SUMMARY

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Acenaphthene and fluorene are two tricyclic hydrocarbons isolated from coal-tar. They exhibit diverse physiological activities. Acenaphthene is an important intermediate in the vat-dye industry. Compared to the other polycyclic hydrocarbons such as naphthalene, anthracene and phenanthrene, these two hydrocarbons have received less attention. Though a large number of oxygen heterocyclics such as α- and γ-pyrones and furan derivatives have been synthesised, the building up of such rings on acenaphthene and fluorene ring systems has not received much attention. It was therefore thought of interest to synthesise such compounds from hydroxyacenaphthene and hydroxyfluorene derivatives. These compounds have also been subjected to some substitution reactions with a view to see the pattern of substitution in these compounds.

The thesis consists of two parts, part I deals with studies on acenaphthene derivatives and part II deals with studies on fluorene and fluorenone derivatives.

In the general introduction to part I some of the previous studies on substitution in acenaphthene and its derivatives has been briefly reviewed so as to indicate the pattern of substitution in acenaphthene and the types of studies made.

Section I of this part deals with the synthesis of some acenaphtho α-pyrones and acenaphtho γ-pyrones. 4'-Methyl-acenaphtho(5,4:6',5')α-pyrone has been synthesised by the Pechmann condensation of 5-hydroxyacenaphthene with ethyl acetoacetate. 5-Hydroxyacenaphthene on formylation with

hexamethylene tetramine gave 5-hydroxy-4-formylacenaphthene which on Perkin acetylation gave acenaphtho(5,4:6',5')α-pyrone. Knoevenagel condensation of this formyl derivative with diethyl malonate gave ethyl acenaphtho(5,4:6',5')α-pyrone-3'-carboxylate which was hydrolysed and decarboxylated to acenaphtho(5,4:6',5')α-pyrone. 5-Hydroxyacenaphthene with ethyl benzoylacetate in the presence of sulphuric acid gave 4'-phenyl acenaphtho(5,4:6',5')α-pyrone. The α-pyrone structure of these derivatives are established by the formation of a substituted acrylic acid derivative on treatment with dimethyl sulphate and alkali which is a diagnostic test for an α-pyrone derivative.

5-Hydroxy-4-acetyl acenaphthene on Kostanecki-Robinson acetylation gave 2'-methyl-3'-acetyl acenaphtho(5,4:6',5')γ-pyrone which was deacetylated to 2'-methyl acenaphtho(5,4:6',5')γ-pyrone. The same compound was also prepared by the condensation of ethyl acetoacetate with 5-hydroxyacenaphthene in boiling diphenyl ether without the use of any condensing agent. The Kostanecki-Robinson benzoylation of 5-hydroxy-4-acetyl acenaphthene gave 2'-phenyl-3'-benzoyl acenaphtho(5,4:6',5')γ-pyrone. Attempts to remove the 3'-benzoyl group were not successful.

5-Hydroxy-4-acetyl acenaphthene on condensation with benzaldehyde in the presence of alcoholic potassium hydroxide gave 5-hydroxy-4-acenaphthyl styryl ketone which on refluxing with selenium dioxide in iso-amyl alcohol did not give any pure product. Therefore the styryl ketone was brominated to the dibromide, which when refluxed with potassium cyanide in alcohol gave the desired 2'-phenyl acenaphtho(5,4:6',5')γ-pyrone.

5-Hydroxy-4-acetyl acenaphthene when condensed with anisaldehyde in the presence of alcoholic potassium hydroxide gave 5-hydroxy-4-acenaphthyl p-methoxy styryl ketone. The dibromide of this ketone on boiling with alcoholic potassium cyanide gave 2'(p-methoxyphenyl)acenaphtho(5,4:6',5')γ-pyrone.

A benzo γ-pyrone derivative with an acenaphthyl group in the 2-position was also synthesised. 5-Methoxy-4-formyl acenaphthene was condensed with o-hydroxy acetophenone. The dibromide of the unsaturated ketone on refluxing with alcoholic potassium cyanide gave 2(5'-methoxy-4'-acenaphthyl) benzo γ-pyrone.

Attempts to synthesise α- and γ-pyrone derivatives from 3-hydroxyacenaphthene were unsuccessful. It did not undergo Pechmann condensation with ethyl acetoacetate in the presence of various condensing agents. Fries rearrangement of 3-acetoxy acenaphthene did not give the desired ortho hydroxy ketone. Formylation also did not succeed.

Section II deals with the synthesis of some acenaphtho furans.

5-Hydroxy-4-formylacenaphthene was condensed with ethyl bromoacetate and the 4-formyl-5-carbethoxymethoxy acenaphthene obtained was hydrolysed to the corresponding acid. This acid on refluxing with sodium acetate and acetic anhydride gave acenaphtho(5,4:5',4')furan. Similarly 5-hydroxy-4-acetyl-acenaphthene, through the same series of reactions gave 3'-methyl acenaphtho(5,4:5',4')furan. This compound was also prepared by brominating 4'-methyl acenaphtho(5,4:6',5')α-pyrone, hydrolysing the 3'-bromo compound obtained with sodium hydroxide

and decarboxylating the coumarilic acid with copper powder in quinoline.

5-Benzoyloxyacenaphthene was subjected to Fries rearrangement, when 5-hydroxy-4-benzoylacenaphthene was obtained. 3'-Phenylacenaphtho(5,4:5',4')furan was synthesised from this through condensation with ethyl bromo acetate, hydrolysis of the ester obtained to the corresponding acid and simultaneously cyclisation and decarboxylation by heating with acetic anhydride and sodium acetate.

Section III deals with the synthesis of a few Mannich bases from 5-hydroxyacenaphthene. When this was reacted with dimethylamine and paraformaldehyde it gave 5-hydroxy-4-dimethylaminomethylacenaphthene. The structure was proved by the formation of 5-hydroxy-4-formylacenaphthene by boiling the Mannich base with hexamethylene tetramine in acetic acid. Similarly the Mannich bases from 5-hydroxyacenaphthene and piperidine and morpholine were prepared. Aniline and benzylamine reacted with 5-hydroxyacenaphthene to give the oxazino derivatives which could not be hydrolysed to the Mannich bases but gave, on heating with hexamethylene tetramine the 4-formyl derivative.

Chloromethylation of 5-hydroxyacenaphthene and 3-hydroxy acenaphthene and their methyl ethers have been attempted. Though various attempts were made using different solvents and conditions, the chloromethyl derivatives could not be obtained.

Part II of this thesis deals with studies on fluorene and fluorenone derivatives.

In the general introduction to this part the previous work on substituion in fluorene, fluorenone and their derivatives is reviewed briefly.

Section I of this part deals with the synthesis of fluoreno α- and γ-pyrones from 2-hydroxyfluorene and 2-hydroxyfluorenone. Fries rearrangement of 2-acetoxyfluorene gave a hydroxy ketone, the methyl ether of which was oxidised by sodium dichromate to a fluorenone derivative which gave a pyridazine derivative with hydrazine showing that the acetyl group is in 1-position.

2-Hydroxy-1-acetylfluorene on condensation with benzaldehyde in the presence of potassium hydroxide gave 2-hydroxy-1-fluorenyl styryl ketone. This ketone on boiling with selenium dioxide in iso-amyl alcohol gave 2'-phenylfluoreno (2,1:6',5')γ-pyrone. 2'-(p-Methoxyphenyl)fluoreno(2,1:6',5') γ-pyrone was also synthesised by condensing 2-hydroxy-1-acetylfluorene with anisaldehyde and then cyclisation and dehydrogenation of the styryl ketone derivative with selenium dioxide.

2-Hydroxyfluorenone, on acetylation and Fries rearrangement gave a ketone, the methyl ether of which was found to be identical with 2-methoxy-1-acetylfluorenone obtained by the oxidation of 2-methoxy-1-acetylfluorene.

2-Hydroxy-1-acetylfluorenone on condensation with benzaldehyde gave 2-hydroxy-9-oxo-1-fluorenyl styryl ketone. This ketone when refluxed in iso-amyl alcohol with selenium dioxide gave 2'-phenyl-9-oxofluoreno(2,1:6',5')γ-pyrone. A similar condensation of 2-hydroxy-1-acetylfluorenone with

anisaldehyde gave the p-methoxy derivative of the above ketone, which on refluxing with selenium dioxide gave 2'(p-methoxy-phenyl)9-oxofluoreno(2,1:6',5')γ-pyrone.

Kostanecki-Robinson acetylation of 2-hydroxy-1-acetyl fluorene gave 2'-methyl-3'-acetylfluoreno(2,1:6',5')γ-pyrone from which the 3-acetyl group could not be removed. Kostanecki-Roninson benzoylation of 2-hydroxy:-1-acetylfluorene did not succeed. Kostanecki-Robinson acetylation and benzoylation of 2-hydroxy-1-acetylfluorenone did not give any pure product.

Pechmann condensation of 2-hydroxyfluorene and 2-hydroxy fluorenone with ethyl acetoacetate also did not take place and the original compounds were obtained back under different conditions and with different condensing agents. With a view to synthesise such compounds through the Perkin and Knoevenagel condensations attempts were made to prepare the formyl derivative but 2-hydroxyfluorene and 2-hydroxyfluorenone did not give the desired formyl derivatives on formylation with hexamethylene tetramine or by Gatterman formylation.

Chloromethylation of 2-hydroxyfluorene and 2-hydroxyfluorenone and their methyl ethers was attempted with a view to prepare the chloromethyl derivatives which could be converted into the formyl derivatives, Mannich bases, etc., but this reaction also did not succeed. Some unworkable products were obtained.

Section II of this part deals with the synthesis of some fluorenofuran derivatives.

2-Hydroxy-1-acetylfluorene was condensed with ethyl bromo acetate and the ester obtained was hydrolysed to the acid. This was cyclised to 3'-methylfluoreno(2,1:5',4')furan.

2-Allyloxyfluorene, on heating gave a hydroxyallylfluorene, the methyl ether of which on oxidation with potassium permanganate gave 2-methoxyfluorenone-1-carboxylic acid, which was also obtained by the haloform reaction on 2-methoxy-1-acetylfluorenone. Therefore the allyl compound has been assigned 2-hydroxy-1-allylfluorene structure. This compound was acetylated and brominated and the dibromide obtained converted in to 2'-methylfluoreno(2,1:5',4')furan by boiling with alcoholic potassium hydroxide.

2-Acetoxyfluorenone on Fries rearrangement gave 2-hydroxy -1-acetylfluorenone. This was condensed with ethyl bromoacetate, The ester obtained was hydrolysed to the acid, which was cyclised to 3'-methyl-9-oxofluoreno(2,1:5',4')furan by refluxing with sodium acetate and acetic anhydride. 2-Benzoyloxy fluorenone on Fries rearrangement gave a hydroxy ketone, the methyl ether of which on refluxing with hydrazine hydrate gave a pyridazine derivative. Therefore 2-hydroxy-1-benzoyl fluorenone structure is assigned to the hydroxy ketone. This compound on refluxing with ethyl bromoacetate gave the corresponding ester, which was hydrolysed to the acid. The acid on refluxing with sodium acetate and acetic anhydride gave 3'-phenyl-9-oxofluoreno(2,1:5',4')furan. 2-Allyloxyfluorenone on heating gave a hydroxy allyl compound which was converted to 2'-methyl-9-oxofluoreno(2,1:5',4')furan through acetylation, bromination and cyclisation with alcoholic potassium hydroxide. This furan on reduction with hydrazine hydrate gave 2'-methyl-fluoreno(2,1:5',4')furan showing that the hydroxyallyl compound was 2-hydroxy-1-allylfluorenone.

Section III deals with the bromination of 2-hydroxyfluorene and 2-hydroxyfluorenone and their methyl ethers.

2-Hydroxyfluorene on bromination with one mole of bromine gave 2-hydroxy-1-bromofluorene. 2-Methoxyfluorene also gave a mono bromo derivative which was identical with the methyl ether of 2-hydroxy-1-bromofluorene. The methoxy bromo compound was oxidised to fluorenone derivative and converted to the corresponding cyano derivative which hydrolysed to 2-methyxyfluorenone-1-carboxylic acid, identical with the acid obtained by haloform reaction on 2-methoxy-1-acetylfluorenone. 2-Methoxyfluorene with 2-moles of bromine gave a dibromo derivative. This was found to be identical with the products obtained by further bromination of 2-methoxy-7-bromofluorene and 2-methoxy-1-bromofluorene. Therefore 2-methoxy-1,7-dibromofluorene structure is assigned to this dibromo compound. 2-Hydroxy and 2-methoxyfluorene on treatment with excess of bromine gave the 1,3,7-tribromo derivative. The orientation of these compounds are established by brominating further 2-methoxy-1-bromofluorene, 2-methoxy-3-bromofluorene obtained from the known 2-methoxy-3-aminofluorene, and 2-methoxy-7-bromofluorene obtained from the known 2-methoxy-7-aminofluorene. In all the cases identical tribromo derivative was obtained.

2-Methoxyfluorenone with one mole of bromine gave 2-methoxy-1-bromofluorenone. 2-Hydroxyfluorenone also gave 2-hydroxy-1-bromofluorenone. This was found to be identical with the oxidised product of 2-methoxy-1-bromofluorene.

2-Hydroxy and 2-methoxyfluorenone with excess of bromine gave a dibromo derivative. The methyl ethers of the hydroxy dibromo derivative was found to be identical with the methoxy dibromo derivative. The orientation of these compounds were established by further brominating 2-methoxy-1-bromo-fluorenone and 2-methoxy-3-bromofluorenone obtained by oxidation of 2-methoxy-3-bromofluorene when dibromo derivative identical with the one obtained above were obtained.