

**THE SYNTHESIS OF 1,8-DIMETHYL PICEIN**

**BY**

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of the University of Maryland in partial fulfillment  
of the requirements for the degree of  
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1938.

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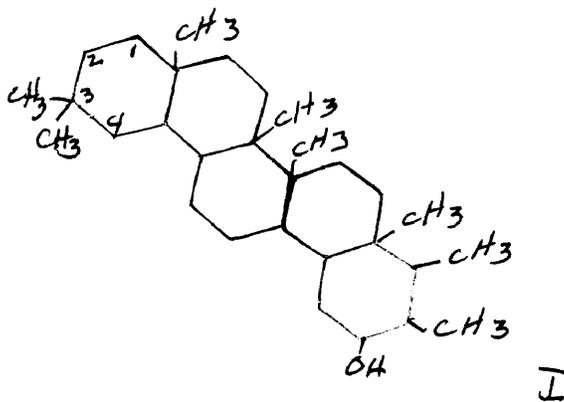
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## I. INTRODUCTORY NOTE

Earlier work by Drake and Haskins (7), and Drake and Duvall (6) has shown that a di- or tri- methyl plicene resulted when friedelinol or ursolic acid was subjected to dehydrogenation. The identification of this hydrocarbon would make possible the determination of the location of certain methyl groups in friedelin and ursolic acid. It is the purpose of this research to investigate the synthesis of this hydrocarbon.

## II. DISCUSSION

The formula for friedelinol proposed by Drake and Haskins (7) was later altered to the formula given below (I), because of additional evidence advanced by Ruzicka (24) on the nature of polyterpenes, of which friedelin is a member (7), (8), (9), (5).



The change made involved a shift of the gem. dimethyl group from carbon #4 to carbon #3.

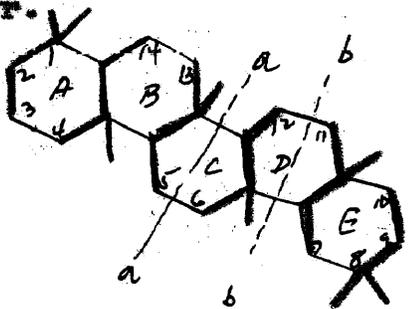
If friedelinol possessed this structure, the polymethyl picene obtained from dehydrogenation (7) should be 3,9,10-trimethyl picene. The reasoning for this supposition is explained by Duvall, (10) who gives a detailed account of dehydrogenation by selenium.

However, in 1936, Ruzicka (25) synthesized 3,9,10-trimethyl picene, and found it to be not identical with the picene homolog obtained by dehydrogenation of polyterpenes (19). The picene hydrocarbon obtained by dehydrogenation of friedelinol was later proved to be identical with the hydrocarbon obtained by Ruzicka and co-workers (23).



phenanthrene and a piceene homolog which is not 3,9,10-trimethyl-, nor 3,8-dimethyl piceene (7).

A formula II which will meet most of these demands was formulated in December, 1936, by Mr. D. F. Houston and the writer.



+ OH at carbon  
#5, 12, or 14

II

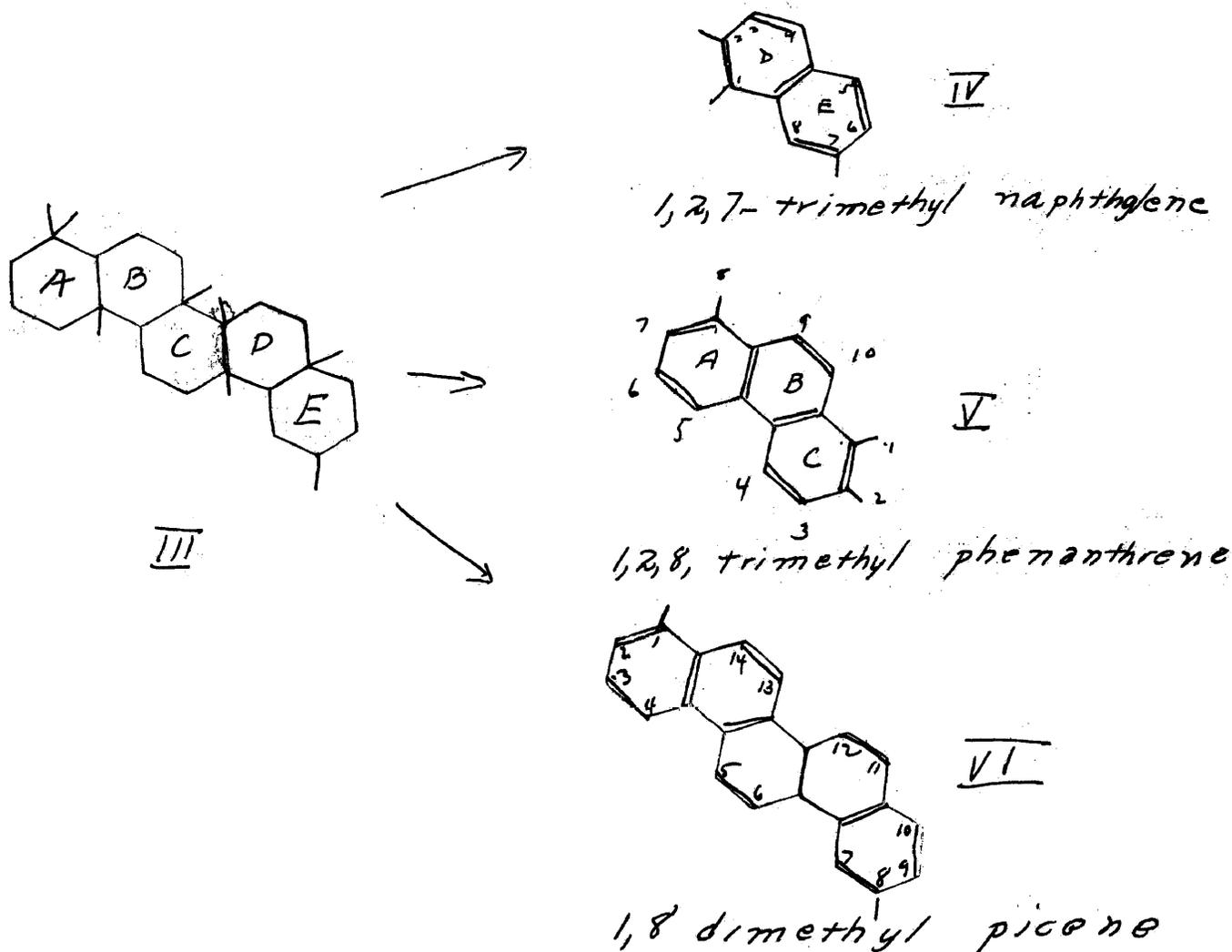
The isoprene nuclei are outlined in blue. It will be noted that they are connected head to tail except in one instance (Ring D-E), and that the molecule is nearly symmetrical. It contains the correct number of fused rings and has the formula  $C_{20}H_{32}O$ . There are only three positions which would allow the oxygen bearing part to be  $\equiv CH-CH(OH)CH_2-$ . These positions are the ones in which the hydroxyl group is attached to carbon #5, 12 or 14. No attempt is made herein to place it definitely, since further evidence is necessary to do so.

The proposed formula predicts the formation of 1,2,8 trimethyl phenanthrene from rings A, B and C by cleavage at b---b. Elimination of all quaternary methyl groups, dehydration and dehydrogenation would result in

the formation of 1,8-dimethyl piceae.

It does not offer a satisfactory explanation for the formation of sapotalene (1,2,7 trimethyl naphthalene). However, it may be formed from rings D and E by cleavage at a-----a, and migration of a methyl group from carbon #6 to the adjacent carbon atom.

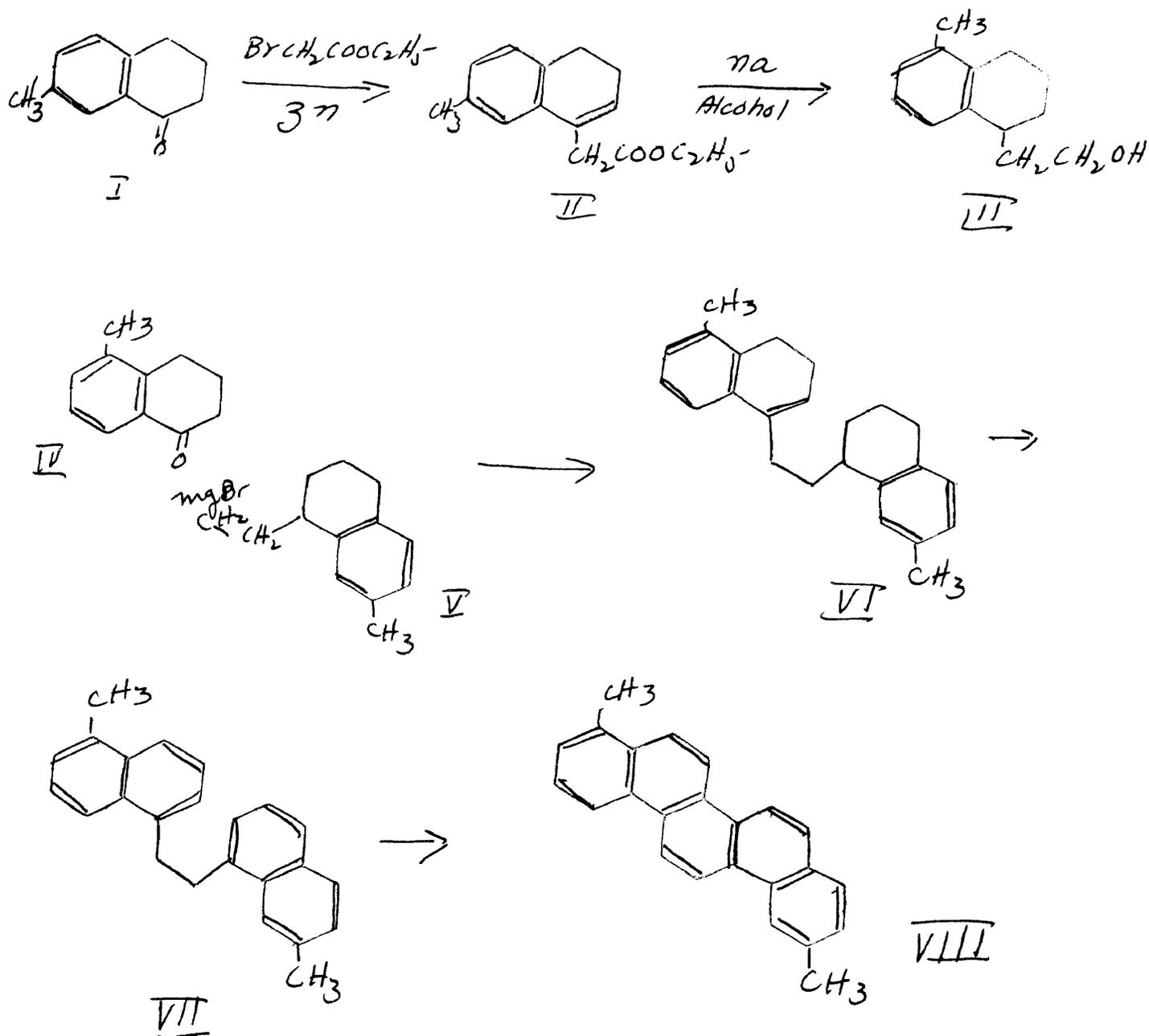
Early in 1937, Rusicka and Giacomello (21) proposed an improved tentative formula for the polyterpenes which more adequately explains the formation of sapotalene, although the isoprene units are not as orderly. This formula III is shown below with its dehydrogenation products.



In order to verify this formula, work was started in April, 1937 on the synthesis of 1,8-dimethyl picene, according to the scheme described in the experimental part.

The work was about half completed, when, in October, Ruzicka and Hoffmann (23) published an account of the synthesis of 1,8-dimethyl picene. Since Ruzicka had used a somewhat different scheme of synthesis than we were using, it was not deemed advisable to discontinue work on the synthesis.

Ruzicka's synthesis is given by the following schematic diagram:

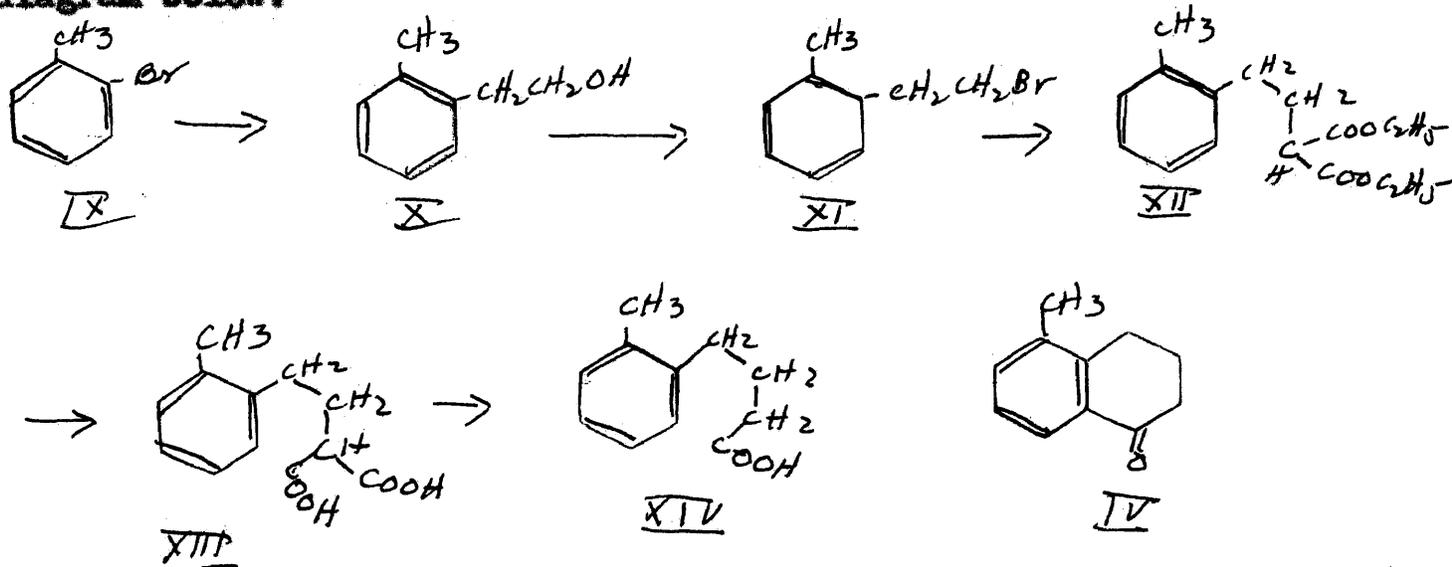


7-methyl-1-tetralone (**I**) prepared as described in this thesis, was reacted with ethyl bromacetate in the presence of zinc. This is a well known reaction named

after its founder, Reformatsky. This reaction gave, in this case, a tertiary alcohol, which lost water when distilled to form the unsaturated ester (II). This ester was reduced by the Beauveault-Blanc method with sodium and alcohol to form the alcohol(III). This alcohol was converted to the bromide with hydrogen bromide, and a grignard reagent made of the bromide.

The author made this compound by a method which required more steps. The tetralone I was dehydrogenated to the corresponding naphthol, which was made to undergo the Bucherer reaction, which replaces the phenolic group with a primary amino group. This amino group was replaced by a bromine atom by the diazonium reaction. The bromide formed a grignard reagent which enabled the replacement of a  $-\text{CH}_2\text{CH}_2\text{OH}$  in place of the bromine by reaction with ethylene oxide. The alcohol thereby formed corresponds to Ruzicka's alcohol III, but with both rings aromatic.

However, the author made 5-methyl, 1-tetralone IV by a much less laborious method than described by Ruzicka. Ruzicka's synthesis of this compound is shown in the diagram below:



The author's synthesis involves only two steps from o-bromotoluene to  $\sqrt{(o\text{-tolyl})}$  butyric acid XIV (see experimental part). Ruzicka's synthesis included a grignard reaction with ethylene oxide on o-bromotoluene to form X (o-tolyl ethanol). The bromide of this alcohol was reacted with diethyl sodium malonate to form XII, which was saponified to XIII and decarboxylated to XIV. Cyclization of XIV to the tetralone IV was accomplished in the same manner by both investigators.

The method of synthesis from this point is essentially the same in both cases. However, in the formation of the dimethyl, dinaphthyl ethane VII, Ruzicka had to remove six hydrogen atoms, while the author had to remove only two. Ruzicka's  $\beta(7\text{-methyl naphthyl-1})$ ,  $\alpha(5\text{-methyl naphthyl-1})$  ethane was probably a mixture of partially dehydrogenated compounds, because he described great difficulty in purifying it. The melting point he gave for this compound does not check with that of the author's compound, which was certainly dehydrogenated, shown to be homogeneous, and gave the correct analysis for carbon and hydrogen. Also, two derivatives of this compound were prepared and analyzed by the present investigator.

Due to the fact that the two methods of synthesis differed in a number of places, it was thought that a confirmation of Ruzicka's work in another laboratory would be pertinent.

### III. EXPERIMENTAL PART

#### A. Purification of materials

Toluene was purified by washing it with concentrated sulfuric acid until fresh acid was not discolored. It was then washed with water, and refluxed over metallic sodium for four hours and distilled.

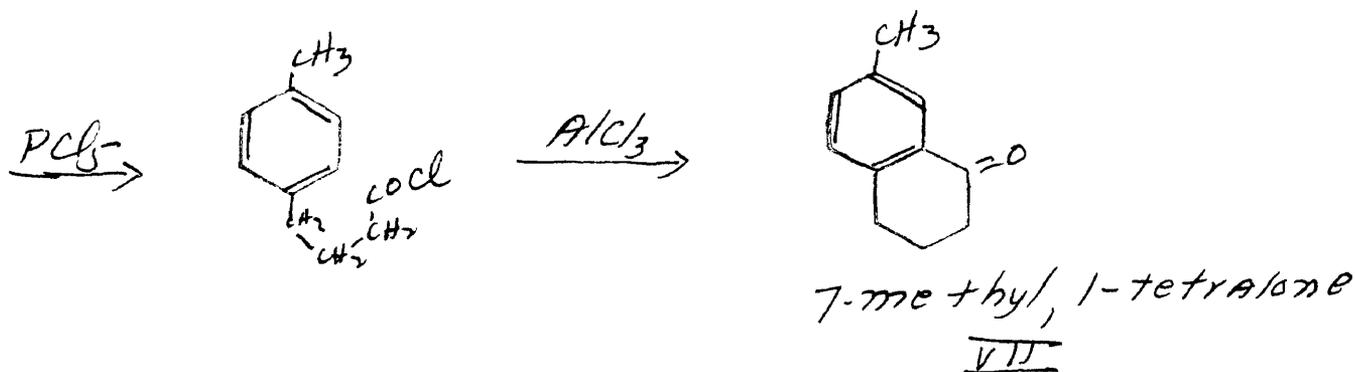
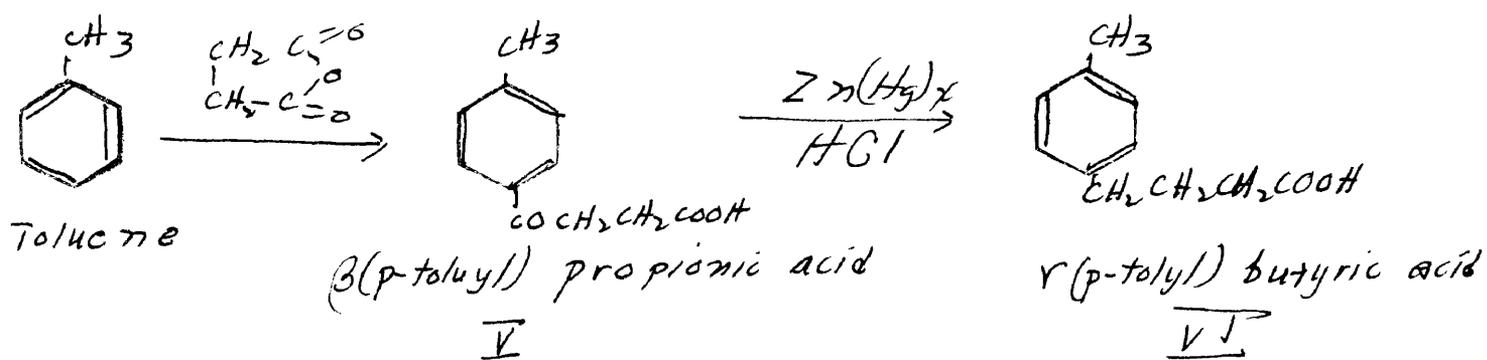
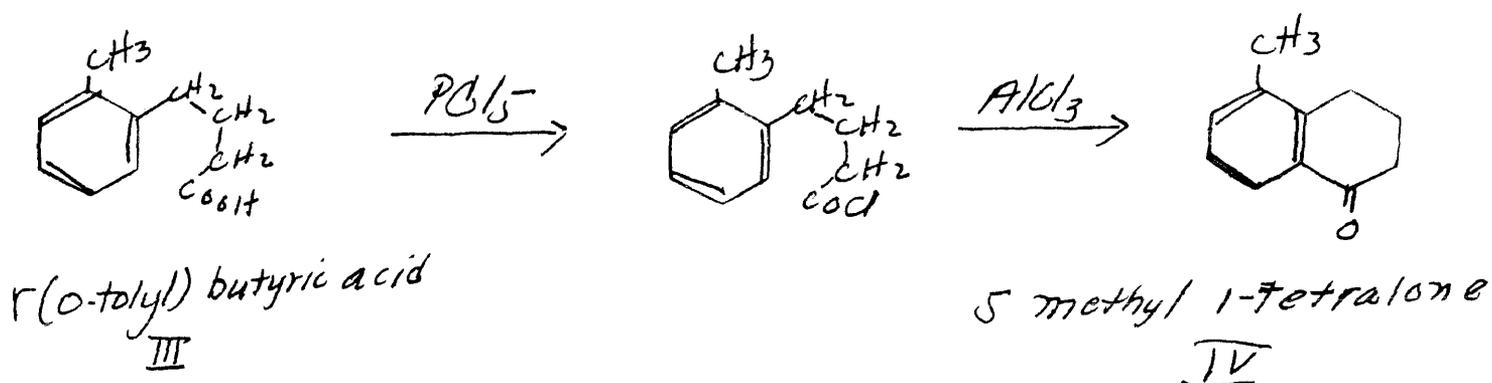
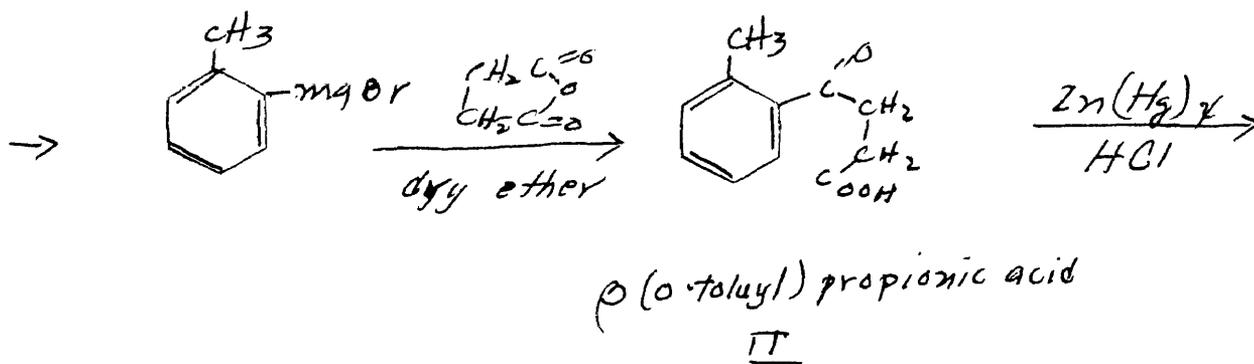
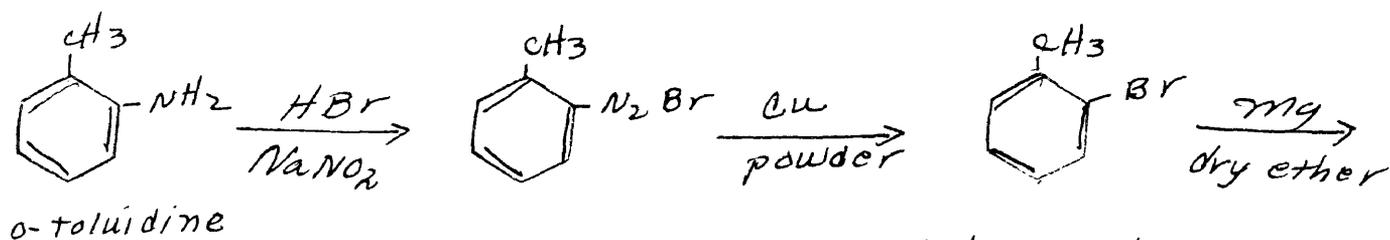
Carbon bisulfide was shaken with mercury until a fresh portion of mercury was not tarnished. It was then dried with phosphorus pentoxide and distilled.

All melting points are given on the Centigrade temperature scale, and are corrected.

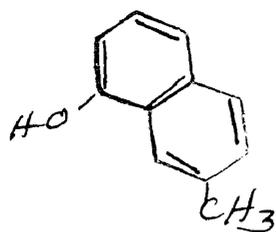
The atomic weight used for carbon is 12.01 units.

#### B. The plan of synthesis

The synthesis of 1,8-dimethyl picene was carried out as represented in the following diagram. The Roman numerals below the formulas of the intermediates are reference numbers used in the detailed description of the synthesis, which follows.

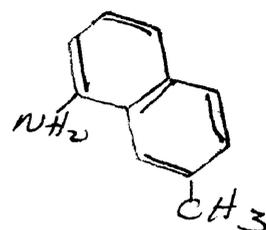


$\xrightarrow[\text{catalyst}]{\text{Pd-C}}$



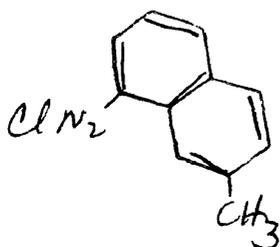
7-methyl, 1-naphthol  
VIII

$\xrightarrow[\text{NH}_4\text{OH}]{(\text{NH}_4)_2\text{SO}_3}$



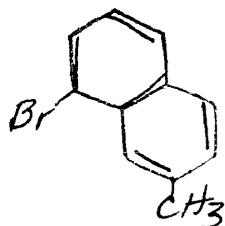
7-methyl, 1-naphthylamine  
IX

$\xrightarrow[\text{HCl}]{\text{NaNO}_2}$

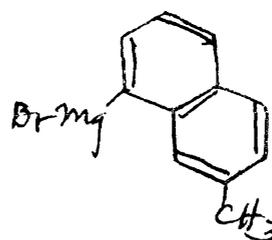


$\xrightarrow{\text{H}_2\text{HgBr}_4}$

$(\text{C}_{11}\text{H}_9\text{N}_2\text{Br})_2\text{HgBr}_2$  heat  
intermediate

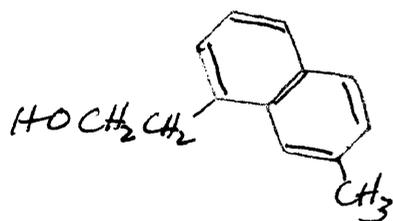


$\xrightarrow[\text{dry ether}]{\text{Mg}}$

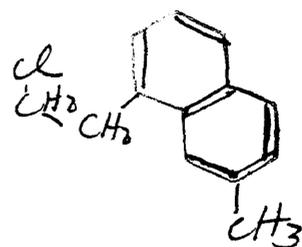


$\xrightarrow{\text{CH}_2=\text{CH}_2}$

7-methyl, 1-bromo naphthalene  
X



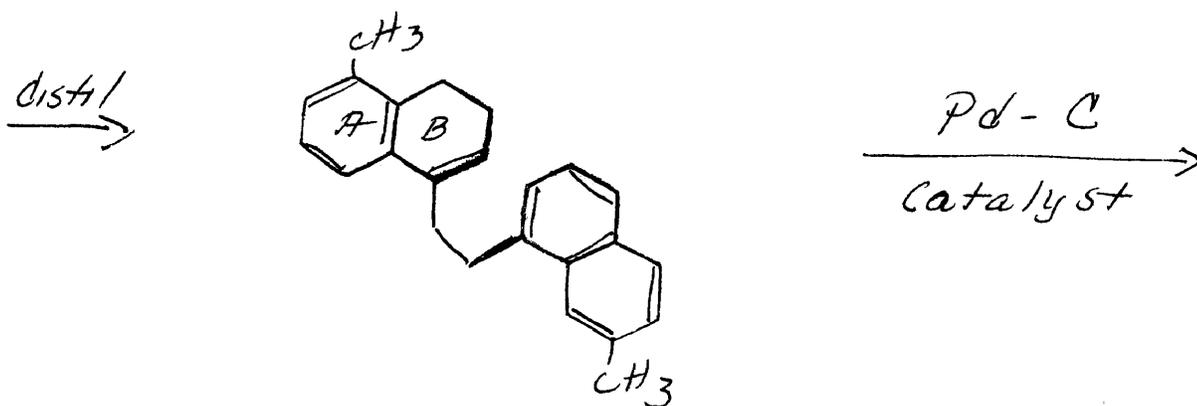
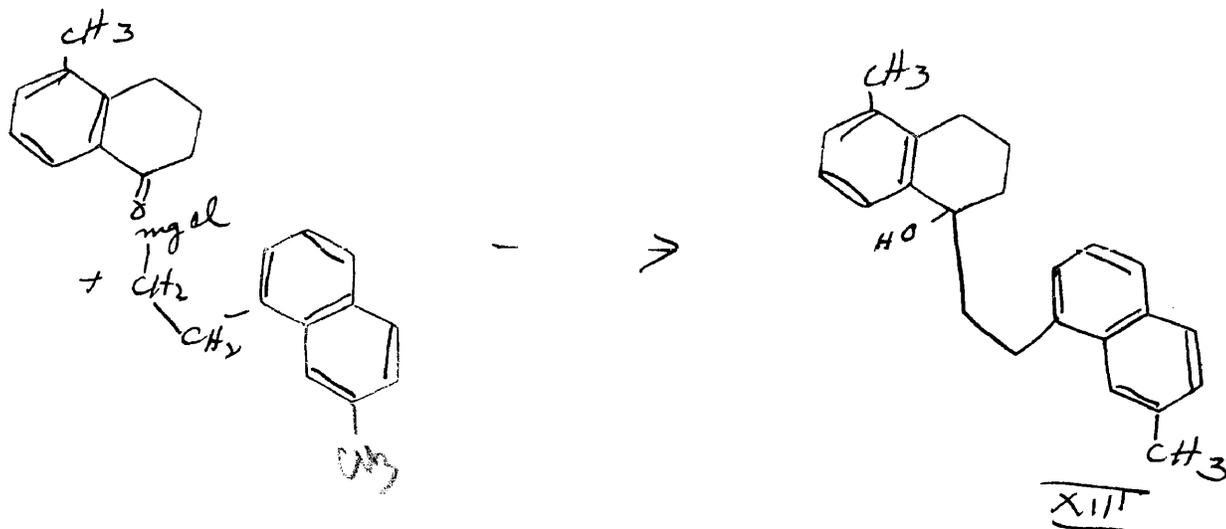
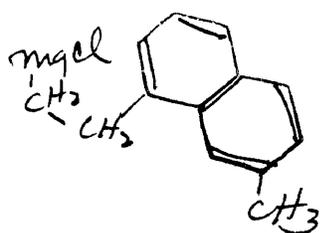
$\xrightarrow[\text{dimethyl aniline}]{\text{SOCl}_2}$



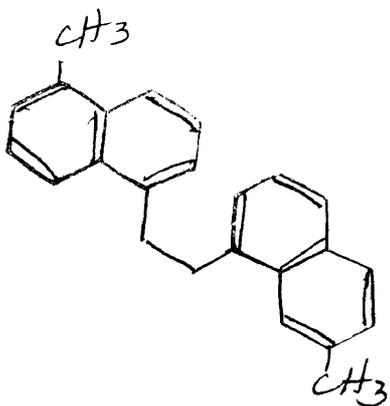
$\xrightarrow[\text{dry ether}]{\text{Mg}}$

β (7-methyl, naphthyl-1)  
ethanol  
XI

β (7-methyl, naphthyl-1)  
ethyl chloride  
XII

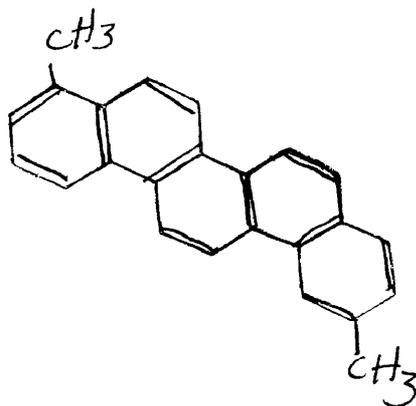


$\beta$ (7-methyl, naphthyl-1)  
 $\alpha$ (5-methyl, 3,4-dihydro naphthyl-1)  
 ethane  
 XIV



$\beta$ (7-methyl naphthyl-1)  
 $\alpha$ (5-methyl naphthyl-1)  
 ethane.

XV



1,8-dimethyl picene

XVI

## C. The synthesis of intermediates

### 1. o-Bromo Toluene (I)

o-Bromotoluene was prepared according to a procedure given in Organic Syntheses (17), with certain modifications. The cold mixture of o-toluidine and hydrobromic acid (16) was stirred mechanically while sodium nitrite was added. This technique was found to cause a more rapid absorption of nitrogen oxide fumes than mere shaking afforded. The product was more carefully purified; care was taken to remove all o-cresol formed as a by-product in the reaction. This undesirable impurity was removed by repeatedly washing the crude o-bromo toluene with 10% sodium hydroxide. The purified product distilled at 80-83° at a pressure of 26-27 mm. of mercury, and remained water white on standing. The yield from 2000 g. of o-toluidine amounted to 1280 g. This represents 40% of the yield theoretically possible.

### 2. $\beta$ (o-toluy) Propionic Acid (II)

A one liter E necked flask was fitted with an efficient mechanical stirrer, a reflux condenser and a dropping funnel. All openings were closed with freshly filled calcium chloride tubes. In the flask were placed 30 g. of magnesium turnings and about 100 ml. of dry, alcohol-free ether. One hundred seventy-one grams of o-bromotoluene was placed in the dropping funnel and about

5 ml. was allowed to drop into the reaction vessel. After the reaction started, more ether (150 ml.) was added. The remainder of the o-bromo toluene was allowed to drop into the well stirred mixture at such a rate as to cause gentle boiling of the ether. After all the o-bromo toluene was added, the mixture was warmed on the water bath for 2 hours, and then allowed to cool.

A 5 liter, 3 necked flask was equipped in the same manner as was the flask used in the preparation of the original reagent. In it were placed 110 g. of succinic anhydride (m.p. 118-119°) and 2000 ml. dry ether, and the mixture warmed on a water bath until the ether boiled. The previously prepared original solution was then added to the well stirred boiling suspension from a 500 ml. dropping funnel at such a rate as to cause gentle boiling. After all the solution was added, the mixture was warmed for 2 hours and allowed to stand for 3 hours.

After decomposition of the reaction mixture with 100 and 10% sulfuric acid, the ether layer was extracted three times with 10% sodium hydroxide. The combined alkaline layers were acidified with 10% sulfuric acid, cooled to 10° and the crude acid which precipitated was filtered with suction and dried. One hundred forty-seven grams (77% of the theoretical amount) of crude acid were thus obtained and were not further purified for use in the next step.

One half gram of the crude acid was crystallized from

50% aqueous alcohol until further recrystallization failed to raise the melting point. The melting point was found to be 105-105.5°. The pure <sup>Acid</sup> oil crystallizes in the form of lustrous white plates.

Analysis. Calcd. for  $C_{11}H_{12}O_3$ : C, 68.73; H, 6.30

Found: C, 68.82; H, 6.30<sup>1</sup>

C, 68.50; H, 6.31

Molecular Weight. Calcd. for  $C_{11}H_{12}O_3$ : 192

Found by East Camphor Method: 190<sup>2</sup>

Found by titration: 189,190

This reaction has been used by Weigmann, Bergmann, and Bergmann (28), and Bergmann and Blum, Bergmann (3) in the preparation of other aryl propionic acids.

### 3. $\alpha$ (o-tolyl) Butyric Acid (III)

$\alpha$ (o-tolyl) Butyric acid was prepared from  $\beta$ (o-tolyl) propionic acid by reduction of the carbonyl group according to Martin's modification of the Clemmenson reduction (15).

An amalgamated zinc was prepared in the following manner. Four hundred thirty grams of mossy zinc, 43 g. of mercuric chloride, 720 ml. of water and 18 ml. of concentrated hydrochloric acid were placed in a 3 l. flask and allowed to

- 
1. The author wishes to thank Mr. J. R. Adams for this analysis.
  2. The author wishes to thank Mr. G. K. Holmes for this molecular weight determination.

stand with frequent shaking for 10 minutes. The liquid was poured off and the zinc amalgam was washed by decantation with three 1 l. portions of water.

To the amalgamated zinc was added 270 ml. of water, 630 ml. of conc. hydrochloric acid, 360 ml. of toluene, and 146 g. of crude  $\beta$ (*o*-toluyl) propionic acid and the mixture was boiled for forty hours. One hundred eighty ml. of hydrochloric acid was added at the end of the tenth, twentieth and thirtieth hour. The mixture was then cooled and the layers separated. The aqueous layer was extracted twice with 200 ml. portions of toluene, and the toluene extracts combined. The combined toluene extracts were concentrated by distillation until the volume was about 300 ml. It was then transferred to a modified Claisen flask and distilled under reduced pressure. The portion which boiled at 135-137° under a pressure of 1-2 mm. of mercury was collected. (The bath temperature was 195-200°). The yield was 114 g. (84.5% of the theoretical amount.)

A small amount was recrystallized from 30-60° petroleum ether. The melting point of the slender needles was found to be 60.5-61°.

Harvey, Hielbron and Wilkinson (12) prepared this compound by a different method and found the melting point to be 60°.

Molecular weight. Calcd. for  $C_{11}H_{14}O_2$ ; 178  
Found (by titration) 177, 175.

#### 4. 5-Methyl, 1-Tetralone (IV)

A 3 necked 3 liter flask was fitted with a mechanical stirrer and reflux condenser. The condenser was equipped with a trap containing water to absorb hydrogen chloride. In the flask were placed 1000 ml. of purified, dry benzene, 120 g. of  $\gamma$ -(o-tolyl) butyric acid, and 154 g. of powdered phosphorus pentachloride. After cessation of the spontaneous reaction, the solution was warmed on a water bath so that the benzene refluxed for two hours. At this time the flask was cooled and 103 g. of anhydrous resublimed aluminum chloride was added to the vigorously stirred solution. Stirring was continued for two hours, after which the mixture was poured onto 500 g. of ice and 150 ml. of concentrated hydrochloric acid. The layers were separated and the benzene layer was washed with 5% sodium hydroxide, and then with water, and distilled. The product which boiled at 114-119<sup>o</sup>C. at 2-3 mm. of Hg was collected. Seventy-six grams (70.5% of the theory) of crystalline product was thus obtained. A small amount was recrystallized from 30-60<sup>o</sup> petroleum ether and formed white needles which melted at 50.0-50.4<sup>o</sup>. Harvey, Heilbron and Wilkinson (12) reported the melting point to be 50-51<sup>o</sup>C.

## Semicarbazone of 5-Methyl, 1-Tetralone

One-half gram of semicarbazide hydrochloride, together with 0.5 g. of the ketone and 0.7 g. of crystallized sodium acetate were dissolved in aqueous alcohol and allowed to stand two hours. The crystals which separated were recrystallized from alcohol until a constant melting point of 237-238° was reached.

Analysis: Calcd. for  $C_{12}H_{15}N_3O$ : C, 66.33; H, 6.96

Found: C, 66.57; H, 6.85

5.  $\beta$ (p-toluyyl) Propionic Acid (V)

$\beta$ (p-toluyyl) propionic acid was made by a modified procedure for the preparation of  $\beta$ benzoyl propionic acid, found in Organic Syntheses (18). Toluene was used instead of benzene in the syntheses.

The quantities of reactants were: 200 g. of succinic anhydride, 1250 ml. of pure toluene, and 585 g. of resublimed anhydrous aluminum chloride. Decomposition was affected with 275 ml. of hydrochloric acid and 820 ml. of water. The crude acid was dissolved in a hot solution of 250 g. of sodium carbonate in 1250 ml. of water. Twenty grams of Nuchar XXX was added and, after boiling for 15 minutes, the mixture was filtered through a layer of macerated filter paper. The filtrate was acidified with hydrochloric acid, and the precipitate filtered by suction. An overage of 593 g. of

damp product was obtained in each run. The acid was nearly white, and after one recrystallization from water, melted at 126-127°. Melting points reported by other investigators are: 124-126° (11), 129° (1) and 127° (2)

#### 6. $\gamma$ (p-tolyl) Butyric Acid (VI)

$\gamma$ (p-toyl) butyric acid was prepared in the same manner as described for the preparation of  $\gamma$ (o-toyl) butyric acid. The product distilled at 150-155° at 3 mm. of Hg pressure. It crystallized from petroleum ether in the form of greasy plates, which melted at 59-59.5°. The yield from 593 g. of wet keto acid amounted to 306 g. This represents an overall yield for the two reactions of 86% of the theory, based on the original succinic anhydride.

Other investigators have reported the melting point of this compound to be: 61-62°C. (15), 60-61° (11), 59° (1).

$\gamma$ -Methyl, 1-tetralone was prepared from  $\gamma$ (p-tolyl) butyric acid in the same way that 5 methyl, 1-tetralone was made from  $\gamma$ (o-tolyl)butyric acid. However, a larger yield was made from  $\gamma$ (o-tolyl)butyric acid. However, a larger yield (83%) was obtained in this case. The product distilled from a Claisen flask at 118-124° under a pressure of 3-3.5 mm. of mercury.

In order to further purify the product for use in the next step, the crude ketone was fractionally distilled in a

30 inch column packed with 1/4" glass helices. Distillation was carried out very slowly, and the temperature of distillation was not taken. Several small fractions (5-6 ml. each) were collected, and only those which showed a refractive index between 1.56000 and 1.56050 at 26.5° were used. Refractive indices were taken on the supercooled liquid.

The data taken on a representative distillation is given in Table I.

TABLE I  
DISTILLATION OF 7-METHYL, 1-TETRALONE  
Charge, 100 g      Pressure 0.5 mm. Hg

Fraction #	T of bath in °C	T of column in °C	R. I. at 26.5°C
1	156	80	1.57510
2	165	96	1.59535
3	165	100	1.57335
4	180	109	1.56050
5	178	109	1.56025
6	175	107	1.56025
7	179	109	1.56000
8	176	107	1.56000
9	180	108	1.56005
10	175	106	1.56041
11	177	106	1.56025
12	183	108	1.56045
13	180	107	1.56065
14	180	112	1.56080
15	180	112	1.56085

In this case fractions 4-12 inc. were considered of sufficient purity, while fractions 1-3 and 13-15 inc. were combined and redistilled. The supercooled liquid fractions, when seeded, crystallized immediately. The purest material melted at 35-35.2°, and had a refractive index of 1.56026 at 26.5°. Crystallization from petroleum ether failed to raise the melting point. Barnett and Sanders (1) reported the melting point to be 35°.

#### Semicarbazone of 7-Methyl, 1-Tetralone

The semicarbazone was prepared in the same manner as was the semicarbazone of 5-methyl, 1-tetralone. The melting point was found to be 225-225-7°. Ruzicka and Mergeli (25) reported the melting point to be 224-225°C.

#### 8. 7-Methyl, 1-Naphthol (VIII)

7-methyl, 1-naphthol was prepared from 7 methyl, 1-tetralone by dehydrogenation with a palladium on carbon catalyst (4). Twenty grams of the ketone, with 10 g. of catalyse were heated on a metal bath at 300-320° until the reaction ceased. (about 1½ hrs.) The reaction mixture was dissolved in ether, and the naphthol extracted with 10% potassium hydroxide solution. The alkaline extracts were acidified with 10% sulfuric acid, whereupon there was precipitated 14-16 g. of crude naphthol. The combined yields of several runs (135 g.) was distilled at a pressure

of 3 mm. of mercury. The fraction which boiled at 135-140° weighed 116 g. and was used in the next step. A small sample, when recrystallized from petroleum ether, formed slender needles which melted at 110.5-111°. Melting points recorded in the literature are 110-111°C (25), 108-109°C. (11) 109° (14).

#### 9. 7-Methyl, 1-Naphthylamine (IX)

An iron pipe (30 inches by  $1\frac{1}{2}$  inches) was capped and tested for flaws and leaks by forcing water into it by means of a hydraulic pump. It was found that pressures up to 600 lbs. per square inch could be exerted in the pipe. It was then wrapped with #18 nichrome wire and well lagged with asbestos paper. Provision was made for temperature determination by including a glass thermometer well under the wire.

Into a glass tube (35x400 mm.) were placed 50 g. of 7-methyl, 1-naphthol, 150 ml. of water, 75 ml. of freshly prepared ammonium sulfite and 75 ml. of 28% ammonia water. The tube was sealed and placed in the iron pipe on a cushion of glass wool. In the pipe was also placed 75 ml. of 28% ammonia water and 150 ml. of water. This served to equalize the pressure in the glass tube.

The caps on the pipe were screwed firmly in place and the whole lashed to a shaking machine so that the pipe traveled 5 inches along its axis. The machine made 70 excursions per minute. Connections to the nichrome wire were made through a rheostat to a 110 volt A.C. line, and

the rheostat regulated so that the tube maintained a temperature of 160-165°C. Heating and shaking was carried on for 30-35 hours. At the expiration of this time the tube was allowed to cool and then opened. The contents were extracted with ether (3-250 ml. portions). The ether extracts were combined and extracted with 10% hydrochloric acid until no more amine was extracted. The acid extracts were made alkaline with 10% sodium hydroxide and the precipitated amine filtered and dried. The yield of crude amine was 43-45 g. (87-90% of the theoretical amount.)

The combined yields from several runs were distilled in a sausage flask at a pressure of 3 mm. of mercury. The bulk of the material boiled at 139-140°C. A small amount was recrystallized from petroleum ether in the form of fine needles, which melted at 58.2-59°. The melting point reported in the literature is 58-59° (25).

Several attempts to carry out this reaction with the tube in a stationary position failed to give any appreciable yield of amine.

The acetyl derivative of 7-methyl, 1-naphthylamine was prepared by bubbling ketene through an acetone solution of the amine. The crystalline material was twice recrystallized from petroleum ether and melted at 180.5-181°. Melting points reported in the literature are 175-176°C (27) and 178-179°C. (25).

## 10. 7-Methyl, 1-Bromonaphthalene (X)

Twenty-seven grams of 7-methyl, 1-naphthylamine was dissolved in a hot solution of 28 ml. of concentrated hydrochloric acid in 565 ml. of water. After all the amine was dissolved, the solution was vigorously stirred mechanically and cooled in an ice bath, and 45 ml. of concentrated acid was added. The sludge of fine crystals which was thus formed was cooled to  $-5^{\circ}$  and a 20% solution of sodium nitrite (12.5 g. of nitrite) was added in three or four portions. Stirring was continued for not more than five minutes.

The cold diazotate was poured into a well stirred, ice cold solution of 115 g. of mercuric nitrate and 180 g. of potassium bromide in 200 ml. of water. Immediately a yellow precipitate of a complex salt,  $(C_{11}H_9N_2)_2 HgBr_4$  (20) (26), formed which was filtered and dried in a vacuum desiccator over phosphorus pentoxide.

The 45 ml. excess hydrochloric acid, by lowering the hydrolysis of amine hydrochloride, retarded the formation of azo amino compound. This compound is formed by coupling of the free amine with diazotized amine. A green color appeared in the yellow complex salt when azo amino compound was present.

The yellow complex salt (about 90 g. from each run)

was intimately mixed with twice its weight of dry, powdered potassium bromide, and placed in a glass tube (100 by 3 cms.), which was sealed at one end. Gentle heating of the mixture at the closed end of the tube caused a spontaneous decomposition of the salt to progress uniformly along the length of the tube toward the open end. When decomposition was complete, the black mass was pulverized and extracted with three 500 ml. portions of ether. The ether extract was washed first with 5% potassium bromide solution to remove dissolved mercuric bromide, then with 10% hydrochloric acid solution to remove any amine, then with water and sodium hydroxide solution to remove naphthol and finally with water.

The ether solution was dried with anhydrous calcium chloride, and the ether distilled off on the steam bath. The residue was distilled at 2 mm. of mercury. The bromide boiled at 110-115° at this pressure. The combined yield from three runs amounted to 68.3 grams. (60.3% of the theoretical amount).

#### Picrate of 7-Methyl,1-Bromonaphthalene

One-fifth gram of the methyl bromonaphthalene was dissolved in alcohol, and an alcohol solution of 0.2 g. of picric acid was added. An immediate orange precipitate

formed which, when recrystallized from alcohol, melted at 101-102°. This agrees with the value reported by Ruzicka (25).

11.  $\beta$ (7-methyl,naphthyl-1) Ethanol (XI)

A 500 ml., 3 necked flask was equipped with a mercury sealed stirrer, a reflux condenser and a dropping funnel. Into the flask was placed 8.5 g. of magnesium turnings and 50 ml. of dry ether. Sixty-seven and four-tenths grams of 7-methyl, 1-bromonaphthalene was placed in the dropping funnel and a few mls. added to the reaction flask. Gentle heating caused the reaction to start, after which 150 ml. more ether was added. The remainder of the bromide was added over a period of one hour, and the mixture warmed on a water bath for an additional hour.

The flask was then surrounded by an ice and salt bath and 23 g. of ethylene oxide was slowly distilled into the mixture. The oxide was made to pass through a tube packed with cracked potassium hydroxide, and was condensed in a spiral condenser surrounded with dry ice. After the addition of the ethylene oxide, the mixture was heated and stirred for an hour and then decomposed with ice (100 g.) and hydrochloric acid (50 ml.). The layers were separated and the aqueous layer extracted twice with 100 ml. portions of ether. The combined ether extracts were washed with dilute sodium hydroxide and then with water, dried with

sodium sulphate and the ether removed by distillation. The residue was distilled at a pressure of 0.5 mm. of mercury from a modified Claisen flask. The portion which boiled at 117.5-120° was collected and weighed 40.5 g. (71.5% of the theoretical amount).

The p-nitro benzoate was prepared by warming 1 g. of the alcohol with 2 g. p-nitro benzoyl chloride. The solid product was dissolved in ether and the ether solution washed with sodium carbonate solution, and then with water, and the ether evaporated. The residue, when recrystallized from petroleum ether, melted at 117-118°. The melting point reported in the literature (25) is 118-119°C.

## 12. $\beta$ (7-methyl naphthyl-1) Ethyl Chloride (XII)

A solution of 28 g. of  $\beta$ (7-methyl naphthyl-1) ethanol in 32.5 g. of dimethyl aniline in a 125 ml. Erlenmeyer flask was cooled in an ice bath, while 19.2 ml. of thionyl chloride was added slowly. The dark mixture was allowed to stand 12 hours at room temperature, and was then warmed on a steam bath for one hour. The mixture was then dissolved in ether and the ether solution washed with dilute hydrochloric acid until no more acid soluble material was extracted. The ether solution was dried with anhydrous

calcium chloride, the ether distilled off on a steam bath and the residue distilled at a pressure of 0.5 mm. of mercury. The product which boiled at 98-100° weighed 24.7 g. (87% of the theoretical amount) and was a light yellow, viscous liquid.

Ruzicka (25) reported the boiling point of this compound to be 124-125° at 0.4 mm. In distillations of this nature, the observed distillation temperature is dependent on the pressure inside the flask, and not on the observed pressure, when the manometer is located at the end of the evacuated system. The pressure in the flask proper is dependent markedly on the design of the apparatus. A flask fitted with a large diameter side arm with no sharp bends will enable the pressure to be reduced more than would be the case with a flask fitted with a small diameter side arm in which sharp bends occurred.

The flask used for the distillation of *β*-7-methyl naphthyl-1) ethanol and subsequent intermediates was of the "sausage" type, with a capacity of about 50 ml., fitted with a side arm in such a manner that a bend of large curvature connected it to the flask. Hence, the boiling points reported herein for subsequent compounds are lower than the corresponding boiling points reported by other investigators.

13.  $\beta$ (7-methyl, naphthyl-1),  $\alpha$ (5-methyl, 3,4-dihydro naphthyl-1) Ethane (XII)

A 200 ml., 3 necked flask was fitted with a mercury sealed mechanical stirrer, a reflux condenser, and a dropping funnel. In the flask was placed 4.0 g. of magnesium turnings, a small crystal of iodine and about 10 ml. of dry ether. In the dropping funnel was placed 12.2 g. of  $\beta$ (7-methyl, naphthyl-1) ethyl chloride, and a few drops were added to the reaction flask. A gentle heat was used to start the reaction. After the reaction had started, more ether (50 ml.) was added; and the rest of the chloride allowed to drop slowly into the reaction. During this addition, which required one hour, the ether was kept boiling by means of a water bath.

After the addition of chloride was completed, the reaction flask was cooled in an ice bath, and a solution of 11.4 g. of 5 methyl, 1-tetralone in 50 ml. of dry ether was added through the dropping funnel over a period of one and one-half hours. When addition was complete, the reaction mixture was stirred and heated so that the ether refluxed for ten hours.

Decomposition was affected by pouring the mixture onto 50 g. of ice and 15 ml. of concentrated hydrochloric acid. The layers were separated, and the aqueous layer

extracted with two 60 ml. portions of ether. The combined ether extracts were washed with water, dried, and the ether distilled off on a steam bath. The residue was distilled in a sausage flask (capacity, 50 ml.) at a pressure of 0.5 mm. of mercury. The product which boiled 189-193° weighed 13 g. (70% of the theoretical amount). It was a very viscous, yellow liquid.

The high temperature necessary for distillation caused the tertiary carbinol (XIII) formed from the reaction to dehydrate and form the unsaturated hydrocarbon (XIV). This is characteristic of tertiary carbinols. The product, in a dry ether solution, failed to react with either sodium or acetyl chloride.

14.  $\beta$  (7-methyl naphthyl-1),  $\alpha$  (5-methyl, naphthyl-1)  
Ethane (XV)

The aromatization of ring B in  $\beta$ (7-methyl, naphthyl-1),  $\alpha$  (5-methyl, 3,4-dihydro naphthyl-1)ethane (XIV) was affected by dehydrogenation with a palladium-on-carbon catalyst (12).

A 50 ml. flask was connected by a ground glass joint to a 50 cm. glass tube (15 mm.o.d.). Near the top of the tube, a side arm connected to a bubble counter. A side arm fitted with a stopcock was sealed near the top of the 50 ml. flask.

The flask was charged with 3.5 g. of hydrocarbon XVI

and 1.0 g. of catalyst, and the air displaced by nitrogen. This mixture of catalyst and hydrocarbon was heated at 220°C in a metal bath until bubbling in the bubble counter ceased, whereupon the flask was cooled and the contents extracted with ether. The catalyst was filtered off and the ether evaporated. A residue (3.3 g.) distilled from a small sausage flask at 195-200° at a pressure of 0.5 mm. of mercury. All attempts to crystallize the distillate failed, so it was again dehydrogenated with 1.0 g. of fresh catalyst, this time at 240-250°. The reaction mixture was worked up as before and distilled. Again, the distillate defied all efforts to crystallize it. It was decided that the hydrocarbon failed to crystallize because it was impure, so an attempt was made to purify it by adsorption on suitable adsorbants.

A solution of the hydrocarbon in 50 ml. of dry petroleum ether was passed through a 20 cm. column of activated alumina (standardized according to Brockmann), and the column washed with two portions of dry petroleum ether. Three separate portions of filtrate were collected, and the petroleum ether evaporated from each. The residues were dissolved in methanol and allowed to stand overnight. The first portion contained white needles, which melted at 69.2-69.5°C. After three recrystallizations from methanol, the melting point was raised to 70.3-70.7°.

Further recrystallizations failed to raise the melting point. The yield amounted to 100 mg.

Ruzicka (23) reported the melting point of this compound to be 74-75°, so it was deemed advisable to attempt further purification in order to bring the melting point up to this figure. Fifty milligrams of hydrocarbon were dissolved in 25 ml. of dry 30-60° petroleum ether and filtered through a 15 cm. column of activated alumina, and the filtrate saved. Then three successive portions (25 ml. each) of 30-60° petroleum ether were used to wash the column, and each filtrate saved separately for later analysis. A final washing of the column with petroleum ether which contained about 3% methanol was made. These five filtrates were all treated in the same manner. The petroleum ether was evaporated and the residue, if any, was recrystallized from methanol.

The first filtrate yielded a small amount of crystalline material (about 10 mg.) which melted at 70.0-70.4°. The second filtrate gave about 30 mg. of crystals which melted at 70.2-70.4°. The third filtrate yielded a very small amount (about 5 mg.) of material which melted at 70.0-70.3°. The fourth and fifth filtrates yielded nothing.

The best recrystallized material from the second

fraction was dissolved in petroleum ether and put through a column of fresh alumina. When this column was observed under ultra violet light, no discontinuity in the bright purplish-blue fluorescence could be noted. It was therefore concluded that the hydrocarbon was chromatographically homogeneous and pure.

Analysis: Calcd. for  $C_{24}H_{22}$ ; C, 92.89; H, 7.11

Found; C, 92.86; H, 7.12<sup>1</sup>

C, 92.77; H, 7.07

The di-picrate of  $\beta$ (7-methyl, naphthyl-1),  $\alpha$ (5-methyl, naphthyl-1) ethane was prepared from 15 mg. of hydrocarbon and 30 mg. of picric acid in about 1.5 ml. of methyl alcohol. After recrystallization, the product, orange needles, melted without decomposition at 167-167.2°.

Analysis: Calcd. for  $C_{36}H_{28}N_6O_{14}$ ; C, 56.25; H, 3.68

Found: C, 56.19; 56.16;

H, 3.87; 3.69

The di-styphnate of the hydrocarbon was prepared in the same manner as was the di-picrate, from 15 mg. of

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1. The author wishes to thank Mr. J. K. Wolfe for this analysis.

hydrocarbon and 30 mg. of styphnic acid. The product, yellow needles, melted without decomposition at 180.5-180.6°. A mixture of styphnate and styphnic acid (m.p. 179-181°) melted at 165-170°. Neither the di-picrate nor the di-styphnate dissociated in methyl alcohol solution.

Analysis: Calcd. for  $C_{36}H_{28}N_6O_{14}$ ; C, 53.99; H, 3.52  
 Found: C, 54.07; 53.99;  
 H, 3.53; 3.62

Another dehydrogenation of 14.9 g. of hydrocarbon XIV at 340° gave, after distillation, 11.0 g. of crude hydrocarbon XV. The first crystallization yielded 4.0 g. of crystals. All material which would not crystallize was again dehydrogenated and repeatedly crystallized. The total yield of pure material was 7.0 g. (38% of the theoretical amount).  $\beta$ (7-methyl, naphthyl-1),  $\alpha$ (5-methyl, naphthyl-1) ethane imparts a light blue fluorescence to its solutions.

#### 15. 1,8-Dimethyl Picene XVI

1,8-dimethyl picene was prepared by cyclicizing  $\beta$ (7-methyl naphthyl-1),  $\alpha$ (5-methyl naphthyl-1) ethane by the action of anhydrous aluminum chloride in carbon bisulfide solution. This method has been used in the preparation of picene (22), 3,9,10-trimethyl, and 3,8-

dimethyl picene (25) and 1,8-dimethyl picene (22).

Three grams of  $\beta$ (7-methyl naphthyl-1)  $\alpha$ (5-methyl naphthyl-1) ethane was dissolved in 30 ml. of dry carbon bisulfide in a 125 ml. glass stoppered Erlenmeyer flask, and 6 g. of resublimed aluminum chloride was added in portions. The flask was stoppered and shaken on a shaking machine for three days at room temperature. The reaction mixture turned dark and viscous during this treatment. The mixture was poured onto 50 g. of ice and 25 ml. of hydrochloric acid, and the carbon bisulfide distilled out with steam. The dark residue was dissolved in 1000 ml. of toluene and the toluene solution washed three times with 1:1 hydrochloric acid, three times with 25% sodium hydroxide solution and finally with water. The toluene was distilled with steam. The residue was scraped from the flask and washed repeatedly with alcohol and ether, until no more soluble material was removed by the ether. Nearly all colored matter was removed by this treatment, and the crude material was transformed into a tan powder.

The resulting tan powder was sublimed at  $260^{\circ}$  in a high vacuum (13). The sublimate was almost pure white and melted at  $303-304^{\circ}$ . One crystallization from toluene gave lustrous white plates which melted at  $304-305^{\circ}$ . Further recrystallization failed to raise the melting point. The total yield was 420 mg.

A pure sample of the picene hydrocarbon obtained by dehydrogenation of ursolic acid (6) was prepared by repeated crystallization and sublimation. This compound melted at 303.5-304°. An intimate mixture of this hydrocarbon and 1,8-dimethyl picene melted at 303.5-305°.

In order to determine whether the reaction could be carried out successfully at a somewhat higher temperature, and a shorter period of time, another experiment was made. Fifteen milliliters of carbon bisulfide, 0.8 g. of

$\beta$ (7-methyl naphthyl-1)  $\alpha$ (5-methyl naphthyl-1) ethane, and 1.65 g. of aluminum chloride were warmed on a steam bath for three hours. The mixture was treated, and the product purified in exactly the same way as just described. The final product (70 mg.) melted at 304-305° and gave no depression in melting point when mixed with the previously prepared 1,8-dimethyl picene. It may be concluded, then, that no rearrangements resulted by raising the reaction temperature to the boiling point of carbon bisulfide.

1,8-dimethyl picene crystallizes from benzene, toluene, xylene, and pyridine in the form of lustrous white plates, which, when pulverized, exhibit a slight blue fluorescence. Solutions of the hydrocarbon possess a blue fluorescence to a marked degree. When dissolved in warm sulfuric acid, the hydrocarbon imparts a green color to the solution, as does the 1,8-dimethyl picene from dehydrogenation of

Friedelinol (7) and ursolic acid (6).

Analysis: Calcd. for  $C_{24}H_{18}$ : C, 94.08; H, 5.92

Found; C, 94.06, 94.23, 93.89

H, 5.86, 5.81, 5.86

## SUMMARY

1. 1,8-dimethyl picene has been synthesized and shown to be identical to the poly alkyl picene obtained by dehydrogenating Friedelinol and ursolic acid.
2. A tentative formula for Friedelinol is proposed.
3.  $\beta$ (o-toluy) propionic acid has been prepared and identified.
4. The cyclization of  $\beta$ (7-methyl naphthyl-1),  $\alpha$ (5-methyl naphthyl-1) ethane has been carried out in boiling carbon bisulfide without rearrangement of methyl groups or lowering the yield of the established procedure.

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