

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.

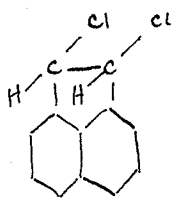
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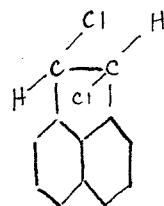
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INTRODUCTION

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 acenaphthylene 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.

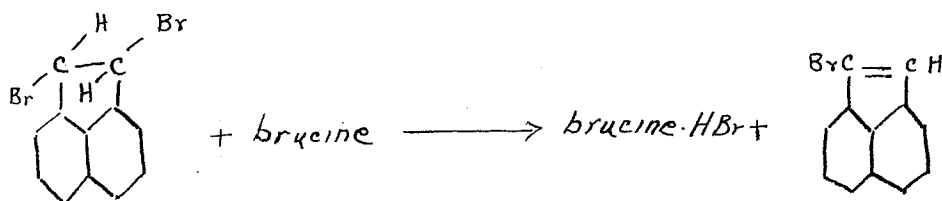


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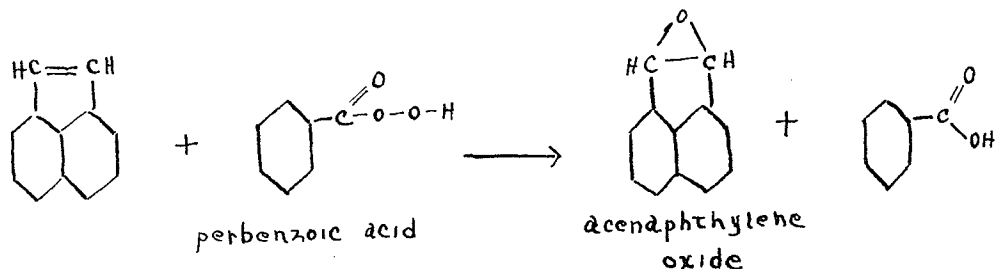
"TRANS"

In 1957, Greene, Remers and Wilson (35) succeeded in determining the configuration of 1,2-dibromoacenaphthene. They used the optically active alkaloid, l-brucine, 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.

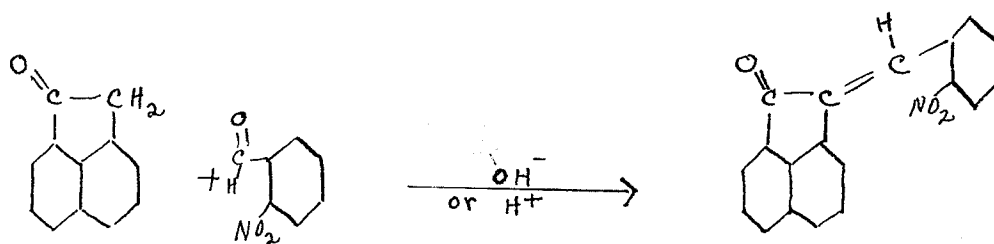


It was proposed that this method of resolution with brucine might be used for determining the configuration of the two dichloroacenaphthenes mentioned above. The cis form would undergo no resolution, whereas the trans isomer should show partial resolution.

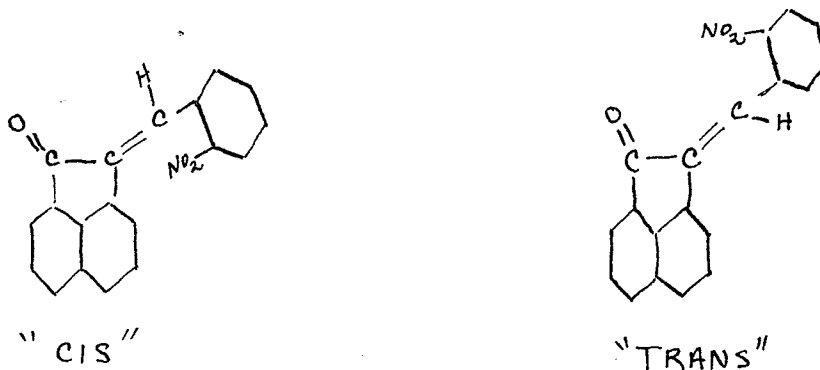
In this investigation, attempts were also made to prepare acenaphthylene oxide by the oxidation of acenaphthylene with perbenzoic acid. This is a standard method of preparing an epoxide ring (45). The reaction would take place as follows.



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.

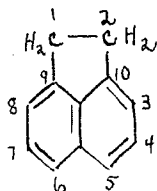


Condensation reactions with acenaphthenone and other substances under both aldol(acid) and Claisen(alkaline) conditions were also tried.

LITERATURE SURVEY

The Chemistry of Acenaphthene

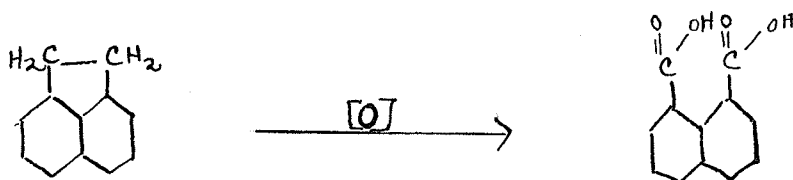
Acenaphthene is a white crystalline hydrocarbon, melting at 95°C., and boiling at 278°C. The accepted structure and numbering system of acenaphthene, according to Patterson's Ring index and Elsevier's Encyclopedia, is shown below.



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.

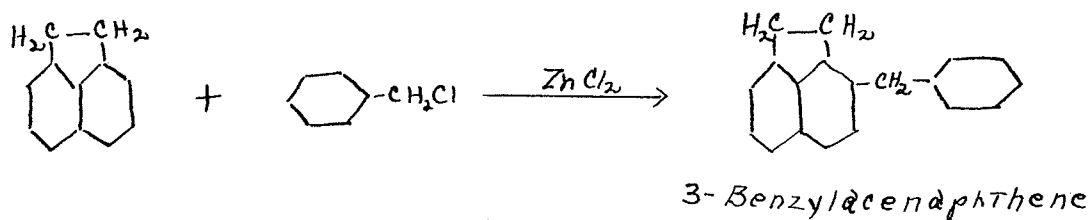
The structure of acenaphthene is very similar to that of naphthalene. Thus, the structures of acenaphthene and of many of its derivatives were determined by oxidation to the known naphthalene derivatives. For example, oxidation of acenaphthene gives naphthalic acid.



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;---

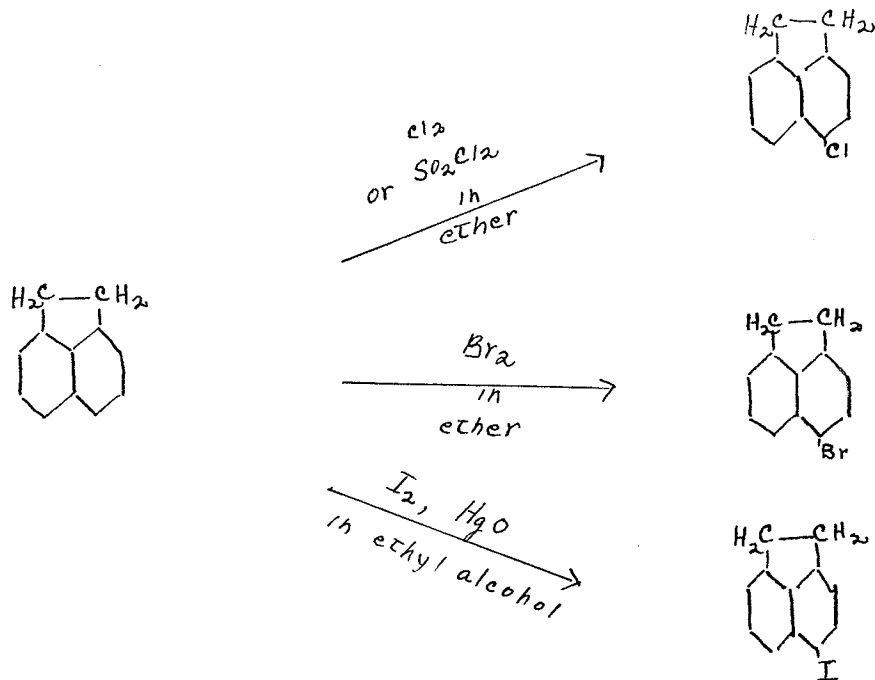


Derivatives of acenaphthene with alkyl or aryl groups substituted in the five membered ring, cannot be

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

Halogen Derivatives

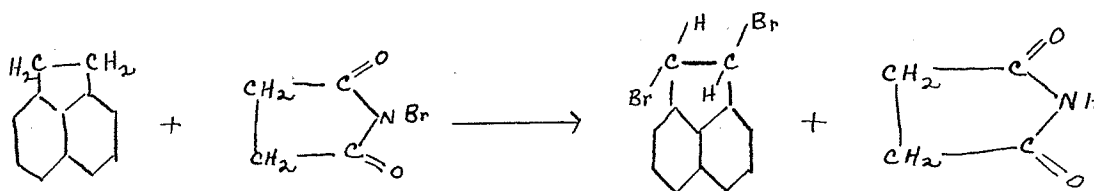
Halogenation of acenaphthene produces products in which the halogen atom may enter either the 1,2-positions, or the naphthalene nucleus. Blumenthal (11), in 1894, investigated some halogen derivatives of acenaphthene. He prepared 1,2-dibromoacenaphthene by brominating acenaphthylene. Other investigators, 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 sulfur chloride in chloroform. Di-, tri-, and tetra bromo compounds have also been prepared.

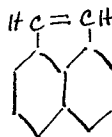
Halogenation of the 1,2-positions has also produced some halogen derivatives of acenaphthene. Jones (41) prepared 1-chloroacenaphthene and 1-bromoacenaphthene by the respective photochemical chlorination and bromination of acenaphthene in carbon tetrachloride solution. These compounds were also obtained 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.

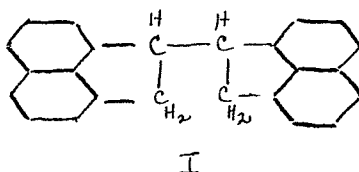
Acenaphthylene



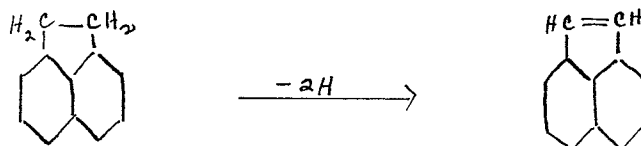
Acenaphthylene forms gleaming yellow plates melting at 93°C. The reactions of acenaphthylene, however, have not been very intensively investigated. The picric acid addition compound melts at 201°C.

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 in ether 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 $(\text{C}_{12}\text{H}_8)_n$.

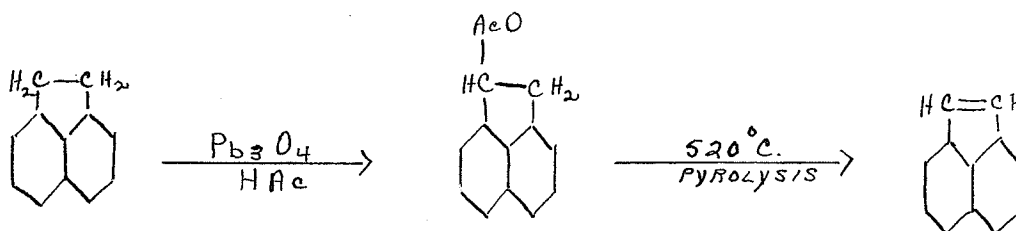


Acenaphthylene is an unsaturated aromatic hydrocarbon which is usually prepared from acenaphthene. It may be prepared from this material by the loss of two hydrogens.



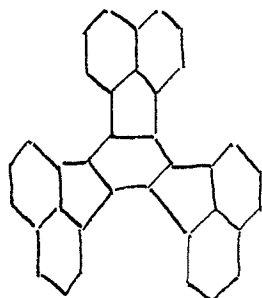
Behr and Van Dorp (6) first prepared acenaphthylene by passing the vapour of acenaphthene over red hot lead oxide. Dziejowski and Rapalski (19) passed acenaphthene vapours through a red hot silicon tube, and extracted the acenaphthylene from the product as a picrate. Numerous other methods have been 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.

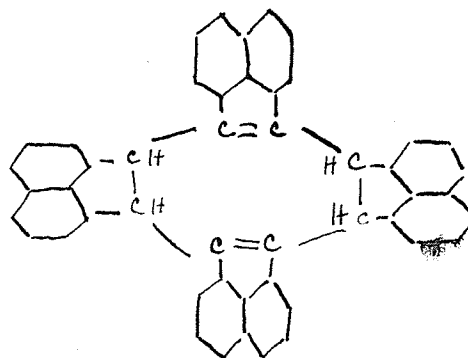


The most attractive method for the large scale production of acenaphthylene is the catalytic dehydrogenation of acenaphthene. Flower and Miller (24) have also given a brief account of this method. Acenaphthene vapours mixed with air were passed at 450°-480°C., over a catalyst consisting of 90% alumina, 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

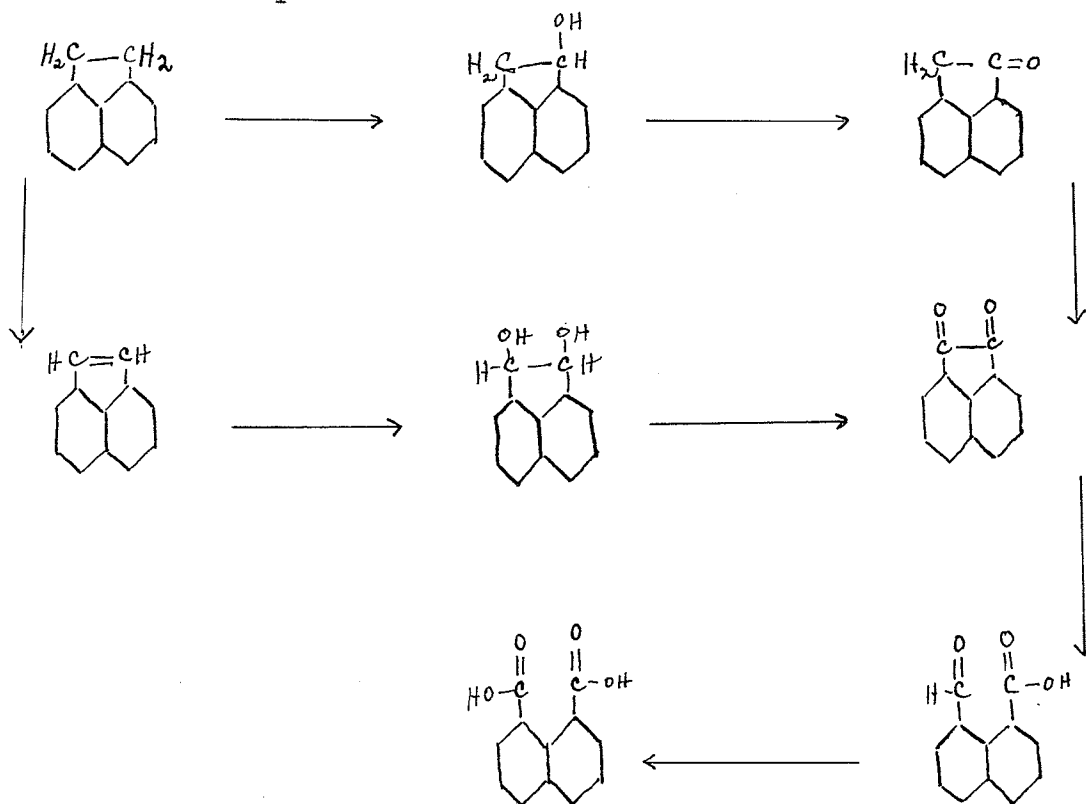


III

Polyacenaphthylene, and allo-polyacenaphthylene have the empirical formula $(C_{12}H_8)_n$, and both are amorphous powders. Polyacenaphthylene melts at $345^{\circ}\text{C}.$ - $350^{\circ}\text{C}.$ with decomposition, while allo-polyacenaphthylene has a melting point of $185^{\circ}\text{C}.$ - $190^{\circ}\text{C}.$ 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

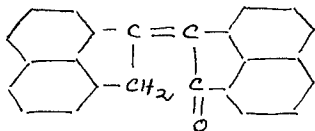
Acenaphthene, under very strong oxidation, yields naphthalic acid. However, if the oxidation is milder, various other products are formed. The various stages of oxidation can be represented as follows.



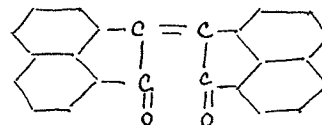
Graebe (33) investigated many of these oxidation products under alkaline conditions.

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).



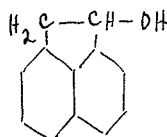
IV



V

Acenaphthenol

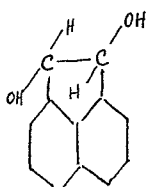
Acenaphthenol is quite a stable substance, except in the presence of strong dehydrating agents, when it tends to lose water and form acenaphthylene.



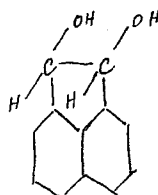
This compound may be prepared by the oxidation of acenaphthene with red lead in glacial acetic acid solution, yielding acenaphthenol acetate, which, under subsequent hydrolysis with sodium hydroxide and methanol, gives acenaphthenol. It crystallizes from alcohol or benzene in the form of colourless needles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



"TRANS"



"CIS"

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,