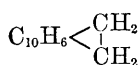


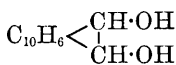
LV.—*Oxidation Products of Acenaphthene.*

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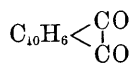
THE following series of experiments was undertaken with the view of preparing the intermediate products of the oxidation of acenaphthene and naphthalic acid. According to the present view of the constitution of acenaphthene (Ekstrand, *Ber.*, 1885, 2881, Philip and Bamberger, *Ber.*, 1887, 237), it should yield on oxidation a dialcohol and diketone of the following constitution:—



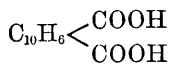
Acenaphthene.



Acenaphthylene glycol.



Acenaphthylene-ketone.



Naphthalic acid.

The present paper contains a preliminary account of these experiments, which are still being carried on.

Action of Lead Oxide, Lead Nitrate, and Water upon Dibromacenaphthene Bromide, C₁₂H₈Br₂Br₄.

Dibromacenaphthene bromide was boiled with water and lead oxide for 2 to 3 days with reflux condenser, and the product distilled in a current of steam. A substance passed over which crystallised in brilliant yellow needles. The same compound was obtained on heating the bromide with lead oxide and water at 150°, and also with a solution of lead nitrate. The yield in all cases was so small that any further investigation as to the constitution of the compound has been postponed. The substance was recrystallised from alcohol, and melts at 126—129°. It gave the following results on analysis:—

	Found.	Calculated for C ₁₂ H ₈ O ₂ Br ₂ .
C.....	45.62	46.15
H.....	3.16	2.53
Br.....	46.80	47.06

Acenaphthylene Glycol Monoacetate.—A better result was obtained by converting acenaphthylene dibromide into the acetate and decomposing the product with potash.

2 grams of the dibromide are boiled with 2 grams of caustic potash and 7—8 c.c. of glacial acetic acid. In a few minutes potassium bromide begins to separate, and the reaction is soon complete.

The product is neutralised with caustic soda, the buff-coloured precipitate collected and washed with water. The precipitate is dried, and crystallised from light petroleum, and recrystallised from acetic acid or alcohol. It forms long, slender, yellow needles, which melt at 122—122·5° (uncorr.); it is easily soluble in alcohol, less soluble in methyl alcohol, very soluble in ether and glacial acetic acid. 40 grams of the bromide give 10 grams of product. The substance gave on analysis the following results:—

	Found.	Calculated for $C_{14}H_{12}O_3$.
C.....	73·65	73·67
H.....	5·7	5·27

The compound is therefore acenaphthylene glycol monoacetate,
 $C_{10}H_6 \begin{array}{c} \text{CH} \cdot \text{OH} \\ | \\ \text{CH} \cdot \text{O} \cdot C_2H_5O. \end{array}$

Acenaphthylene Glycol Diacetate.—The monoacetyl compound was boiled with excess of acetic anhydride for half an hour, and the mass poured into water. When the excess of anhydride was decomposed, a brown solid residue remained, which was collected, washed with water, and crystallised from methyl alcohol. It melts at 130°, and gave on analysis the following results:—

	Found.	Calculated for $C_{10}H_6 \begin{array}{c} \text{CH} \cdot \text{O} \cdot C_2H_5O \\ \\ \text{CH} \cdot \text{O} \cdot C_2H_5O \end{array}$
C.....	70·75	71·11
H.....	5·54	5·20

It is a yellow, crystalline substance.

Acenaphthylene Glycol.—1·6 gram of the monacetyl compound and 1 gram of caustic potash are dissolved in methyl alcohol and boiled for 2 to 3 hours on the water-bath. On cooling, long needles separate, which may be recrystallised from methyl alcohol. They are colourless, melt at 204—205°, and are slightly soluble in cold methyl alcohol or hot water. The substance gave the following results on analysis:—

	Found.	Calculated for $C_{10}H_6 \begin{array}{c} \text{CH} \cdot \text{OH} \\ \\ \text{CH} \cdot \text{OH} \end{array}$
C.....	77·18	77·42
H.....	5·62	5·38

On oxidation with an alkaline 4 per cent. permanganate solution in the cold, a white, crystalline acid is formed, melting at 266—267°,

which is doubtless naphthalic acid. No intermediate oxidation product of the glycol could be obtained in this way.

Acenaphthylene Glycol Monobenzoate.—1 gram acenaphthylene bromide was dissolved in ether, and 1.44 gram of silver benzoate added. The reaction goes on in the cold. The product was collected and the ether evaporated. The residue may be crystallised from methyl alcohol or toluene, and forms small, colourless plates melting at 189–190°. A second portion dissolved in alcohol was treated with excess of moist silver benzoate, extracted with light petroleum, and recrystallised from glacial acetic acid. The product was the same.

	Found.		Calculated for
	I.	II.	$C_{10}H_6 \begin{matrix} \text{CH}\cdot\text{OH} \\ \\ \text{CH}\cdot\text{O}\cdot C_7H_5O \end{matrix}$
C	78.73	78.71	78.62
H	5.38	5.04	4.83

Acenaphthene Ketone.—To obtain the methyl-derivative of acenaphthylene glycol, we acted on the glycol with methyl iodide and sodium alcoholate. The result turned out very different from what we anticipated. 2 grams of the glycol were mixed with alcohol insufficient for complete solution, and 0.5 gram of sodium, dissolved in about 5 c.c. of absolute alcohol, added. 3.1 grams of methyl iodide were introduced, and the mixture heated for two hours at 150–160°. Sodium iodide separated. The product was diluted with water, extracted with ether, the ethereal solution dehydrated over calcium chloride, and evaporated. The residue solidified, and was recrystallised from alcohol. The substance forms pale yellow needles melting at 119–119.5°. It gave on analysis the following results:—

	Found.	Calculated for
		$C_{12}H_8O$.
C	85.71	85.78
H	4.78	5.21

It is not acted on by dry, gaseous hydrochloric acid when passed through its solution in toluene, or when boiled with glacial acetic acid. It combines with phenylhydrazine acetate, but the amount of product obtained was insufficient for analysis. The compound will therefore be a ketone of the following constitution: $C_{10}H_6 \begin{matrix} \text{CH}_2 \\ | \\ \text{CO} \end{matrix}$. We

explain the reaction by supposing that the sodium alcoholate has a dehydrating action on the glycol, removing 1 mol. of water.

To prepare the alkyl ethers of acenaphthylene glycol, we had recourse to the action of sodium ethylate on acenaphthylene dibromide, and the results, although they have not yielded the desired

compound, may be of some interest. 2 grams of acenaphthylene bromide, 0.35 gram sodium, and 10 c.c. of alcohol were allowed to stand in the cold for one hour and then heated just to boiling. On cooling, the whole solidified; after crystallisation from alcohol the product was obtained in long needles melting at 94—95°. It gave the following results on analysis:—

	Found.	Calculated for $C_{12}H_{10}$.
C.....	92.90	93.56
H.....	6.76	6.45

It formed a crystalline compound with picric acid, melting at 161—162°. The substance is, therefore, acenaphthene.

If the acenaphthylene bromide be dissolved in anhydrous benzene, and then heated with dry sodium alcoholate, a brown oil is formed, which readily combines with picric acid to form a yellow, crystalline compound, melting at 201—202°, and gives the following results on analysis:—

	Found.	Calculated for $C_{12}H_8 \cdot C_6H_2(OH)(NO_2)_3$.
C.....	56.94	56.70
H.....	3.16	2.87

The compound is doubtless the picric acid derivative of acenaphthylene.

We cannot as yet attempt a satisfactory explanation of the course of these reactions, but we intend to investigate them further.

Tetrabromacenaphthene.—To obtain the diketone we first prepared the tetrabromo-derivative of acenaphthene.

2 grams of acenaphthylene bromide dissolved in carbon bisulphide and 1.75 gram of bromine, were allowed to stand overnight. Rosettes of crystals separated, which, when pure, melt at 161—162° with decomposition. It is insoluble in alcohol. The following results were obtained on analysis:—

	Found.	Calculated for $C_{12}H_6Br_4$.
Br	67.73	68.08

Tribromacenaphthene.—This compound was obtained in one experiment in the preparation of the tetrabromo-derivative; but the conditions were not specially noted at the time, and we have not been able, so far, to obtain it a second time.

It is a yellow crystalline substance, soluble in ether, glacial acetic acid, and hot alcohol. It melts at 88—90°.

It gave the following results on analysis:—

	Found.	Calculated for $C_{12}H_7Br_3$.
C.	36.45	36.83
H.	2.08	1.79

Action of Chromium Oxychloride upon Acenaphthene.

To obtain the dialdehyde corresponding to naphthalic acid, we adopted Étard's method. 2 grams of acenaphthene were dissolved in 20 grams of anhydrous carbon bisulphide and 2 grams of CrO_2Cl_2 , dissolved in carbon bisulphide, were slowly added to the cold solution of the acenaphthene. A dark brown, amorphous precipitate was formed, which was filtered through glass-wool, washed with carbon bisulphide, and dried in a vacuum over concentrated sulphuric acid. It was analysed with the following result:—

	Found.	Calculated for $C_{12}H_{10}(CrO_2Cl_2)_2$.
Cr.	22.10	22.41

On bringing the compound into water, a green solution is obtained; but the insoluble brown amorphous product obstinately retains chromium, even after prolonged boiling, and in spite of repeated attempts, it was impossible to prepare a pure product. It dissolves also with difficulty in the usual solvents.

To obtain the dialdehyde and diketones of naphthalic acid, we distilled the barium salt of the latter with the lime salt of the fatty acid, and obtained distillates which readily crystallised. The acid chlorides readily react on acenaphthene in presence of aluminium chloride to form well crystallised ketones; but the ketone-group appears to go into the nucleus and not into the ethylene side-chain.

Naphthalimide forms a crystalline chlorine-derivative when acted on by phosphorus pentachloride. The investigation of these compounds will form the subject of a subsequent communication.