

THE CHEMISTRY OF ACENAPHTHENE

AND

ACENAPHTHYLENE

THE ATTEMPTED SYNTHESIS OF

ACENAPHTHYLENE OXIDE

Thesis submitted by

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TO

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TO

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TO

Dr. E.H. Charlesworth, without whose kind and generous
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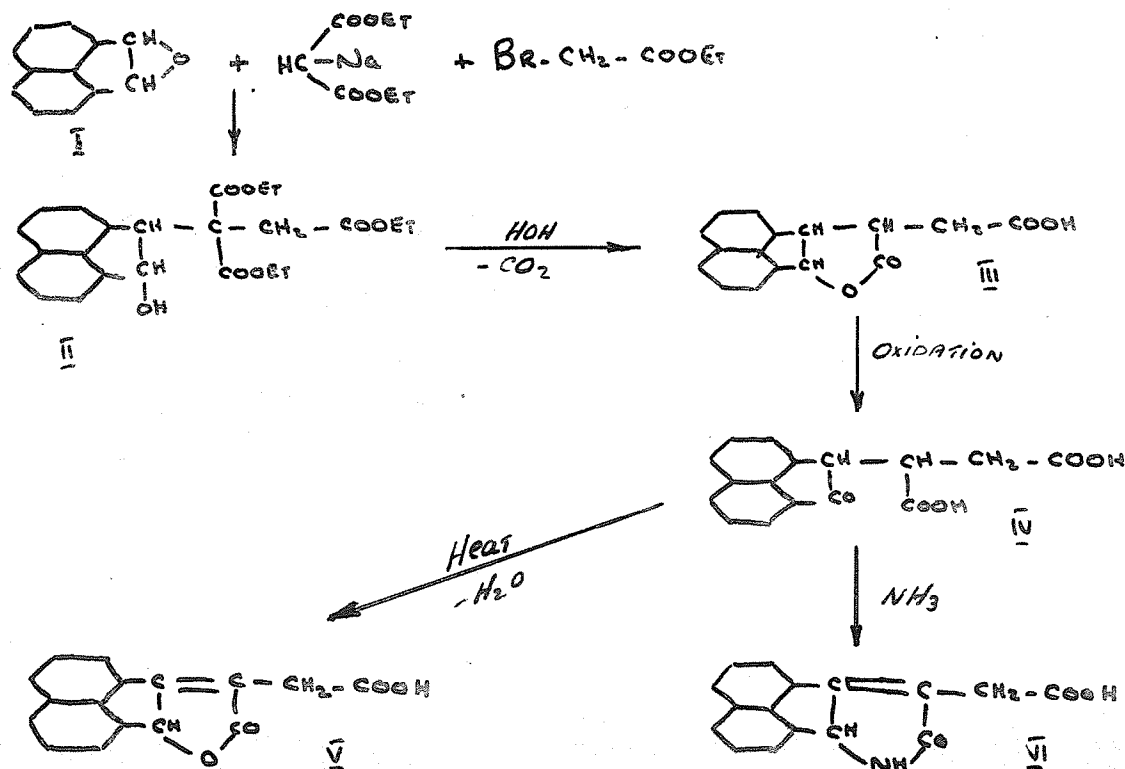
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INTRODUCTION

Condensations of the ethylene oxides with active methylene compounds have been investigated by Charlesworth, McRae, and others. This research was intended to extend the work of these authors to the oxide of acenaphthylene.

The proposed plan was for acenaphthylene oxide (I) to be condensed with ethyl sodio-malonate and ethyl bromoacetate to yield the tricarboxylic ester (II), which, following hydrolysis and decarboxylation, would produce the lactone of acenaphthylsuccinnic acid (III). Oxidation of this lactone (III) should have yielded 2-ketoacenaphthylsuccinnic acid (IV). The preparation of the unsaturated lactone (V), and the lactam (VI) was also to have been attempted.



DISCUSSION OF RESULTS

The preparation of acenaphthylene oxide had not been recorded in the literature, and its preparation had to be investigated. The proposed scheme of synthesis was (1) to prepare it from acenaphthylene chlorohydrin (VII), or (2) to prepare it by the direct oxidation of acenaphthylene with an oxidizing agent such as perbenzoic acid. The first steps in the synthesis were to prepare a sufficiently large supply of acenaphthylene, and to investigate the nature of the double bond in the side ring. If this bond was found to be ethylenic in type, the chlorohydrin of acenaphthylene would be prepared, and, from it, the oxide would also be prepared.



A number of methods for the preparation of acenaphthylene from acenaphthene and substituted acenaphthenes have been found in the literature, and are discussed in a later section. Most of these were of little value since the yields were quite small. The remaining methods dealt mainly with the vapour phase oxidation of acenaphthene at high temperatures, with and without the aid of catalysts. Several attempts to prepare the acenaphthylene by these latter methods proved to be of little value. The methods were of poor yield, and required the tedious fractional crystallization of the reaction product to separate the unoxidized acenaphthene from the acenaphthylene. The passage

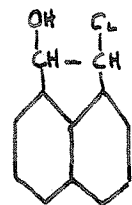
of acenaphthene vapours, along with dry carbon dioxide gas as a diluent, through a red hot quartz tube produced acenaphthylene in 10% yields. However, on subsequent runs, this yield was cut down considerably by a coating of black carbonaceous matter on the inner surface of the tube. The passage of a mixture of air and acenaphthene vapours through a glass combustion tube, heated to red heat and containing powdered manganese dioxide as a catalyst, also produced acenaphthylene in 10% yield. A similar method described in the literature indicated that a yield of almost 100% should be expected.

Attempted oxidations of acenaphthene by potassium permanganate and potassium dichromate in acetone solutions have failed to produce any acenaphthylene at all, although there was evidence that some sort of oxidation had occurred. An attempt to oxidize acenaphthene to either acenaphthylene or acenaphthylene oxide by the action of perbenzoic acid also failed, the reaction yielding only unoxidized acenaphthene. It had been reported in the literature by L. Monti that selenium dioxide on acenaphthene yielded acenaphthylene in 16% yields. Using both C.P. and commercial grades of selenium dioxide, it was experimentally found that the yields were considerably lower than reported.

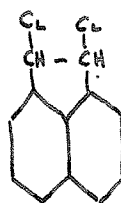
By far the most successful method for preparing acenaphthylene was that of R.G. Flower¹, in which 1-acetoxy-acenaphthene, with dry carbon dioxide gas as a diluent, was passed through a quartz tube heated at 520°C. The product obtained is quite free from acenaphthene. The yields of acenaphthylene are as high as 80% and the method was very well adapted to the large scale continuous production of acenaphthylene.

To prepare the chlorohydrin of acenaphthylene, excess acenaphthylene was treated with fairly strong hypochlorous acid solutions. Hypochlorous acid solutions of strength about 16% hypochlorous acid were obtained by the acidification of a solution of monochlorourea prepared according to Detoef². The progress of the reaction was followed by titration of samples of the reaction mixture for hypochlorous acid with sodium thiosulphate in the usual manner. Steam distillation of the reaction mixture yielded only a small amount of unreacted acenaphthylene. In the distilling flask there remained a small amount of a dark brown gummy residue which was unaffected by organic solvents. This gummy residue is quite possibly a condensation product of acenaphthylene.

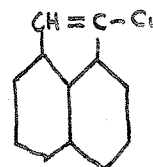
By using a more concentrated hypochlorous acid solution, and by extracting the reaction mixture with ether instead of steam distilling it, a considerable quantity of product was isolated. Distillation of the dried ethereal extract under reduced pressure yielded a light yellow oil which distilled over a fairly wide range of temperature. The chlorine content of the oil was determined to be 19.93% Chlorine. This is different from the chlorine content of any of the known chlorine substituted compounds of acenaphthylene. The only chlorine substituted compound with a chlorine content near to that of the oil were the chlorohydrin of acenaphthylene and 1-monochloroacenaphthylene (VIII)



Acenaphthylene
Chlorohydrin
17.32% Cl



1,2-dichloro-
Acenaphthylene
31.79% Cl



1-monochloro-
Acenaphthylene.
19.00% Cl

VIII

It is assumed that the oil must be a mixture of two or more of the chlorine compounds, whose structural configuration has been illustrated on the previous page.

Upon standing for several weeks, the light yellow oil darkened considerably and a crop of colorless crystals were observed in the oil. These crystals were filtered from the oil and were recrystallized several times from ethyl alcohol to give fine white crystals which melted sharply at 64°C . It was hoped that these crystals were those of the chlorohydrin of acenaphthylene but their chlorine content was found to correspond with that of a dichloroacenaphthene, within experimental error. In 1915, B.A. Campbell³ had reported 1,2-dichloroacenaphthene as a white solid melting sharply at 115°C . It has been assumed that these two dichloroacenaphthenes are geometric isomers. This assumption was not made ~~as a wild guess~~ ^{without justification.} Acenaphthylene is known to have two isomeric dihydroxy derivatives which are cis-acenaphthylene glycol, melting at $210-212^{\circ}\text{C}$., and trans-acenaphthylene glycol, melting at $157-8^{\circ}\text{C}$. Thus it is reasonable to assume that there might possibly be two corresponding dichloro derivatives. The final identity of the dichloro derivatives would be established if they could be converted into the corresponding dihydroxy derivative, and also if the two glycols were to be converted into their corresponding dichloro derivatives. P.A. Hawkins and N. Bennett⁴ have obtained the chlorohydrin of dihydropyran from the corresponding dichloride by means of water and calcium carbonate. A similar treatment of the two dichloride isomers of acenaphthylene might result in the production of one or even two isomeric chlorohydrins of acenaphthylene.

In 1915, B.A. Campbell had prepared a yellow oil from 1,2-dichloroacenaphthene. None of the oil's physical properties were given except the chlorine analysis which corresponded to that of 1-monochloroacenaphthylene. Campbell's work was repeated and several of the properties of the oil were determined. Under a reduced pressure of 6mm. of mercury the oil distilled at 135-140°C. A picrate derivative of the oil was made and its melting point was determined to be 150-2°C.

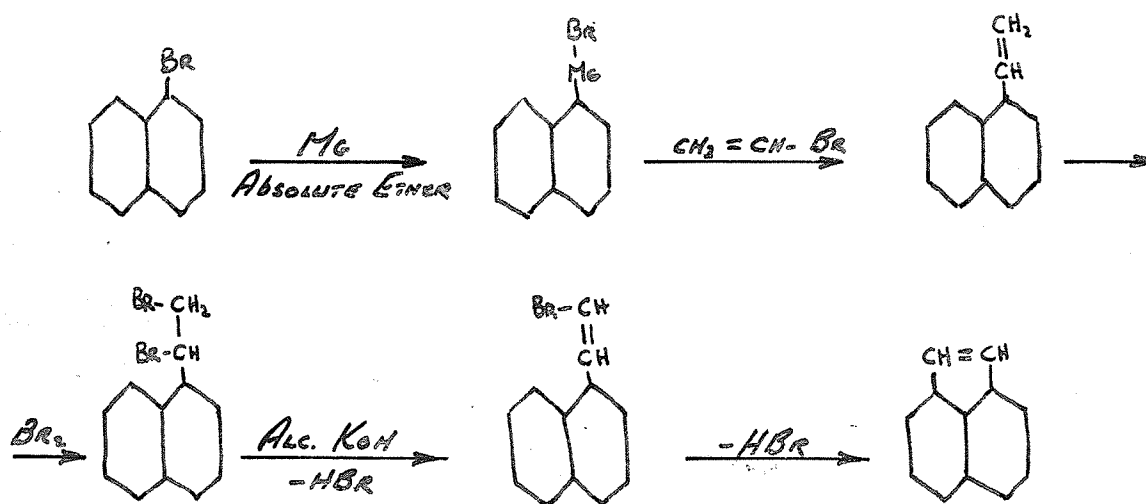
The yellow oil formed by the action of the hypochlorous acid upon acenaphthylene was fractionally distilled under a reduced pressure of 6 mm. of mercury into three fractions- (1) 130-140°C., (2) 140-145°C., (3) 145-150°C. Fraction (1) did not form a picrate derivative, but fraction (2) did form a picrate which melted at 151-153°C. A mixed melting point of this picrate and that from 1-monochloroacenaphthylene was determined to be 149-151°C.

When left overnight in an ice chest, the three fractions each behaved in a different manner. Fraction(1) remained liquid, Fraction (2) became very viscous, and Fraction (3) became entirely solid. The first two fractions were analysed for their chlorine content. Fraction (1) had a chlorine content of 17.12%, which is almost identical with the chlorine content of 17.23% for the chlorohydrin of acenaphthylene. Fraction (2) had a chlorine content considerably higher than that for either the chlorohydrin or 1-monochloroacenaphthylene. It is believed that this fraction and also the third fraction contain some of the lower melting dichloro derivative of acenaphthylene.

At the present time the acenaphthylene chlorohydrin has not been identified conclusively among the products of the reaction of hypochlorous acid upon acenaphthylene.

An attempt to prepare the oxide directly from acenaphthylene by the action of perbenzoic acid was made. Two solid products were obtained in small quantity. The lower melting product, melting at 121-2°C., was proved to be benzoic acid. The higher melting product, white flakes melting at 175-8°C., has not been identified as yet. The mother liquor of the reaction mixture was a dark red, viscous liquid, and has not been identified.

Acenaphthene had been synthesized by Berthelot from α -ethylnaphthalene. The author had intended to attempt a similar synthesis of acenaphthylene using α -vinylnaphthalene. The scheme



of synthesis is outlined above. Unfortunately, the work was held up due to lack of time.

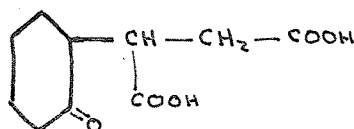
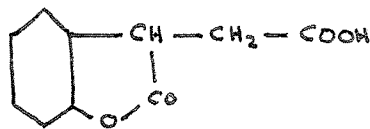
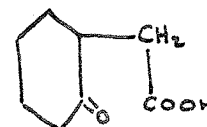
For the preparation of acenaphthylene chlorohydrin it was necessary to prepare a fairly strong hypochlorous acid solution.

Solutions up to 16% hypochlorous acid have been prepared by Detoeuf² from monochlorourea solutions. Chlorine was passed into a mixture of urea, water, and precipitated chalk. The chlorine and urea combined to form monochlorourea and urea hydrochloride. The chalk reacted with urea hydrochloride to regenerate urea, leaving a solution of urea and monochlorourea. For best results the monochlorourea solution should be used as soon as possible after preparation because the monochlorourea hydrolyses, with the hypochlorous acid being lost as hydrochloric acid and oxygen. To generate the hypochlorous acid, the monochlorourea solution was acidified with glacial acetic acid, which also acts as a solvent to some extent in subsequent reactions.

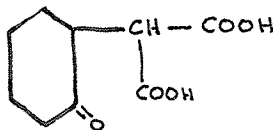
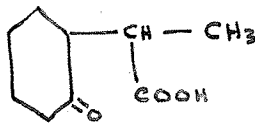
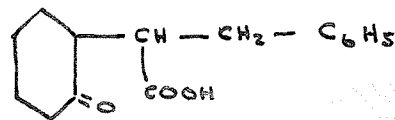
LITERATURE SURVEY

A: Condensation of Ethylenic Oxides With Substituted Malonic Esters.

This work was to be an extension of a series of experiments carried out by McRae, Charlesworth, and Alexander⁶ concerning the synthesis of 2-ketocyclohexylsuccinic acid (X), and related substances. The 2-ketocyclohexylsuccinic acid was synthesized by the oxidation of the lactone of cyclohexylsuccinic acid (IX), which resulted from the condensation of cyclohexene oxide, ethyl sodio-malonate, and ethyl bromoacetate, followed by hydrolysis and decarboxylation.

XIXXI

This reaction had been extended to prepare 2-ketocyclohexylacetic acid (XI), and 2-ketocyclohexylmalonic acid (XII). By substituting the alkyl halides, methyl iodide and benzyl chloride, for ethyl bromoacetate, 2-ketocyclohexyl- α -propionic acid (XIII), and 2-ketocyclohexylbenzylacetic acid (XIV) were produced.

XIIXIIIXIV

Charlesworth, McRae, and MacFarlane⁷ prepared the 2-ketocyclohexylacetic acid and 2-ketocyclohexyl- α -propionic acid by the condensation of the sodio-derivative of ethyl cyclohexanone-2-