducing conditions, with ethanol present as a proton source, an unstable dihydropyrene product (mp 56-8°C) has been isolated.^{10a} When no proton source was available in the solvent the unstable dihydropyrene could not be isolated upon hydrolysis with methanol^{10a} or mineral acid.²⁰ The product quickly autoxidizes to 1. With ammonia/ether as solvents the stable 4,5-dihydropyrene (2a) is obtained (15%) after hydrolysis with NH₄Br.^{10a}

The pyrene dianion produced by sodium or lithium in ether has been

2b2c2d2e16a16b

shown to react with carbon dioxide to form pyrene dicarboxylic acids. Bergman and Bograchov²⁰ suggest diacids 17a and 17b as possible structures. Diacids 17c and 17b would be the most probable structures based on dianions 16a and 16b which afford 2b and 2c respectively upon protonation. Neunhoeffer and Woggon^{10a} have isolated two pyrene dicarboxylic acids (mp 310°C and mp 360°C) but do not suggest possible structures. Other workers²¹ have suggested that the radical anion of pyrene preferentially adds to the 1,8 positions which is consistent with structures 2c and 17b.

Nucleophilic attack appears to occur primarily from the four position of pyrene when a mixture of ammonia and diethyl ether is used. Pyrene reduced with sodium in this solvent system followed by addition of CO₂ affords 4-pyrenecarboxylic acid (18).^{10a} Substituting benzylchloride for CO₂ yields 19 (10%) and 20 (trace).²² Radical anion 21 and



dianion 22 have been suggested as the reacting species. In contrast, pyrene reacts with electronically neutral free radicals at position 1.²² For example, 1 reacts with toluene and t-butylhydroperoxide to give 23 (25%). It has been reported that electronically neutral free radicals attack at the point of maximum free valence (position 1 of pyrene) and

radical anions are formed across the carbob-carbon bond with the highest bond order (4,5 positions of pyrene).²² This does not, however, explain the formation of 2b, 2c, 17b, and 17c from the one electron reactions mentioned previously. Apparently, solvent effects are critical for the products formed.

Reductions of pyrene (1) by one electron reducing systems in NH_3 , diethyl ether, and ethanol solvent are of limited utility. The pyrene dianion formed is apparently insoluble in this solvent and further reduction ceases. Other solvents, discussed below, which enhance the further reduction of pyrene in dissolving metal reactions have been investigated. These reducing systems are synthetically more useful and represent excellent alternatives to catalytic hydrogenation.

Reduction of pyrene with sodium in 1-pentanol was first reported in 1907.^{8a} This procedure has been modified^{18b-d,13} and used by other workers for the preparation of sym-hexahydropyrene (4b). as-Hexahydropyrene was also characterized and identified. The reduced pyrene products 2a, 3a, 4a, and 4b have also been treated with sodium and 1-pentanol,¹⁵ however, the product analyses were incorrect. The reduction of other PNA compounds under similar conditions has been described.^{16c-e} Reduction of anthracene at the 9,10 positions occurs more readily than reduction of the 9,10 positions of phenanthrene.^{16e} Phenanthrene reduces at the 9,10 positions in aprotic solvents but the 1,2,3,4 positions are more easily reduced in protic solvents.^{16e}

The reduction of some PNA hydrocarbons with lithium and ethylenediamine has been studied^{8c,23} and the following conclusions were reported:^{8c}

(i) Aromatic hydrocarbons, highly substituted by alkyl or alicyclic

groups are resistant to reduction.

- (ii) The less substituted benzene hydrocarbons and diphenyl-type structures yield, in addition to a proportion of fully reduced material, compounds containing isolated single olefinic bonds which tend to resist further reduction.
- (iii) Highly condensed hydrocarbons (pyrene and coronene) yield some perhydro derivatives, but a part of the product consists of less completely reduced compounds with aromatic and olefinic features; these compounds are more resistant to further reduction than the parent hydrocarbons.
- (iv) Condensed polynuclear hydrocarbons also yield some products containing hydroxyl (phenolic) and carbonyl groups.

Lithium-ethylenediamine systems are also reported to exhibit isomerization of double bonds while sodium-ethylenediamine systems do not promote olefin isomerization.²⁴

CHAPTER III

RESULTS AND DISCUSSION

Pyrene was reduced with sodium in various alcohol and amine solvents. The reaction product consisted of a complex mixture of hydrogenated pyrenes as indicated by gas chromatography. Previous workers have isolated hexahydropyrene isomers 4a and 4b from reduction of pyrene with sodium and 1-pentanol but the remainder of the reaction mixture was not studied.^{8a-d} A detailed product analysis and a study of product formation curves for the dissolving metal reductions and catalytic hydrogenation of pyrene indicate that the reduction sequence is substantially different for these two reducing systems.

The gas chromatography (gc) retention patterns for the products obtained by catalytic hydrogenation and by dissolving metal reduction of pyrene is shown in Figure 5. The perhydropyrenes (stereochemistry not resolved) appear at ca. 2 minutes on the gc pattern. They are obtained only after prolonged reaction times or by high pressure catalytic hydrogenation. Traces of these perhydropyrenes can also be detected when a large excess of metal is used in dissolving metal reductions. Decahydropyrenes 5a and 5b (stereochemistry not resolved) are obtained in near equal quantities by catalytic hydrogenation of 1 as shown in Figure 1. In contrast, dissolving metal reductions of pyrene gives a much higher 5b:5a ratio which is solvent dependent. Dissolving metal reductions yield 5a only when large quantities of metal

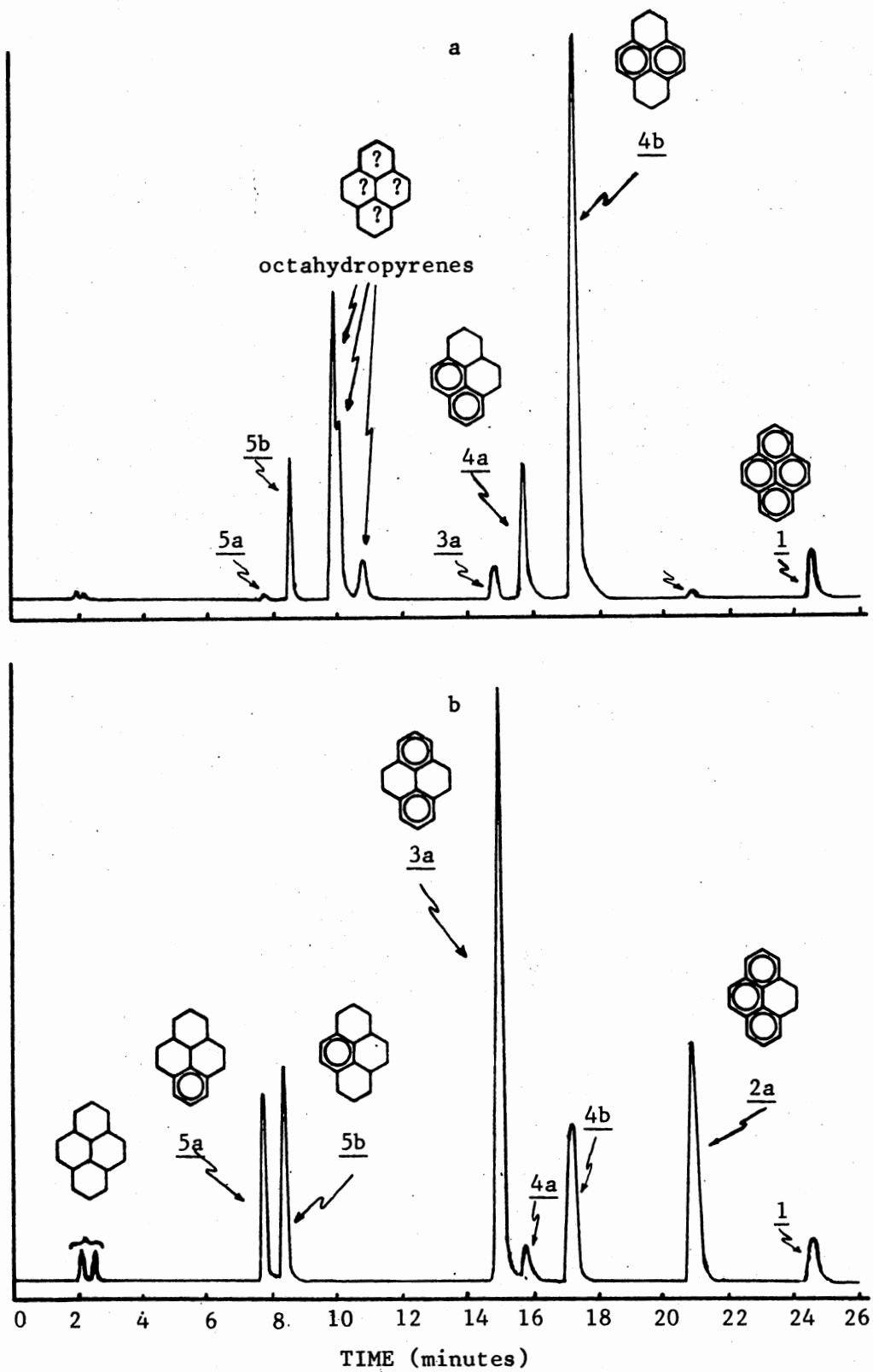


Figure 5. G.C. Retention Pattern for Products Obtained from
 a) Dissolving Metal Reduction of 1 and b) Catalytic
 Hydrogenation of 1.

are used. The three peaks represented by question marks in Figure 5 are not present in the catalytic hydrogenation of 1 but are significant in dissolving metal reductions. Separation of these hydrocarbons for structure determination was not successful but other evidence indicates that they are octahydropyrenes. 4,5,9,10-Tetrahydropyrene (3a) is the major product obtained by catalytic hydrogenation of 1 but exists in low quantities in dissolving metal reductions. Hexahydropyrenes 4a and 4b are obtained as minor products from catalytic hydrogenation of 1. Dissolving metal reduction affords 4a in low yield (13%) but 4b now becomes the major product (50%). 4,5-Dihydropyrene (2a), a major product by catalytic hydrogenation of 1, is obtained in trace amounts in dissolving metal systems. Catalytic hydrogenations and dissolving metal reductions are therefore complementary in selectivity and each is of synthetic value.

The product formation curves for reducing pyrene (1) with sodium in selected alcohol and amine solvents are shown in Figures 6, 7, and 8. The solvent is critical for these reductions. The low boiling solvents (ethanol, bp 78°C, and 2-propanol, bp 82°C: Figure 6) are less effective in the reduction of 1 with sodium. The ratio of octahydropyrenes 6a and 6b to the remainder of the other reduction products is greater with these solvents than with the higher boiling solvents. In contrast, t-butyl alcohol (bp 82°C, part c of Figure 6) affords 4b as the major product with yields superior to other solvents investigated. These low boiling solvents are synthetically less desirable due to the limited solubility of 1 and the slow reaction of sodium metal even at reflux. Reaction of the metal is greatly enhanced above the melting point of the metal; 97°C for Na. The metal not only provides electrons which reduce

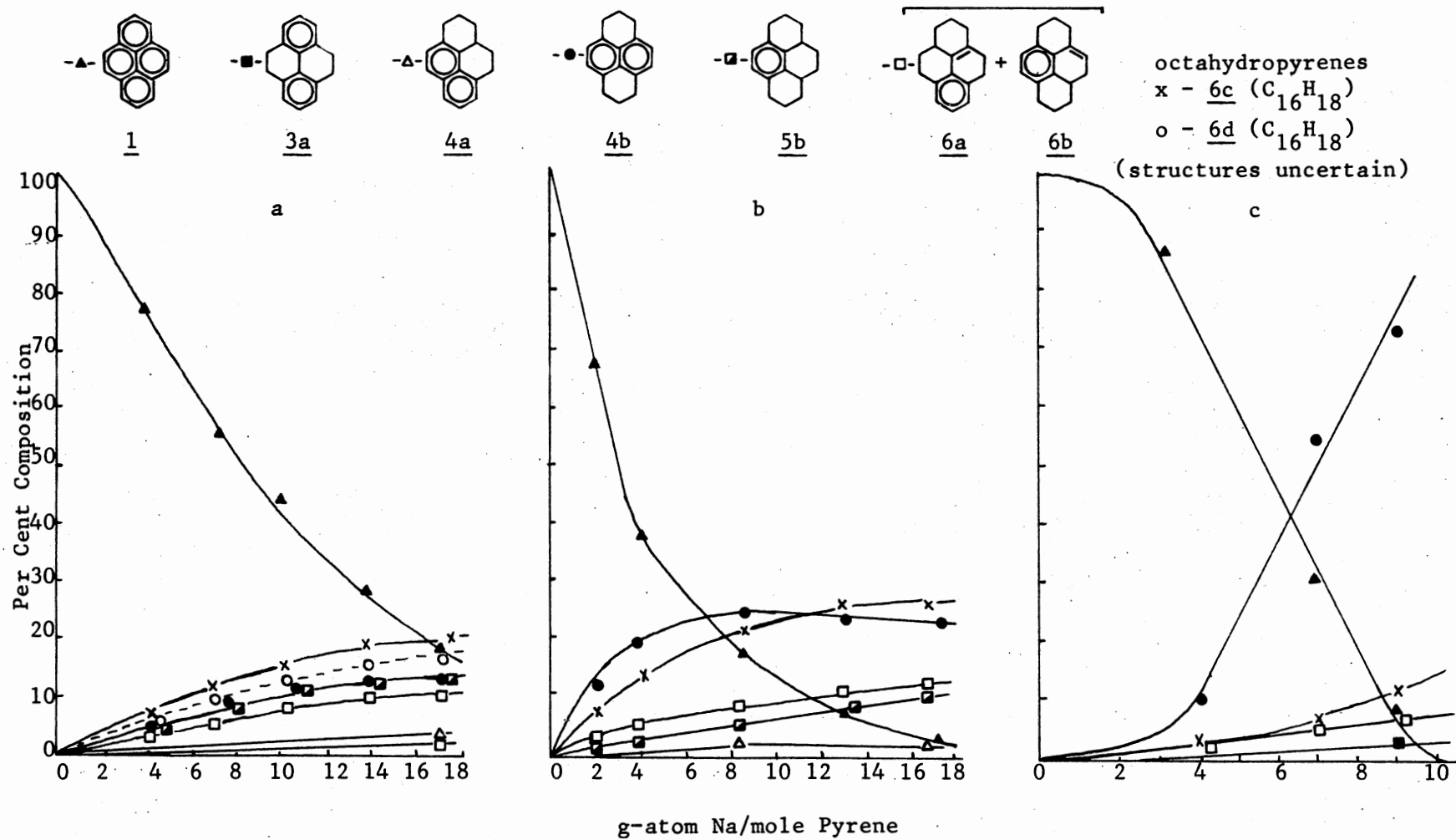


Figure 6. Product Formation in the Reduction of **1** with Na in a) Ethanol, b) 2-Propanol, and c) t-Butyl Alcohol.

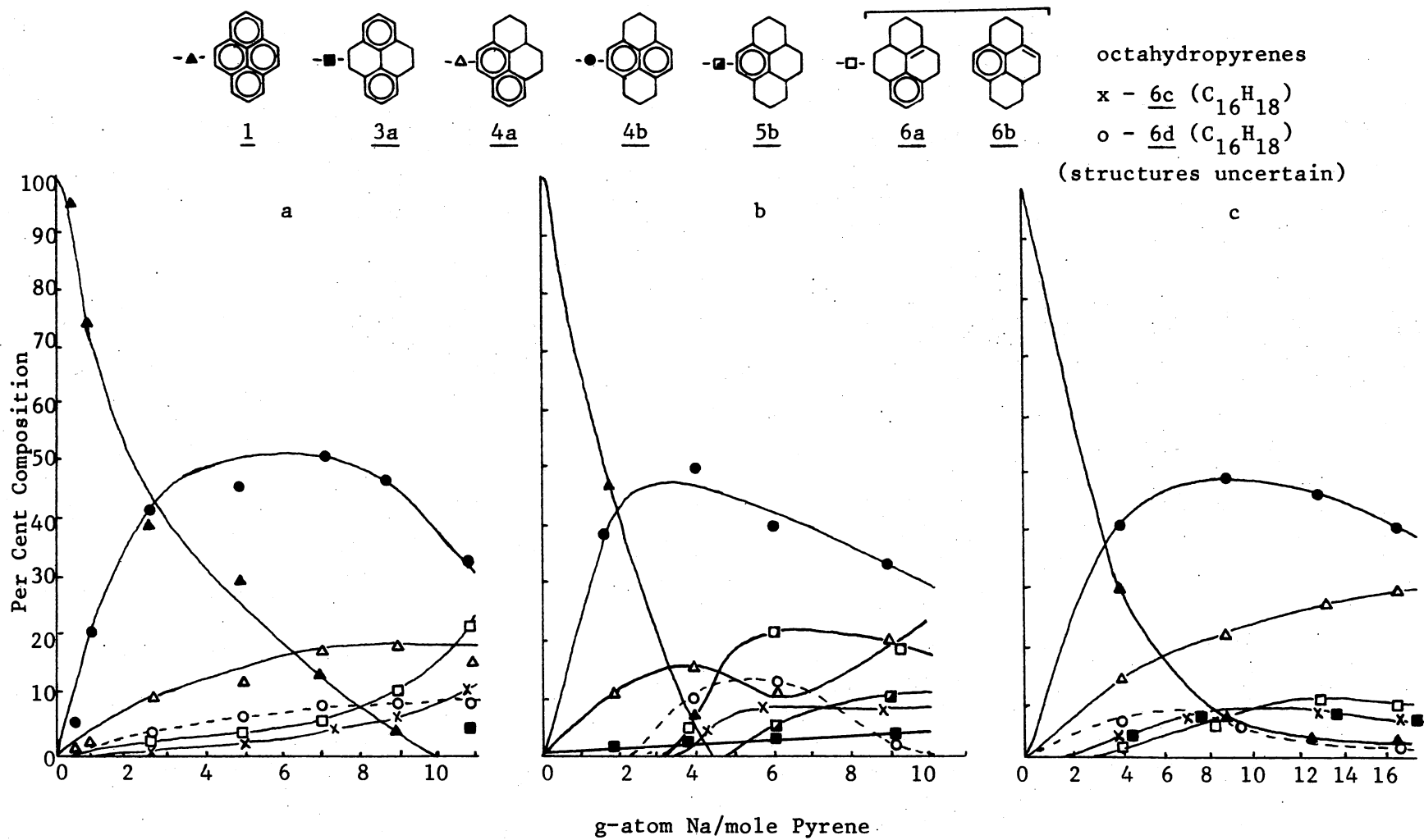


Figure 7. Product Formation in the Reduction of **1** with Na in a) 1-Pentanol, b) 3-Methyl-1-butanol, and c) 1-Octanol.

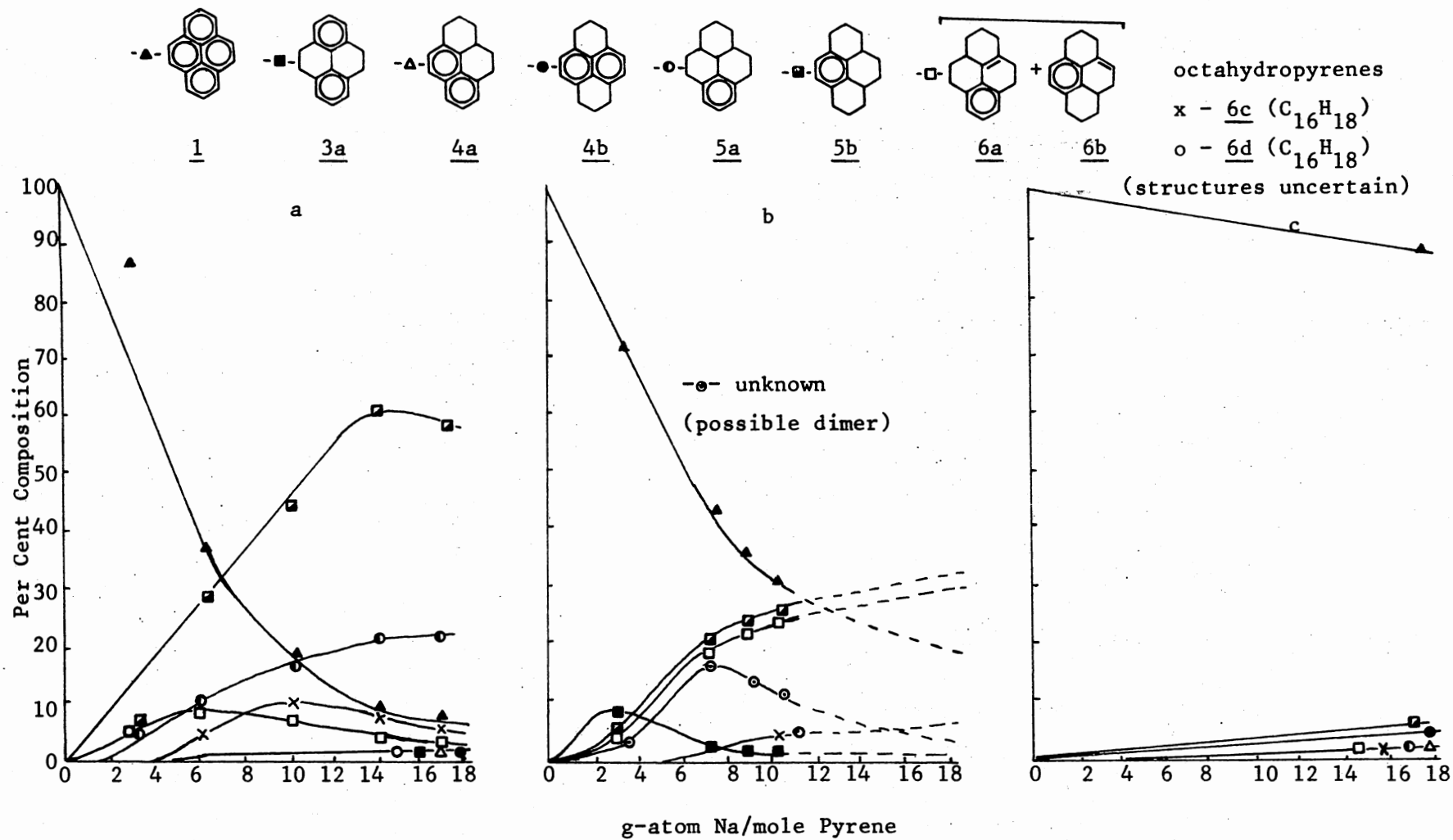


Figure 8. Product Formation in the Reduction of 1 with Na in a) Ethanolamine, b) Ethylenediamine, and c) Ethylene Glycol

the substrate, but also reacts with the solvent as indicated by H_2 evolution and alkoxide salt formation. This competing process seems to have little effect on the actual reduction process.

Primary and secondary alcohols with similar structures and boiling points react similarly. No correlation was made for tertiary alcohols since t-butyl alcohol was the only one investigated. Reductions of 1 with higher boiling alcohols are similar as shown in Figure 7. Unlike the simple alcohols, ethanolamine (bp $170^\circ C$, part a of Figure 8) and sodium reduce pyrene (1) to obtain 5a and 5b as the major products while 4a and 4b become minor components. Similarly, ethylenediamine (bp $117^\circ C$, part b of Figure 8) and sodium reduce pyrene more extensively than sodium in alcohol solvents. Sodium-ethylenediamine, unlike sodium-ethanolamine, gave only traces of decahydropyrene 5a and an unknown compound was detected, but not isolated, which was not found in other solvent systems investigated. This compound (indicated by \ominus in part b of Figure 8) has a retention time longer than the retention time of 1 and is possibly a reduced pyrene dimer. Sodium-ethylenediamine has been shown to produce reduced naphthalene dimers.^{16a,19b-e} This is apparently a reversible process since the concentration of the unknown product decreased with no appearance of new products. Although ethanolamine and ethylenediamine produce the more highly reduced pyrenes, the alcohol solvents require less sodium for complete conversion of pyrene to reduction products. Surprisingly, ethylene glycol (bp $178^\circ C$, part c of Figure 8) with sodium is a poor reducing system for 1.

The influence of solvents on product formation is not well understood. Almost certainly a combination of interrelated factors are responsible for the variety of observations noted in dissolving metal

reductions. Among these factors are 1) boiling point of solvent, 2) solubility of substrate and metal, 3) ionization potential between solvent and metal,¹³ 4) ion pair formation,¹³ and 5) competing reactions between solvent and metal (i.e. alkoxide salt formation). Product analysis for reducing systems with sodium and various solvents are presented in Table 1.

Pyrene (1), 4,5-dihydropyrene (2a), 4,5,9,10-tetrahydropyrene (3a), 1,2,3,3a,4,5-hexahydropyrene (4a), and 1,2,3,6,7,8-hexahydropyrene (4b) were reduced with Na/1-pentanol. Complete conversion of 1 and 2a was accomplished with 8-10 molar equivalents of sodium to substrate. Hydrocarbons 3a and 4a were more resistant to reduction and required 35 and 37 molar equivalents of Na respectively for complete conversion to more highly reduced pyrenes. *sym*-Hexahydropyrene (4b) was most resistant to reduction; 35% 4b remained after addition of 90 molar equivalents of sodium to 4b. Product formation curves for reducing 2a, 3a, 4a and 4b are presented in Figures 9 and 10.

Preparation of 4b was consistently accomplished in 50% yield by carefully controlling the amount of sodium added. Earlier literature^{8b} cites a 23% yield of 4b. This low yield is probably due to addition of excess sodium which further reduces 4b. As 4b decreases due to further reduction an increase of octahydropyrene (6b) is observed (part a of Figure 7). Reduction of 1 with Na/1-pentanol proceeds through the competing pathways presented in Figure 11. Reduction sequence *a-d-i* predominates as indicated by the rapid rate of 4b formation and the occurrence of 4b as the major product. Intermediate structures 2b and 2c have been isolated from dissolving metal reduction of 1 (Na/NH₃, EtOH).^{9,10b} Intermediates 3b (60%) and 3c (30%) have been obtained by Na/NH₃ reduction

TABLE I

SODIUM REDUCTION PRODUCTS OF PYRENE

Hydrocarbon g(mol)	Na g(g-atom)	Solvent mL(bp °C)	% Composition of Products									
			<u>1</u>	<u>2</u>	<u>3</u>	<u>4a</u>	<u>4b</u>	<u>5a</u>	<u>5b</u>	<u>6a + 6b</u>	<u>6c^g</u>	<u>6d^g</u>
25(0.124) ^a	50(2.17)	Ethanol 1500(78)	19	-	2	2	14	1	15	12	19	16
25(0.124) ^a	50(2.17)	2-propanol 1500(82)	4	-	2	2	24	1	12	12	24	21
10(0.05) ^a	10(0.44)	t-Butyl alcohol 600(82)	7	-	2	-	53	-	-	7	-	11
20(0.1) ^a	23(1.0)	ethylenediamine ^f 650(117)	28	1	2	1	1	-	25	26	3	3
125(0.62) ^a	200(8.7)	2-methyl-1-butanol 3000(129)	-	-	-	-	20	-	-	42	38	-
125(0.62) ^a	190(8.3)	3-methyl-1-butanol 3000(129)	-	-	7	20	36	-	-	13	24	-
200(1.0) ^a	180(7.8)	n-pentanol 4500(137)	-	-	2	17	58	-	-	9	8	6
20(0.1) ^a	40(1.7)	ethanolamine 600(170)	8	-	-	-	-	22	57	6	8	-
10(0.05) ^a	20(0.87)	n-octanol 500(195)	4	-	6	30	42	-	2	8	7	4
20(0.1) ^a	40(1.7)	ethylene glycol 800(198)	87	-	-	1	4	1	5	1	1	-
3(0.015) ^b	5(0.22)	n-pentanol 300(137)	-	-	48	2	-	-	7	44	-	-
4.4(0.021) ^c	44(1.91)	n-pentanol 400(137)	-	-	-	-	48	-	32	20 ^h	-	-
5(0.025) ^d	50(2.17)	n-pentanol 1000(137)	-	-	-	-	-	6	52	37	6	-
5(0.024) ^e	20(0.87)	n-pentanol 500(137)	-	-	3	-	-	27	4	66 ⁱ	-	-

^a Pyrene (1). ^b 4,5-Dihydropyrene (2a). ^c Hexahydropyrene (4b). ^d Hexahydropyrene (4a). ^e 4,5,9,10-tetrahydropyrene (3a). ^f Na-ethylenediamine gave an isomer (10.8%) with retention time greater than pyrene. ^g Octahydropyrene, C₁₆H₁₈ (structures uncertain). ⁱ Contains 6a only.

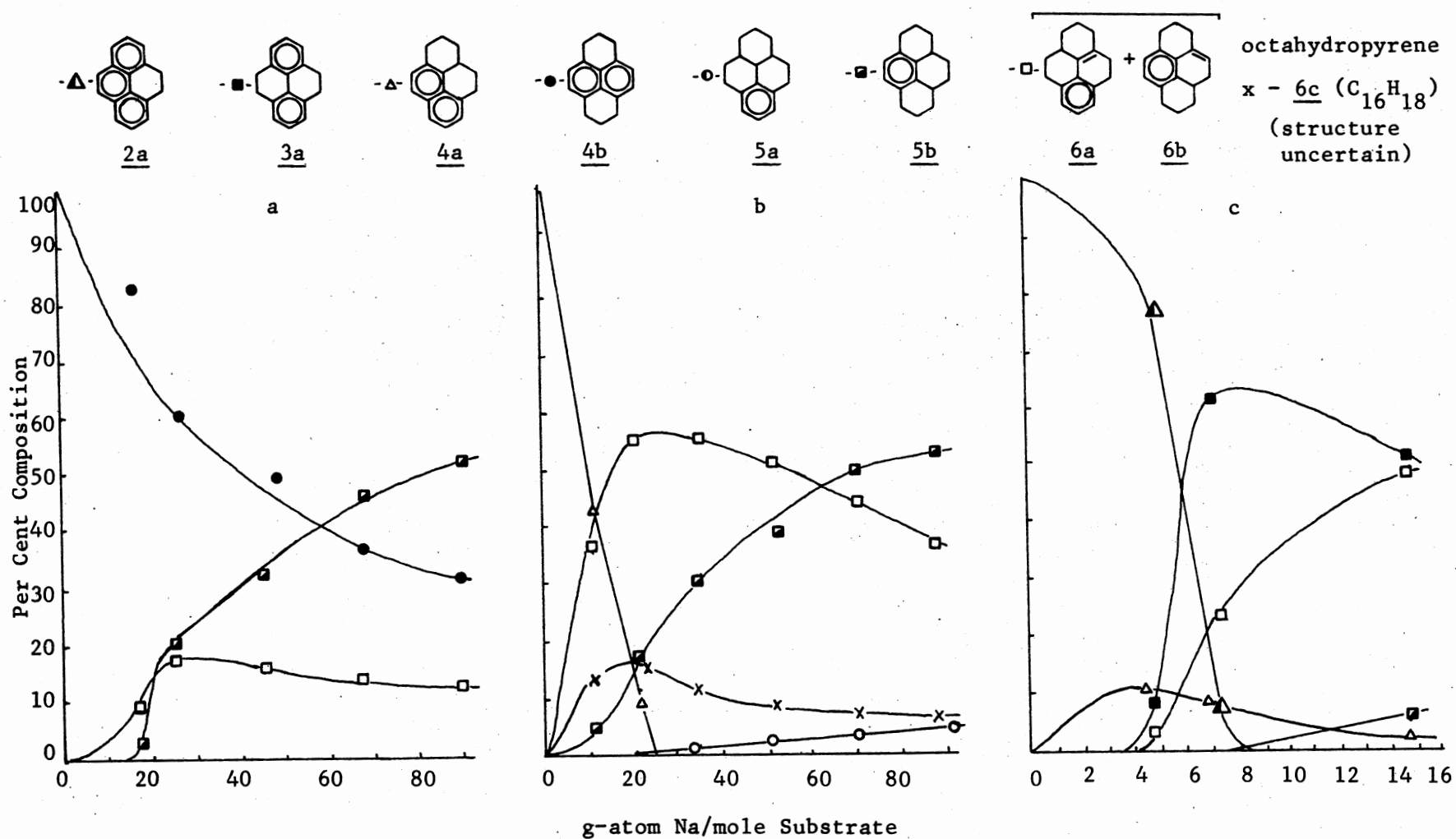


Figure 9. Product Formation in the Reduction of a) 1,2,3,6,7,8-Hexahydropyrene (4b), 1,2,3,3a,4,5-Hexahydropyrene (4a), and c) 4,5-Dihydropyrene (2a) with Sodium in 1-Pentanol.

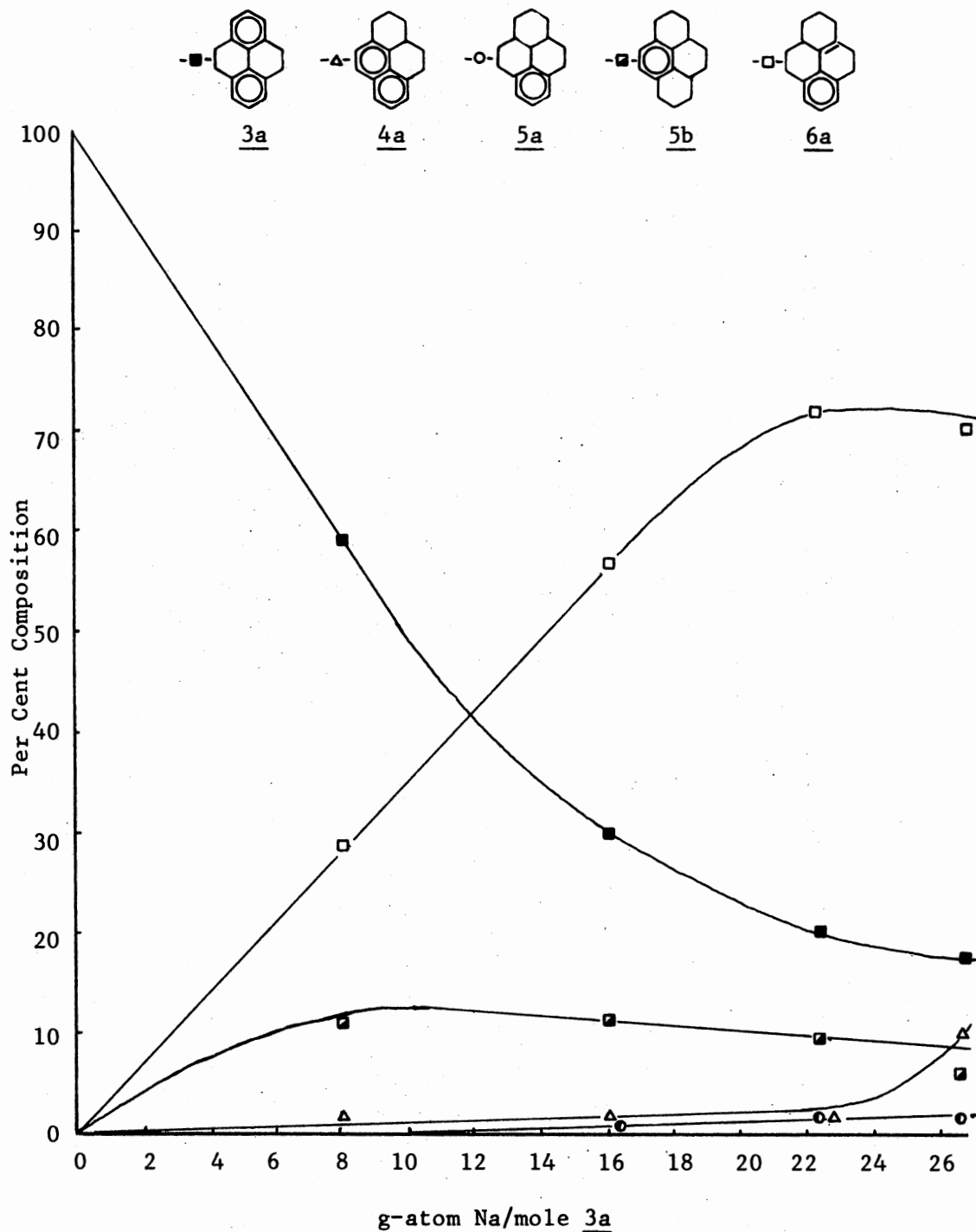


Figure 10. Product Formation in the Reduction of 4,5,9,10-Tetrahydropyrene (**3a**) with Sodium in 1-Pentanol.

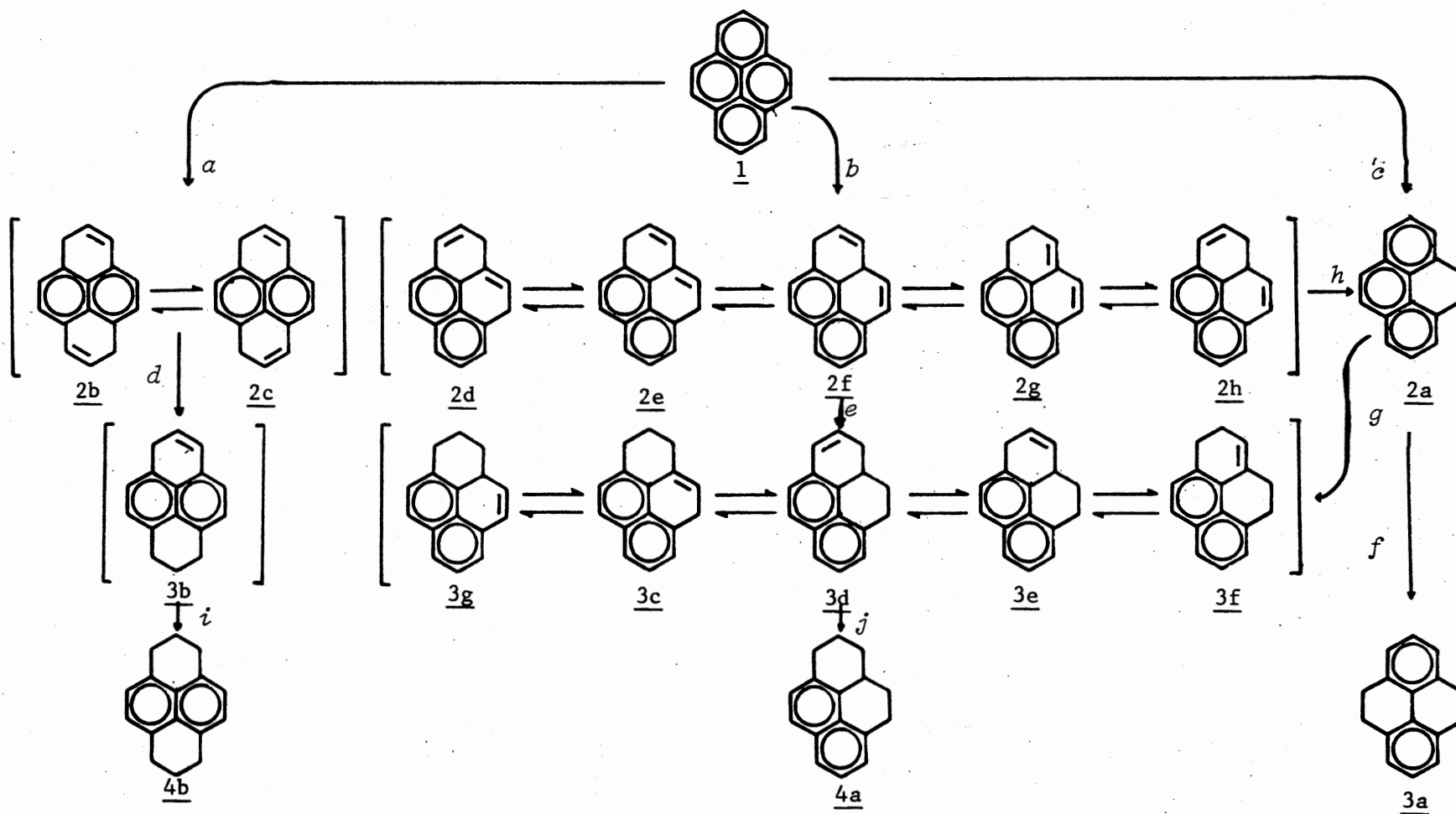


Figure 11. Pathways of Initial Reduction of Pyrene (1) in Na/1-Pentanol.

of 1¹² while controlled electron potential (CEP) reductions of 1 yield tetrahydropyrenes 3d and 3e.¹³ Intermediates 2b, 2c, and 3b are representative of sequence *a-d-i* of Figure 11 while structures 3c, 3d, and 3e are involved in sequence *b-e-j* of Figure 11. Reduction via steps *c-f* or *b-h-f* is minimal as indicated by low yields of 3a and only traces of 2a. The fast rate of 2a conversion requires a low steady state concentration of 2a which accounts for its low abundance. Reduced products 3a, 4a, and 4b obtained from these competing processes are further reduced to octahydro- and decahydropyrenes.

The above rationalization and reduction sequences are valid when two assumptions are considered: 1) when structures containing both aromatic and olefinic double bonds undergo reduction of the olefin prior to reduction of the aromatic rings and 2) when there is no significant isomerization of aromatic rings (i.e. 2c \neq 2d, etc.). Fortunately these restrictions appear to be applicable in dissolving metal reductions of 1.

The products obtained by reducing 1 with Na/1-pentanol correlate well with the expected products based on ESR experiments on the radical anion of pyrene. Electron densities of pyrene (1) obtained from ESR experiments^{25a-c} agree well with calculated values^{26a,b} and indicate the densities to decrease in the order: position one > position four > position two. This supports the primary formation of 2b, and 2c which reduce to the major product 4b.

Treatment of 1 with Na in ethanolamine and ethylenediamine (parts a and b of Figure 8) gives a reduction similar to the high boiling solvents. Low concentrations of 3a, 4a, and 4b are observed as a result of rapid further reduction in amine solvents. Low boiling solvents, ethanol and 2-propanol (parts a and b of Figure 6), favor reduction sequence *b-e-j*

in Figure 11. This is supported by the formation of octahydropyrenes 6c and 6d, (structures uncertain), as the major products. These octahydropyrenes are not obtained by reducing 3a or 4b but are obtained by reduction of 4a. Formation of these octahydropyrenes also accounts for the low occurrence of 4a which is expected from sequence *b-e-j*. A certain degree of selectivity is observed in this reduction process. Hansen and coworkers¹³ noted the same phenomena from controlled electron potential experiments.

4,5-Dihydropyrene (2a) was reduced with Na/1-pentanol to a mixture containing 3a (47%), 4a (3%), 5b (5%), and 6a (42%) - (part c of Figure 9). Traces of 6c, 6d, and 5a were also detected. Dihydropyrene (2a) is analogous to phenanthrene and is reduced similarly. Reduction of phenanthrene occurs predominantly at the middle ring with Na/NH₃^{16e} but reduction of the end ring is enhanced with Na/1-pentanol.^{16e,27a,b} Reduction of the 9,10 positions of 2a affords 3a which is then reduced to 6a (Figure 12, steps *a* and *b*). Reduction of 2a produces 4a by two competing reaction sequences: 1) by direct reduction of positions 1, 2, 3, and 3a of 2a (Figure 11, steps *g* and *j*) and 2) reduction of 2a to 3a (Figure 11, step *f*) followed by reduction to 4c and isomerization to 4a (Figure 12, steps *a* and *d*). The latter sequence was verified by reducing 3a with Na/1-pentanol to give a small amount of 4a (8%). Direct reduction of the end ring of 3a (Figure 12, steps *a* and *b*) is preferred to the isomerization process (Figure 12, step *d*). This is supported by the larger 6a:4a ratio found in the Na/1-pentanol reduction of 3a (Figure 10). Octahydropyrenes 6a, 6c, and 6d, (structures 6c and 6d uncertain), are obtained by reduction of 3a and 4a which are formed in the reaction. Reduction of 2a with Na/1-pentanol correlates well with

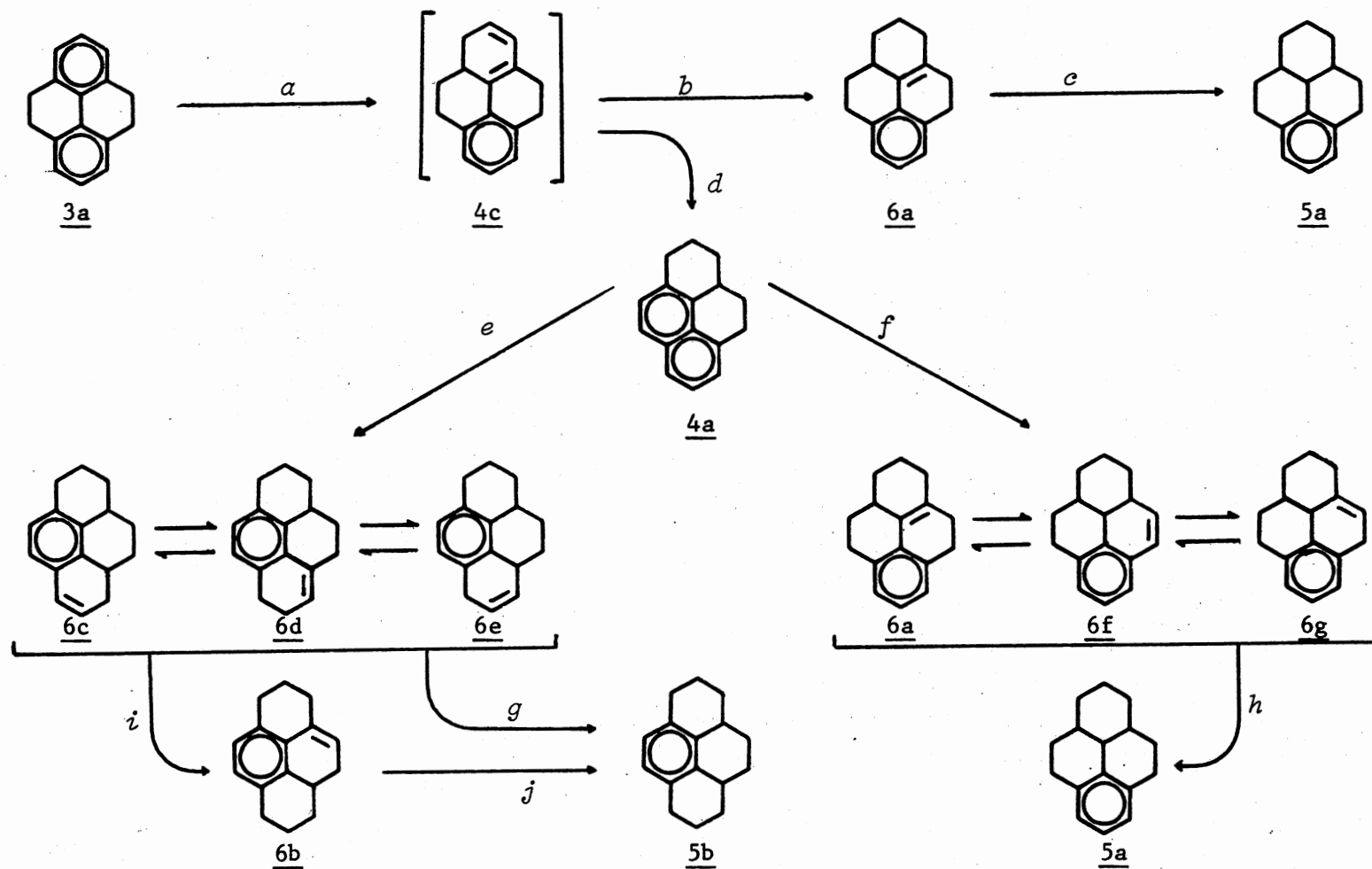


Figure 12. Reduction Sequence for 4,5,9,10-Tetrahydropyrene (**3a**) and 1,2,3,3a,4,5-Hexahydropyrene (**4a**) with Sodium in 1-Pentanol.

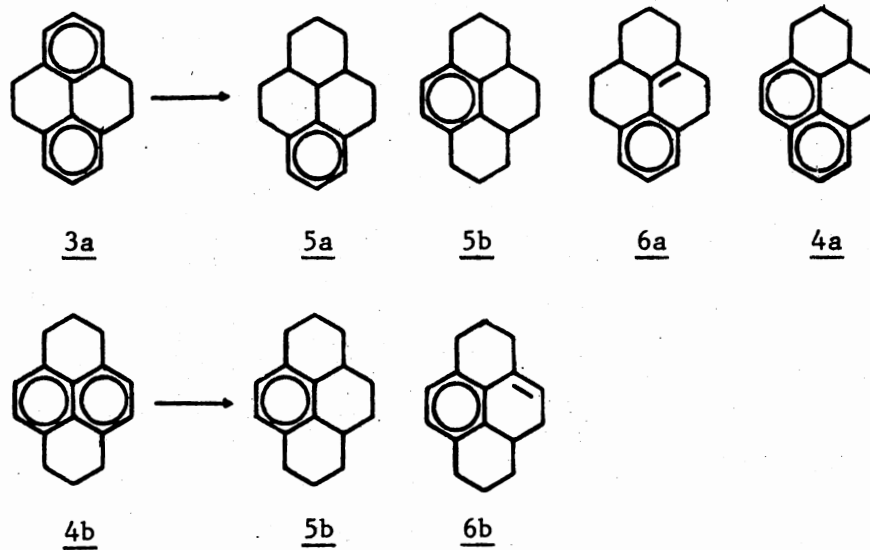
the predicted results based on ESR studies of 2a.^{28,29}

1,2,3,3a,4,5-Hexahydropyrene (4a) was reduced with Na/1-pentanol to produce an octahydropyrene which afforded 5b upon further reduction. Direct reduction of 4a could possibly give the octahydropyrene compounds listed in Figure 12, steps *e* and *f*. Only structures 6c, 6d, and 6e will reduce to 5b. However, the major octahydropyrene formed in this reduction was identified as 6b. Consequently, isomerization of 6c, 6d, and/or 6e to 6b probably occurs before further reduction to 5b (Figure 12, sequence *e-i-j*). This type of isomerization probably occurs in the reduction of 1 and 2a but is difficult to establish due to the complexity of the reaction mixtures. Octahydropyrenes 6c and 6d were also observed by gc studies in the reduction of 4a. ESR experiments on 4a are not currently in the literature, making it impossible to correlate ESR data to the observed product formation curve. However, reduction is expected to proceed predominantly at the least substituted aromatic ring^{8c} and this is observed in the reduction of 4a with Na/1-pentanol.

4,5,9,10-Tetrahydropyrene (3a) was reduced with Na/1-pentanol to produce 4a, 5a, 5b, and 6c (structure uncertain). Formation of 4a probably occurs by isomerization of 4c to 4a (Figure 12, step *d*). Reduction of 4b with Na/1-pentanol was very slow and afforded 5b and 6b. Isomerization of 6a and 6b is not observed in the reduction of 3a and 4b respectively. ESR studies of 3a^{29,30} and 4b^{30,31} indicate the benzylic positions to have the highest electron density which accounts for their resistance to further reduction in the dissolving metal process.

Reduction of pyrene with Na/1-pentanol provided at least three reduced compounds, observed by gc, which are not present in the catalytic hydrogenation of 1. Reaction mixtures containing these compounds

readily decolorized bromine and provided 5a and 5b upon low pressure (810 mm Hg) catalytic hydrogenation with 5% Pd/C in ethyl acetate. Based upon gc retention times and the above information, the unidentified reduction products were proposed to be octahydropyrenes. Further confirmation was obtained by dehydrogenation with Pd/C in toluene. Low temperature dehydrogenation has been shown to selectively dehydrogenate substituted dihydronaphthalene systems while leaving tetrahydronaphthalene systems unaffected.³² Figure 13 illustrates the results obtained by dehydrogenation of the product mixture obtained from Na/1-pentanol reduction of 1. The disappearance of the two unidentified components with the longest retention times occur simultaneously with the formation of 4a. The octahydropyrene peak which corresponded to 6a and 6b was unaffected and no formation of 4b was observed.



Identification of these octahydropyrene components was difficult due to the inability to separate them by chromatography techniques. The octahydropyrenes were removed from the remaining reduction products by preparative HPLC.³³ Octahydropyrenes 6a and 6b were obtained

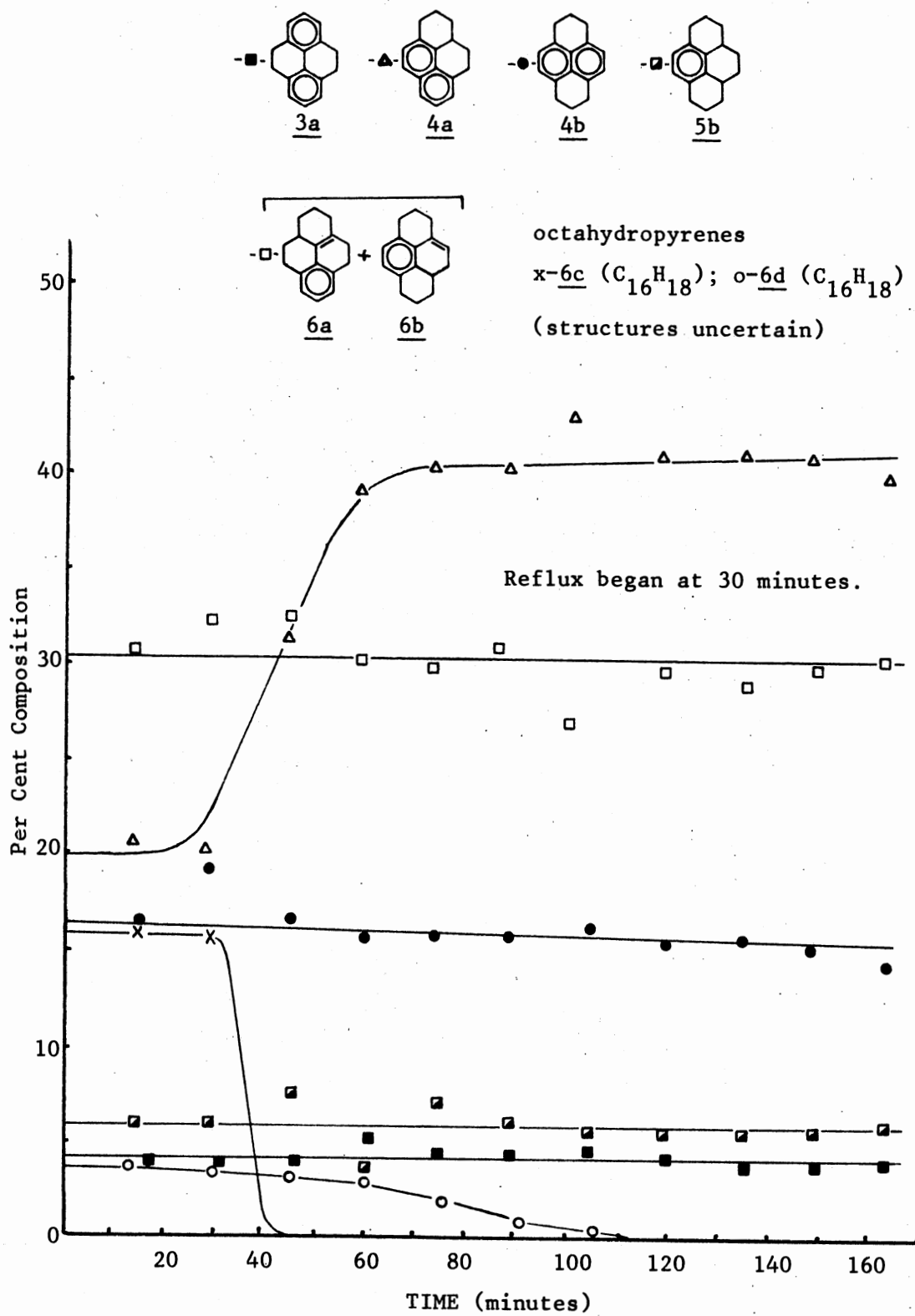
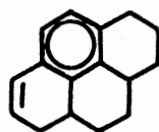
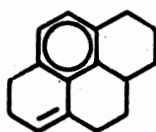
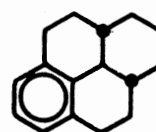


Figure 13. Low Temperature Dehydrogenation of a Mixture of Pyrenes with 5% Pd/C in Toluene.

by reducing 3a and 4b respectively with Na/1-pentanol followed by HPLC separation.³³ Isomers 6a and 6b had identical packed column gc³⁴ retention times and mixed injection gave a single peak corresponding to the octahydroxyrene peak with the lowest retention time. Consequently, at least four octahydroxyrene isomers must be present in the Na/1-pentanol reduction of 1 since the first of the three octahydroxyrene peaks contains two components. Gas chromatography (glass capillary)-mass spectrometry³⁵ separated these isomers into four components (M^+ 210) but identification by mass spectra could not be accomplished since all spectra were very similar. Since four components existed by GC/MS and two of these are present in the first peak by packed column gc, then the remaining two octahydroxyrene peaks observed by packed column gc must contain only one component each.

Catalytic hydrogenation of a mixture of the reduced pyrenes which contained 2% 4a, 38% 6a, 35% 6b and 24% of the second octahydroxyrene product yielded 4% 4a, 36% 5a, 55% 5b, and 5% unreacted 6a and 6b. Since hydrogenation of 6a and 6b afford 5a and 5b respectively, the second octahydroxyrene product must have structure 6c or 6d which would afford 5b upon catalytic hydrogenation.

Dissolving metal reduction of 1 selectively gave 1,2,3,3a,4,5,9,10,10a,10b-decahydroxyrene (5c) which was confirmed by melting point and ¹³C-nmr. Hansen and coworkers¹³ previously observed all of the stereoisomers of 5a in controlled electron potential studies.

6c6d5c

CHAPTER IV

EXPERIMENTAL

General Procedure for Reduction of Pyrene(1) with Sodium and Alcohol. Reductions were conducted in a multi-port glass vessel equipped with a stainless steel turbine stirrer, reflux condenser, thermocouple, heating mantle, and N₂ flow. Solvent and substrate were placed in the reaction vessel and stirred with warming to affect solution. Depending on the solubility, the solvent:substrate ratio ranged from 50 mL-300 mL/g. The solution was heated and the alkali metal was introduced, in small portions, through Gooch tubing attached to one of the ports. The reactions proceeded slowly at temperatures below 95°C (mp of Na) but accelerated at the boiling point of the solvent. In some instances it was necessary to add more solvent to maintain solubility of the alkali metal salts. In all cases, the reactions were sampled periodically and analyzed through gc studies.³⁴ The solution was cooled, poured into water (dil. HCl when amine solvents were used) and extracted. The aqueous layer was extracted once with ethyl ether. The organic phases of high boiling solvents were concentrated by rotary evaporation which simultaneously removed water as an azeotrope. Low boiling solvents were dried (MgSO₄), filtered, and concentrated. The reductions of 1, 2, 3, 4a, and 4b in various solvents are presented in Table 1.

Reduction of Pyrene (1) with Sodium in 1-Pentanol. Pyrene (1), 200 g, 1.0 mol) was reduced with 180 g (7.8 g-atom) Na in 4.5 L 1-pentanol at reflux. GC analysis³⁴ of the final product indicated the reaction mixture contained 6a and 6b (9%), 6c (9%), 6d (6%), 3a (2%), 4a (17%), and 4b (58%). Crystallization from n-hexane afforded 99% pure 4b (106 g, 0.51 mol, 51% yield). The yield of 4b ranged from 35% to 58% (average 48%). When the amount of Na is increased or decreased the yield of 4b decreases sharply.

After removing crystals of 4b by filtration, the mother liquor was analyzed by gc-mass spectrometry³⁵ (glass capillary GC gave separation of some products not separated by the packed gc column used previously. The mother liquor contained the following components presented in order of elution from the GC-MS glass capillary column.³⁵

5b (1.1%); retention time 18:14; MS m/z (rel. intensity) 212 (M^+ , 79.1), 211 (20.7), 210 (26.7), 184 (49.3), 183 (21.3), 181 (28.9), 170 (49.5), 169 (100), 156 (24.9), 141 (37.5); Identical to standard 6b from catalytic hydrogenation.

6c unidentified octahydropyrene $C_{16}H_{18}$ (1.7%); retention time 18:27; MS m/z (rel. intensity) 210 (M^+ , 100), 209 (25.8), 208 (18.7), 182 (37.1), 181 (32.5), 168 (21.2), 167 (62.1), 166 (18.1), 165 (40.0), 89 (18.2). MS similar to MS of 6a.

6a (13.4%); retention time 18:36; MS m/z (rel. intensity) 210 (M^+ , 100), 209 (23.4), 208 (29.9), 182 (30.8), 181 (26.4), 168 (17.2), 167 (70.6), 166 (19.1), 165 (40.4), 152 (17.5).

6b (2.7%); retention time 18:46; MS m/z (rel. intensity) 211 ($M+1^+$, 16.8), 210 (M^+ , 100), 209 (21.9), 208 (20.2), 182 (33.37), 181 (82.8), 167 (39.5), 166 (16.7), 165 (37.5), 89 (15.9).

6d unidentified octahydropyrene $C_{16}H_{18}$ (6.2%); retention time 18:52; MS m/z (rel. intensity) 210 (M^+ , 100), 209 (29.3), 208 (43.4), 207 (22.9), 182 (36.3), 181 (42.3), 180 (26.4), 167 (54.1), 165 (48.0), 89 (25.2).

unidentified hexahydropyrene $C_{16}H_{16}$ (3%); retention time 18:58; MS m/z (rel. intensity) 208 (M^+ , 100), 207 (38.1), 202 (16.8), 193 (17.9), 180 (36.4), 179 (32.3), 178 (23.9), 165 (38.9), 95 (17.0), 89 (29.6).

MS similar to MS of 4b.

3a (22.5%); retention time 19:07; MS m/z (rel. intensity) 207 ($M+1^+$, 15.2), 206 (M^+ , 100), 205 (64.4), 204 (18.5), 203 (35.3), 202 (38.6), 189 (16.0), 101 (23.7), 100 (14.0), 89 (19.8); Identical to standard 3a from catalytic hydrogenation.

unidentified hexahydropyrene $C_{16}H_{16}$ (0.9%); retention time 19:20; MS m/z (rel. intensity) 209 ($M+1^+$, 17.1), 208 (M^+ , 100), 207 (48.1), 206 (14.5), 202 (30.4), 180 (30.3), 179 (24.4), 178 (22.4), 165 (42.1), 89 (26.9).

4a (26.7%); retention time 19:41; MS m/z (rel. intensity) 209 ($M+1^+$, 17.0), 208 (M^+ , 100), 207 (37.7), 206 (26.2), 205 (20.5), 180 (68.8), 179 (33.0), 78 (27.7), 165 (64.8), 89 (34.7); Identical to standard 4a from catalytic hydrogenation.

4b (18.8%); retention time 20:08; MS m/z (rel. intensity) 209 ($M+1^+$, 16.9), 208 (M^+ , 100), 207 (32.6), 202 (9.3), 180 (20.6), 179 (19.4), 178 (16.4), 165 (32.7), 90 (13.9), 89 (22.5); Identical to standard 4b from catalytic hydrogenation.

2a (0.7%); retention time 20:51; MS m/z (rel. intensity) 205 ($M+1^+$, 15.1), 204 (M^+ , 89.9), 203 (100), 202 (95.9), 201 (31.9), 200 (27.7), 102 (7.9), 101 (52.8), 88 (10.6); Identical to 2a from catalytic hydrogenation.

1 (1.8%); retention time 21:35; MS m/z (rel. intensity) 203 ($M+1^+$, 18.0), 202 (M^+ , 100), 201 (25.5), 200 (30.7), 199 (5.2), 198 (3.6), 101 (30.6), 100 (13.7), 99 (3.2), 88 (9.1); Identical to 1 from starting material.

Purification of 1,2,3,6,7,8-Hexahdropyrene (4b). Hydrocarbon 4b (250 g, 99% pure) was eluted through a picric acid column by Soxhlet extraction with n-hexane. Fractions were collected and analyzed by gc.³⁴ The purest fractions (ca. 200 g, 99.5% pure) were chromatographed on a dual column of basic alumina (100 g) above silica gel (150 g). Fractions were collected and 4b was allowed to crystallize and was then filtered. These crystals (mp 133-134, lit.^{5a} 132-133.5°C) were analyzed by gc and all those exceeding 99.90% purity were combined and zone refined. Less pure fractions were combined and reprocessed in a similar manner. IR (KBr) 3050 (ArH str.) cm^{-1} ; 1H NMR³⁷ ($CDCl_3$) δ 1.84-2.10 (pentet, $J=6Hz$, 4, $ArCH_2CH_2$), 2.92-3.04 (t, $J=6Hz$, 8, $ArCH_2$), 7.02 (s, 4, ArH); ^{13}C NMR³⁸ ($CDCl_3$) ppm 23.2 ($ArCH_2CH_2$), 31.3 ($ArCH_2$), 123.1 (C-4, C-5, C-9, C-10), 123.4 (C-10b, C-10c), 133.7 (C-3a, C-5a, C-8a, C-10a).

Reduction of Pyrene (1) with Sodium in Ethanol. Pyrene (1), (25 g, 0.124 mol) was added to 1.5 L ethanol and the resulting solution was brought to reflux (78°C). Sodium (50 g, 2.17 g-atoms) was added in 80 min. The reaction mixture contained 10% pyrene, 2% 3a, 2% 4a, 14% 4b, 1% 5a, 15% 5b, 12% 6a and 6b, 19% 6c and 6d (structures uncertain) as determined by gc.³⁴

Reduction of Pyrene (1) with Sodium in 2-Propanol. Pyrene (1), (25 g, 0.124 mol) was added to 1.5 L 2-propanol and dissolved after reaching reflux (82°C). Sodium (50 g, 2.17 g-atoms) was added in 2 h to obtain 4% pyrene, 2% 3a, 2% 4a, 24% 4b, 1% 5a, 12% 5b, 12% 6a and 6b, 24% 6c

and 21% 6d (structures uncertain) as determined by gc.³⁴

Reduction of Pyrene (1) with Sodium in t-Butyl Alcohol. Ten grams (0.05 mol) of 1 was dissolved in 600 mL t-butyl alcohol at reflux (82°C) and 10 g (0.44 g-atom) of sodium was added in 1 h. After 20 min continued stirring and heating, ca. 1 g of sodium remained unreacted and was destroyed by careful addition of H₂O. The reaction mixture contained 7% pyrene, 2% 3a, 73% 4b, 7% 6a and 6b, and 11% 6d (structure uncertain) as indicated by gc.³⁴

Reduction of Pyrene (1) with Sodium in 2-Methyl-1-butanol. Pyrene (125 g, 0.62 mol) was dissolved in 3 L 2-methyl-1-butanol and brought to 60°C. Sodium (200 g 8.7 g-atom) was added to the solution over 35 min at a rate to maintain reflux (128°C). After an additional 1 h reflux the solution was extracted with water and the alcohol phase was distilled, leaving 116 g of crude product mixture which was Kugelrohr distilled (130-140°C, 0.1 mm) to afford 112 g of material containing 20% 4b, 42% 6a and 6b, and 38% 6c (structure uncertain) by gc.³⁴

Reduction of Pyrene (1) with Sodium in 3-Methyl-1-butanol. Pyrene (125 g, 0.62 mol) was dissolved in 3 L of 3-methyl-1-butanol and heated to 100°C. Sodium (190 g, 8.3 g-atom) was added in 1 h so as to maintain reflux (128°C). After refluxing an additional 20 min the solution was extracted with water and the alcohol was distilled, leaving 115 g crude material which was Kugelrohr distilled (145°C, 0.16 mm) to give 108 g material composed of 18% 4a, 32% 4b, 12% 5b, 21% 6a and 6b, 10% 6c and 1% 6d (structures uncertain) as indicated by gc.³⁴

Reduction of Pyrene (1) with Sodium in 1-Octanol. Ten grams (0.05 mol) of pyrene were dissolved in 500 mL 1-octanol at 140°C and 20 g (0.87 g-atom) of Na was added in 30 min to reach reflux (195°C). The reaction

mixture contained 4% 1, 6% 3a, 30% 4a, 42% 4b, 2% 5b, 8% 6a and 6b, and 7% 6c (structure uncertain) as determined by gc.³⁴

Reduction of Pyrene (1) with Sodium in Ethylenediamine. Twenty grams (0.1 mol) of 1 was reduced in 650 mL refluxing ethylenediamine (bp 117°C) by adding 23 g (1.0 g-atom) of sodium in 3 h to afford 28% 1, 1% 2a, 2% 3a, 1% 4a, 25% 5b, 26% 6a and 6b, 3% 6c and 3% 6d (structures uncertain), and 10% of an unidentified product with retention time greater than for pyrene as indicated by gc.³⁴ The solution turned green and then red as the reaction proceeded.

Reduction of Pyrene (1) with Sodium in Ethanolamine. Twenty grams (0.1 mol) of pyrene was reduced in 600 mL ethanolamine (bp 170°C) at 150°C by adding 40 g (1.7 g-atom) in 32 min to obtain 8% 1, 22% 5a, 57% 5b, 6% 6a and 6b, and 8% 6c (structure uncertain) as determined by gc.³⁴

Reduction of Pyrene (1) with Sodium in Ethylene Glycol. Pyrene (20 g, 0.1 mol) was dissolved in 800 mL ethylene glycol (bp 198°C) at 100°C and 40 g (1.7 g-atom) of Na was added in 45 min as the solution was heated to 170°C. A blue color appeared at the surface of the sodium. The product mixture contained 87% pyrene, 1% 4a, 4% 4b, 1% 5a, 5% 5b, 1% 6a and 6b, and 1% 6c (structure uncertain) as determined by gc.³⁴

Reduction of 4,5-Dihydropyrene (2a) with Sodium in 1-Pentanol. Three grams (0.15 mol) of 2a was dissolved in 300 mL 1-pentanol at 55°C and 5 g (0.22 g-atom) of sodium was added in 20 min as the solution was brought to reflux (137°C). The reaction mixture contained 48% 3a, 2% 4a, 7% 5b, and 44% 6a and 6b as determined by gc.³⁴

1,2,3,3a,4,5,9,10-Octahydropyrene (6a) from Reduction of 4,5,9,10-Tetrahydropyrene (3a) with Sodium in 1-Pentanol. Ten grams (0.05 mol) of 3a were dissolved in 500 mL 1-pentanol at 50°C and 30 g (1.3 g-atom)

of Na were added at reflux (137°C) to obtain 16.8% 3a, 8.8% 4a, 2.2% 5a, 5% 5b, and 67% 6a as determined by gc³⁴ and GC-MS.³⁵ Five g of reaction mixture was dissolved in 40 mL n-hexane and was separated by preparative HPLC.³³ Fractions were collected and analyzed by gc³⁴ to determine the best fraction containing 6a. Concentration of the n-hexane yielded 1.3g (93% pure) of hydrocarbon 6a, mp 73-4°C [lit.^{14b} 76-7°C]: IR (melt) 3040 (ArH str.) cm⁻¹; ¹H NMR³⁷ (DCCl₃) δ 1.15-2.5 (m, 11, aliphatic C-H), 2.6-2.9 (m, 4, benzylic CH); ¹³C NMR³⁸ (DCCl₃) ppm 22.1, 28.0, 29.2, 29.7, 31.2, 31.6, 31.8, and 35.4 (aliphatic CH), 124.7, 125.2, 126.1, 126.6, 128.3, 130.8, 134.3, and 134.8 (aromatic and vinyl CH).

Reduction of 1,2,3,3a,4,5-Hexahydropyrene (4a) with Sodium in 1-Pentanol. Five grams (0.025 mol) of 4a was dissolved in 1L of 1-pentanol at 125°C and 50 g (2.17 g-atom) of Na was added in 70 min as the solution was brought to reflux (127°C). The reaction mixture contained 6% 5a, 52% 5b, 37% 6a and 6b, and 6% 6c as determined by gc.³⁴

Reduction of 1,2,3,6,7,8-Hexahydropyrene (4b) with Sodium in 1-Pentanol. *sym*-Hexahydropyrene (4b), (4.42 g, 0.021 mol) was dissolved in 400 mL 1-pentanol at 100°C and 44 g (1.91 g-atom) of sodium was added in 1 h as the solution was brought to reflux (137°C). The reaction mixture contained 48% 4b, 32% 5b, and 20% 6b as indicated by gc³⁴ and GC-MS.³⁵

1,2,3,3a,4,5-Hexahydropyrene (4a) from Dehydrogenation of Reduced Pyrene Mixture. A mixture of reduced pyrene (115 g) composed of 4% 3a, 20% 4a, 18% 4b, 7% 5b, 32% 6a and 6b, 16% 6c, and 4% 6d was dehydrogenated with 5 g of 10% Pd/C in 1 L toluene at reflux for 2 h and the reaction was followed by gc (see Figure 12). The mixture was filtered while hot through a bed of dicalite to remove the catalyst. The products

consisted of 5% 3a, 41% 4a, 14% 4b, 8% 5b, and 31% 6a and 6b as determined by gc.³⁴ The toluene was removed by rotary evaporation and the crude reaction mixture was eluted through a Soxhlet column containing 40g basic alumina over 30 g silica gel by percolating isohexane solvent. Successive fractions were taken to obtain 39 g (34% yield) of 4a (95% pure by gc³⁴), mp 104-105°C [lit.^{28b} 105-105.5°C] : IR (KBr) 3045 (ArH str.) cm⁻¹; ¹H NMR³⁷ (DCCl₃) δ 1.2-2.2 (m, 6, aliphatic H), 2.6-3.2 (m, 5, benzylic H), 7.0-7.6 (m, 5, ArH); ¹³C NMR³⁸ (DCCl₃) ppm 22.8, 29.9, 30.6, 30.9, 31.1, 37.7 (aliphatic and benzylic C), 124.0, 124.2, 125.3, 125.5, 126.4, 127.4, 131.3, 132.0, 134.1, 135.9 (aromatic C).

Catalytic Hydrogenation of Reduced Pyrenes. A mixture (0.5 g) of reduced pyrenes which contained 2% 4a, 38% 6a, 35% 6b, and 24% of the second octahydropyrene component (by GC-MS³⁵) was reduced with 0.05 g 5% Pd/C in 60 mL EtOAc at 810 mm Hg pressure. The hydrogenation consumed 247 mL H₂. The mixture was filtered through dicalite and concentrated to give 0.5 g crude material which contained 4% 4a, 36% 5a, 55% 5b, and 5% unreacted 6a and 6b as determined by gc.³⁴

1,2,3,3aα,4,5,9,10,10aα,10bβ-Decahydropyrene (5a). Low boiling reduced pyrenes, ca. 150 g from combined reaction mother liquors, was vacuum distilled 120-150°C (0.02 mm) and fractions were collected. The first fractions were enriched in perhydropyrenes, dehydropyrenes, and octahydropyrenes. The latter fractions were enriched in octahydropyrenes, 3a, 4a, and 4b. Upon standing ca. 2 weeks, crystals appeared in the oily distillate of the middle fractions. The oil was decanted and the crystals were recrystallized from n-hexane to give ca. 5 g (92% pure) hydrocarbon 5a, mp 118-120 [lit. 118°C¹³, 129°C^{7a}] : IR (melt) 3055 (ArH str.) cm⁻¹; ¹H NMR³⁷ (DCCl₃) δ 1.0-1.5 (m, 5H), 1.5-2.1 (m, 7H), 2.70-

2.95 (m, 5, benzylic H), 6.75-7.15 (m, 3, ArH); ^{13}C NMR³⁸ (DCCl_3) ppm
25.1, 25.7, 26.0, 28.4, 35.6, and 39.6 (aliphatic C), 124.8, 126.0,
133.7, and 135.8 (aromatic C).

PART II

SYNTHESIS OF 1-¹³C-NAPHTHALENE AND

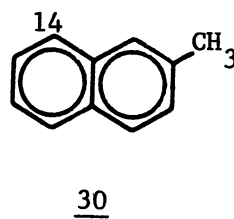
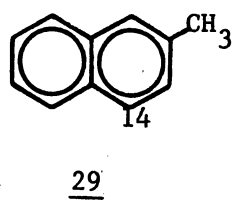
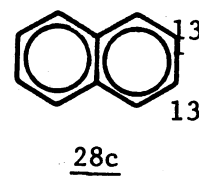
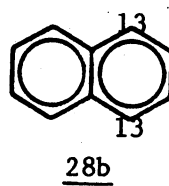
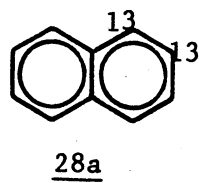
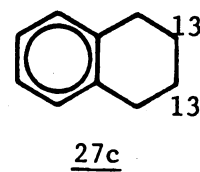
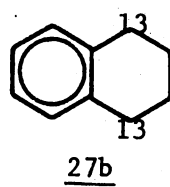
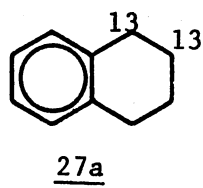
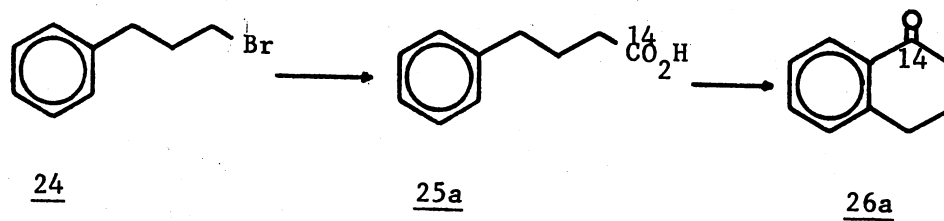
4-¹³C-2,6-DIMETHYLNAPHTHALENE

CHAPTER V

INTRODUCTION AND HISTORICAL

Hydroaromatic compounds are valuable as solvents and as hydrogen transfer agents in the thermally induced depolymerization of coal to coal liquids.^{39a,b} In model studies, tetralin and related hydroaromatic hydrocarbons have proven useful to further the understanding of the kinetics and mechanism(s) of these reactions.^{39c,d} Labeled compounds show promise in determining the fate of solvents in these reaction processes. Consequently, we undertook the synthesis of the title compounds to be used later in coal depolymerization studies. Due to cost of the label, we sought a synthesis which permitted introduction of ^{13}C at a late stage.

Introduction of labeled ^{13}C and ^{14}C isotopes is generally accomplished by reaction of a Grignard reagent with commercially available $^*\text{CO}_2$ (obtained from Ba^*CO_3) or by nucleophilic attack of $^*\text{CN}^-$ on a carbon atom which contains a labile leaving group.⁴⁰ Both of these methods have been previously utilized in the conversion of 3-phenylpropylbromide (24) to ^{14}C -labeled 4-phenylbutyric acid (25a) and 1-tetralone (26a).^{41a,b,c} Budzikiewicz and Stoltze⁴² have prepared hydrocarbons 27a-c and 28a-c having two carbon-13 labels in each molecule. Other workers have described the synthesis of ^{14}C -labeled 2-methylnaphthalenes 29⁴³ and 30⁴⁴.



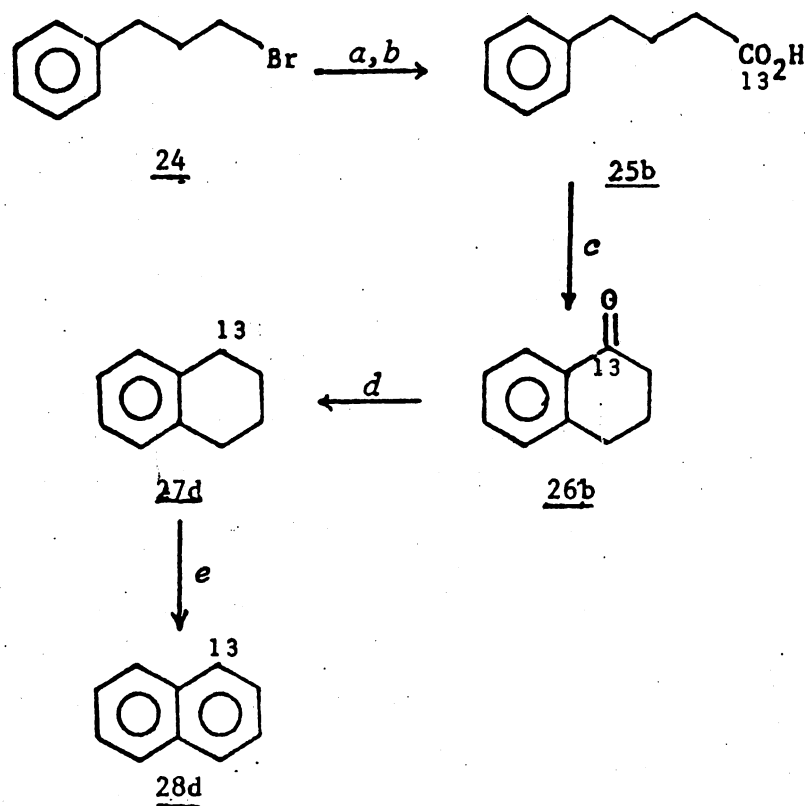
CHAPTER VI

RESULTS AND DISCUSSION

The synthesis of 1-¹³C-1,2,3,4-tetrahydronaphthalene (27d) and 4-¹³C-2,6-dimethyl-1,2,3,4-tetrahydronaphthalene (36) was undertaken to be used later in coal depolymerization studies.⁴⁵ Due to cost of the label, a synthesis was sought which permitted introduction of ¹³C at a late stage.

The route used for the synthesis of 1-¹³C-naphthalene (28d) is illustrated in Figure 14 and the route used for the synthesis of 4-¹³C-2,6-dimethylnaphthalene (37) is outlined in Figure 15. Both reaction sequences involve similar reactions and ¹³C is introduced through the use of labeled carbon dioxide⁴⁶ via an improved procedure⁴⁷ for carbonation of Grignard reagents.

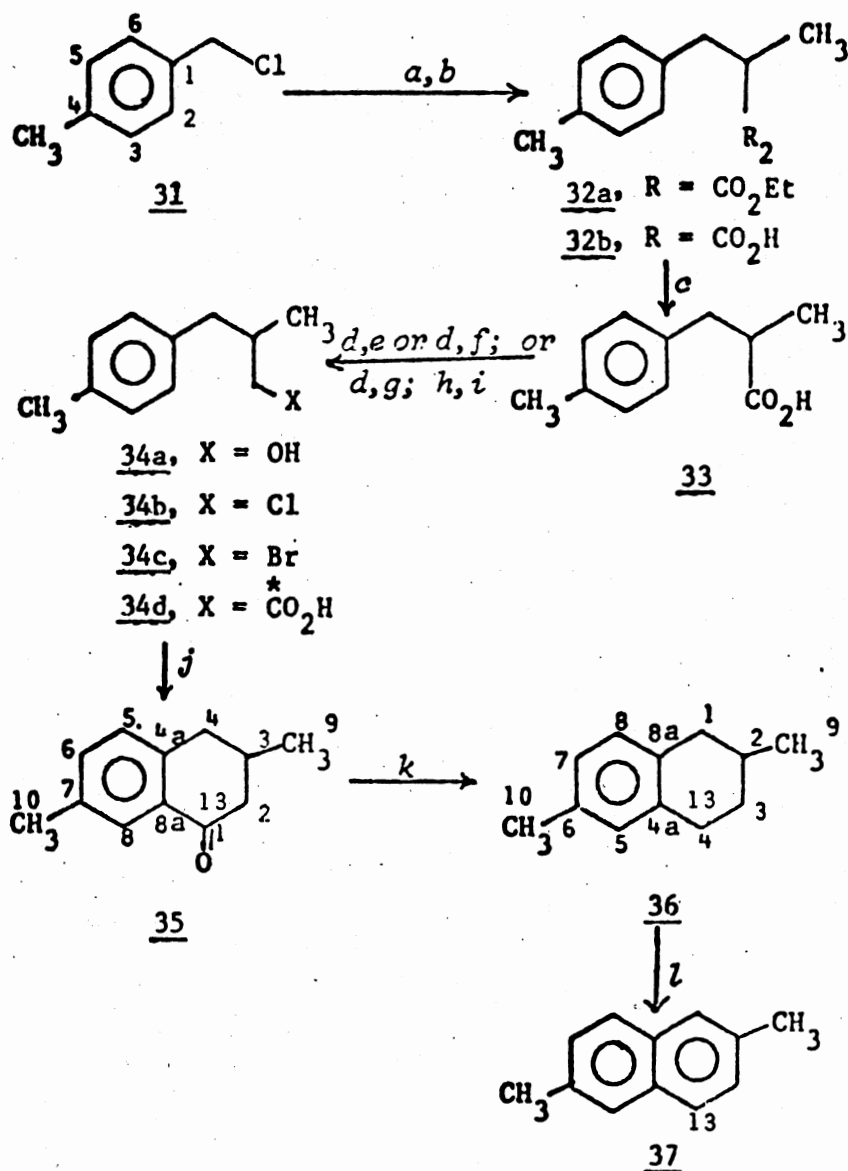
An all-metal reactor assembly was developed which is capable of operating at 50-60 psig and thus insures safe handling of the expensive ¹³C label in relatively large quantities (0.2-0.4 mol). The details of the carbonation step and the operation of the apparatus have been described.⁴⁷ The ¹³CO₂ was generated by adding H₃PO₄ to a slurry of Ba¹³CO₃ and H₂O (part a of Figure 16). The ¹³CO₂ that evolved was transferred and condensed into a gas bottle (part b of Figure 16) where it was stored until needed. The Grignard reagent was prepared in a glass apparatus (part c of Figure 16) and transferred by siphoning into an all-metal carbonation reactor (Figure 17). The previously prepared ¹³CO₂ (part b of Figure 16) was then transferred and condensed into



a Mg, THF, C₆H₆ (1:9). *b* ¹³CO₂. *c* PPA, Δ.

d H₂, Pd/C, HOAc, Δ. *e* Pd/C, Δ.

Figure 14. Reaction Sequence for the Synthesis of 1-¹³C-Naphthalene (28d).



a C₂H₅O⁻, C₆H₅CH₃; CH₃CH(CO₂C₂H₅)₂, Δ. *b* OH⁻, Δ; H₃O⁺.
c Δ. *d* (iC₄H₉)₂AlH, CH₃C₆H₅. *e* (C₆H₅)₃P, Br₂, Δ. *f* SOCl₂.
g C₆H₆, Py. *h* PBr₃, C₆H₅CH₃, Δ. *i* Mg, THF, C₆H₆ (1:9).
j ¹³CO₂. *k* PPA, Δ. *l* H₂, Pd/C, HOAc, Δ. *m* Pd/C, Δ.

Figure 15. Reaction Sequence for the Synthesis of 4-¹³C-2,6-Dimethylnaphthalene (**37**).

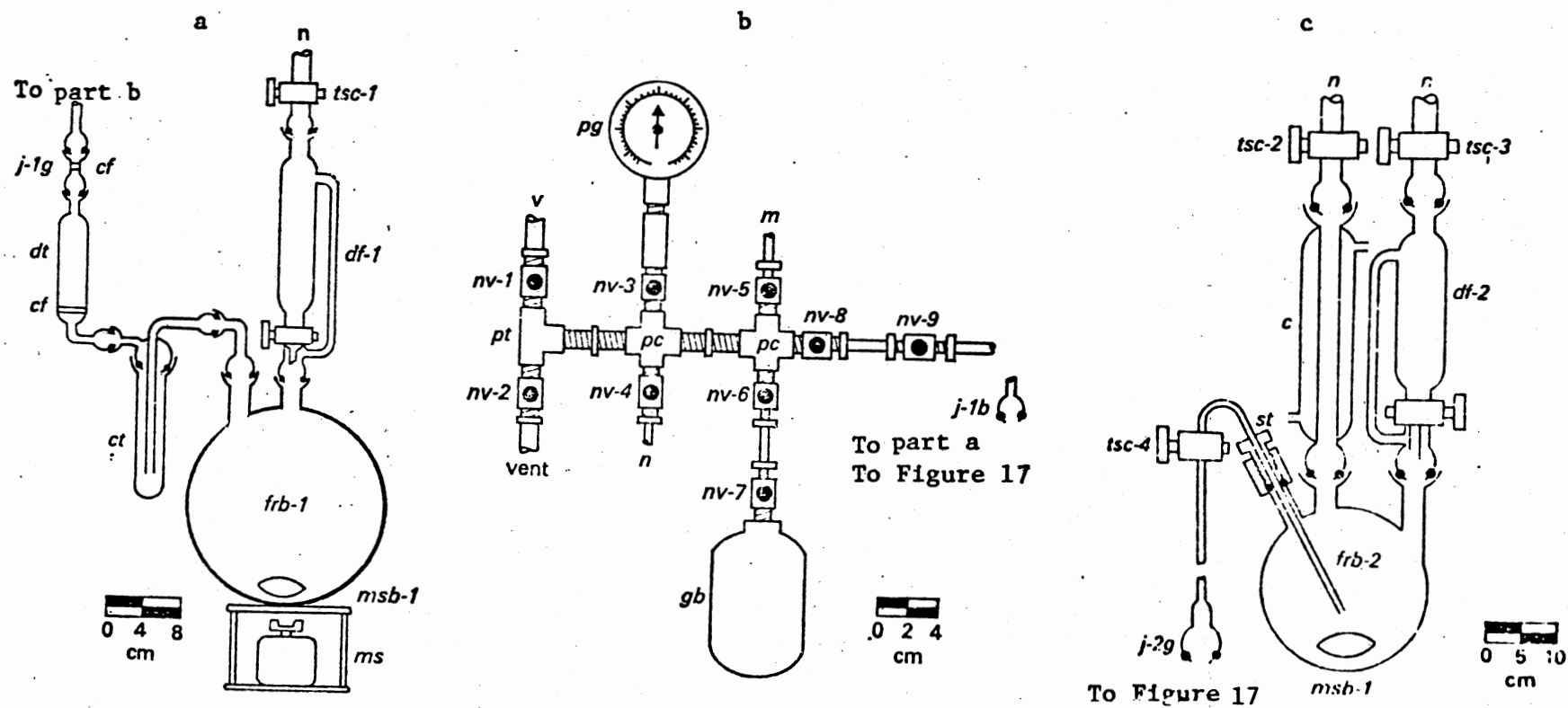


Figure 16. Grignard Carbonation Apparatus for a) Generation of $^{13}\text{CO}_2$, b) Transfer and Storage of $^{13}\text{CO}_2$ Through All Metal Vacuum Train, and c) Generation and Transfer of Grignard Reagent.

Legend for Figures 16 and 17.

<i>c</i>	condenser, water-cooled, sj 35/20 (sj spherical joint)
<i>cf</i>	coarse frit
<i>ct</i>	cold trap, 250ml, sj 50/30 O-ring joint and sj 18/9 O-ring joint side arm
<i>df-1</i>	dropping funnel, pressure equalising, 150ml, Teflon stopcock and sj 35/20 O-ring joints
<i>df-2</i>	dropping funnel, pressure equalising, 500ml, Teflon stopcock and sj 35/20 O-ring joints
<i>dt</i>	drying tube, 75ml with sj 28/15 O-ring joint at top and sj 18/9 O-ring joint at bottom
<i>frb-1</i>	flask, round-bottom, 500ml, 2-neck, sj 35/20
<i>frb-2</i>	flask, round-bottom, 1litre, 2-sj 35/20 and siphon tube; adapter constructed from Ace Glass, Inc thread connector No. 5027
<i>gb</i>	gas collection bottle, 1 litre, 0.25in pipe
<i>j-1b</i>	joint, brass, sj 18/9, Ace Glass, Inc, No. 7659-02, P.O. Box 688, Vineland, NJ 08360; O-ring added locally
<i>j-1g</i>	joint, O-ring ball and socket, glass, sj 18/9, Quartz Glass Corporation, 12440 Exline Street, El Monte, Calif. 91732
<i>j-1s</i>	joint, socket, stainless steel, sj 18/9, Ace Glass, Inc, No. 7658-22
<i>j-2g</i>	joint, O-ring ball, glass, sj 35/20, Quartz Glass Corp.
<i>j-2s</i>	joint, socket, stainless steel, sj 35/20, Ace Glass, Inc, No. 7548-40
<i>m</i>	to manometer
<i>ms</i>	magnetic stirrer
<i>msb-1</i>	magnetic stirring bar, Teflon-enclosed, egg-shaped, 12 x 36mm
<i>msb-2</i>	magnetic stirring bar, Teflon-enclosed, egg-shaped, 25 x 70mm
<i>n</i>	to nitrogen
<i>nv-1,2,4,5,6,7,8</i>	needle valve, brass, 0.25in pipe, 0.25in Swagelok
<i>nv-3</i>	needle valve, brass, 0.25in pipe
<i>nv-9</i>	needle valve, brass, 0.25in Swagelok
<i>nv-10</i>	needle valve, stainless steel, 0.5in pipe, or needle valve, ss, 0.375in pipe and two each 0.375in to 0.5in pipe reducer
<i>pc</i>	pipe cross, brass, 0.25in female
<i>pg</i>	pressure gauge, 0-200lb in ² , 0.25in pipe
<i>pt</i>	pipe T, brass, 0.25in female
<i>rv</i>	reaction vessel, stainless steel, 1700ml; see reference 8 for construction details of a similar vessel
<i>st</i>	siphon tube and threaded bushing, Ace Glass, Inc No. 5029
<i>tsc-1 through tsc-4</i>	Teflon stopcock, 2mm
<i>v</i>	to vacuum

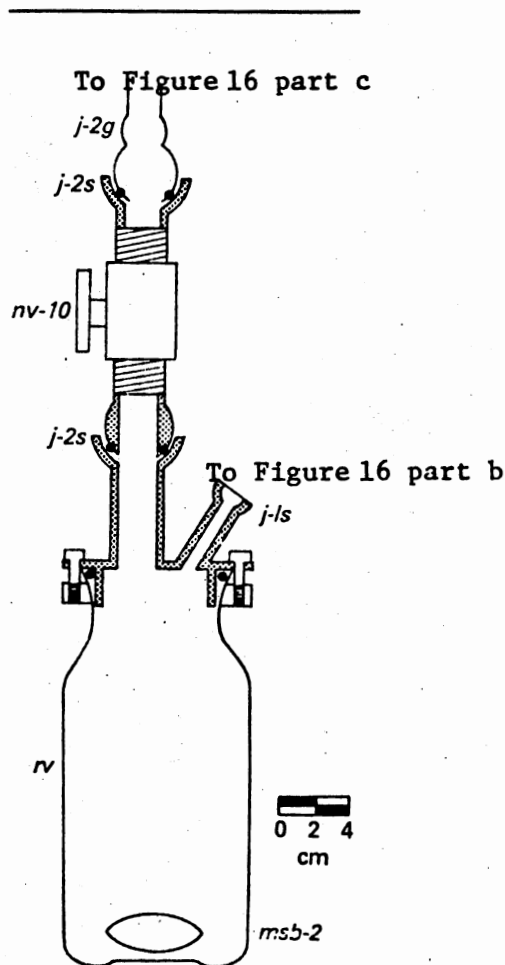


Figure 17. All Metal Reactor for Carbonation of Grignard Reagent

the carbonation vessel (Figure 17) where the mixture was allowed to warm and stir until the reaction reached completion. Unreacted $^{13}\text{CO}_2$ was recovered by bubbling into a $\text{Ba}(\text{OH})_2$ trap. Trial carbonation reactions with commercial dry ice⁴⁸ proved to be unsatisfactory, and were a contributing factor in the need to develop the all-metal reactor and the currently used carbonation procedure.

Other reaction steps involved in Figures 14 and 15 are well known and widely documented. However, some steps deserve comment. Diester 32a was unchanged by prolonged hydrolysis in refluxing $\text{HCl}/\text{HOAc}/\text{H}_2\text{O}$.⁴⁹ However, conversion of 32a to 32b was accomplished in high yield by alkaline hydrolysis ($\text{NaOH}/\text{ethanol}$) followed by acidification. Decarboxylation of 32b to 33 is best carried out by heating the diacid 32b at 175-220°C.

Three routes were investigated for the conversion of alcohol 34a to the corresponding halide 34b or 34c. The chloro-compound 34b was obtained in 56% yield from 34a using thionyl chloride and pyridine.⁵⁰ A substantial polymeric pot residue remained after distillation. The bromo-compound 34c was synthesized from 34a using triphenylphosphine and bromine in CCl_4 at 40°C in 86% yield.⁵¹ In contrast, treatment of 34a with PBr_3 gave 34c in 37% yield.⁵² As with the chloro-compound 34b, 34c from the PBr_3 reaction gave considerable pot residue.

Formation of the Grignard reagent from the bromo-compound 34c proceeded much faster than from the corresponding chloride 34b and appears to be quantitative. Reaction conditions for the formation of the Grignard reagents of both 34b and 34c were critical. Attempts to initiate Grignard reagent formation by intermittent warming with a heat gun failed, and constant heating at reflux with a heating mantle was required. Preformed methylmagnesium iodide was superior to iodine or dichloroethane for

initiating the formation of Grignard reagent. Initiation without this treatment occurs slowly. Grignard reagent formation from 24, 34b, and 34c requires 1.5-2.5 h at reflux regardless of the initiation method. Pure THF and ethyl ether were found to be inferior to benzene/THF (9:1, V/V) as solvents.⁵³

CHAPTER VII

EXPERIMENTAL

1-¹³C-4-phenylbutanoic Acid (25b). Labeled carbon dioxide (¹³CO₂, 0.21 mol) was generated⁴⁷ by adding 200 mL of H₃PO₄ to an aqueous slurry of 46.1 g of Ba¹³CO₃ (92% ¹³C).⁴⁶ Preparation of the Grignard reagent was accomplished using the previously described Grignard apparatus.⁴⁷

In a three-necked flask was placed 6.7 g (0.28 mol) of Mg turnings and 300 mL of 9:1 benzene:THF solution. This solution was brought to reflux as 50 g (0.25 mol) of 3-phenyl-1-propylbromide (24) was added slowly through an addition funnel. After the reaction was initiated, reflux was maintained an additional 45 min with most of the Mg reacted.

The Grignard reagent was transferred by siphoning to a stainless steel reactor.⁴⁷ After cooling the stainless reaction vessel to liquid nitrogen temperature, ¹³CO₂ was sublimed into it, and the system was gradually warmed (overnight), after which unreacted ¹³CO₂ was recovered.

The stainless steel vessel was removed, and its contents were poured over 500 g of ice. The mixture was acidified with conc. HCl and extracted 3x with ethyl ether. The combined ether layers were washed 2x with saturated Na₂CO₃ (ca. 1 L), filtered through MgSO₄ and concentrated to give 10 g of neutral product.

The Na₂CO₃ extracts containing the labeled acid were acidified with conc. HCl followed by extraction (2x) with ethyl ether. The organic layer was filtered through MgSO₄ and concentration of the ether fraction

yielded 26.9 g (0.16 mol) of ^{13}C -labeled 25b (76.2% yield) as white crystals (mp 50–51°C) [lit.⁵⁴ 52°C for unlabeled acid]: IR (melt) 2955 (–CO₂H), 1660 (C=O), 745,700 (C=CH bend) cm⁻¹; ^1H NMR³⁷ (DCCl₃) δ 2.65–3.1 (m, 2, ArCH₂CH₂), 7.05–7.25 (m, 5, ArH), 11.04 (s, 1, CO₂H); ^{13}C NMR⁵⁵ (DCCl₃) ppm 26.0 (ArCH₂CH₂), 33.2 (ArCH₂), 34.8 (CH₂CO₂H), 125.7 (C-4), 128.1 (C-2, C-3, C-5, and C-6), 140.8 (C-1), 180.0 (C=O); MS m/z (rel. intensity), 165.2 (M⁺, 1.6), 163.2 (4.7), 147.2 (11.5), 104.3 (84.7), 91.2 (100).

1- ^{13}C -3,4-dihydro-1(2H)-naphthalenone (26b). The labeled acid, 25a, (61.0 g, 0.37 mol) was added to 500 g of polyphosphoric acid and mechanically stirred. The mixture was heated at 95–105°C for 1 h, then poured over ice and stirred to yield greenish-white crystals. The product was extracted with ether, filtered through MgSO₄, and concentrated. After Kugelrohr distillation (64°C, 0.07 mm) [lit.^{41c} 133 (15 mm) for ^{14}C -labeled ketone], compound 26b was obtained in 99% yield (54 g, 0.37 mol) as a transparent colorless liquid: IR (neat) 1575 (C=O), 1625 (C=C str), 760, 725 (C=CH bend) cm⁻¹; ^1H NMR³⁷ (DCCl₃) δ 1.90–2.20 (pentet, J=6 Hz, 2, ArCH₂CH₂), 2.48–2.68 (q, J=7 Hz, 2, ArCH₂), 2.82–2.96 (t, J=6 Hz, 2, ArCOCH₂), 7.10–7.46 (m, 3, ArH), 7.85–8.05 (m, 1, ArH peri to C=O); ^{13}C NMR⁵⁵ (DCCl₃) ppm 22.7 (C-3), 29.0 (C-4), 38.5 (C-2), 125.8 (C-6), 126.2 (C-7), 128.1 (C-5), 131.8 (C-8), 132.6 (C-8a), 143.7 (C-4a), 197.1 (C=O); MS m/z (rel. intensity), 147.1 (M⁺, 58.1), 119.0 (100), 115.0 (14.5), 91.0 (15.5), 90.0 (70.7), 89.0 (25.7).

1- ^{13}C -1,2,3,4-tetrahydronaphthalene (27d). A mixture, containing 56.8 g (0.39 mol) of labeled ketone 26b and 5 g 5% Pd/C in 500 mL acetic acid, was hydrogenated at 70–80°C and 35 psig. The reaction was stopped after hydrogen uptake ceased. The mixture was filtered, concentrated,

neutralized with Na_2CO_3 , extracted with isohexane, and dried (MgSO_4). The hydrocarbon, 27d, was obtained in 98.5% yield (50.6 g, 0.38 mol) after concentration and Kugelrohr distillation (35°C , 0.13 mm) [lit.⁵⁶ 45°C (0.3 mm) for the unlabeled hydrocarbon]: IR (neat) 1500, 1450 (C=C str), 740 (C=C-H bend) cm^{-1} ; $^1\text{H NMR}^{37}$ (DCCl_3) δ 1.70-1.90 (m, 4, ArCH_2CH_2), 2.00-2.20 (m, 1, $\text{Ar}^{13}\text{CH}_a\text{H}_b$), 2.65-2.90 (m, 2, ArCH_2), 3.30-3.50 (m, 1, $\text{Ar}^{13}\text{CH}_a\text{CH}_b$), 7.05 (s, 4, ArH); $^{13}\text{C NMR}^{55}$ (DCCl_3) ppm 23.3 (C-2,C-3), 29.3 (C-1, C-4), 125.1 (C-6,C-7), 128.8 (C-5, C-8), 136.6 (C-4a,C-8a); MS m/z (rel. intensity), 133.1 (M^+ , 69.2) 129.1 (31.4), 105.1 (100), 104.1 (60.7), 92.1 (33.6), 91.1 (37.4).

1- ^{13}C -Naphthalene (28d). Labeled tetralin 27d (1.52 g, 0.011 mol) was heated at $180\text{--}200^\circ\text{C}$ with 0.2 g of 10% Pd/C until H_2 evolution ceased. The mixture was then brought to reflux for an additional 15 min. After cooling, the solid was dissolved in ether and filtered through dicalite to remove the catalyst. The ether was concentrated, leaving an off-white product which was chromatographed on silica gel with cyclohexane as solvent. After concentrating the cyclohexane, hydrocarbon 28d (1.24 g, 0.01 mol) was obtained in 84% yield as white crystals, mp 76°C . Additional purification via picrate formation and regeneration raised the mp to 80°C [lit.⁵⁷ 80°C for unlabeled hydrocarbon]: IR (KBr) 1575 (C=C str), 785 (Ar-H bend) cm^{-1} ; $^1\text{H NMR}^{37}$ (DCCl_3) δ 7.05-7.90 (m, ArH); $^{13}\text{C NMR}^{55}$ (DCCl_3) ppm 126.0 (C-2, C-3, C-6, C-7), 128.1 (C-1, C-4, C-5, C-8), 133.7 (C-4a, C-8a); MS m/z (rel. intensity), 129.2 (M^+ , 100), 128.2 (19.0), 127.1 (6.92), 103.2 (6.35), 102.1 (4.33).

Diethyl Methyl(4-methylphenylmethyl)malonate (32a). In a 12 L fluted flask equipped with a turbine stirrer, addition funnel, heating mantle, Dean-Stark trap, thermometer, and nitrogen bubbler, was placed 1300 mL of anhydrous ethanol. Sodium (76 g, 3.3 g-atom) was added slowly over

30 min with stirring. The solution was maintained at reflux until all of the sodium had reacted, then 600 mL of ethanol was removed by distillation and 3 L of dry toluene was added. Diethyl methylmalonate (523 g, 3 mol) was added to the solution over 15 min, after which the toluene/ethanol azeotrope was removed until the temperature reached 108°C with sufficient toluene being added to maintain a homogeneous solution. p-Methylbenzylchloride (450 g, 3.2 mol) was added to the solution over 30 min and the addition funnel was rinsed with toluene. The mixture was then cooled, acidified with conc. HCl, and the organic layer was washed twice with water. The organic layer was dried (MgSO₄), filtered, concentrated by rotary evaporation, and vacuum-distilled at 115-130°C (0.1 mm) [lit.⁵⁸ 220°C (20 mm)] to give a 79% yield (662 g, 2.38 mol) of diester 32a: IR (neat) 1730 cm⁻¹ (C=O); ¹H NMR³⁷ (DCCl₃) δ 1.25 (t, J=7 Hz, 6, -CH₂CH₃), 1.32 (s, 3, CCH₃), 2.30 (s, 3, ArCH₃), 3.18 (s, 2, ArCH-), 4.18 (q, J=6 Hz, 4, -CH₂CH₂-), 7.02 (s, 4, ArH); ¹³C NMR⁵⁵ (DCCl₃) ppm 14.0 (OCH₂CH₃), 19.7 (CCH₃), 20.9 (ArCH₃), 54.9 (CCH₃), 61.1 (OCH₂), 128.9 (C-3, C-5), 130.2 (C-2, C-6), 133.3 (C-1), 136.3 (C-4), 171.7 (C=O); MS m/z (rel. intensity) 278 (M⁺, 23.4), 204 (54.5), 158 (28.8), 130 (21.3), 105 (100), 91 (11.1).

Methyl(4-methylphenylmethyl)malonic Acid (32b). In a 5 L 1-neck flask equipped with reflux condenser was placed 355 g (1.27 mol) of the diester 32a. Ethanol (1500 mL) and 10% NaOH (2500 mL) were added and the solution was stirred at reflux for 4 h. The reflux condenser was then replaced with a distillation head and ethanol was removed by distillation. The distillation residue was cooled and extracted with ether. The aqueous layer was poured over ice, and acidified (conc. HCl) to give white crystals, mp 170-171°C (dec.). Recrystallization from ethyl ether afforded a 97% yield (275 g, 1.24 mol) of the diacid 32b,

mp 173-174°C (dec) [lit.⁵⁹ 178-180°C]: IR (KBr) 3000 ($-\text{CO}_2\text{H}$), 1725 ($\text{C}=\text{O}$) cm^{-1} ; $^1\text{H NMR}^{37}$ (acetone d_6) δ 1.30 (s, 3, RCH_3), 2.27 (s, 3, ArCH_3), 3.18 (s, 2, ArCH_2-), 7.09 (s, 4, Ar-H); $^{13}\text{C NMR}^{55}$ (DCCl_3) ppm 20.0 (CCH_3), 21.0 (ArCH_3), 41.3 (ArCH_2), 54.9 (CCH_3), 129.5 (C-3,C-5), 130.9 (C-2,C-6), 131.3 (C-1), 136.8 (C-4), 173.6 ($\text{C}=\text{O}$); MS m/z (rel. intensity) 178.05 ($\text{M}-\text{CO}_2^+$, 12), 117.04 (5.87), 106.03 (9.29), 105.04 (100), 91.05 (7.04), 77.06 (7.19). Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{O}_4$: C, 64.85; H, 6.35. Found: C, 65.00; H, 6.35.

2-Methyl-3-p-tolylpropionic Acid (33). To a 500 mL flask equipped with thermometer, Vigreux column, and gas bubble tube were added 127 g (0.57 mol) of diacid, 32b. The temperature was increased to 140°C at which evolution of CO_2 was observed. Heating was continued until at 220°C, CO_2 evolution ceased. Distillation (Kugelrohr, 110°C, 0.1 mm Hg) [lit.⁶¹ 168-169°C (9 mm)] gave 99 g (0.56 mol, 98%) or monocarboxylic acid, 33, as white crystals, mp 39-41°C: IR (KBr) 3278 (CO_2H), 1695 ($\text{C}=\text{O}$) cm^{-1} ; $^1\text{H NMR}^{37}$ (DCCl_3) δ 1.11 (d, $J=3$ Hz, 3, RCH_3), 2.26 (s, 3, ArCH_3), 2.46-3.06 (m, 3, ArCH_2- , $-\text{CHCH}_3$), 7.08 (s, 4, ArH); $^{13}\text{C NMR}^{55}$ (DCCl_3) ppm 16.4 (CHCH_3), 21.0 (ArCH_3), 38.9 (ArCH_2), 41.4 (CH), 128.9 (C-3,C-5), 129.1 (C-2,C-6), 135.8 (C-4), 136.0 (C-1), 183.0 ($\text{C}=\text{O}$); MS m/z (rel. intensity) 178.05 (M^+ , 9.92), 117.02 (9.20), 106.05 (10.36), 105.05 (100), 91.05 (10.56), 77.03 (8.73). Anal. Calcd for $\text{C}_{11}\text{H}_{14}\text{O}_2$: C, 74.13; H, 7.92. Found: C, 74.31; H, 8.00.

2-Methyl-3-p-toyl-1-propanol (34a). To a solution of 353 g (2.5 mol) of diisobutylaluminumhydride in 1 L of dry toluene was added a solution of 127 g (0.71 mol) of monoacid 33 in 300 mL of toluene over a 1 h period at 30°C. After addition was complete, excess reducing agent was destroyed by the addition of 82 mL of ethyl acetate. The solution was poured carefully over 3 Kg ice, and acidified with 1.5L

of concentrated HCl. The mixture was placed in a separatory funnel and the organic layer was removed. The aqueous layer was extracted twice with toluene, and the organic layers were combined, washed twice with water, dried (MgSO_4), and filtered. Distillation (Kugelrohr, 103°C , 1 mm Hg) [lit.^{6.0} 129°C (12 mm)] afforded an 84% yield (98 g, 0.60 mol) of alcohol 34a: IR (neat) 3333 (OH), 1036 (C-O) cm^{-1} ; $^1\text{H NMR}$ ³⁷ (acetone-d) δ 7.05 (s, 4, ArH), 3.45 (d, $J=6\text{Hz}$, 2, $-\text{CH}_2\text{O}-$), 2.85-2.21 (m, 2, ArCH₂), 2.3 (s, 3, ArCH₃), 1.9 (octet, $J=6\text{ Hz}$, 1, 3°H), 0.88 (d, 3, $J=6\text{ Hz}$, R-CH₃); $^{13}\text{C NMR}$ ⁵⁵ (DCCl_3) ppm 16.4 (CHCH₃), 20.9 (ArCH₃), 37.8 (CH), 39.2 (ArCH₂), 67.2 (CH₂OH), 128.9 (C-3,C-5), 129.0 (C-2,C-6), 135.0 (C-4), 137.6 (C-1); MS m/z (rel. intensity) 164.00 (M^+ , 20.81), 130.99 (25.36), 106.09 (30.09), 105.09 (100), 91.10 (18.81), 77.21 (12.24). Anal. Calcd for $\text{C}_{11}\text{H}_{16}\text{O}$: C, 80.44; H, 9.83. Found: C, 80.16; H, 9.79.

2-Methyl-3-p-tolyl-1-chloropropane (34b). To a cooled (ice bath) solution containing 100 g (1.27 mol) of pyridine and 110 g (0.72 mol) of alcohol 34a was slowly added 107 g (0.9 mol) of thionyl chloride. The solution was stirred for an additional 15 min, and then heated to 60°C .

The mixture was then poured into a separatory funnel and extracted with ethyl ether. The ether extract was washed with 10% HCl, and then twice more with 800 mL portions of H_2O . The organic layer was dried (Na_2SO_4), filtered, and the solvent concentrated to yield 110 g (0.6 mol) of chloride 34b.

Distillation (Kugelrohr; 85°C , 0.1 mm) gave 74 g (0.404 mol, 56.2%) of chloride 34b: IR (neat) 833, 795 (C-Cl) cm^{-1} ; $^1\text{H NMR}$ ³⁷ (DCCl_3) δ 1.00 (d, $J=7\text{ Hz}$, 3, RCH₃), 1.90-2.25 (m, 1, CH), 2.30 (s, 3, ArCH₃),

2.40-2.90 (m, 2, ArCH₂), 3.40 (d, J=5 Hz, 2, CH₂Cl), 7.05 (s, 4, ArH);
¹³C NMR⁵⁵ (DCCl₃) ppm 17.6 (CHCH₃), 21.0 (ArCH₃), 37.5 (CH), 39.7 (ArCH₂),
 50.2 (CH₂Cl), 129.0 (C-2, C-3, C-5, C-6), 135.4 (C-4), 136.6 (C-1); MS
 m/z (rel. intensity) 184.01 (M+2⁺, 3.86), 181.95 (M⁺, 10.87), 130.98
 (5.69), 105.06 (100), 91.00 (6.05), 77.10 (8.73). Anal. Calcd. for
 C₁₁H₁₅Cl: C, 72.33; H, 8.22. Found: C, 72.45; H, 8.20.

2-Methyl-3-p-tolyl-1-bromopropane (34c). A. To a CCl₄ solution
 containing 149 g (0.91 mol) of alcohol 34a was added 261 g (1.0 mol) of
 P(C₆H₅)₃.⁶¹ Through an addition funnel was added 160 g (1.0 mol) of Br₂,
 keeping the temperature approximately 40°C. The reaction mixture was
 allowed to stir overnight under N₂. The resulting precipitate was
 filtered and washed with CCl₄, then twice with H₂O. The CCl₄ wash was
 filtered through MgSO₄ and concentrated under vacuum. The residue was
 fractionally distilled at 75°C (0.13 mm) [lit.⁶⁰ 125°C (12 mm)] to give
 an 86% yield (177 g, 0.78 mol) of bromide 34c.

B. To a cooled (ice bath) solution containing 150 mL of toluene and
 68.5 g (0.42 mol) of alcohol 34a was slowly added 40 g (0.15 mol) of
 phosphorous tribromide. After one hour, the ice bath was removed and the
 solution was stirred overnight. The mixture was poured over ice and
 acidified with conc. HCl. The resulting mixture was poured into a separ-
 atory funnel and extracted. The aqueous layer was extracted again with
 toluene. The organic layers were combined and washed with saturated
 Na₂CO₃ and water respectively. The organic phase was filtered through
 MgSO₄ and concentrated by rotary evaporation.

Distillation (Kugelrohr, 115°C, 0.18 mm) afforded 35.3 g (0.16 mol,
 37%) of the bromide 34c: IR (neat) 650, 792 (C-Br) cm⁻¹; ¹H NMR³⁷ (DCCl₃)
 δ 1.01 (d, J=6 Hz, 3, RCH₃), 1.8-2.2 (m, 1, -CH-), 2.31 (s, 3, ArCH₃),

2.55 (d, J=6 Hz, 1, ArCH₂-), 2.66 (d, J=6 Hz, 1, ArCH₂-), 3.29 (d, J=2 Hz, 1, CH₂Br), 3.35 (d, J=2 Hz, 1, CH₂Br), 7.07 (s, 4, ArH); ¹³C NMR⁵⁵ (DCCl₃) ppm 18.7 (CHCH₃), 20.9 (ArCH₃), 37.1 (CH), 40.5 (ArCH₂, CH₂Br), 129.0 (C-2, C-3, C-5, C-6), 135.4 (C-4), 136.5 (C-1); MS m/z (rel. intensity) 228 (M+2⁺, 6.74), 226 (M⁺, 6.74), 145 (55.2, -HBr), 130 (100), 105 (94.61), 91 (84.80).

1-¹³C-3-Methyl-4-p-tolylbutanoic Acid (34d). Labeled carbon dioxide⁴⁶ (¹³CO₂, 0.22 mol) was generated as described⁴⁷ by adding 200 mL of H₃PO₄ to an aqueous slurry of 48.5 g of Ba¹³CO₃ (92% ¹³C).⁴⁶ Preparation of the Grignard reagent was accomplished using the Grignard apparatus described previously.⁴⁷ In the 3-necked flask was placed 7.1 g (0.29 mol) of Mg turnings and 300 mL of 9:1 benzene:THF solution. This solution was brought to reflux as 60 g (0.26 mol) of bromide 34c was added slowly through the addition funnel. After the reaction was initiated, reflux was maintained for an additional 45 min with most of the Mg reacted.

The Grignard reagent was transferred by siphoning to a stainless steel reactor.⁴⁷ After cooling the stainless reaction vessel to liquid nitrogen temperature, ¹³CO₂ was sublimed into it, and the system was gradually warmed (overnight), after which unreacted ¹³CO₂ was recovered.

The stainless steel vessel was removed, and its contents were poured over 500 g ice. The mixture was acidified with conc. HCl and extracted 3x with ethyl ether. The combined ether layers were washed 2x with saturated Na₂CO₃ (ca. 1 L), filtered through MgSO₄, and concentrated to give 9 g of neutral product.

The Na₂CO₃ extracts containing the labeled acid were acidified with conc. HCl followed by extraction (2x) with ethyl ether. The organic

layer was filtered through MgSO_4 and concentration of the ether fraction yielded 40.5 g (0.23 mol) of ^{13}C -labeled acid, 34d (94.5).

Distillation of the product (Kugelrohr, 113°C , 0.13 mm) [lit.⁶² $180\text{--}181^\circ\text{C}$ (15 mm) for unlabeled acid] afforded 39.3 g (0.22 mol) of 34d in 92% yield: IR 3000 ($-\text{CO}_2\text{H}$), 1700 ($\text{C}=\text{O}$) cm^{-1} ; $^1\text{H NMR}^{37}$ (DCCl_3) δ 0.95 (d, $J=6$ Hz, 3, RCH_3), 2.15–2.40 (m, 3, CH , $\text{CH}_2\text{CO}_2\text{H}$), 2.29 (s, 3, ArCH_3), 2.49 (d, $J=3$ Hz, 1, ArCH_2), 2.57 (d, $J=3$ Hz, 1, ArCH_2), 7.05 (s, 4, ArH); $^{13}\text{C NMR}^{55}$ (DCCl_3) ppm 19.5 (CHCH_3), 20.9 (ArCH_3), 32.1 (CH), 42.5 (ArCH_2 , $\text{CH}_2\text{CO}_2\text{H}$), 129.1 (C-2, C-3, C-5, C-6), 135.4 (C-4), 136.9 (C-1), 180.0 (CO_2H); MS m/z (rel. intensity) 193.02 (M^+ , 12.17), 131.96 (58.03), 116.96 (10.41), 104.99 (100), 77.02 (9.15).

1- ^{13}C -3,7-Dimethyl-3,4-dihydro-1(2H)-naphthalenone (35). To 485 g of polyphosphoric acid was added 54 g (0.28 mol) of ^{13}C -labeled carboxylic acid, 34d. The mixture was heated at $95\text{--}105^\circ\text{C}$ for 1 h, then poured over ice and stirred to yield greenish-white crystals. The product was extracted with ether, filtered through MgSO_4 , concentrated, and vacuum-distilled at 80°C (0.1 mm) lit.⁶² $140\text{--}150^\circ\text{C}$ (15 mm) for unlabeled ketone to give a 97% yield (47 g, 0.27 mol) of labeled ketone 35 as white crystals, mp $49\text{--}50^\circ\text{C}$ [lit.⁶² $52\text{--}53^\circ\text{C}$ for unlabeled ketone]: IR (KBr) 1670 ($\text{C}=\text{O}$), 1645 (Ar) cm^{-1} ; $^1\text{H NMR}^{37}$ (DCCl_3) δ 1.12 (d, $J=5$ Hz, 3, RCH_3), 2.10–3.10 (m, 5, ArCH_2 , CH , $\text{CH}_2\text{C}=\text{O}$), 2.35 (s, 3, ArCH_3), 7.05–7.40 (two doublets, $J=8$ Hz ea., 3, ArH-5,6), 7.84 (s, 1, ArH-8); $^{13}\text{C NMR}^{55}$ (DCCl_3) ppm 20.9 (CHCH_3), 21.2 (ArCH_3), 36.6 (C-3), 37.7 (C-4), 48.2 (C-2), 127.1 (C-6), 128.6 (C-5), 128.8 (C-8), 134.4 (C-4a, C-7, C-8a), 198.6 ($\text{C}=\text{O}$); MS m/z (rel. intensity) 175.11 (M^+ , 1.78), 160.6 (52.96), 132.98 (100), 131.99 (16.14), 103.99 (79.61), 78.00 (18.92).

4- ^{13}C -2,6-Dimethyl-1,2,3,4-tetrahydronaphthalene (36). A solution

of 30.9 g (0.18 mol) of labeled ketone, 35, in 500 mL of acetic acid containing 3 g of 5% Pd/C was hydrogenated at 70-95°C at 35 psig. Hydrogen uptake ceased after 25 psig H₂ was consumed. The solution was filtered, concentrated, neutralized with Na₂CO₃, extracted with isohexane, and dried (MgSO₄). Kugelrohr distillation at 57°C (0.1 mm) [lit.⁶³ 241°C (760 mm) for unlabeled hydrocarbon] gave a 73% yield (20.7 g, 0.13 mol) of labeled hydrocarbon, 36: IR (neat) 1475, 1450 (C=C str), 800 (C=C-H bend), cm⁻¹; ¹H NMR³⁷ (DCCl₃) δ 1.02 (d, J=6 Hz, 3, RCH₃), 1.2-1.5 (m, 1, CH), 1.6-2.0 (m, 2, ArCH₂CH₂), 2.25 (s, 3, ArCH₃), 2.65-2.80 (2 doublets, J=4 Hz ea., 4, ArCH₂CH₂), 6.88 (s, 3, ArH); ¹³C NMR⁵⁵ (DCCl₃) ppm 20.9 (ArCH₃), 22.1 (CHCH₃), 29.3 (C-4), 29.5 (C-2), 31.7 (C-3), 37.8 (C-1), 126.3 (C-7), 128.9 (C-8), 129.0 (C-5), 133.6 (C-8a), 134.5 (C-6), 136.2 (C-4a); MS m/z (rel. intensity) 161.1 (M⁺, 62.6), 146.0 (36.9), 119.0 (100), 117.9 (28.3), 115.9 (18.3), 106.0 (18.6).

4-¹³C-2,6-Dimethylnaphthalene (37). Labeled hydrocarbon 36 (1.79 g, 0.01 mol) was heated at 180-200°C with 0.2 g of 10% Pd/C until H₂ evolution ceased and was then refluxed an additional 15 min. After cooling, the solid was dissolved in ether and filtered through dicalite. The ether was concentrated, leaving an off-white product which was chromatographed on silica gel with cyclohexane as solvent. After concentrating, 37 was obtained as white flakes (1.5 g, 0.01 mol, 96% yield) mp 111°C [lit.⁶⁴ 110-111°C for unlabeled hydrocarbon]: IR (KBr) 1600 (C=C str), 820, 890 (Ar-H bend) cm⁻¹; ¹H NMR³⁷ (DCCl₃) δ 2.46 (s, 6, ArCH₃), 7.18-7.68 (m, 6, ArH); ¹³C NMR⁵⁵ (DCCl₃) ppm 21.5 (ArCH₃), 126.6 (C-3, C-7), 127.0 (C-4, C-8), 128.1 (C-1, C-5), 132.0 (C-4a, C-8a), 134.4 (C-2, C-6); MS m/z (rel. intensity) 157.0 (M⁺, 100), 156.0 (43.1), 154.0 (10.7), 141.0 (50.2), 129.0 (13.6), 115.9 (10.9).

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33. Analytical and preparative HPLC separations were performed on a
Waters Associates system and Prep 500 system respectively
using Microporasil (silica gel) columns manufactured by Waters
Associates. n-Hexane was used as solvent. Analytical HPLC
separations were also accomplished on Microbondapak (C-18)
columns with CH₃CN:H₂O (4:1) but solubility limitations
prohibited preparative HPLC separation.
34. GC analysis of the reduction products of 1, 2a, 3a, 4a, and 4b were
done with a Hewlett-Packard 5750B instrument using a 6-ft x
0.25-in copper tubing column of 1.5% OV-17 and 1.95% QF-1 on
80-100 mesh Chromosorb Q at 200°C.
35. The author thanks Dr. G.W. Keen, CONOCO Inc., Ponca City, Oklahoma
74601, for obtaining GC-MS data on mixtures described in Part I
of this study. The GC-MS data was obtained on a Finnigan Model
4023 GC-MS system with a 30 m SP-2100 glass capillary column.
The spectra were scanned with a 1.1 sec. interval with a head
pressure of 30 psig programmed from 60-260°C at 8°C per minute.
Probe temperature 140°C.
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37. ¹H NMR spectra were recorded at 100.1 MHz on a Varian XL-100A.
Spectra were run in DCCl₃ using a deuterium lock and are re-
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38. ¹³C NMR spectra were recorded at 25.2 MHz in the FT mode on a
Varian XL-100A interfaced with a 12 K Nicolet 1080 computer

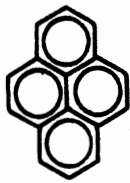
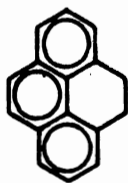
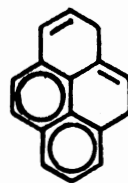
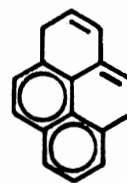
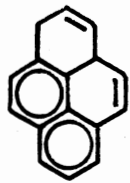
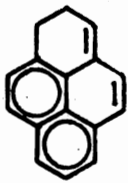
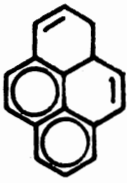
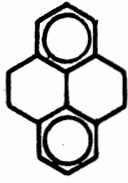
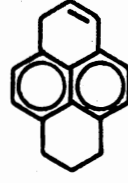
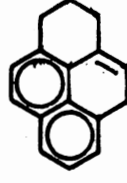
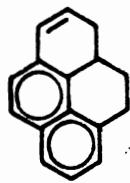
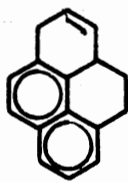
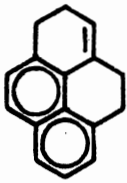
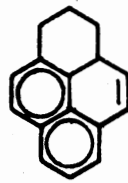
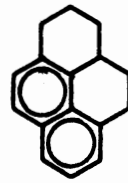
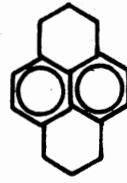
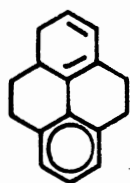
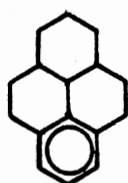
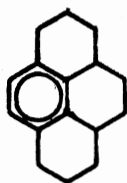
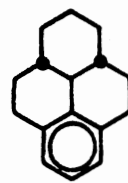
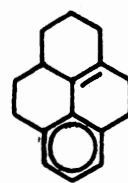
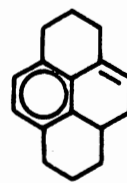
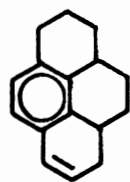
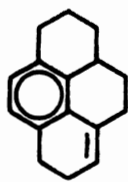
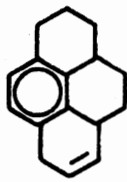
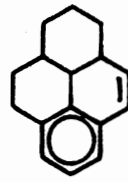
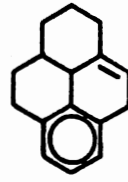
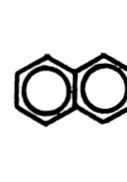
system. Spectra were run in DCCl_3 using a deuterium lock and are reported in ppm downfield from TMS.

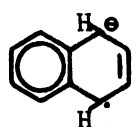
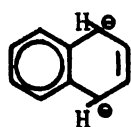
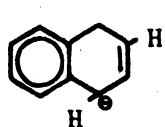
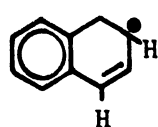
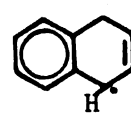
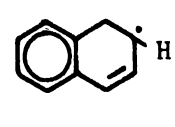
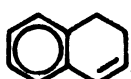
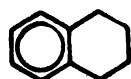
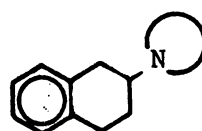
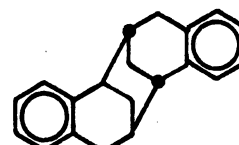
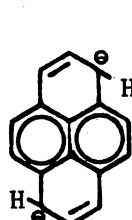
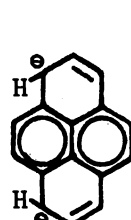
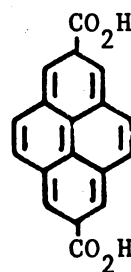
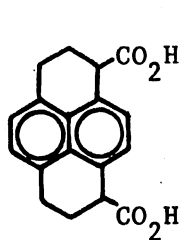
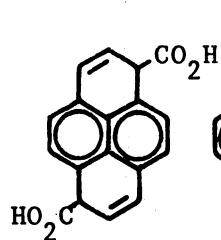
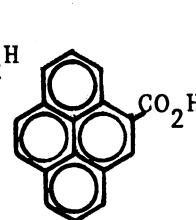
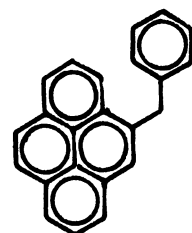
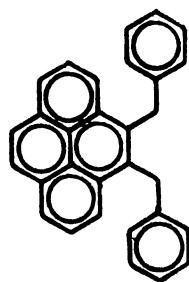
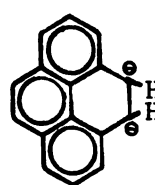
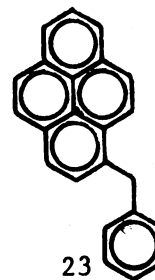
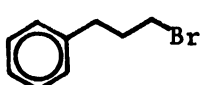
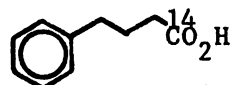
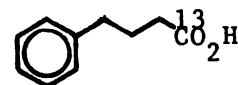
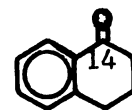
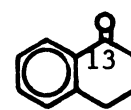
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45. Funding of this research study was provided by the U.S. Energy Research and Development Administration under Project E(49-18)-2305. We wish to also acknowledge our indebtedness to L. Kindley (DOE), D.C. Cronauer, and A.B. King for helpful suggestions.
46. The $^{13}\text{CO}_2$ as 90% $\text{Ba}^{13}\text{CO}_2$ (92% $^{13}\text{CO}_2$) was obtained from Mound Laboratories, Miamisburg, Ohio 45342.
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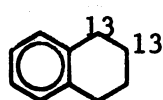
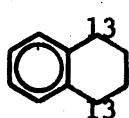
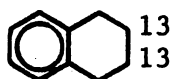
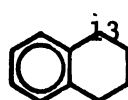
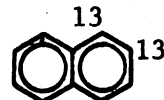
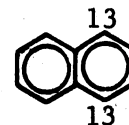
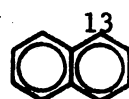
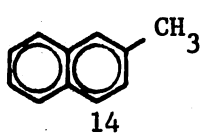
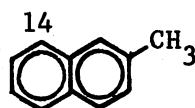
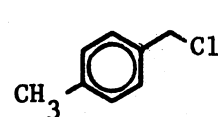
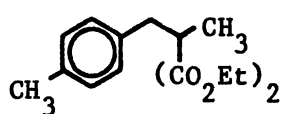
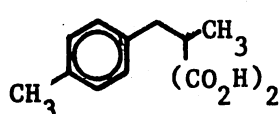
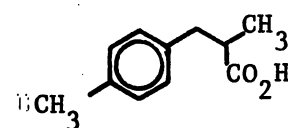
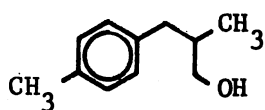
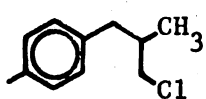
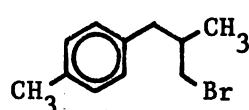
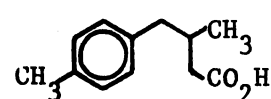
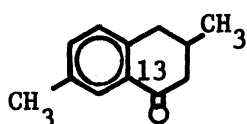
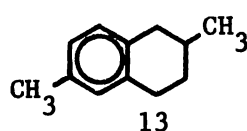
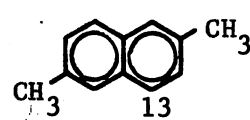
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55. The author thanks Drs. D.M. Jewell and K.S. Seshadri, Gulf Research and Development Company, Pittsburg, Pennsylvania, 15230, for the generous amount of time spent in obtaining and interpreting ^{13}C NMR and mass spectra. NMR spectra in Part II of this study were obtained by the pulsed FT technique at 20 MHz on a Varian CFT-20 spectrometer, equipped with 620/L computer with 16 K memory. The free induction decays, after a sufficient number of transients had been accumulated, were smoothed with an exponential function and Fourier transformed. Samples were studied in an 8 mm tube at a probe temperature of 36°C . Spectra were run using a deuterium lock and values are reported in ppm downfield from internal TMS.
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APPENDIX

GLOSSARY OF STRUCTURES

12a2b2c2d2e2f2g2h3a3b3c3d3e3f3g4a4b4c5a5b5c6a6b6c6d6e6f6g7

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27a27b27c27d28a28b28c28d29303132a32b3334a34b34c34d353637

VITA²

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II. SYNTHESIS OF 1-¹³C-Naphthalene and 4-¹³C-2,6-DIMETHYL-
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