

A STUDY OF THE ACID CATALYZED REARRANGEMENT  
OF 4-OXO-3,3-DIMETHYL-3,4-DIHYDROPHENANTHRENE

by

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INTRODUCTION

Six-membered cyclic ketones containing two double bonds (dienones) either exocyclic or endocyclic rearrange under acid catalysis to form phenolic derivatives by migration of certain attached alkyl groups and subsequent aromatization of the ring. Many examples of this rearrangement appear in the literature and the name dienone-phenol was first applied to it by Wilds and Djerassi in 1946 (32, p.1712). It is interesting to note that there is little or no evidence in the literature concerning the susceptibility of the reaction to steric hindrance.

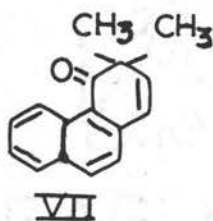
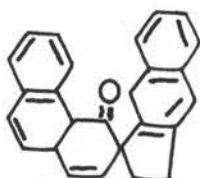
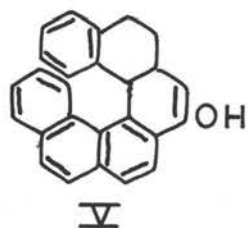
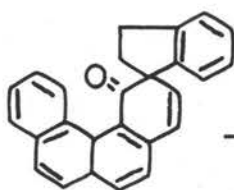
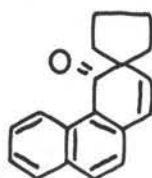
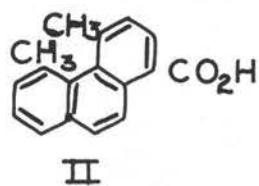
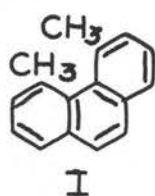
The dienone-phenol rearrangement has found wide application as a synthetic tool. Aside from the obvious use for the synthesis of 3,4-dialkylnaphthols which proceed in good yields, much valuable use of the rearrangement has been made in the synthesis of steroidal materials. These possibilities could be appreciably

broadened if the reaction were found to be reasonably insensitive to steric factors.

In 1940 it was predicted (25, p.450) that 4,5-dimethylphenanthrene (I) should be optically active because of the methyl groups in the hindered positions. Later work with the related acid (II) confirmed this prediction and X-ray analysis revealed that optical activity in these hindered compounds can arise from both bending of the alkyl groups out of the plane of the ring or by bending of the ring itself (23, p.4765).

Newman and co-workers investigating optically active aromatic polycyclic compounds have prepared the optically active hexahelicene (III) (23, p.4765). The dienone-phenol rearrangement could be useful not only for the synthesis of similar hindered aromatic compounds such as (IV), (V) and (VI) assuming no steric limitations but could also make possible the study of the absolute configuration of such hindered aromatic rings.

It is, therefore, desirable to study further some molecules so constructed as to permit assessment of the influence of steric effects on the oxygen migration mechanism. The dienone 4-oxo-3,3-dimethyl-3,4-dihydro-phenanthrene (VII) supplies the simplest case for such a study.



## HISTORICAL

Although numerous examples of the dienone-phenol rearrangement are to be found in the literature, the early work (prior to 1952) was adequately surveyed by Geiszler (16, p.4-11), so that only the work since that time need be covered here. It should be noted that the dienone-phenol rearrangement is particularly useful as a structural diagnostic weapon and recently as a synthetically useful process.

A variety of routes are available for the synthesis of dienones. Winstein (33, p.756) has synthesized dienones of the spiran type such as (I) and (II) by means of  $Ar_1$ -participation from the corresponding para-substituted phenoxide. Although the dienone (II) was of transitory existence, its presence could be detected spectrophotometrically.

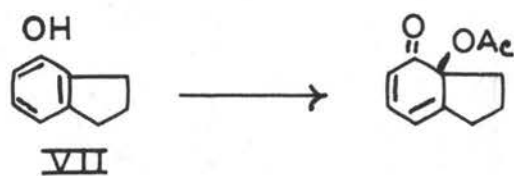
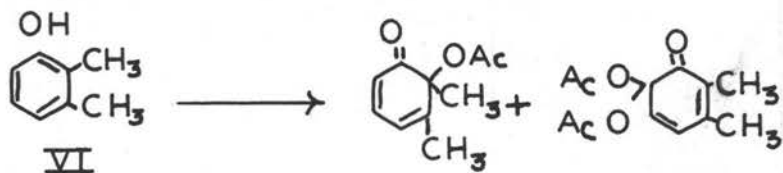
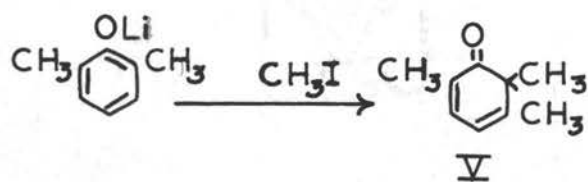
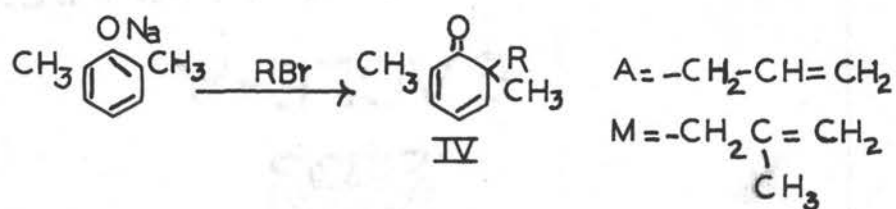
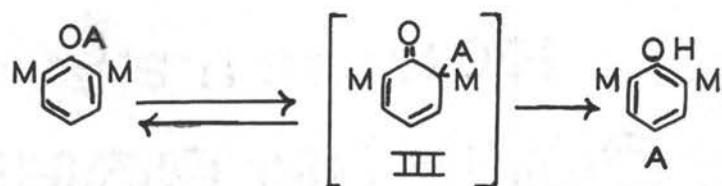
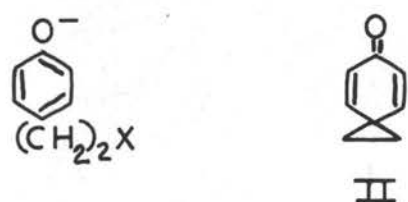
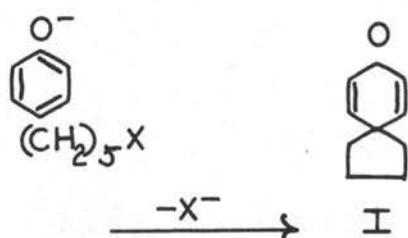
Curtin has postulated the formation of a dienone intermediate (III) during the para-Claisen rearrangement of phenyl ethers (11, p.2611). In the process of proving his postulate, he has developed a method of synthesis for dienones based on a report by Claisen (20, p.210) which suggested that the sodium salts of phenols undergo

ortho-alkylation. Utilizing this procedure, he has prepared dienones of type (IV) by reaction of an allyl or benzyl bromide with the sodium salt of 2,6-dimethylphenol (9, p.3156). Using the lithium salt of the phenol, dienones such as (V) could be prepared since the reaction is no longer restricted to the use of allyl or benzyl halides (7, p.4339 and 10, p.6016). The latter procedure has been suggested by Curtin as a method of obtaining pure dienones since the dienone produced dimerizes to a solid which can be purified by crystallization and the dienone recovered by vacuum distillation.

Wessely has prepared dienones of the quinol type by oxidation of phenols with lead tetraacetate. A few representative examples are illustrated by the oxidation of the phenols (VI), (VII) and (VIII) to produce the quinol mono- and diacetates (30, p.69). Work has been done substituting acetyl and benzoyl peroxides for lead tetraacetate (31, p.425).

Alder has carried out the synthesis of dienones having exocyclic double bonds by reacting cyclopentene-3-one-1 with benzaldehyde to produce the dienone (IX) and (X) (2, p.1732) and has also prepared the cyclohexadienone (XI) by pyrolysis of fulvene oxide (3, p.1709). Newman and others have prepared cyclohexadienones having



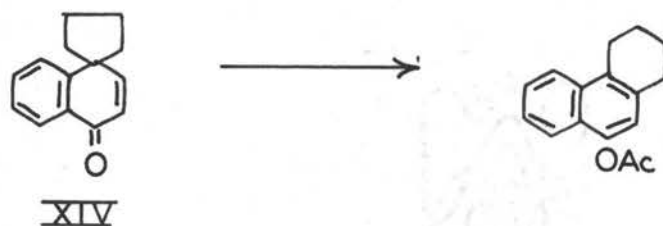
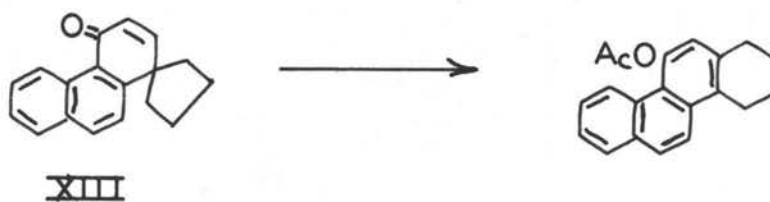
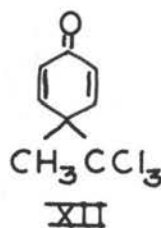
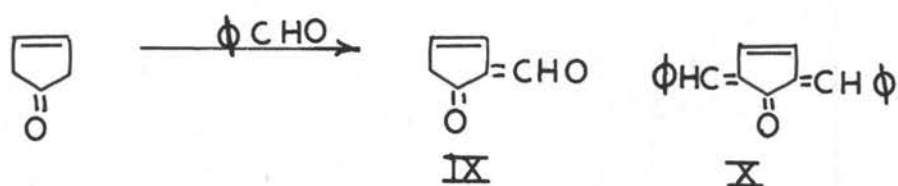
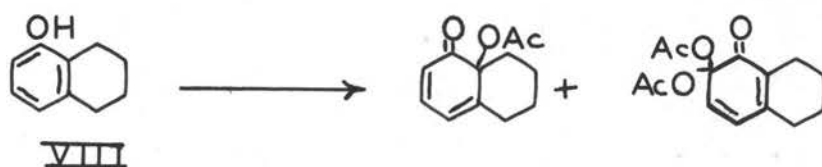


a trichloromethyl group such as (XII) by reaction of alkyl substituted phenols with carbon tetrachloride in the presence of aluminum chloride (24, p.978).

Examples of the usefulness of the dienone-phenol rearrangement in synthesis are supplied by Fenton et al., and also by Burnell and Taylor who have used the rearrangement for the synthesis of six- and seven-membered rings by the expansion of suitable five- and six-membered rings. Examples of six-membered ring synthesis are given by Fenton et al. (14, p.5983) and by Burnell and Taylor (8, p.3486) who produced the desired polycyclic compound by rearrangement of (XIII) and (XIV) respectively. Seven-membered ring synthesis is illustrated by the same authors in the rearrangement of the dienones (XV) and (XVI).

Wilds and Djerassi synthesized the hormone  $\alpha$ -estradiol using a procedure which employed the dienone-phenol rearrangement as one of the key steps in the synthesis (32, p.2125). Other workers likewise have made valuable use of this rearrangement in the synthesis of steroidal materials by partial aromatization of suitable sterol derivatives (35, p.494).

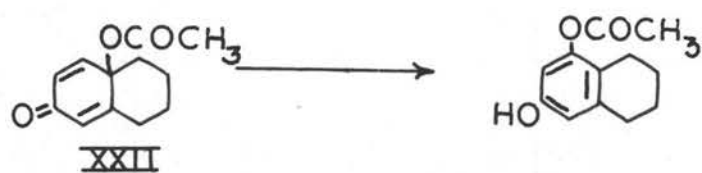
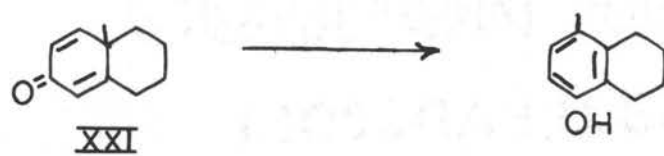
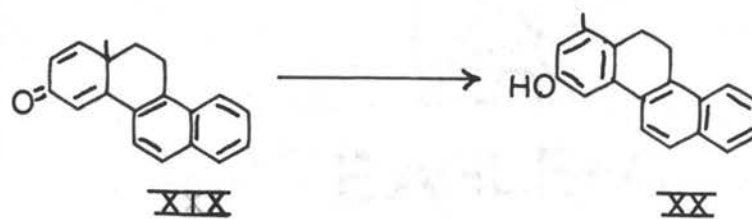
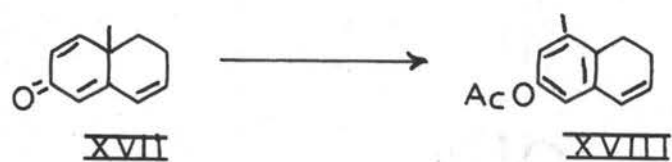
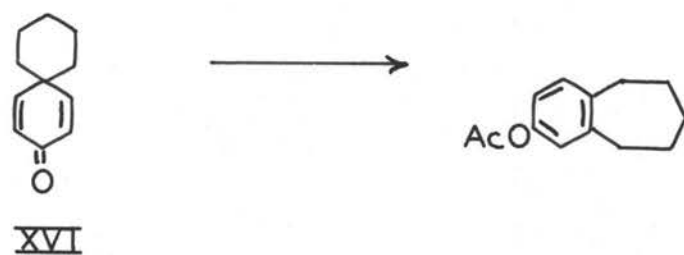
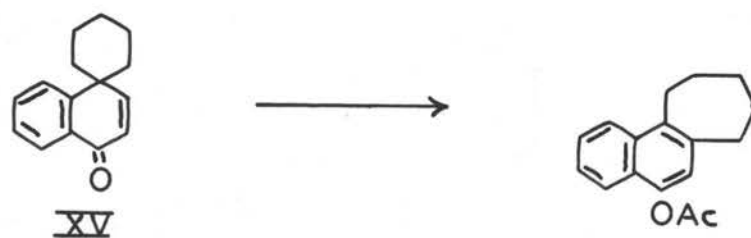
As a structural analysis device, the dienone-phenol rearrangement has also found application. It was learned that introduction of a double bond in a dienone



to form the corresponding trienone (XVII) causes migration of the methyl group during rearrangement rather than the secondary alkyl substituent forming (XVIII). Djerassi and Rosenkranz (27, p.896) gave added evidence for preferential methyl group migration in trienones.

By analogy the rearrangement product of ketone (XIX) can be assigned the structure (XX). That this assignment is correct has been proven by synthesis. Likewise the rearrangement of the dienone (XXI) to the 1,4-disubstituted tetralin and its application to the rearrangement of more complex structurally related molecules has made it possible to assign structures to the rearrangement products of other complex ketones by the principle of analogy. Goodwin and Witkop (17, p.179), in a synthesis having application in biological oxidation mechanisms, have used the dienone-phenol rearrangement of (XXII) to produce the corresponding phenol.

Woodward (34, p.33) has shown by an elegant proof that the dienone (XXIII) rearranges to the phenol (XXIV) via a spiran intermediate. This could occur only if the more highly substituted carbon atom migrates in preference to the least substituted one. Recently, Bloom (6, p.6280) has provided the first detailed experimental evidence for the existence of the spiran intermediate in

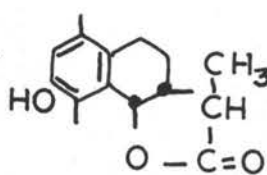
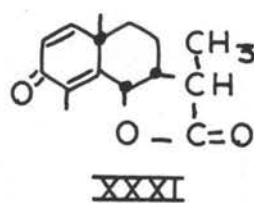
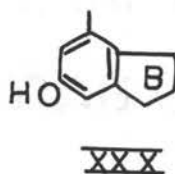
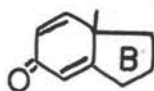
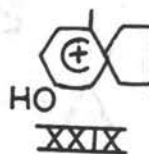
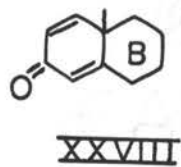
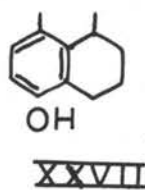
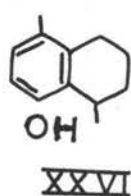
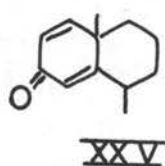
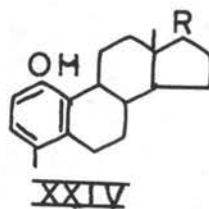
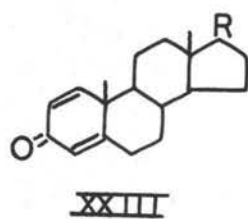


the dienone-phenol rearrangement as well as verifying Woodward's assignment of the correct structure (XXIV) by demonstrating that the dienone (XXV) rearranges to (XXVI) and not (XXVII).

Bloom has also demonstrated that ring size influences the course of the dienone-phenol rearrangement (5, p.4728). The rearrangement of the ketone (XXVIII) has been shown to proceed by the spiran intermediate (XXIX). Bloom has shown that if the ring B in the ketone (XXVIII) is small, the strain occurring in the spiran intermediate is sufficient to prevent the rearrangement from taking this course and the angular methyl group migrates instead forming the phenol (XXX).

Abe, et al. (1, p.1416) have used the dienone-phenol rearrangement in their studies of the optically active and optically inactive members of the santonin series. One example, the rearrangement of racemic santonin D (XXXI) will suffice. The black dots employed show that the attached group lies above the plane of the molecule.

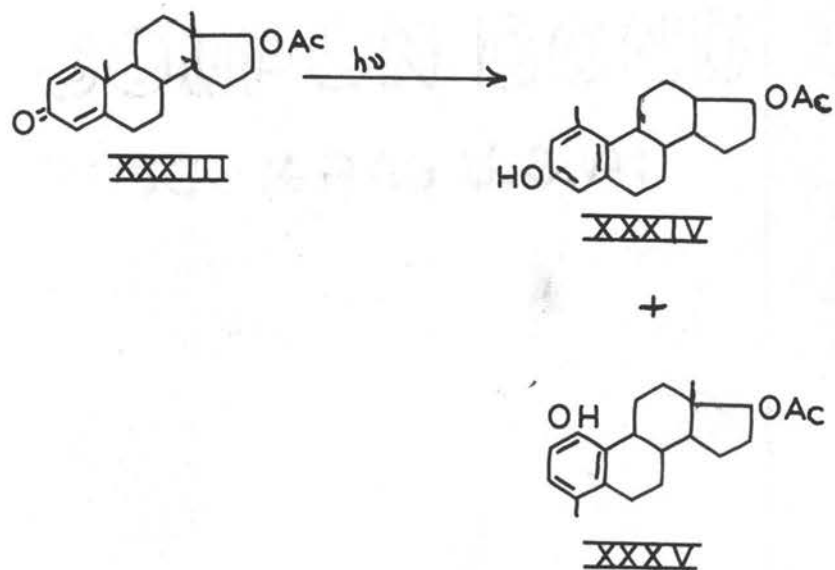
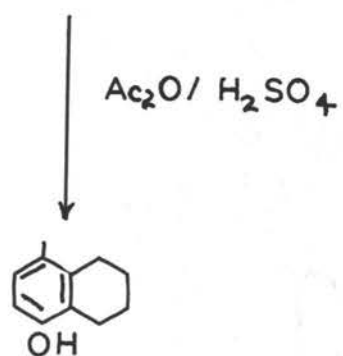
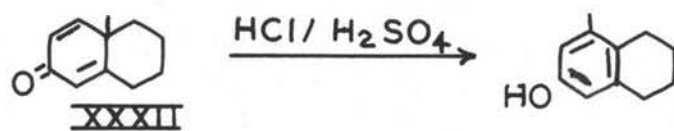
There are a variety of acidic media to choose from in rearranging dienones to phenols. Drieding, et al. (12, p.3159) noted that the dienone (XXXII) produced different rearrangement products depending upon whether



the rearrangement media was a mixture of hydrochloric and sulfuric acids or whether it was a mixture of acetic anhydride and sulfuric acid.

Although Woodward and Singh originally formulated the dienone-phenol rearrangement as an acid catalyzed reaction (35, p.494), it has been recently shown that it is possible to promote the dienone-phenol rearrangement by long periods of irradiation with ultraviolet light. Dutler, et al. (13, p.494) have rearranged the dienone (XXXIII) by long term irradiation with ultraviolet light to a mixture of isomers (XXXIV) and (XXXV). Shorter irradiation periods produced isomeric tetracyclic and pentacyclic ketones which are probably intermediate products to the phenols.





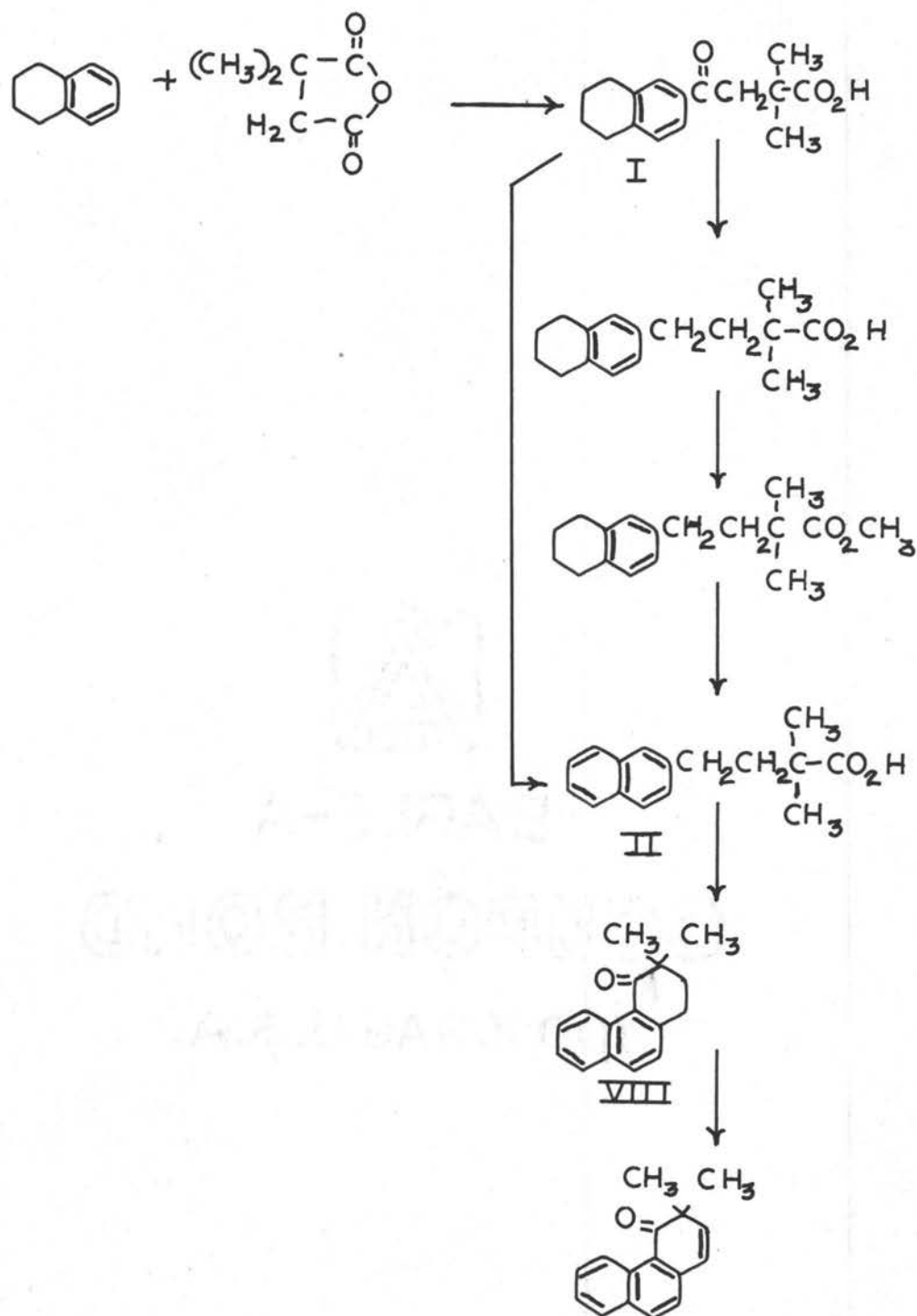
## DISCUSSION

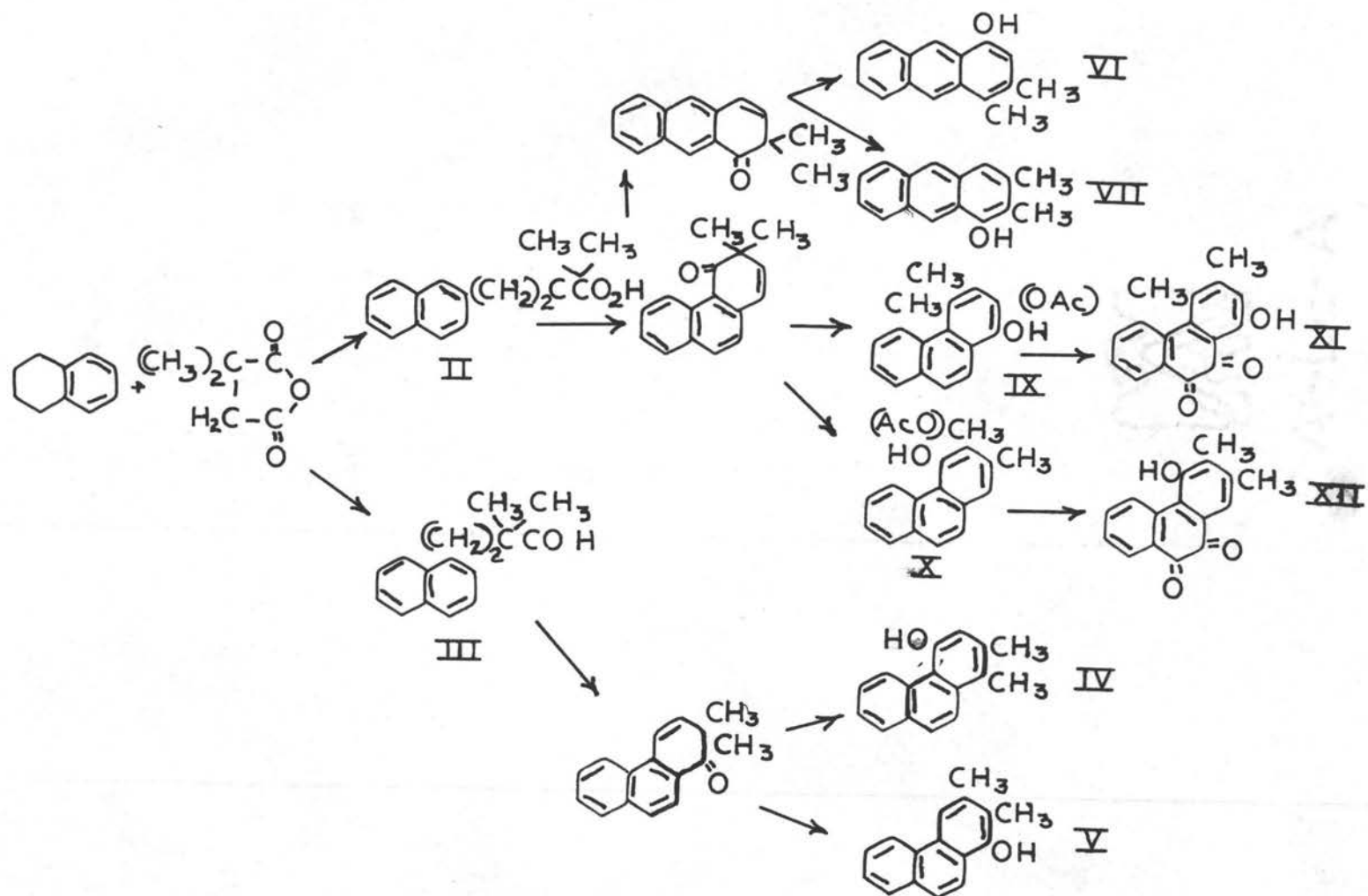
### I. Synthetic Procedure

The details of the synthesis of 4-oxo-3,3-dimethyl-3,4-dihydrophenanthrene (page 16) have been discussed previously (19, p.19) and it is the intent here to deal with the rearrangement of 4-oxo-3,3-dimethyl-3,4-dihydrophenanthrene. One modification resulting in decreasing the number of steps in the synthesis was introduced. It has been shown that a carbon-oxygen double bond adjacent to an aromatic nucleus is reduced to a methylene group during the dehydrogenation (26, p.1099). This made it possible to go directly to the acid (II) from the methyl ester of acid (I).

The synthetic scheme employed (page 17) could conceivably lead to three products, two dihydrophenanthrenes and a dihydroanthracene. Since each could rearrange via either of the two available paths six possible products must be considered after dienone-phenol rearrangement.

Thus it can be seen that it is most important to prove the identity of the starting material before proceeding with the rearrangement of the dienone proper.





Krollpfeiffer and Schäfer report that tetralin produces almost exclusive beta substitution but some alpha substitution does occur (21, p.620). However, both acids (II) and (III) have been synthesized by Sengupta (28, p.9). and the structures proven by oxidation to either alpha- or beta-naphthoic acid. According to Sengupta, the acid (II) melts at 133-135° and (III) at 99-101°. The acid obtained in this work by condensation of tetralin with dimethylsuccinic anhydride melted at 139.5-140° leaving no doubt of its being a very pure sample of the desired acid (II) thus eliminating the isomers (IV) and (V).

In Sengupta's method of synthesis of the acids it is possible to obtain a difficult to separate mixture of the alpha- and beta-naphthoic acids. This probably explains why his acids melt over a wider range than do the acids synthesized in this work.

The anthracene isomers (VI) and (VII) can be eliminated also on the basis of first, the infrared spectra, and second on the basis of work done on the synthesis of a number of alkylphenanthrenes by Haworth. Werner, Kennard, and Rayson (29, p.346) have reported the infrared spectra of a number of substituted naphthalenes among them being the 1,2- and the 2,3- disubstituted naphthalenes. Since the cyclized ketone will be in

essence either a 1,2- or a 2,3-disubstituted naphthalene depending upon whether cyclization is angular or linear, comparison of spectra should provide evidence for the structure of the tricyclic ketone.

The following table shows the infrared absorption maxima for the disubstituted naphthalenes as listed by Werner et al. and the cyclized ketone. The regions of absorption for distinguishing the two isomeric naphthalenes lie in the  $740\text{--}770\text{ cm}^{-1}$  region and the  $800\text{--}840\text{ cm}^{-1}$  region. Of these, according to the above mentioned authors, the former is the more reliable.

<u>2,3-Disubstituted naphthalenes</u>	<u>1,2-Disubstituted naphthalenes</u>	<u>Tricyclic ketone</u>
748 $\text{cm}^{-1}$	724 $\text{cm}^{-1}$	721 $\text{cm}^{-1}$
	743 $\text{cm}^{-1}$	750 $\text{cm}^{-1}$
	786 $\text{cm}^{-1}$	780 $\text{cm}^{-1}$
	808 $\text{cm}^{-1}$	808 $\text{cm}^{-1}$
	865 $\text{cm}^{-1}$	865 $\text{cm}^{-1}$

It can be seen quite readily that the infrared spectra give very convincing evidence for angular cyclization.

Haworth (18, p.2248) obtained a number of alkyl substituted phenanthrenes by cyclization of the corresponding naphthoylbutyric acids. This parallels our route of synthesis in going from (II) to (VIII). Of eighteen cyclizations of naphthoylbutyric acids, seventeen produced the angular-cyclized product. In none of these seventeen cases was Haworth able to obtain a linear

cyclized product. In the one case where linear cyclization occurred, the cyclized product was obtained in 15% yield and here steric factors which inhibit the formation of the angular isomer were present.

It seems quite apparent then that the tricyclic ketone is indeed 4-oxo-3,3-dimethyl-1,2,3,4-tetrahydrophenanthrene and that attention may then be directed to the introduction of the double bond in the 1,2-position. The bromide of 4-oxo-3,3-dimethyl-1,2,3,4-tetrahydrophenanthrene was prepared by bromination using N-bromosuccinimide. The bromide produced was isolated by distillation under a high vacuum but no attempt to obtain a pure sample was made. Dehydrobromination was accomplished by heating the bromide intermediate in  $\gamma$ -collidine at 135-140° for 30 minutes. An infrared spectrum of this dienone showed the expected 1660  $\text{cm}^{-1}$  carbonyl frequency. In order to prove that no skeletal rearrangement occurred during introduction of the double bond, a sample of the unsaturated ketone was submitted to quantitative hydrogenation. It took up 107% of the theoretical amount of hydrogen and gave 4-oxo-3,3-dimethyl-1,2,3,4-tetrahydrophenanthrene as proven by a comparison of the infrared spectra with that of the original tetrahydroketophenanthrene. The dienone was chromatographed over alumina before use.

The dienone was extremely difficult to purify for analytical purposes, the major contaminant being probably bromoketone. A distilled sample of the dienone was placed on a chromatastrip. Development of the strip, and examination under ultraviolet light revealed a number of fluorescent areas corresponding to impurities in the dienone. Careful chromatography over silicic acid and over alumina followed by careful drying under vacuum yielded a sample of the dienone which still produced fluorescent areas on the chromaplate under ultraviolet light and failed to give an exact analysis.

## II. Rearrangement

The attempts to rearrange the dienone under conditions commonly employed (acetic anhydride and catalytic amounts of sulfuric acid) gave after 37 hours and after 3 weeks only polymeric materials and starting material. Since it seemed probable that the catalyst under these conditions is the acetylum ion, the steric hindrance about the oxygen function might inhibit attack at that point. To minimize this factor, rearrangement was attempted in glacial acetic acid using concentrated hydrochloric acid as a catalyst but without success.



The dienone was then subjected to rearrangement under forced conditions using acetic anhydride in which was dissolved a large excess of concentrated sulfuric acid. The mixture was allowed to stand two weeks. Though this produced only a red oil which could not be induced to crystallize, it was definitely encouraging because the oil showed a peak in the infrared at  $1759\text{ cm}^{-1}$ . Examination of the oil by the chromatastrip technique indicated the presence of several compounds, and suggested the feasibility of separating the components on a silicic acid column. The mixture was chromatographed on silicic acid and the eluates examined at intervals in the  $1500\text{-}1800\text{ cm}^{-1}$  region. Two substances were obtained. The first, having carbonyl absorption at  $1683\text{ cm}^{-1}$  was a yellow crystalline material melting at  $93.5\text{-}94.0^\circ$  which was identified as 1-bromo-4-oxo-3,3-dimethyl-1,2,3,4-tetrahydrophenanthrene. The second material having an acetate band at  $1759\text{ cm}^{-1}$ , melted at  $130\text{-}132^\circ$ . No other acetates were found.

### III. Identification of the Rearrangement Product

There remains the problem of ascertaining whether the acetate isolated has the structure (IX) or (X). This problem was complexed by the isolation only  $354\text{ mg.}$  of

material and the difficulties attendant upon providing a larger sample.

A portion of the acetate was hydrolyzed by the procedure of L. Fieser (15, p.2468) to a phenol which melted at 178-179° d. An infrared spectrum showed the expected hydroxyl maxima at about 3370  $\text{cm}^{-1}$ . A second portion of the acetate was oxidized to an acetoxy-phenanthraquinone and hydrolyzed to the corresponding hydroxyquinone. Unfortunately the overall yield was too low to provide material for an analytical sample.

It should prove possible to judge whether (IX) or (X) is obtained on the basis of the variance in their hydrogen bonding behavior and the quinones derived from them. If hydrogen bonding involves the H of an O-H group, the characteristic O-H stretching frequency of this group in the infrared is lowered and the stronger the hydrogen bonding is, the greater the lowering of the frequency. This lowering of the frequency will occur whether the hydrogen bonding is intermolecular or intramolecular and in order to distinguish between inter- and intramolecular hydrogen bonding a series of spectra at different concentrations must be obtained (4, p.215).

If the hydrogen bonding in the molecule is intermolecular, continued dilution of a concentrated solution of the material in question will cause the bonded O-H

frequency to disappear because dilution destroys the hydrogen bonding. On the other hand, however, if the type of hydrogen bonding occurring is intramolecular, no amount of dilution will cause the bonded O-H frequency to disappear.

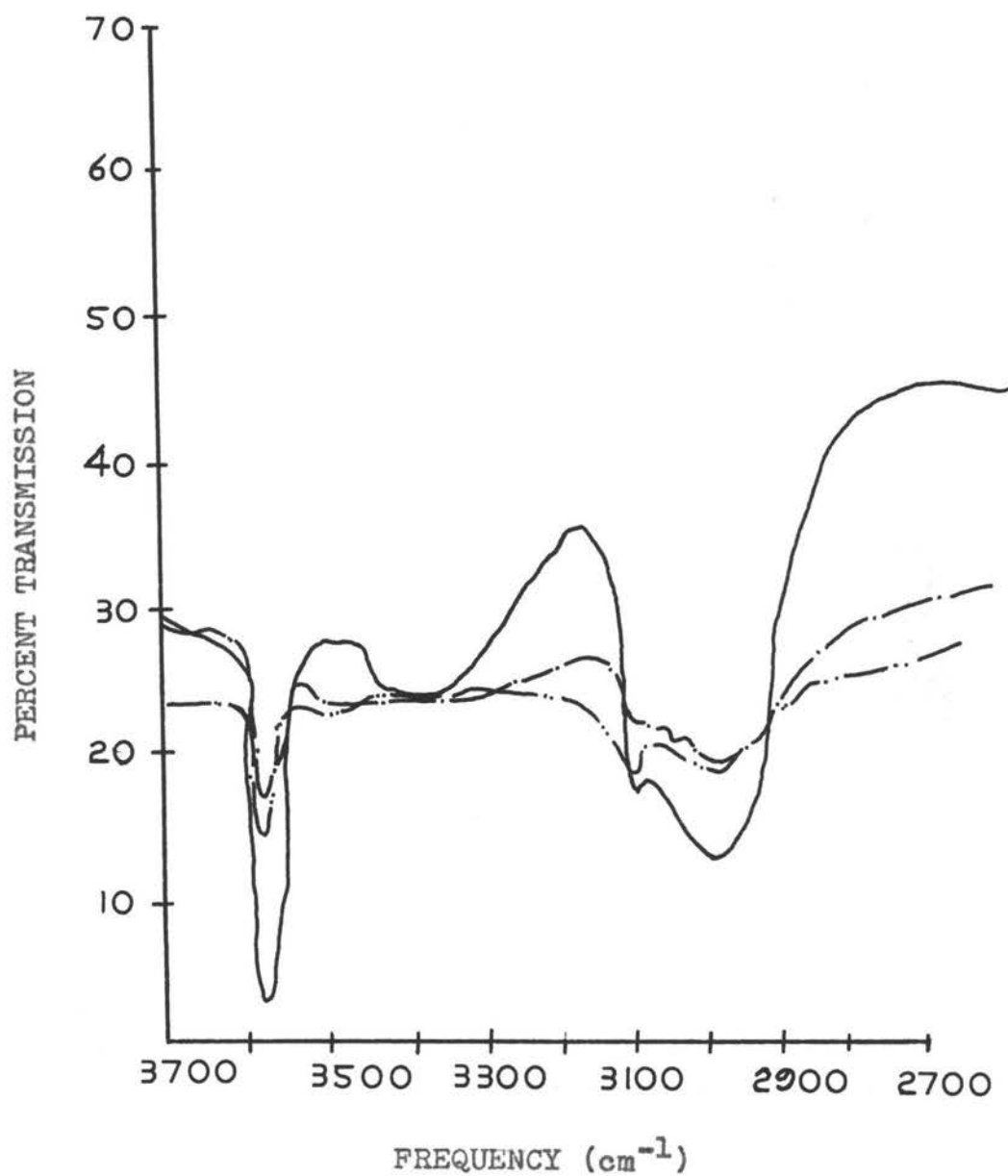
If either of the phenols (IX) or (X) was obtained, intermolecular hydrogen bonding would be expected to occur and dilution spectra as described above would show a disappearance of the bonded O-H frequency although, perhaps, slightly more rapidly in the case of the hindered phenol (X). However with the corresponding quinones (XI) and (XII), only in the case of (XI) can intramolecular hydrogen bonding occur. Thus an examination of the O-H stretching region for the hydroxyquinone should show significant differences upon dilution and permit unequivocal identification of the product.

On the following pages are shown the dilution spectra of the phenol and the quinone. It can be seen by the disappearance of the  $3374\text{ cm}^{-1}$  peak and also the appearance of the sharp peak at  $3600\text{ cm}^{-1}$  in the case of the phenol and the persistence of the  $3440\text{ cm}^{-1}$  peak in the case of the quinone that the existence of an intramolecular hydrogen bond is shown. This could only be the case if 3,4-dimethyl-1-hydroxyphenanthrene (IX) had been

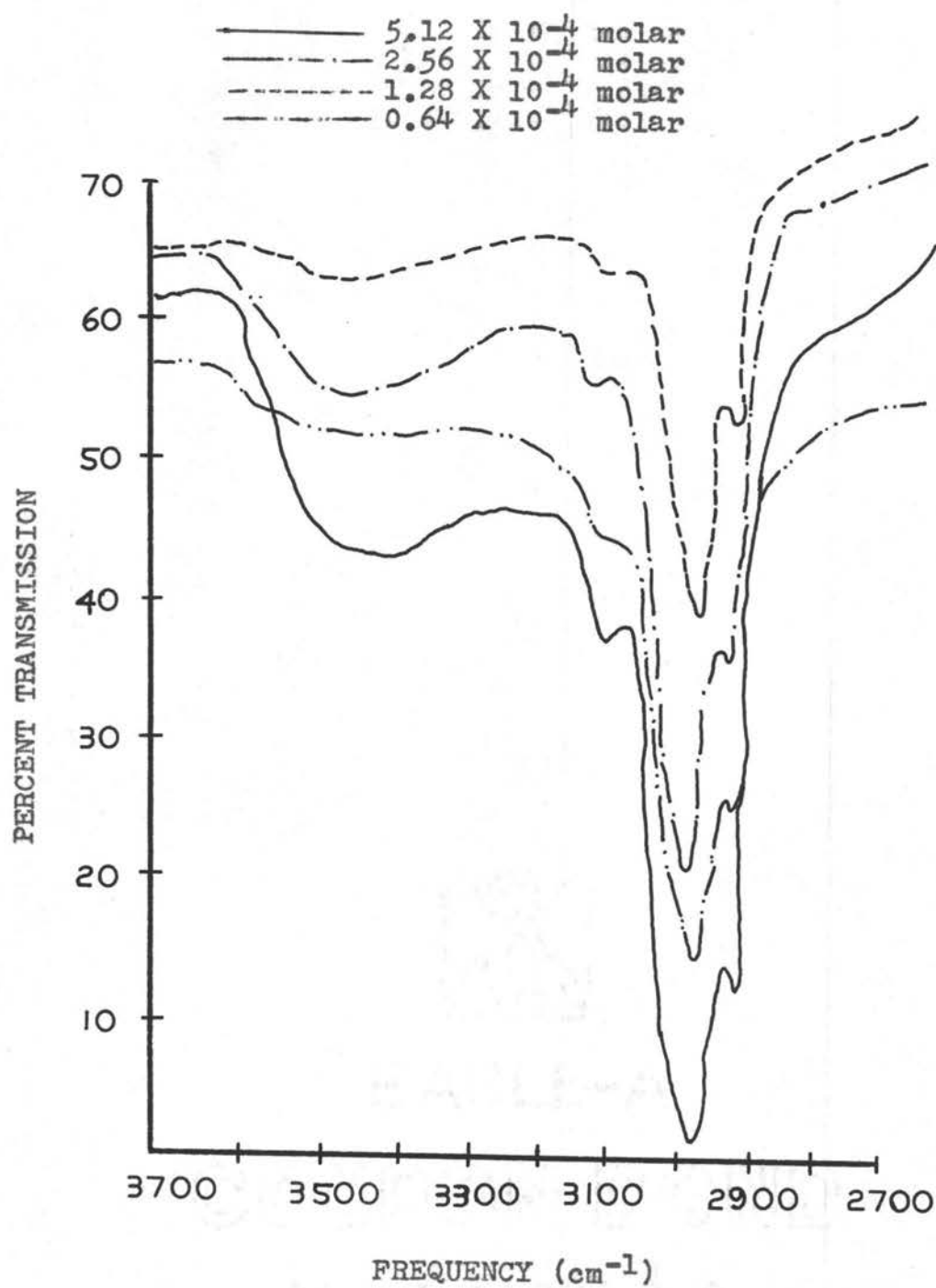
produced in the rearrangement, assuming that no major and unexpected skeletal rearrangement occurred.

DILUTION SPECTRA OF  
1-HYDROXY-3,4-DIMETHYLPHENANTHRENE

—  $9.0 \times 10^{-5}$  molar  
- - -  $3.6 \times 10^{-5}$  molar  
- · -  $1.8 \times 10^{-5}$  molar



DILUTION SPECTRA OF 1-HYDROXY-  
3,4-DIMETHYL-9,10-PHENANTHRAQUINONE



## EXPERIMENTAL

 $\gamma$ -(2-Naphthyl)- $\alpha,\alpha$ -dimethylbutyric acid

A mixture containing 12.8 g. (0.049 mole) of  $\gamma$ -(5,6,7,8-tetrahydro-2-naphthoyl)- $\alpha,\alpha$ -dimethylpropionic acid and 0.2 g. of 10% Pd-C catalyst was prepared and heated to 200° under a nitrogen atmosphere. Stirring was started, the nitrogen flow decreased and the temperature was raised to 270° very slowly over a period of nine hours. The mixture was cooled, dissolved in methanol and the spent catalyst removed by filtration. The product crystallized when the methanol solution was cooled, yielding 9.0 g. (81%) of white crystals melting at 139-140° (reported 133-135°) (28, p.9-19).

4-Oxo-3,3-dimethyl-3,4-dihydrophenanthrene

A solution of 7.07 g. (0.032 moles) of 4-oxo-3,3-dimethyl-1,2,3,4-tetrahydrophenanthrene in 200 cc. of carbon tetrachloride was treated with 8.0 g. (0.045 mole) of N-bromosuccinimide and 1.04 g. of dry benzoyl peroxide. The mixture was held under reflux for 2½ hours, the insoluble imide removed by filtration and the bromide distilled in vacuo, b.p. 140° C (0.250-0.200 mm.). The crude

material readily crystallized and melted at 115-118° C. The yield was 7.45 g. or 77%. The product gave a good test for bromine (sodium fusion) but was not further investigated.

The crude bromide was dissolved in 22 cc. of  $\gamma$ -collidine, and heated to 135-140° in an oil bath for half an hour. The collidine hydrobromide was removed from the reaction mixture by filtration and the filtrate was extracted with 5% sodium hydroxide, water, 5% hydrochloric acid, again with water and then dried over anhydrous magnesium sulfate. The dienone was isolated by distillation under reduced pressure, yielding 5.39 g. (99%) light yellow oil boiling at 127° (0.15 mm.) and having  $n_D^{24}$  1.6462.

The dienone took up 107% of the theoretical amount of hydrogen when treated with hydrogen at atmospheric pressure over palladized carbon. The dienone was purified by chromatography on alumina using petroleum ether as eluant.

Anal: Calc. for  $C_{16}H_{14}O$  : C, 86.50%; H, 6.30%

Found: C, 84.04%; H, 6.38%

C, 84.41%; H, 6.86%



Rearrangement of 4-oxo-3,3-dimethyl-3,4-dihydro-phenanthrene via the sulfuric acid-acetic anhydride method

To 3.6 g. of the dienone was added 200 cc. of acetic anhydride containing 3 cc. of concentrated sulfuric acid. The mixture was swirled until the dienone had completely dissolved, the reaction vessel flushed with nitrogen, and then allowed to stand in the dark. The rearrangement mixture turned first yellow, then green, and after one week a dark red color. Rearrangement was allowed to proceed for two weeks after which time the solution was poured onto a stirred mixture of cracked ice and water. After hydrolysis, the aqueous phase was extracted with chloroform and the chloroform layer washed with water and dried over anhydrous magnesium sulfate. Removal of the chloroform yielded a very viscous red oil. The acetate was isolated from the oil by chromatography on silicic acid. The acetate so obtained when recrystallized from alcohol melted at 130-132°.

I.R. Maxima at 765, 816, 933, 1017, 1073, 1165, 1369, 1380, 1451, 1620, 1758  $\text{cm}^{-1}$

U.V. Maxima at 208, 226, 256, 296, 308  $\text{m}\mu$

Anal: Calc. for  $\text{C}_{18}\text{H}_{16}\text{O}_2$  : C, 81.90%; H, 6.06%

Found: C, 81.52%; H, 6.34%

A yellow crystalline material isolated from the oil was identified as the bromoketone and melted at 93.5-94.0° when crystallized from alcohol.

I.R. maxima at 753, 795, 844, 965, 1006, 1015, 1090, 1144, 1174, 1194, 1221, 1274, 1361, 1374, 1428, 1458, 1514, 1591, 1630, 1673, 2954  $\text{cm}^{-1}$

U.V. maxima at 230, 258, 266, 280, 344  $\text{m}\mu$

Anal: Calc. for  $\text{C}_{16}\text{H}_{13}\text{BrO}$  : C, 63.80%; H, 4.32%

Found: C, 63.29%; H, 4.83%

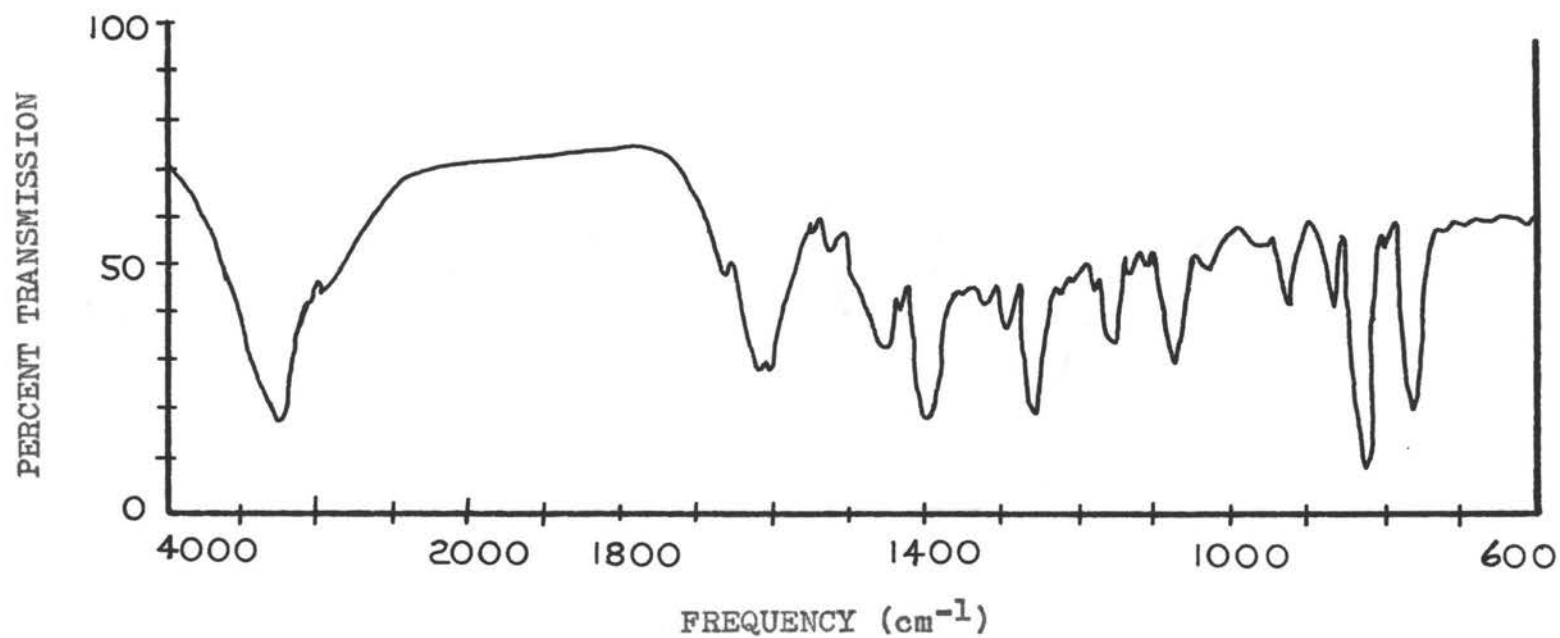
#### 1-Hydroxy-3,4-dimethylphenanthrene

A 50 mg. (18 X 10<sup>-5</sup> mole) sample of 1-acetoxy-3,4 dimethylphenanthrene was placed in a small flask and 2 cc. of absolute alcohol was added followed by 1 cc. of 6-N sodium hydroxide solution. The mixture took on a green hue when the sodium hydroxide was added. Nitrogen was bubbled through the mixture continuously while the flask was warmed in a water bath to 45° briefly until the solid acetate had dissolved. The resulting solution was cooled, diluted with 3 cc. of cold distilled water and brought to a pH of 2 (about 1.5 ml. of 5% hydrochloric acid). The green color disappeared and a white solid 34.1 mg. (78%) precipitated. It melted at 178-179° d. after recrystallization from alcohol. The analysis was unsatisfactory.

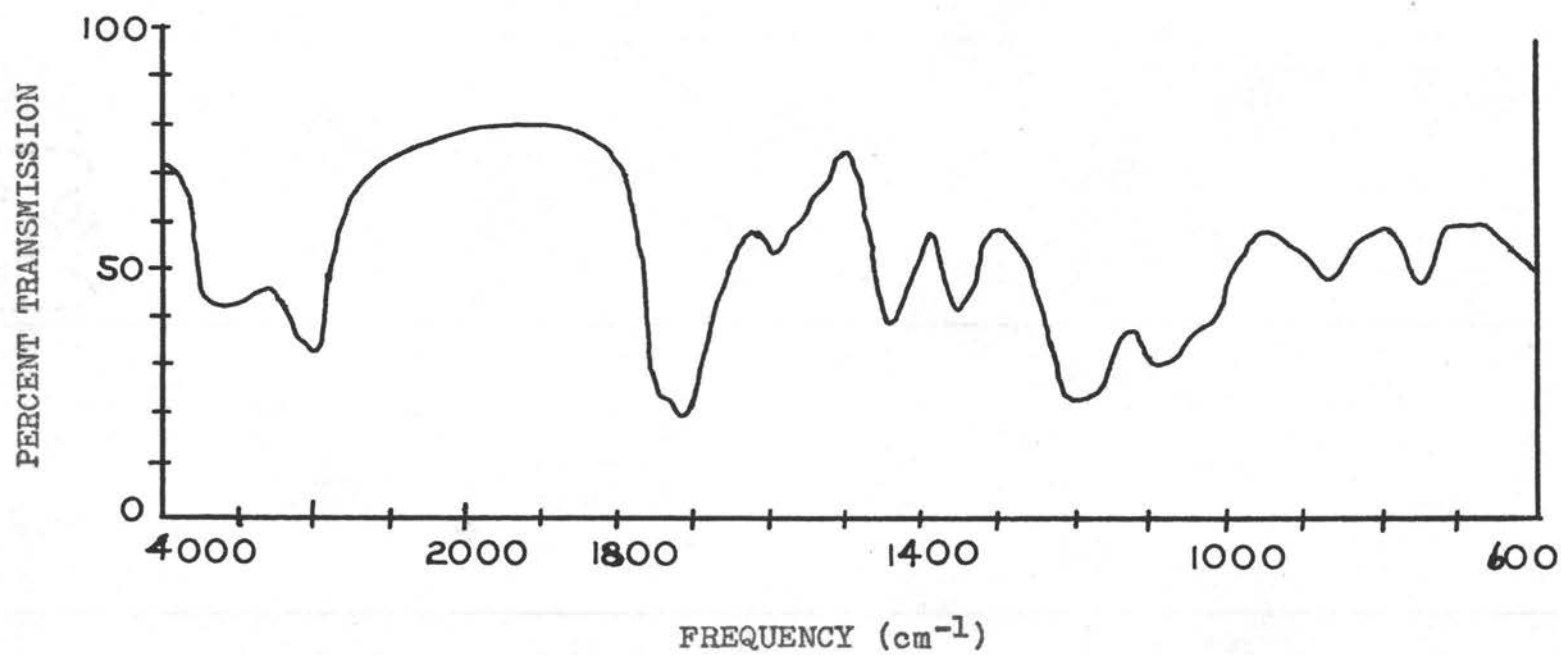
1-Hydroxy-3,4-dimethyl-9,10-phenanthraquinone

A 50 mg. ( $18 \times 10^{-5}$  mole) sample of 1-acetoxy-3,4-dimethylphenanthrene was added to 0.6 ml. of glacial acetic acid. A solution of 60 mg. ( $6 \times 10^{-4}$  mole) of chromic anhydride in glacial acetic acid was added and the solution heated on a steam bath to  $70^{\circ}$  for a half hour after which time it was cooled, diluted with water and the resulting quinoneacetate isolated by extraction with ether. The ether was removed by evaporation and a concentrated solution of sodium bisulfite was added to the residue followed by heating on a steam bath for one hour. The product was isolated by an ether extraction and after removal of the ether, weighed 6.4 mg. (13%).

INFRARED SPECTRA OF  
1-HYDROXY-3,4-DIMETHYLPHENANTHRENE



INFRARED SPECTRA OF 1-HYDROXY-  
3,4-DIMETHYL-9,10-PHENANTHRAQUINONE



## SUMMARY

The desired substrate for this study, 4-oxo-3,3-dimethyl-3,4-dihydrophenanthrene, was synthesized by an improved procedure and its rearrangement studied. Several attempts under standard conditions led to failure and only in the presence of excess sulfuric acid in acetic anhydride was rearrangement observed. The longest time previously reported for the rearrangement of a dienone is five days (22, p.5177) while this dienone required two weeks.

Two products were isolated by chromatography: (1) a yellow crystalline material having a ketone carbonyl frequency at  $1683\text{ cm}^{-1}$ , m.p.  $93-94^{\circ}$ . (2) a white crystalline solid having an acetate carbonyl frequency at  $1759\text{ cm}^{-1}$ , m.p.  $130-132^{\circ}$ .

The acetate was tentatively identified by examination of the infrared spectra at various dilutions of both the corresponding phenanthrol and hydroxyphenanthraquinone. This data indicated the hydroxyl group to be in the 1-position on the phenanthrene nucleus.

From these results, two conclusions can be drawn: (1) 4-oxo-3,3-dimethyl-3,4-dihydrophenanthrene rearranges only under drastic conditions suggesting that the

rearrangement is subject to steric hindrance, (2) the rearrangement product is 1-acetoxy-3,4-dimethylphenanthrene indicating a preference in this case for the mechanism involving migration of the oxygen function. Thus despite the steric factors and the greater double bond character, the reaction still does not involve the o-quinoid intermediate.

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