

THE SYNTHESIS OF
4-OXO-3,3-DIMETHYL-3,4-DIHYDROPHENANTHRENE

by
ARTHUR MADISON IMEL

A THESIS
submitted to
OREGON STATE COLLEGE

in partial fulfillment of
the requirements for the
degree of

MASTER OF SCIENCE

June 1958

APPROVED:

Redacted for Privacy

Assistant Professor of Chemistry

In Charge of Major

Redacted for Privacy

Chairman of Department of Chemistry

Redacted for Privacy

Chairman of School Graduate Committee

Redacted for Privacy

Dean of Graduate School

Date thesis is presented _____

Typed by Lois Metzger

ACKNOWLEDGMENT

To Dr. E. N. Marvell whose suggestions have made this work possible. Also, the author is indebted to Dr. B. E. Christensen and Dr. C. H. Pease who have proofread the manuscript during Dr. Marvell's absence and have offered helpful criticisms.

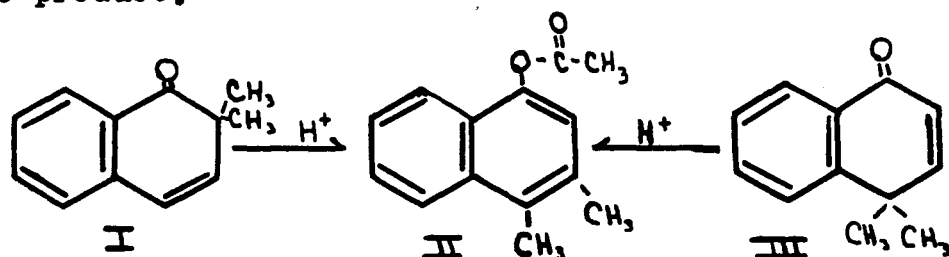
TABLE OF CONTENTS

| | |
|---|----|
| INTRODUCTION. | 1 |
| HISTORICAL. | 4 |
| DISCUSSION. | |
| A. Synthetic Procedures. | 9 |
| B. Mechanism | 14 |
| EXPERIMENTAL | |
| α,α -Dimethylsuccinic acid. | 19 |
| α,α -Dimethylsuccinic anhydride | 19 |
| β -2(5,6,7,8-Tetrahydronaphthoyl) α,α -dimethyl- propionic acid. | 19 |
| γ -2-Tetrallyl- α,α -dimethylbutyric acid | 20 |
| Methyl- γ -2-tetrallyl- α,α -dimethyl butyrate | 21 |
| γ (2-Naphthyl)- α,α -dimethylbutyric acid | 22 |
| 3,3-Dimethyl-1,2,3,4-tetrahydrophenanthrene- 4-one | 23 |
| 3,3-Dimethyl-3,4-dihydrophenanthrene-4-one | 24 |
| SUMMARY | 27 |
| BIBLIOGRAPHY. | 28 |

THE SYNTHESIS OF 4-OXO-3,3-DIMETHYL-
3,4-DIHYDROPHENANTHRENE VIA AN UNAMBIGUOUS ROUTE

INTRODUCTION

Arnold, Buckley, and Richter (2,p.2322) have reported that the acid catalyzed rearrangement of 1-oxo-4,4-dimethyl-1,2-dihydronaphthalene (III) produces the 3,4-dimethyl naphthyl acetate (II). Marvell and Geiszler (13,p.1259) have reported that the rearrangement of 1-oxo-2,2-dimethyl-1,2-dihydronaphthalene (I) produces the same product:



Two mechanisms were proposed to account for the products obtained, the one by Marvell and Geiszler suggesting migration of the oxygen function and that by Arnold, Buckley, and Richter involving no oxygen function migration.

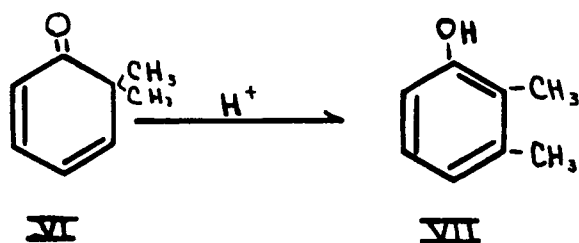
Thus two modes of rearrangement are open to a dienone: the one involving a migration of the oxygen

function by Geiszler and the other involving no migration by Arnold. A study of the mechanisms involved for the different modes of rearrangement reveals that in the case of the Arnold mechanism an ortho quinoid intermediate is formed during the course of the rearrangement. In order for this intermediate to form, the aromatic double bond of the dienone must be ruptured. (See mechanisms page 14).

Since the breaking of this bond involves a large amount of energy, an energy barrier is presented to the dienone following this mechanism, and the dienone is forced to take an abnormal path of less energy involving migration of the oxygen function.

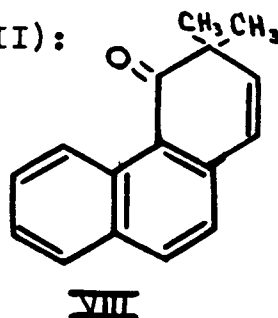
To determine the height of this energy barrier, dienones having a double bond with varying degrees of aromatic character should be synthesized and their path of rearrangement studied.

The dienone (VI) having double bonds which are olefinic was synthesized and its rearrangement studied by Geiszler (9, p.2). Of three possible modes of rearrangement, this compound yielded mainly the 2,3-dimethylphenol (VII) indicating a preference for the Arnold mechanism (normal path) in this case because of the ease of bond rupture of the olefinic bond to form the quinoid intermediate.



In both the dienone (I) and similar dienones studied by Stephenson (17, p.3) and Magoon (12, p.3) the dienone contained a double bond which was incorporated into a benzene ring and thus highly aromatic. In all of these cases the rearrangement was forced to take the abnormal path involving oxygen function migration because of the stability of the benzene double bond to rupture.

Since there is less aromatic character in the naphthalene ring than in the benzene ring, a dienone having one of the double bonds incorporated into a naphthalene ring would provide additional information about the energy barrier between the two mechanisms. A compound fulfilling this requirement is 4-oxo-3,3-dimethyl-3,4-dihydrophenanthrene (VIII):

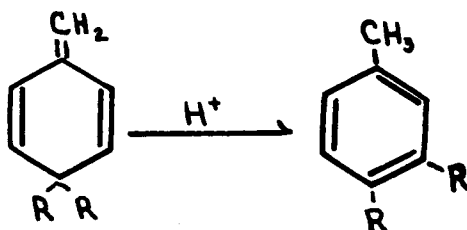


The purpose of this work will be to synthesize this dienone for later study.

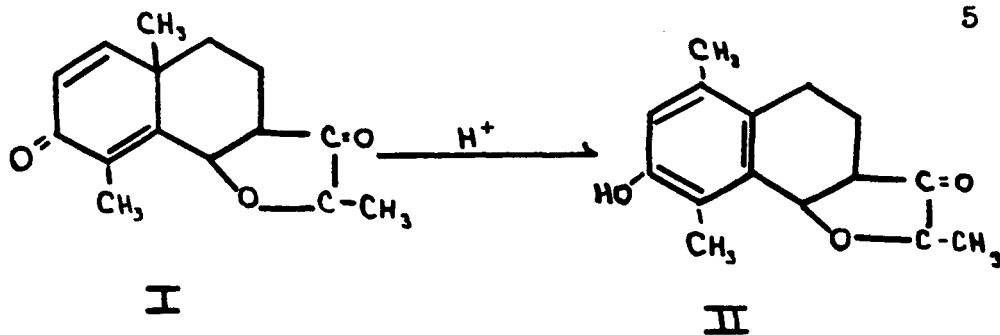
HISTORICAL

In 1879 Benedikt (5,p.127) reported a rearrangement resembling the dienone-phenol rearrangement. Although he did not propose a structure for his compound, he did report a product which gave tests characteristic for phenols.

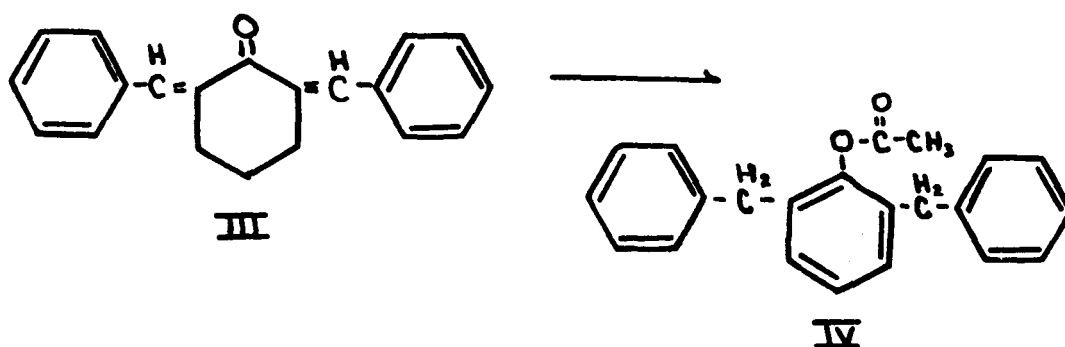
Anwers and his co-workers (1,p.3598) studied a rearrangement known as the semi-benzene rearrangement which differs from the dienone-phenol rearrangement only in that the ketone function is replaced by a methylene group.



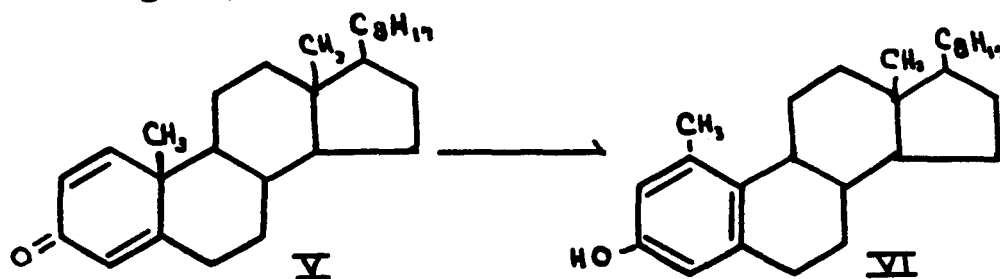
In 1930 Clemo, Haworth and Walton (7, p.1110) reported the classic example of the dienone phenol rearrangement in their study of santonin. They treated santonin (I) with acid and found that it rearranged to desmotropic santonin (II).



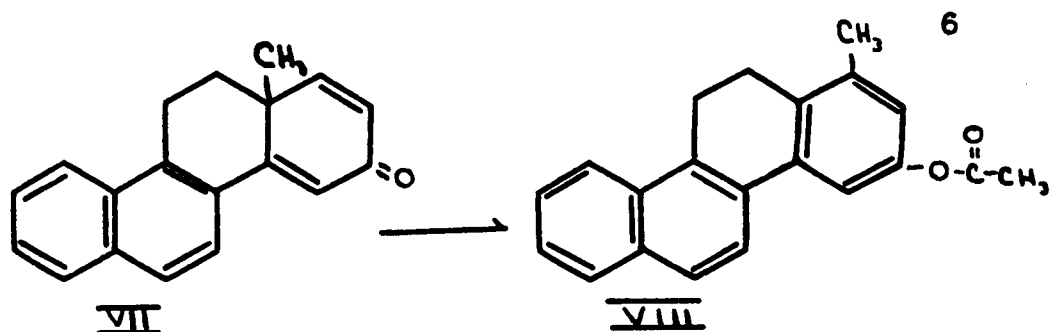
A case of the dienone-phenol rearrangement involving exocyclic double bonds was reported by Weiss and Ebert (18, p.399) when they rearranged the cyclo-dienic ketone (III) to a substituted phenol derivative (IV).



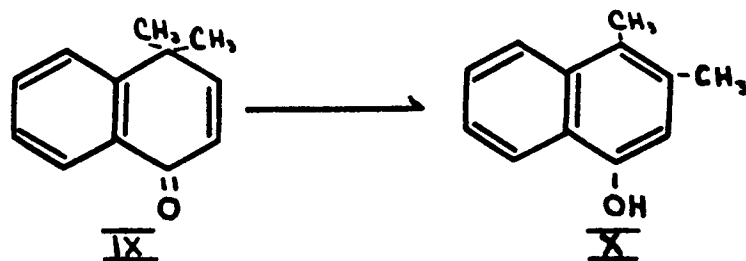
Inhoffen, (10, p.473) working with the steroids rearranged (V) to (VI).



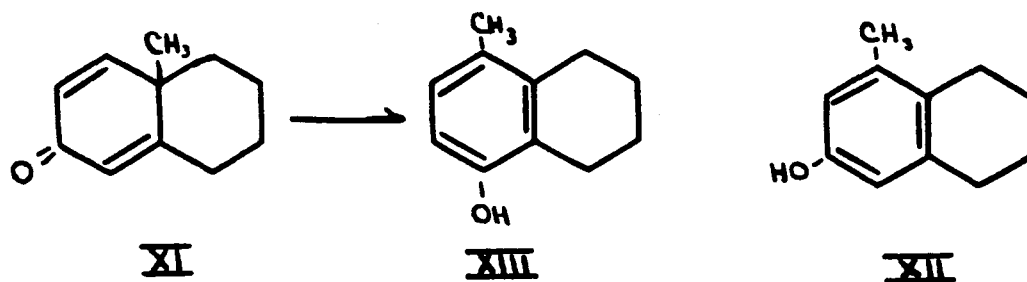
Later, in 1946, Wilds and Djerassi (21, p.1712) proposed the name "dienone-phenol" for the rearrangement from their work in the chrysene series in which (VII) was rearranged to (VIII).



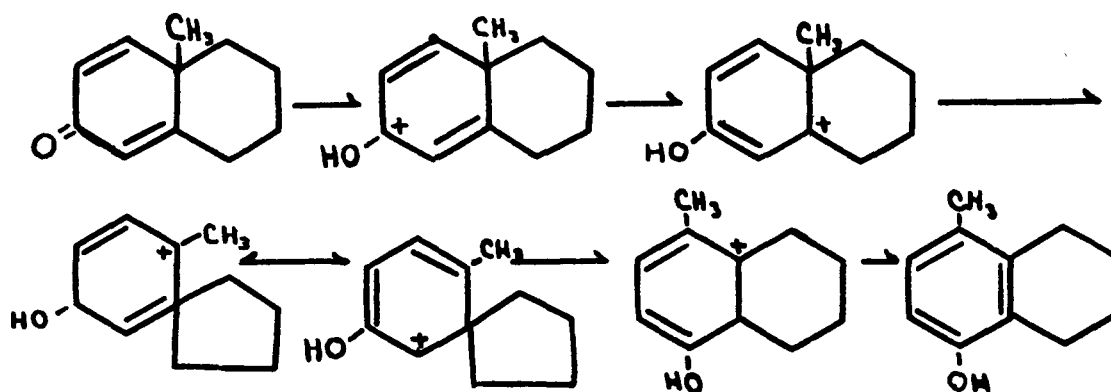
Arnold, Buckley and Richter (2, p.2322) began an investigation of the dienone-phenol rearrangement by the examination of gamma-blocked dienones in which neither of the substituents in the para position are part of a fused ring system. They subjected (IX) to conditions which brought about its rearrangement to (X). They proposed a mechanism for the rearrangement. (See mechanisms).



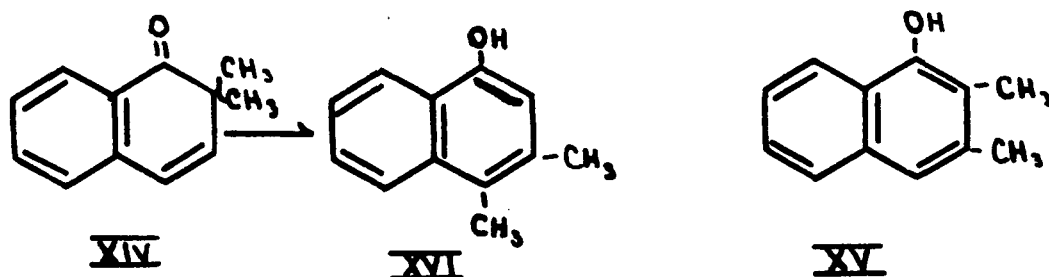
Woodward and Singh (22, p.494) were first to notice a seeming discrepancy in the above mechanism when they rearranged (XI) and instead of finding the expected (XII) found (XIII). They noticed if either the methyl group or the ring could rearrange, that the ring rearranges.



They proposed the following mechanism:



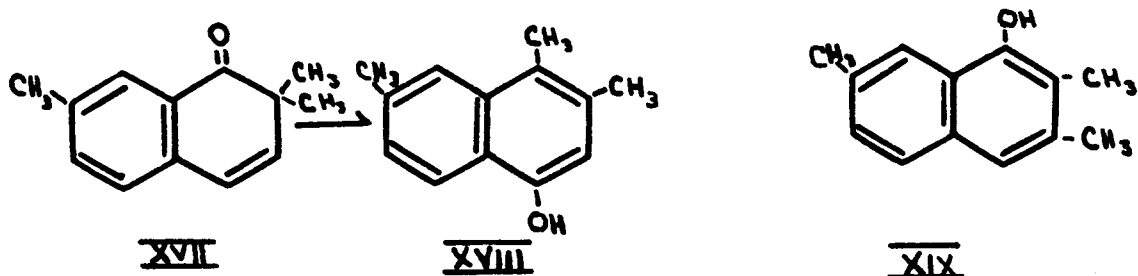
In 1952 Marvell and Geiszler (9, p.1259) studied the alpha-blocked dienone (XIV) and also found that it did not give the expected product (XV) but, instead (XVI).



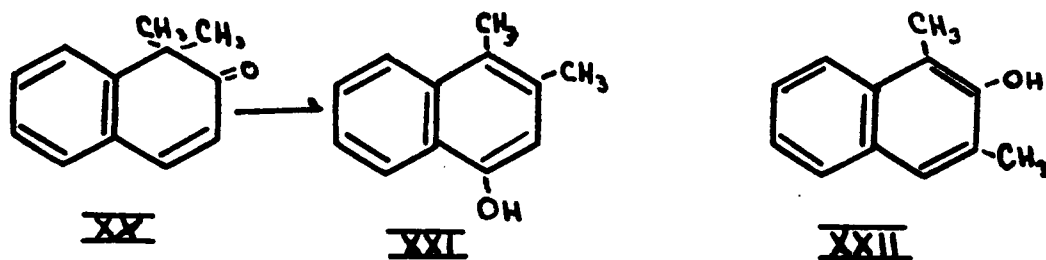
Once again, to explain this result, a mechanism was devised. This time the mechanism involved migration of the oxygen function. (See mechanisms).

This mechanism was substantiated by Magoon (12,

p.22) when he rearranged (XVII) and obtained (XVIII) instead of the product expected by the mechanism proposed by Arnold (XIX).



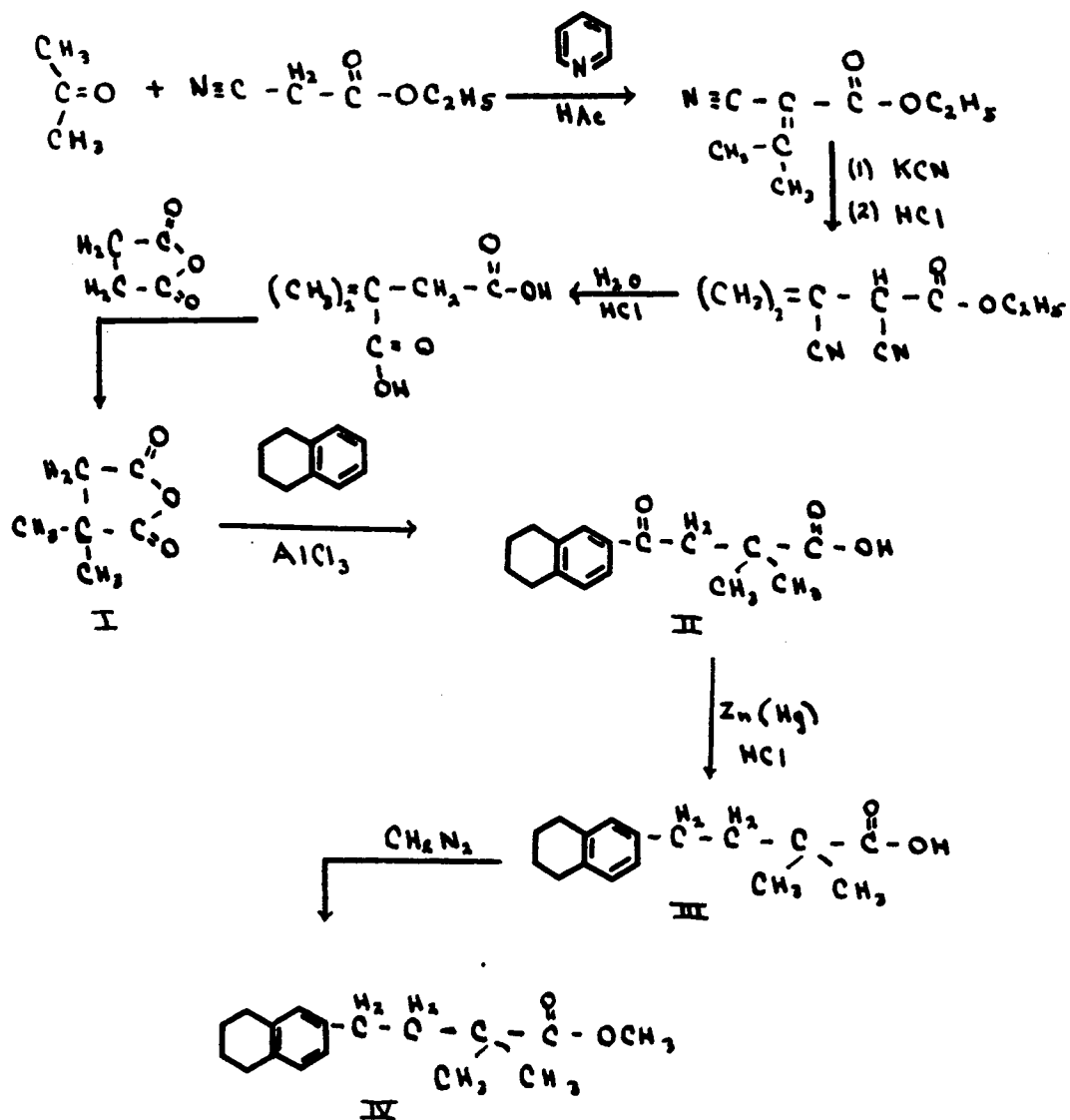
Stephenson (17, p.15) further substantiated the mechanism when he rearranged (XX) finding (XXI) in place of the otherwise expected (XXII), showing also that either double bond when in the ring fails to play a part in the reaction.

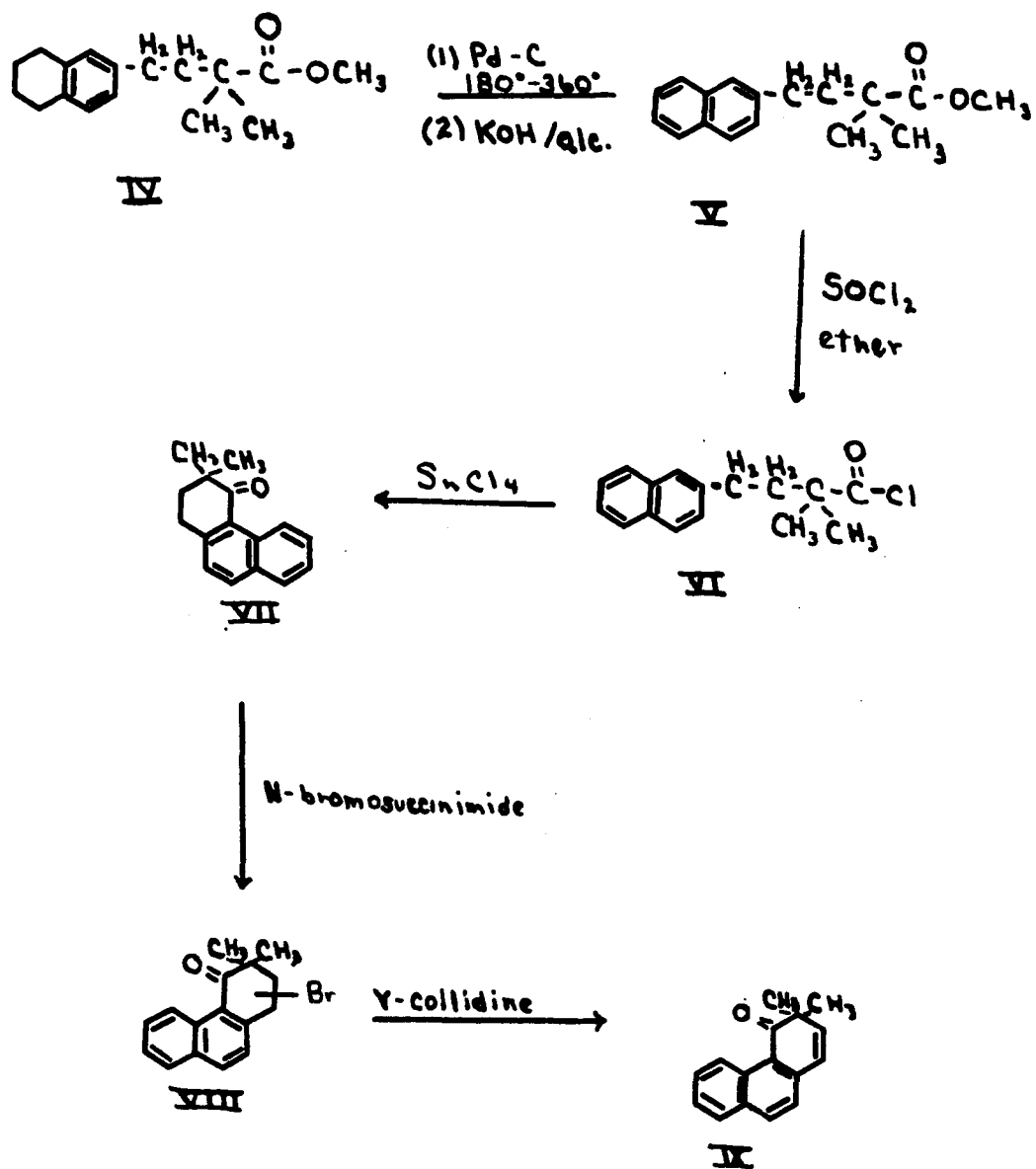


DISCUSSION

A. Synthetic Procedure

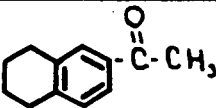
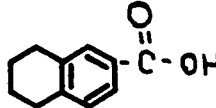
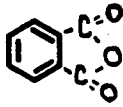
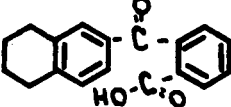
In these laboratories, the following synthetic procedures have been performed:





It was important to insure beta substitution in the synthesis of the keto acid (II) since this would determine which keto isomer would be obtained at the end of the synthesis.

Krollpfeifer and Schäfer (11, p.620) have reported that tetralin substitutes exclusively in the beta position since only the beta isomer is obtained in a number of substitution reactions with tetralin. (See table).

| Condensing agent | Product |
|---|---|
| $\text{CH}_3\text{-}\overset{\text{O}}{\parallel}\text{C}\text{-Cl}$ |  |
| $\text{CO}_2 + \text{HCl}$ ($\text{Cl}\text{-}\overset{\text{O}}{\parallel}\text{C}\text{-OH}$) |  |
|  |  |

For this reason, tetralin rather than naphthalene was decided to be the better choice since separation of the alpha and beta isomers obtained with naphthalene is very difficult.

α,α -Dimethylsuccinic anhydride was prepared by the usual well known methods and was used to succinoylate tetralin to produce β -2(5,6,7,8-tetrahydronaphthyl), α,α -dimethylpropionic acid (II) according to a modification of the procedure by Newman and Zahn (14, p.1097) in which

they prepared a similar acid having no methyl groups.

It was found that better yields of the reduced acid (III) were obtained if toluene was omitted in the Martin modification of the Clemensen reduction and additional acetic acid was added to increase the solubility of the keto acid. The linear distance of the keto acid, which floats on the top of the acid layer during reduction, to the zinc amalgam should be as great as possible to prevent gumming of the zinc. An attempt to prepare the 2,4-dinitrophenyl hydrazide from the reduction product failed indicating that there was none of the keto acid present.

It was necessary to form the ester (IV) before dehydrogenating the acid (V) since, under the conditions for dehydrogenation, the acid would decarboxylate (14, p.1099). An initial attempt to prepare the ester (IV) from the reduced acid by the Fischer-Spier method failed but it was found that the ester could easily be prepared using diazomethane (20, p. 179).

The ester was dehydrogenated using 10% palladium-charcoal catalyst and temperatures as high as 360°. Optimum yields were obtained if only 5 g. portions were used and the apparatus were scrupulously cleaned after each run. The dehydrogenated acid gave a melting point of 139.5-140°. The same acid reported by Sengupta

(15, p.9) gave a melting point of 133-135°. However, his method of synthesis made possible the likelihood of contamination of his acid with the isomer, γ (1-naphthyl), α,α -dimethylbutyric acid, and thereby causing a low melting point. The fact that the acids compare so closely in melting points is additional proof that tetralin has succinoylated in the beta position. For the melting point of the isomer he reports 99-101°.

The cyclic ketone (VII) when prepared by the sulfuric acid method (3, p.164) was obtained in such low yields that the Friedel-Crafts method of cyclization was used. This involved the formation of the acid chloride (VI) by purified thionyl chloride. The cyclic ketone was obtained in 91% yield by this method.

The possibility of obtaining the isomeric ketone 1-oxo-2,2-dimethyl-1,2,3,4-tetrahydrophenanthrene has been ruled out because of the beta substitution of tetralin. The other possibility, that of formation of the corresponding keto anthracene angular isomer does not take place because of the higher reactivity of the alpha position on the naphthalene nucleus.

Infra-red absorption maxima in the 740-775 and 800-840 cm^{-1} region confirm the 1,2-disubstitution of the naphthalene nucleus (19, p.346).

The dimethyl cyclic ketone (VII) has been prepared

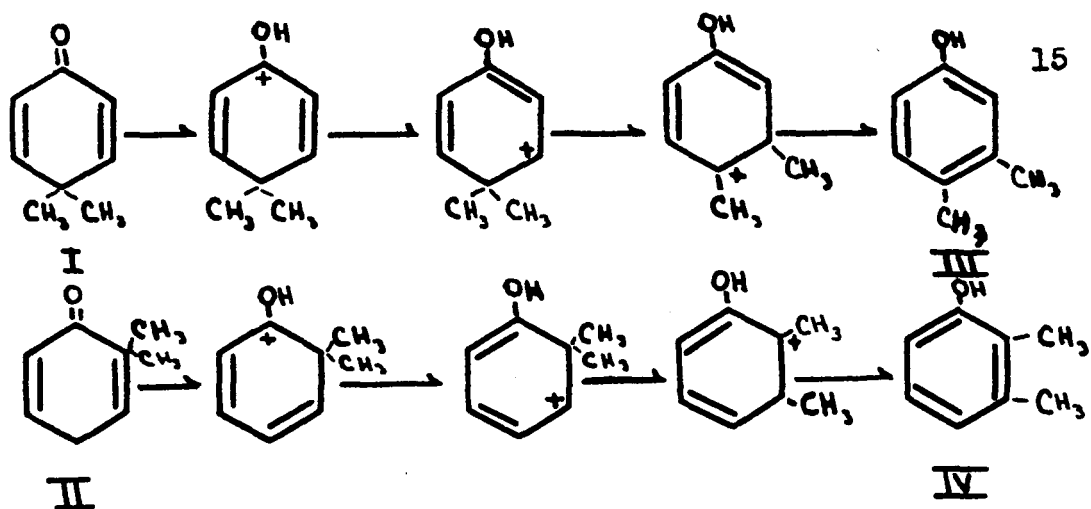
by Sengupta (15, p.9) who reports a boiling point of 155-157° (7mm). Our ketone distilled at 138-141° (0.5 mm), had a refractive index of 1.6084 at 26.8° and a specific gravity of 1.0706 at 23°. The molar refractivity was calculated to be 69.38 and found to be 72.47.

4-oxo-3,3-dimethyl-1,2,3,4-tetrahydrophenanthrene (VII) was converted to 4-oxo-3,3-dimethyl-3,4-dihydrophenanthrene by bromination with N-bromosuccinimide in carbon tetrachloride to insure bromination in the allyl position and dehydrohalogenating the resulting bromide with collidine.

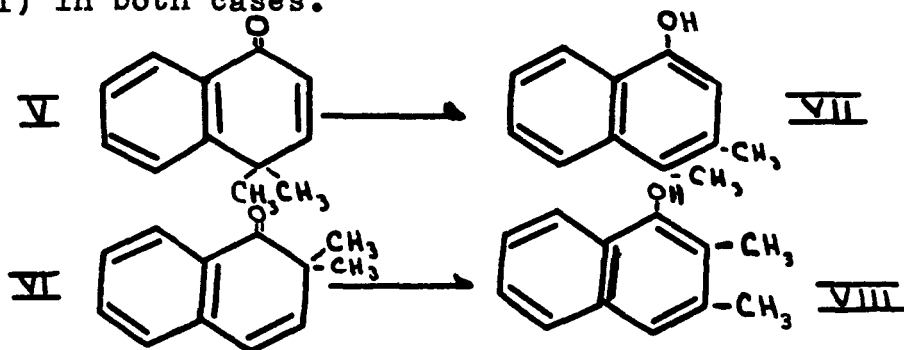
The dienone was hydrogenated in a micro-quantitative hydrogenation apparatus and absorbed 102% of the theoretical amount of hydrogen.

B. Mechanism

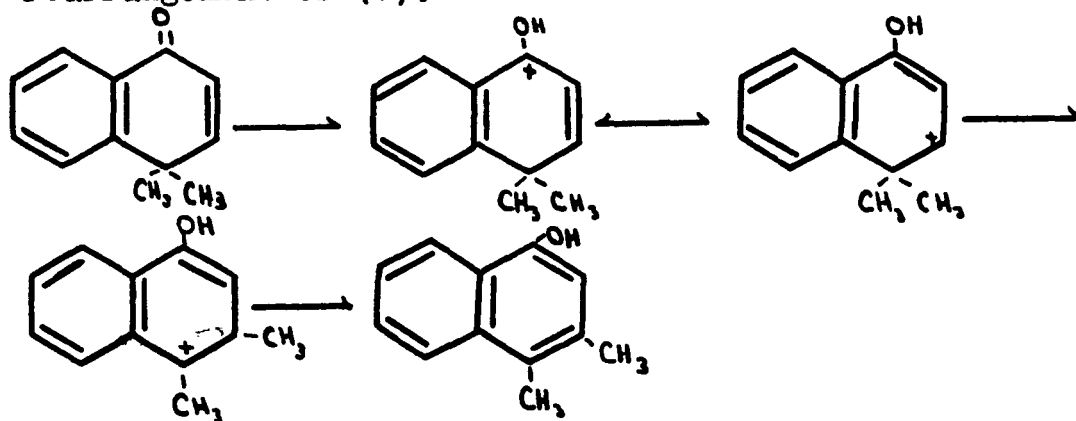
In the cyclohexadienone system, both of the cyclohexadienones (I) and (II) (12, p.21) can be expected to rearrange in the usual manner predicted by Arnold's mechanism (2, p.2322) forming 3,4-dimethylphenol (III) and 2,3-dimethylphenol (IV) respectively.



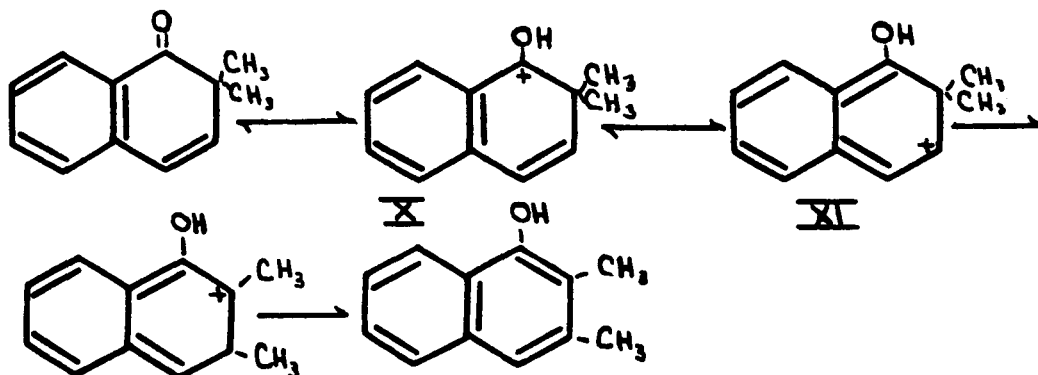
The rearrangement of analogous compounds in the naphthalene series (V) (2, p.2322) and (VI) (13, p.1259) would be expected to produce the corresponding 3,4- and 2,3-dimethylphenols. However, the rearrangement produces only (VII) in both cases.



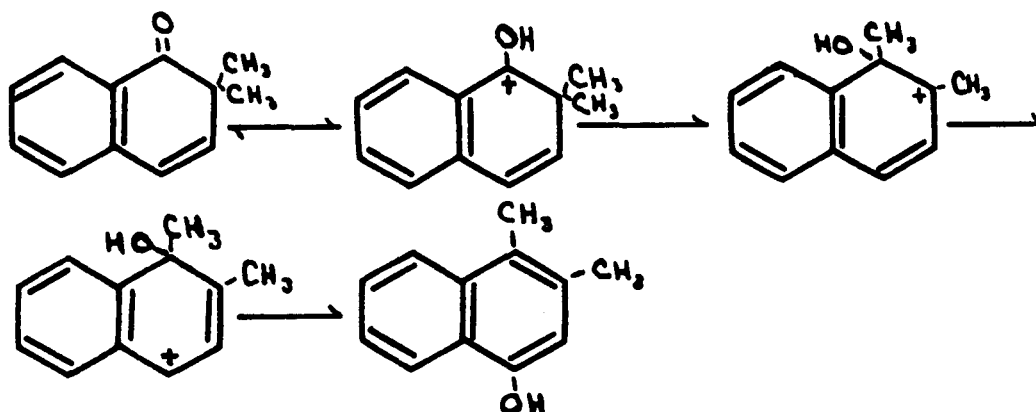
Arnold has proposed the following mechanism for the rearrangement of (V).



When applied to the rearrangement of (VI), the mechanism involved the formation of an ortho quinoid intermediate (XI) which would be less stable than the benzenoid form (X).

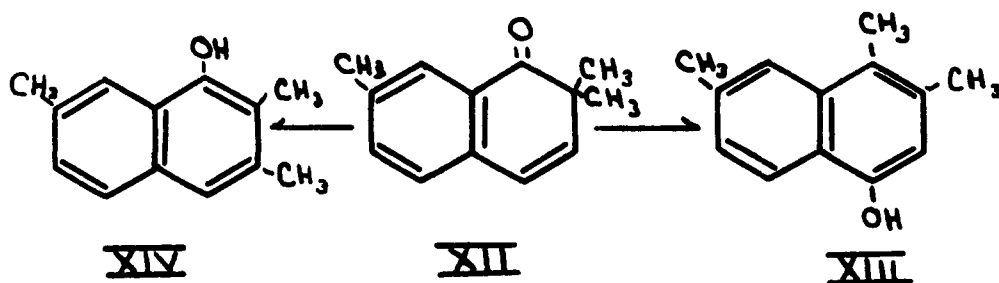


Marvell and Geiszler (13, p.1259) have devised a mechanism following a path of lower energy involving migration of the oxygen function.

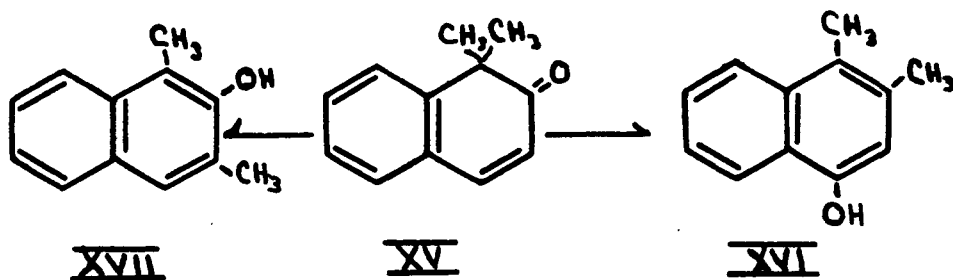


Evidence to support the latter mechanism was brought forth when Marvell and Magoon (12, p.15) rearranged the dienone (XII) and found (XIII) as the only product whereas, had the Arnold mechanism been in effect, the dienone

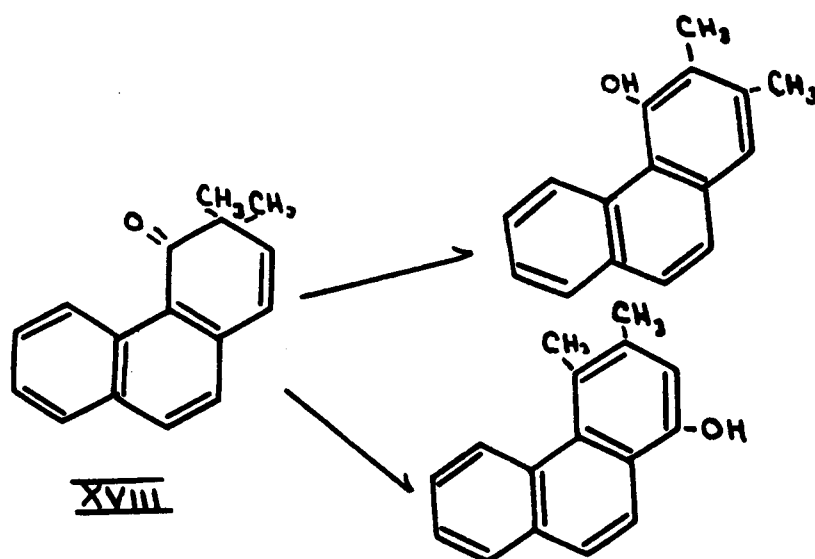
(XIV) would have been the only expected product.



Again Marvell and Stephenson (17, p.19) rearranged the dienone (XV) finding the phenol (XVI) in accordance with the Geiszler mechanism instead of the phenol (XVII) as the Arnold mechanism would predict.



In 4-oxo-3,3-dimethyl -1,2-dihydrophenanthrene (XVIII) the double bond involved in the rearrangement is part of a naphthalene nucleus instead of a benzene nucleus as in the preceding examples. If this compound is rearranged, two products could be expected depending upon which mechanism is followed.



The rearrangement of this phenanthrene will be studied at a later date. This work will be directed to the synthesis of the dienone for the succeeding study.

EXPERIMENTAL

 α,α -Dimethylsuccinic acid

This acid was prepared according to a procedure given by Smith and Horwitz (16, p.3418). It seemed advisable to extract the acid from the salt cake, which was formed in the reaction, by using ether and a Soxhlet extractor. The yield was 216.4 g. (100%) of slightly impure acid melting at 136-143°. The melting point from the literature is 139°.

 α,α -Dimethylsuccinic anhydride

The anhydride was synthesized according to well known means. Best results were obtained if a stirrer was introduced during the refluxing period. The yield was 116.7 g. (87%) of a colorless, somewhat viscous liquid boiling at 125° (50mm).

 β -2(5,6,7,8-tetrahydronaphthoyl), α,α -Dimethylpropionic acid

To a well-stirred mixture of 353.5 g. (2.7 moles) of tetralin and 100 g. (0.75 mole) of anhydrous aluminum chloride was added 47.5 g. (0.38 mole) of α,α -dimethylsuccinic anhydride with cooling to keep the temperature at 15-20°. After addition of the anhydride was complete, the mixture was allowed to stand at room temperature for

one hour, then heated on a steam bath for one hour and poured while still hot onto cracked ice and hydrochloric acid. The excess tetralin was steam distilled from the mixture which was then made basic with sodium bicarbonate, boiled with Norite, filtered, extracted with ether and acidified to a pH of 2 with concentrated hydrochloric acid. The total yield was 52.5 g. (44%) of material melting at 158.5-162°. When pure the acid was found to melt at 164.7-164.9°.

Anal: Calc. for $C_{16}H_{20}O_3$: C, 73.8% ; H, 7.69%

Found: C, 73.8%; H, 7.70%

γ -2-Tetrallyl- α,α -dimethylbutyric acid

Zinc was amalgamated in the usual fashion. There was added 154 cc. of water, 359 cc. of concentrated hydrochloric acid, 51.2 g. of β -2(5,6,7,8-tetrahydronaphthoyl) α,α -dimethylpropionic acid and 25 cc. of glacial acetic acid. The mixture was heated to boiling for 36 hours then poured out into a beaker, allowed to cool and the solid which formed was isolated by filtration. The filtrate was extracted with benzene and the benzene extract washed with 5% sodium carbonate. The solid was added to the sodium carbonate extract and enough 5% sodium carbonate added to dissolve all the acid. The carbonate solution was extracted once with ether and

acidified with hydrochloric acid to precipitate the acid which was filtered and dried before recrystallization from hexane to yield 41.2 g. (87%) of material melting at 110° .

Anal: Calc. for $C_{16}H_{22}O_2$: C, 78.1%; H, 8.94%

Found: C, 78.1% ; H, 9.06%

Neutral equivalent: Calc. for $C_{16}H_{22}O_2$: 246

Found: 251

I.R. maxima at 1207, 1274, 1459, 1477, 1490, 1571, 1620, 1707, 2935 $cm.^{-1}$

Methyl- γ -2-tetraallyl- α,α -dimethyl butyrate

An ethereal solution containing an excess of diazomethane (6, p.165) was added to 20 g. (0.081 mole) of the acid to be esterified and allowed to stand at room temperature until the reaction was complete as evidenced by the ceasing of the evolution of nitrogen.

When the reaction was complete, the excess diazomethane was destroyed using acetic acid, the ether removed by distillation on a steam bath and the ester distilled in vacuo yielding 17 g. (80.3%) of a yellow viscous oil, b.p. 164° (3.6 mm), n_D^{20} 1.5142, d^{20} 1.013.

M_D : Calc. for $C_{17}H_{24}O_2$: 76.58

Found : 77.45

I.R. maxima at 809, 829, 1736, 2917 $cm.^{-1}$

γ (2-Naphthyl) α,α -dimethylbutyric acid

A mixture of 5 g. (0.0216 mole) of methyl- γ -2-tetrallyl- α,α -dimethylbutyrate and 0.1 part by weight of 10% palladium-charcoal catalyst was heated in a carbon dioxide atmosphere to 180-360°. When the reaction was complete as evidenced by the collection of a quantitative volume of hydrogen, the reaction mixture was taken up in a benzene-ligroin mixture and the catalyst removed by filtration. As much as possible of the solvent was removed by distillation and 1.7 g. (0.03 mole) of potassium hydroxide in alcohol was added and the mixture put under reflux for four hours to hydrolyze the ester. The acid was dissolved in sodium carbonate, extracted with ether, and precipitated with hydrochloric acid.

Optimum yields were obtained if dehydrogenation was performed on 5 g. portions. A total of 50 g. of the ester was dehydrogenated yielding 24.6 g. of the dehydrogenated acid (53.4%) melting at 139.5-140°.

Anal: Calc. for $C_{16}H_{18}O_2$: C, 79.3% ; H, 7.44%

Found: C, 79.4% ; H, 7.50%

Neutral equivalent: Calc. for $C_{16}H_{18}O_2$: 242

Found: 244

I.R. maxima at 737, 819, 1205, 1219, 1366, 1378, 1390, 1436, 1471, 2882, 2918 $cm.^{-1}$

3,3-Dimethyl-1,2,3,4-tetrahydrophenanthrene-4-one

In a dry 200 cc. 3-necked flask equipped with a calcium chloride drying tube and thermometer was placed 25 cc. of dry ether containing two drops of pyridine. To the cooled mixture was added 8 cc. (0.1 mole) of purified thionyl chloride (8, p.381) and 13.4 g. (0.055 mole) of γ (2-naphthyl) α , α -dimethyl butyric acid. The flask was allowed to stand at room temperature with occasional swirling for a half hour. A piece of porous plate was introduced and the mixture warmed ten minutes on the steam bath. The excess ether and thionyl chloride was removed by gradually applying full suction from an aspirator pump, adding 5 cc. of dry benzene and again reducing the pressure. The process was repeated and the last traces of volatile material removed by reducing the pressure on a vacuum pump for five minutes. At no time should the temperature be allowed to exceed 40°.

The residual acid chloride was taken up in 60 cc. of dry benzene and transferred to a dropping funnel. Fifteen cc. of stannic chloride in 15 cc. of dry, thiophene-free benzene was added and the mixture chilled in an ice-salt bath. A mercury sealed stirrer was attached and the benzene solution of the acid chloride was dropped in at such a rate that the temperature of the mixture did not exceed 5°. When addition was complete, the mixture

was swirled for 10-15 minutes at 5° and hydrolyzed by pouring onto 50 cc. of concentrated hydrochloric acid in ice. Ether was added to dissolve the stannic chloride complex and the organic layer separated and washed several times with 5% hydrochloric acid, water, 5% sodium hydroxide, and again with water and dried over anhydrous magnesium sulfate. The ketone was distilled under reduced pressure after removal of the solvent, yielding 11.16 g. (91%) of a yellow viscous oil, b.p. 138-141° (0.5 mm), d^{23}_4 1.0706, $n^{26.8}_D$ 1.6084.

Anal: Calc. for $C_{16}H_{16}O$: C, 85.52% ; H, 7.14%

Found: C, 85.56% ; H, 7.22%

M_D : Calc. for $C_{16}H_{16}O$: 69.38

Found: 72.47

m.p. of picrate : 145.5°

I.R. maxima at 754, 809, 830, 863, 960, 979, 998, 1097, 1156, 1206, 1217, 1330, 1362, 1402, 1464, 1621, 1707, 2970 $cm.^{-1}$

U.V. maxima at 252 and 274 $m\mu$

3,3-Dimethyl-3,4-dihydrophenanthrene-4-one (4-oxo-3,3-dimethyl-3,4-dihydrophenanthrene)

In 45 cc. of dry carbon tetrachloride was dissolved 1.82 g. (0.008 mole) of 3,3-dimethyl-1,2,3,4-tetrahydrophenanthrene-4-one. To this solution was added

1.45 g. (0.008 mole) of N-bromosuccinimide which had been held over phosphorous pentoxide for eight hours at 0.5 mm. and was mixed with 10 mole percent (.197 g.) of benzoyl peroxide. The mixture was brought to reflux until the reaction was complete as evidenced by a disappearance of the color of the ketone and the appearance of the insoluble imide which floated. The imide was filtered, washed with solvent and the solvent was removed at reduced pressure.

To the bromide intermediate was added 2.71 cc. (0.024 mole) of collidine and the mixture was heated for half an hour in an oil bath at 135-140°. The reaction mixture was shaken with several portions of ether and the collidine hydrobromide removed by filtration. The filtrate was washed with dilute hydrochloric acid, water, 5% sodium hydroxide and again with water. The ether solution was dried over anhydrous magnesium sulfate, the ether removed via distillation and the residue remaining was distilled yielding 1.26 g. (70%) of orange viscous oil, b.p. 170-185° (2.5 mm.), $n_D^{20.5}$ 1.6474, d^{20} 1.1370.

Anal: Calc. for $C_{16}H_{14}O$: C, 86.50% ; H, 6.36%

Found: C, 83.3% ; H, 6.18%

M_D : Calc. for $C_{16}H_{14}O$: 61.89

Found : 71.07

m.p. of picrate : 158.5-159.5°

I.R. maxima at 742, 787, 837, 857, 957, 984, 1006,
1008, 1088, 1150, 1169, 1187, 1220, 1274, 1330, 1427,
1593, 1665, 2950 cm.^{-1}

U.V. maxima at 252, 333, and 370 $\text{m}\mu$

SUMMARY

The existence of an energy barrier to the rearrangement of alpha-blocked dienones according to expected paths was discovered when attempts to rearrange these dienones led to unexpected products. An important factor in this energy barrier is the stability of the double bond involved in the rearrangement. Information has been obtained about the stability of double bonds of olefin and benzene character to rupture; however, no work has been undertaken to determine the stability of a double bond of naphthalene character. As a step in this direction the synthesis of a molecule incorporating a double bond of naphthalene character into such a position that it would be involved in the rearrangement was undertaken. A suitable molecule having this requirement was decided to be 4-oxo-3,3-dimethyl-3,4-dihydrophenanthrene.

The synthesis of this molecule has been performed, care being taken during the synthesis to eliminate the possibility of isomers. Molar refractivity data, carbon hydrogen analysis, ultra-violet and infra-red data, neutral equivalents, and indices of refraction are supplied as proof of structure.

BIBLIOGRAPHY

1. Anwers, K. Uber die Einwirkung von Chloroform und Alkali auf *as. o*-Xylenol. *Berichte der Deutschen Chemischen Gessellschaft* 32:3598-3599. 1899.
2. Arnold, R. T., J. S. Buckley and J. Richter. Dienone-phenol rearrangement. *Journal of the American Chemical Society* 69:2322-2325. 1947.
3. Bachmann, W. E., et al. *Organic reactions*. Vol. 2. New York, Wiley, 1944. 461 p.
4. Bellamy, L. J. *The infra-red spectra of complex molecules*. New York, Wiley, 1954. 321 p.
5. Benedikt, R. Uber Bromoxylderivative des Benzols. *Annalen der Chemie, Justus Liebig's* 199:127-128. 1879.
6. Blatt, A. H. (ed.). *Organic synthesis*. Rev. ed. Vol. 2. New York, Wiley, 1943. 654 p.
7. Clemo, G. R., R. D. Haworth and E. Walton. The constitution of santoin. II. The synthesis of racemic desmotroposantonin. *Journal of the Chemical Society*, p. 1110-1115, 1930.
8. Fieser, Louis F. *Experiments in organic chemistry*. 2d ed. New York, D.C. Heath, 1941. 381 p.
9. Geiszler, A. O. The rearrangement of α,α -disubstituted cyclic dienones. Ph. D. thesis. Corvallis, Oregon State College, 1955. 37 numb. leaves.
10. Inhoffen, H. H. Ubergang von Steinen in aromatische Verbindungen. *Angewandte Chemie* 53:471-475. 1940.
11. Krollpfeiffer, F. and W. Shafer. Uber Ringschlüsse von γ -aryl-n-buttersäuren zu Derivaten des 1-keto-tetrahydro-naphthalins. *Berichte der Deutschen Chemische Gessellschaft* 56:620-632. 1923.
12. Magoon, Eugene F. Possible paths for the alpha-blocked dienone-phenol rearrangement. Ph. D. thesis. Corvallis, Oregon State College, 1955. 37 numb. leaves.

13. Marvell, E. N. and A. O. Geiszler. An unusual dienone-phenol rearrangement. *Journal of the American Chemical Society* 74:1259-1263. 1952.
14. Newman, M. S. and H. V. Zahm. The catalytic dehydrogenation of 2-substituted-5,6,7,8-tetrahydronaphthalene derivatives. *Journal of the American Chemical Society* 65:1097-1101. 1943.
15. Sengupta, S. C. Dehydrogenation. II. *Journal für Praktische Chemie* 152:9-19. 1939.
16. Smith, P. A. S. and J. Horwitz. Synthesis for unsymmetrically substituted succinic acid. *Journal of the American Chemical Society* 71:3418-3419. 1949.
17. Stephenson, John L. Rearrangement of 1,1-dimethyl 2-oxo-1,2-dihydronaphthalene. Master's thesis. Corvallis, Oregon State College, 1954. 24 numb. leaves.
18. Weiss, R. and J. Ebert. Transformation of dialkylidenecyclohexanones into the isomeric dialkylphenols (I) dibenzalicyclohexanone. *Monatshefte für Chemie und Verwandte teile anderer Wissenschaften* 65:399. 1935.
19. Werner, R. L., W. Kennard, and D. Rayson. An infra-red spectroscopic study of naphthalene substitution. *Australian Journal of Chemistry* 8:346. 1955.
20. Weygand, C. *Organic reactions*. New York, Interscience Publishers, 1945. 534 p.
21. Wilds, A. L. and C. Djerassi. The preparation and partial aromatization of 1,4-cholestadienone-3 by the dienone-phenol rearrangement. *Journal of the American Chemical Society* 68:1712-1715. 1946.
22. Woodward, R. B. and Tara Sigh. Synthesis and rearrangement of cyclohexadienones. *Journal of the American Chemical Society* 72:494-500. 1950.