SOME ASPECTS OF THE CHEMISTRY OF ACENAPHTHENE

By

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ABSTRACT

During the course of this investigation, it was discovered that the 64°C. melting dichloroacenaphthene isomer could only be obtained by using hypochlorous acid on acenaphthylene which had been prepared by passing acenaphthenol acetate through a pyrolysis tube. Repeating the reaction a number of times, using a commercial grade of acenaphthylene, failed to yield the 64°C. melting isomer.

The method of partial resolution using the alkaloid brucine, which had been used for determining the configuration of 1,2-dibromoacenaphthene, was applied to the dichloroacenaphthene isomers. Although this method succeeded in partially resolving the dibromoacenaphthene, it failed with both of the dichloroacenaphthene isomers.

The reaction between acenaphthylene and perbenzoic acid did not yield the expected acenaphthylene oxide. The product that was obtained was acenaphthylene glycol monobenzoate. A mechanism was proposed for this reaction, which indicated that ring strain was the reason for not being able to isolate acenaphthylene oxide. This mechanism also explained why acenaphthylene glycol benzoate was obtained.

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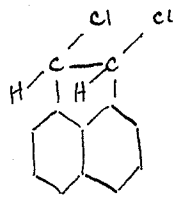
INTRODUCTION

In 1915, B. A. Campbell (14) prepared a compound, 1,2-dichloroacenaphthene, by chlorinating acenaphthylene in carbon tetrachloride solution. In 1948, J. J. Conn (16), in attempting to prepare acenaphthlene oxide, isolated a new dichloroacenaphthene. C. T. Elston (21), in 1951, showed that the two chlorine atoms were in the 1,2, positions. Thus it appeared that the two 1,2-dichloro-acenaphthenes were geometric isomers, but Elston was unable to determine the respective configurations.



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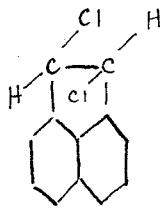

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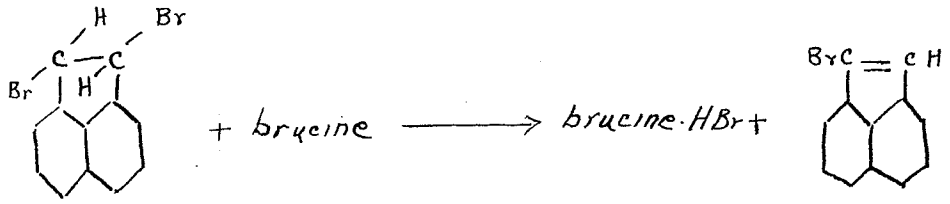
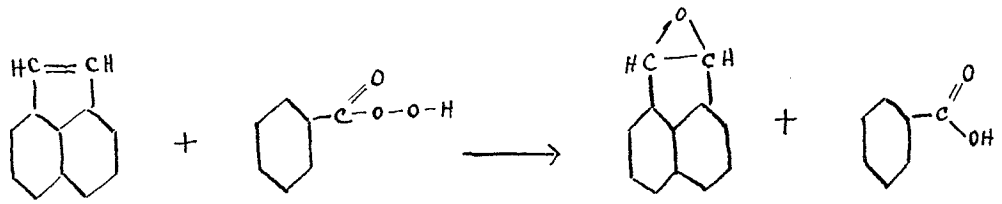
In 1957, Greene, Remers and Wilson (35) succeeded in determining the configuration of 1,2-dibromoacenaphthene. They used the optically active alkaloid, l-orucine, to partially resolve the d,l optical enantiomorphs of the trans isomer. l-Brucine reacts differentially with the d- and l- enantiomorphs, reacting faster with the dextro form than with the laevo. This differential reaction thus leaves a greater proportion of the laevo form than of the dextro, and this may be seen in the polarimeter.

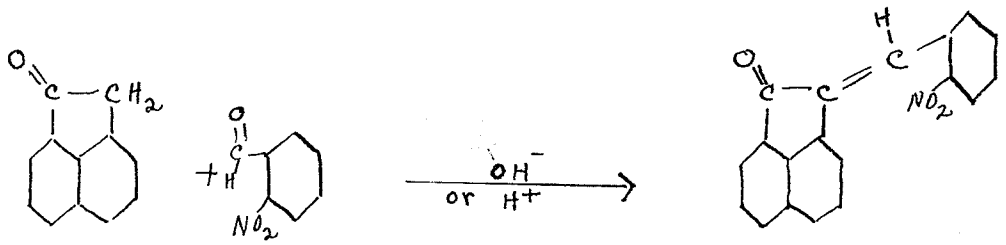


It was proposed that this method of resolution with brucine might be used for determining the configuration of the two dichloroacenaphthenes mentioned above. The cis form would undergo no resolution, whereas the trans isomer should show partial resolution.

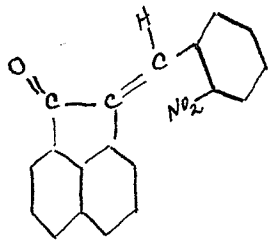
In this investigation, attempts were also made to prepare acenaphthylene oxide by the oxidation of acenaphthylene with perbenzoic acid. This is a standard method of preparing an epoxide ring (45). The reaction would take place as follows.



Another aspect of acenaphthene chemistry which was investigated was the condensation reactions of acenaphthenone with aromatic aldehydes. A representative reaction of this type would be the condensation of acenaphthenone with o-nitrobenzaldehyde.



Under acid conditions this reaction gave a product melting at 164°C., and under alkaline conditions, another substance melting at 238°C. These were thought to be geometric isomers, and attempts were made to convert the higher melting isomer to the lower melting one by refluxing with alcoholic hydrogen chloride solution.



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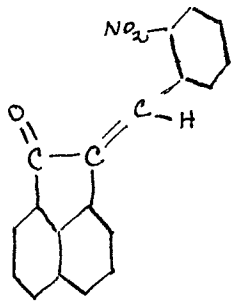


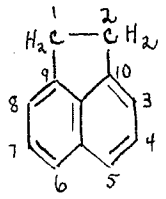
"TRANS"

Condensation reactions with acenaphthenone and other substances under both aldol(acid) and Claisen(alkaline) conditions were also tried.

LITERATURE SURVEY

The Chemistry of Acenaphthene

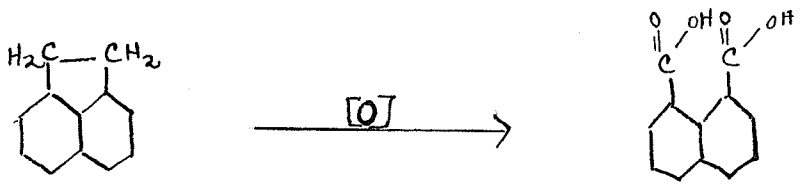
Acenaphthene is a white crystalline hydrocarbon, melting at 95°C., and boiling at 278°C. The accepted structure and numbering system of acenaphthene, according to Patterson's Ring index and Elsevier's Encyclopedia, is shown below.



There are several ways of synthesizing acenaphthene, such as the pyrolysis of 1-ethyl naphthalene (8), or the Friedel Craft's reaction with naphthalene and oxalyl chloride and subsequent reduction of the acenaphthenequinone formed.

Acenaphthene was first discovered and synthesized by Bertholet (7,8), in 1867. Large quantities of the material became available when it was discovered that it could be isolated from coal tar.

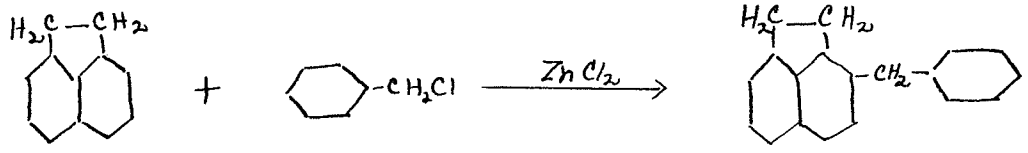
The structure of acenaphthene is very similar to that of naphthalene. Thus, the structures of acenaphthene and of many of its derivatives were determined by oxidation to the known naphthalene derivatives. For example, oxidation of acenaphthene gives naphthalic acid.



Derivatives of acenaphthene with the substituents in the 1,2-positions, also give naphthalic acid upon oxidation. Derivatives with substituents in the ring will yield substituted naphthalic acids on oxidation. The positions in the ring most susceptible to substitution reactions are the 3 and 5 positions.

Acenaphthene is a reactive compound which enters into a wide variety of reactions. It forms a number of addition compounds quite readily. Of these, the picrate is probably the most important, since it is frequently used to separate acenaphthene from other hydrocarbons.

Acenaphthene, like benzene and naphthalene, undergoes Friedel-Craft's and related reactions quite readily. An example of this type of reaction is;---



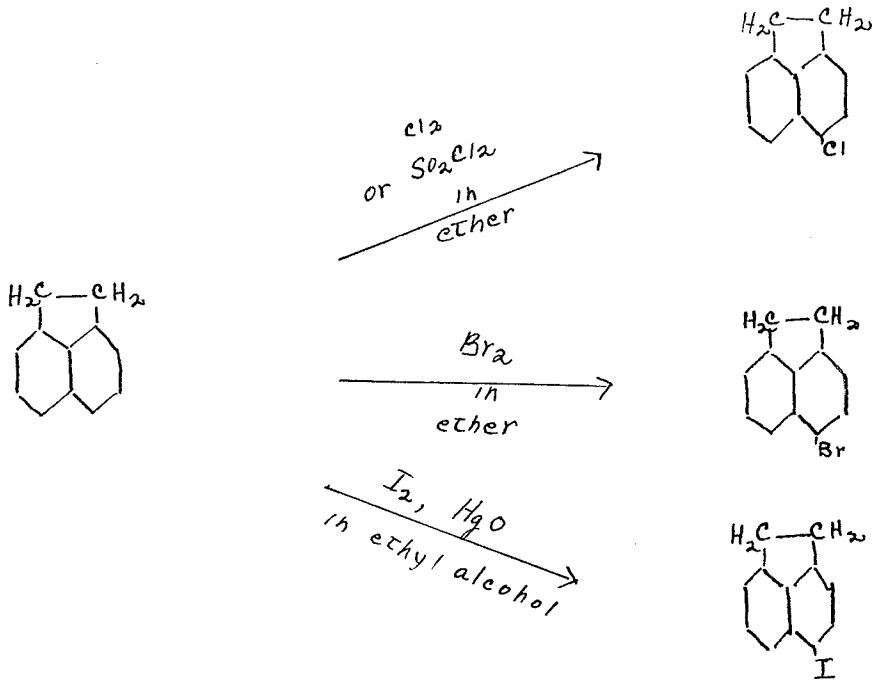
3-Benzylacenaphthene

Derivatives of acenaphthene with alkyl or aryl groups substituted in the five membered ring, cannot be

prepared by direct alkylation, but several have been prepared by indirect methods (12).

Halogen Derivatives

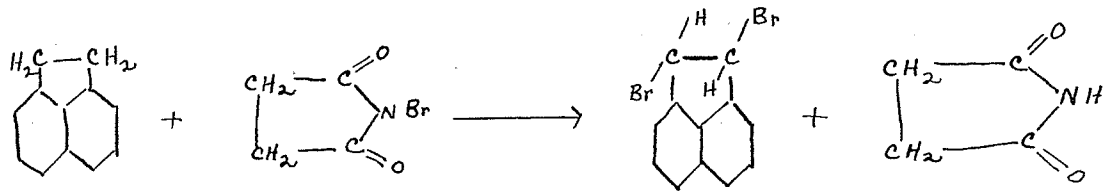
Halogenation of acenaphthene produces products in which the halogen atom may enter either the 1,2-positions, or the naphthalene nucleus. Blumenthal (11), in 1894, investigated some halogen derivatives of acenaphthene. He prepared 1,2-dibromoacenaphthene by brominating acenaphthylene. Other investigators, such as J. T. Kebler (40), E. Bamberger (4), and Compton (15), showed that halogenation of acenaphthene yielded derivatives with the halogen mainly in the naphthalene nucleus, and predominantly in the 5-position.



Derivatives of acenaphthene with more than one halogen atom are also known. Morgan (36) prepared 5,6-di-

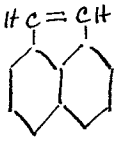
chloroacenaphthene by treating 5-chloroacenaphthene with sulfuryl chloride in chloroform. Di-, tri-, and tetra bromo compounds have also been prepared.

Halogenation of the 1,2-positions has also produced some halogen derivatives of acenaphthene. Jones (41) prepared 1-chloroacenaphthene and 1-bromoacenaphthene by the respective photochemical chlorination and bromination of acenaphthene in carbon tetrachloride solution. These compounds were also obtained by Gault (25) and Backman (3) by treating the acenaphthenol with phosphorus trichloride, or phosphorus tribromide. The iodine analogue of these compounds has not yet been prepared. These materials are quite unstable, losing hydrogen halide quite readily. The acenaphthylene formed polymerizes in the presence of the liberated acid, to yield one of its polymers. Photochemical bromination of acenaphthene, using two moles of bromine, yielded 1,2-dibromoacenaphthene. The dichloro analogue cannot be formed in this way. B. A. Campoell (14) prepared 1,2-dichloroacenaphthene by chlorinating acenaphthylene in carbon tetrachloride solution. The 1,2-dibromoacenaphthene has also been prepared by Blumenthal (11) through the direct bromination of acenaphthylene in ether solution. Green, Remers and Wilson (35) prepared this compound by the reaction of N-bromosuccinimide on acenaphthene.



These workers also determined that this compound had the "trans" configuration. This configuration was determined by partial resolution of the "trans" isomer, using the optically active alkaloid l-brucine. The brucine reacted differentially with the dextro and laevo optical forms of the trans isomer. It reacted faster with the d-form than with the laevo, thus leaving an excess of the l-form over the dextro at the end of the reaction.

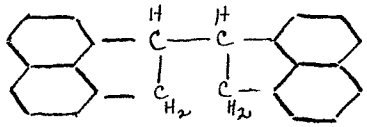
There are very few iodine derivatives of acenaphthene known, and all of these have the iodine in the naphthalene nucleus.

Acenaphthylene 

Acenaphthylene forms gleaming yellow plates melting at 93°C. The reactions of acenaphthylene, however, have not been very intensively investigated. The picric acid addition compound melts at 201°C.

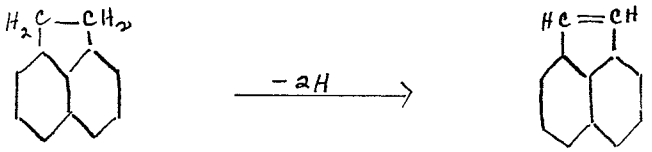
Acenaphthylene displays many reactions characteristic of unsaturated compounds. It forms 1,2-dichloroacenaphthene with chlorine in carbon tetrachloride solution, and also 1,2-dibromoacenaphthene with bromine inether solution. The iodine analogue has not been prepared, and attempts to prepare it have resulted only in the formation of

polyacenaphthylene. Both the dichloride and the dibromide are relatively unstable, and tend to lose hydrogen halide on heating, yielding the corresponding mono substituted acenaphthylene. In the presence of hydrogen chloride and other mineral acids at 100°C., acenaphthylene produces biacene (I), and its acid polymer allopolyacenaphthylene $(C_{12}H_8)_n$.



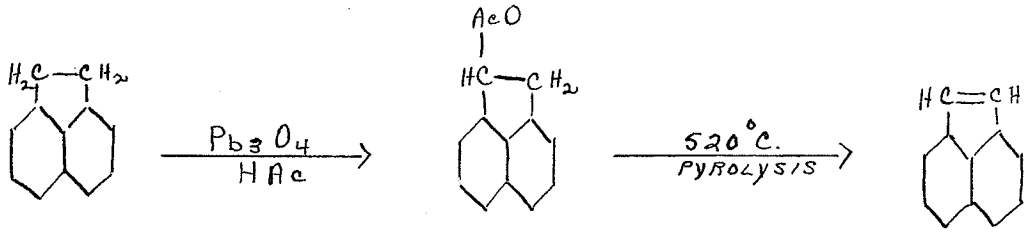
I

Acenaphthylene is an unsaturated aromatic hydrocarbon which is usually prepared from acenaphthene. It may be prepared from this material by the loss of two hydrogens.



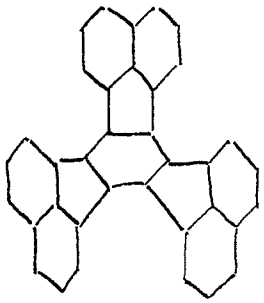
Behr and Van Dorp (6) first prepared acenaphthylene by passing the vapour of acenaphthene over red hot lead oxide. Dziewonski and Rapalski (19) passed acenaphthene vapours through a red hot silicon tube, and extracted the acenaphthylene from the product as a picrate. Numerous other methods have been employed by various investigators (20, 39, 43, 48). The most successful method of preparation has been that of Flower and Miller (24), who obtained an 80% yield. They used the method of Fieser and Cason (23) for preparing acenaph-

thenol acetate. This was done by treating acenaphthene with lead tetraacetate in acetic acid solution. The acenaphthenol acetate was then passed through a quartz tube maintained at 520°C. This method produced acenaphthylene which was not contaminated by acenaphthene, and could be obtained pure by simple recrystallization.

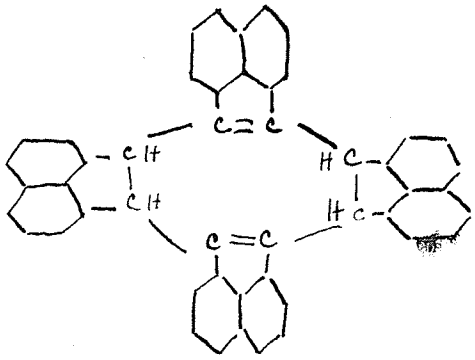


The most attractive method for the large scale production of acenaphthylene is the catalytic dehydrogenation of acenaphthene. Flower and Miller (24) have also given a brief account of this method. Acenaphthene vapours mixed with air were passed at 450°-480°C., over a catalyst consisting of 90% alumina, and 10% manganese dioxide. This gave a yield of 70%. Kynaston and Jones (41) have reported yields up to 92% acenaphthylene.

Acenaphthylene undergoes polymerization quite readily. At its boiling point, Acenaphthylene polymerizes to yield polyacenaphthylene, together with decacyclene (II) and fluocyclene (III).



II

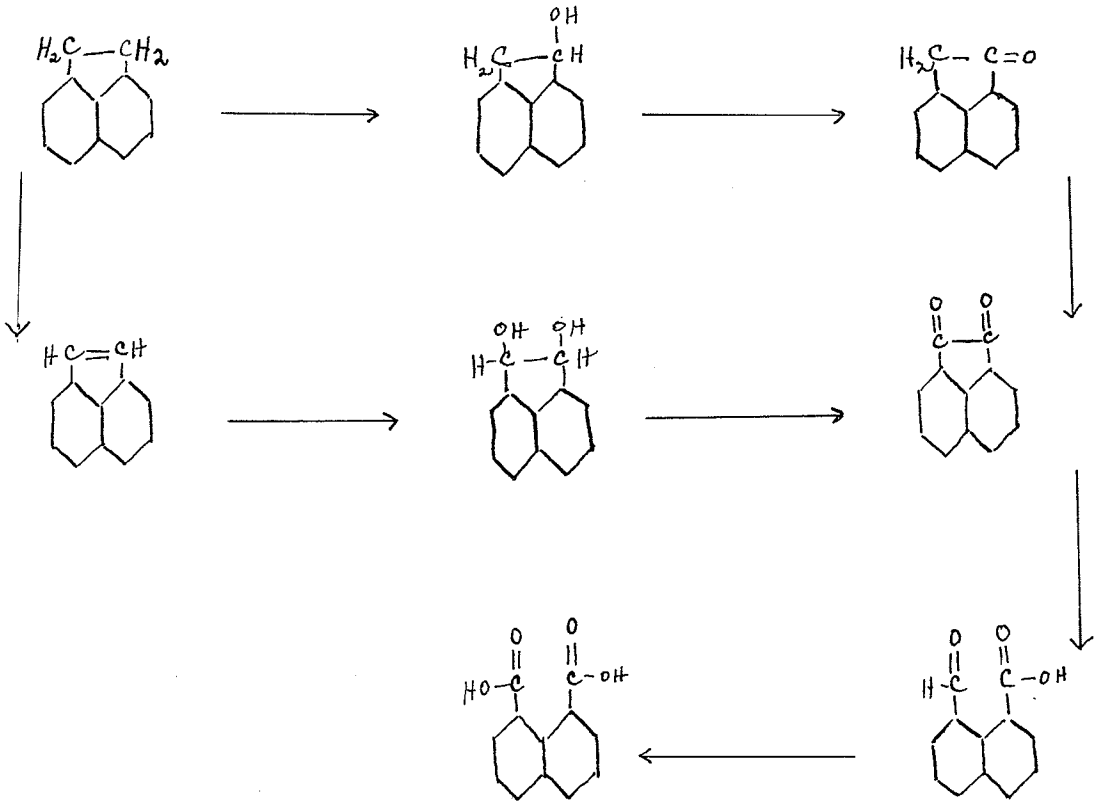


III

Polyacenaphthylene, and allo-polyacenaphthylene have the empirical formula $(C_{12}H_8)_n$, and both are amorphous powders. Polyacenaphthylene melts at 345°C. - 350°C. with decomposition, while allo-polyacenaphthylene has a melting point of 185°C. - 190°C. They are soluble in chloroform or benzene, but insoluble in alcohol or ether. Oxidation of these polymers with dichromate yields the same product as that obtained from acenaphthylene itself, namely, naphthalic acid. Acenaphthylene has also been used to polymerize and copolymerize with other monomers, giving potentially useful plastics (38).

Oxidation Products of Acenaphthene

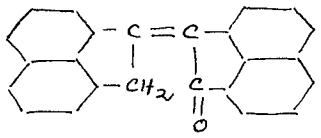
Acenaphthene, under very strong oxidation, yields naphthalic acid. However, if the oxidation is milder, various other products are formed. The various stages of oxidation can be represented as follows.



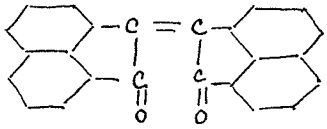
Graebe (33) investigated many of these oxidation products under alkaline conditions.

Certain condensation reactions could also lead to products which have two acenaphthene nuclei in the molecule. For instance, acenaphthene condensed with acenaphthene quinone yields biacenone (IV), and also, acenaphenone condensed with

acenaphthene quinone, yields biacenedione (V).



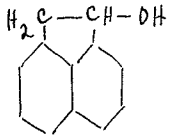
IV



V

Acenaphthenol

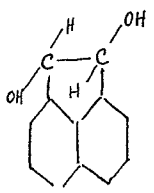
Acenaphthenol is quite a stable substance, except in the presence of strong dehydrating agents, when it tends to lose water and form acenaphthylene.



This compound may be prepared by the oxidation of acenaphthene with red lead in glacial acetic acid solution, yielding acenaphthenol acetate, which, under subsequent hydrolysis with sodium hydroxide and methanol, gives acenaphthenol. It crystallizes from alcohol or benzene in the form of colourless needles melting at 146°C.

Acenaphthenol reacts with acid chlorides to yield the corresponding esters. The reaction with thionyl chloride in pyridine solution, yields acenaphthylene as the main product. Gault (25) treated acenaphthenol in acetic acid with hydrogen bromide, and obtained 1-bromoacenaphthene.

Acenaphthylene Glycol



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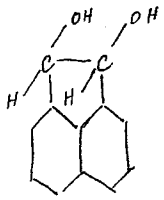

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These two hydroxyl groups, similar to any other 1,2-disubstituted group, may exist as geometric isomers. These geometric isomers result from the fact that the two hydroxyl groups may lie, either both above the plane of the naphthalene ring, or, one above, and one below. The two geometric forms, cis and trans, have both been isolated. In 1896, Graebe (34) obtained both geometric forms by direct hydrolysis of the dibromide. The trans form was found to exist as colourless needles melting at 159°C., and the cis form, as colourless needles melting at 212°C. These glycols were insoluble in all common organic solvents, but dissolved readily in water, the cis form being much less soluble than the trans. This difference in solubility afforded an easy method of separation when they were formed together. Other methods by which these glycols may be formed are; the reduction of acenaphthene quinone with sodium mercury in alcohol (10), or with hydrogen over a platinum catalyst (37), and, the direct action of selenium dioxide on acenaphthene (43).

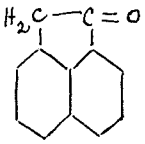
Jack and Rule (37) first utilized the fact that the trans form can exist as d,l optical enantiomorphs. In 1938,

they used this fact in establishing definitely that the lower melting isomer was the trans form. Their method involved the resolution of the optically active trans form by ester formation with l-menthoxy acetyl chloride.

Upon boiling with concentrated hydrochloric acid, the glycols undergo a pinacol rearrangement to give acenaphthenone.

The reaction between the glycols and lead tetraacetate to yield naphthalic dialdehyde hydrate, has been used to determine the configuration of 1,2-disubstituted glycols. With lead tetraacetate in acetic acid, glycols usually show similar differences in reaction velocity. The cis glycol in this reaction was found to have a specific rate constant about 4×10^6 greater than that for the trans.

Acenaphthenone



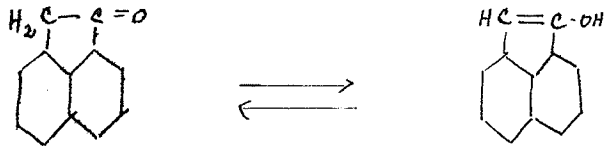
Acenaphthenone may be prepared in very good yield by the method employed by Fieser and Cason (23). This method essentially involves the oxidation of acenaphthenol by chromic annydride. Various other methods may be used for the preparation of acenaphthenone, acenaphthene quinone being the starting material in most cases (5, 34, 50, 51).

The first practical method developed for the preparation of acenaphthenone was that of Graebe and Jequier (34). These workers reduced 2,2-dichloroacenaphthenone, prepared by the action of phosphorus pentachloride on acenaphthene quinone, with zinc and acetic acid. Ghigi (27,29) improved their method by effecting the reduction with powdered iron in acetic acid.

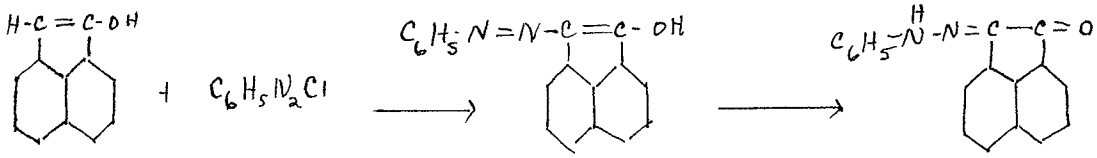
Rule and Thompson (51) prepared acenaphthenone by the reduction of the phenylhydrazone of acenaphthene quinone with iron and hydrochloric acid.

Acenaphthenone may be crystallized from alcohol in the form of needles melting at 121°C. It is usually separated from the reaction mixtures by steam distillation. In the presence of alcoholic sodium or potassium hydroxide, it gives a characteristic very dark violet color.

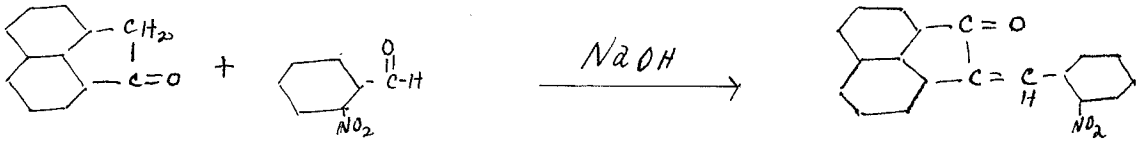
Acenaphthenone contains both a carbonyl group and a methylene group, hence there are a large number of possibilities for a reaction. Under certain conditions, acenaphthenone reacts with Grignard reagents to regenerate the Grignard hydrocarbon. Since this type of behaviour is typical of compounds of the acetoacetic ester type, Ghigi (26) has proposed that acenaphthenone exists as tautomeric keto and enol forms. However, this has never been proven, and the enol form is known only through its derivatives.



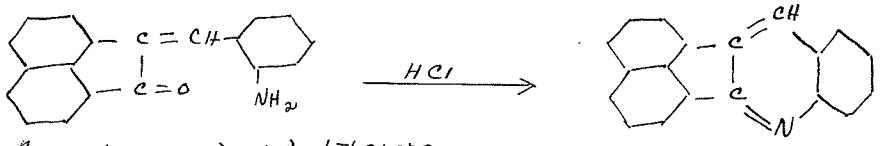
Ghigi (27) considered that the coupling of diazonium salts (benzenediazonium chloride) with acenaphthenone in alcoholic solution, to yield benzenediazoacenaphthenone, was further evidence for the enol form. The reaction is assumed to proceed as follows.



The methylene group of acenaphthenone has been shown to undergo condensation reactions with various aromatic aldehydes (27,30,31,32). A typical example of this type of reaction is the condensation of o-nitrobenzaldehyde and acenaphthenone according to Claisen-Schmidt conditions.

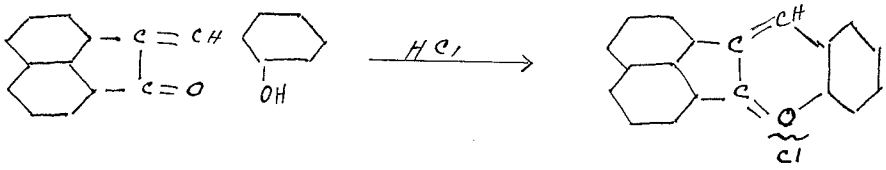


If the aromatic aldehyde contains an ortho amino or hydroxyl group, the condensation product may undergo ring closure, if hydrogen chloride is the condensing agent (31,32).



2-o Amino benzal acenaphthenone

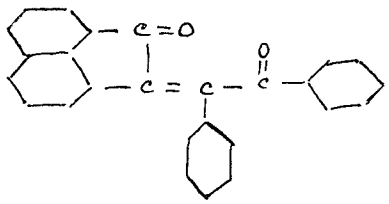
Acenaphthylene 1,2':2,3 quinoline



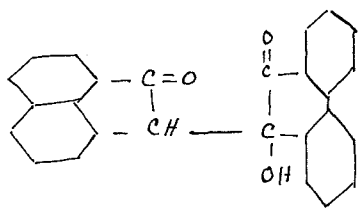
2-o Hydroxy benzal acenaphthenone

Acenaphthylene 1,2':2,3 Benzpyrylium Chloride

Some aromatic ketones also condense with acenaphthenone. For instance, benzil in alcoholic potassium hydroxide yields 2-α-benzoylbenzalacenaphthenone (30).

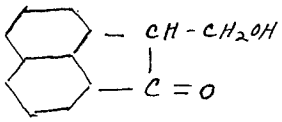


Acenaphthenone also condenses with acenaphthene quinone in the presence of acetic acid and sodium acetate to produce biacenedione (V) and the aldol 1-hydroxy-2,2-diketo-1,1-biacenaphthyl (VI).



VI

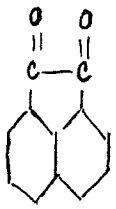
Formaldehyde is the only aliphatic aldehyde reported (25) to have undergone condensation with acenaphthenone. This reaction takes place in aqueous medium in the presence of sodium carbonate or barium hydroxide, forming the aldol (VII).



VII

Grignards react with the carbonyl group of acenaphthenone to yield tertiary alcohols. These are fairly unstable, and readily lose water to give alkylated acenaphthylenes.

Acenaphthenequinone



Acenaphthenequinone is one of the most important commercial derivatives of acenaphthene. It is used extensively in the manufacturing of dyes. It is quite a reacive substance, and its reactions are many and varied.

Acenaphthenequinone may be crystallized from alcohol in the form of yellow needles melting at 261°C. It is easily soluble in alcohol, acetic acid, or benzene, and

with sodium sulfide and a trace of water it gives a characteristic blue coloration.

Under suitable conditions, acenaphthenequinone may be prepared by the dichromate oxidation of acenaphthene (17, 33). The reaction is very sensitive, and the rate of reaction, and the conditions of extraction must be carefully controlled. The quinone is usually separated as its bisulfite addition product or its oxime (50).

Reduction of acenaphthenequinone yields, either the mono ketone acenaphthenone, or acenaphtnylene glycol, depending on the conditions of the reduction. The preparation of the glycols by this reduction is perhaps the best method of preparing these compounds.

Acenaphthenequinone reacts with Grignard reagents to form 1,2-dialkyl-1,2-dihydroxyacenaphthenes (1,2,43), which undergo pinacol rearrangements giving 2,2-dialkyl acenaphthenones.

This acenaphthenequinone has two reactive keto groups, and thus enters intomany condensation reactions. These condensation reactions may be classified into four general classes.

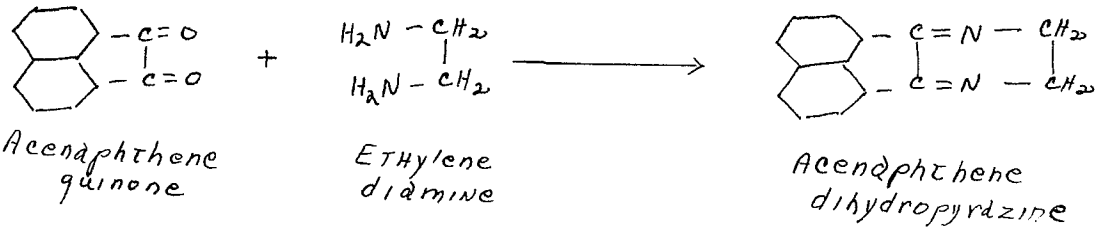
1. In the presence of phenols and sulfuric acid, acenaphthenequinone condenses to yield mainly substituted acenaphthenones. With phenol, under such circumstances,

2,2-bis-p-hydroxyphenylacenaphthenone is produced (42).

2. The hydrogen atoms of aromatic hydrocarbons, or their derivatives, in the presence of aluminum chloride, unite with the carbonyl oxygen of the quinone to eliminate water (54). The substances belonging to this class are of the fluorescin type dyes.

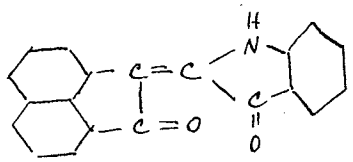
3. Acenaphthenequinone condenses quite readily with carbon atoms containing an active hydrogen. With acetone, the quinone in aqueous potassium hydroxide yields 2-hydroxy-2-acetylacenaphthenone (52). Under similar conditions, ethyl acetoacetate yields α-2 keto-1-acenaphthylidene acetoacetic acid (49).

4. Acenaphthenequinone also condenses with ammonia, amines, hydrazines, and other compounds containing the $-NH_2$ group. A typical example of this type of reaction is as follows.

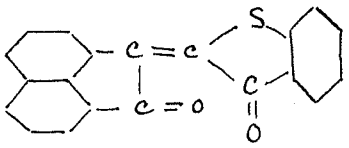


A condensation of acenaphthene quinone which is of considerable commercial importance, is that leading to the indigoid class of vat dyes. With indoxyl in sodium carbon-

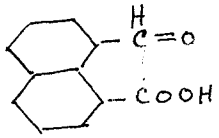
ate solution, or in acetic acid solution, it gives acenaphthene indigo



Another dye, acenaphthene-thio-indigo, may be prepared by reacting acenaphthenequinone with S -Phenythioglycollic-o-carboxylic acid plus acetic anhydride (9). This product is also sold under the trade name of Ciba Scarlet

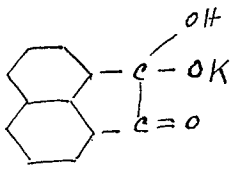


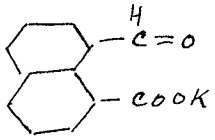
Naphthaldehydic Acid



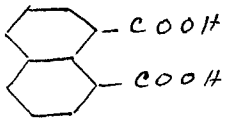
This compound may be prepared by dissolving acenaphthenequinone in 30% potassium hydroxide solution (33). The free acid may be precipitated by adding mineral acids and purified by recrystallization from alcohol.

The salts of naphthaldehydic acid appear to exist in two isomeric forms.





Naphthalic Acid



This substance is the normal end product of the oxidation of acenaphthene with dichromate (33). This compound readily loses water on heating to yield the anhydride. It also gives a characteristic blue fluorescence in the presence of conc. sulfuric acid.

Work done on these compounds, in this laboratory, will be discussed in a later section.

DISCUSSION OF RESULTS

The purpose of this investigation was to attempt to establish the configuration of the two geometric 1,2 dichloroacenaphthene isomers. During the course of this research, there was considerable difficulty involved in obtaining the 64°C. melting isomer. Numerous attempts to obtain this compound, using the method of Elston (21), hypochlorous acid treatment of acenaphthylene, met with failure. After testing every other source of errorin the procedure, it was decided that perhaps the inability to obtain this compound was involved with the preparation of acenaphthylene. The acenaphthylene used in all the experimental work was of a commercial grade which was unavilable at the time of Elston's work. Therefore it was decided that Elston's complete procedure should be followed, including his method of preparation of acenaphthylene, in order to obtain this 64°C. melting isomer. This method of preparation of acenaphthylene, that of Flower and Miller (24), involved, first, the formation of acenaphthenol acetate, followed by a pyrolysis of this material in a silicon tube. Although a mixed melting point of the two acenaphthylenes (prepared and purchased) gave no depression, and gas chromatograph curves showed very little difference between them, the prepared sample yielded the 64°C. melting isomer, whereas the pur-

chased sample would not yield this material. The commercial grade of acenaphthylene would probably not be prepared by the method used here (Flower and Miller's), since, if it were, the acenaphthylene would be quite expensive, and it was purchased quite cheaply. A private communication with the Aldrich Chemical Co. of Milwaukee, suppliers of this material, gave no additional information, since they purchased this material from a German chemical firm. However, the most probable commercial preparation of acenaphthylene is a catalytic dehydrogenation, which would only involve one step in the preparation. In this method, acenaphthene vapours are passed, at a temperature of 450°C. - 485°C. over a mixture of 90% alumina and 10% manganese dioxide, and the acenaphthylene then collected and redistilled. Kynaston and Jones (41) have reported yields up to 92% acenaphthylene using this method. A speculation as to why only the prepared sample yielded the 64°C. melting isomer might be the fact that hydroquinone was used as a polymerization inhibitor during the purification by distillation. During this distillation enough hydroquinone might distill over with the acenaphthylene to inhibit polymerization long enough for the reaction to take place.

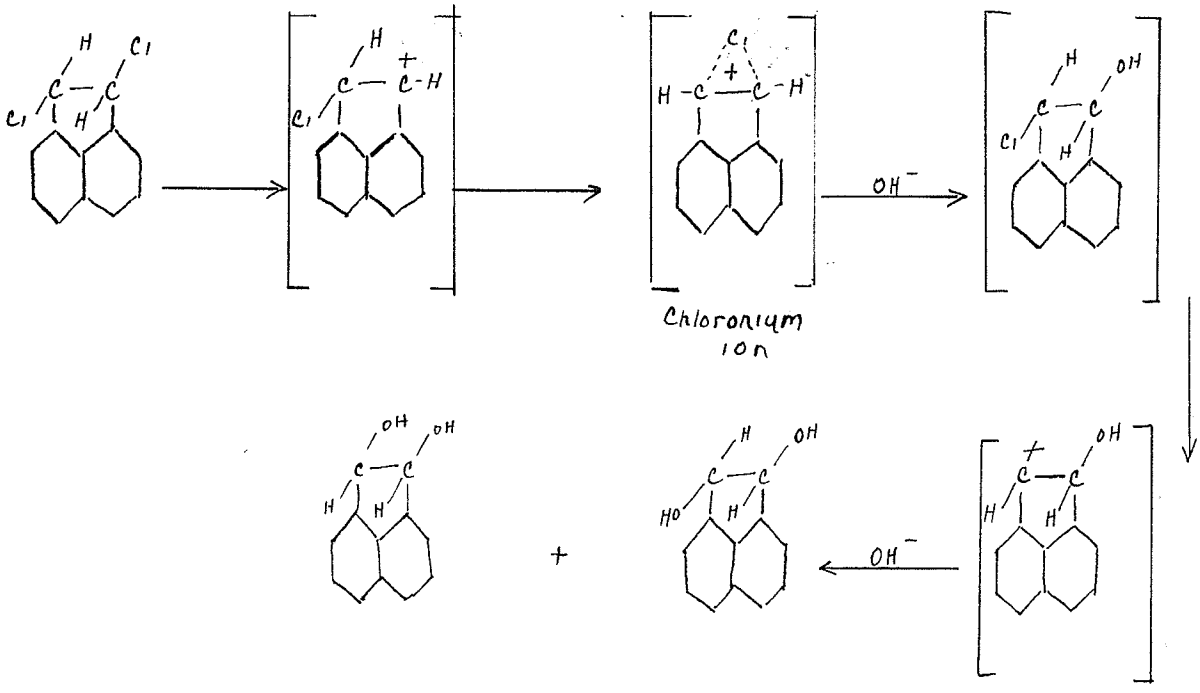
Greene, Remers and Wilson (35) had determined the configuration of trans-1,2-dibromoacenaphthene, by the method of partial resolution using the optically active alkaloid, l-brucine. Their experiment was repeated, and it was found

that brucine did partially resolve the racemic 1,2-dibromoacenaphthene mixture. The reaction took place differentially, l-brucine reacting faster with the dextro isomer than with the laevo (Lucas, H.J., Gould Jr., C.W. J. Am. Chem. Soc. 601: 64. 1942.) However, when this method (page 8) was tried on the 1,2-dichloroacenaphthene, it was found to be inapplicable. Neither the 115°C. melting isomer, nor the 64°C. melting isomer showed any partial resolution. In both these reactions the amount of brucine used was calculated to leave 1 g. of each isomer unreacted. There were 0.5 g. of the 115°C. melting isomer, and 0.7 g. of the 64°C. melting isomer recovered after the attempted partial resolution. Thus it appears that the reaction did take place. A possible explanation for the inability to resolve the isomers might be that the difference in the rates of reaction of brucine with the d and l forms is not sufficiently great to be detectable.

The brominations with N-bromosuccinimide were found, by Greene, Remers and Wilson (35), to give stereospecific trans addition. The reaction between N-chlorosuccinimide and acenaphthene, under the conditions used by Greene, Remers and Wilson (35) for N-bromosuccinimide and acenaphthene, was found not to work. The only product isolated was the starting material, acenaphthene. Repeating the

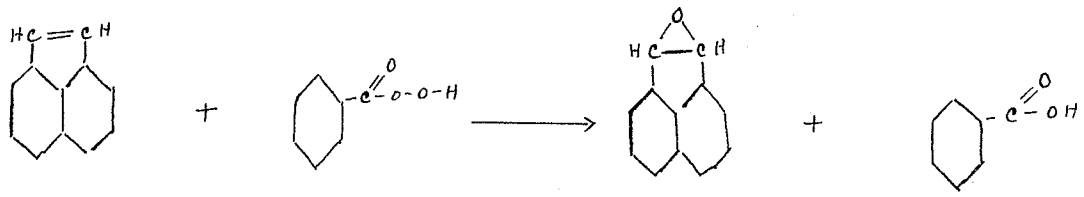
experiment at successively higher temperatures, a reaction was found to take place at about 110°C. This reaction yielded 1-monochloroacenaphthylene and the starting material, acenaphthene. This reaction was also tried at temperatures of 135°C. - 140°C., but the only product obtained at this temperature was 1-monochloroacenaphthylene. Thus it appears that if the desired reaction did take place, it was so exothermic that hydrogen chloride was eliminated immediately.

An attempt was made to try to convert the 1,2-dichloroacenaphthenes, by hydrolysis, to the geometrically known 1,2-dihydroxyacenaphthenes. It was found that both the glycol isomers(cis and trans) were obtained from each isomer during the hydrolysis. The mechanism for the hydrolysis would probably proceed through a chloronium ion in the transition state, and would thus give equal probability of obtaining both the cis and trans glycols.

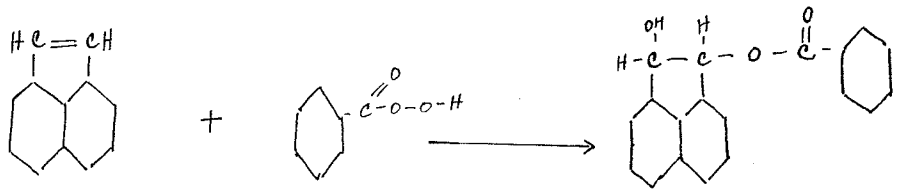


In attempting to go back the other way, from the known glycols to the dichloroacenaphthenes, using phosphorus trichloride, it was found that no reaction took place, and the glycols were recovered unchanged.

In this investigation, attempts were also made to obtain the unknown epoxide, acenaphthylene oxide, by means of the oxidation of acenaphthylene with perbenzoic acid.

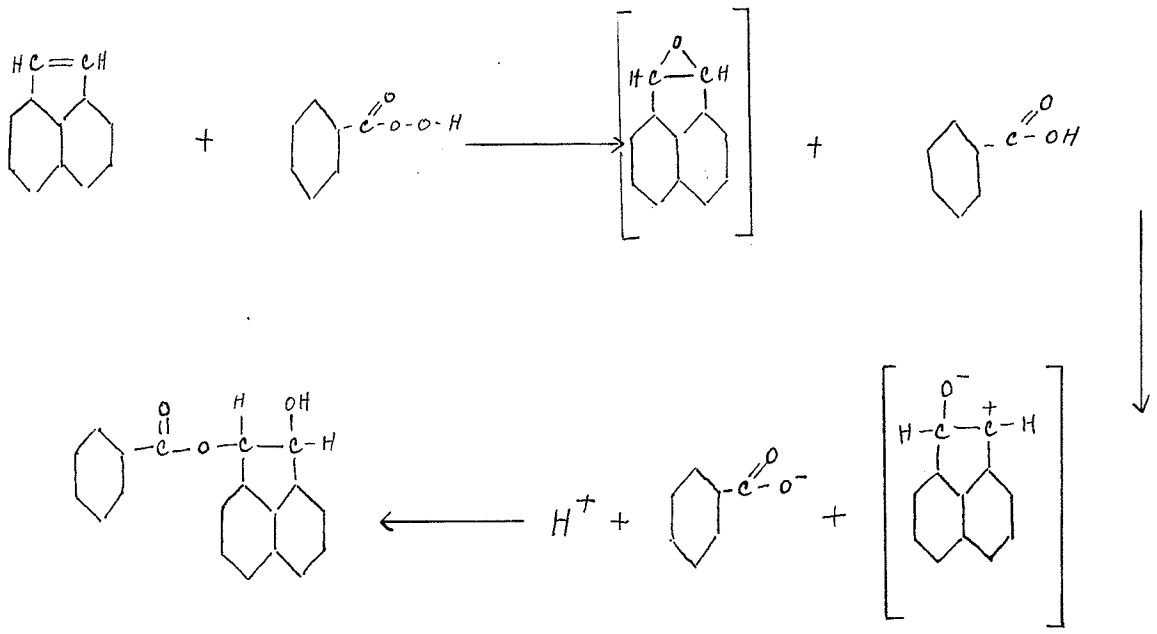


This reaction did not proceed as indicated above. A white solid was obtained from this reaction, which, when recrystallized, was found to melt at 188°C. - 190°C. Analysis, although it was not too close, indicated that this compound might be acenaphthylene glycol monobenzoate. A synthesis of this material was then carried out according to the method of Ewan and Cohen (22). A mixed melting point of the two products gave no depression, hence this newly formed product was acenaphthylene glycol monobenzoate. Thus the reaction between acenaphthylene and perbenzoic acid actually took place as follows.

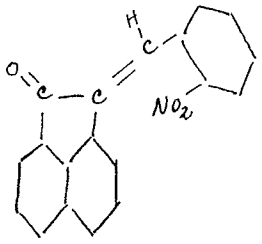


Thus a new and shorter method of forming acenaphthylene glycol monobenzoate has been arrived at. It may be done in one step only, whereas the method of Ewan and Cohen (22) involved the formation of intermediate products.

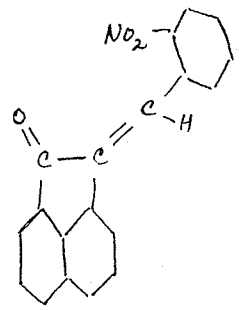
This method for forming an epoxide ring, perbenzoic acid on a double bond, is a standard method for this preparation. Since this method failed to produce the desired epoxide with acenaphthylene, it would seem that there might be too much strain in the five membered ring of acenaphthylene for the formation of this epoxide structure. As a result of the product formed, acenaphthylene glycol monobenzoate, it might be considered that the oxidation of the double bond did take place. But, since the ring strain is too great to allow the epoxide ring to remain, one oxygen to carbon bond is broken, and the ion formed then reacts with benzoic acid, formed during the reaction, to put hydrogen on the oxygen, and the benzoate anion on the other carbon.



Another aspect of acenaphthene chemistry which was investigated, was an attempt to convert the 238°C. melting o-nitrobenzalacenaphthenone into the lower melting isomer (164°C.).



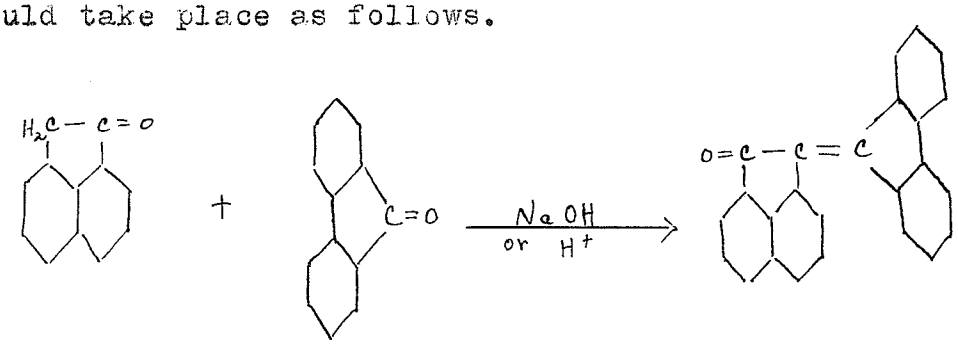
"CIS"



"TRANS"

In the past, several investigators (Stachiw (53), Campbell (13)) had attempted to convert the lower melting isomer (164°C.) into the higher melting one (238°C.). They had employed various methods, including irradiation with ultra violet light and heating above the melting point. In this investigation, attempts were made to go from the higher melting isomer to the lower one, by refluxing with alcoholic hydrogen chloride solution. This yielded a substance which melted about 260°C., and which was probably some decomposition product of the isomer.

A condensation reaction between fluorenone and acenaphenone was also tried. It was hoped that this reaction would take place as follows.



It was found that the above reaction did not take place under either aldol (acid) or Claisen (alkaline) conditions. The only product obtained from this reaction was the self condensation product of acenaphthenone, biacenone(IV).

EXPERIMENTAL

Preparation of Acenaphthenol Acetate

Acenaphthenol acetate was prepared by the method of Fieser and Cason (23).

Acenaphthene (154 g.) and glacial acetic acid (1100 ml.) which had been distilled over potassium permanganate were placed in a 2 liter beaker fitted with a mechanical stirrer and a thermometer extending below the surface of the liquid. The solution was stirred and heated to 60°C., at which point the source of heat was removed and red lead (820 g.) was added in portions of about 50 g. each. A new portion was added as soon as the color due to the previous portion had been discharged. During this operation, which required thirty to forty minutes, the temperature was maintained at 60-70°C. by external cooling. When the test for lead tetraacetate with moistened starch-iodide paper was negative, it was assumed that the reaction was complete. The dark red syrupy solution was then poured into water (2 litres) and the acetate was extracted with two portions of ether (350 ml. and 250 ml.). The total extract was washed, first with water (100ml.), and then with a saturated solution of sodium chloride (300ml.), and was finally dried over anhydrous sodium sulfate (50g.). The sodium sulfate was removed by filtration and washed colourless with three portions of ether (50ml.). After removal of the ether, the acetate was distilled under reduced pressure, the fraction boiling between 180°-190°C. at 16mm. being

collected. The average yield over several runs was 171g. or 80% of the theoretical amount.

Preparation of Acenaphthylene

Acenaphthylene was prepared by the pyrolysis of acenaphthenol acetate according to the method outlined by Flower and Miller (24).

The apparatus for the pyrolysis was set up as shown in the diagram. A quartz pyrolysis tube three-fourths of an inch in diameter, and fifteen inches long, was wound with nichrome wire, and then insulated with asbestos. The tube was heated by a 110 volt source, thecurrent being controlled by a powerstat. The appropriate setting of the powerstat to maintain a reaction temperature of 520°C. was determined by means of a direct reading thermocouple. The acenaphthenol acetate was admitted slowly (approximately 50 drops per minute) to the pyrolysis tube by means of a dropping funnel with the tip drawn out to a fine jet. The tip of the jet extended approximately two inches into the tube. Dry nitrogen gas from a cylinder served as a diluent and was admitted at the rate of two bubbles per second. The hot vapours issuing from the pyrolysis tube were passed through a steam heated condenser, and then collected in an air-cooled receiver. The crude product obtained was a reddish solid which gradually turned green upon exposure to air. The crude acenaphthylene was washed well with water, and then allowed to dry. Several recrystallizations from alcohol using decolorizing carbon produced pure acenaphthylene

as lemon-yellow plates melting at 92°C. The purification of the crude product, without previous crystallization, may be greatly simplified by vacuum distillation using hydroquinone as polymerization inhibitor. The distillate is almost pure acenaphthylene, boiling point 135-140°C. at 15-16mm., but yields are a little lower due to partial polymerization of the acenaphthylene. An average yield of acenaphthylene obtained during a run was about 180g. from 170g. of acenaphthenol acetate, or about 62% of the theoretical

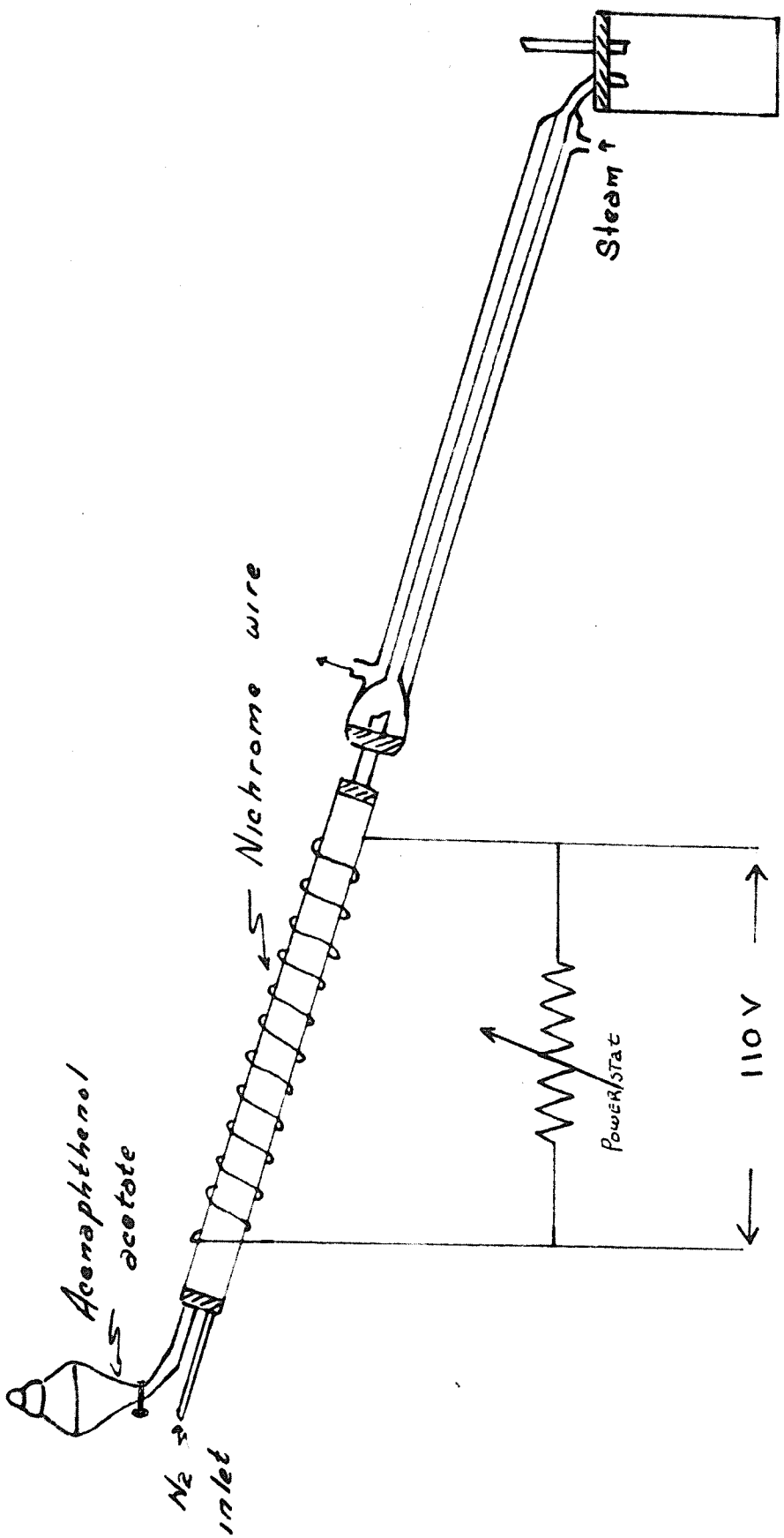
The optimum rate of flow of the acetate appeared to be when the vapour issuing from the pyrolysis tube was thin and pale orange in colour. On the average, about two hours were required to put 100g. of acetate through the tube. The efficiency of the tube is somewhat reduced by carbonaceous deposits, and for best results should be cleaned after every run of about 200g.

To prevent oxidation and photochemical polymerization, the acenaphthylene was stored in stoppered bottles, and kept in the dark.

Preparation of Hypochlorous Acid

The method followed here was that outlined by Detoeuf (18).

Precipitated chalk (28g.), urea (40g.) and water (31ml.) were placed in a 250 ml. Erlenmeyer flask fitted with an inlet tube extending below the surface of the liquid, and an


Steam
Nichrome wire
Acenaphthenol acetate
N2 inlet
Power Stat
110 V

outlet tube leading to the fume hood. A rapid stream of chlorine from a cylinder was passed into the mixture until the flask had increased in weight by approximetely 25g. During the chlorine addition, the flask and its contents were cooled in an ice bath, and shaken occasionally. When the chlorine had been added, the solution was diluted to a volume of 200ml. with water, and then filtered. The filtrate was stored in the ice chest until required. This filtrate, (hypochlorous acid), was not stored any longer than was necessary, since it decomposed fairly rapidly.

The potential hypochlorous acid content of the solution was determined in the following way. A 1ml. sample of the solution was placed in a 250ml. Erlenmeyer flask, diluted with water (24ml.), and acidified with acetic acid. Excess 10% potassium iodide solution was added and the liberated iodine was titrated with N/10 sodium thiosulfate solution using starch indicator. The hypochlorous acid content varied from one run to another, the range of concentration obtained being from 9%-12.5%. The following data are typical.

1 ml. HOCl solution 40.2 ml. of N/10 $Na_2S_2O_3$

Thus, 1000 ml. of solution would contain

$$\frac{52.5}{2} \times 40.2 \quad 105 \text{ gm. HOCl}$$

Reaction of Hypochlorous Acid with Acenaphthylene

Acenaphthylene (24g.), hypochlorous acid (250 ml. 9.9%) and acetic acid (15 ml.) were placed in a 500 ml. round bottom

flask and stirred slowly with a mechanical stirrer. The rate of reaction was followed by withdrawing a 1 ml. sample and titrating in the previously described method. No visible reaction occurred in the first couple of hours, and the hypochlorous acid concentration remained almost constant. After twenty-four hours, the acenaphthylene had turned brown in color and had collected on the bottom of the flask as a gummy solid. The decrease in hypochlorous acid during this time was approximately 10% greater than the rate of spontaneous decomposition of the acid. After five days, the hypochlorous acid had completely disappeared, but the mixture had changed little in appearance.

The gum and solution were then extracted with ether. The extract was washed with water, 5% sodium bicarbonate solution, and then again with water. After drying with anhydrous sodium sulfate, the ether was removed under reduced pressure, leaving a dark brown oil. Distillation under reduced pressure gave a light yellow oil, boiling point 170-180°C. at 14-15 mm. This purified product yielded a crop of light yellow crystals after being in the ice chest for two days. The viscous mixture was filtered under suction. Further solid was separated from the filtrate by repeatedly dissolving it in alcohol, and allowing it to crystallize. Using these methods, a total of 4.8g. of light yellow crystals were obtained from the oil. After being recrystallized from alcohol using decolorizing charcoal,

they appeared as fine white needle-like crystals, melting at 64-65°C.

Analysis:	Calculated	C,64.57	H,3.58	Cl,31.83
	Found	D,64.43	H,3.51	Cl,31.71

Preparation of 1,2-Dichloroacenaphthene

1,2-Dichloroacenaphthene melting at 115°C. was prepared according to the method of B. A. Campbell (14).

A solution of acenaphthylene (25g.) in carbon tetrachloride (150ml.) was placed in a 250 ml. flask fitted with an inlet tube extending below the surface of the liquid, and an outlet tube leading to the fume hood. The flask was cooled in an ice bath, and a rapid stream of chlorine gas passed into the solution until an increase in weight of 11.7g. was observed. The flask was then transferred to the ice chest, and allowed to cool for five hours. At the end of this time, a heavy crop of light green crystals had formed, and they were filtered off. The filtrate was evaporated to half of its original volume, and then cooled once again. The crystals were recrystallized from ethyl alcohol using decolorizing charcoal to yield 12.0g. of fine white needle-like crystals, melting point 115-116°C.

Preparation of 1,2-Dibromoacenaphthene

There were two methods used for the preparation of this compound; that of Blumenthal (11), and that of Greene,

Remers and Wilson (35).

Blumenthal's Method (11)

Acenaphthylene was dissolved in ether solution. Bromine was added very slowly to this solution, until the solution became distinctly colored. The ether was then evaporated under reduced pressure, yielding a reddish yellow solid. Recrystallization from alcohol using decolorizing charcoal gave fine white crystals melting at 124-125°C..

The method of Greene, Remers and Wilson (35)

A mixture of acenaphthene (0.77g. (0.005 mole) m.p. 93.5-95.0°C.), N-bromosuccinimide (1.78g. (0.01 mole)), and benzoyl peroxide (5 mg.) in carbon tetrachloride (10 ml.) was heated at reflux for 30 minutes. The orange mixture was cooled and filtered (strong odor of hydrogen bromide), and the residue, which consisted chiefly of succinimide, was washed with carbon tetrachloride. The filtrate was taken to dryness under reduced pressure, affording 1.5g. of a pale yellow solid. Recrystallization from pentane gave a crop of colorless crystals melting at 118-121°C. A second recrystallization gave a crop of colorless crystals melting at 124-125°C.

A mixed melting point of the products prepared by the two different methods gave no depression.

Chlorination of Acenaphthylene in Ether

This reaction was carried out under conditions

analogous to that used by Blumenthal (11) for preparing 1,2-dibromoacenaphthene. It was necessary to take the temperature of the ether down to -75°C., since at room temperature the reaction was too exothermic, yielding only 1-monochloroacenaphthylene.

Acenaphthylene was dissolved in ether solution. The temperature of this solution was then taken down to -75°C. by means of an acetone-dry ice bath. Dry chlorine gas was then passed through this solution, until a white precipitate settled out. This precipitate was filtered from the cold ether solution. The white precipitate was recrystallized from ethyl alcohol, yielding white crystals which melted at 115°C. A mixed melting point of this product and that obtained by the method of B. A. Campbell (14) gave no depression.

Attempted Hydrochlorination of 1-Monochloroacenaphthylene

1-Monochloroacenaphthylene was prepared by passing dry chlorine gas over dry acenaphthylene. This reaction would normally form a dichloride, but under these conditions the reaction was so exothermic that hydrogen chloride was eliminated from the molecule, leaving 1-monochloroacenaphthylene.

1-Monochloroacenaphthylene was dissolved in ether. The ethereal solution was cooled with dry ice and acetone to -75°C. Dry hydrogen chloride gas was then bubbled into the ether solution for one hour, at this same temperature. At the

end of this time, a dark brown gummy mass had settled to the bottom of the test tube. This substance was probably a polymer of acenaphthylene. Since this substance was insoluble in ether, and both the dichloro compounds are readily soluble in ether, the experiment was discontinued.

Reaction of N-Chlorosuccinimide on Acenaphthene

This reaction was carried out by a method analagous to that of Greene, Remers and Wilson (35) for the formation of 1,2-dibromoacenaphthene.

A mixture of acenaphthene (2g.), N-chlorosuccinimide (4g.), and benzoyl peroxide (5mg.) in carbon tetrachloride (10 ml.) was heated at reflux for 30 minutes. At the end of this time, the suspension was still white colored, and no visible reaction took place. The mixture was cooled, filtered, and the filtrate taken to dryness. This gave a white solid which was found to melt at 95°C. A mixed melting point with this compound and acenaphthene gave no depression.

A series of experiments were then carried out, using successively higher temperatures for the reaction. The solvent used was 1,1,2,2-tetrachloroethane. A reaction was found to occur at about 110°C. The products isolated from this reaction by the above methods, were 1-monochloroacenaphthylene and unchanged acenaphthene. If a dichloroacenaphthene were formed, it readily lost hydrogen chloride at this temperature.

Partial Resolution of 1,2-Dibromoacenaphthene

This is the method employed by Greene, Remers and Wilson (35) for definitely establishing the configuration of the trans-1,2-dibromoacenaphthene.

A solution of 1,2-dibromoacenaphthene (1.56g. (0.005 mole))and brucine (1.16g. (0.0025 mole)) in chloroform (10ml.) was left at room temperature for 64 hours. The chloroform was removed under reduced pressure, and the residual oil was treated with ether and 2N hydrochloric acid. The ether layer was extracted twice with 2N hydrochloric acid, with water, dried over magnesium sulfate, filtered, and the solvent removed under reduced pressure, leaving a semi-solid. Several recrystallizations from pentane gave colorless crystals melting at 125°C. A mixed melting point with this material and the racemic mixture gave no depression.

A solution of this partially resolved material (0.22g.) in chloroform (8ml.) was prepared. A portion of this solution was examined in the polarimeter, in a tube of length 2 dm. A rotation of -2.5° was observed. This corresponds to $[\alpha]_D = -45°$.

Attempted Partial Resolution of the 115°C. 1,2-Dichloroacenaphthene

The previous method outlined above was used on the 1,2-dichloroacenaphthene.

A solution of 1,2-dichloroacenaphthene (2.264g.) and brucine (2.27g.) in chloroform (10ml.) was left at room temp-

erature for 64 hours. The chloroform was removed under reduced pressure, and the residual oil treated with ether and 2N hydrochloric acid. After drying the ether and removing the solvent, the solid remaining was recrystallized several times from pentane. This gave crystals melting at 115°C.

A solution of this material (.240g.) in chloroform (8ml.) was prepared, and examined in the polarimeter. There was no rotation obtained from this material.

A series of experiments was then carried out, using increasingly larger amounts of the 1,2-dichloroacenaphthene in the reaction, and also increasing the amounts of this material in the chloroform solution to be put into the polarimeter. The amounts of 1,2-dichloroacenaphthene and of brucine were increased up to 14.4g. of the dichloro compound and 17.2g. of brucine. This also gave no rotation in the polarimeter.

Experiments were also carried out in which the 1,2-dichloroacenaphthene was refluxed gently with brucine. This also produced no rotation.

Attempted Partial Resolution of the 64°C. melting 1,2-Dichloroacenaphthene

1,2-Dichloroacenaphthene (2.942g.) and brucine (3.88g.) were dissolved in chloroform (20ml.) and left at room temperature for four days. The chloroform was removed under reduced pressure, and the residual oil treated with ether and 2N hydrochloric acid. After drying the ether and removing

the solvent, the solid remaining was recrystallized several times from pentane. This gave crystals melting at 64°C.

A solution of this material (0.7g.) in chloroform (6ml.) was prepared and examined in the polarimeter. There was no rotation obtained from this compound.

Attempted Preparation of 1,2-Iodoacenaphthene

This experiment depended on the fact that sodium iodide is soluble in acetone, whereas sodium bromide is not.

Sodium iodide was dissolved in cold acetone. 1,2-dibromoacenaphthene was also dissolved in this same solution. Upon gentle heating, a solid (sodium bromide) settled out of the solution, and the solution changed color from colorless to yellow, and then to dark red.

The sodium bromide was filtered and the solvent removed under reduced pressure. The solid residue was extracted with ether and washed with water. After drying and removing the solvent, the resulting solid was recrystallized from alcohol, yielding a very small amount of a pale brown powder (0.1g.). This was found to melt at 248-250°C. This material could be a polymer of acenaphthylene, or perhaps naphthalic acid.

Preparation of Acenaphthylene Glycols by Hydrolysis of 1,2-Dichloroacenaphthene

1,2-Dichloroacenaphthene (5g. melting point 115°C.)

was boiled under reflux with water (75ml.) for two hours. After refluxing, the hot solution was filtered to remove any unaltered dichloride. The filtrate was treated with charcoal, filtered while hot, and then allowed to cool. Upon cooling, 1.5 gm. of a white crystalline solid separated from the solution. It melted at 207-208°C. This corresponds to the cis-glycol, melting at 209-210°C. The filtrate obtained after the separation of the cis-glycol was allowed to evaporate until it was reduced to a small volume. Further crystallization occurred to yield 1.2g. of a white solid, melting at 155-157°C. This corresponds to the trans glycol, melting point 159°C.

Reactions of Phosphorus Trichloride on the Glycols

Cis acenaphthylene glycol (1g.) was dissolved in dioxane. Hydrolysis of the solution and subsequent ether extraction failed to yield any soluble material.

The experiment was also tried in ether solution, but the glycol would not dissolve in ether, and hence no reaction took place.

The glycols are soluble in phosphorus trichloride, and upon extraction, yield an oil which will not crystallize.

Preparation of Perbenzoic Acid

Perbenzoic acid was prepared by the method given in "Reactions of Organic Chemistry" - Hickinbottom, page 231-2.

Finely ground benzoyl peroxide (62g.) was suspended in dry toluene (800ml.) in a 3-litre flask equipped with a stopper, and cooled to below -5°C. by means of a freezing bath. An ice cold solution of sodium ethoxide (12g. of sodium in 250ml. of absolute ethyl alcohol) was added and the mixture was stirred vigorously. When all of the ethoxide had been added, 1 litre of ice-cold water was added and the contents of the flask were stirred until all of the benzoyl peroxide had disappeared. The toluene layer was separated in a cooled separatory funnel, and the aqueous layer was extracted with ether. The sodium salt of perbenzoic acid was present in the aqueous layer which was cooled to 0°C. and acidified by the cautious addition of an ice-cold solution of sulfuric acid (27g.) in water (25ml.). The perbenzoic acid separated as a thick oil which was extracted by three 150ml. portions of chloroform. The chloroform extract was dried over anhydrous sodium sulfate, and kept in an ice chest until required.

The Reaction of Perbenzoic Acid and Acenaphthylene

Acenaphthylene (10.5g.) was added to the chloroform solution (275ml.) of perbenzoic acid in a 500ml. round bottom flask. The flask was stoppered and allowed to stand at room temperature until reaction was completed, as shown by titration of a sample of the solution with sodium thiosulfate solution. The flask was shaken occasionally. The reaction was complete in 5 days. The chloroform solution was washed with dilute

sodium hydroxide solution until the alkaline washings ceased to produce benzoic acid upon acidification with hydrochloric acid. The solution was then washed free of alkali with water, and finally dried over anhydrous sodium sulfate. The chloroform was evaporated under reduced pressure. During the evaporation of the chloroform, a heavy white solid settled out of solution. This was filtered off, and further evaporation of the solvent yielded more of this white solid which melted at 170-175°C. A recrystallization from chloroform gave white crystals which melted at 188-190°C. The yield of this material was (7g.). An analysis of the compound indicated that it might be acenaphthylene glycol monobenzoate.

Analysis:	Calculated	C,74.21	H,4.81
	Found	C,77.36	H,4.85

Preparation of Acenaphthylene Glycol Monobenzoate

The method followed was that outlined by T. Ewan and J. B. Cohen (22).

The silver benzoate used in this preparation was prepared according to A. A. Noyes and O. Schwartz (47). Benzoic acid was added to a solution of sodium carbonate. This solution was then boiled until it was free from carbon dioxide. The solution was then treated with silver nitrate, and the resulting precipitate crystallized twice from hot water, yielding fine snowy white silver benzoate (5g.).

1,2-Dibromoacenaphthene (1g.) was dissolved in ether, and silver benzoate (1.44g.) added. The reaction took place at

room temperature. The product was collected, and the ether evaporated. The product was recrystallized from methyl alcohol. It melted at 188-190°C. The yield of material was (0.7g.)

A mixed melting point of this acenaphthylene glycol monobenzoate, and the product obtained from the perbenzoic acid oxidation of acenaphthylene, gave no depression.

Preparation of Acenaphthenol

Acenaphthenol was prepared by the method of Fieser and Cason (23).

Acenaphthenol acetate (170g.) was refluxed with sodium hydroxide (40g.) in a mixture of water (400ml.) and methyl alcohol (275ml.) for two hours. Crystalline acenaphthenol began to separate almost immediately, and the liquor acquired a dark violet color, probably due to the presence of acenaphthenone. After cooling to room temperature, the precipitated product was collected, washed with water and then dried overnight in a vacuum desicator. The crude acenaphthenol was dissolved in hot benzene (1 liter), treated with charcoal and cooled. The first crop of crystals thus obtained were in the form of colorless needles melting at 145°C. The yield was 119 g. Further evaporation of the solvent to one-third of its original volume, yielded a second crop of crystals weighing 3g. and melting at 142-145°C. The overall yield was 122g.

Preparation of Acenaphthenone

The method of Fieser and Cason (23) was used in this preparation.

A suspension of acenaphthenol (100g.) in glacial acetic acid (300ml.) was maintained in a 1 liter flask by means of a mechanical stirrer. An oxidizing solution was prepared by dissolving chromic anhydride (43g.) in the minimum amount of water, and then diluting with acetic acid (240ml.). The oxidizing solution was added in the course of fifty minutes while maintaining a reaction temperature of 28-32°C. by external cooling. The solution was stirred for an additional hour at this temperature, and then poured into ice water (6 liters). The precipitated ketone was filtered off, washed with water, and then purified by steam distillation. The distillate (35 liters) was cooled below 20°C. and the practically colorless ketone was collected and dried. The yield for one run was 58.0g. Pure acenaphthenone may be obtained by recrystallizing the above product from alcohol. It exists as colorless needles melting at 121°C.

Preparation of o-Nitrobenzalacenaphthenone

Acenaphthenone (2g.) and o-nitrobenzaldehyde (1.9g.) were dissolved in ethyl alcohol (50ml.). A solution of 50% sodium hydroxide (10g. sodium hydroxide in 10ml. water) was added slowly over a period of an hour. The mixture was allow-

ed to stand for 24 hours, and the yellow crystals were then filtered off, washed with water and dried. Recrystallization from glacial acetic acid gave yellow crystals melting at 241-243°C.

Attempted Conversion of the Higher Melting O-nitrobenzalacenaphthenone into the Lower One

It was felt that it might be possible to convert the higher melting isomer into the lower one, by refluxing with alcoholic hydrochloric acid. This method had been used in converting the higher melting benzalacenaphthenone into the lower one (46).

O-nitrobenzalacenaphthenone (1g.) and conc. hydrochloric acid (5ml.) and alcohol (5ml.) were refluxed for one hour. The solution was filtered, washed with water, and recrystallized from glacial acetic acid, yielding a dark brown crystalline substance which melted at 250-257°C. The yield of this substance was (0.3g.).

Mixed melting points indicated that this material was neither of the isomers, nor biacenone or acenaphthenequinone.

Attempted Condensation of Acenaphthenone with Fluorenone

A. Under aldol conditions.

Acenaphthenone (2g.) and fluorenone (2g.) were dissolved in alcohol (50ml.). Dry hydrogen chloride gas was

bubbled through this solution until the solution turned dark red and a solid started separating out. This solid was filtered, recrystallized from glacial acetic acid, and dried. It melted at 255°C. A mixed melting point with biacenone gave no depression.

B. Under alkaline conditions

Acenaphthenone (2g.) and fluorenone (2g.) were again dissolved in alcohol (50ml.). A solution of 50% sodium hydroxide (10g. sodium hydroxide in 10ml. water) was added slowly over a period of an hour. After standing 24 hours, the solid was filtered off, wasned, and recrystallized from glacial acetic acid. This material melted at 256°C. A mixed melting point with biacenone indicated no depression.

SUMMARY

1. The 64°C. melting dichloroacenaphthene isomer could only be obtained by using acenaphthylene which had been prepared by the method of Flower and Miller (24), and could not be obtained from commercial acenaphthylene.

2. The method of Greene, Remers and Wilson (35), for determining the configuration of 1,2-dibromoacenaphthene, failed to give a partial resolution of either of the dichloroacenaphthenes.

3. The hydrolysis of the 1,2-dichloroacenaphthene isomers yielded both of the acenaphthylene glycols from either of the dichloroacenaphthene isomers.

4. The reaction of perbenzoic acid on acenaphthylene failed to yield the expected acenaphthylene oxide. The only product obtained from this reaction was acenaphthylene glycol monobenzoate. This product, together with the mechanism proposed, seems to indicate pretty definitely that acenaphthylene oxide cannot be obtained due to the ring strain involved in its formation.

5. The attempted conversion of the 238°C. melting o-nitrobenzalacenaphthenone into the lower melting isomer (164°C.) met with little success.

6. The condensation of acenaphthene and fluorenone yielded only biacenone, under both acid and alkaline conditions.

RECOMMENDATIONS FOR FUTURE WORK

1. The alkaloids, quinine and ephedrine could be tried, first on the dibromoacenaphthene, and if successful, on the dichloroacenaphthene isomers, to attempt partial resolution.

2. A kinetics experiment might be tried, in which the rate of elimination of hydrogen bromide from 1,2-dibromoacenaphthene could be compared to the rates of elimination of hydrogen chloride from the dichloroacenaphthenes. The trans dichloroacenaphthene should have a rate constant about the same order of magnitude as the trans dibromoacenaphthene, whereas the cis dichloroacenaphthene should have a rate constant considerably different from the previous two compounds.

3. An investigation into the reasons why only the acenaphthylene prepared by the method of Flower and Miller (24) yielded the 64°C. melting dichloroacenaphthene isomer could be conducted.

4. An experiment using hypobromous acid, prepared by the method of Detoeuf (18), could also be tried on the acenaphthylene prepared by the method of Flower and Miller(24).

5. Further experiments could be conducted for attempting to determine the configuration of the o-nitrobenzalacenaphthenones.

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