

THE SYNTHESIS AND DEHYDROGENATION OF
SOME KETOTETRAHYDRONAPHTHALENES

By

Charles William Hinman

"

Bachelor of Science

Western Illinois University

Macomb, Illinois

1962

Submitted to the Faculty of the Graduate School of
the Oklahoma State University
in partial fulfillment of the requirements
for the degree of
Master of Science
May, 1965

Thesis

1060

4430

copy

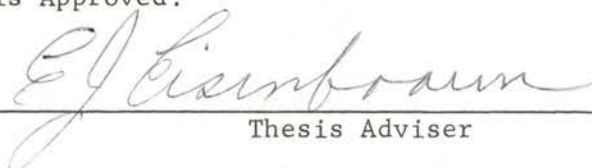
THE UNIVERSITY OF CHICAGO
DIVISION OF THE PHYSICAL SCIENCES
DEPARTMENT OF CHEMISTRY
5708 SOUTH CAMPUS DRIVE
CHICAGO, ILLINOIS 60637

OKLAHOMA
STATE UNIVERSITY
LIBRARY

SEP 20 1965

THE SYNTHESIS AND DEHYDROGENATION OF
SOME KETOTETRAHYDRONAPHTHALENES

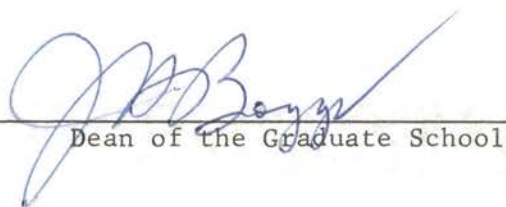
Thesis Approved:



Thesis Adviser



Thesis Adviser



Dean of the Graduate School

587516

ACKNOWLEDGMENTS

The author is grateful for the friendship, encouragement, and assistance of Dr. E. J. Eisenbraun, without whom this thesis would not have been possible. The author also wishes to thank A. B. Carel, P. W. Flanagan, M. Evans, and M. Hamming, for use of their facilities at Continental Oil Company, at Ponca City, Oklahoma, and also for their assistance in structure determination.

Appreciation is also extended to the American Petroleum Institute for financial aid in the form of a research assistantship.

TABLE OF CONTENTS

Chapter	Page
I. HISTORICAL	1
II. DISCUSSION OF RESULTS	5
III. EXPERIMENTAL	15
β -(<u>p</u> -Xyloyl-2)- α -methylpropionic Acid (I)	15
γ -(<u>p</u> -Xylyl-2)- α -methylbutyric Acid (II)	17
1-Keto-1,2,3,4-tetrahydro-2,5,8-trimethyl- naphthalene (III)	18
1,2,3,4-Tetrahydro-2,5,8-trimethylnaphthalene (IV)	19
1,2,3,4-Tetrahydro-2,5,8-trimethyl-1-naphthol (V)	20
3,4-Dihydro-2,5,8-trimethylnaphthalene (VI)	21
1,4,6-Trimethylnaphthalene (VII)	22
β -(<u>p</u> -Xyloyl-2)- β -methylpropionic Acid (VIII)	23
γ -(<u>p</u> -Xylyl-2)- β -methylbutyric Acid (IX)	24
1-Keto-1,2,3,4-tetrahydro-3,5,8-trimethyl- naphthalene (X)	24
1,2,3,4-Tetrahydro-3,5,8-trimethyl-1-naphthol (XI)	25
3,4-Dihydro-3,5,8-trimethylnaphthalene (XII)	25
4-Hydroxy-2-methyl-4-(<u>p</u> -xylyl-2)-3-butenoic Acid γ -Lactone (XIII)	26
4-Hydroxy-3-methyl-4-(<u>p</u> -xylyl-2)-3-butenoic Acid γ -Lactone (XIV)	26
1,4,5-Trimethylnaphthalene (XX)	27
Dehydrogenation of 1,2,3,4-Tetrahydro-2,5,8- trimethyl-1-naphthol (V) with 5% Palladium on Carbon	29
Dehydrogenation of 1,2,3,4-Tetrahydro-3,5,8- trimethyl-1-naphthol (XI) with 5% Palladium on Carbon	30
Dehydrogenation of 1,2,3,4-Tetrahydro-4,5,8- trimethyl-1-naphthol (XVII) with 5% Palladium on Carbon	30
Dehydrogenation of 1-Keto-1,2,3,4-tetrahydro- 2,5,8-trimethylnaphthalene (III) using Palladium on Carbon	30
Dehydrogenation of 1-Keto-1,2,3,4-tetrahydro-3,5,8- trimethylnaphthalene (X) with Palladium on Carbon	31
Dehydrogenation of 1-Keto-1,2,3,4-tetrahydro-4,5,8- trimethylnaphthalene (XVI) with Palladium on Carbon	32

Chapter	Page
Reaction of the 1-Ketotetrahydrotrimethyl- naphthalenes with Anhydrous Caustic	32
Dehydrogenation of 1-Keto-1,2,3,4-tetrahydro- phenanthrene (XXI) with 5% Palladium on Carbon	33
Dehydrogenation of 1-Keto-1,2,3,4-tetrahydro- phenanthrene (XXI) with 5% Palladium on Carbon in the Presence of Naphthalene	34
Dehydrogenation of α -Tetralone (XXV) with Pd/C and Pt/C	35
Dehydrogenation of α -Tetralone (XXV) using NaOH and KOH	36
Dehydrogenation of β -Tetralone (XXVII) using Pd/C	36
Dehydrogenation of β -Tetralone (XXVII) using NaOH and KOH	37
Friedel-Crafts Reaction Study in Three Solvent Systems	38
BIBLIOGRAPHY	40

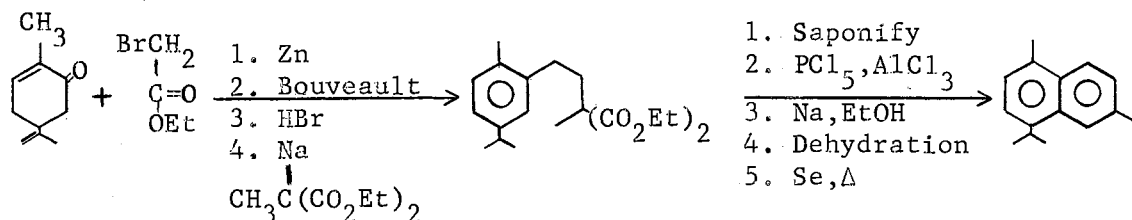
LIST OF FIGURES

Figure		Page
1	Synthetic Route to 1,4,6-Trimethylnaphthalene	6
2	Synthetic Route to 1,4,5-Trimethylnaphthalene and Dehydrogenation of Tetrahydrotrimethylnaphthols.	9
3	Dehydrogenations of 1-Ketotetrahydrophenanthrene and 1-Ketotetrahydronaphthalenes.	12

CHAPTER I

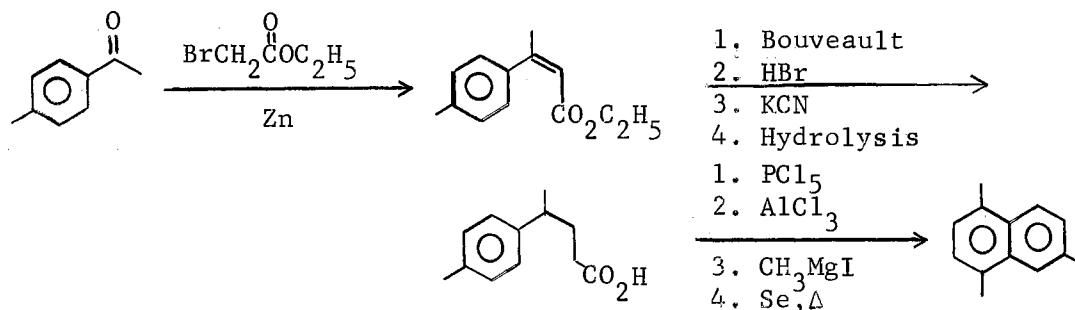
HISTORICAL

Several routes to the synthesis of polyalkylnaphthalenes have been described. In 1922, Ruzicka and Seidel (1) reported the synthesis of cadalene starting with carvone, ethyl bromoacetate, and zinc in a typical Reformatsky reaction. The Reformatsky reaction product arranges to ethyl 1-methyl-4-isopropylphenyl-2-acetate. The Bouveault reaction with sodium and alcohol reduced the ester to a primary alcohol, which was in turn converted to the bromide and then reacted with the sodio derivative of diethyl methylmalonate. Saponification and distillation gave γ -(*p*-cymyl-2)- α -methylbutyric acid. The acid chloride formed from this butyric acid was cyclized to the 1-ketotetrahydronaphthalene, which in turn was reduced with sodium and ethanol, dehydrated, and aromatized to cadalene.



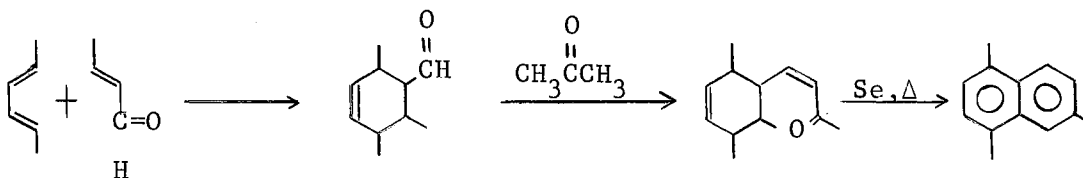
Ruzicka and Ehmman (2) condensed *p*-methylacetophenone with ethyl bromoacetate in the presence of zinc. The resulting hydroxy ester was reduced with moist sodium to give the primary alcohol. The primary alcohol was converted to the corresponding bromide with hydrogen bromide, then to the nitrile with potassium cyanide, and finally hydrolyzed

to γ -(tolyl-4)- γ -methylbutyric acid. The acid chloride was prepared and cyclized to the ketotetrahydronaphthalene which in turn was reacted with methylmagnesium iodide followed by dehydrogenation with selenium to give 1,4,6-trimethylnaphthalene:



Heilbron and Wilkinson (3) also used this approach to prepare trimethylnaphthalenes.

Schorygin and Gussewa (4) synthesized 1,4,6-trimethylnaphthalene, starting with 1,4-dimethyl-1,3-butadiene and crotonaldehyde in a Diels-Alder reaction. The resulting product was condensed with acetone, and after heating with selenium gave 1,4,6-trimethylnaphthalene.



Succinic anhydride and polyalkyl benzenes (5, 6, 7, 8) have been used as starting materials for the syntheses of polyalkylnaphthalenes.

Abadir, Cook, and Gibson (9) prepared octamethylnaphthalene starting

with 1,2,3,4-tetramethylbenzene and 2,3-dimethylsuccinic anhydride. Dev and Guha (10) used *p*-cymene and methylsuccinic anhydride in a multistep synthesis of cadalene.

Mosby (11) prepared a number of tri- and tetramethylnaphthalenes using γ -valerolactone and *o*, *m*, and *p*-xylenes in a Friedel-Crafts reaction. This step was followed by cyclization, reduction, dehydration, and dehydrogenation to give the appropriate naphthalene. Because of our interest in polyalkylnaphthalene synthesis, we repeated the work of Dev and Guha and obtained essentially the same results.

In 1937 Du Feu, McQuillin, and Robinson (12) studied the dehydrogenation of α,β -unsaturated cyclic ketones in the presence of palladium on carbon. β -Naphthol was obtained from 2-keto- $\Delta^{1:9}$ -octalin in 66% yield. No mention was made of the formation of naphthalene. In 1945, Horning (13) reported the formation of 2,6-dibenzylphenol in 91% yield from the dehydrogenation of 2,6-dibenzalicyclohexanone with 10% palladium on carbon. Horning and Horning (14) reacted 3-methyl-5-aryl-2-cyclohexen-1-ones with palladium on carbon in a variety of solvents to obtain phenolic products in 52% to 84% yield. Their studies showed that the higher boiling solvents, *p*-cymene, triethylbenzene, and phenylether, gave the highest yields of phenolic compounds. There was no indication that aromatic hydrocarbons were present as products due to hydrogenation of the carbonyl group and subsequent dehydration. Horning, Horning, and Walker (15) in a continuation of their dehydrogenation studies of α,β -unsaturated ketones reported that variation of alkyl groups and aryl groups at the 5-position to the carbonyl function had little effect in altering the nature of the products. Again there was no mention of the formation of aromatic hydrocarbons.

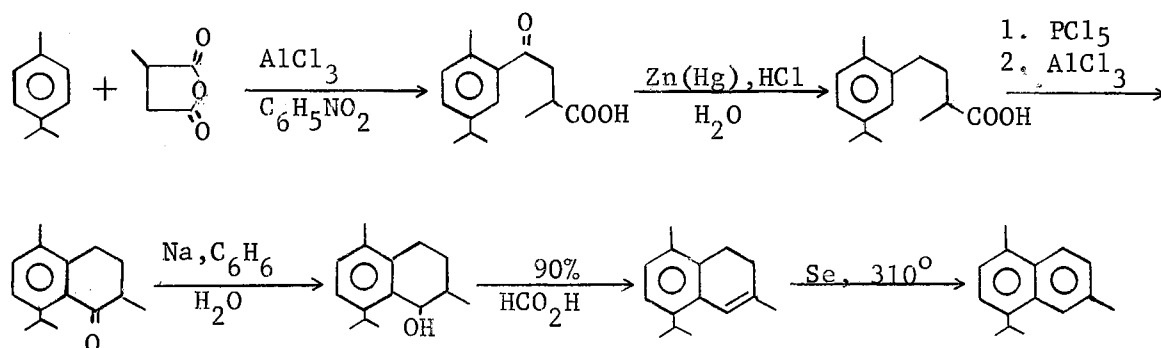
Mosettig and Duvall (16) reported the isolation of 1- and 4-phenanthrol from heating 1- and 4-ketotetrahydrophenanthrene in the presence of palladium on carbon in a variety of solvents. Naphthalene proved to be the better solvent. In some cases they obtained side products in small yield, and in one case they mentioned the possible formation of phenanthrene.

As recently as 1964, Birch and White (17) reported the dehydrogenation of α -tetralone to naphthalene using a 1:1 mixture of solid sodium hydroxide and potassium hydroxide. This reaction is unusual since conventional dehydrogenation reagents were not employed. However, since this is an alkali-promoted dehydration reaction and hydrogen is not evolved, this process does not appear to be in the same category as that previously described.

CHAPTER II

DISCUSSION OF RESULTS

The synthesis of cadalene and related hydrocarbons was of interest to us because cadalene has an isoprenoid structure and hydrocarbons of this type are suspected to be present in petroleum. A search of the literature showed cadalene had been prepared by several routes (1, 6, 10, 18, 19). The best of these routes appears to be that of Dev and Guha, who reacted methylsuccinic anhydride with *p*-cymene in a Friedel-Crafts reaction as the first step of a seven-step synthesis as shown.



Since the reaction of *p*-xylene and methylsuccinic anhydride would eventually yield a single trimethylnaphthalene, *p*-xylene was selected for large-scale synthesis as shown in Fig. 1. Some of the synthetic steps described by Dev and Guha are impractical for large-scale reactions. The Friedel-Crafts reaction, which is the first step of the synthesis, came under immediate scrutiny because of the difficulty in removing the nitrobenzene solvent from the reaction product. Steam

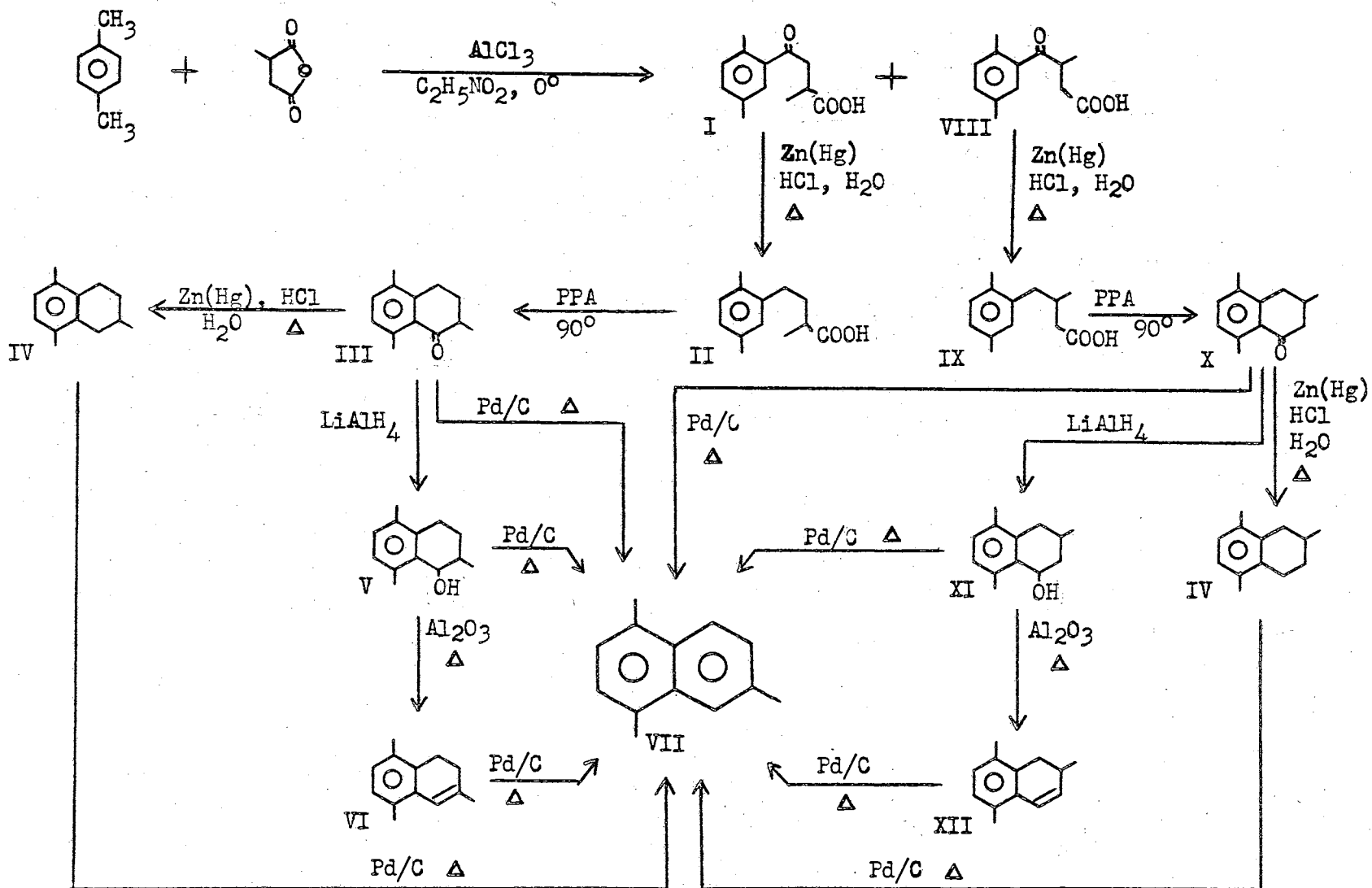


FIG. I SYNTHETIC ROUTE TO 1,4,6-TRIMETHYLNAPHTHALENE

distillation was attempted, but proved to be time consuming for removing nitrobenzene on a large scale. The problem of solvent removal was overcome by substituting nitroethane, which is easily removed by distillation. Most Friedel-Crafts reactions are allowed to stand for several hours after the addition of the aluminum chloride and then stirred for an additional two hours. For the large-scale reactions, we found this inconvenient and troublesome because accumulated gases caused considerable foaming when stirring was begun after a few hours of standing. A single turn of the stirring propeller was enough to cause a sudden release of gases, which resulted in an overflow of the flask contents. Comparison of nitrobenzene, nitroethane, and nitromethane as solvents for Friedel-Crafts reactions of *p*-xylene and methylsuccinic anhydride showed nitroethane to be superior in regard to yield and selectivity of reaction.

The Clemmensen reduction (20) was well adapted to the large-scale reactions and proved to be superior to the Wolff-Kishner reduction for converting the keto-acid to the desoxy acid. With large-scale reactions, caution should be exercised when the reaction mixture is first brought to reflux since there is a brisk evolution of gases when the reaction mixture begins to boil. This can be avoided by reducing the temperature of the heating mantle when the solution appears to be near the boiling point. Once the solution boils, heating may be resumed.

The conversion of the acid to the acid chloride followed by ring closure with aluminum chloride is time consuming and inconvenient for large-scale preparation of tetralones. Our studies showed polyphosphoric acid (PPA) to be a superior reagent for cyclization of γ -arylbutyric acids to tetralone (21).

The 1-keto-1,2,3,4-tetrahydrotrimentylnaphthalenes III, X, and XVI were reduced with lithium aluminum hydride, instead of moist benzene and

sodium (22). With proper precautions, reductions of ten moles of ketone may be accomplished with ease.

Formic acid dehydration of the 1,2,3,4-tetrahydrotrimethyl-1-naphthols V, XI, and XVII is a satisfactory reaction. However, we wished to include the study of the dehydration by pyrolysis on a column of alumina (23). Therefore, the latter reaction was used to convert the tetrahydrotrimethylnaphthols V, XI, and XVII to the dihydrotrimethylnaphthalenes VI, XII, and XVIII as shown in Figs. 1 and 2. Several small scale reactions were necessary to determine the proper parameters to be used for maximum yield of the desired product. These yields ranged from 66 to 84%. Dehydration of the tetrahydronaphthols V, XI, and XVII leads to a mixture of isomeric dihydronaphthalenes. Isomerization during dehydration of this series of tetrahydronaphthols was observed for both acidic and basic dehydrating agents, i.e., formic acid and alumina.

The use of selenium for dehydrogenation was not acceptable because of the difficulties encountered in trapping the toxic hydrogen selenide given off during dehydrogenation. Palladium on carbon (11) was therefore employed for all dehydrogenations, although the possibility of some disproportionation existed.

Because of our interest in reducing the number of steps in the synthesis, methods for direct conversion of the tetrahydrotrimethylnaphthols V, XI, and XVII and the 1-keto-1,2,3,4-tetrahydrotrimethylnaphthalenes III, X, and XVI to the trimethylnaphthalenes VII and XX were sought. Direct dehydrogenation of the tetrahydrotrimethylnaphthol V, Fig. 1, with palladium on carbon catalyst, appeared to be the most effective route to 1,4,6-trimethylnaphthalene (VII) and reduced the total number of steps

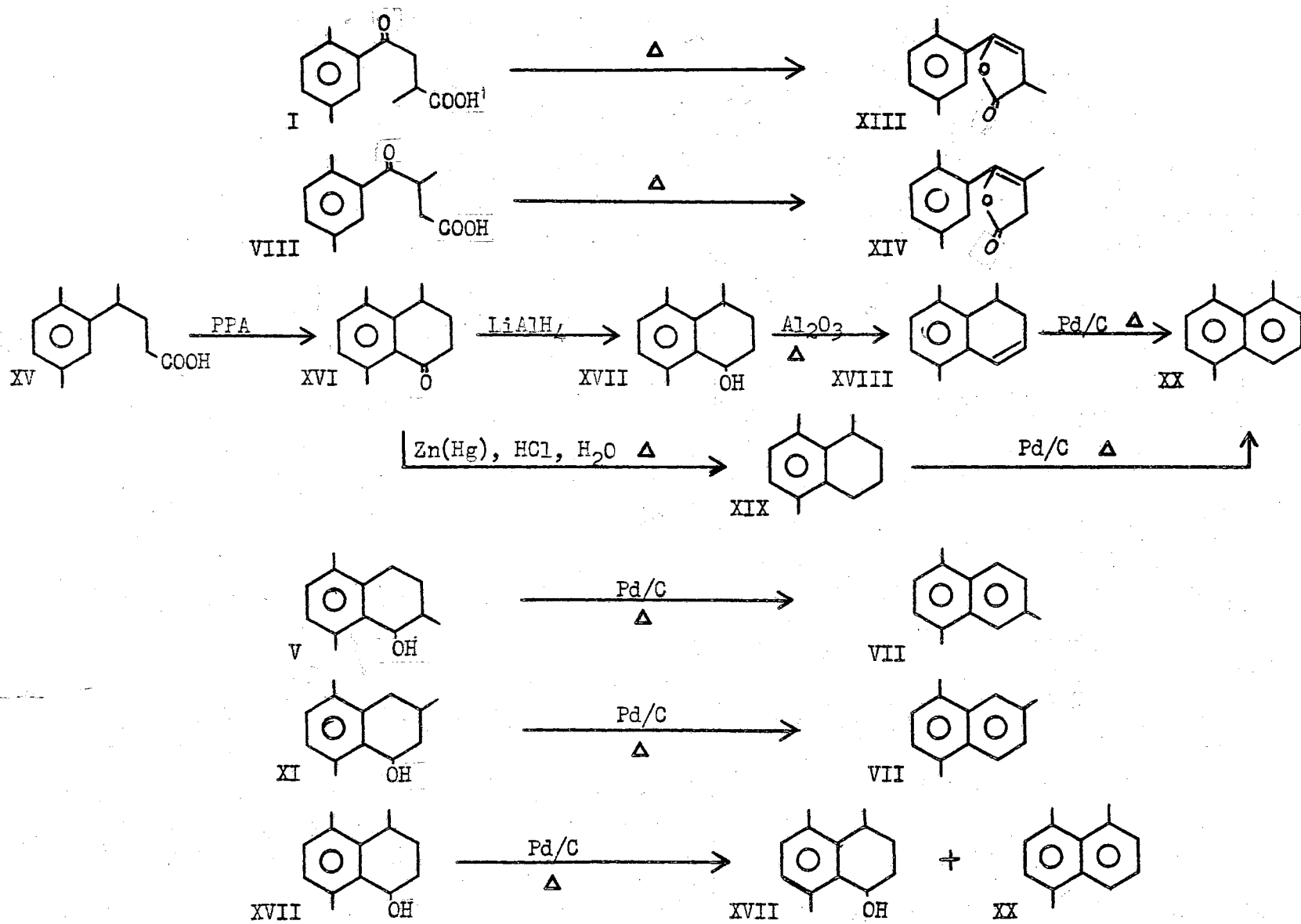
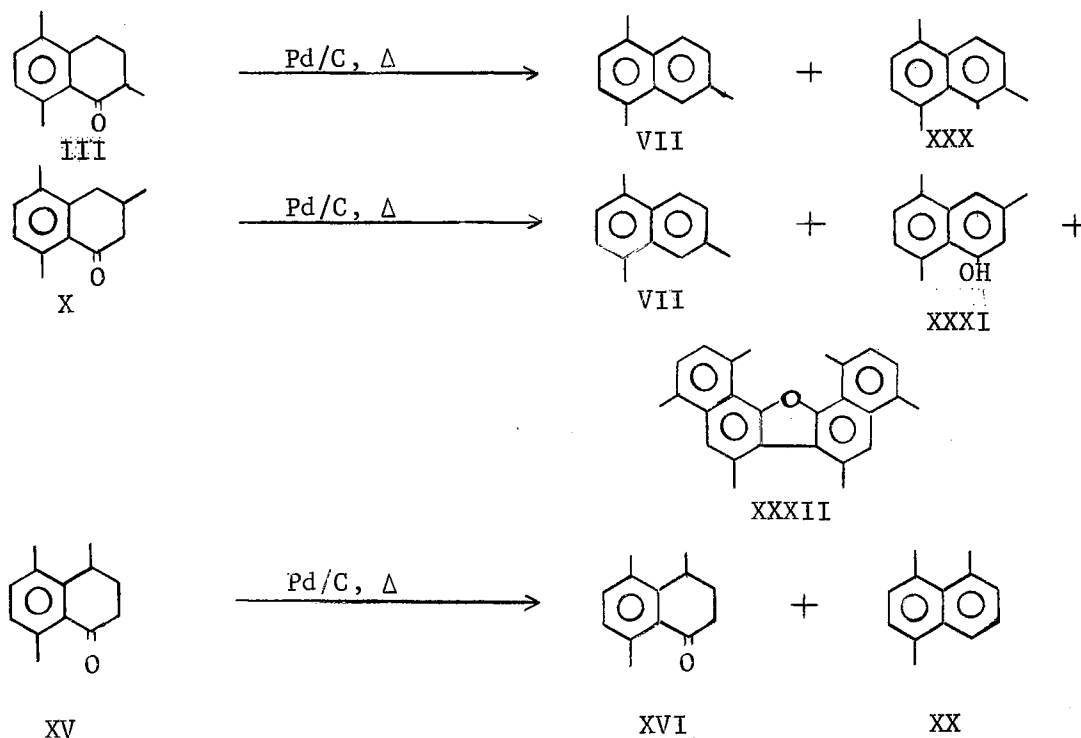


Fig. 2 Synthetic Route to 1,4,5-Trimethylnaphthalene, and Dehydrogenation of Tetrahydrotrimethylnaphthols

in the synthesis from six to five. The overall yield was also increased to 66% using this sequence.

Direct dehydrogenation of the tetrahydrotrimethylnaphthols proved to be effective for those cases where the methyl group was α or β to the hydroxyl. However, placing a methyl group γ to the hydroxyl group slowed the dehydrogenation reaction so that for this particular arrangement the reaction is not practical. We assume that the 4,5,8-arrangement of the methyl groups of the 1,2,3,4-tetrahydro-4,5,8-trimethyl-1-naphthol (XVII) produces a steric effect which retards approach to the catalyst surface, and consequently blocks or slows the dehydrogenation step. Dehydrogenation with platinum on carbon and palladium on carbon appears to be equally effective. Since there appeared to be no advantage to the use of platinum on carbon, and since this catalyst is considerably more expensive, our studies were mainly directed toward dehydrogenation with palladium on carbon. It is of interest that naphthols did not appear among the products of dehydrogenation of the tetrahydrotrimethylnaphthols.

We sought to remove an additional step from the synthesis of trimethylnaphthalenes by direct dehydrogenation of the 1-keto-1,2,3,4-tetrahydrotrimethylnaphthalenes III, X, and XVI, and thus avoid preparation of the tetrahydrotrimethylnaphthols. Dehydrogenation of the 1-ketotetrahydrotrimethylnaphthalenes III, X, and XVI appears to be more complex than dehydrogenation of the tetrahydrotrimethylnaphthols, in that the trimethylnaphthols XXX, XXXI were among the products. These trimethylnaphthols were not encountered in the tetrahydrotrimethylnaphthol dehydrogenation studies.



The dehydrogenation studies were extended to other cyclic ketones. In one set of reactions using 1-keto-1,2,3,4-tetrahydrophenanthrene (**XXI**) (Fig. 3) with palladium on carbon alone, and also with added solvent, it was found that 1-phenanthrol was obtained in much better yield when a solvent was present. In the absence of solvent, a small quantity of phenanthrene was obtained. However, phenanthrene was not obtained when naphthalene was present. Phenanthrene was found to be steam volatile; therefore, if any phenanthrene had been formed in Mosettig and Duvall's work it would have steam distilled and consequently remained undetected. We found a small quantity of 1,2,-dihydro-1-phenanthrol (**XXIV**) formed in this reaction when naphthalene was used as solvent. A portion of this compound was readily converted to 1-phenanthrol in 83% yield by heating with palladium on carbon using naphthalene as solvent. The neutral portion of the reaction remaining after 1-phenanthrol was extracted with base, was shown

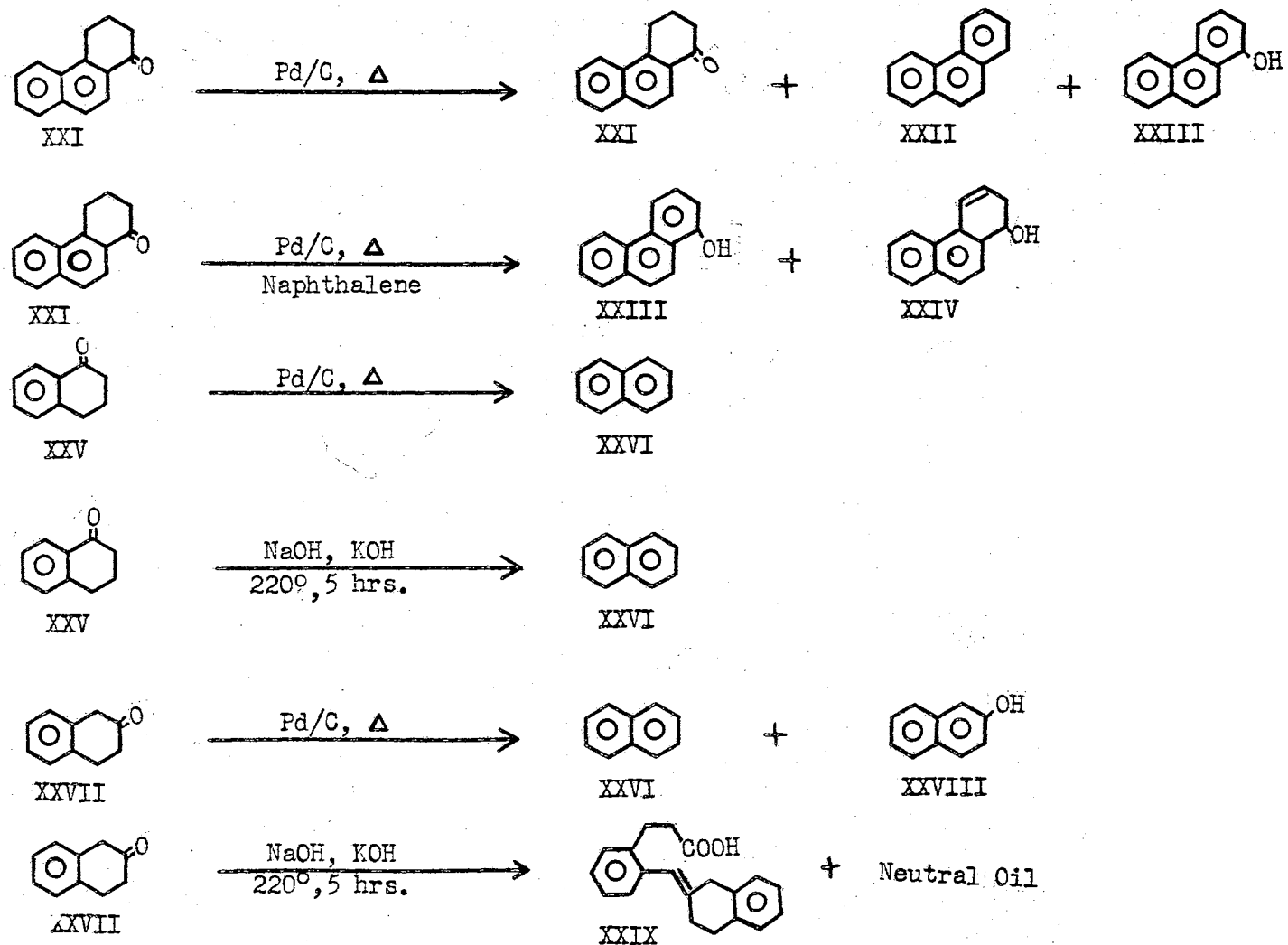
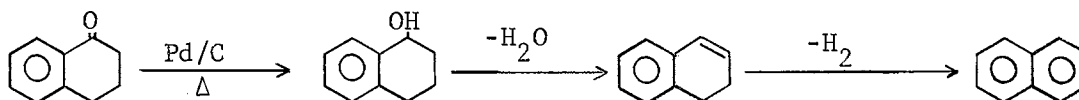


Fig. 3 Dehydrogenations of 1-Ketotetrahydrophenanthrene and 1-Ketotetrahydronaphthalenes

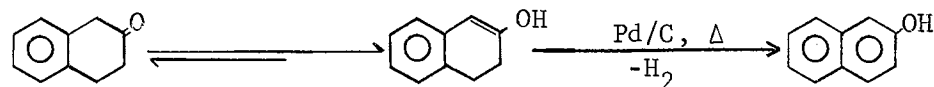
to contain phenanthrene through gas chromatography analysis. There was no evidence of any starting material in the reaction flask.

The dehydrogenation of α -tetralone (Fig. 3) with palladium on carbon to naphthalene was accompanied by formation of water. This would suggest reduction of the carbonyl group and very rapid dehydration followed by dehydrogenation to naphthalene as shown.

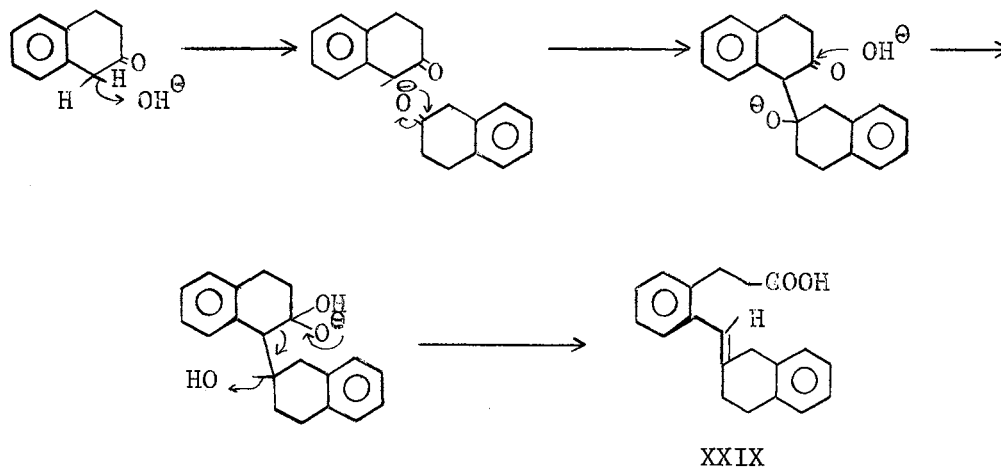


The hydrogen necessary for the reduction of the ketone carbonyl function could result from other dehydrogenation processes.

The formation of β -naphthol (26%) during the dehydrogenation of β -tetralone to naphthalene (54%) may be the result of dehydrogenation of the enol form of β -tetralone.



The base catalyzed reaction described by Birch (17), smoothly converts α -tetralone to naphthalene (Fig. 3). When β -tetralone was subjected to identical conditions, only a trace of naphthalene was obtained. The major product was a neutral oil. Two molecules of β -tetralone condensed to form 3-(o-[(1,2,3,4-tetrahydro-2-naphthylidene)methyl]phenyl) propionic acid (XXIX). This reaction may be rationalized through the following sequence:



The structure of 3-(o-[(1,2,3,4-tetrahydro-2-naphthylidene)methyl]-phenyl) propionic acid (XXIX) has been confirmed by elemental analysis and by the N.M.R. and infrared spectra of the acid and the N.M.R. spectrum of its methyl ester.

CHAPTER III

EXPERIMENTAL

For large-scale Friedel-Crafts reactions a 22-liter, round-bottomed, 3-necked flask, equipped with an XP Lightnin stirrer mounted on a heavy duty stand was used. The flask was supported on an 8" rubber vehicle tire and placed inside a large plastic tub which contained a mixture of cracked ice and salt for cooling the reaction. The center neck of the flask contained a size-fourteen Neoprene stopper, fitted with an asbestos and shredded Teflon packing gland capable of sealing around the $\frac{1}{2}$ ", 316 stainless steel, stirring shaft, such that a light pressure could be maintained inside the flask, and gases were prevented from escaping around the stirring shaft.

One side neck was used to add aluminum chloride through a Gooch tube to the reaction. The other side neck was fitted with an open-bore reflux condenser which permitted lowering a thermometer well into the reaction mixture. An exhaust tube for escaping gases led from the top of the condenser to the rear of the hood. The interior of the flask and condenser were thoroughly dried with a hot stream of air from a heat gun before addition of any reagents. This apparatus is effective for Friedel-Crafts reactions in the range of 15 to 30 moles of reactants.

β -(p-Xyloyl-2)- α -methylpropionic Acid (I).

Methylsuccinic anhydride (2,109 g., 18.5 moles), p-xylene (2,162 g.,

2,520 mls., 20.4 moles), and distilled nitroethane (6 l.) were added to the above-described flask. The solid methylsuccinic anhydride dissolved readily in nitroethane and p-xylene. The tub was filled with ice and salt mixture, and the mixture stirred and cooled to 10°. Anhydrous aluminum chloride (12 lbs., 5,435 g., 40.7 moles) was added slowly through the side neck over a period of five hours, the temperature being held at 15°. Approximately fifteen minutes after the final addition, ice and water were removed from the tub. The reaction mixture was stirred for an additional 90 minutes. The dark-colored reaction product was poured onto approximately fifty pounds of ice and stirred until the red-brown complex had decomposed.

Hydrochloric acid (3 l.) was then poured into the solution to complete the decomposition. The organic layer (a grayish paste) was taken up by several extractions of the aqueous solution with ether. The ether solution was then washed with water, saturated sodium chloride solution, dried over anhydrous magnesium sulfate, and filtered. Most of the ether was removed on a steam bath. The remaining solution was placed in the refrigerator for crystallization of the keto-acid, after which the liquid was decanted and the crystals broken up and filtered. Nitroethane was then distilled under aspirator vacuum. The solution remaining was placed in the refrigerator and more keto-acid crystallized to give a total yield of 3,322 g. (15.1 moles, 81.6%) of I, m. p. 118-119°C; 2,4-dinitrophenylhydrazone, m. p. 122.5-123.5°C; methyl ester, m. p. 22-23°C.

The molecular weight of I was determined by mass spectrometry to be 220. The ultraviolet spectrum of I showed $\lambda_{\max}^{\text{EtOH}}$ 211, 245 and 293 m μ , log ϵ (4.33, 3.95, and 3.18).

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.9%; H, 7.27%. Found: C, 70.9%; H, 7.02%.

γ -(p-Xylyl-2)- α -methylbutyric Acid (II).

A 12-liter, two-necked, round-bottomed flask, heated with a mantle was used as the reaction vessel for a Clemmensen reduction of I. One neck contained a large reflux condenser and the other neck was used for adding the reactants. Mossy zinc (reagent grade 1,760 g., 27 g. atom) was amalgamated by stirring with mercuric chloride (90 g.), concentrated hydrochloric acid (88 ml.), and water (2,288 ml.) for fifteen minutes. The acid was decanted from the zinc; the amalgamated zinc, I (880 g., 4 moles), concentrated hydrochloric acid (1,760 ml.), water (1,820 ml.), and a second portion of concentrated hydrochloric acid (1,320 ml.) were added to the flask in the order given. The heating mantle was turned on. After the reaction mixture began to boil,¹ concentrated hydrochloric acid (440 ml.) was added every three hours. The reaction was stopped after 38 hours of reflux, the aqueous layer was siphoned from the cooled reaction flask, and the organic layer was taken up in ether. The remaining zinc (397 g. recovered) was washed thoroughly with small portions (200 ml.) of ether. These washings were added to the original ether solution along with extracts from the aqueous layer. The ether solution was washed with water and saturated sodium chloride solution, dried over anhydrous magnesium sulfate, filtered, and the ether removed to

¹When the reaction mixture temperature approaches the boiling point, the Variac should be turned down until boiling has begun. There is a vigorous evolution of gases when the reaction first begins to boil. Any subsequent starts after the initial heating are normal.

approximately half volume. The solution was placed in the refrigerator for crystallization to give γ -(p-xylyl-2)- α -methyl-butyrlic acid (II), 89%, (739 g., 3.58 moles), m. p. 54.5-55.5°.

The molecular weight of II was determined by mass spectrometry to be 206. The ultraviolet spectrum of II showed $\lambda_{\max}^{\text{EtOH}}$ 215, 268 and 276 m μ , log ϵ (4.03, 2.75 and 2.77).

Anal. Calcd. for C₁₃H₁₈O₂: C, 75.72%; H, 8.73%. Found: C, 75.8% H, 8.59%.

1-Keto-1,2,3,4-tetrahydro-2,5,8-trimethylnaphthalene (III).

To a 12-liter, two-necked, round-bottomed flask equipped with a Lightnin F stirring motor with shaft and two three-bladed propellers (2" dia.) was added 7,248 g. (1 gal.) polyphosphoric acid. The acid in the flask was heated to 90° with a mantle, the stirrer started, and solid γ -(p-xylyl-2)- α -methylbutyrlic acid (2,126 g., 10.32 moles) was added. The reaction immediately became a dark brown color. Stirring was continued for twenty minutes. The exothermic reaction caused the temperature to rise to 115-120°. The temperature was maintained at 90-100° throughout the reaction except for this period following addition of the solid acid. Another gallon of PPA was added to the reaction; stirring was continued for thirty minutes. The reaction flask was removed from the heating mantle, and the reaction mixture allowed to cool to 60°. The reaction mixture was then poured onto a mixture of ice (25 lbs.) and water (20 l.) for decomposition. When all the dark brown material had decomposed, the organic layer was extracted from the aqueous layer with ether. Unreacted acid was then extracted from the ether solution with several portions of 5% sodium hydroxide. The ether solution was

washed free of base with water, and saturated sodium chloride solution, dried over anhydrous magnesium sulfate (450 g.), filtered and concentrated by stripping under aspirator vacuum.

The product, 1-keto-1,2,3,4-tetrahydro-2,5,8-trimethylnaphthalene (III), was distilled at 95-100°/0.2 mm. On cooling, the product crystallized from isopropyl alcohol as colorless crystals melting at 20°. Since the crystalline material melts readily, filtration is difficult. The 2,4-dinitrophenylhydrazone melts at 183.5-184-5°.

The molecular weight was determined by mass spectrometry to be 188. The ultraviolet spectrum of III showed $\lambda_{\max}^{\text{EtOH}}$ 213, 254 and 300 m μ , log ϵ (4.73, 4.18 and 3.62).

Anal. Calcd. for C₁₃H₁₆O: C, 82.97%; H, 8.5%. Found: C, 82.89%; H, 8.43%.

1,2,3,4-Tetrahydro-2,5,8-trimethylnaphthalene (IV).

In a one-liter, three-necked, round-bottomed flask containing a reflux condenser in the center neck, was added 100 g. (15.4 g. atom) of reagent grade mossy zinc (amalgamated), concentrated hydrochloric acid (100 ml.) and water (75 ml.). A 50 g. (0.27 mole) sample of III and concentrated hydrochloric acid (75 ml.) were added next. The reaction was heated at reflux for seventeen hours, with fifty milliliters of concentrated hydrochloric acid being added after each three hours of reflux time. The organic layer was extracted from the aqueous layer with ether; the ether layer was washed with several portions of water to remove traces of acid, then washed with saturated sodium chloride solution, dried over anhydrous magnesium sulfate, filtered, and distilled to remove the ether.

The resulting product was distilled at $77^{\circ}/0.6$ mm. to give an 85.7% yield (39.7 g., 0.23 mole) of 1,2,3,4-tetrahydro-2,5,8-trimethylnaphthalene (IV), which melted at $3-6^{\circ}$.

The molecular weight was determined by mass spectrometry to be 174. The ultraviolet spectrum of IV showed $\lambda_{\text{max}}^{\text{isooctane}}$ 268 and 273 m μ , log ϵ (2.39 and 2.28).

Anal. Calcd. for $C_{13}H_{18}$: C, 89.65%; H, 10.35%. Found: C, 89.68%; H, 10.43%.

1,2,3,4-Tetrahydro-2,5,8-trimethyl-1-naphthol (V).

In a 12-liter, three-necked, round-bottomed flask equipped with a dropping funnel on one side neck, a condenser on the other side neck, and a stirring shaft in the center neck, was added 3.5 liters of dry ether and lithium aluminum hydride (40 g.). A heating mantle was used for initial warming of the reaction. The lithium aluminum hydride-ether suspension was heated with stirring at reflux temperature for fifteen minutes. 1-Keto-1,2,3,4-tetrahydro-2,5,8-trimethylnaphthalene (III) (376 g., 2 moles) in dry ether (500 ml.) was added dropwise to the lithium aluminum hydride-ether suspension over a period of ninety minutes. The heating mantle was turned off during addition of III as the reaction is exothermic. After addition of III the mixture was heated at reflux temperature for two hours thirty minutes. To test for completion of the reaction, a small quantity of lithium aluminum hydride was added to the solution. If no reaction is visible the reduction is complete. The heating mantle was replaced with a plastic tub in order to cool the reaction mixture with an ice-water bath during decomposition.

A saturated solution of sodium sulfate was added to the reaction flask as rapidly as practical from the dropping funnel. After the excess lithium aluminum hydride had been decomposed, the ether solution was decanted from the white precipitate into a separatory funnel. The precipitate was washed 2-3 times with ether; these washings were then added to the separatory funnel. The ether solution was washed 2-3 times with water (250 ml. portions) and saturated sodium chloride solution and dried over anhydrous magnesium sulfate, filtered, and the ether removed under aspirator vacuum. 1,2,3,4-Tetrahydro-2,5,8-trimethyl-1-naphthol (V) was distilled at $95^{\circ}/0.35$ mm., giving 360.7 g. (1.9 moles) in 95% yield. The naphthol V crystallizes from petroleum ether and melts at $79-81^{\circ}$.

3,4-Dihydro-2,5,8-trimethylnaphthalene (VI).

1,2,3,4-Tetrahydro-2,5,8-trimethyl-1-naphthol (V) (20 g., 0.105 mole) was dissolved in distilled cyclohexane (100 ml.) and passed through a preheated column (30 mm. x 38 cm.) containing 33 cm. of Harshaw alumina (A1-0104, 1/8", B901). The temperature of the column was maintained between 250 and 270° . The naphthol V, which vaporized on contact with the alumina, was swept through the column with gentle flow of N_2 gas. The naphthol V was metered onto the column by means of a bellows pump over a period of two hours. A second 100 ml. portion of cyclohexane was passed through the system as a rinse. The collected solution was washed with water and saturated sodium chloride solution, dried over anhydrous magnesium sulfate, and filtered. The cyclohexane was removed by distillation. The product was then distilled under vacuum to give 14.8 g. (75%) of the

hydrocarbon, boiling at 81-93^o/0.7 mm. A sample of the product was analyzed by gas chromatography on a Carbowax column ($\frac{1}{4}$ " x 10', acid washed Chromosorb W, 80-100 mesh) at 200^o and found to contain four components. These were separated by preparative gas chromatography on a 10' x 4" diameter column of 20% Carbowax on 60/80 mesh Chromosorb W. The largest peak was 81.5% (66% yield of the product and was shown by comparison through gas chromatography to be 3,4-dihydro-2,5,8-trimethylnaphthalene (VI). The other peaks were shown to be 3,4-dihydro-3,5,8-trimethylnaphthalene (XII) (4%), 1,4,6-trimethylnaphthalene (VII) (66%), and 1,4-dihydro-2,5,8-trimethylnaphthalene (4.4%).

A gas chromatography purified sample of VI boiled at 66^o/0.2 mm. and was analyzed.

Anal. Calcd. for C₁₃H₁₆: C, 90.7%; H, 9.30%. Found: C, 89.92%; H, 9.89%.

1,4,6-Trimethylnaphthalene (VII) from IV.

A 2-liter, three-necked flask, equipped with a reflux condenser in the center neck and a thermometer in one side neck, was used for dehydrogenation with Pd/C catalyst. A 1,097 g. (6.3 moles) sample of IV and 10% Pd/C (12 g.) were added to the flask. The reaction mixture was heated for thirteen hours, and the progress of the reaction was followed with gas chromatography. The contents of the flask were filtered through a sintered glass funnel containing a bed of Celite. Ether was used to rinse the product out of the Celite. 1,4,6-Trimethylnaphthalene (VII) was distilled under vacuum to give 1,051.6 g. (6.18 moles) boiling at 90^o/0.85 mm. (98%). The picrate (orange crystals) melted at 134-135^o (lit. 133^o) (2). The molecular weight of VII was determined by mass spectrometry to be 170.

β -(p-Xylo1-2)- β -methylprionic Acid (VIII).

This keto-acid was formed during the preparation of β -(p-xyloyl-2)- α -methylpropionic (I). The isolation was accomplished by flash distilling all residues left after removing the major portion of the α -methylpropionic acid I by crystallization. Water, resulting from formation of the γ -enol-lactones (Fig. 2) of the keto acids I and VIII, was observed in the early part of the distillation. The distilled material, a mixture of acids and enol-lactones, was stirred with a saturated sodium bicarbonate solution to remove any free acid remaining from enol-lactone formation. The organic layer was extracted from the bicarbonate solution with ether. The ether solution was washed with water, saturated sodium chloride solution, dried over anhydrous magnesium sulfate, filtered, and the ether removed to give mainly the β -methyl enol-lactone XIV. It was later discovered that the enol-lactone XIII of the α -methyl series is least stable and is hydrolyzed by bicarbonate solution, whereas the enol-lactone XIV is stable under these conditions.

A 20 g. portion of the β -methyl enol-lactone XIV was added to a quantity of 10% sodium hydroxide solution. As the organic compound dissolved in the basic solution, more sodium hydroxide pellets were added until solution was complete. The basic solution was then extracted with ether. The alkaline layer was acidified with concentrated hydrochloric acid to give a crystalline acid. The remainder of the organic material was then hydrolyzed using 30% sodium hydroxide solution. The organic material was extracted with ether and the ether layer was washed with water and saturated sodium chloride solution, dried over anhydrous magnesium sulfate, and filtered. After removal of ether, the compound was crystallized from petroleum ether (b.p. 66-67^o) to give colorless crystals

of the β -methyl acid VIII, m. p. 81-82 $^{\circ}$, whose 2,4-dinitrophenylhydrazone and methyl ester melted at 96.5-98 $^{\circ}$ and 62-63 $^{\circ}$, respectively. The molecular weight was determined by mass spectrometry to be 220. The ultraviolet spectrum of VIII showed $\lambda_{\max}^{\text{EtOH}}$ 211, 245 and 290 m μ , log ϵ (4.34, 2.92 and 3.16).

Anal. Calcd. for $\text{C}_{13}\text{H}_{16}\text{O}_3$: C, 70.9%; H, 7.27%. Found: C, 70.6%; H, 7.56%.

γ -(p-xylyl-2)- β -methylbutyric Acid (IX).

A Clemmensen reduction of β -(p-xyloyl-2) β -methylpropionic acid (VIII) was carried out in the same manner as previously described for II. A 440 g. sample of VIII (2 moles), amalgamated zinc (880 g. 13.5 g. atom), concentrated hydrochloric acid (1540 ml. total), water (660 ml.) were used. The total reaction time was forty-one hours, and concentrated hydrochloric acid (1190 ml. total) was added at three hour intervals during this period. The reaction was worked up as described for the other Clemmensen reductions to give 287 g. (1.39 moles) of γ -(p-xylyl-2)- β -methylbutyric acid (IX), m.p. 68-68.5 $^{\circ}$. The molecular weight was determined by mass spectrometry to be 206.

The ultraviolet spectrum of the β -methyl butyric acid IX showed $\lambda_{\max}^{\text{EtOH}}$ 215, 268 and 277 m μ , log ϵ (4.05, 2.78 and 2.82).

Anal. Calcd. for $\text{C}_{13}\text{H}_{18}\text{O}_2$: C, 75.72%; H, 8.73%. Found: C, 76.2%; H, 8.7%

1-Keto-1,2,3,4-tetrahydro-3,5,8-trimethylnaphthalene (X).

The preparation of X was similar to that of the 1-keto-tetrahydro-trimethylnaphthalene III. Polyphosphoric acid (387 g.) and γ -(*p*-xylyl-2)- β -methylbutyric acid (IX) (106.5 g., 0.51 mole) were allowed to react in a three-liter flask. A second portion of polyphosphoric acid (339 g.) was added after the initial stirring time. The reaction was worked up as previously described to give a 91% yield (87.5 g., 0.47 mole) of 1-keto-1,2,3,4-tetrahydro-3,5,8-trimethylnaphthalene (X) m.p. 71-72^o, whose 2,4-dinitrophenylhydrazone melted at 249-250^o. The molecular weight was determined by mass spectrometry to be 188. The ultraviolet spectrum of X showed $\lambda_{\max}^{\text{EtOH}}$ 213, 254 and 306 m μ , log ϵ (4.67, 4.08 and 3.42).

Anal. Calcd. for C₁₃H₁₆O: C, 82.97%; H, 8.5%. Found: C, 82.9%; H, 8.65%.

1,2,3,4-Tetrahydro-3,5,8-trimethyl-1-naphthol (XI).

In a manner similar to the preparation of the tetrahydronaphthol V, 188 g. (1 mole) of 1-ketotetrahydrotrimethylnaphthalene X was reduced with lithium aluminum hydride (10 g.) to give 182 g. (0.96 mole) of 1,2,3,4-tetrahydro-3,5,8-trimethyl-1-naphthol (XI), m.p. 76-77^o, in 96% yield. The molecular weight was determined by mass spectrometry to be 190. The ultraviolet spectrum of XI showed $\lambda_{\max}^{\text{EtOH}}$ 217, 270 and 279 m μ , log ϵ (4.03, 2.77 and 2.75).

Anal. Calcd. for C₁₃H₁₈O: C, 82.1%; H, 9.47%. Found: C, 82.48%; H, 9.61%.

3,4-Dihydro-3,5,8-trimethylnaphthalene (XII).

The hydrocarbon XII was prepared from 15 g. of the tetrahydrotri-methylnaphthol XI using the procedure described for the preparation of

the dihydronaphthalene VI. Two fractions totaling 10.45 g., distilling at 73-80°/0.7 mm., were obtained. The two fractions were analyzed on a gas chromatography column (4' x ¼", SE 30 on Chromosorb P, 130°) to determine the yield of XII (8.94 g., 0.052 mole, 65% yield). The molecular weight was determined by mass spectrometry to be 172.

Anal. Calcd. for C₁₃H₁₆: C, 90.7%; H, 9.3%. Found: C, 90.38%; H, 9.47%.

4-Hydroxy-2-methyl-4-(p-xylyl-2)-3-butenic Acid γ-Lactone (XIII).

A 15-gram sample of the keto-acid I was placed in a 200-ml., three-necked, round-bottomed flask equipped with a thermometer in one side neck and an elongated U-tube in the center neck leading to a three-necked flask. The reaction flask was heated with a heating mantle at atmospheric pressure. When the temperature of the reaction mixture reached 247° water appeared in the side tube. At 252°, the reaction mixture began to boil. Heating was continued for eighty-five minutes, at which time no more water vapor appeared to be forming. The top temperature was 300°. The dark brown oil was distilled at 128-157°/0.05 mm. to give 9 grams of a light yellow oil which crystallized from ether-petroleum ether (65-70°) as colorless crystals of XIII, m.p. 98-98.5°.

The molecular weight was determined by mass spectrometry to be 202. The ultraviolet spectrum of XIII showed $\lambda_{\max}^{\text{EtOH}}$ 212, 271 and 278 mμ, log ε (4.53, 2.98 and 2.96).

Anal. Calcd. for C₁₃H₁₄O₂: C, 77.22%; H, 6.93%. Found: C, 77.7%; H, 7.22%.

4-Hydroxy-3-methyl-4-(p-xylyl-2)-3-butenic Acid γ-Lactone (XIV).

The same type of reaction apparatus was used for this preparation as was described for the preparation of the α -methyl enol-lactone XIII. Water vapor appeared at 240° , and the compound began boiling at 258° . The compound was heated for two hours and twenty-five minutes. The top temperature was 320° . The light yellow viscous material was distilled at $151-155^{\circ}/0.9$ mm. The oil obtained from the distillation crystallized upon cooling and the solid was recrystallized from ether-petroleum ether ($40-45^{\circ}$) to give colorless crystals of XIV, m.p. $72-73^{\circ}$.

The molecular weight was determined by mass spectrometry to be 202. The ultraviolet spectrum of XIV showed $\lambda_{\max}^{\text{EtOH}}$ 271 and 279 m μ , log ϵ (2.93 and 2.93).

Anal. Calcd. for $\text{C}_{13}\text{H}_{14}\text{O}_2$: C, 77.22%; H, 6.93%. Found: C, 77.44%; H, 7.1%.

1,4,5-Trimethylnaphthalene (XX)

γ -(*p*-xylyl-2)- γ -methylbutyric acid (XV) was prepared by reacting *p*-xylene and γ -valerolactone in the presence of aluminum chloride (Fig. 2). The crude acid XV (279 g.) was purified by esterifying it in a mixture of methanol (164 ml., 129.6 g.), methylene chloride (500 ml.), and concentrated sulfuric acid (20 ml.) during a thirty-hour heating period at the boiling temperature (24). The solution was washed with water and saturated sodium bicarbonate solution to remove sulfuric acid and unesterified acid. The solution was washed with water, saturated sodium chloride solution, dried over anhydrous magnesium sulfate, filtered, and the methylene chloride distilled from the ester. The product was distilled at $104^{\circ}/1.5$ mm. to give 238 g. (1.08 mole, 80% yield) of methyl γ -(*p*-xylyl-2)- γ -methylbutyrate. The ester (33 g., 0.15 mole) was hydrolyzed by boiling with 15%

sodium hydroxide solution, 2 g. of *p*-toluene sulfonic acid, and 60 ml. of methanol for 22 hours. The water was drained from the condenser, and a splash head with attached downward condenser for distilling the methanol from the reaction flask was attached to this. After removal of methanol, the solution was cooled and extracted with ether to remove organic material. The basic layer was acidified and the acid XV was taken up in ether. The ether solution containing the acid XV was washed with water, saturated sodium chloride solution, dried over anhydrous magnesium sulfate, filtered, and the ether partially removed. The acid XV was allowed to crystallize to give 29 g. (0.14 mole, 94.6% yield) of colorless crystals melting at 111-112°.

A 110 g. portion of the crude acid XV was cyclized with PPA to 1-keto-1,2,3,4-tetrahydro-4,5,8-trimethylnaphthalene (XVI) in 75% yield.

A sample of 1,2,3,4-tetrahydro-1,5,8-trimethylnaphthalene (XIX) was prepared by Clemmensen reduction of the 1-ketotetrahydronaphthalene XVI and purified using preparative scale gas chromatography (10' Carbowax on Chromosorb W at 200°). The molecular weight of XIX was determined by mass spectrometry to be 174. The ultraviolet spectrum of XIX showed $\lambda_{\text{max}}^{\text{isooctane}}$ 268 and 273 m μ , log ϵ (2.39 and 2.28).

Anal. Calcd. for C₁₃H₁₈: C, 89.66%; H, 10.34%. Found: C, 89.73%; H, 10.33%.

1,2,3,4-Tetrahydro-4,5,8-trimethyl-1-naphthol (XVII) was prepared by the reduction of the ketone XVI with lithium aluminum hydride. Pyrolysis of the tetrahydronaphthol XVII at 250° on a 33 cm. 30 mm. column of alumina in a Pyrex tube gave 3,4-dihydro-4,5,8-trimethylnaphthalene (XVIII) in an 84% yield. The ultraviolet spectrum of XVIII showed

$\lambda_{\text{max}}^{\text{isooctane}}$ 223, 270 and 305 μ , $\log \epsilon$ (4.54, 4.03 and 2.72).

1,2,3,4-Tetrahydro-1,5,8-trimethylnaphthalene (XIX) was dehydrogenated with 10% palladium on carbon at 260-270 $^{\circ}$ to give 1,4,5-trimethylnaphthalene (XX) as colorless, waxy crystals melting at 62.5-63.5 $^{\circ}$.

Apparatus for Small Scale Dehydrogenation Studies.

The small scale dehydrogenations (10 g. or less) were carried out in a 50 ml., round-bottomed, three-necked flask, fitted with a condenser with attached splash head. A thermometer was passed through the top of the splash head into the reaction mixture. A Wood's metal bath containing a submerged heating unit was used to heat the flask.

Dehydrogenation of 1,2,3,4-Tetrahydro-2,5,8-trimethyl-1-naphthol (V) with 5% Palladium on Carbon.

Ten grams of the tetrahydronaphthol V and 0.5 g. of palladium on carbon (5%) were placed in the flask. The apparatus was assembled, and the flask was lowered into the preheated bath. After five minutes of heating time, the temperature in the reaction flask was 181 $^{\circ}$, and at the end of the reaction time (8 hours) the temperature was 272 $^{\circ}$. Water was observed 15 minutes after the flask was immersed in the bath. Samples (0.2 ml.) were taken at 1,2,4,6, and eight-hour intervals, and analyzed through gas chromatography ($\frac{1}{4}$ " x 8', 15% Phenyl-diethanolamine Succinate (PDEAS) on Acid Washed Fire Brick at 200 $^{\circ}$) in order to observe the progress of the reaction. The remaining mixture in the flask at the end of the reaction time was filtered through a sintered glass funnel containing a bed of Celite. The tetrahydronaphthol V was converted almost

entirely to 1,4,6-trimethylnaphthalene (VII) after 4 hours with complete conversion at the end of the 8-hour heating period.

Dehydrogenation of 1,2,3,4-Tetrahydro-3,5,8-trimethyl-1-naphthol (XI) with 5% Palladium on Carbon.

Ten grams of tetrahydronaphthol XI and 0.5 g. of palladium on carbon (5%) were used for the reaction which was carried out as described for V. Water was observed after 10 minutes of heating, and the temperature after five minutes was 168°. At the end of eight-hour heating period, the temperature was 270°. This reaction proceeded nearly to completion with a trace of impurities showing at the end of eight hours.

Dehydrogenation of 1,2,3,4-Tetrahydro-4,5,8-trimethyl-1-naphthol (XVII) with 5% Palladium on Carbon.

Ten grams of the tetrahydronaphthol XVII and 0.5 g. of palladium on carbon (5%) were heated in the Wood's metal bath in the manner previously described. Water was observed after six minutes of heating time, and the temperatures after five minutes and eight hours were 186° and 267°, respectively. The filtered reaction mixture was deep lavender in color, but this color disappeared with time. At the end of eight hours the gas chromatography analysis showed the presence of four peaks. The larger was the unreacted tetrahydronaphthol XVII; the second major peak was 1,4,5-trimethylnaphthalene (XX). The 1,4,5-trimethylnaphthalene peak increased with time and was approximately 35% of the total peak areas at the end of eight hours.

Dehydrogenation of 1-Keto-1,2,3,4-tetrahydro-2,5,8-trimethylnaphthalene (III) Using Palladium on Carbon.

Ten grams of 1-keto-1,2,3,4-tetrahydro-2,5,8-trimethylnaphthalene (III) and 5% palladium on carbon (0.5 g.) were placed in the flask. The apparatus was assembled, and the flask was lowered into the Wood's metal bath. The temperature after five minutes and after twelve hours was 213° and 260°, respectively. Water was present in the apparatus within one hour after heating began. Samples for gas chromatography were taken at 1,2,4,6,9 and twelve-hour intervals to observe the progress of the reaction. At the end of twelve hours, the remaining reaction mixture was cooled, ether added, and the contents of the flasks were filtered. The percentages of the total peak areas were as follows: 1,4,6-trimethylnaphthalene (VII), 62.0%; 2,5,8-trimethyl-1-naphthol (XXX), 28.2%; and unreacted 1-ketotetrahydronaphthalene III, 9.8%. A ¼" x 8', 15% PDEAS on AWFB column at 200-210°, or a ¼" x 4' SE 30 on Chromosorb P column at 150°, can be used for analyzing the results of the reaction.

Dehydrogenation of 1-Keto-1,2,3,4-tetrahydro-3,5,8-trimethylnaphthalene (X) with Palladium on Carbon.

Ten grams of 1-keto-1,2,3,4-tetrahydro-3,5,8-trimethylnaphthalene (X) and 5% palladium on carbon (0.5 g.) were heated for twelve hours with samples being taken at 1,2,4,6,9 and twelve-hour intervals. The temperature at twelve hours was 259°. Water was present in the reaction flask an hour after heating began. A solid, identified as 3,5,8,3',5',8'-hexamethyldinaphtho-[1,2-b:2',1'-d]furan (XXXII), was observed in the filtered samples and appeared to be insoluble in ether. It was later found that this solid could be crystallized from chloroform by adding a few drops of ether to the chloroform solution in which the compound had been dissolved. This procedure gives crystals of XXXII melting at 210-211°.

Mass and N.M.R. spectra support the proposed structure. The N.M.R. spectrum indicates a symmetrical molecule with peaks at 7.51 ppm. equivalent to 2 protons, 7.13 ppm. equivalent to 4 protons, and 6 protons at 3.05 ppm., 2.90 ppm., and 2.62 ppm. The latter peaks were completely resolved and essentially equal in height as well as area.

Anal. Calcd. for $C_{26}H_{24}O$: C, 88.64%; H, 6.82%; O, 4.54%. Found: C, 88.4%; H, 6.95%; O, 4.64%.

Attempts at gas chromatographic analysis of XXXII on columns containing SE 30, PDEAS, XE 60, and Apiezon L as substrates were unsuccessful. In a separate reaction carried out on 10 g. of X in which no samples were taken during the reaction period, 3.59 grams (0.01 mole, 19% yield) of XXXII were crystallized from the filtered reaction material. The following percentages were calculated for: 1,4,6-trimethylnaphthalene (VII), 61%; 1-keto-1,2,3,4-tetrahydro-3,5,8-trimethylnaphthalene (X), 10%; and 3,5,8-trimethyl-1-naphthol (XXXI), 10%.

Dehydrogenation of 1-keto-1,2,3,4-tetrahydro-4,5,8-trimethylnaphthalene (XVI) with Palladium on Carbon.

This reaction was carried out on 10 g. of XVI using 5% palladium on carbon (0.5 g.) in the same manner as the previous dehydrogenations of III and X. The samples injected onto a $\frac{1}{4}$ " x 8' column of 15% PDEAS on AWFB at 210°, revealed a very small peak besides the one corresponding to unreacted XVI. At the end of twelve hours, the peak corresponding to 1,4,5,-trimethylnaphthalene (XX) was only 11.7% of the total areas of the two peaks.

Reaction of the 1-Ketotetrahydrotrimethylnaphthalenes III, X and XVI with Anhydrous Caustic.

The alkali-catalyzed reactions were carried out in 25 ml., round-bottomed flasks with attached condenser and splash head. In each reaction, the 1-ketotetrahydronaphthalene (5 g.) was heated for five hours with NaOH:KOH (0.8 g. each) at 220°. The reaction mixture was transferred to a larger flask for steam distillation at the end of the five-hour reaction period. The steam distillate was extracted with ether, washed with saturated sodium chloride solution, dried over anhydrous magnesium sulfate, filtered, and the ether was removed. The steam distillation residue was acidified and extracted with ether; the ether solution was washed and dried in the same manner as the steam distillate extract. The weights of the steam volatile material were obtained for the three reactions. The small quantity of non-steam volatile material extracted from the steam distillation pot in each case was a black tar. The steam volatile compounds were injected onto a gas chromatography column (SE 30 on Chromosorb P, $\frac{1}{4}$ " x 4' at 150°) for analysis. In each case the starting material was the only compound present. The following percentages of starting materials recovered from the three identical runs were: 1-keto-1,2,3,4-tetrahydro-2,5,8-trimethylnaphthalene (III), 4.82 g., 96.4%; 1-keto-1,2,3,4-tetrahydro-3,5,8-trimethylnaphthalene (X), 4.88 g., 97.6%; 1-keto-1,2,3,4-tetrahydro-4,5,8-trimethylnaphthalene (XVI) 4.71 g., 94.2%.

Dehydrogenation of 1-Keto-1,2,3,4-tetrahydrophenanthrene (XXI) with 5% Palladium on Carbon.

Two grams of 1-keto-1,2,3,4-tetrahydrophenanthrene (XXI) and 5% palladium on carbon (0.067 g.) were placed in a 50-ml., round-bottomed, three-necked flask equipped with a splash head. The flask was placed in

a heated Wood's metal bath. The temperature was maintained at 220° to 225° for twenty-four hours. The contents of the flask were allowed to cool, ether was added, and the reaction product was filtered through a sintered glass funnel containing a layer of Celite. The ether was evaporated, and the residue was heated on a steam bath for 15 minutes with an excess of 5% KOH solution. Upon cooling, the organic material was extracted with ether, washed with three (10 ml.) portions of 5% KOH solution which were added to the original basic solution. The combined basic solutions were acidified with concentrated hydrochloric acid, and extracted with ether. The ether was evaporated, and the resulting residue was sublimed to give 0.36 g. (18% yield) of 1-phenanthrol (XXIII), which melted at 154.5-156°. The material extracted from the basic solution gave (0.56 g.) of a mixture of phenanthrene (XXII) and starting material. This mixture was identified on the gas chromatograph ($\frac{1}{4}$ " x 4', SE 30 on Chromosorb P column at 190°). Considerable tar remained in the sublimation tube.

Dehydrogenation of 1-Keto-1,2,3,4-tetrahydrophenanthrene (XXI) with 5% Palladium on Carbon in the Presence of Naphthalene.

Two grams of 1-Keto-1,2,3,4-tetrahydrophenanthrene (XXI), naphthalene (20 g.), and 5% palladium on carbon (0.067 g.) were placed in a 50-ml. round-bottomed flask. A reflux condenser was attached, and the flask and contents were heated in a Wood's metal bath at 220-225° for twenty-four hours. The contents of the flask were dissolved in ether and filtered into a 500-ml. round-bottomed flask. Naphthalene was steam distilled from the reaction mixture. The remaining organic material was extracted from the steam distillation pot, the ether evaporated, and the

residue heated fifteen minutes with an excess of 5% potassium hydroxide solution. These washings were added to the original basic solution. The basic solution was acidified with concentrated hydrochloric acid, and the organic material extracted with ether. The ether solution containing the base-soluble organic material was washed with water, saturated sodium chloride solution, dried over anhydrous magnesium sulfate, filtered, and the ether was removed. The residue was sublimed to give 1.44 g. (71% yield) of 1-phenanthrol (XXIII) melting at 155-156°. The ether soluble and alkali insoluble fraction gave 0.23 g. of solid 1,2-dihydro-1-phenanthrol (XXIV) melting at 115-116.5°. The molecular weight was determined by mass spectrometry to be 196.

Anal. Calcd. for $C_{14}H_{12}O$: C, 85.71%; H, 6.12%. Found: C, 85.52%; H, 6.06%.

Dehydrogenation of α -Tetralone (XXV) with Pd/C and Pt/C.

Five grams of α -tetralone (XXV), 5% Pd/C (0.25 g.), and 5% Pt/C (0.25 g.) were placed in a 50-ml., three-necked, round-bottomed flask fitted with a thermometer, a silicone rubber sampling septum, and condenser, which, in turn, was fitted with a splash head. The temperature after five minutes of heating in a Wood's metal bath was 200°. The final temperature after twelve hours was 242°. Water was observed in the condenser after two hours of heating. Samples taken at 1,2,4,6,8, and twelve-hour intervals were analyzed at 180° on a $\frac{1}{4}$ " x 8' of PDEAS 15% on AWFB. The reaction showed naphthalene (XXVI) plus a trace of an impurity after six hours. This reaction gave a quantitative yield of naphthalene after twelve hours heating.

Dehydrogenation of α -Tetralone (XXV) Using NaOH and KOH .

One gram α -tetralone (XXV) and 1:1 ratio of NaOH:KOH (0.32 g.) were added to a 50-ml., round-bottomed flask. The neck of the flask contained a reflux condenser fitted with a splash head. A Teflon sleeve was used to prevent freezing of the condenser and flask joints due to alkali. The flask and contents were heated in a Wood's metal bath at 220° for 5 hours. The reaction mixture was cooled and rinsed into a larger flask for steam distillation. The steam distillate was extracted with ether, the ether solution dried over anhydrous magnesium sulfate, filtered, and distilled. The product was injected onto a $\frac{1}{4}$ " x 4' SE 30 on Chromosorb P column at 115°. Two peaks were present, one corresponding to naphthalene (XXVI), the other unreacted α -tetralone (XXV). By using percentage of peak areas and the weight of the reaction product obtained, a 92.5% yield of naphthalene (XXVI) was calculated.

Dehydrogenation of β -Tetralone (XXVII) Using Pd/C .

Three grams of β -tetralone (XXVII) and 5% Pd/C (0.15 g.) were placed in a 25-ml., round-bottomed flask. The apparatus was similar to the other small-scale reactions. Water was observed in the condenser after forty-five minutes of heating. After heating 11 hours at 250-282°, the flask was removed from the bath and allowed to cool. Ether was added and the reaction mixture was filtered through a sintered glass funnel containing a bed of Celite. The ether was removed to give a residue weighing 2.22 g. Injection onto a $\frac{1}{4}$ " x 4' column of SE 30 on Chromosorb P at 120° showed peaks corresponding to naphthalene (XXVI) and β -naphthol (XXVIII) but none of unreacted XXVII. Using percentage of peak areas,

yields of 54.5% and 26.6% were obtained for naphthalene (XXVI) and β -naphthol (XXVIII), respectively.

Dehydrogenation of β -Tetralone (XXVII) Using NaOH:KOH.

The same type apparatus used for dehydrogenation of α -tetralone (XXV) with base was used for this reaction. Three grams of β -tetralone (XXVII), sodium hydroxide (0.48 g.), and potassium hydroxide (0.48 g.) were heated at 220^o for 5 hours. The reaction mixture developed a deep blue color when it was rinsed into the flask for steam distillation. This color disappeared on heating during the steam distillation. The steam distillate was extracted with ether, dried over anhydrous magnesium sulfate, filtered and the ether removed. The residue (0.18 g.) showed a very small peak corresponding to naphthalene (XXVI), the major peak was unreacted β -tetralone (XXVII), and in addition two impurities were present. The gas chromatography analysis was conducted in a manner identical to the α -tetralone studies (same column of SE 30 at 120^o).

The steam distillation pot was extracted with ether, and the remaining alkaline layer was acidified with concentrated hydrochloric acid. The acidified solution was extracted with ether. These two ether extractions were separately washed with water, saturated sodium chloride solution, dried over anhydrous magnesium sulfate, filtered, and the ether was removed. The material obtained before acidification was a dark viscous oil, weighing 1.84 g. The residue (0.95 g.) obtained from the acidified basic solution was a dark green color, but yielded white crystals, melting at 119-120^o to which structure XXIX was assigned. A few crystals were dissolved in ether and injected onto an SE 30 column at 200^o, but no

peaks were observed. The neutral oil was also injected at this temperature, but no peaks were observed.

An infrared spectrum of the solid XIX showed typical carboxyl and carbonyl absorption at 2900 and 1700 cm^{-1} .

The N.M.R. spectrum showed a peak for a carboxyl group proton at approximately 12 ppm., 4 phenyl protons at 7.2 ppm., 4 phenyl protons at 7.0 ppm., one vinyl proton at 6.1 ppm., 2 protons at 3.6 ppm. between a phenyl group and a double bond, and 8 other protons one being a vinyl proton, and the other 7 methylene protons. One of the phenyls is under the influence of an adjacent group believed to be the vinyl group, and its protons give a peak of less intensity than the peak resulting from the protons on the other phenyl.

Friedel-Crafts Reaction Study in Three Individual Solvent Systems.

Three separate Friedel-Crafts reactions were carried out in the same apparatus using nitrobenzene, nitroethane, and nitromethane as the solvents. A 2-liter round-bottomed flask having four necks was used for the reaction. A Lightning F stirring motor was attached to a stirring shaft inserted in the center neck of the flask. The three side necks were used for a thermometer, a gas outlet, and the addition of the anhydrous aluminum chloride through a Gooch tube. The flask was placed in a container, so the reaction could be cooled with an ice-salt bath. In each reaction the following quantities of reagents were used: Methylsuccinic anhydride (58.14 g., 0.51 mole), *p*-xylene (70 ml.), and solvent (300 ml.) The stirring motor was started and when the mixture had cooled to 0° , the aluminum chloride (151 g., 1.13 moles) was added in thirty minutes. The

temperature during this time remained at 10° or below. After addition of the aluminum chloride, the reaction mixture was stirred for ninety minutes at the ice-salt bath temperature. The ice-salt bath was removed, and stirring was continued for an additional ninety minutes. The reaction mixture was poured onto ice and after the brown reaction mixture had decomposed, concentrated hydrochloric acid (100 ml.) was added. The organic material was extracted with ether, washed with water, saturated salt solution, dried over anhydrous magnesium sulfate, and filtered. A sufficient quantity of ether was removed, and the separate reaction products transferred to 500 ml. volumetric flasks and diluted to that volume. A 20-ml. aliquot was taken from each flask and esterified with diazomethane. Some ether was removed in order to transfer the samples to 5-ml. volumetric flasks. After dilution, these solutions were injected onto an analytical gas chromatography (10' x $\frac{1}{4}$ " Carbowax on Chromosorb W at 200°) in an effort to determine the quantity of each isomer formed in the different solvent systems. The percentages of the peak areas for the two isomers in the separate solvent systems were as follows:

Nitrobenzene: α isomer - 97.8%, β isomer - 2.2%

Nitroethane: α isomer - 98.4%, β isomer - 1.6%

Nitromethane: α isomer - 98.3%, β isomer - 1.7%

BIBLIOGRAPHY

1. Ruzicka, L. and Seidel, C. F., *Helv. chim. Acta*, 5, 369 (1922).
2. Ruzicka, L. and Ehmann, L., *Helv. chim. Acta*, 15, 140 (1932).
3. Heilbron, I. M. and Wilkinson, D. G., *J. Chem. Soc.*, 1930, 2537.
4. Schorygin, P. P. and Gussewa, A. R., *J. Gen. Chem. U.S.S.R.*, 6, 1569 (1936).
5. Barnett, E. de Barry and Cook, J. W., *J. Chem. Soc.*, 1933, 22.
6. Barnett, E. de Barry and Sanders, F. G., *J. Chem. Soc.*, 1933, 434.
7. Baddar, F. G. and Warren, F. L., *J. Chem. Soc.*, 1939, 944.
8. Dev, S., *Current Sci.*, 16, 377 (1947).
9. Abadir, B. J., Cook, J. W., and Gibson, W. L., *J. Chem. Soc.*, 1953, 8.
10. Dev. S. and Guha, P. C., *J. Ind. Chem. Soc.*, 25, 13 (1948).
11. Mosby, W. L., *J. Am. Chem. Soc.*, 74, 2564 (1952).
12. Du Feu, E. C., McQuillin, F. J., and Robinson, R., *J. Chem. Soc.*, 1937, 53.
13. Horning, E. C., *J. Org. Chem.*, 10, 263 (1945).
14. Horning, E. C. and Horning, M. G., *J. Am. Chem. Soc.*, 69, 1359 (1947).
15. Horning, E. C., Horning, M. G., and Walker, G. N., *J. Am. Chem. Soc.*, 71, 169 (1949).
16. Mosettig, E. and Duvall, H. M., *J. Am. Chem. Soc.*, 59, 367 (1937).
17. Birch, A. J. and White, D. A., *J. Chem. Soc.*, 1964, 4086.
18. Chatterjee, N. N., *J. Ind. Chem. Soc.*, 13, 588 (1936).
19. Dutta, P. C., *J. Ind. Chem. Soc.*, 18, 233 (1941).
20. Martin, E. L., "Organic Reactions," Vol. I, R. Adams, Ed., John Wiley and Sons, Inc., New York, N. Y., 1942, p. 157.

21. Snyder, H. R. and Werber, F. X., "Organic Syntheses," Coll. Vol. III, E. C. Horning, Ed., John Wiley and Sons, Inc., New York, N. Y., 1955, p. 798.
22. Nystrom, R. F. and Brown, W. G., J. Am. Chem. Soc., 69, 1197, (1947).
23. Pines, H. and Haag, W. O., J. Am. Chem. Soc., 83, 2847 (1961).
24. Clinton, R. O. and Laskowski, S. C., J. Am. Chem. Soc., 70, 3135, (1948).

VITA

Charles William Hinman

Candidate for the Degree of

Master of Science

Thesis: THE SYNTHESIS AND DEHYDROGENATION OF SOME KETOTETRAHYDRONAPHTHALENES

Major Field: Organic Chemistry

Biographical:

Personal Data: The author was born in Niota, Illinois, on January 29, 1926, the son of Novel and Mary Elizabeth Hinman.

Education: The author attended grade school at Victory, Niota, Illinois. He graduated from Dallas City Community High School, Dallas City, Illinois, in 1943. He received the Associate in Arts degree from Keokuk Community College, Keokuk, Iowa, in June, 1959; received the Bachelor of Science degree from Western Illinois University, Macomb, Illinois, in June, 1962.

Professional Experience: The author was employed by Clinton Corn Processing Company during the summers of 1960 and 1961.

Membership in Professional Societies: American Chemical Society and Phi Lambda Upsilon.