ELECTROLYTIC REDUCTION OF POLYNUCLEAR

AROMATIC HYDROCARBONS

By

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PREFACE

I wish to express my gratitude to Dr. E. J. Eisenbraun for his invaluable guidance and counsel during the course of my graduate work. The author is grateful to Dr. Paul Arthur for his advice concerning electrolytic processes. Thanks are also due to Dr. P. W. K. Flanagan and Mr. M. C. Hamming of the analytical division of the Continental Oil Company, Ponca City, Oklahoma, for the instrumental analyses. I wish to thank Mr. R. C. Bansal for his help and for authentic samples from his collection. I wish to express appreciation to my wife, Patricia, for her patience and understanding.

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CHAPTER I

INTRODUCTION

This study was undertaken in connection with the American Petro-
leum Institute's Standard Samples Program in an attempt to find new
routes for synthesis of certain hydrocarbons which are difficult to
prepare through conventional methods. An important aspect of this
synthetic method is to gain a better understanding of electrolytic
reduction. Electrolytic reduction of polynuclear aromatic hydro-
carbons using platinum metal electrodes, alkali metal salts as elec-
trolytes, and low-molecular-weight amines as solvents has not been
extensively studied. Consequently, there is little known about the
effects produced by varying the structure of the amine solvent, the
structure of the aromatic hydrocarbon, the temperature of the reaction
and the nature and concentration of the alkali metal salt used as
electrolyte. It has been suggested[1] that this electrolytic process is
related to metal-amine reductions and accordingly, the mechanism devel-
oped to explain the Birch reduction and related reactions[2] may be uti-
lized in explaining electrolytic reduction.

The purpose of this research was to study the effects produced by
varying the reaction parameters and through analysis of products to
arrive at an explanation of how the various hydrocarbon reduction
products are formed.

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CHAPTER II

HISTORICAL

The first electrolytic reduction of an aromatic ring was reported in 1906. This was accomplished by Mettler,[3] who reduced benzoic acid to cyclohexene carboxylic acid using a mercury cathode and aqueous potassium hydroxide as the electrolyte and solvent.
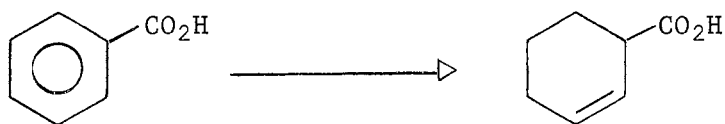

Since that time, there have been a few investigations into the polarographic reduction of benzene,[4] naphthalene,[5] and phenanthrene[6] at a dropping mercury electrode, i.e. a micro-electrode, but there have been only a few studies of reduction of aromatic nucleii at macro-electrodes. The literature review for this thesis will be concerned primarily with reductions at macro-electrodes. Reaction products from micro- and macro-electrodes have been shown to differ due to charge density and concentration of the reactive species in the vicinity of the electrodes.[7]

Benzoic acid in aqueous sulfuric acid solution has also been reduced with platinized platinum electrodes prepared by depositing platinum from a solution of chloroplatinic acid onto smooth platinum. It had been shown that smooth platinum electrodes were not effective in this solvent.[8]

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Polarographic reduction of naphthalene has been used to show the electrolytic reduction mechanism involves a two-electron transfer proceeding via 1,4-addition.[9] The only report of electrolytic reduction of a naphthalene nucleus at macro-electrodes is that of 2-methoxy- and 1,2,7-trimethoxynaphthalene to the corresponding enol ether.[10] A lead cathode and aqueous sulfuric acid-dioxane solvent was used.
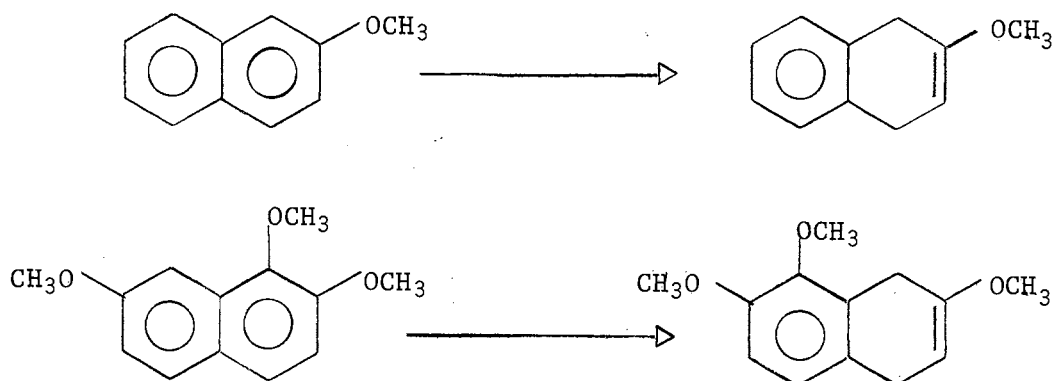
Coupling products usually result from electrolytic reduction of heterocyclic aromatic amines in aqueous sulfuric acid using a lead cathode.[11]
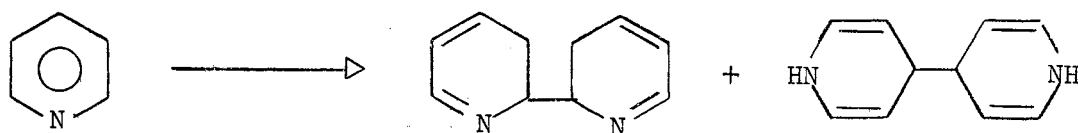
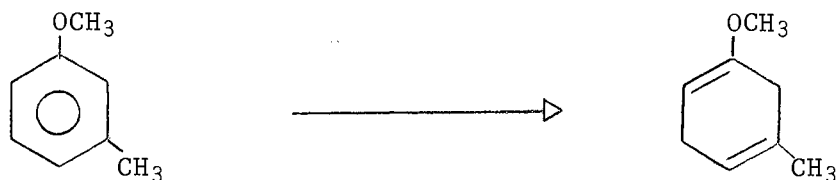However, the electrolytic reduction of indole results in hydrogenation of the heterocyclic ring:[12]
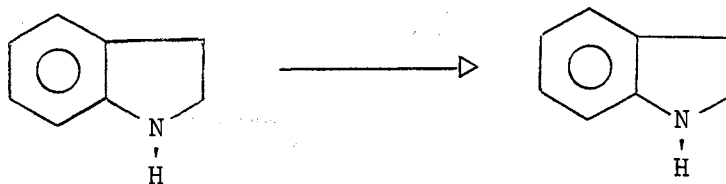
Lyons[13] reported reduction potentials of -1.89 and -2.88 V for

naphthalene and benzene respectively. These data may be used to explain the ease of reduction of naphthalene to tetralin and the resistance of tetralin to further reduction in a sodium-ammonia system.

Until 1946, all electrolytic reductions were carried out in water, aqueous ethanol, or aqueous-dioxane solvents, using electrodes of platinized platinum, mercury, or lead and a sulfuric acid electrolyte.

In 1946, Birch[14] reported electrolytic reduction of 3-methylanisole to 2,5-dihydro-3-methylanisole using liquid ammonia as solvent, sodium ethoxide as electrolyte, and a smooth copper cathode at -40°.

There have been two additional investigations into the electrolytic reduction of a benzenoid hydrocarbon.[15,16] One investigator was able to obtain selective reduction.[15] Selective reduction was also observed in Mettler's original work[3] in which phthalic acid was reduced at a mercury cathode. The use of aqueous sulfuric acid electrolyte gave 1,2,3,4-tetrahydrophthalic acid, while an aqueous potassium hydroxide electrolyte gave 1,2-dihydrophthalic acid.
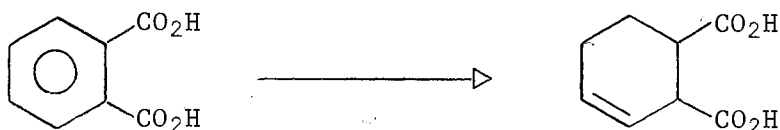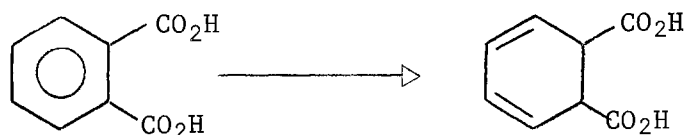
Benkeser and Kaiser[15] reported selective reduction of benzene and alkyl-substituted benzenes using methylamine solvent, lithium chloride electrolyte and a smooth platinum cathode. By separating the anode and cathode compartments, 1,2,3,4-tetrahydro derivatives were obtained. However, dihydro products were reported when the electrodes were not placed in separate compartments.
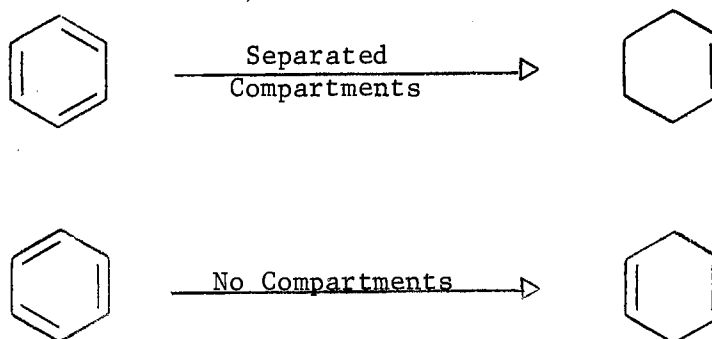
Reduction to tetrahydro products when separate cell compartments were used was attributed to an excess of lithium methylamide in the cathode compartment,[17] since it has been shown that excess lithium alkylamide will isomerize non-conjugated cyclic dienes to conjugated dienes. These conjugated dienes are then subject to further reduction by the lithium-amine system.

Sternberg[16] et al. reported no selectivity during electrolytic reduction using compartmented electrodes; however, in this case, a graphite cathode, ethylenediamine solvent and tetra-n-butylammonium-iodide electrolyte vide ante were used. The divider in this case was a sintered glass membrane, whereas Benkeser and Kaiser used an asbestos divider.[15]

The multistep mechanism of Krapcho and Bothner-By[1] may be used as modified by Sternberg et al. as shown in Fig. 1 to explain the reduction of aromatic hydrocarbons during electrolysis.

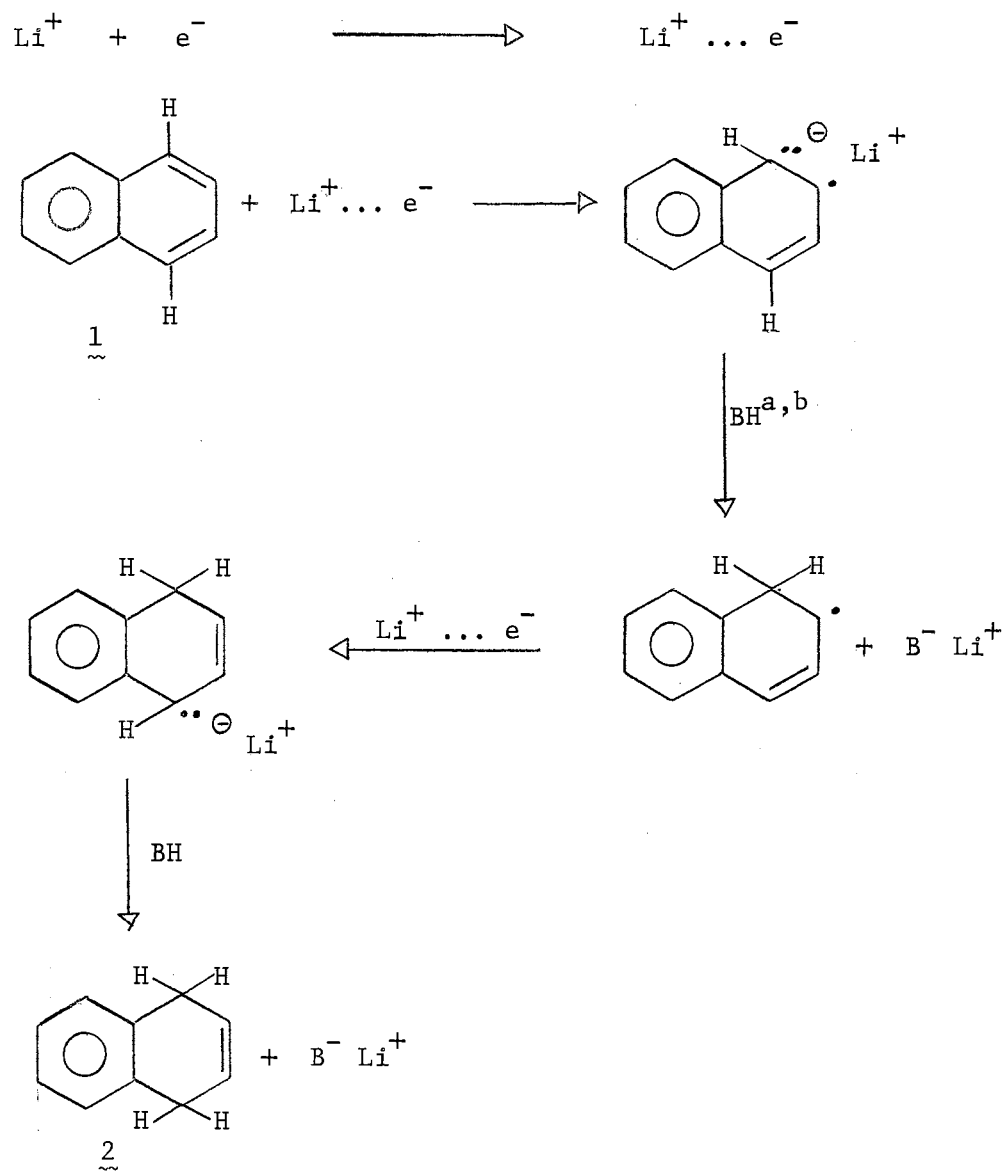$$Li^+ \; + \; e^- \longrightarrow Li^+ \ldots e^-$$

Figure 1. Mechanism for Electrolytic Reduction

[a]Krapcho and Bothner-By[1] originally suggested BH = C_2H_5OH.

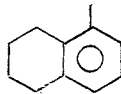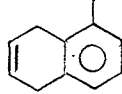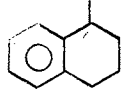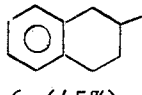[b]Sternberg, Markby, and Wender[16] suggested the amine solvent functions as BH.

CHAPTER III
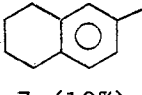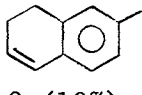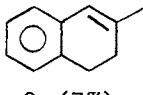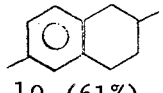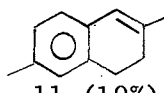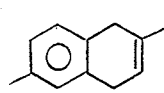
RESULTS AND DISCUSSION

Electrolytic reduction of aromatic hydrocarbons using lithium-chloride as electrolyte and a low-molecular-weight amine as solvent has been restricted to benzenoid hydrocarbons.[15,16] It was felt that extension of this reduction system to polynuclear aromatic hydrocarbons would allow synthesis of unsaturated hydrocarbons which are ordinarily not available through conventional routes. Thus, electrolytic reduction could be a step in the partial reduction of aromatic hydrocarbons to cyclic olefins. Since benzenoid hydrocarbons can only be catalytically hydrogenated under high pressure and at elevated temperatures, electrolytic reduction is an attractive approach toward destruction of the ring aromaticity because low temperatures and atmospheric pressure are generally used. Other manipulations would be feasible once the pi system is disrupted.

Before applying electrolytic reduction to polynuclear aromatic hydrocarbons, it was felt that a better understanding of the parameters affecting the reaction pathways was necessary. These parameters are the nature of the electrode, temperature, concentration of metal salt, structure of amine, and structure of the hydrocarbon. The results of our studies are reported in Tables I, II, III, and IV. The composition of these reaction products was determined through the use of gas chromatography, NMR, and mass spectroscopy analyses. In

TABLE I
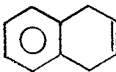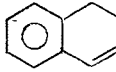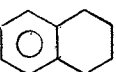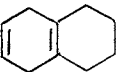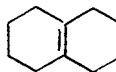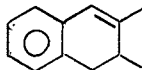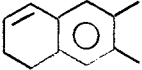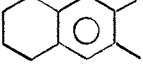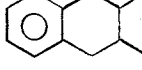
ELECTROLYTIC REDUCTION OF SELECTED NAPHTHALENES USING ETHYLAMINE AND PROPYLAMINE SOLVENT

Starting Material	Solvent	Recovered Starting Material, %	Distribution of Hydrocarbons				
			Structure of Reduced Hydrocarbons				
1-Methyl-naphthalene	Ethyl amine	1	3 (61%)	4 (10%)	5 (8%)		Unknown mixture of hexahydro and octahydro products, 4 peaks 20%
1-Methyl-naphthalene	Ethyl amine	28	(32%)	(10%)	(4%)		Unknown mixture of dihydro products, 5 peaks 26%
2-Methyl-naphthalene	Ethyl amine	1	6 (45%)	7 (19%)	8 (10%)	9 (7%)	Unknown mixture of hexahydro products, 2 peaks 18%
2-Methyl-naphthalene	Propyl amine	15	(33%)	(16%)	(3%)	(30%)	Unknown compound. Possibly a dihydro product 2%
2,6-Dimethyl-naphthalene	Ethyl amine	0	10 (61%)	11 (10%)	12 (4%)		Unknown compound. Possibly a hexahydro product 25%
2,6-Dimethyl-naphthalene	Propyl amine	32	(20%)	(48%)			

The electrolyses were carried out at the boiling point of the solvents (17° and 49°) for 20 hours.

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TABLE II

ELECTROLYTIC REDUCTIONS USING THE SMALL REDUCTION APPARATUS[a]

Starting Material	Total Yield of Hydrocarbon Products, %	Distribution of Hydrocarbons		
		Recovered Starting Material, %	Structure of Hydrocarbons	
Naphthalene	88	6	2 (11%) 13 (37%) 14 (11%) 15 (33%) 16 (2%)	
2,3-Dimethyl-naphthalene[b]	90	7	17 (1%) 18 (3%) 19 (48%) 20 (13%)	Unknown mixture of hexahydro & octahydro products, 5 peaks 23%

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[a]The electrolyses were carried out in ethylamine solvent for 20 hrs.
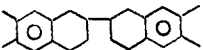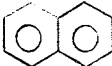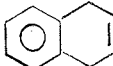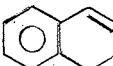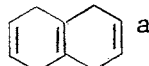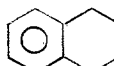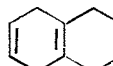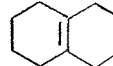
[b]Trace quantities of [structure] were isolated.

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TABLE III

PREPARATIVE REDUCTION OF NAPHTHALENE WITH ETHYLAMINE SOLVENT

Reaction Time (Hours)	1 %	2 %	13 %	28 %	14 %	15 %	16 %
24	63	28	4	1	2	2	>1
48	63	28	4	1	2	2	>1
72	33	42	6	7	5	5	2
96	1	73	0	3	13	6	4
120	1	65	0	4	18	7	7

[a]Tentative structure assignment

TABLE IV

PREPARATIVE REDUCTION OF ACENAPHTHALENE WITH ETHYLAMINE[a]
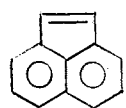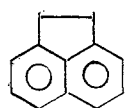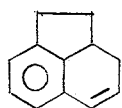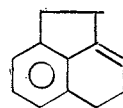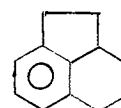
21 (0%)   22 (4%)   23 (50%)   24 (2%)   25 (21%)   26 (19%)   27 (3%)
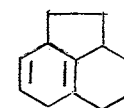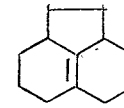
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[a]After 60 hours reaction time

the usual procedure for gas chromatography analysis, a chromatogram was first obtained for the entire reaction mixture; then the reaction mixture was enriched with an authentic sample of a compound thought to be present among the reaction products. The analysis was then repeated using the enriched mixture. If any component of the reaction mixture corresponded to the authentic sample, then its peak intensity increased. In some cases in which authentic samples were not available, preparative gas chromatography was used for separation and purification of samples for identification through use of other instruments.

The gas chromatography purification was facilitated by use of flow programming. When flow programming is used, all gas flow is stopped and a sample is injected onto the column. Flow is resumed and increased at a linear rate until maximum flow is obtained. This linear increase in flow causes improved separation of the reaction mixture. An additional advantage is the increased ease of large sample injection when there is no back pressure on the column.

When 1-methylnaphthalene was reduced in the presence of ethyl-amine solvent, there was obtained 61% of 3 and 8% of 5 as shown in Table I; this is a ratio of 3/5 = 7.6/1. The use of propylamine as the solvent gives a ratio of 3/5 = 8/1.

In the reduction of 2-methylnaphthalene with ethylamine solvent, there was obtained 45% of 6 and 19% of 7; this is a ratio of 6/7 = 2.4/1. When the solvent was changed to propylamine, the ratio was 6/7 = 2.1/1.

From these data, it is seen that changing the solvent does not appreciably change the reduction product ratio for the tetralins.

However, the yield of tetralins is substantially less when propyl-amine is used since 28% starting material is recovered when 1-methyl-naphthalene was reduced. Similarly, 15% starting material was recovered from the reaction with 2-methylnaphthalene and 32% starting material was recovered from reduction of 2,6-dimethylnaphthalene, whereas the starting hydrocarbon was essentially consumed when ethyl amine was used. It is our conclusion that propylamine is a less effective reducing agent. When ethylenediamine at 50° was used, considerable tar was encountered and no useful product was isolated. An attempt was made to carry out an electrolytic reduction in hexamethyl-enimine solvent at 50°, but no reaction took place since the lithium chloride electrolyte was insoluble, and consequently, there was no current flow. Our attempt to substitute sodium chloride for lithium chloride in ethylamine solvent failed due to the insolubility of sodium chloride.

One attempt was made to use sodium metal as a source of sodium cations and amide ion as a source of anions to cause transport of current:
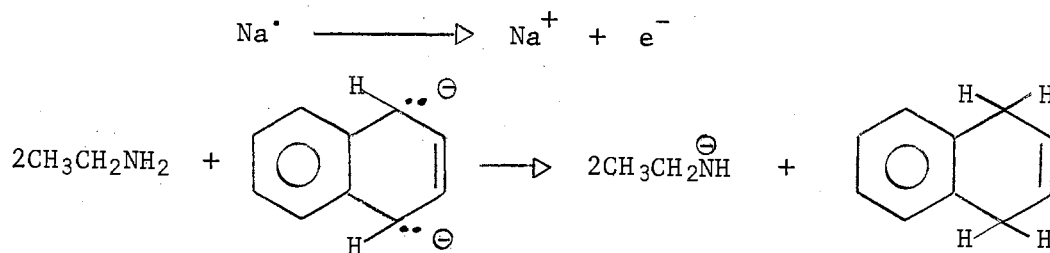
However, this approach was not successful and will require modification of the electrolysis apparatus since particles of free floating sodium metal caused a short circuit across the electrodes and greatly increased the explosion and fire hazard.

If temperature alone is an important factor in electrolytic reduction, greater reduction should be observed when propylamine is used. The opposite is true as may be seen in Table I.

In one sense, the use of propylamine is more selective in its reduction than ethylamine: if a tetrahydronaphthalene is desired, then propylamine would be the preferred solvent. However, if more extensive reduction is sought, then ethylamine would be the better solvent choice.

Much of this inequality of reduction product formation may be attributed, as previously pointed out, to differences in solubility of lithium chloride in these solvents. The insolubilities of many metal salts (sodium chloride, potassium chloride, calcium chloride, lithium carbonate, etc.) in low-molecular-weight amines prohibit their use in electrolytic reductions.

The role of metal salt in electrolytic reduction is not fully understood. Sternberg, Markby, and Wender[16] suggested that the electron involved in electrolytic reduction is transferred from the electrode to the solution, becomes solvated and stabilized by the metal cation and is then transferred to the hydrocarbon to form a radical anion as shown in Fig. I. Krapcho and Bothner-By[1] had suggested essentially the same mechanism. Both research groups concluded that the electron is not directly transferred from electrode to hydrocarbon. This was substantiated by polarographic studies[16] with tetralin, and tetralin in the presence of lithium chloride-ethylenediamine. It has been suggested that lithium metal is formed from the cation during electrolytic reduction at the cathode[16] and the metal

cation. Since it has long been recognized that a solvated electron[19] and solvated cation[20] play an important role in these reactions, it is entirely possible that the oxidation and reduction reactions take place in solution rather than at electrode interface. This overall process from electrons at the cathode surface to reduced hydrocarbon may be rationalized as follows:

$$LiCl \quad + \quad nNH_2CH_2CH_3 \quad \rightleftharpoons \quad [Li(NH_2CH_2CH_3)_n]^{\oplus}$$

Added
electrolyte

$$e^- \quad + \quad nNH_2CH_2CH_3 \quad \rightleftharpoons \quad [e(NH_2CH_2CH_3)_n]^{\ominus}$$

From
cathode

$$[e(NH_2CH_2CH_3)n]^-$$

$$2NH_2CH_2CH_3$$

$$2NHCH_2CH_3^{\ominus}$$
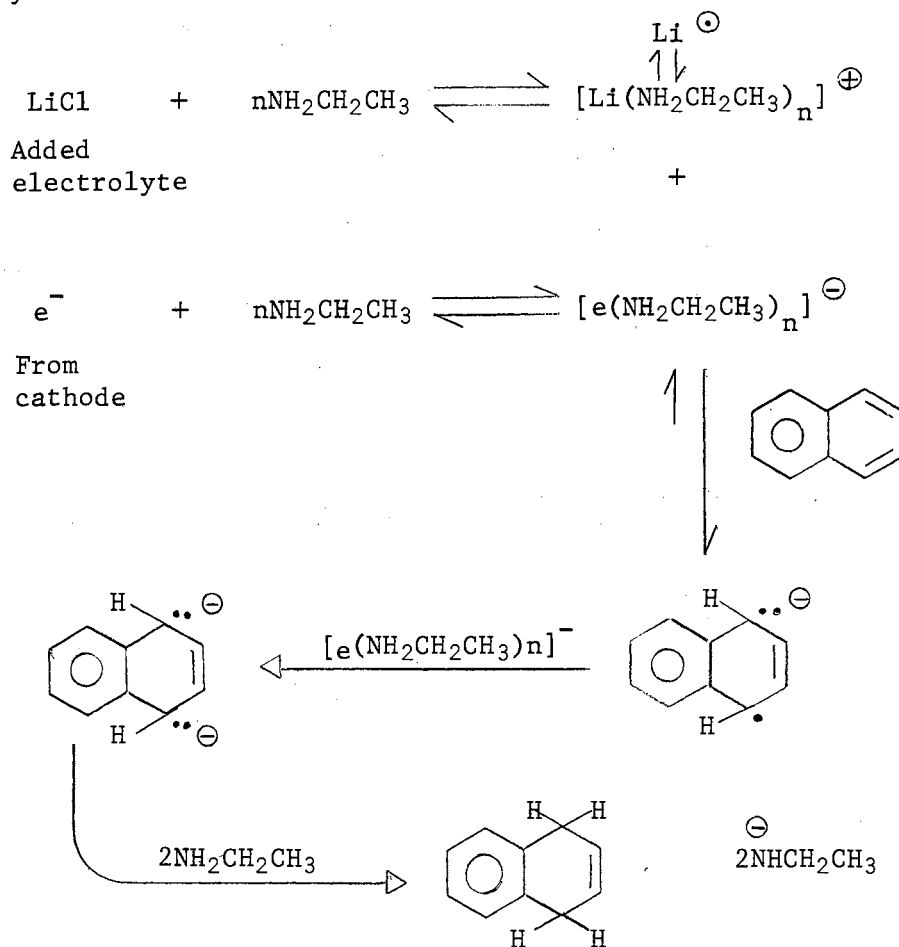
A possible objection to this explanation would be that lithium metal may be expected to accumulate. However, the reversible conversion of lithium metal to cation is favored by utilization of electrons in the reduction of hydrocarbons.

It has been our custom to occasionally reverse the potential of

the electrodes and when this is done, bits of white material flake away from the electrode which had been the cathode. It is our belief that this white material is lithium ethylamide since it is hard and brittle and burns when exposed to water. It is also possible that this material is lithium metal or a combination of these.

The metal salt-hydrocarbon molar ratios appear to play an important role in the rate of the electrolytic reduction reaction (Table II and III; Fig. 2). In the reduction of naphthalene in the small electrolytic reduction apparatus, the molar ratio of lithium chloride to naphthalene was 3.3:1. After 20 hours of reaction time, only 6% of the starting material had not reacted (Table II). When naphthalene was reduced in the preparative electrolytic reduction apparatus, the initial lithium chloride-naphthalene molar ratio was 1:1. After reacting for 24 hours, there was 63% of the naphthalene remaining (Table III). Additional lithium chloride was added at the end of 48 hours of reaction as it was apparent no further reduction had occurred between the 24th to 48th hour (Fig. 2). This additional lithium chloride changed the lithium chloride-naphthalene molar ratio to 2.4:1. In the 48 hours of reaction time following this molar ratio increase, an additional 62% of naphthalene was consumed.

One can infer from the curves in Fig. 2 that 1,4-dihydronaphthalene is the initial reaction product and is more stable to further reduction than any of the succeeding reaction products. 1,4-Dihydronaphthalene (2) may react by isomerization to 1,2-dihydronaphthalene and subsequent reduction to tetralin or by reduction to isotetralin. That both of these pathways are utilized is evidenced by the presence of both 1,2-dihydronaphthalene (13) and isotetralin (28) in the
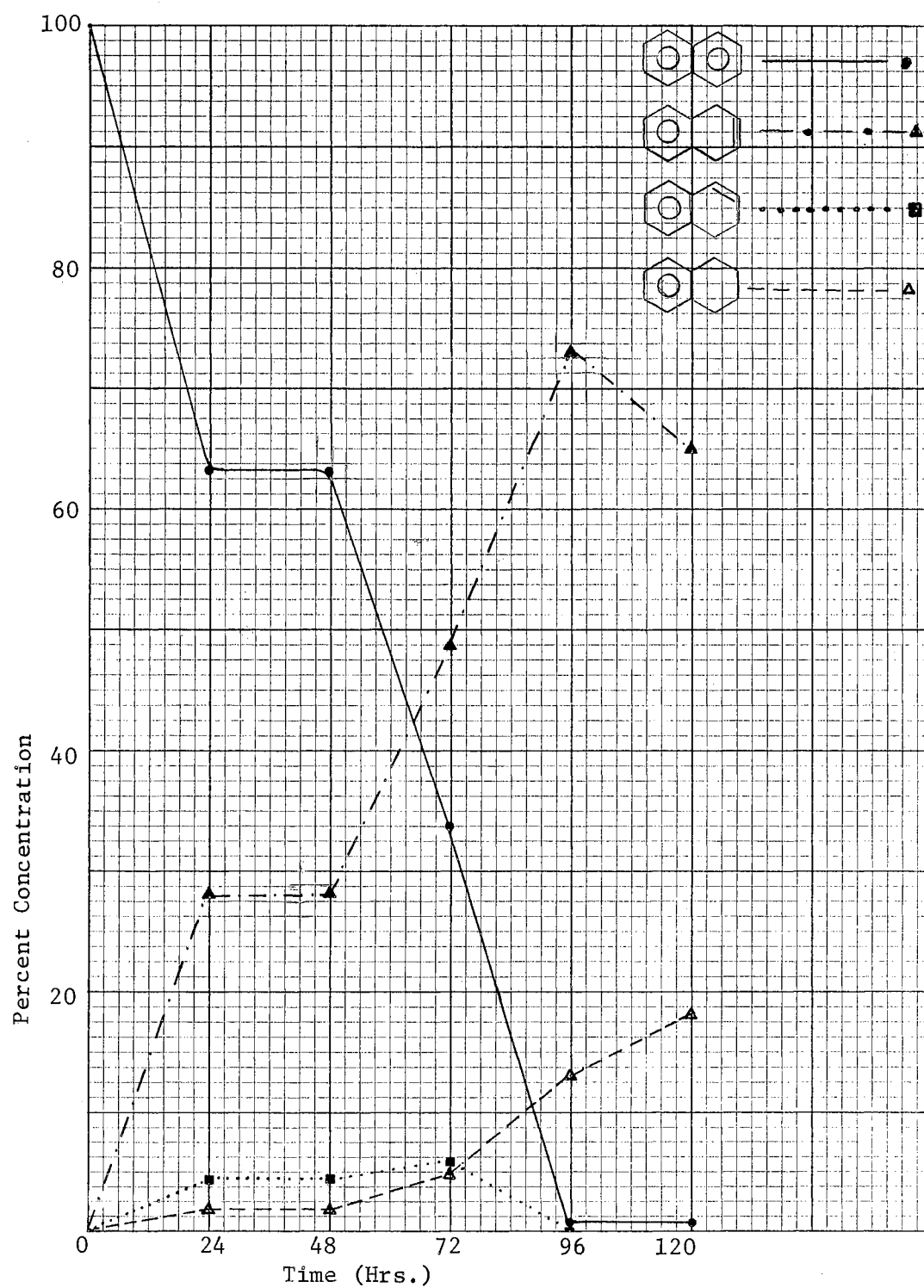
Figure 2. Naphthalene Reduction Products Measured at 24-Hour Time
Intervals, Part a
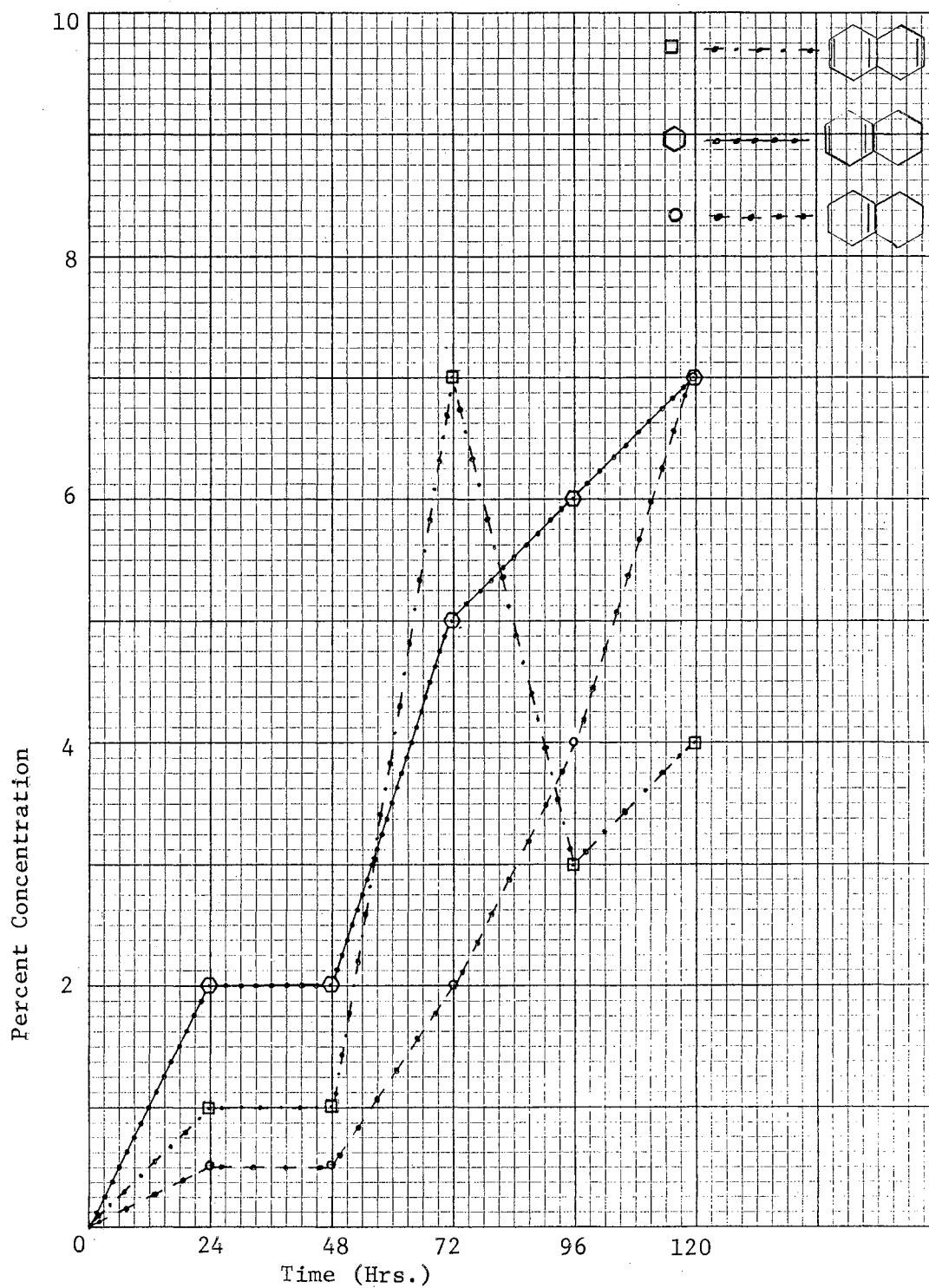
Figure 3.   Naphthalene Reduction Products Measured at 24-Hour Time
Intervals, Part b

reaction mixture. The former is only observed in the early stages.

$$H \quad H \quad \xrightarrow{CH_3CH_2NH^-} \quad \overset{\ominus}{NHCH_2CH_3} \quad H^{\nearrow}\overset{\cdot}{N}HCH_2CH_3 \quad \longrightarrow$$

$$2[e(NH_2CH_2CH_3)n]^- \quad \longrightarrow \quad \overset{\ominus}{\cdot\cdot}H \quad \overset{\ominus}{\cdot\cdot}H \quad \xrightarrow{2NH_2CH_2CH_3}$$
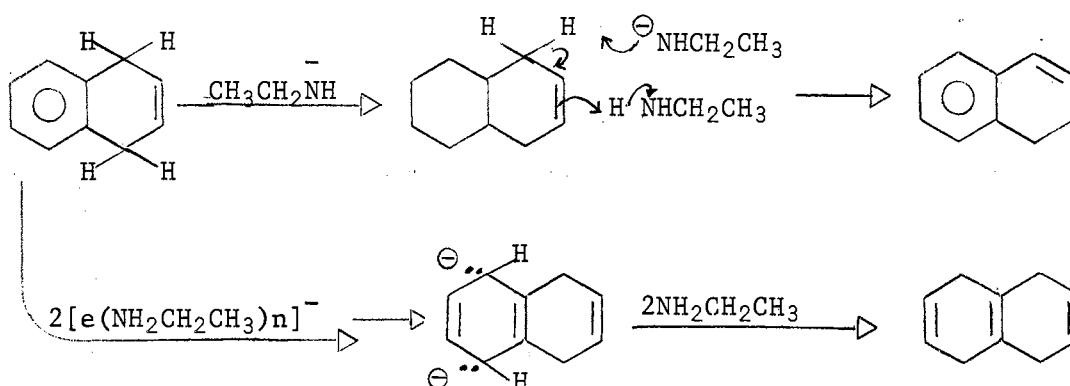
It is believed that the rate-determining step in the reduction of naphthalene to tetralin is the formation of 1,2-dihydronaphthalene. It is not apparent at this time whether hexahydronaphthalene is formed from tetralin or isotetralin.

From these studies, it may be concluded that electrolytic reduction of polynuclear hydrocarbons can be used to obtain cyclic olefins. The degree of saturation in the products is determined largely by the length of reaction time since a stepwise process is probably involved.

CHAPTER IV

EXPERIMENTAL

Nuclear magnetic resonance spectra were obtained with a Varian
HR-60 spectrometer, using tetramethyl silane as an internal standard
($\delta = 0$). Mass spectra were obtained with a Consolidated Electronics
Corporation Model 21-103C mass spectrometer. All temperatures are in
degrees centigrade. An F and M Model 700 gas chromatography apparatus
equipped with a termal conductivity detector was used for the analyses
and preparative separations. With the exception of the reduction pro-
ducts from 1-methylnaphthalene, all hydrocarbons were satisfactorily
separated and analyzed on a Carbowax 20 M column (25% on acid washed
Chromosorb W, 10' x 1/4"; helium flow 40 cc/min) operating at 190°.
The reduction products from 1-methylnaphthalene were best resolved on
a LAC 886 column (25% on acid washed Chromosorb W, gas flow 40 cc/min)
operating at 190°.

Gas chromatography analyses of all starting materials showed
greater than 99% purity. The identity of many of the reduction products
were determined by successive enrichment of reaction mixtures with authen-
tic samples and observing the expected increase in a given peak intensity.

Selected steam distilled reduction products from preparative
reductions of naphthalene and acenaphthalene were purified by preparative
gas chromatography (Carbowax 20 M, 25% on base washed Chromosorb W,

10' x 3/8", 180°, helium flow programmed from 0 to 200 ml/min).
Collection of naphthalene reduction products requires cooling the
traps in ice water, whereas collection of acenaphthalene reduction
products necessitates heating the traps to prevent formation of an
aerosol. The chromatogram is presented in Fig. 4.

Purification of Ethylamine. Ethylamine (bp 15°)as drawn directly
from the metal cyclinder contains colloidal iron. Since iron would be
expected to foul the electrodes, iron free amine was desired. The
cylinder containing the amine was connected by rubber tubing to a 2-1.,
two-necked flask containing sodium hydroxide pellets. This flask
served as a distillation flask. A 6" Vigreux column surmounted by a
distillation head with attached condenser and receiver was fitted to
the distillation flask. A soda lime drying tube at the exit vent pro-
tected the amine from atmospheric gasses.

Preparative Electrolytic Reduction Apparatus. The electrolytic
reduction vessel consisted of a glass cylinder (15 cm wide x 29 cm high)
with a flat ground lip (1 cm rim width) and a matching cover having two
$ 24/40 outer joints equidistance around the top and one $ 34/45 outer
joint in the middle. The cylinder and top were held together by means
of a steel clamp as shown in Plate I. A Teflon gasket was used to in-
sure a tight seal and prevent loss of amine.

One of the $ 24/40 joints was fitted with a high capacity reflux
condenser equipped with a soda-lime tube, the second $ 24/40 joint was
stoppered and used to add chemicals or withdraw samples.

The $ 34/45 center joint was used as a port for the sandwich of
three platinum electrodes which were suspended on 18 gauge platinum

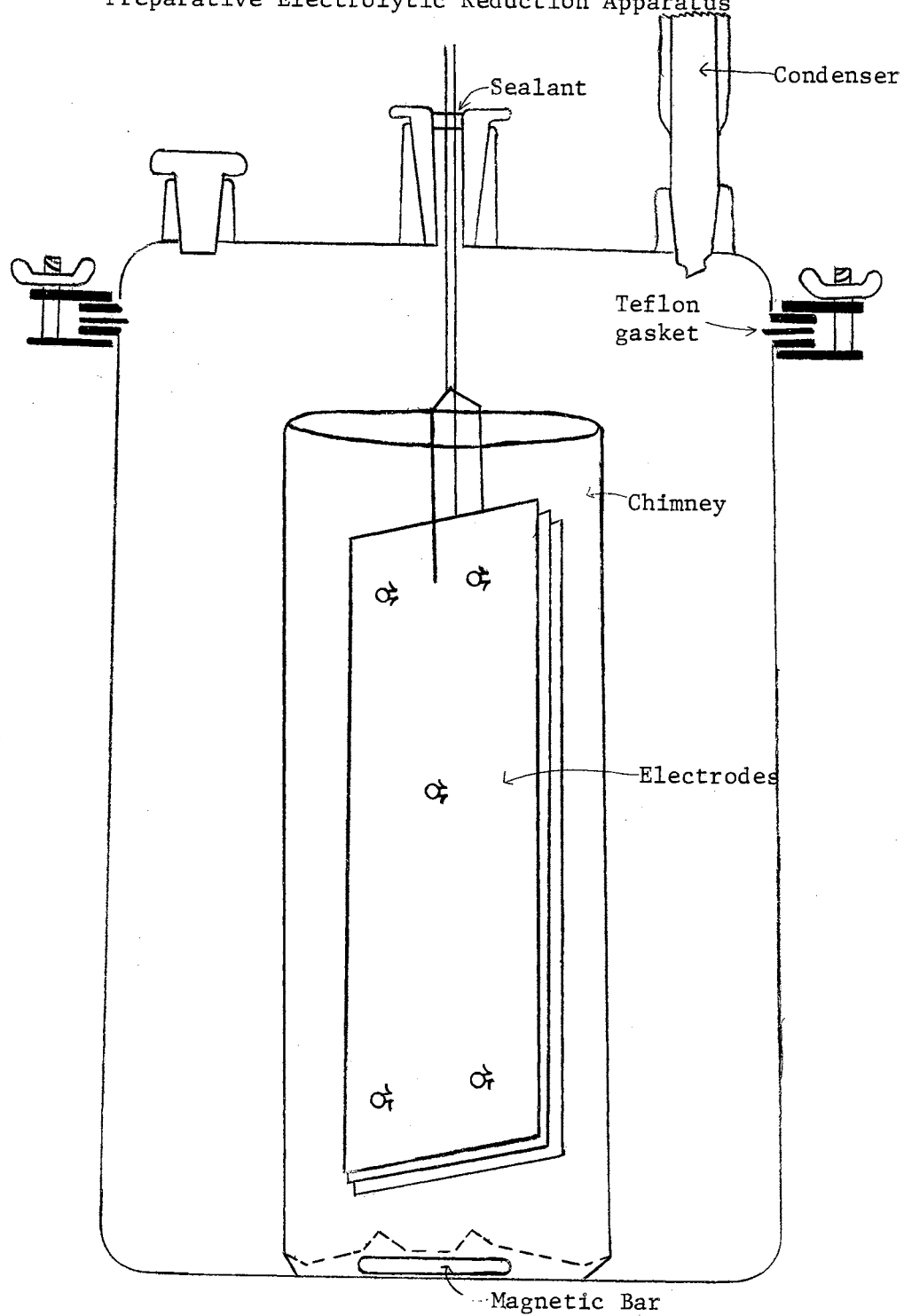Preparative Electrolytic Reduction Apparatus

Plate I

wire. To obtain a sealed system, the electrode wires were passed through a Teflon thermometer adapter which in turn was sealed with Silastic silicone rubber sealant.

Agitation of the solution being electrolyzed was accomplished by a magnetic stirring bar at the bottom of the flask and the use of a chimney surrounding the electrodes. The chimney with perforations at the bottom served as an efficient pump by directing the upward flow of warmed and partially vaporized amine solvent. Fresh amine solvent and hydrocarbon automatically entered the bottom of the chimney to complete the pumping cycle. The chimney also served as a baffle to prevent marbles from coming in contact with the electrodes. The marbles were added as an aid toward regulation of solvent volumes[21]. In some cases it was desirable to alter the volume of solvent and hydrocarbon. The addition of marbles to fill the void and provide complete coverage of electrodes served admirably. Thus the need for a variety of vessel sizes was avoided.

The electrodes consisted of three platinum sheets (2" x 6" x 0.004"). These were separated by Teflon rods and spacers to a distance of 14 mm. The outer electrodes of the sandwich were joined with 18 gauge platinum wire which in turn was connected to the lead wire. The inner electrode was formed by connecting the second 18 gauge lead wire to the center platinum sheet. The center lead was sheathed in a Teflon tube to prevent electrical contact.

The heat from the electrolysis was dissipated by circulating chilled water around the outside of the reaction flask. The direct current electrical circuit for the electrodes incorporated a double-pole,

double-throw switch and a 0-5 amp. ammeter.

Preparative Reduction of Naphthalene. The reaction vessel was
charged with 1800 ml ethylamine, the vessel contents were cooled to
5°, and 42 g (1.0 mole) of lithium chloride were added slowly from an
Erlenmeyer flask by means of a Gooch tube. Slow addition was necessary
due to heat of solution. After all lithium chloride had been added and
dissolved, 128 g (1.0 mole) of naphthalene were added to the solution.
Electrolysis was started at 15 volts and 0.5 amperes. After 48 hours,
58 g (1.38 moles) of lithium chloride were added since the reduction
had virtually ceased during the 24 to 48 hour period. After addition
of lithium chloride the current rose to 3 amps. Samples for gas chrom-
atography analysis were withdrawn every 24 hours. At the end of 120
hours, 98% of the naphthalene had been reduced. These results are
shown in Table III.

At the completion of the electrolysis, a distillation head with
attached condenser and receiving flask was fitted to the reaction vessel
and the major portion of the amine solvent was distilled. The reaction
product was poured onto ice, acidified with concentrated hydrochloric
acid and extracted with three 200 ml portions of ether. The extract
was dried over anhydrous sodium sulfate, filtered and the ether removed
by distillation. The resulting dark colored viscous oil weighed 112 g.
This oil was steam distilled, the steam distillate was extracted with
ether, dried over anhydrous sodium sulfate, filtered and distilled.
The colorless concentrated oil weighed 85.4 g. This oil was separated
by preparative gas chromatography vide ante to obtain pure samples of
the individual reaction product components for NMR and mass spectroscopy

Gas Chromatogram of Products from Electrolytic Reduction of Naphthalene
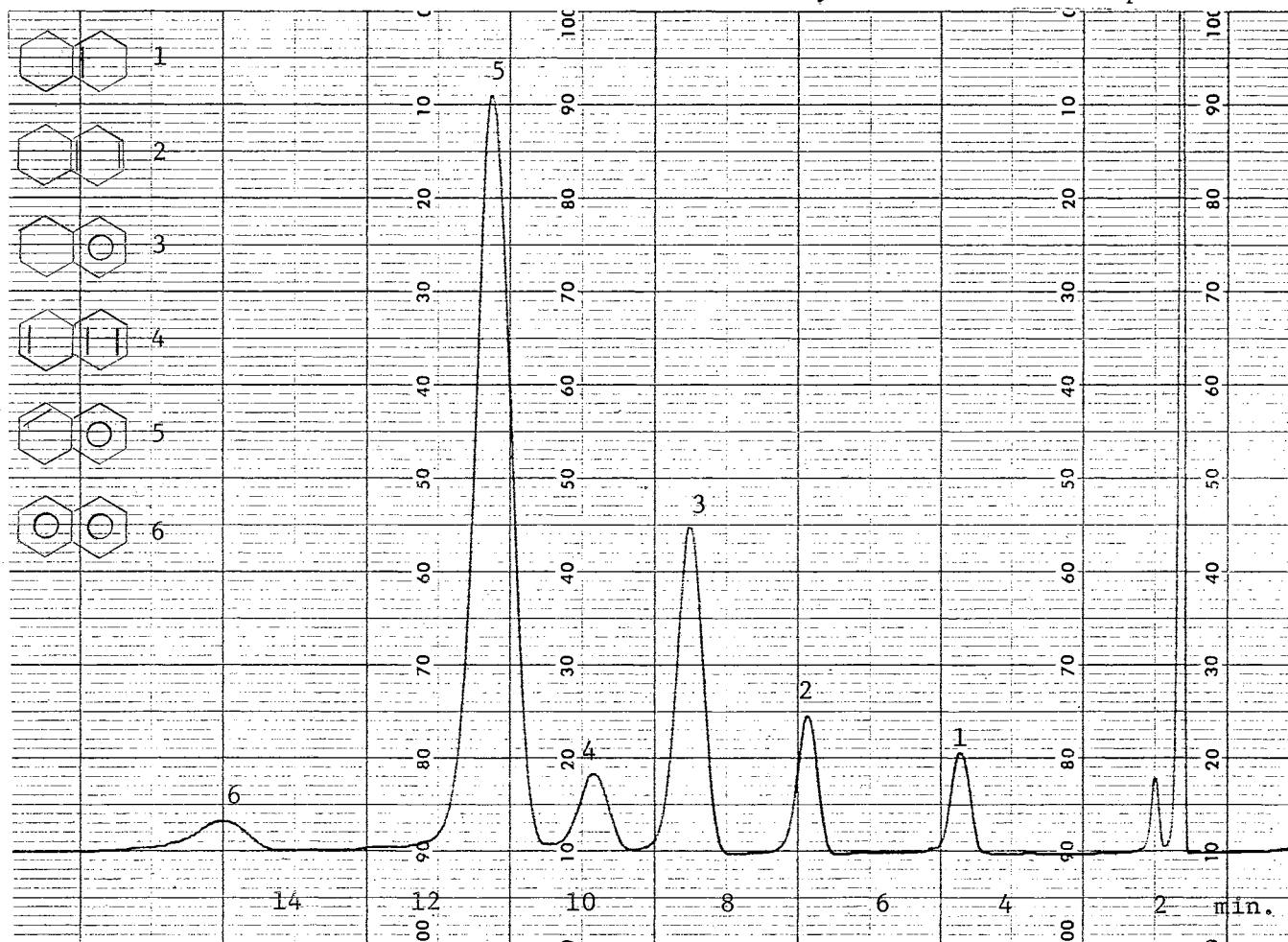
Plate II

Gas Chromatogram of Products from Electrolytic Reduction of Acenaphthalene
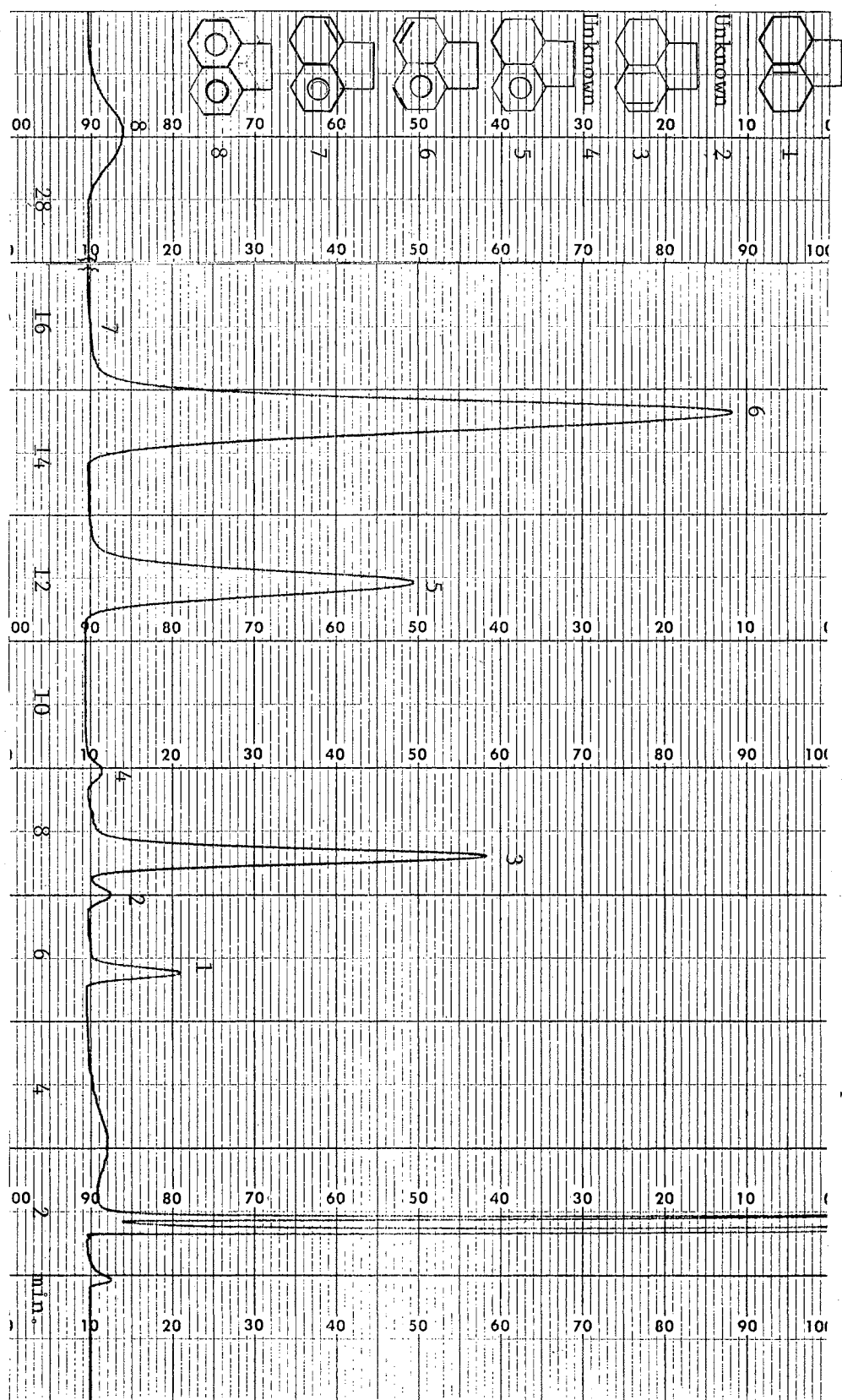
Plate III

studies.

The steam distillation pot residue was extracted with ether, the ether solution was dried over anhydrous sodium sulfate, filtered and the ether was then removed by evaporation. The dark colored residue weighed 20 g and on distillation yielded 8 g of colorless viscous oil.

Acenaphthalene was also reduced in the preparative electrolytic reduction apparatus. The reduction products are shown in Table IV.

Identification of the Products from Electrolytic Reduction of Naphthalene. The structures of 2, 13, and 14 were assigned on the basis of comparison with authentic samples in gas chromatography analysis.

The structures of 15 and 16 were assigned on the basis of their mass and NMR spectra.

The mass spectrum of 15 showed a parent ion peak at m/e = 134 and the NMR spectrum showed adsorption at δ = 1.78 (4H, two equivalent methylene groups, multiplet); 1.84 (4H, protons allylic to 1 double bond, doublet); 2.75 (4H, protons allylic to 2 double bonds, singlet); 5.62 (2H, vinylic protons, singlet).

The mass spectrum of 16 showed a parent ion peak m/e = 136 and the NMR spectrum showed adsorption at 1.67 (8H, four equivalent methylene groups, multiplet); 1.84 (8H, allylic protons, doublet).

Similar studies were used to establish the structures of the products obtained from the electrolytic reduction of acenaphthalene. These results are presented in Table IV.

Small Reduction Cell. This apparatus was used for runs of 0.05 moles hydrocarbon and consisted of a 200 ml three-necked round bottomed flask fitted with a high capacity reflux condenser, a polyethylene

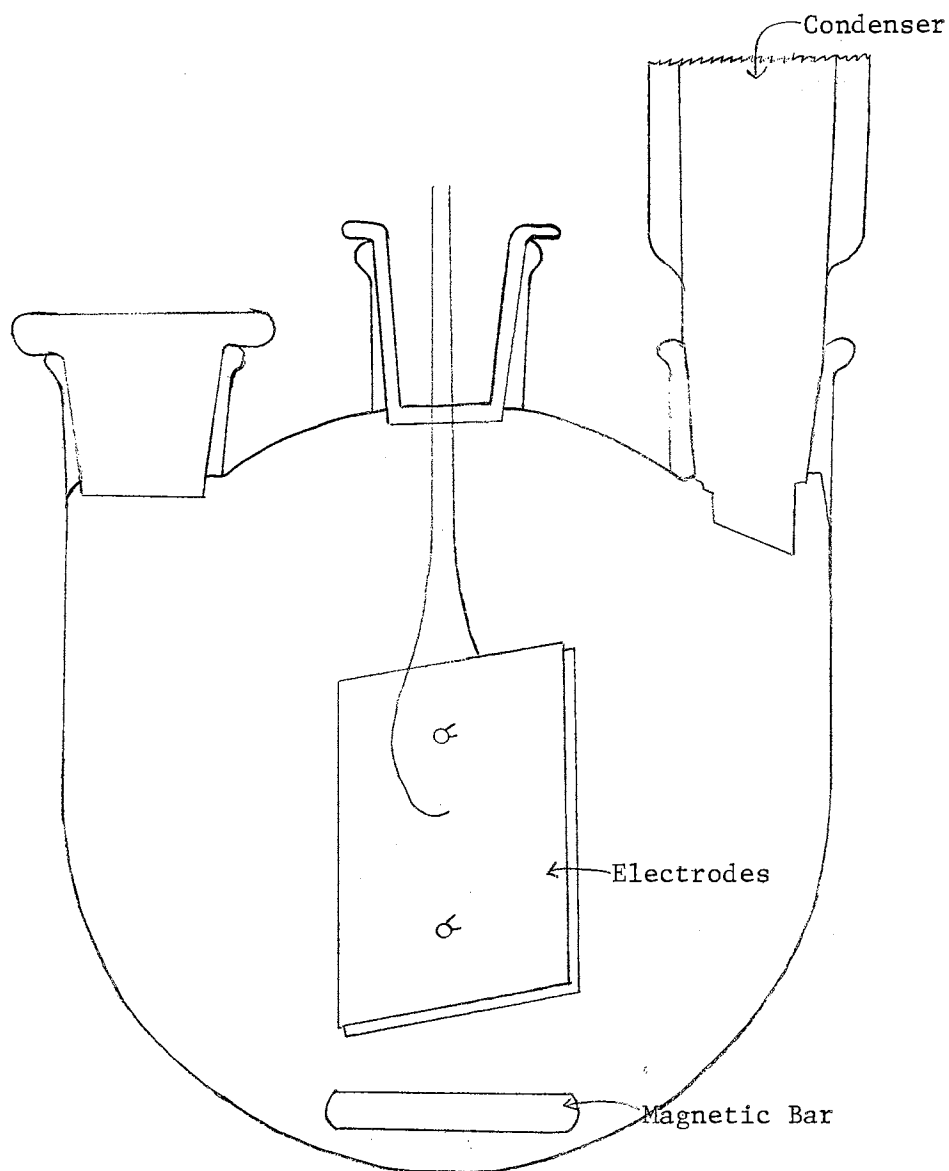Small Electrolytic Reduction Apparatus

Plate IV

stopper in the middle neck and a glass stopper in one of the side necks through which chemicals were added and samples were removed. Stirring was accomplished by a magnetic bar. This flask, in contrast to the preparative reduction apparatus, was not cooled in a water bath since the condenser cooling capacity was sufficient to recondense vaporized amine solvent.

The electrode assembly consisted of two platinum sheets (2 cm x 4 cm x 0.004") spot welded to an 18 gauge platinum wire. The electrodes were separated by two 4 mm Teflon spacers. The lead wires from the electrodes were fed through the polyethylene cap and sealed in place by Silastic silacone rubber sealant. The electrical circuit was the same as that used with the preparative reduction apparatus.

Reduction of 2,3-Dimethylnaphthalene. The small reaction flask was charged with 150 ml ethyl amine and 7.2 g (0.17 moles) of lithium chloride were added slowly through a Gooch tube from an Erlenmeyer flask. After the lithium chloride disolved, 7.9 g (0.05 mole) of 2,3-dimethylnaphthalene were added and electrolysis initiated. The reaction was run at 30 V. and 0.8 amperes for 20 hours. At the end of this time, the amine solvent was distilled and the resulting viscous residue poured onto ice. The solution was then acidified with concentrated hydrochloric acid and extracted with three 50 ml portions of ether. The ether solution was then dried over anhydrous sodium sulfate, filtered and then removed by distillation to give 7.1 g of reduction products. Gas chromatography analysis revealed 10 components in the reduction mixture. This chromatogram is shown in Plate V.

Gas Chromatogram of Products from Electrolytic Reduction of 2,3-Dimethylnaphthalene
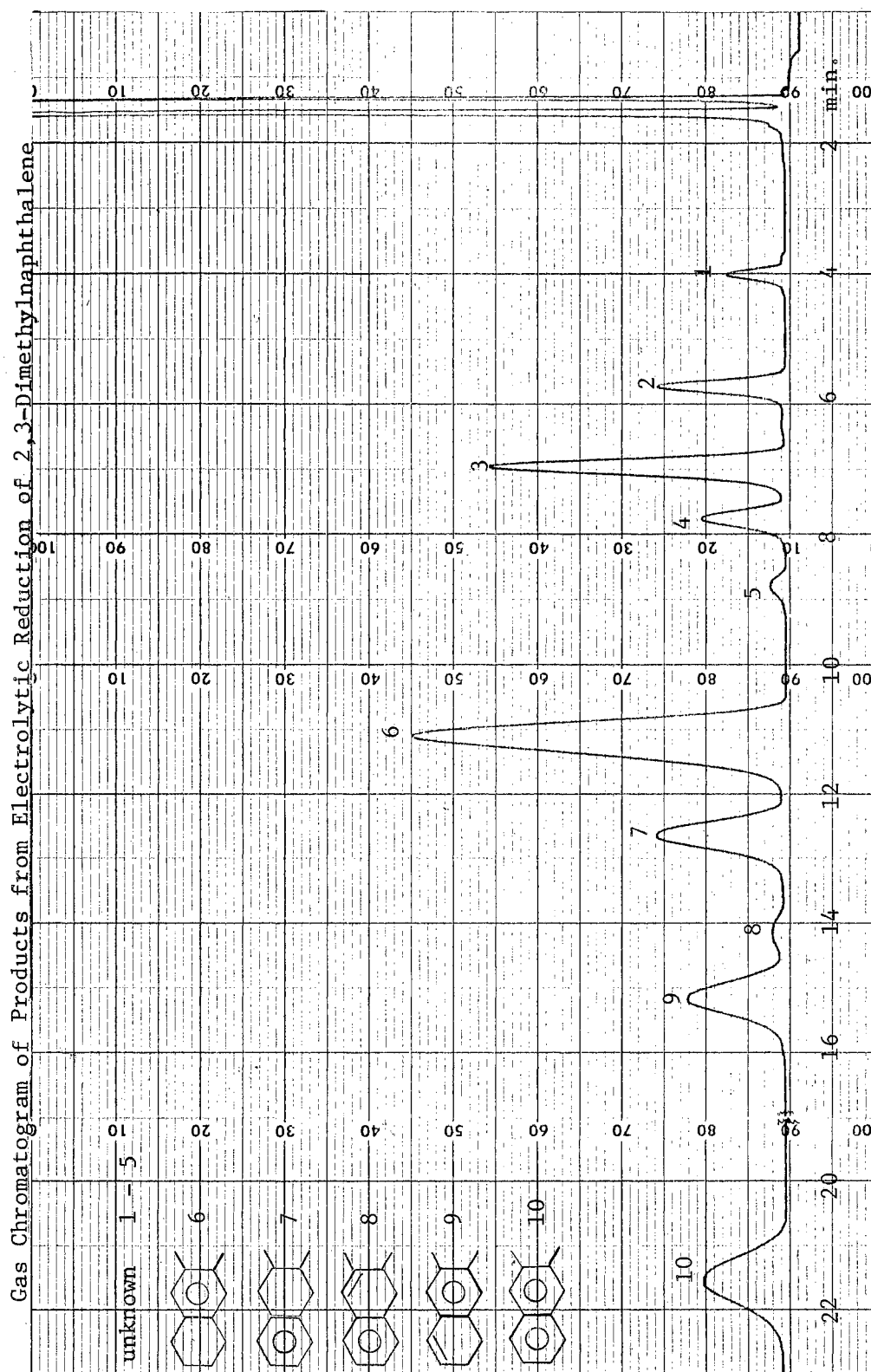
Plate V

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