

SOME CHEMICAL REACTIONS OF ACENAPHTHENE

AND RELATED COMPOUNDS

By

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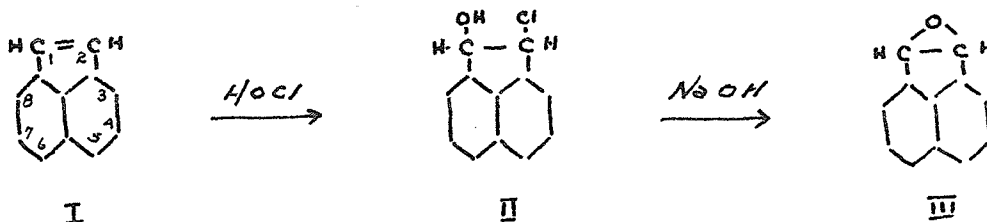
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INTRODUCTION

The present investigation was originally intended to be a continuation of the work ^{it} initiated by J. J. Conn Jr. in 1948 (24). Conn had attempted the preparation of acenaphthylene chlorohydrin (II) as an intermediate in the formation of acenaphthylene oxide (III). The chlorohydrin was to be prepared by the action of hypochlorous acid on acenaphthylene (I).



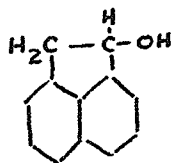
He was unable to isolate any chlorohydrin from the hypochlorous acid reaction mixture, but did however, isolate as a side product, what he believed to be a new 1,2-dichloro-acenaphthene (IV) melting at 64°C. This new dichloro compound appeared to be a geometrical isomer of a similar compound melting at 115°C. prepared by B. A. Campbell in 1915 (20) by the direct chlorination of acenaphthylene in carbon tetrachloride solution.



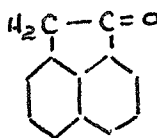
The problem then, was to reinvestigate the above reaction for possible chlorohydrin formation and to prove the

structure and the configuration of the new 1,2-dichloroace-
naphthene (IV).

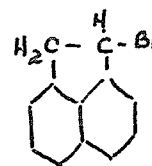
Having carried this problem as far as seemed feasi-
ble, attention was then directed to the reactions of
several other compounds derived from acenaphthene, notably:
acenaphthenol (V), acenaphthenone (VI) and 1-bromoace-
naphthene (VII).



V



VI

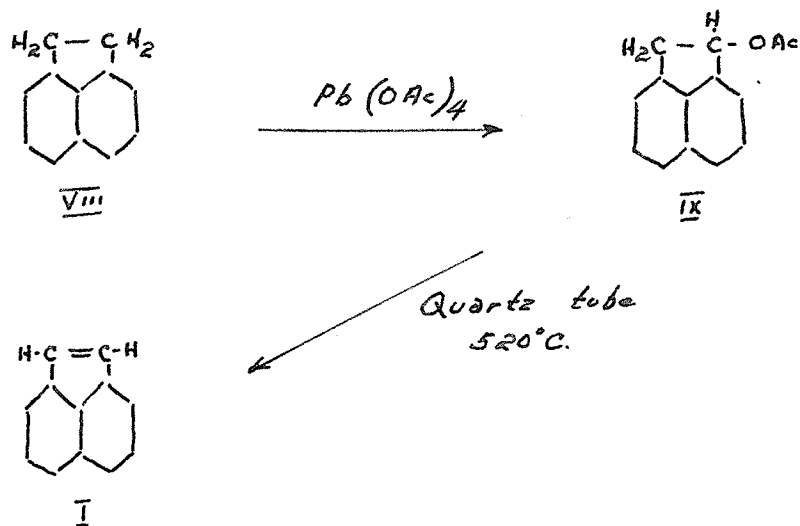


VII

All melting points determined in the course of
this investigation were corrected.

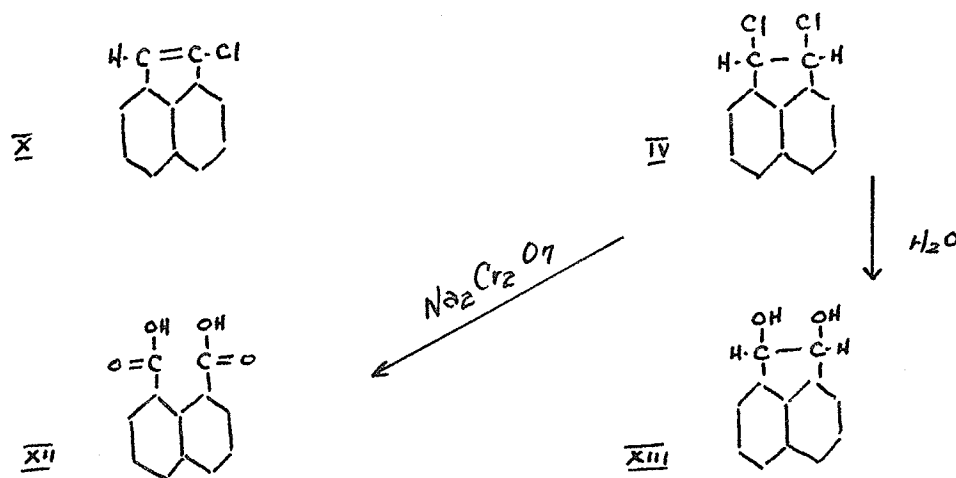
DISCUSSION OF RESULTS

Acenaphthylene (I) was prepared from acenaphthene (VIII) by the method of Flower and Miller (41) with yields of 62%. The method involves the selective oxidation of the 1-position of acenaphthene by lead tetraacetate, thereby giving 1-acenaphthenol acetate (IX). Pyrolysis of this acetate in a heated quartz tube gave acenaphthylene. Vacuum distillation of the crude product gave pure acenaphthylene, melting at 92-93°C.



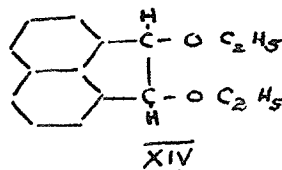
The nature of the double bond in the five-membered ring of acenaphthylene has been investigated with respect to its reaction with hypochlorous acid. The acid was prepared by Detoeuf's (30) and the mercuric oxide method (65). This investigation has revealed little tendency for chlorohydrin formation. In aqueous medium, in which the acenaphthylene is insoluble, the reaction with hypochlorous acid proceeds very slowly, almost paralleling the rate of spontaneous decomposition of the acid. There was extensive

polymerization of the acenaphthylene but the following products were isolated: 1-monochloroacenaphthylene (X), a yellow liquid, boiling point 165-170°C. at 14-15 mm., and a new dichloroacenaphthene (IV) melting sharply at 64°C. In alcoholic solution, the reaction proceeds more smoothly with increased yields but the products are the same. These products were shown to be identical with those obtained by Conn (24). The chlorine atoms in the new dichloroacenaphthene were shown to be in the 1,2 positions by oxidation to naphthalic acid (XII) with sodium dichromate, and also by hydrolysis to the known acenaphthylene glycols (XIII). The new dichloroacenaphthene must therefore be a geometrical isomer of a similar compound, melting point 115°C., prepared by Campbell (20) by the direct chlorination of acenaphthylene.



Attempts to determine the configuration of the two isomeric 1,2-dichloroacenaphthenes were unsuccessful. The configuration of the glycols corresponding to these dichloro compounds was determined in 1938 by Jack and Rule (53).

Their method involved the resolution of the optically active trans form by ester formation with l-menthoxy acetyl chloride. Present attempts to relate the two have met with little success. Direct hydrolysis is rendered useless by the fact that each of the dichloro isomers gives both of the glycols. Treatment of the glycols with various halogenating agents failed to give a crystalline solid containing halogen. Several esters of the glycols are known and they hydrolyze without inversion to the respective glycols. However, ester formation from the dichlorides yielded in both cases the ester of the cis glycol. The dipole moments of the two dichloro isomers did not show enough significant difference to permit identification. The isomers, upon solution in ethyl alcohol and exposure to sunlight, did not undergo interconversion, but rather produced a new compound containing no halogen and melting at 272-273°C. Time did not permit a detailed investigation of the nature of this compound but it seems probable that it is an ether of the type (XIV) or a photochemically produced complex of the dichlorides themselves.

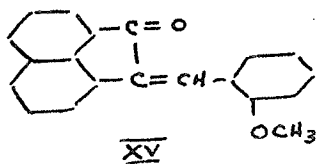


Acenaphthenol was readily obtained by the hydrolysis of acenaphthenol acetate (21), the intermediate in the formation of acenaphthylene. Acenaphthenol reacted with p-nitrobenzoyl chloride and with 3,5-dinitrobenzoyl chloride to yield the corresponding esters. Both existed as light yellow

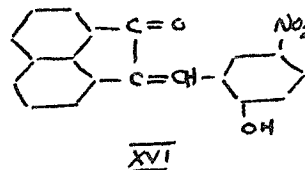
crystals, the former melted at 117.5-118°C., while the latter melted at 166°C. With α -naphthyl isocyanate, acenaphthenol gave colorless crystals of acenaphthenol α -naphthyl urethan, melting at 206°C.

Gault and Kalopissis (42) found that a suspension of acenaphthenol in acetic acid yielded 1-bromoacenaphthene when treated with dry hydrogen bromide. 1-Bromoacenaphthene was prepared by this method in the present investigation and the reactivity of its halogen atom was investigated. It was found to react with Grignard reagents to yield an amorphous material resembling a polymorphic form of acenaphthylene and an uncrystallizable oil. When the bromide was treated with magnesium in dry ether it similarly appeared to undergo decomposition to acenaphthylene with ensuing polymerization rather than forming a Grignard compound.

A study of the condensation reactions of acenaphthenone with various aldehydes in the presence of alcoholic sodium hydroxide was attempted. With o-methoxybenzaldehyde and 5-nitrosalicylaldehyde acenaphthenone yielded the corresponding condensation products: 2-(o-methoxybenzal)-acenaphthenone (XV), and 2-(5-nitrosalicylal)-acenaphthenone (XVI). Under the

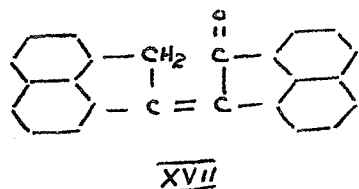


Yellow, needle-like crystals,
melting point 192-192.5°C.



Yellow crystals,
melting point
242-243°C.

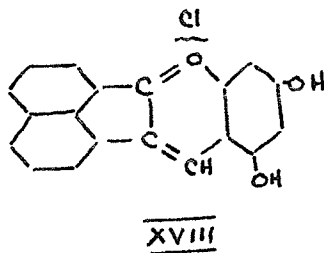
same conditions, m-methoxybenzaldehyde and acenaphthenone gave naphthalic acid (XII), page 4, while m-tolualdehyde condensed with acenaphthenone to yield a compound melting at 274°C. Analysis showed that this compound was not the expected 2-(m-tolual)-acenaphthenone but a substance of a different structure. It contained, C- 71.29%, H- 3.02%. Time did not permit a more thorough investigation of the exact nature of this product. Acenaphthenone showed little tendency to condense with aliphatic aldehydes under these conditions. The main product, both in the condensation with propionaldehyde and with n-butyraldehyde was biacenone (XVII). This compound is formed by the union of two molecules of acenaphthenone with resulting loss of water.



Biacenone (XVII) was also the product obtained when attempts were made to alkylate the active methylene group of acenaphthenone, either with sodium ethoxide in absolute ethyl alcohol or with sodium in benzene.

Phloroglucinaldehyde, prepared by Adams and Levine's modification (2) of Gattermann's hydroxy aldehyde synthesis, was reacted with acenaphthenone in the presence of acetic acid and dry hydrogen chloride in an attempt to form the corresponding pyrylium salt (XVIII). However, the only product obtained from the reaction mixture was an amorphous material, which was

also obtained from phloroglucinaldehyde itself in the presence of dry hydrogen chloride.



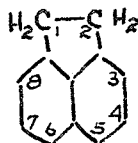
In the presence of alcoholic sodium hydroxide, acenaphthenone did not react with phloroglucinaldehyde to yield 2-phloroglucinalacenaphthenone, but rather condensed with itself to yield biacenone. (XVII).

LITERATURE SURVEY

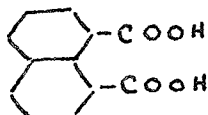
The Chemistry of Acenaphthene

Much of the early history of acenaphthene was a result of investigations carried on by Bertholet. It was he who discovered the compound in 1867 (11) and also synthesized it by the action of acetylene on naphthalene (12) and by heating α -ethyl naphthalene at red heat (13). Fairly large quantities of acenaphthene first became available in 1873 when it was observed to separate in the form of flat prisms from coal tar distillates collected between the temperatures 250-300°C.

Acenaphthene is a white crystalline hydrocarbon, melting at 95°C. and boiling at 278°C. It has the structure shown below. This figure also includes the present accepted numbering system for the carbon atoms of acenaphthene.



Due to its similarity to naphthalene, the structures of acenaphthene and its derivatives were elucidated by oxidation to known derivatives of naphthalene. Oxidation of acenaphthene by dichromate in sulfuric acid solution gives naphthalic acid,

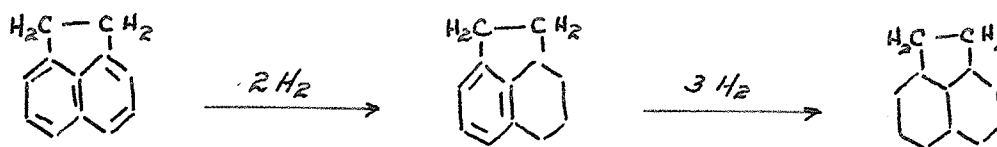


the structure of which was early determined by Bomberger and Phillip (6). Derivatives of acenaphthene with the substituents in the 1,2-positions likewise

oxidize to naphthalic acid. If a substituent is in the six-membered ring then oxidation yields a substituted naphthalic acid. This method has enabled investigators to establish the constitution of all substituted acenaphthenes.

Acenaphthene is a reactive compound and enters into a wide variety of reactions. It forms addition compounds readily, a total of twenty-four have been reported in the literature. Of these, the picrate is possibly the most important and is often used in separating it from mixtures of other hydrocarbons.

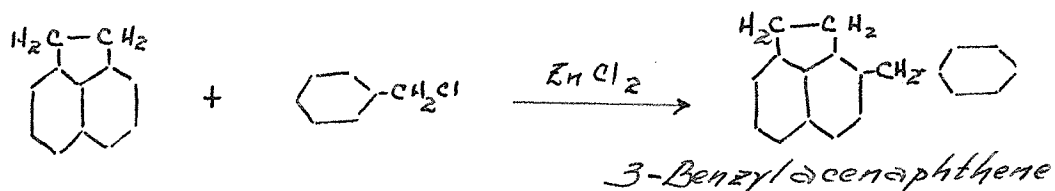
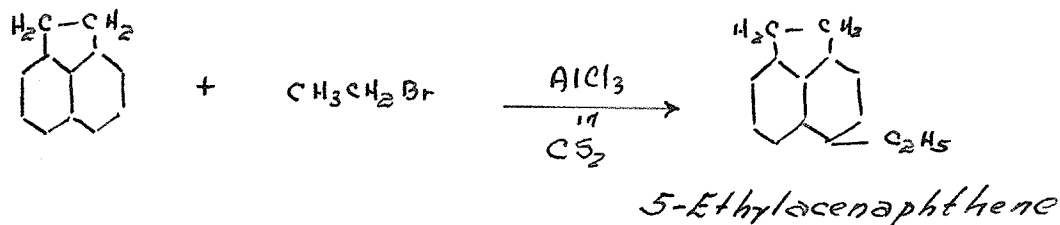
Acenaphthene can be reduced by hydrogen on nickel catalysts to yield tetrahydro- and decahydroacenaphthene.



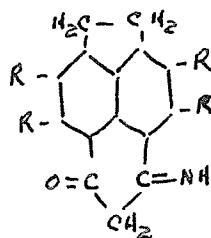
Known substitution products of acenaphthene are numerous but do not of course equal the theoretical number of isomers possible. From inspection of the formula of acenaphthene there should be four different monosubstituted acenaphthenes, with three of these having the substituent in the naphthalene nucleus. Also there should be seventeen disubstituted products, of which nine would have two substituents in the naphthalene nucleus. The positions in the ring most susceptible to attack are the 3 and 5 positions.

Alkylation of Acenaphthene

Like benzene, acenaphthene undergoes the Friedel-Craft and related reactions readily. Examples of compounds formed in this way are:



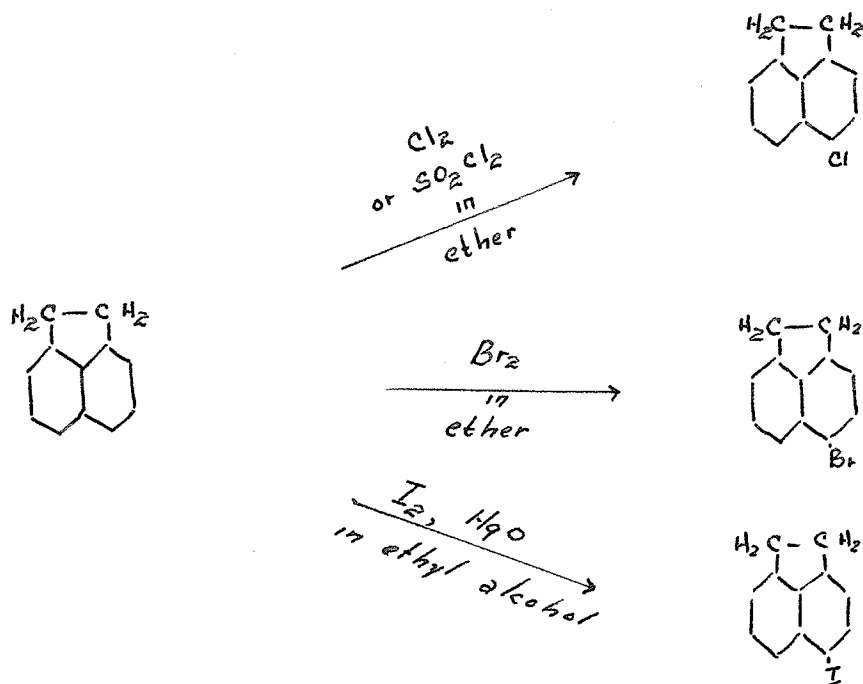
Acenaphthene was found to condense with maleic anhydride, using aluminum chloride in nitrobenzene as a catalyst to yield cyclic ketone carboxylic acids (39). With cyanoacetyl chloride in the presence of the same catalyst acenaphthene gives ketimides of acenaphthene-peri-indandiones, which are useful intermediates for dyes (40). They have the general formula.



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. (18)

Halogen Derivatives

Halogenation of acenaphthene gives rise to products in which the halogen atom may enter the 1 and 2 positions or the naphthalene nucleus. Blumenthal began the investigation of halogen derivatives of acenaphthene in 1874 (16). The results of his investigation and also others which followed: J. T. Kebler (56), E. Bamberger (7), T. Ewan (38) and Compton (23) showed that halogenation of acenaphthene yielded mainly derivatives with the halogen in the 5 position.



By varying the above conditions and means of various catalysts, halogenation has been carried further. Morgan (52) prepared 5,6-dichloroacenaphthene by treating 5-chloroacenaphthene with sulfuryl chloride in chloroform. Di-, tri- and tetrabromo compounds have also been isolated from the products of the reaction of acenaphthene with bromine in chloroform.

Halogen derivatives of acenaphthene in which halogenation has occurred in the 1,2-positions are also known. Jones (57) found that the photochemical halogenation of acenaphthene with chlorine or bromine in carbon tetrachloride solution yielded 1-chloroacenaphthene and 1-bromoacenaphthene respectively. He obtained these derivatives as uncrystallizable oils. However, 1-bromoacenaphthene has also been prepared by other investigators (4, 42) from 1-acenaphthenol and was obtained as a white crystalline solid. The iodine analogue has not been prepared as yet. Both the chloride and the bromide are very unstable substances, losing hydrogen halide readily even at room temperature. The acenaphthylene which is at first formed polymerizes in the presence of the liberated acid to yield its acid polymer. Photochemical bromination of acenaphthene using two moles of bromine yields crystalline 1,2-dibromoacenaphthene, melting point 124°C. The corresponding dichloro compound does not form under these conditions. Both these compounds however, may be obtained by the direct halogenation of acenaphthylene and will be discussed under the chemistry of that substance.

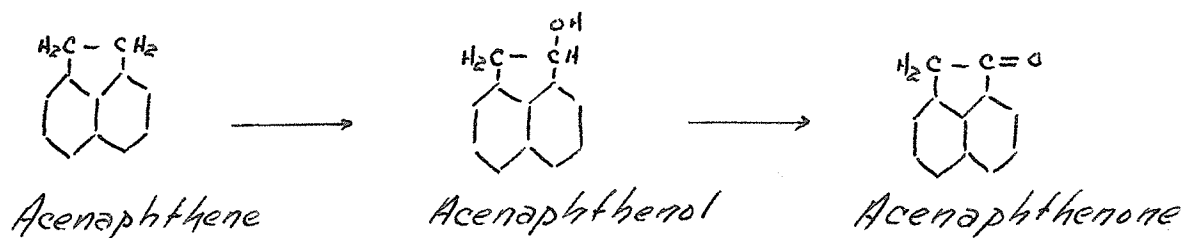
Nitro and Sulfonic Acid Derivatives of Acenaphthene

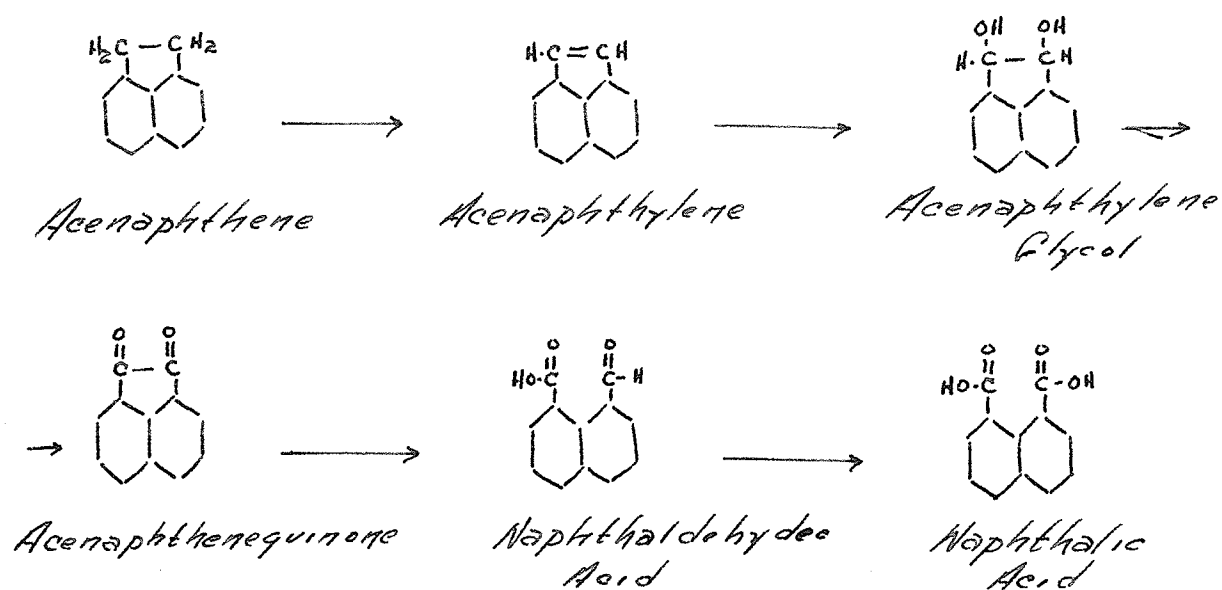
Electrophilic substitution of acenaphthene by these reagents usually takes place ortho or para to one of the methylene groups. Morgan and Sheasby (63) nitrated acenaphthene under both hydrous and anhydrous conditions. They found that hydrous conditions generally yielded para substituted products

and that anhydrous conditions generally resulted in ortho substitution. Early investigation on sulfonation of acenaphthene (64, 36) revealed that the acids obtained depended upon the conditions under which the sulfonation was carried out as well as the nature of the sulfonating agent. Concentrated sulfuric acid on acenaphthene at a low temperature (0°C.) yields chiefly acenaphthene-3-sulfonic acid, while at 100°C. the product obtained is the isomer acenaphthene-5-sulfonic acid. It is interesting to note that fusion of the above sulfonic acids with potassium hydroxide yields not the corresponding hydroxy derivatives but rather acenaphthylene. Presumably the sulfonic acid group migrates to the 1 position and then splits off to yield the unsaturated acenaphthylene.

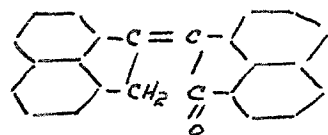
Oxidation Products of Acenaphthene

Oxidation of acenaphthene by dichromate, as was mentioned earlier, usually leads to naphthalic acid. However, by proper modifications in the conditions of the reaction and by the use of other oxidizing agents, acenaphthene oxidation may yield a great variety of products. The oxidation in its various stages may be schematically represented as follows.

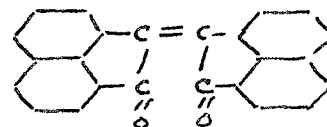




Graebe (49) pioneered in this field of investigation and established the most favorable conditions for the maximum yields of some of the more important products. The primary oxidation products may also give rise to a series of compounds containing two acenaphthene nuclei. Thus acenaphthene may condense with acenaphthenequinone to yield biacenone, while the condensation of acenaphthenone with acenaphthenequinone would yield biacenedione.

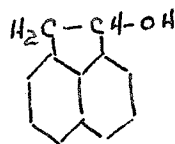


Biacenone



Biacenedione

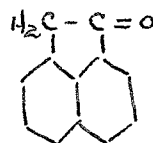
Acenaphthenol



The acetate of acenaphthenol is formed in a yield of approximately 75-80% by oxidation of acenaphthene with lead tetraacetate in acetic acid solution (21). Hydrolysis of the ester with sodium hydroxide in a mixture of water and methanol yields acenaphthenol (21). It crystallizes from alcohol or benzene in the form of colorless needles melting at 146°C.

Acenaphthenol is a stable substance except under the influence of strong dehydrating conditions when it loses water to yield acenaphthylene. When acenaphthenol is treated with thionyl chloride in pyridine solution acenaphthylene is the main product. With phosphorous tribromide in ether solution (4) or with hydrogen bromide in acetic acid (42) acenaphthenol gives 1-bromoacenaphthene. It reacts with acid chlorides readily to yield the corresponding esters. Oxidation with chromic acid gives the ketone, acenaphthenone.

Acenaphthenone



Acenaphthenone crystallizes from alcohol in colorless needles, melting point 121°C. It is volatile in steam and is

usually separated from reaction mixtures in this way. In the presence of alcoholic sodium or potassium hydroxide it gives a red-violet color.

Various methods are available for the preparation of acenaphthenone, acenaphthenequinone being the starting material in most cases: (50,43,68,59,67,69,33,22,8).

Graebe and Jequier (50) developed the first practical method for its preparation. 2,2-Dichloroacenaphthenone, obtained by the interaction of acenaphthenequinone and phosphorous pentachloride, was reduced to acenaphthenone with zinc and acetic acid. The yield obtained was 30%. Ghigi (43) improved the yield to 60% by effecting the reduction with powdered iron in acetic acid.

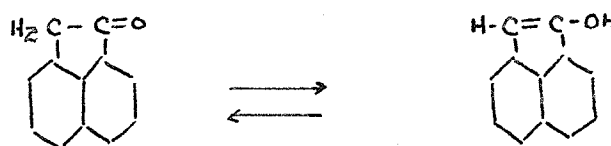
Rule and Thomson (68) obtained acenaphthenone in 45% yield by the reduction of the phenyl hydrazone of acenaphthenequinone with iron and hydrochloric acid.

Another very excellent method is that first developed by Marquis (59) and later used by Fieser and Cason (21) involving the oxidation of acenaphthenol with chromic anhydride in acetic acid. The average yield by this method is about 65% based on the acenaphthenol or 47% based on acenaphthene.

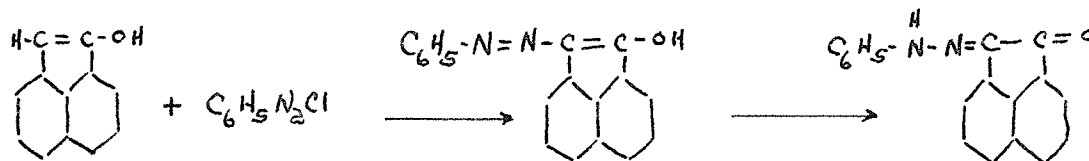
Reactions of Acenaphthenone

Acenaphthenone contains both an active methylene group and a carbonyl group, thus affords many possibilities for reaction. As is common with compounds containing active

methylene groups it reacts with amyl nitrite to yield an oxime, in this case, acenaphthenequinone oxime (46). Also under certain conditions acenaphthenone reacts with Grignard reagents to regenerate the Grignard hydrocarbon. This reaction is typical of compounds of the acetoacetic ester type and has lead Ghigi (44) to propose that acenaphthenone exists in two forms, keto and enol. The enol form has never been isolated



and is known only through its derivatives. Ghigi (45) cites the coupling of diazonium salts with acenaphthenone in alcoholic solution as further evidence for the enol form. The reaction is assumed to proceed as follows.



The product obtained from this reaction is identical with that obtained from the reaction of the corresponding aryl hydrazine on acenaphthenequinone.

The activity of the methylene group in acenaphthenone is well illustrated by the numerous condensation reactions between itself and various aromatic aldehydes. The condensation of acenaphthenone and benzaldehyde in alcoholic alkali is typical of the reactions of this type.

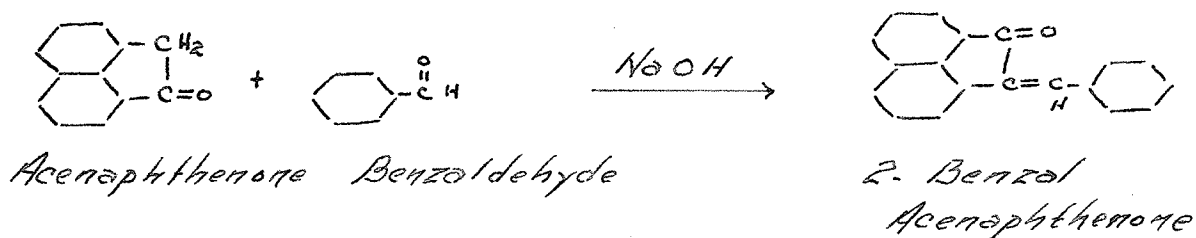


Table I (page 20) lists the reported condensation products of acenaphthenone with aromatic aldehydes in alcoholic alkali. Their formation is in all cases similar to that given above for the condensation with benzaldehyde.

It will be observed that different melting points are given for five products listed in the table. The reason for this discrepancy has not yet been found.

The condensation product with aromatic aldehydes containing an amino or hydroxyl group in the ortho position may undergo ring closure in the presence of dry hydrogen chloride giving 2,3-quinoline or 2,3-pyrylium derivatives respectively (48, 47).

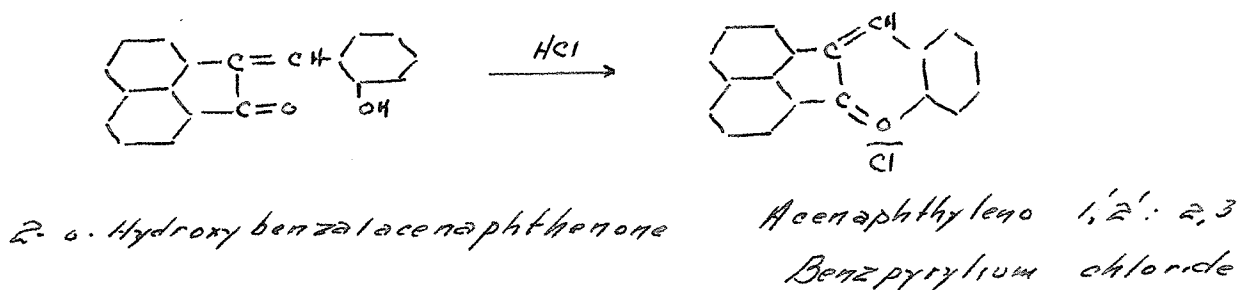
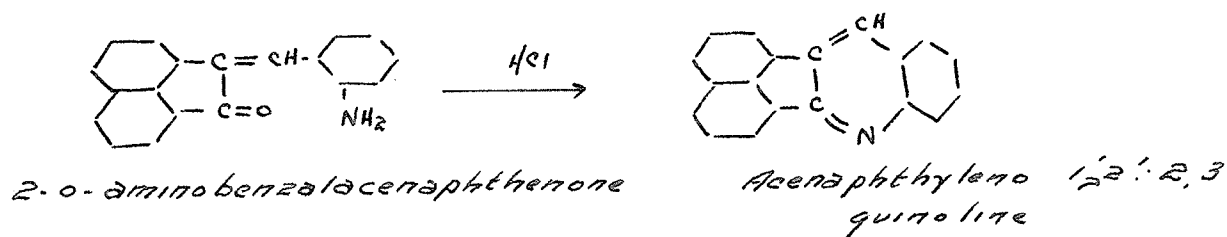
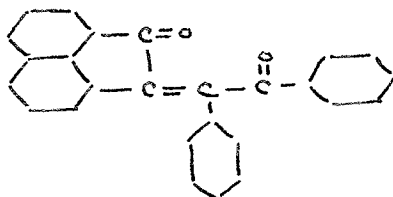


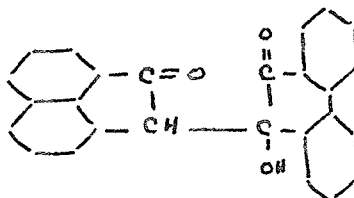
Table I

Aldehyde	Color of Product	M.P.	Reference
Benzaldehyde	Yellow	107	(45)
o-Nitrobenzaldehyde	Yellow	241-3	dec. (29)
		157	(47)
m-Nitrobenzaldehyde	Straw-yellow	177-8	(46)
p-Nitrobenzaldehyde	Yellow	202-3	(29)
		239-40	(46)
p-Acetoaminobenzaldehyde	Yellow	255-6	(46)
p-Dimethylaminobenzal	Garnet	158-60	(29)
o-Hydroxybenzaldehyde	Maroon	168	(29)
		Yellow	186-7 (48)
o-Glucosidoxybenzal	Light yellow	246-8	dec. (29)
m-Hydroxybenzaldehyde	Pale yellow	191-2	(46)
Anisal	Yellow	97-8	(29)
		126-7	(46)
Vanillal	Maroon	149-50	(29)
2,4-Dihydroxybenzal	Red-brown	167-9	dec. (29)
			(48)
Piperonal	Yellow	159-60	(29)
Phenylethyliidene	Orange-yellow	95-7	(29)
Cinnamal	Yellow	167-8	(46)
		214-5	(29)
Furfural	Golden-yellow	142-3	(29)

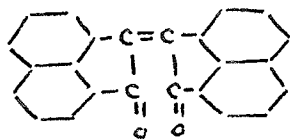
Certain aromatic ketones similarly condense with acenaphthenone. With benzil in alcoholic potassium hydroxide, acenaphthenone yields 2- α -benzoylbenzalacenaphthenone (46).



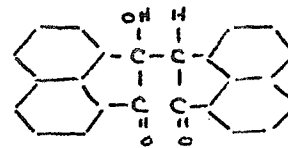
With phenanthrenequinone in acetic acid and sodium acetate the product is the aldol, 2-(10-hydroxyphenanthroxyl)-acenaphthenone (46).



Acenaphthenequinone and acenaphthenone condense in the presence of acetic acid and sodium acetate to produce biacenedione (XIX) and the aldol, 1-hydroxy-2,2'-diketo-1,1'-biacenaphthyl (XX) (46).



XIX

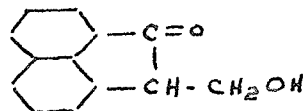


XX

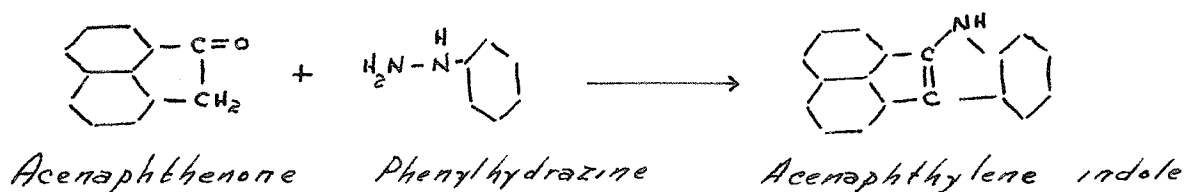
The latter upon heating with acetic anhydride and sodium acetate loses water and gives biacenedione.

With the exception of formaldehyde, no condensation reactions between acenaphthenone and aliphatic aldehydes have so far been reported in the literature. In aqueous medium, in the presence of sodium carbonate or barium hydroxide, form-

aldehyde unites with acenaphthenone to form the corresponding aldol (42).



Acenaphthenone condenses with phenylhydrazine or with methyl phenylhydrazine to yield acenaphthylene indole or 1-methyl acenaphthylene indole respectively (19,47).

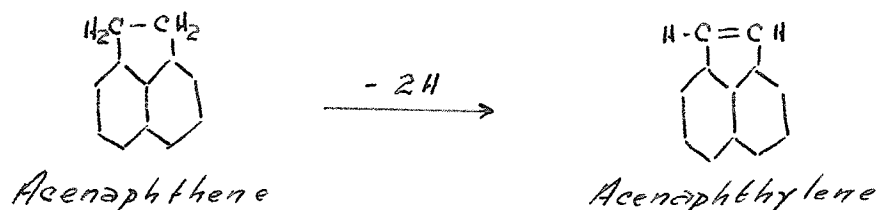


Acid anhydrides react with acenaphthenone in the presence of their sodium salt or in pyridine solution to yield a wide variety of products depending upon the conditions of the reaction (45). The structure of many of the compounds thus obtained is still rather uncertain.

Grignard reagents react with the carbonyl group of acenaphthenone to yield tertiary alcohols (21, 18). Such compounds are relatively unstable and readily lose water to give alkylated acenaphthylenes.

Acenaphthylene

Acenaphthylene is an unsaturated aromatic hydrocarbon closely related to acenaphthene, from which it may be prepared by the loss of two atoms of hydrogen.

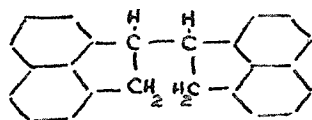


It was first prepared by Bohr and van Dorp (10) by passing the vapor of acenaphthene over red hot lead oxide. Dziewonski and Rapalski (35) merely passed the acenaphthene vapors through a red hot silicon tube and extracted the acenaphthylene from the product as the picrate. These procedures have been widely adopted as laboratory methods of preparation giving variable results (16,22,20,53,17,25). Numerous other methods have been employed by various investigators: (55,37,64,62) but the yields have generally been low. Fieser and Cason (21) found that the oxidation of acenaphthene with lead tetraacetate in acetic acid solution yielded mainly acenaphthenol acetate. Starting with acenaphthenol acetate Flower and Miller (41) have recently evolved an improved method of preparing acenaphthylene. By passing the acetate through a quartz tube maintained at 520°C. acenaphthylene is obtained in 80% yield. This method has the distinct advantage that the product is not contaminated with acenaphthene and may be obtained in a pure state by simple recrystallization.

For continuous large scale production of acenaphthylene, catalytic dehydrogenation of acenaphthene is the most attractive method and lends itself to industrial practice. Flower and Miller (41) have given a brief account of the preparation of acenaphthylene by this method. Acenaphthene vapors,

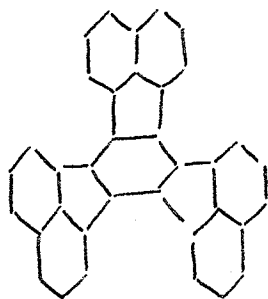
mixed with air, were passed at 450-485°C. over a catalyst consisting of 90% alumina and 10% manganese dioxide, giving a product which after distillation showed a yield of 70% acenaphthylene. Kynaston and Jones (57) have recently made a very thorough investigation of the catalytic dehydrogenation of acenaphthene and have reported yields up to 92% acenaphthylene.

The reactions of acenaphthylene have not been investigated to any great extent. It forms gleaming lemon-yellow plates from alcohol, melting at 92-93°C. With picric acid it yields an addition compound melting at 201°C. Acenaphthylene displays many of the reactions characteristic of an unsaturated compound. With chlorine in carbon tetrachloride solution (20) and with bromine in ether solution (16) it gives 1,2-dichloroacenaphthene and 1,2-dibromoacenaphthene respectively. With iodine in ether solution (20) however, the reaction is not one of addition but rather of polymerization, polyacenaphthylene being formed. Both the dichloride and the dibromide of acenaphthylene are unstable and upon heating tend to lose hydrogen halide yielding the corresponding mono substituted acenaphthylene. Osmium tetroxide reacts with acenaphthylene to give the osmic ester of cis acenaphthylene glycol (26). In the presence of hydrogen chloride and other mineral acids at 100°C. acenaphthylene produces biacene and its acid polymer allo-polyacenaphthylene.

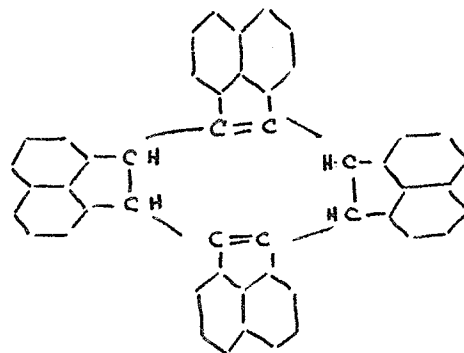


Biacene

At its boiling point acenaphthylene polymerizes to yield polyacenaphthylene together with decacyclene and fluocyclene (32).

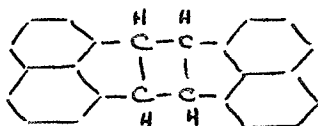


Decacyclene



Fluocyclene

In benzene or ligroin solution acenaphthylene polymerizes photochemically giving α and β -heptacyclene (34).

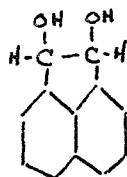


Heptacyclene

Polyacenaphthylene and allo-polyacenaphthylene have the empirical formula $(C_{12}H_8)_n$ and are both amorphous powders. The former melts at 345-350°C. with decomposition while the latter has a melting point of 185-190°C. They are freely soluble in benzene or chloroform but insoluble in alcohol or ether. At its melting point polyacenaphthylene breaks down giving acenaphthylene, acenaphthene, fluocyclene and decacyclene. Oxidation of the polymers with dichromate yields the same product as that obtained from acenaphthylene itself,

namely naphthalic acid. Special interest also attaches to acenaphthylene by virtue of its ability to polymerize and copolymerize with other monomers to give potentially useful plastics (54).

Acenaphthylene Glycol



As is the case with all 1,2 disubstituted acenaphthenes acenaphthylene glycol can exist in two isomeric forms. The geometrical isomerism arising from the fact that the hydroxyl groups can lie above or below the plane of the naphthalene ring. The two glycols, cis and trans, have been isolated.

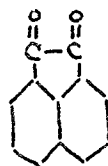
The cis form was first obtained as colorless needles, melting point 212°C . by transforming 1,2-dibromoacenaphthene into the acetate and then saponifying the ester. In 1896 Graebe (50) obtained both forms by direct hydrolysis of the bromide. The trans form exists as colorless needles melting at 159°C . The glycols are insoluble in all common organic solvents but dissolve readily in water, the cis form being much less soluble than the trans form. The two isomeric glycols may also be obtained by reduction of acenaphthenequinone with sodium-mercury in alcohol (15) or with hydrogen over a platinum catalyst (53). They are also the product of the direct oxidation of acenaphthene using selenium dioxide (62).

By inspection of the configuration of these substances it will be seen that the trans form can exist as optical enantiomers. This fact was utilized by Jack and Rule (53) in 1938 in definitely establishing 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.

The glycols react with lead tetraacetate in acetic acid to yield naphthalic dialdehyde hydrate. The cis glycol has a specific rate constant for this reaction at 20°C. approximately 4×10^6 greater than that for the trans glycol. This reaction has been used to determine the configuration of 1,2 disubstituted glycols, which usually show a similar difference in reaction velocities.

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

Acenaphthenequinone



Acenaphthenequinone crystallizes from alcohol in the form of yellow needles melting at 261°C. It is soluble in alcohol, acetic acid or benzene. With sodium sulfide and a trace of water it gives a characteristic blue coloration.

At present, this diketo compound is one of the most important commercial products derived from acenaphthene. It

finds extensive application in the manufacture of dyes. It is an extremely reactive substance and though its reactions are many and varied they have been quite thoroughly investigated.

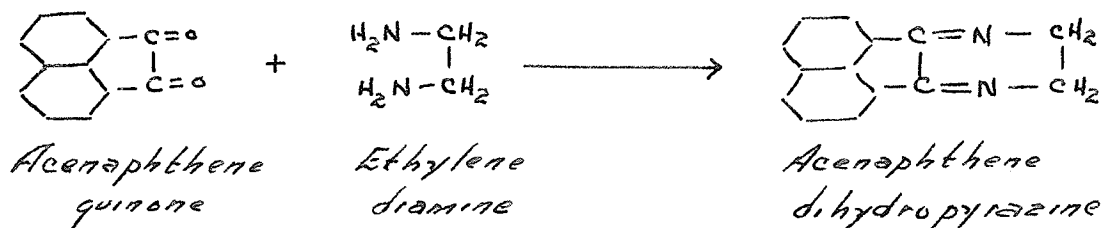
Under suitable conditions the oxidation of acenaphthene by dichromate gives acenaphthenequinone in 40-50% yields (49,27). The speed with which the oxidation proceeds and the conditions of extraction from the reaction mixture must be carefully controlled. The quinone is usually separated as its bisulfite addition product or as its oxime (67), as the use of alkali often causes transformation to a salt of naphthaldehydic acid or to biacenaphthylidenedione (XIX page 21).

Reduction of acenaphthenequinone may yield the mono ketone, acenaphthenone (9) or acenaphthylene glycol (53) depending upon the conditions of the reduction. The reduction to the acenaphthylene glycols affords possibly the best method of preparing these substances.

With Grignard reagents (1,62,5) acenaphthenequinone yields 1,2-dialkyl-1,2-dihydroxyacenaphthenes. These disubstituted glycols undergo pinacol rearrangement giving 2,2-dialkylacenaphthenones when treated with hydrogen chloride in acetic acid.

Acenaphthenequinone, by virtue of its reactive keto groups, enters into many condensation reactions. These may conveniently be divided into four general types. The first involves the condensation with ammonia, amines, hydrazines

and other compounds containing -NH_2 groups. A complete survey of such reactions is beyond the scope of the present work but the following is typical (3).

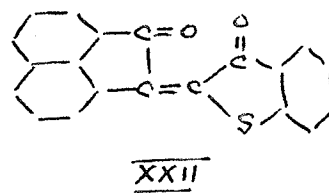
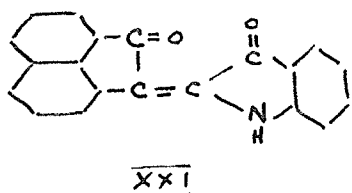


A second type of condensation is that with aromatic hydrocarbons or their derivatives in the presence of aluminum chloride (71). Here the hydrogen atoms of the aromatic coupling compound unite with the carbonyl oxygen of the quinone to eliminate water, forming substances which belong to the fluorescein type dyes.

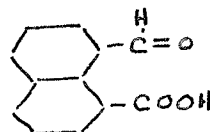
In the presence of phenols and sulfuric acid acenaphthenequinone condenses to yield mainly substituted acenaphthenones. With phenol under such circumstances is produced 2,2-bis-p-hydroxyphenylacenaphthenone (60).

Acenaphthenequinone also condenses readily with carbon atoms containing active hydrogen. Acetone and the quinone in aqueous potassium hydroxide yield 2-hydroxy 2-acetylacenaphthenone (70). Under somewhat similar conditions (66) ethyl acetoacetate yields α -(2-keto-1-acenaphthylidene) acetoacetic acid. Of more commercial importance is the condensation reaction of acenaphthenequinone which leads to indigoid class vat dyes. With indoxyl in sodium carbonate solution or in acetic acid solution it gives acenaphthene-indole-indigo (XXI) (14). With S-phenylthioglycolic-o-carboxylic acid plus acetic anhy-

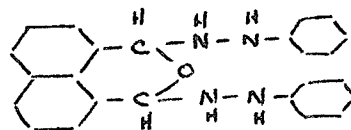
dride or with 3-hydroxythionaphthalene plus hydrogen chloride in acetic acid acenaphthenequinone yields acenaphthene-thio-naphthene-indigo (XXII) (14). The latter product is sold by the Ciba Co. under the trade-name of Ciba Scarlet.



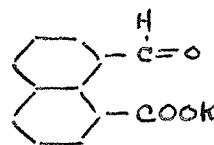
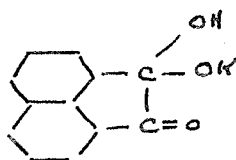
Napthaldehydic Acid



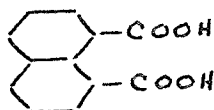
This compound is formed in almost quantitative yields when acenaphthenequinone is dissolved in 30% aqueous potassium hydroxide solution (49). The free acid may be precipitated by the addition of mineral acids and purified by recrystallization from alcohol. It reacts with phenylhydrazine to give a compound of the following structure.



Salts of naphthaldehydic acid appear to exist in two isomeric forms.



Naphthalic Acid



Naphthalic acid is the normal end product of the oxidation of acenaphthene with dichromate, and may under suitable conditions be obtained in almost 100% yields (49). If however, the oxidizing conditions become too severe or are too prolonged the naphthalic acid decomposes to smaller oxidative fragments. When heated, naphthalic acid readily loses water to form a monomeric anhydride. In the presence of concentrated sulfuric acid it gives a characteristic blue fluorescence.

EXPERIMENTAL

Preparation of Acenaphthenol Acetate

Acenaphthenol acetate was prepared by the method of Fieser and Cason (21).

Acenaphthene (154 gm.) 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 gm.) was added in portions of about 50 gm. 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 liters) and the acetate was extracted with two portions of ether (350 ml. and 250 ml.). The total extract was washed first with water (100 ml.) and then with a saturated solution of sodium chloride (300 ml.) and was finally dried over anhydrous sodium sulfate (50 gm.). The sodium sulfate was removed by filtration and washed colorless with three portions of ether (50 ml.). After removal of the ether, the acetate was distilled under reduced pressure, the fraction boiling between 180-190°C. at

16 mm. being collected. The average yield over several runs was 171 gm. 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 (41).

The apparatus for the pyrolysis of acenaphthenol acetate was set up as shown on page 35. 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, the current being controlled by a variable rheostat. The appropriate setting of the rheostat 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 vapors 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 average yield was 75-80% based on the acenaphthenol acetate. The purification of the crude product may be greatly simplified by vacuum distillation using hydroquinone as a polymerization inhibitor. The distillate is almost pure acenaphthylene, boiling point 135-140°C. at 15-16mm., but yields are somewhat lower due to partial polymerization of the acenaphthylene.

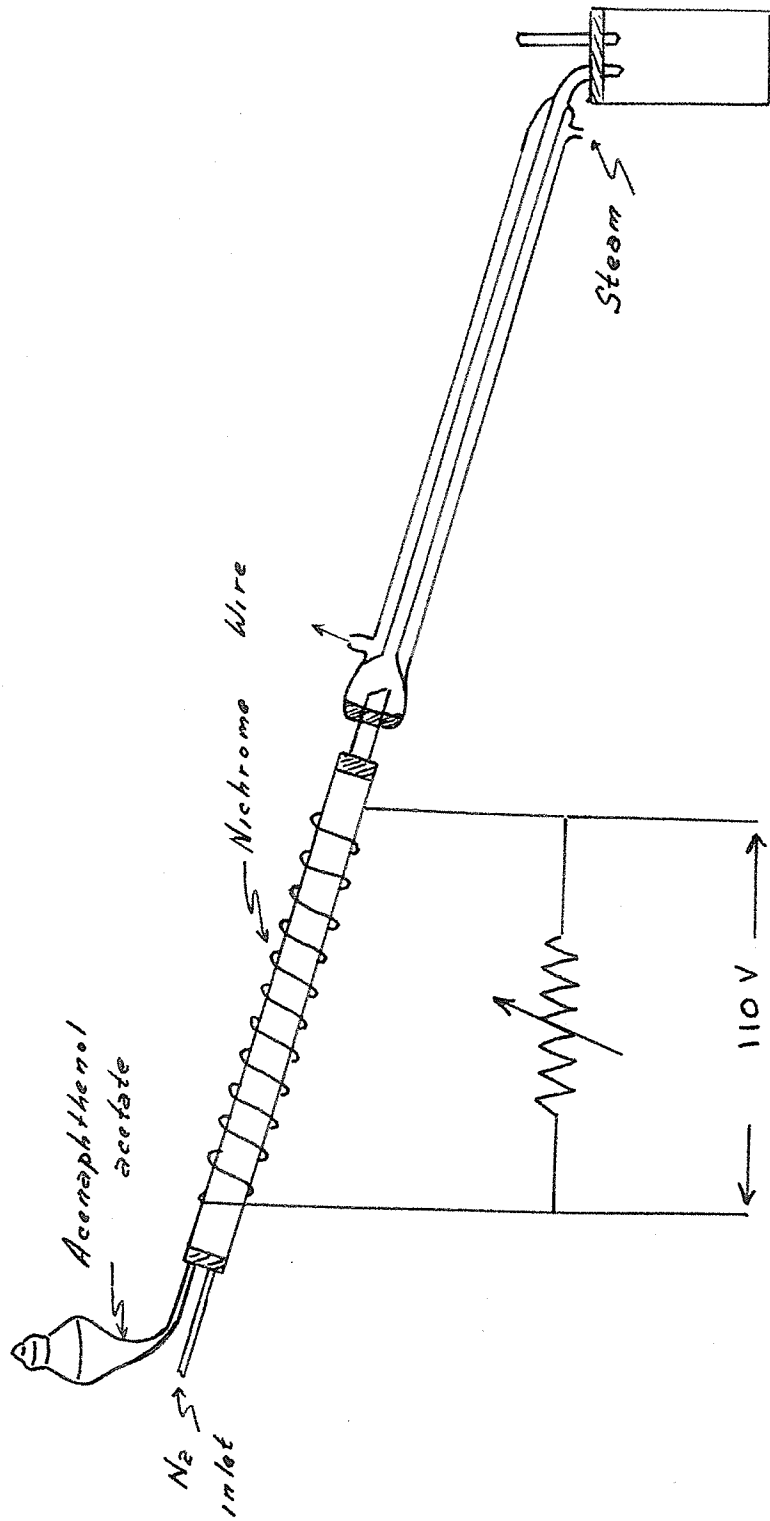
The optimum rate of flow of the acetate appeared to be when the vapor issuing from the pyrolysis tube was thin and pale orange in color. On the average, about two hours were required to put 100 gm. of acetate through the tube. The efficiency of the tube is somewhat reduced by carbonaceous deposits and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

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

Preparation of Hypochlorous Acid

A. Detoeuf's Method (30)

Precipitated chalk (28 gm.), urea (40 gm.) and water (31 ml.) were placed in a 250 ml. Erlenmeyer flask fitted with an inlet tube extending below the surface of the liquid and an 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 approximately 25 gm. 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 200 ml. with water and then filtered. The filtrate was stored in the ice chest until required but could not be kept for a period greatly exceeding twenty-four hours.

The potential hypochlorous acid content of the solution was determined in the following way. A 1 ml. sample of the solution was placed in a 250 ml. Erlenmeyer flask, diluted with water (25 ml.) 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 but the following data is typical.

1 ml. HOCl solution = 40.2 ml. of N/10 Na₂S₂O₃

Therefore, 1000 ml. of solution would contain

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

B. Mercuric Oxide Method (65)

Mercuric chloride (3.1 gm.) was dissolved in water (62 ml.) in a 500 ml. flask and cracked ice (100 gm.) was added to the cool solution. A cold solution of sodium hydroxide (23.7 gm.) in water (62 ml.) was added and a rapid stream of chlorine gas from a cylinder was passed into the

mixture. During the addition of chlorine the flask was cooled externally to prevent the temperature from rising above 5°C. When the yellow color of the mercuric oxide had just disappeared the stream of chlorine was stopped and the solution was diluted with 75 ml. of cold nitric acid (1.5 N) with stirring. The hypochlorous acid content of this solution was determined by titration with thiosulfate as explained above. Only one run was made using this procedure and it was found to contain 3.4% hypochlorous acid.

Reaction of Hypochlorous Acid with Acenaphthylene

The reaction of hypochlorous acid with acenaphthylene was studied under the following conditions.

Reaction Medium	Method of HOCl Preparation	Proportion of Reactants
I Water	Detoef	Excess HOCl
II Water	"	Stoichiometric
III Alcohol	"	Excess HOCl
IV Water	Mercuric oxide	Stoichiometric

I

Acenaphthylene (25 gm.), 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 usual manner. No visible

reaction occurred in the first six 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 concentration 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 mixture was 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 16.0 gm. of a dark brown oil. The oil was placed in the ice chest for several days but no crystals appeared. Distillation under reduced pressure gave 14.7 gm. of 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 centrifuged for one hour and then filtered. Further solid was separated from the filtrate by repeatedly dissolving it in alcohol and allowing to crystallize. Using these methods a total of 4.8 gm. of light yellow crystals were obtained from the oil. After being recrystallized from alcohol using decolorizing carbon they appeared as fine white needle-like crystals, melting sharply at 64°C. A mixed melting point of this solid with the similar compound obtained by Conn (24) showed no

depression. His investigation showed that this compound corresponded in chlorine content to a dichloroacenaphthene. After separation of the solid the remaining yellow oil was redistilled under reduced pressure to yield a product boiling at 165-170°C. at 13-14 mm. The yellow oil formed a picrate derivative upon treatment with a saturated solution of picric acid in alcohol. This picrate melted at 152-153°C. A mixed melting point of this picrate and that of 1-monochloroacenaphthylene was found to be 151-152°C. No further products could be isolated from the yellow oil either by fractional distillation or crystallization.

II

Acenaphthylene (25 gm.), hypochlorous acid (262 ml. 3.3%) and glacial acetic acid (15 ml.) were placed in a 500 ml. flask and stirred slowly with a mechanical stirrer for six hours. The flask was shielded from direct sunlight over the course of this reaction. At the end of this period the stirrer was stopped and the flask was placed in the dark until the test for hypochlorous acid was negative. The reaction mixture was then extracted with ether as outlined in I. The product obtained from the ether extraction after removal of the solvent was a viscous brown oil weighing 10 gm. Vacuum distillation revealed that the oil contained 50% of its weight as unreacted acenaphthylene. The remainder was a light yellow oil similar in properties to that obtained from I.

III

Acenaphthylene (25 gm.) was dissolved in ethyl alcohol (125 ml.) and glacial acetic acid (15 ml.). To this solution was added hypochlorous acid (125 ml., 14%). The suspension was stirred for six hours and then allowed to stand in the dark for four days. The reaction mixture was then diluted to 500 ml. with water and extracted with ether. The ether extract was treated as in I. Removal of the ether under reduced pressure yielded 20.1 gm. of a dark brown oil. No crystallization occurred upon being placed in the ice chest for five days. Vacuum distillation of this product gave a light yellow oil, boiling point 175-180°C. at 14 mm. and similar in properties to that obtained in I except that it yielded a much lower percentage of the white solid, melting point 64°C. No other components could be isolated from the oil.

IV

A suspension of acenaphthylene (25 gm.) in water (25 ml.) was maintained in a 500 ml. flask by means of a mechanical stirrer. Hypochlorous acid prepared by the mercuric oxide method (290 ml., 3.0%) was added in amounts equal to one-quarter that necessary for complete reaction. The reaction per quarter took approximately one and a half hours. By the time the last quarter was added the solid in suspension had turned black and viscous and this last quarter reacted very slowly. After one day the hypochlorous acid was

completely gone. The product in the reaction vessel consisted of a clear liquid and a very gummy black solid. Extraction with ether and other common organic solvents failed to yield any soluble material. It was assumed that a polymerization product of acenaphthylene had been obtained and no further identification was attempted.

Preparation of 1,2-Dichloroacenaphthene

1,2-Dichloroacenaphthene melting at 115°C . was prepared by the method of B. A. Campbell (20).

A solution of acenaphthylene (25 gm.) in carbon tetrachloride (150 ml.) 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 was passed into the solution until an increase in weight of 11.7 gm. 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 12.0 gm. of fine white needle-like crystals, melting point 115°C .



Preparation of 1-Monochloroacenaphthylene

1-Monochloroacenaphthylene was prepared by the method of B. A. Campbell (20).

A solution of sodium metal (1.2 gm.) in absolute ethyl alcohol (70 ml.) was prepared in a 125 ml. round bottom flask fitted with a reflux condenser. 1,2-Dichloroacenaphthene (10 gm.) was added to the solution and the mixture was refluxed for one hour. After cooling, the solution was poured into ice water (150 ml.) and extracted with ether. The ether extract was washed with water, dried over anhydrous sodium sulfate and then distilled under reduced pressure. The product was a light yellow oil, boiling point 165-170°C. at 14-15 mm. Treatment of the oil with a saturated solution of picric acid in alcohol yielded an orange colored addition product melting at 151-152°C.

Photochemical Bromination of Acenaphthene

The procedure used in this reaction is that described by Kynaston and Jones (57).

Acenaphthene (15.4 gm.) was dissolved in carbon tetrachloride (100ml.) in a 500 ml. Pyrex flask fitted with a reflux condenser and a dropping funnel. The funnel contained bromine (32 gm.) in carbon tetrachloride (100 ml.). The apparatus was placed in brilliant sunshine, the solution of acenaphthene was refluxed gently and the bromine solution was added slowly over a period of one-half hour. The reaction

proceeded smoothly with a copious evolution of hydrogen bromide. When all the bromine had been added the solution was evaporated under reduced pressure to half of its original volume. The solution was then placed in the ice chest for four hours and the light yellow crystals which formed were filtered off. After recrystallization from alcohol they yielded 16.5 gm. of white crystals of 1,2-dibromoacenaphthene melting at 123°C.

Photochemical Chlorination of Acenaphthene

This reaction was carried out in a manner analogous to that for the photochemical bromination of acenaphthene. The chlorinating agent was prepared by dissolving chlorine gas (14.2 gm.) in carbon tetrachloride (100 ml.). The partially evaporated solution resulting from the reaction was placed in the ice chest for two days but crystallization failed to occur. Vacuum distillation of this solution proceeded with the evolution of hydrogen chloride and yielded 2.0 gm. of acenaphthylene as the first fraction, boiling point 133-138°C. at 14-15 mm. The second fraction consisted of a yellow oil, boiling point 165-170°C. at 14-15 mm. No solid material could be separated from the yellow oil. It gave a picrate derivative melting at 150-152°C. which indicated that it contained mainly 1-monochloroacenaphthylene.

Attempted Partial Hydrolysis of 1,2-Dichloroacenaphthene

1,2-Dichloroacenaphthene (5 gm., melting point 115°C.) was placed in a small flask to which was added sodium carbonate solution (25 ml.) of the calculated strength for partial hydrolysis and the mixture was stirred mechanically for six hours. The mixture was then allowed to stand at room temperature for two days. At the end of this time no reaction could be observed. The solid was filtered off and found to be essentially unchanged dichloroacenaphthene.

Preparation of Acenaphthylene Glycols

A. Hydrolysis of 1,2-Dichloroacenaphthene

1,2-Dichloroacenaphthene (5 gm., melting point 115°C.) was boiled under reflux with water (75 ml.) 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 206-208°C. This corresponds to the cis glycol, melting point 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 1.2 gm. of a white solid, melting at 154-156°C. This corresponds to the trans glycol, melting point 159°C.

B. Oxidation of Acenaphthene with Selenium Dioxide

Selenium dioxide (155 gm.) was added slowly to fused acenaphthene (100 gm.) heated to 150-170°C. in a 600 ml. beaker. After all the selenium dioxide had been added the mixture was kept at the above temperature for one-half hour. The black sticky mass was allowed to cool to room temperature and was then pulverized in a mortar. Exhaustive extraction of this finely ground material with boiling water yielded upon cooling 3 gm. of a white solid, melting point 205-208°C., corresponding to the cis glycol. The other isomer could not be obtained by further evaporation of the filtrate due to the high amount of inorganic impurities present.

Determination of the Structure of the New Dichloroacenaphthene

The new dichloroacenaphthene (2.0 gm., melting point 64°C.) and sodium dichromate (10 gm.) were dissolved in glacial acetic acid (30 ml.) and refluxed for four hours. At the end of this time the mixture was diluted with water (150 ml.) and the resulting precipitate was filtered off. The precipitate was transferred to a small beaker, leached with sodium carbonate solution and then filtered. The filtrate was decolorized with charcoal and then acidified with hydrochloric acid. The precipitate was purified by a repetition of this process followed by a recrystallization from alcohol. The purified product was a white crystalline solid melting at 268-270°C. It contained no halogen and gave a decided blue

fluorescence in concentrated sulfuric acid. These properties agree with those of naphthalic anhydride, melting point 270°C . The two chlorine atoms in the new dichloroacenaphthene must therefore be in the 1,2 positions and it must be a geometrical isomer of the 1,2-dichloroacenaphthene prepared by Campbell (20) in 1915.

Attempts to Determine the Configuration of the Two Isomeric
1,2-Dichloroacenaphthenes

A. Hydrolysis to the Known Glycols

As was mentioned on page 44 of this work, hydrolysis of 1,2-dichloroacenaphthene melting at 115°C . gave both the cis and trans glycol. This hydrolysis experiment was repeated for the 1,2-dichloroacenaphthene melting at 64°C . and was also found to yield both the isomeric glycols.

B. Reaction of the Glycols with Halogenating Agents

(i) Cis acenaphthylene glycol (2 gm.), fused zinc chloride (2.4 gm.) and concentrated hydrochloric acid (5.5 ml.) were placed in a small flask equipped with a reflux condenser and heated on the steam bath for one hour. At the end of this time the glycol had turned to a dark brown gummy material. Ether extraction failed to yield any soluble product and since the dichlorides are readily soluble in ether the experiment was discontinued.

(ii) A suspension of cis acenaphthylene glycol (1 gm.)

in anhydrous ether (25 ml.) was treated with phosphorous trichloride (0.27 gm.) and allowed to stand at room temperature for twenty-four hours. At the end of this time the glycol had not entered solution and was recovered by filtration.

(iii) Cis acenaphthylene glycol (0.5 gm.) was treated with excess thionyl chloride at room temperature. The mixture was shaken frequently for one-half hour, at the end of which time the glycol had completely dissolved. Hydrolysis of the mixture with water yielded a small amount of brownish material, melting point 135-140°C. Further attempts to obtain more of this material were unsuccessful. The hydrolysis in each case yielded an oily material from which no crystalline material could be obtained. Treatment of 1,2-dichloroacenaphthene (melting point 115°C.) and of acenaphthene with thionyl chloride under the same conditions yielded the starting material upon hydrolysis. The cis glycol was also soluble in phosphorous trichloride and in phosphorous pentachloride. However, as was the case with thionyl chloride the product obtained after hydrolysis was an uncrystallizable oil.

(iv) Cis acenaphthylene glycol (2 gm.), pyridine (20 ml.) and thionyl chloride (1 ml.) were placed in a small flask fitted with a condenser. The reactants quickly entered solution at room temperature but in a moment a white solid separated. Upon gentle heating this solid redissolved and the

solution turned a very dark brown. The warm solution was allowed to stand for fifteen minutes and was then diluted with twice its volume of water. The product separating was a dark brown viscous mass. This residue was dissolved in alcohol, treated with charcoal and allowed to crystallize. A small amount of greyish solid was thus obtained. It had a melting point of 160-170°C. (very indefinite). Sodium fusion showed it to be halogen free. No other crystalline products could be obtained from the reaction mixture.

C. Ester Formation

1,2-Dichloroacenaphthene (2 gm., melting point 115°C.) was added to a solution of potassium acetate (4 gm.) in acetic acid (8 ml.). The mixture was refluxed for one hour and then diluted to twice its volume with water. The resulting precipitate was recrystallized three times from alcohol using decolorizing charcoal to yield fine white needle-like crystals melting at 123°C. This corresponds to the monoacetate of cis acenaphthylene glycol, melting point 123°C.

The above procedure was repeated with the new dichloroacenaphthene and similarly yielded white needles melting at 123°C. A mixed melting point of the two esters thus obtained showed no depression.

D. Dipole Moments

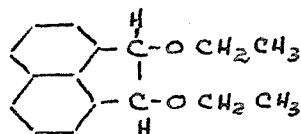
An apparatus similar to that described in J. Chem. Ed. 23: 179. 1946 was used to determine whether any

appreciable differences existed in the dielectric constants of the solutions of the two dichloro isomers and hence in their dipole moments. For this purpose two solutions were prepared. The first contained the new dichloride (0.5 gm.) in benzene (15 ml.) while the second contained the other isomer (0.5 gm.) in the same volume of solvent. The relative dielectric constants of the two solutions were determined. However, due to the low sensitivity of the apparatus used, the difference between the two was found to be no more than the margin of error involved.

Attempted Photochemical Interconversion of
1,2-Dichloroacenaphthene Isomers

Two solutions were prepared, each containing one of the isomers (1 gm.) in ethyl alcohol (50 ml.). The solutions were placed in 100 ml. Pyrex round bottom flasks fitted with reflux condensers. The solutions were exposed to brilliant sunshine for a period of ten days. At the end of this time the solutions were evaporated to one-third of their original volume and then placed in the ice chest. Upon cooling, both solutions yielded a light brown crystalline precipitate. The solids were filtered off, washed with a small amount of alcohol and then recrystallized from this solvent using decolorizing charcoal. The recrystallized products appeared as practically colorless crystals. Both had a melting point of 272-273°C. A mixed melting point of the two derivatives showed no depression. Preliminary analysis showed that the

compound contained no halogen. It was felt that the product was an ether of the type,



or a photochemically produced complex of the dichlorides themselves. Time was not available to proceed further along these lines.

Preparation of Acenaphthenol

Acenaphthenol was prepared by the method of Fieser and Cason (21).

Acenaphthenol acetate (170 gm.) was refluxed with sodium hydroxide (40 gm.) in a mixture of water (400 ml.) and methyl alcohol (275 ml.) for fifteen minutes. The reaction requires a short incubation period but once initiated proceeds to completion almost at once. After cooling to room temperature the precipitated product was collected, washed with water and then dried overnight in a vacuum desiccator. 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 gm. Further evaporation of the solvent to one-third of its original volume yielded a second crop of crystals weighing 3 gm. and melting at 142-145°C. The overall yield was 122 gm. or 72% of the theoretical.

Preparation of Acenaphthenol 3,5-Dinitrobenzoate

Acenaphthenol (2 gm.) was placed in a small flask and dissolved in pyridine (10 ml.). To this solution was added 3,5-dinitrobenzoyl chloride (2.7 gm.). The mixture was warmed over a low flame for two minutes and then poured with vigorous stirring into water (30 ml.). The precipitate was allowed to settle and the supernatant liquid was decanted. The residue was mixed thoroughly with 5% sodium bicarbonate solution (20 ml.), filtered, washed with water and then dried. Several recrystallizations from acetone using decolorizing charcoal yielded 3 gm. of pale yellow crystals, melting point 166°C. Analysis by the semi-micro method revealed: C- 62.35%, H- 3.30%. Calculated for acenaphthenol 3,5-dinitrobenzoate $C_{19}H_{12}O_6N_2$: C- 62.64%, H- 3.32%.

Preparation of Acenaphthenol p-Nitrobenzoate

Acenaphthenol (2 gm.) was dissolved in dry pyridine (10 ml.). p-Nitrobenzoyl chloride (2.18 gm.) was added and the mixture was treated in a manner similar to that outlined for the 3,5-dinitrobenzoate. Three recrystallizations from alcohol using decolorizing charcoal yielded 2.8 gm. of light yellow crystals, melting point 117.5-118°C. Semi-micro analysis showed: C-71.52%, H-4.13%. Calculated for acenaphthenol p-nitrobenzoate $C_{19}H_{13}O_4N$: C- 71.47%, H- 4.10%.

Preparation of Acenaphthenol α -Naphthyl Urethan

Acenaphthenol (3 gm.) and α -naphthyl isocyanate (3 gm.) were dissolved in dry pyridine (15 ml.). The solution was warmed gently for a few minutes and then cooled to room temperature. The urethan readily separated under these conditions and was filtered off. The solid was washed with pyridine and then recrystallized from a hot solution of this solvent. The urethan existed as colorless crystals melting at 206°C. with decomposition. The yield was 4.6 gm. Semi-micro analysis showed: C- 81.20%, H- 5.06%. Calculated for the acenaphthenol α -naphthyl urethan $C_{23}H_{17}O_2N$: C- 81.38%, H- 5.05%.

Preparation of Acenaphthenone

Acenaphthenone was prepared by the method of Fieser and Cason (21).

A suspension of acenaphthenol (100 gm.) in glacial acetic acid (300 ml.) was maintained in a 1 liter beaker by means of mechanical stirrer. An oxidizing solution was prepared by dissolving chromic anhydride (43 gm.) in the minimum amount of water and then diluting with acetic acid (240 ml.). 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 58.6 gm. or 58% of the theoretical. Pure acenaphthenone may be obtained by recrystallizing the above product from alcohol. It exists as colorless needles and melts at 121°C.

Preparation of 2-o-Methoxybenzalacenaphthenone

Acenaphthenone (1 gm.) and o-methoxybenzaldehyde (0.81 gm.) were dissolved in ethyl alcohol (50 ml.) in a 125 ml. Erlenmeyer flask. A solution of sodium hydroxide (5 gm.) in water (5 ml.) was added slowly over a period of two hours. A yellow precipitate formed shortly after the addition of the sodium hydroxide had begun. When all the base had been added the mixture was allowed to stand at room temperature for twenty-four hours and was then filtered. The precipitate was washed with alcohol and then recrystallized from a chloroform alcohol mixed solvent. The condensation product crystallized as orange-yellow crystals, melting point 192-192.5°C. Semi-micro analysis showed: C- 83.79%, H- 4.96%. Calculated for 2-o-methoxybenzalacenaphthenone $C_{20}H_{14}O_2$: C- 83.90%, H- 4.93%.

Preparation of 2-(5-Nitrosalicylal)-Acenaphthenone

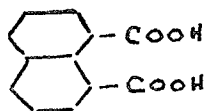
Acenaphthenone (1 gm.) and 5-nitrosalicylaldehyde (1 gm.) were dissolved in ethyl alcohol (50 ml.) and treated

with sodium hydroxide in a manner similar to that outlined above. A dark red solid formed almost immediately and the alcoholic solution became so thick that stirring was no longer possible. One hour after the base had been added the product was filtered and washed with alcohol. Two recrystallizations from acetic acid using decolorizing charcoal yielded 1.2 gm. of fluffy orange-yellow crystals melting at 242-243°C. with decomposition. Semi-micro analysis revealed: C- 71.62%, H- 3.53%. Calculated for 2-(5-nitrosalicylal)-acenaphthenone $C_{19}H_{11}O_4N$: C- 71.92%, H- 3.50%.

Attempted Alkali Condensation of Acenaphthenone with
m-Methoxybenzaldehyde

Acenaphthenone (1 gm.) and m-methoxybenzaldehyde (0.81 gm.) were dissolved in alcohol (50 ml.) and treated with sodium hydroxide following the same procedure as that given for o-methoxybenzaldehyde. No precipitate formed until the mixture had been standing at room temperature for approximately seventy-two hours. The solid was filtered off and washed with alcohol. It was dissolved in water, treated with decolorizing charcoal, filtered and then acidified with hydrochloric acid. The white solid precipitating from the acid solution was washed with water and then dried. It dissolved readily in sodium bicarbonate solution to yield its sodium salt and liberate carbon dioxide. It melted at 274°C. In the presence of concentrated sulfuric acid it gave a yellow color with a

decided blue fluorescence. Analysis showed: C- 66.75%, H- 3.70%. A neutralization equivalent determined by the semi-micro method was 110. All these properties agree closely with those of naphthalic acid, which has the structure.



Calculated for naphthalic acid $C_{12}H_8O_4$: C- 66.65%, H- 3.72%, neutralization equivalent 108.1.

Attempted Alkali Condensation of Acenaphthenone with m-Tolualdehyde

Acenaphthenone (2 gm.) and m-tolualdehyde (1.43 gm.) were dissolved in alcohol (50 ml.) and treated with aqueous sodium hydroxide as outlined above. A white precipitate slowly formed over a period of three to four days. This solid was filtered from the solution, washed well with alcohol and then recrystallized from glacial acetic acid using decolorizing charcoal. Two such recrystallizations yielded 0.9 gm. of fine white needles melting at $274^{\circ}C$. Semi-micro analysis showed: C- 71.29%, H- 3.02%. These figures do not agree with those calculated for 2-(m-tolual)-acenaphthenone $C_{20}H_{14}O$: C- 88.85%, H- 5.22%. Time was not available for a more detailed investigation of the structure of this condensation product.

Reaction of Acenaphthenone with Aliphatic Aldehydes
in the Presence of Alcoholic Alkali

A. With Propionaldehyde

Acenaphthenone (2 gm.) and propionaldehyde (0.70 gm.) were dissolved in alcohol (100 ml.) and treated slowly with a solution of sodium hydroxide (10 gm.) in water (10 ml.). After twenty-four hours a small quantity of light yellow crystals had separated from the solution. They were filtered off, washed well with alcohol and then crystallized from chloroform. The product thus obtained was a yellow solid melting at 260°C. with decomposition. In the presence of sulfuric acid it gave a deep violet color. Semi-micro analysis showed: C- 90.34%, H- 4.43%. These properties indicate that the product of the reaction was biacenone. Calculated for biacenone $C_{24}H_{14}O$: C- 90.54%, H- 4.43%. The structure of biacenone is given on page 15 of this work. It has a melting point of 262°C. Calculated for 2-propionalacenaphthenone $C_{15}H_{12}O$: C- 86.50%, H- 5.81%.

B. With n-Butyraldehyde

The procedure for this condensation and the purification of the product was identical with that given in A. The product, after crystallization from chloroform, existed as yellow crystals melting at 259-260°C. with decomposition. A mixed melting point of biacenone with this substance showed no depression.

Attempted Alkylation of the Active Methylene Group
of Acenaphthenone

Dry sodium metal (0.78 gm.) was added to absolute ethyl alcohol (20 ml.) in a small three-neck flask fitted with a reflux condenser (protected with a calcium chloride tube) and a dropping funnel. When all the sodium had been added the solution was treated with acenaphthenone (5.7 gm.). The solution turned a dark violet immediately and a precipitate formed after a few minutes. A small amount of the solid was withdrawn from the flask and its chemical properties were investigated. It was completely insoluble in water but soluble in chloroform. After being recrystallized from this solvent it melted at 258-260°C. A mixed melting point of this substance and biacenone showed no depression. Since practically all of the original acenaphthenone used in the reaction had precipitated in this manner the alkylation experiment was not continued any further.

Using the same apparatus as described above, the following modification was performed. Pure acenaphthenone (4.4 gm.) was dissolved in anhydrous benzene (50 ml.) and then metallic sodium (0.60 gm.) was added. The result was identical with that obtained in the presence of sodium ethoxide. The acenaphthenone precipitated almost completely in the form of its self-condensation product, biacenone.

Preparation of 1-Bromoacenaphthene

1-Bromoacenaphthene was prepared by the method of Gault and Kalopissis (42).

Acenaphthenol (10 gm.) was dissolved in acetic acid (100 ml.) and then the solution was cooled to 20°C. This temperature or slightly lower was maintained throughout the reaction. An excess of dry hydrogen bromide was passed into the suspension until a heavy precipitate of 1-bromoacenaphthene formed. The mixture was then filtered, washed with a small amount of alcohol, water and finally alcohol again. The resulting white solid was placed in a vacuum desiccator and dried for two to three hours. The yield of dried product was 11.1 gm. or 75% of the theory. It had a melting point of 68-70°C. 1-Bromoacenaphthene is very unstable and fumes readily in moist air.

Attempted Grignard Formation with 1-Bromoacenaphthene

1-Bromoacenaphthene (3.5 gm.), dry magnesium turnings (0.36 gm.) and dry ether (10 ml.) were placed in a dry eight inch test tube fitted with a reflux condenser and calcium chloride tube. A kernel of iodine was added and after gentle warming a vigorous reaction set in. The mixture was refluxed gently for one hour and then it was cooled and poured into dry ice in ether. After evaporation of the carbon dioxide the ethereal solution was washed with dilute hydrochloric acid, water and then with 5% sodium hydroxide solution. Acidification

of the alkaline wash revealed that no acid had been formed in the reaction. The ethereal layer was then dried over anhydrous sodium sulfate and evaporated to a small volume. Addition of alcohol to this solution yielded a light buff colored precipitate. Further attempts to obtain it in a crystalline form were unsuccessful. It had a very indefinite melting point 135-235°C. and appeared to be a mixture of solid acenaphthylene polymers.

Reaction of Grignard Reagents with 1-Bromoacenaphthene

p-Bromotoluene (2.57 gm.), magnesium turnings (0.36 gm.) and dry ether (10 ml.) were placed in an eight inch test tube fitted with a reflux condenser and a calcium chloride tube. After the Grignard had formed the solution was cooled in an ice bath and 1-bromoacenaphthene (3.5 gm.) was added slowly over a period of one-half hour. The solution was kept cold for twenty-four hours, then it was washed with dilute hydrochloric acid, water, sodium bicarbonate and then again with water. The ether solution was dried over anhydrous sodium sulfate and the ether was removed under reduced pressure. The residue was a viscous oil, soluble in petroleum ether and chloroform but insoluble in alcohol. Repeated attempts at crystallization yielded a small amount of amorphous material of very indefinite melting point (130-170°C.). The rest of the product remained as an oil. The oil was dissolved in chloroform and treated with a saturated solution of picric acid in alcohol but failed to yield a picric acid



derivative. The solid of melting point 130-170°C. corresponds to a similar product obtained by Jones (57) by the spontaneous decomposition of the bromide in benzene solution.

The reaction of 1-bromoacenaphthene with the Grignard of α -bromonaphthalene was conducted in a similar manner and yielded the same results.

Preparation of Phloroglucinaldehyde

Phloroglucinaldehyde was prepared by the Adams and Levine modification (2) of the Gattermann synthesis of hydroxy aldehydes.

The zinc cyanide catalyst was prepared by dissolving sodium cyanide (20 gm.) in water (30 ml.) and adding rapidly a solution of dry zinc chloride (35 gm.) dissolved in the minimum amount of 95% alcohol. The resulting precipitate of zinc cyanide was filtered at the pump, washed with a small amount of water, alcohol and finally with ether. The pure white solid was dried in an electric oven at 50-60°C. for four hours.

Phloroglucinol (10 gm., previously dried in the oven at 130°C. for twelve hours) and dry ether (100 ml.) were placed in a three-neck round bottom flask fitted with a reflux condenser (with exit tube to the fume hood), a mercury seal stirrer and an inlet tube extending below the surface of the liquid. The suspension was stirred mechanically and a rapid stream of dry hydrogen chloride was passed in. The hydrogen chloride addition was continued for two hours after the oil

which had at first formed, had solidified. The solid material was then filtered off, washed well with ether and dissolved in hot water (200 ml.). This solution was boiled gently for five minutes, saturated with sulfur dioxide gas and then cooled in an ice bath. 8 gm. of light brown crystals of phloroglucin-aldehyde separated upon cooling. Phloroglucinaldehyde has no definite melting point.

Reaction of Acenaphthenone with Phloroglucinaldehyde in the Presence of Dry Hydrogen Chloride

Acenaphthenone (1 gm.) and phloroglucinaldehyde (1.22 gm.) were dissolved in glacial acetic acid (20 ml.) in a 50 ml. round bottom flask fitted with a reflux condenser and a calcium chloride tube. The flask was cooled in an ice bath and a rapid stream of dry hydrogen chloride was passed into the solution for two hours. At the end of this time the solution had turned quite red in color and a small amount of a red solid material had separated. Addition of ether to the solution caused a further precipitation of this red solid. It was amorphous in appearance and had no definite melting point. A blank run carried out under the same conditions with the exception that no acenaphthenone was added to the mixture, yielded what appeared to be the same reddish amorphous solid. This product was assumed to be a decomposition or condensation product of phloroglucinaldehyde.

Attempted Alkali Condensation of Acenaphthenone with
Phloroglucinaldehyde

This reaction was performed in a manner entirely analogous to that given on page 53. A yellow solid separated shortly after the addition of the base had been completed. It was filtered off, washed with alcohol and then crystallized from chloroform. It appeared as yellow needles, melting point 261-262°C. Semi-micro analysis revealed: C- 90.28%, H- 4.42%. Calculated for biacenone, melting point 262°C., $C_{24}H_{14}O$: C- 90.54%, H- 4.43%. Calculated for 2-phloroglucin-alacenaphthenone $C_{19}H_{12}O_4$: C- 74.99%, H- 3.98%.

SUMMARY

1. This investigation has revealed little tendency for chlorohydrin formation in the reaction between hypochlorous acid and acenaphthylene.

2. The new dichloroacenaphthene melting at $64^{\circ}\text{C}.$, which was first isolated by Conn (24) from the hypochlorous acid reaction mixture, was shown to be a 1,2-dichloroacenaphthene and hence a geometrical isomer of the 1,2-dichloroacenaphthene prepared by Campbell (20) by the direct chlorination of acenaphthylene.

3. Attempts to determine the configuration of the two isomeric 1,2-dichloroacenaphthenes have met with little success. Interconversion was found to occur in all reactions involving the replacement of the chlorine atoms.

4. When dissolved in ethyl alcohol and exposed to sunlight, both the isomeric 1,2-dichloroacenaphthenes gave rise to a new product, melting point $272-273^{\circ}\text{C}.$ The structure of this product has not yet been determined.

5. Three new derivatives of acenaphthenol have been prepared:

(i) Acenaphthenol p-nitrobenzoate, light-yellow crystals, melting point $117.5-118^{\circ}\text{C}.$

(ii) Acenaphthenol 3,5-dinitrobenzoate, pale yellow crystals, melting point $166^{\circ}\text{C}.$

(iii) Acenaphthenol α -naphthyl urethan, colorless needles, melting point $206^{\circ}\text{C}.$ with decomposition.

6. Three new compounds have been obtained from an extension of the condensation reactions of acenaphthenone with aromatic aldehydes:

(i) 2-(*o*-Methoxybenzal)-acenaphthenone, yellow needle-like crystals, melting point 192-192.5°C.

(ii) 2-(5-Nitrosalicylal)-acenaphthenone, yellow crystals, melting point 242-243°C.

(iii) An unidentified compound obtained by the condensation of *m*-tolualdehyde with acenaphthenone, melting point 274°C. Analysis showed: C- 71.29%, H 3.02%.

7. Acenaphthenone has shown little tendency to condense with aliphatic aldehydes in the presence of alcoholic sodium hydroxide. The reaction was predominantly one of self-condensation, yielding biacenone, melting point 262°C.

8. Attempts to prepare a pyrylium salt from the acid condensation of acenaphthenone and phloroglucinaldehyde were unsuccessful. Decomposition of the phloroglucinaldehyde predominated over any tendency for pyrylium salt formation.

RECOMMENDATIONS FOR FUTURE WORK

1. The compound obtained from the condensation of m-tolualdehyde with acenaphthenone in alcoholic sodium hydroxide should be investigated further. A molecular weight determination and an analysis for functional groups should give the necessary clues for its positive identification.

2. Although the alkylation of the active methylene group of acenaphthenone could not be accomplished through its sodium salt, there is a possibility that the desired reaction would go in the presence of an acid catalyst, such as boron trifluoride.

3. The photochemical reaction between 1,2-dichloro-acenaphthene and ethyl alcohol should receive further study and the unknown compound identified. If this product is dependent upon the alcohol used, other homologues of a similar type may possibly be prepared using higher alcohols. The desired photochemical reaction may be promoted by using another solvent, or with the use of ultraviolet light rather than sunlight.

4. Pyrylium salt formation might be effected with the use of 2-O-benzoylphloroglucinaldehyde and acenaphthenone, rather than with the unprotected phloroglucinaldehyde. Robinson (58) used this device for preventing the self-condensation of phloroglucinaldehyde in similar reactions.

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