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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 assistance this thesis could not have been written

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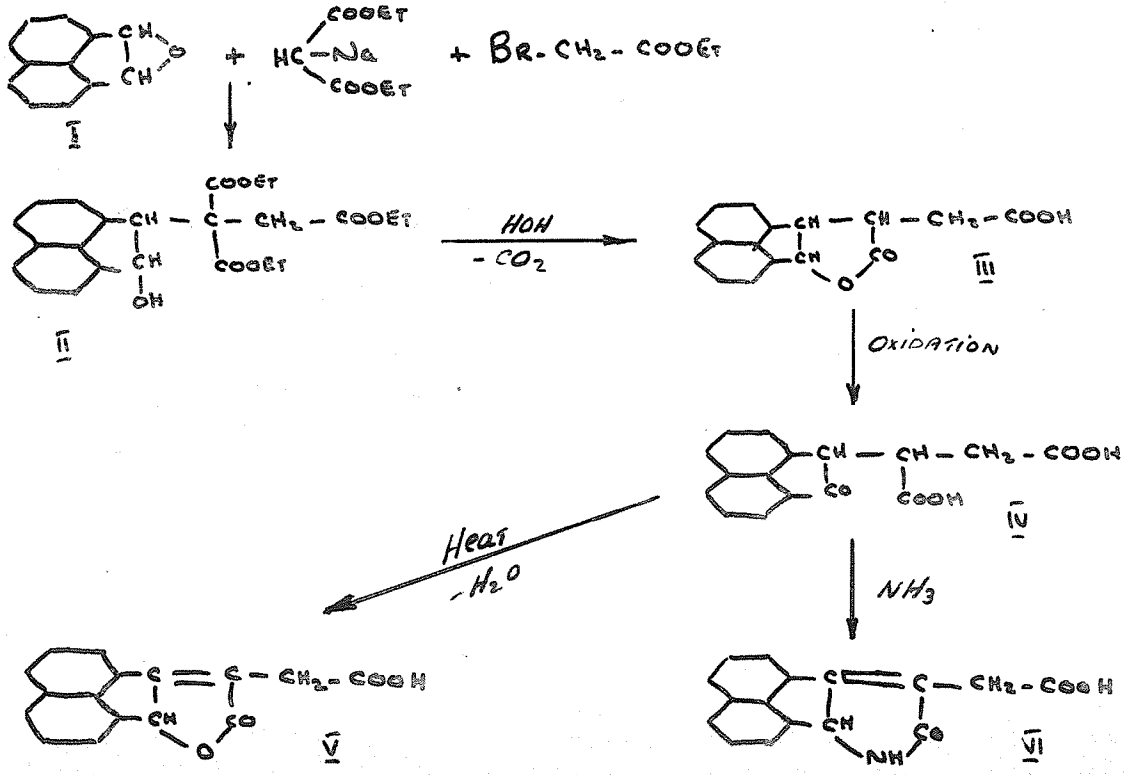
INTRODUCTION

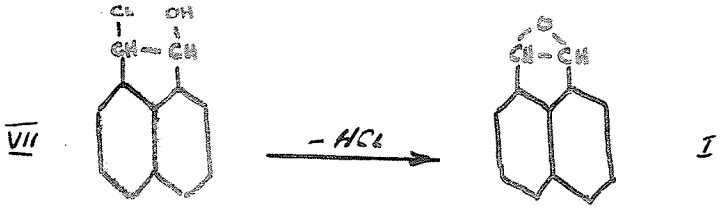
Condensations of the ethylene oxides with active methylene compounds have been investigated by Charlesworth, McRae, and others. This research was intended to extend the work of these authors to the oxide of acenaphthylene.

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

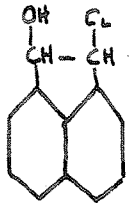
of acenaphthene vapours, along with dry carbon dioxide gas as a diluent, through a red hot quartz tube produced acenaphthylene in 10% yields. However, on subsequent runs, this yield was cut down considerably by a coating of black carbonaceous matter on the inner surface of the tube. The passage of a 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.

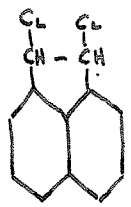
By far the most successful method for preparing acenaphthylene was that of R.G. Flower,[1] in which 1-acetoxy-acenaphthene, with dry carbon dioxide gas as a diluent, was passed through a quartz tube heated at 520°C. The product obtained is quite free from acenaphthene. The yields of acenaphthylene are 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 Detoeuf[2]. 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.

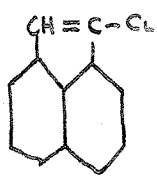
By using a more concentrated hypochlorous acid solution, and by extracting the reaction mixture with ether instead of steam distilling it, a considerable quantity of product was isolated. Distillation of the dried ethereal extract under reduced pressure yielded a light yellow oil which distilled over 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-Acenaphthene
31.79% Cl



VIII

1-monochloro-acenaphthylene.
19.00% Cl

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. Campbell[3] 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°C., and trans-acenaphthylene glycol, melting at 157-8°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. Bennett[4] 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.

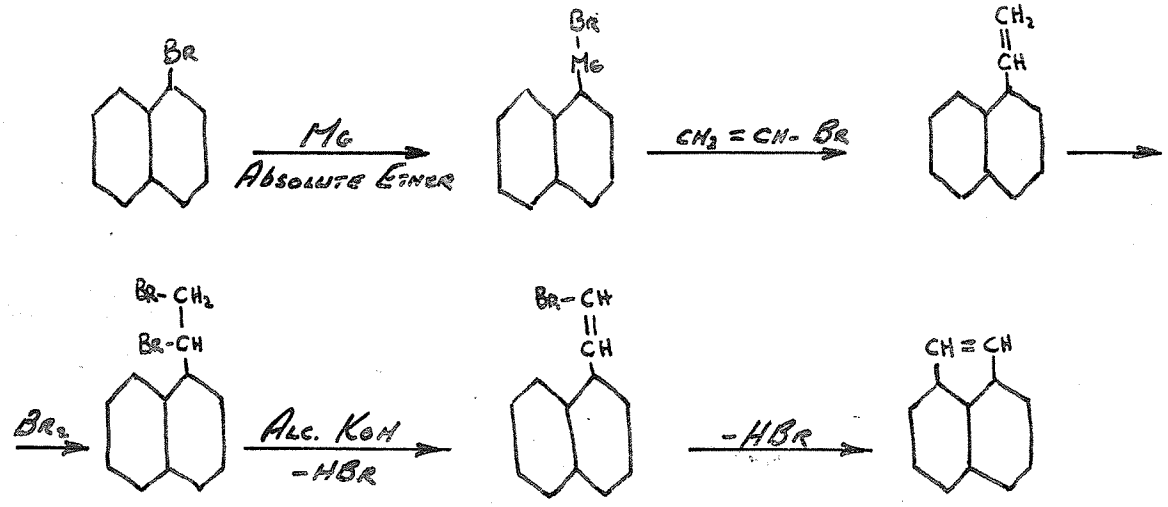
The yellow oil formed by the action of the hypochlorous acid upon acenaphthylene was fractionally distilled under a reduced pressure of 6 mm. of mercury into three fractions- (1) 130-140°C., (2)140-145°C., (3)145-150°C. Fraction (1) did not form a picrate derivative, but fraction (2) did form a picrate 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 acenaphth--ylene 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[5] 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.

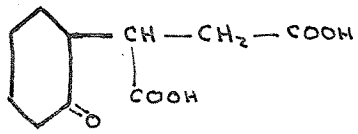
For the preparation of acenaphthylene chlorohydrin it was necessary to prepare a fairly strong hypochlorous acid solution.

Solutions up to 16% hypochlorous acid have been prepared by Detoeuf[2] 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.

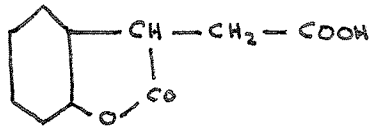
LITERATURE SURVEY

A: Condensation of Ethylenic Oxides With Substituted Malonic Esters.

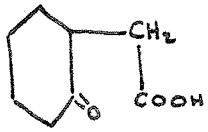
This work was to be an extension of a series of experiments carried out by McRae, Charlesworth, and Alexander[6] concerning the synthesis of 2-ketocyclohexylsuccinic acid (X), and related substances. The 2-ketocyclohexylsuccinic acid was synthesized by the oxidation of the lactone of cyclohexylsuccinic acid (IX), which resulted from the condensation of cyclohexene oxide, ethyl sodiomalonate, and ethyl bromoacetate, followed by hydrolysis and decarboxylation.



X

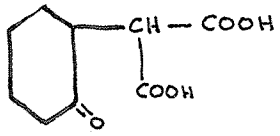


IX

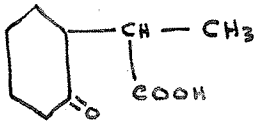


XI

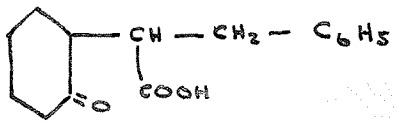
This reaction had been extended to prepare 2-ketocyclohexylacetic acid (XI), and 2-ketocyclohexylmalonic acid (XII). By substituting the alkyl halides, methyl iodide and benzyl chloride, for ethyl bromoacetate, 2-ketocyclohexyl-α-propionic acid (XIII), and 2-ketocyclohexylbenzylacetic acid (XIV) were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



XII



XIII

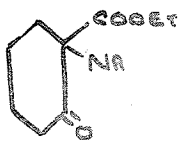


XIV

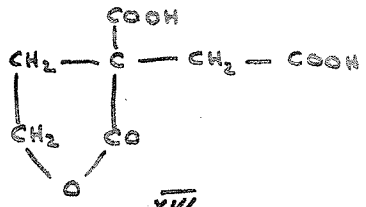
Charlesworth, McRae, and MacFarlane[7] prepared the 2-ketocyclohexylacetic acid and 2-ketocyclohexyl-α-propionic acid by the condensation of the sodio-derivative of ethyl cyclohexanone-2-

-carboxylate (XV) with ethyl bromoacetate and ethyl α-bromo-propionate respectively, followed by hydrolysis.

The synthesis of 2-ketocyclohexylsuccinic acid (X) from cyclohexene oxide suggested that this method might be extended to include other ethylene oxides. Condensations using other ethylenic



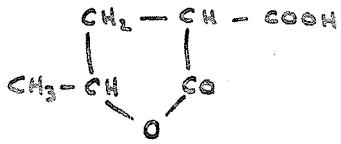
XV



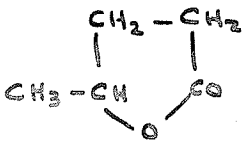
XVI

oxides were investigated by McRae, Charlesworth, Archibald, and Alexander[6]. Ethylene oxide, ethyl sodio-malonate, and ethyl chloro-acetate were condensed and the product was hydrolysed to yield 2-oxo-3-carboxytetrahydrofuran-3-acetic acid (XVI). This acid, when decarboxylated, yielded 2-oxotetrahydrofuran-3-acetic acid. Using ethyl β-bromopropionate in place of ethyl chloroacetate in the above condensation, 2-oxotetrahydrofuran-3-propionic acid (XVII) was obtained as the final product.

XVII



XVIII



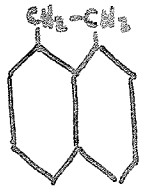
XIX

When propylene oxide was employed in place of the ethylene oxide, the final product was 2-oxo-5-methyltetrahydrofuran-3-carboxylic acid (XVIII), which could be decarboxylated to yield γ-valerolactone (XIX).

B: The Chemistry of Acenaphthene.

Acenaphthene is a white crystalline hydrocarbon found in coal tar to the extent of as much as 2%. It was first discovered in 1867 by Berthelot,[9] who later synthesized it by the action of acetylene upon naphthalene.[10] It had also been synthesized by heating α-ethylnaphthalene at red heat.[5] The main source of acenaphthene is from coal tar distillate of which it comprises most of the fraction boiling at 250-300°C. When pure, acenaphthene melts at 95°C., and distills at 278°C.

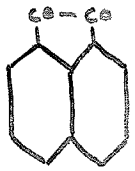
The first thing to note when considering the chemistry of acenaphthene is the similarity between its structure and that of naphthalene. It was this similarity of structure which enabled the earlier investigators to establish the constitution of several of the substitution products of acenaphthene. When subjected to oxidation by potassium bichromate and sulphuric acid, acenaphthene yielded a white crystalline compound melting at 266°C., and having the composition $C_{12}H_8O_4$. This latter compound was found to be identical with an acid, prepared by Bamberger and Phillip[11] from Estrand's nitronaphthalic acid, which had been established as the



α,α'-dicarboxylic acid of naphthalene, or naphthalic acid. From this data, the only conclusion was that acenaphthene had the above configuration. This was later confirmed by Baly and Tuck[12] from their investigations on the absorption spectra of naphthalene and

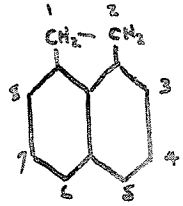
acenaphthene.

Once the constitution of acenaphthene was established, it was relatively an easy matter to determine the structures of the various products of oxidation which occurred along with naphthalic acid. One of the compounds isolated from among the oxidation products had the formula $C_{12}H_6O_2$, and could be further oxidized to naphthalic acid.[13] Its constitution was thus determined as



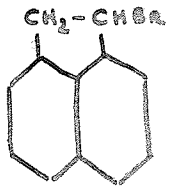
and the compound was called acenaphthene quinone.

For the method of nomenclature of the various substitution products of acenaphthene, it is generally adopted that the carbon atoms of acenaphthene be numbered[14] as in the figure below.

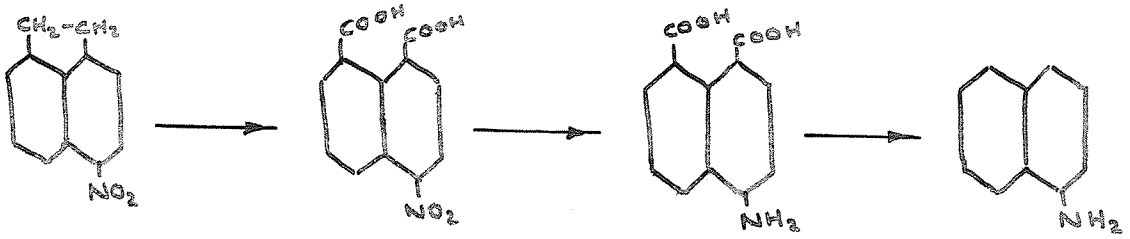


From the figure it is obvious that there should be four different monosubstituted acenaphthenes, with three of these having the substituent in the naphthalene nucleus. Also there should be seventeen disubstituted products, of which nine would have the two substituents in the naphthalene nucleus. In determining the position of a halogen substituent, Blumenthal[15] found it most convenient to employ oxidation reactions. For example, if a compound had the formula $C_{12}H_9Br$ and was found to oxidize to naphthalic acid and not to a bromonaphthalic acid, the bromine atom was

obviously substituted in one of the methylene groups, and the compound had the configuration



The oxidation of substituted acenaphthenes to known naphthalene derivatives has enabled investigators to establish the constitution of all substituted acenaphthenes.[16] The oxidation of nitroacenaphthene to α-naphthylamine, as in the following diagram, by Graebe estab-



-lished the nitro group in the 5-position of acenaphthene. With the constitutions of most of the substituted acenaphthenes firmly established, the constitutions of the various substituted oxidation products could be determined. Buri-Hoi and Cagneant[17] have reduced 3- and 5-substituted acenaphthene quinones by the Clemmenson method to the correspondingly substituted acenaphthene hydrocarbons which were readily identified.

Apart from oxidation to oxygen-containing compounds like acenaphthenone and acenaphthene quinone, acenaphthene can be oxidized to a very similarly constituted compound, called ace--naphthylene, by the loss of two hydrogen atoms from the methylene groups. The oxidation of acenaphthene to acenaphthylene will be discussed in detail in a later section.

The passage of acenaphthene vapours over reduced nickel in the presence of hydrogen yielded two hydrogenated products- tetrahydroacenaphthene, b.p. 240°C., and decahydroacenaphthene, b.p. 235°C. Tetrahydroacenaphthene appeared to be stable indef--initely in closed vessels and yellowed only slightly in air. It decolorized potassium permanganate solution like an unsaturated compound and is vigorously attacked by a chromic acid and sulphuric acid mixture.

Halogen Derivatives

Blumenthal, in 1874, made the first recorded investig--ations of the halogen derivatives of acenaphthene. His paper mentioned several different substances containing halogens, but these were of such doubtful purity that their constitution was very much in doubt. He did, however, succeed in preparing 5-bromo--acenaphthene by the action of bromine upon acenaphthene in ether solution. Further investigations conducted by J.T.Kebler, E. Bam--berger, and T.Ewan were all equally indefinite. It seemed probable that in all of these cases the separation of pure products was hampered by the presence of eutectic mixtures. In 1903, pure 5-bromoacenaphthene was isolated and found to be identical with the white bromine compound prepared by Blumenthal. It was prepared in excellent yield by a modification of Blumenthal's method. In 1903 Crompton prepared 5-chloroacenaphthene and 5-iodoacenaphthene by application of the same method. Crompton used chlorine gas or sulphuryl chloride as chlorinating agents, bromine in ethereal solution as the brominating agent, and iodine with yellow mercuric

oxide in methyl or ethyl alcohols as the iodinating agent. The 5-chloro- and 5-bromo-acenaphthenes form isomorphous mixtures. This is indicated by the fact that the addition of 5-chloro--acenaphthene to 5-bromoacenaphthene does not depress the freezing point of the latter, but the freezing points of mixtures of the two compounds lie on a continuous curve between those of the two pure compounds. Moreover, 5-chloroacenaphthene does not form isomorphous mixtures with either acenaphthene or 5-iodoacenaphthene. It is expected that 5-bromoacenaphthene does not form isomorphous mixtures with either of the two compounds.

The spectrochemical behavior of the two halo-acenaphthenes have been investigated by J.E.Purvis[25] and by K. von Auwers.[26] F.Sachs and G.Mosebach[27] confirmed the constitution of the 5-chloro-, 5-bromo-, and 5-iodoacenaphthenes in 1910 by preparing these substances from 5-aminoacenaphthene. Paillard and Favarger,[28] in 1933, stated that a maximum yield (83%) of 5-chloroacenaphthene could be obtained from the chlorination of acenaphthene in either methyl alcohol, ethyl alcohol, or glacial acetic acid as solvent and with iodine or antimony pentachloride as catalyst. Dashevski and Karishin,[29] in 1937, chlorinated acenaphthene in organic solvents, in the cold and at elevated temperatures, with and without catalysts of iodine, sulphur, bismuth, copper, lead, iron, or aluminum. Contrary to the findings of Paillard and Favarger, acenaphthene with two moles of chlorine in glacial acetic acid and alcohol at 80°C. in the presence of iodine and other catalysts does not give 82% of 5-chloro--acenaphthene but a mixture of chlorides containing 55% of 5,6-dichloroacenaphthene. However, reaction of acenaphthene in 5 parts of boiling 75% ethyl alcohol with 10-15% excess chlorine, and no

catalyst, yielded 90% of 5-chloroacenaphthene. With 2.5 moles of chlorine the products were 55% of 5,6-dichloroacenaphthene, some 5-chloroacenaphthene, and some trichloro- and pentachloro-acenaphthenes. Oxidation of 5,6-dichloroacenaphthene with chromic acid in glacial acetic acid yielded 4,5-dichloronaphthalic acid which changes at 194°C. to the anhydride.

Oxidation of 5-chloroacenaphthene with sodium dichromate in 95% acetic acid yielded 94% of 4-chloronaphthalic acid. Oxidation with ammonium dichromate yielded α,α'-dichlorobiacenaphth--ylidenedione, 4-chloronaphthalic acid, and 5-chloroacenaphthene quinone. The quinone yield of 26% could not be raised above that figure by any means. When oxidized with ammonium dichromate, 5-6--dichloroacenaphthene yielded almost 100% of 5,6,5',6'-tetrachloro-biacenaphthylidenedione. Depending upon the conditions of oxidation with sodium dichromate, 5,6-dichloroacenaphthene yielded 94-95% of 5,6-dichloroacenaphthene quinone, or about 10% of 4,5-dichloro--naphthalic acid. Dashevski and Karishin also prepared lemon yellow crystals of 1,1,2,5,6-pentachloroacenaphthene.

Bromination of acenaphthene in boiling 75% alcohol yielded 92-95% of 5-bromoacenaphthene and, with a variation of conditions, yielded 30-40% of 5,6-dibromoacenaphthene. The oxidation of 5-bromo-acenaphthene with sodium dichromate under various conditions yielded 91-96% of 4-bromonaphthalic acid, or 78% of α,α'-dibromoacenaphth--ylidenedione, or 9-10% of 5-bromoacenaphthene quinone.

Oxidation of 5,6-dibromoacenaphthene with sodium and ammonium dichromates, by methods similar to those used for the oxidation of 5-chloroacenaphthene, resulted in the preparation of

4,5-dibromonaphthalic acid, 5,6,5',6'-tetrabromoacenaphthylidene--dione, and 5,6-dibromoacenaphthene quinone.

The sulphonic acid derivatives of the halogen-substituted acenaphthenes had also been investigated by Dashevski and Karishin.[30] Heating with two parts by weight of concentrated sulphuric acid converted 5,6-dichloroacenaphthene into 5,6-dichloroacenaphthene--3-sulphonic acid. The amide of this acid, when treated with sodium amalgam in absolute alcohol, yielded acenaphthene-3-sulphonamide. Oxidation of the acid by potassium dichromate produced 4,5-dichloro--2-sulphonaphthalic acid. Using excess concentrated sulphuric acid, 5,6-dichloroacenaphthene was converted into 5,6-dichloroacenaphthene--3,8-disulphonic acid, as well as the -3-sulphonic acid. Dashevski and Karishin investigated the oxidation products of the mono--sulphonic acid and the disulphonic acid of 5,6-dichloroacenaphthene, and also those of the monosulphonic acid and disulphonic acid of 5,6-dibromoacenaphthene.

There was only one halogen substituted acenaphthene with the halogen substituted in the side ring. This compound was 1-monobromoacenaphthene, which had been prepared by Fieser and Cason[31] from 1-acenaphthenol by the action of potassium pentabromide. The chlorine analogue has not been prepared as yet. The dibromo-, and dichloro--acenaphthenes with both halogens in the side ring will be discussed in a later section of 'The Chemistry of Acenaphthylene'.

Table I lists the halogenated acenaphthenes and their melting points, as well as the melting points of a few of their derivatives.

TABLE I

MELTING POINTS OF HALOACENAPHTHENES AND SOME OF THEIR DERIVATIVES

Haloacenaphthene	Melting Point	Derivative
5-chloroacenaphthene	70.5°C.	picrate 137°C.
5-bromoacenaphthene	52.0°C.	
5-iodoacenaphthene	62.0°C.	picrate 102.5°C.
5,6-dichloroacenaphthene	169-70°C.	
?-trichloroacenaphthene	178-80°C.	
?-pentachloroacenaphthene	198-9°C.	
5,6-dichloroacenaphthene quinone	496°C. &305°C.	
4,5-dichloronaphthalic acid	194°C. &337.5°C.	
4-chloronaphthalic acid	206°C.	
1,1,2,5,6-pentachloroace--naphthene	198-9°C.	
5,6-dibromoacenaphthene	140°C.	
4,5-dibromonaphthalic acid	260°C.	
5,6-dibromoacenaphthene quinone	258°C.	
5,6-dichloroacenaphthene-3--sulphonic acid	192°C. (dec.)	chloride 175°C. amide 270-2°C.
4,5-dichloro-2-sulphonaphth--alic acid	229-30°C.	sulphonyl chloride 219-20°C. amide 380-2°C.
5,6-dichloroacenaphthene-3,8--disulphonic acid	265-6°C.	chloride 198-200°C. diamide over 400°C.
4,5-dichloro-2,7-disulphona--phthalic acid	176-7°C. (dec.)	
5,6-dibromoacenaphthene-3--sulphonic acid	240°C. (dec.)	chloride 190-1°C. amide 260-2°C.
4,5-dibromo-2-sulphonaphth-alic acid	235-6°C. (dec.)	
5,6-dibromoacenaphthene-3,8--disulphonic acid	252°C. (dec.)	chloride 197-8°C. diamide 274-5°C.
4,5-dibromo-2,7-disulphonaph--thalic acid	159-60°C. (dec.)	
1-monobromoacenaphthene	70.5-71.5°C.	

Nitro Derivatives

F. Quincke,[32] in 1887, was the first investigator to nitrate acenaphthene. He obtained a mixture containing two substances later identified as 5-nitroacenaphthene and 5,6-dinitroacenaphthene. E. Jandrier,[33] in the same year, under what appeared to be the same experimental conditions as used by Quincke, obtained a mononitro-derivative melting at 155°C. (cf. 102°C. for Quincke). C. Graebe,[34] and N. Briones[35] both confirmed the investigations of Quincke. Graebe modified Quincke's method of nitration to greatly increase the yield, and was the first investigator to prepare pure 5-nitroacenaphthene, melting at 106°C. Graebe's method was further modified by F. Sachs and G. Mosebach[36] who obtained yields of 84% for 5-nitroacenaphthene and 40% for 5,6-dinitroacenaphthene (XXVI), and established the constitution of the latter. They also prepared 4-nitro-5-amino-acenaphthene, and 4-nitro-5-oxyacenaphthene as a result of nitrating the acetyl derivative of 5-aminoacenaphthene.

Substitution in acenaphthene usually takes place para to one of the methylene groups, but this is perhaps preceded by ortho substitution. Morgan and Sheasby[37] nitrated acenaphthene under both hydrous and anhydrous conditions. They found that hydrous conditions generally yielded para-substituted compounds and that anhydrous conditions generally resulted in ortho substitution. Nitration with benzoyl nitrate in cold petroleum ether yielded 3-nitroacenaphthene as the sole product. Nitration with acetylnitric acid yielded 65-70% of 3-nitroacenaphthene (XXI), the remainder of the product being mainly 5-nitroacenaphthene (XXII) produced by a secondary reaction of the 3-nitroacenaphthene. This was established by the preparation of 5-nitroacenaphthene by heating 3-nitroacenaphthene with a little

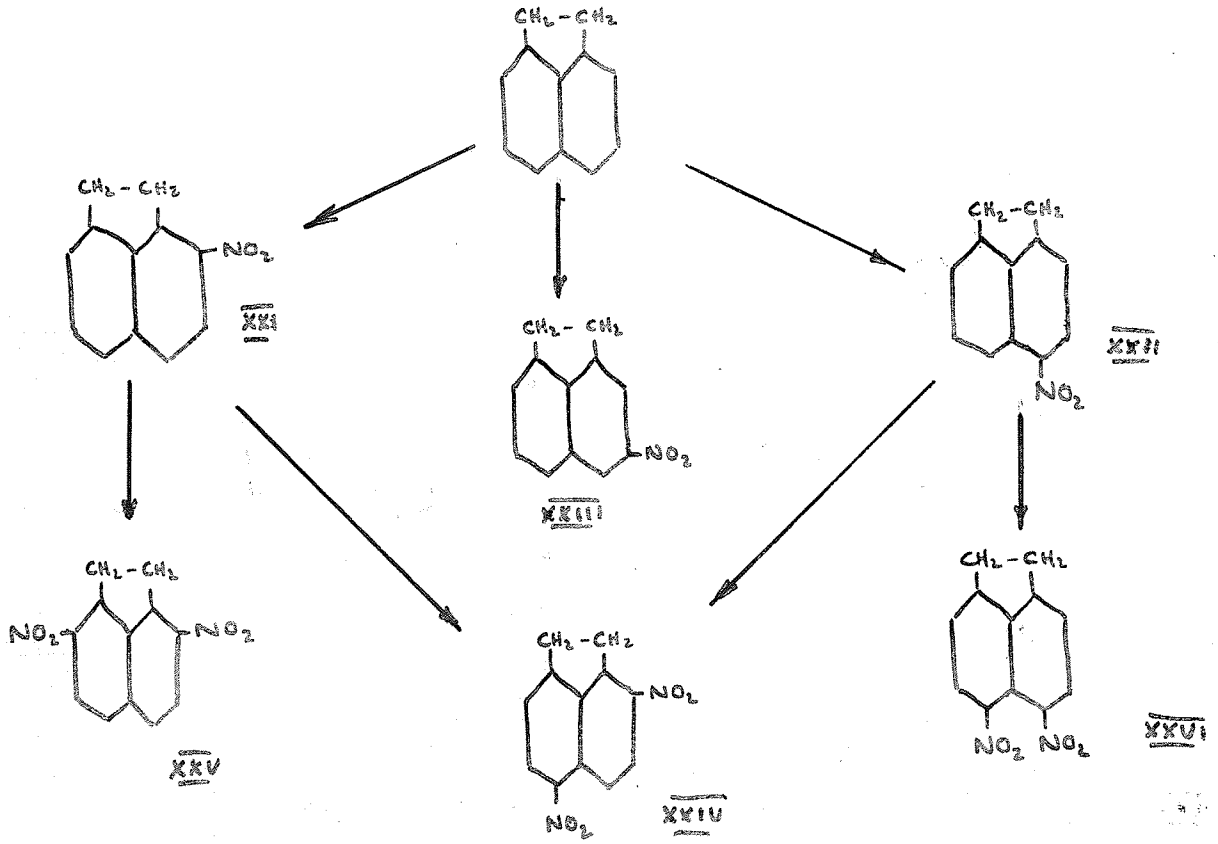
nitric acid or sulphuric acid in glacial acetic acid. There was some indication that the reaction was reversible, but, if so, the equilibrium was well to the para side.

A characteristic greyish-blue coloration was obtained when 3-nitroacenaphthene was treated with cold concentrated sulphuric acid. With sulphuric acid, 5-nitroacenaphthene gave a bluish-red coloration. These distinctive colorations and certain differences in solubility have rendered possible the detection of 3-nitro--acenaphthene among the nitration products of acenaphthene produced under ordinary hydrous conditions.

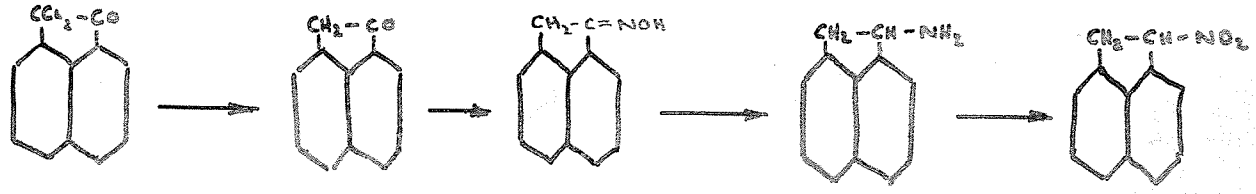
After nitration under anhydrous conditions with diacetyl orthonitric acid, there was evidence of a 4-nitroacenaphthene (XXIII) produced. This product was not isolated from the nitration product, but 4-aminoacenaphthene was isolated from among the products of reduction of the crude nitration product, showing that there had been a substitution in the 4-position of acenaphthene.

Morgan and Harrison[38] found that the further nitration of 3-nitroacenaphthene under hydrous conditions yielded principally 3,6-dinitroacenaphthene (XXIV), which was also produced from 5-nitro-acenaphthene using diacetylorthonitric acid. These two modes of formation do not exclude a 3,5- orientation of the nitro groups, but the new dinitro compound, melting at 205-6°C., furnished, upon partial reduction, 6-nitro-3-aminoacenaphthene, which is isomeric with but not identical with 5-nitro-3-aminoacenaphthene derived from 3-formamidoacenaphthene.

The by-product of nitration, under hydrous conditions, of 3-nitroacenaphthene was regarded as 3,8-dinitroacenaphthene (XXV). It was probable that it was also formed in small amounts during anhydrous nitration of acenaphthene, in as much as the basic product obtained on reduction of crude 3-nitroacenaphthene with aluminum amalgam contained a diamine which diazotized to a clear yellow soluble diazonium compound, a property possessed by 3-amino- but not by 4-aminoacenaphthene, which, upon diazotization, displayed intense green or blue colorations. Hence it was inferred that neither of the amino groups of the diamine was in the 5- or 6-positions, and the base was assumed to be 3,8-diaminoacenaphthene. The following diagram indicates the relationships existing among the mononitro- and dinitro-acenaphthenes.



Morgan and Stanley[39] succeeded in preparing 2-nitro-acenaphthene indirectly. Acenaphthene quinone was converted to 1,1-dichloroacenaphthenone, which on reduction gave acenaphthenone. The oxime of acenaphthenone, when reduced, yielded 2-amino-acenaph--thene. The oxidation of this amine produced 2-nitroacenaphthene. The 2-aminoacenaphthene was a base of mixed aromatic and aliphatic type, resembling benzylamine.

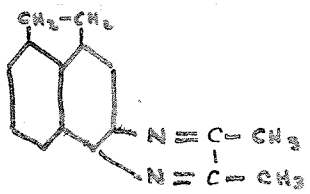


Amino Derivatives

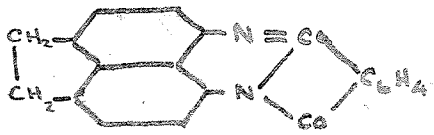
Many different methods for reduction of nitroacenaphthenes have been investigated.[40] Of the earlier investigators, Sachs and Mosebach had the best yields of 5-aminoacenaphthene with yields of 77% as compared with 50% for Graebe. Rodionov and Mel'nik have reported yields as high as 94% for 5-aminoacenaphthene using a platinum black catalyst. Numerous amino- and diamino-derivatives of acenaphthene have been prepared, among which are 4-nitro-5-amino--acenaphthene, 4,5-diaminoacenaphthene, and 5,6-diaminoacenaphthene. The study of the reactions of the monoamino- and diamino-derivatives of acenaphthene should prove of great interest because of the numerous reactions which are possible involving the amino hydrogen. Diazotization and coupling are two such reactions. Compounds like acenaphthene-azo-β-naphthol, azotol, and Schiff's base have been prepared from 5-aminoacenaphthene.[41]

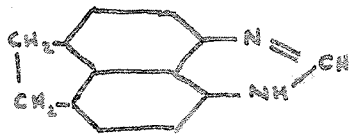
The diaminoacenaphthenes also provide many interesting

reaction products. 4,5-Diaminoacenaphthene condensed with diacetyl to give



5,6-Diaminoacenaphthene yielded a variety of products under the action of carbonyl oxygen. This diamino- compound reacts with phthalic anhydride, and with formic acid to give, respectively,





It had been found that acenaphthene quinone condensed with aromatic amines quite readily. Interesting results might be obtained if the diamines were the diamines of acenaphthene itself. The cond--ensations of acenaphthene quinone with amines, with hydroxylamine, and with hydrazine have been investigated by G. Ampola and V. Recchi,[42] A. Cruto,[43] G. Charrier,[44] L. Behrend,[45] J. Hermes,[46] K. Auwers,[47] F. Ullmann and E. Cassirer,[48] L. Fransconi and F. Pirazzoli.[49] It would be well worth noting that if the monoamino- and diamino- derivatives of acenaphthene were condensed in reactions involving the amino hydrogen the reaction products would still have the methylene groups of acenaphthene available for further condensation reactions.

Sulphonic Acid Derivatives

The first recorded preparation of a sulphonic acid derivative of acenaphthene, that of acenaphthene-5-sulphonic acid, was made by E. Oliveri-Mandala.[50] In 1923, Dziewonski and Stolyhwo[51] investigated the sulphonic acids of acenaphthene and found two isomeric monosulphonic acids and four isomeric disulphonic acids. The acids that were obtained were found to depend upon the condition under which the sulphonation was carried out as well as upon the nature of the sulphonating agent.[52] The sulphonating agents used were concentrated sulphuric acid and chlorosulphonic acid. The use of the calculated amount of sulphonating agent produced the isomeric monosulphonic acids. At low temperatures, near 0°C., the -3-mono--sulphonic acid was the chief product, and at high temperature, near 100°C., the -5-monosulphonic acid was the main product. The mono- and di-sulphonic acids were difficult to separate as their salts, but their derivatives, especially the amides, were very well suited to the purpose. The sodium and barium salts of the monosulphonic acids were considerably less soluble than those of the disulphonic acids. The sodium and barium salts of the -5-mono--sulphonic acid were less soluble than those of the -3-monosulph--onic acid. To establish the position of the sulphonic group in the acenaphthene molecule, the following procedure was employed. The monosulphonic acid was oxidized to a sulphonaphthalic acid, from which, after alkali fusion at 250°C., a compound, melting at 257°C., was obtained. This was previously supposed to be identical with 4-hydroxynaphthalic anhydride. This compound had the formula $C_{12}H_6O_3$, and gave β-naphthol when distilled with calcium hydroxide. It formed 1,8-phenylpyridazone-2-naphthoquinone without the loss

of carbon dioxide. This established the compound as 7-hydroxy-1-naphthoic acid. The sulphonaphthalic acid was 2-sulphonaphthalic acid, and the acenaphthene-sulphonic acid had the sulphonic acid group in the -3-position. The other monosulphonic acid was therefore the acenaphthene-5-sulphonic acid.

Fusion of the -3-sulphonic acid with potassium hydroxide did not produce the corresponding hydroxy derivative, but lost sulphurous acid and yielded acenaphthylene. For this reason, the acid was described in a German patent[53] as acenaphthene-1-sulphonic acid. This reaction furnished no evidence as to the structure of the -3-and -5-sulphonic acids because both acids reacted in the same way, not only with potassium hydroxide, but also with potassium cyanide and potassium ferrocyanide, and even upon distillation in vacuo. In addition to acenaphthylene, there is also produced, in much larger quantities, polyacenaphthylene, $(C_{10}H_8)_{22}$, which was always formed as a polymerization product of acenaphthylene. The most probable explanation for the formation of acenaphthylene was that, on heating the acid, the sulphonic acid group migrated to the -1-position, and the unstable sulphonic acid then decomposed to give acenaphthylene and polyacenaphthylene.

Employing a large excess of concentrated or fuming sulphuric acid, two isomeric disulphonic acids were isolated. These acids were characterized by the extremely high solubility of their barium salts in water, while their sodium salts were almost entirely insoluble in alcohol. The exact positions of the sulphonic acid groups were not known. However, de-sulphonation with sodium amalgam gave, in both cases, acenaphthene-5-sulphonic acid, showing that one of the acid groups was in the -5-position.

The preparation of 5-hydroxyacenaphthene-3-sulphonic acid was described in a German patent.[54] 5-Aminoacenaphthene was treated with 80% sulphuric acid to obtain 5-aminoacenaphthene-3-sulphonic acid, which was then converted to the -5-hydroxy derivative by heating with water in a pressure vessel.

The nitro- and amino-derivatives of acenaphthene mono--sulphonic acids were studied by Dziewonski and Orzelski in 1926. They noted that, in the nitration of acenaphthene-3-sulphonic acid or in the sulphonation of 4-nitroacenaphthene, the unsubstituted ring was attacked. Thus, using chlorosulphonic acid in nitrobenzene, 5-nitroacenaphthene was converted into 5-nitroacenaphthene-7--sulphonic acid. This latter compound was oxidized by sodium dichromate to 5-nitro-3-sulphonaphthalic acid. The reduction of the 5-nitroacenaphthene-7-sulphonic acid yielded 5-aminoacenaphthene--7-sulphonic acid. The diazonium derivative of the amino-sulph--onic acid derivative of acenaphthene, with sodium formate, formic acid, and copper powder yielded a monosulphonic acid derivative of acenaphthene which was isomeric with the known -3- and -5-sulphonic acids. To establish the structure of the two isomeric nitroacenaph--thene sulphonic acids, the following procedure was employed. The sodium salt of acenaphthene-3-sulphonic acid, when treated with nitric acid (d.-1.38) in glacial acetic acid, yielded 6-nitro--acenaphthene-3-sulphonic acid, which, on oxidation, yielded 5--nitro-2-sulphonaphthalic acid. Reduction of 6-nitroacenaphthene--3-sulphonic acid produced the 6-aminoacenaphthene-3-sulphonic acid, which was desulphonated with sodium amalgam to 5-aminoace--naphthene.

Hydroxy and Carboxyl Derivatives

There were relatively few acenaphthene compounds to be found in the literature in which the hydrogen atoms of the aromatic nucleus were substituted by hydroxyl groups. Sachs and Mosebach prepared 5-hydroxy-4-nitroacenaphthene and its reduced counterpart, 5-hydroxy-4-aminoacenaphthene. The preparation of 5-acenaphthenol, which was used in the production of indigoid dyes, had been covered by a patent.[56] Hydroxy compounds with the hydroxyl groups substituted into the methylene groups of acenaphthene will be dealt with in the next section.

Berthelot[57] used phosgene in an unsuccessful attempt to substituted a carbonyl group into the aromatic nucleus of acenaph--thene. Using chlorocarbamic acid, E.P. Harris[58] obtainedan acid which was hydrolysed to acenaphthene-5-carboxylic acid, commonly called acenaphthoic acid. Acenaphthoic acid had been prepared by Liebermann[59] in 30% yield using oxalyl chloride, and by Grignard[60] (1) by the action of carbon dioxide upon the magnesium derivative of acenaphthene, and (2) by hydrolysis of the nitrile obtained by treating 5-bromoacenaphthene with magnesium and cyanogen chloride.

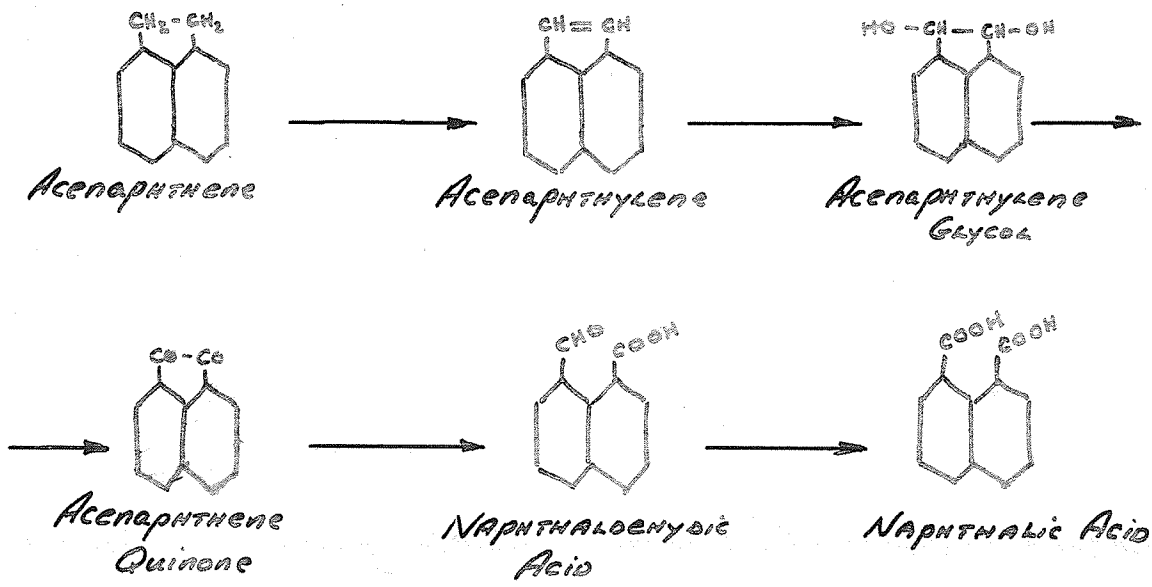
There were several patents[61] covering the preparation of mono- and di-carboxylic acids of acenaphthene. Acenaphthene-5-carb--oxylic acid and acenaphthene-5,6-dicarboxylic acid were prepared by condensing acenaphthene with an alkyl phenylurea or an alkyl phenylcarbamyl chloride (which may have a chlorine or methyl group substituted in the phenyl nucleus) in the presence of an aluminum halide, and then hydrolysing the resulting alkylanilides.

Oxidation Products

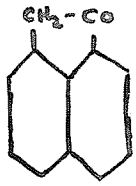
Most of the work done in the field of acenaphthene chemistry has been the investigation of the oxidation products of acenaphthene. Investigations took their natural course, which was the perfection of methods for preparing the individual products and for separating the various products from crude oxidation mixtures. It was indeed shown in the earliest experiments that the yields of the individual products depended very definitely upon the reaction conditions, and also that a great variety of products were formed.

Graebe[62] established the relationship between acenaphthene and its oxidation products, and also established the most favorable conditions for maximum yields of some of the more important products. These conditions have not been improved upon until quite recently. Graebe reported yields of 40% for acenaphthene quinone, whereas Dashevski and Karishin[63] have modified his method to raise the yield to 71%.

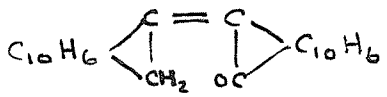
The oxidation of acenaphthene proceeds through the following stages-



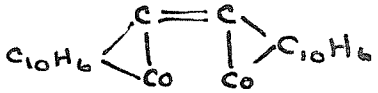
Intermediate between acenaphthene and acenaphthylene there is another product which also may be regarded as a product of direct oxidation. This product is acenaphthenone.



There are also a number of secondary oxidation products formed from the primary oxidation products. These secondary oxidation products are biacenaphthylidene ketone and biacenaphth--ylidenedione, formed by the condensation of one molecule of



Biacenaphthylidene Ketone

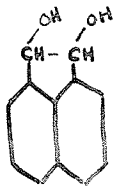


Biacenaphthylidenedione

acenaphthene quinone with one molecule of acenaphthene or one molecule of acenaphthenone respectively. Biacenaphthylidenedione has been found in nearly all of the oxidation reaction products. the three most common compounds found in the product of oxidation of acenaphthene were acenaphthene quinone, naphthalic acid, and biacenaphthylidenedione. Acenaphthenone and naphthaldehydic acid were also found in small amounts in oxidation mixtures. Graebe determined the experimental conditions for the best yields of acenaphthene quinone and naphthalic acid. His efforts succeeded in yields of 40% for acenaphthene quinone, and almost 100% for the naphthalic acid. However, later researchers[64] were unable to duplicate Graebe's yield of 100% for naphthalic acid, no matter how precisely the conditions were duplicated. Graebe emphasised the fact that

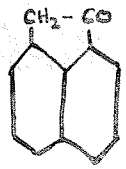
great care was needed in carrying out the oxidation reaction. Also care had to be exercised in extracting acenaphthene quinone, for the concentrations of the sodium hydroxide solutions used in the extraction were of utmost importance. If dilute (5%) sodium hydroxide solution were used during the extraction of the quinone, practically all of the quinone was precipitated by the addition of a mineral acid. If more concentrated caustic solutions (30%) were used, an almost quantitative yield of naphthaldehydic acid resulted upon the addition of the mineral acid. The more important oxidation products are now to be considered in detail.

Acenaphthylene Glycol

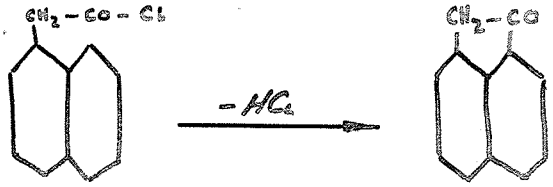


Up until 1938, this product had not been isolated from the products of direct oxidation of acenaphthene. It had been prepared from acenaphthylene bromide by (1) transforming the bromide into the acetate and saponifying the result[65], and (2) boiling the bromide with water[66]. In 1938, L. Monti[67] reported the isolating of two acenaphthylene glycols from the products of direct oxidation of acenaphthene with selenium dioxide. The two glycols were believed to be cis and trans geometric isomers.

Acenaphthenone



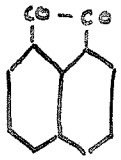
This product appears to be midway between acenaphthene and acenaphthylene. It has been prepared from acenaphthylene glycol (1) by treating the glycol with sodium alcoholate and methyl iodide,[68] and (2) by boiling the glycol with concentrated hydrochloric acid, and then steam distilling the solution, the acenaphthenone appear--ing in the distillate.[69] The oxidation of acenaphthenol with chromic acid in glacial acetic acid also yielded acenaphthenone.[70] There were several methods of preparation from acenaphthene quinone. The direct reduction of the quinone in acetic acid with zinc dust, or the conversion of the quinone to the dichloride with phosphorus pentachloride, followed by reduction both produced the desired acenaphthenone in 35-37% yields. Acenaphthenone is also produced by the action of aluminum chloride on ∝-naphthylacetyl chloride in nitrobenzene according to the equation[71]



Being part quinone in nature, it would be expected that acenaphthenone exhibit some of the characteristics of quinones. It polymerized to yield biacenaphthylidenedione. Derivatives of acenaphthenone, in which the hydrogen of the methylene groups had not been replaced, were condensed with isatin or naphthisatin, which contain an ∝-ketone oxygen atom, to form indigoid dyes.[72]

The possibilities of reaction of acenaphthenone are many in view of the fact that the substance, in addition to a reactive carbonyl group, possesses a methylene group which is very reactive. The dichloro- derivative also has many possibilities for reaction.

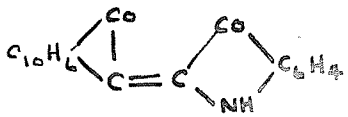
Acenaphthene Quinone

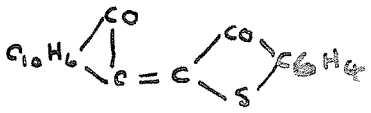


This is by far the most important commercial oxidation product of acenaphthene. Its greatest application is found in the field of dye chemistry. It has been found that neither the character nor the quantity of the oxidizing agent had little effect upon the yield of quinone from acenaphthene, whereas the speed at which the reaction was carried out appeared to be of utmost importance. The yields generally ran around 40% under the most favorable conditions. Dashevski and Karishin,[73] in 1936, using ammonium dichromate reported a yield of 71% for the quinone. The reason for the generally low yields was the fact that the quinone itself was very reactive and condenses with other of the oxidation products. In the earlier investigations where alkali was employed to separate the quinone, it was observed that acenaphthene quinone underwent a number of transformations, among which were the formation of a salt of naphthaldehydic acid and the formation of biacenaphthylidenedione. The separation of the quinone was generally affected by precip-itation of the quinone as the bisulphite addition product[74] or as its monoxime.[75] This latter process removed some of the difficulties but not all of them.

Acenaphthene quinone undergoes four general types of condensation reactions. The first of these involves the condens--ation of one molecule of quinone with one or more molecules of another substance. For example, the condensing substance could be an amine with the amino hydrogen and the carbonyl oxygen being eliminated as water. A second type is the condensation of the quinone with aromatic hydrocarbons or their derivatives in the presence of aluminum chloride.[76] 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. A third type of condensation, with halogen substituted hydrocarbons, is one which does not involve the carbonyl oxygen. The hydrogen atoms of the peri positions of acenaphthene and the halogen atoms of the condensing hydrocarbon are eliminated as the halogen acid. The hydrocarbon residue att--aches itself to the acenaphthene molecule in the peri positions. Certain of the higher indandiones are synthesized in this manner.

The fourth and most important type of reaction involves the preparation of indigoid class vat dyes. These reactions are covered by a large number of patents. The first references to this type of reaction were by A. Grob,[77] A. Bezdrik and P. Friedlander.[78] They condensed acenaphthene quinone with indoxyl and 3-oxythio--naphthene to get indigoid type products.





The product of condensation with 3-oxythionaphthene is known as Ciba Scarlet G. (B.A.S.F.), Thio-indigo Scarlet 2G. (Kalle & Co.),

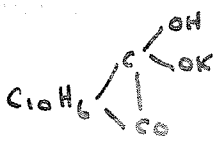
and Helidone Scarlet C. (M.L.B.). Patents have been issued covering all of the halogenated products which may be derived from acenaphthene quinone, its homologues, and all substances analogous to it. All of the patents covering the condensation of acenaphthene quinone with indoxyl, 3-oxythionaphthene, and similar substances are phrased so as to include all possible reactions between carbonyl oxygen, present in every variety of α-diketone grouping, and reactive methylene or methine group present in any form of combination.

Other Oxidation Products

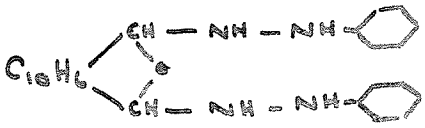
Biacenaphthylidenedione and biacenaphthylidene ketone are secondary oxidation products formed by the action of various reagents upon acenaphthenone and acenaphthene quinone.

The end product of acenaphthene oxidation is naphthalic acid or its anhydride, and was one of the earliest oxidation products investigated.[79] Most of the early investigations involved the use of sodium or potassium dichromates with concentrated sulphuric acid, and the yields varied from 16-20% for Behr and Van Dorp to almost 100% for Graebe. Ullmann[80] repeated Graebe's work but was not able to obtain over a 40% yield. The main difficulty appeared to be stopping the reaction before the naphthalic acid was appreciably decomposed.

Naphthaldehydic acid is quite an interesting substance whose salts appear to exist in two tautomeric forms.



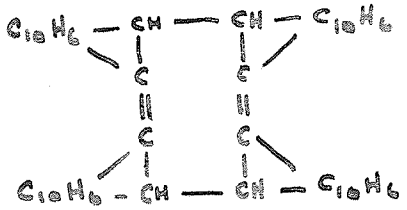
It was formed almost quantitatively when acenaphthene quinone was dissolved in 30-33% aqueous potassium hydroxide solution.[81] The free acid was precipitated by mineral acids, and purified by recrystal--lization from alcohol. It condenses readily with phenylhydrazine to give



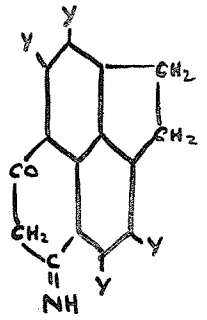
The preparation of naphthaldehydic acid from acenaphthene quinone is covered by patents.[82]

Condensation Reactions

Oxidation of acenaphthene in a solvent yields the usual products, such as acenaphthene quinone. However, if ace--naphthene is heated to 340°C under pressure with PbO, decacyclene, $C_{36}H_{18}$, is formed; using PbO_2 at lower temperatures (180-200°C.) fluorocyclene, $C_{48}H_{22}$, shown below, is obtained in 30% yield with only a little decacyclene.[83]

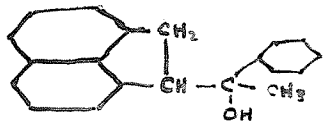


Acenaphthene condensed in a large number of reactions with various substances. Some of the condensations involved the hydrogen atoms of the naphthalene nucleus, whereas others involved the hydrogen atoms of the methylene groups of acenaphthene. Acenaphthene was found to condense with maleic anhydride in the presence of acid condensing agents, such as aluminum chloride, sodium aluminum chloride, or ferric chloride, in nitrobenzene as solvent, first forming open chain carboxylic acids which, on further condensation, yielded cyclic ketone carboxylic acids.[84] One compound which had been isolated from such a reaction was 1-ace--naphthylsuccinic acid, a glass-like substance which sublimed in vacuo in a carbon dioxide stream at about 200°C.[85] The condensation of acenaphthene or substituted acenaphthenes with cyanoacetyl chloride in the presence of aluminum chloride at 90-160°C. yielded products of the general formula

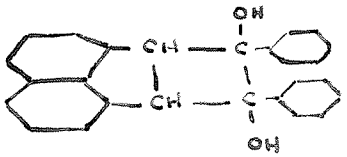


which are ketimides of acenaphthene-peri-indandiones, and are useful as intermediates for dyes.[86]

E. Oliveri-Mandala[87] had investigated the effect of sunlight upon condensations of acenaphthene with acetophenone and benzil. The product from the condensation of acenaphthene with acetophenone had the formula $C_{20}H_{18}O$, and its configuration was assumed to be



Acenaphthylene was also detected in the reaction product, but no acetophenone pinacol was found, even though its presence was thought likely due to a partial reduction of acetophenone in the conversion of acenaphthene to acenaphthylene. The condensation of acenaphthene and benzil yielded a product, $C_{26}H_{20}O_3$, which was considered to be



Acenaphthylene and benzylbenzoin were also found to be formed, the benzylbenzoin being formed by partial reduction of the benzil.

Exposure of acenaphthene in purified acetone to sun light yielded traces of acenaphthenone. There appeared to be no photochemical reaction between acenaphthene and diphenylmethane, nor between acenaphthene quinone and diphenylethane.

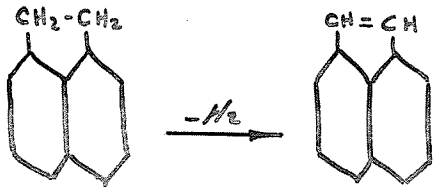
Like many aromatic hydrocarbons, acenaphthene combined with a number of aromatic nitro compounds to form readily dissociated addition compounds.[88] Picryl bromide and chloride formed molecular addition compounds with acenaphthene, melting at 104.3°C. and 113.2°C., respectively. Acenaphthene formed molecular compounds with both chlorodinitrobenzene and bromodinitrobenzene,

melting at 65.8°C. and 58.6°C. respectively. Mononitrohalobenzenes do not form molecular compounds with acenaphthene, but frequently do give eutectic points. In the system of acenaphthene and o-chloronitrobenzene, a eutectic was formed at 26.8% acenaphthene, melting at 25.7°C. Meta-dinitrobenzene formed with acenaphthene a molecular compound melting at 72.6°C. Acenaphthene united with two molecules of 2,4-dinitrotoluene to form a compound congruently melting at 51.7°C. While mononitro compounds, such as nitrophenols, fail generally to give addition compounds with most hydrocarbons, o-nitrophenol united with acenaphthene to form a readily dissociated compound melting at 65.5°C. With three molecules of m-aminonitrobenzene, acenaphthene formed a compound congruently melting at 119.5°C.

A rather unusual use for acenaphthene was indicated by investigations of Remo de Fazi[89]. Cyclic aldehydes gave a red-violet coloration with acenaphthene and sulphuric acid. All attempts by de Fazi to isolate the colored complex have failed. The mechanism of the reaction has not been fully determined. The characteristic red-violet coloration was obtained only when cyclic aldehydes were tested, and did not appear when aliphatic aldehydes were tested. Many sugars gave the red-violet coloration when treated with acenaphthene and sulphuric acid. This was believed to be due to the presence of minute quantities of furfural.

C: The Chemistry of Acenaphthylene.

Acenaphthylene is an aromatic hydrocarbon, very similar in structure to acenaphthene, from which it is formed by the loss of two hydrogen atoms from the methylene groups, as indicated by the equation



Many methods of preparation have been found in the literature. A goodly number of the methods dealt with the vapour phase oxidation of acenaphthene. Dziewonski[90] prepared acenaphthylene by passing acenaphthene vapours through a red-hot quartz tube in a carbon dioxide atmosphere. Bowen and Marsh[91] employed a silica tube under similar conditions. Fischer, Schrader, and Meyer[92] used a tin-plated tube heated to 760-770°C. to effect the preparation of acenaphthylene from acenaphthene vapours. Several investigators had employed catalysts as well as high temperatures. Goswami[93] used reduced nickel as catalyst, and Marek and Hahn[94] used powdered manganese dioxide as catalyst. Two patents[95] had been issued covering the use of catalysts containing elemental silicon and carbon, and also metals of the second to seventh groups which form difficultly reduced oxides or compounds of these metals, for example, zinc molybdate and magnesium oxide, zinc oxide and aluminum oxide, magnesium oxide and carbon. There were few yields given in the above methods of preparation, except for that of Marek and Hahn, who gave a yield figure of almost 100%. The

indications were that the yields for most of the methods were very low.

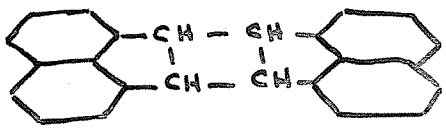
Acenaphthylene had been prepared from several substituted acenaphthenes.[96] Mayer and Kaufmann prepared acenaphthylene by the zinc dust distillation of 5-ethylacenaphthene. Dziewonski[97] obtained acenaphthylene from acenaphthene-3-, or -5-sulphonic acids by (1) distillation of the sulphonic acid with potassium cyanide under reduced pressure, and (2) fusion with alkali. Acenaphthylene was prepared in small yield by E. Oliveri-Mandala[98] by the distillation of the potassium salt of acenaphthene-5-sulphonic acid with potassium ferrocyanide. Braun, Hahn, and Seemann[99] prepared acenaph--thylene by the passage of 5-acetylacenaphthene through a tube heated at 700°C. in the presence of lead dioxide.

L. Monti[100] obtained acenaphthylene in 16% yield by the oxidation of fused acenaphthene with selenium dioxide. Acenaphth--ylene glycols were also isolated from the oxidation product. L. Monti[101] also employed lead tetraacetate as the oxidizing agent, but the results were only fair. R. Marquis[102] oxidized acenaphthene with lead dioxide in glacial acetic acid to acenaphthenol, and found that the action of thionyl chloride upon acenaphthenol yielded a small amount of acenaphthylene.

The best yields of acenaphthylene were obtained by R. G. Flower.[103] Acenaphthylene was prepared in 70% yield by the passage of acenaphthene vapours through a stainless steel column heated at 450-485°C., and packed with a catalyst of 10% manganese dioxide and 90% alumina, the whole system being maintained at a pressure of 100 mm. of mercury. Flower also passed 1-acetoxyacenaphthene

through a quartz tube heated at 520°C., with dry carbon dioxide gas as a diluent, or through a stainless steel column heated at 520°C., and packed with a catalyst of 10% copper borate and 90% alumina, the latter system being maintained at a pressure of 2 mm. of mercury. The yields of acenaphthylene in these last two methods were 82% and 87% respectively.

The chemistry of acenaphthylene had not been investigated to any great extent. Acenaphthylene forms gleaming lemon yellow plates, from alcohol, melting at 92-3°C. It forms an addition compound with picric acid melting at 201°C. Acenaphthylene is soluble in alcohol and ether, and is readily polymerized into polyacenaphthylene,[104] $(C_{12}H_8)_{22}$, a pale yellow powder which is insoluble in alcohol and ether. Another polymer,[105] allopolyacenaph-thylene, $(C_{12}H_8)_6$, was formed by the action of strong acids upon acenaphthylene. Dziewonski and Rapalski[106] investigated the action of sunlight upon acenaphthylene in benzene, and succeeded in isolating dinaphthylenecyclobutane.



Dinaphthylenecyclobutane crystallized in silky needles melting at 306-7°C., and was very resistant to chemical reagents.

There were very few of the common derivatives of ace-naphthylene, such as the halogen substituted acenaphthylenes and the nitro- or sulphonic acid substituted acenaphthylenes. Only three halogenated acenaphthylenes were listed in the literature. Beilstein lists 1,2-dibromoacenaphthylene, melting

at 121-3°C. B. Campbell[107] prepared 1,2-dichloroacenaphthene by the action of chlorine upon acenaphthylene. The 1,2-dichloroace--naphthene melted at 115°C. From 1,2-dichloroacenaphthene, Campbell prepared 1-monochloroacenaphthylene, a yellow oil.

EXPERIMENTAL WORK

ATTEMPTED OXIDATION OF ACENAPHTHENE BY POTASSIUM PERMANGANATE

Several hundred millilitres of acetone were refluxed with potassium permanganate until the pink color of the permanganate was permanent, and then were purified by distillation. The process removed all of the oxidizable materials from the acetone.

Acenaphthene (3 gm.) was added to acetone (50 ml.) in a 125 ml. Erlenmeyer flask and refluxed with potassium permanganate until the pink color was permanent. The brown residue of manganese dioxide was filtered from the reaction solution and most of the acetone was removed by distillation. The reaction product crystallized out from the solution in the form of long white needles, melting at 94-5^{o}C. The picrate derivative of the oxidation product melted at 160-1^{o}C. These two melting points correspond to those of acenaphthene. There was no acenaphthylene produced in the reaction.

Purified acetone (35 ml.), acenaphthene (1 gm.), and potassium permanganate (5 gm.) were placed in a 125 ml. stoppered Erlenmeyer flask, and allowed to stand for several weeks at room temperature with occasional shaking. The manganese dioxide residue was filtered from the reaction solution, and the acetone was allowed to evaporate. Again, the product was long white needles, melting at 94-5^{o}C. No acenaphthylene was produced in the reaction.

The experiments were repeated using potassium dichromate in place of the potassium permanganate. Only unchanged acenaphthene

was recovered from the acetone solutions. Although there was evidence of some oxidation taking place, nothing but unoxidized acenaphthene could be isolated.

ATTEMPTED PERBENZOIC ACID OXIDATION OF ACENAPHTHENE

Perbenzoic acid was prepared by the method given in "Reactions of Organic Chemistry"- Hickinbottom, page 231-2.

Finely ground benzoyl peroxide (62 gm.) was suspended in dry toluene (800 ml.) in a 3-litre flask equipped with a stopper, and cooled to below -5°C. by means of a freezing bath. An ice-cold solution of sodium ethoxide (12 gm. of sodium in 250 ml. of absolute ethyl alcohol) was added and the mixture was stirred vigorously. When all of the ethoxide had been added, 1 litre of ice-cold water was added and the contents of the flask were stirred until all of the benzoyl peroxide had disappeared. The toluene layer was separated in a cooled separatory funnel, and the aqueous layer was extracted with ether. The sodium salt of perbenzoic acid was present in the aqueous layer which was cooled to 0°C. and acidified by the cautious addition of an ice-cold solution of sulphuric acid (27 gm.) in water (25 ml.). The perbenzoic acid separated as a thick oil which was extracted by three 150 ml. portions of chloroform. The chloroform extract was dried over anhydrous sodium sulphate, and kept in an ice chest until required.

The chloroform solution, containing 12.5 gm. of per--benzoic acid, was cooled to 0°C. and acenaphthene (7 gm.) was added. The reaction mixture was allowed to stand for three days

at 0°C., at the end of which time it was found that there had been little change in the perbenzoic acid concentration. The temperature of the reaction mixture was raised to room temperature. At the end of three days it was found that the perbenzoic acid had completely reacted. The solution was washed with a dilute solution of sodium hydroxide until acidification of the alkaline washings ceased to produce benzoic acid. The chloroform solution was washed with water to remove the sodium hydroxide, and finally was dried over anhydrous sodium sulphate. The dried solution was distilled to remove the chloroform. The dark brown residue was dissolved in ethyl alcohol and allowed to crystallize. Long white needles of acenaphthene separated out, and there remained behind a few drops of a very thick brown viscous liquid. As far as could be determined, there was no acenaphthylene produced by the reaction.

VAPOUR PHASE OXIDATIONS OF ACENAPHTHENE

Using Glass Tube and Manganese Dioxide

A mixture of air and acenaphthene vapours (15 gm.) was passed through a glass combustion tube filled with powdered manganese dioxide, and heated to around 400°C. A yellow condensate was deposited in the receiver connected to the end of the combustion tube. The condensate was dissolved in ethyl alcohol and the picrate derivative was prepared by the addition of an equal volume of alcoholic picric acid. The picrate derivative was fractionally crystallized to separate the picrate of acenaphthylene, melting at 201°C., from that of acenaphthene, melting at 161°C.

When the separation of the two picrates was complete, as shown by the sharpness of the melting points of the two fractions, the acenaphthylene was regenerated from its picrate by treatment of the picrate with dilute ammonia solution. The yield of acenaph--thylene was 1.5 gm. or 10%.

Using A Silica Tube Alone

A silica tube was wound with nichrome wire, as a heating coil, and insulated with asbestos. Acenaphthene vapours (10 gm.) mixed with dry carbon dioxide gas as a diluent were passed through the tube which was heated to red heat electrically. A black powder was condensed in the receiver attached to the end of the silica tube. This powder was dissolved in ethyl alcohol and purified by recrystallization. The yellow recrystallized product was converted into the picrate derivative and the picrate was fractionally crystallized from ethyl alcohol. The acenaphthylene picrate was decomposed by ammonia solution to yield .9 gm. of pure acenaphthylene, a yield of 9%.

ATTEMPTED SYNTHESIS FROM α-VINYLNAPHTHALENE

Bromonaphthalene was prepared according to the method in "Organic Syntheses", Collective Volume I, page 121.

Vinyl bromide was prepared in 85% yield by treating ethylene dibromide with excess of 20% alcoholic potassium hydroxide.

The synthesis of α-vinylnaphthalene was not carried out

because of a lack of ferric chlorode catalyst necessary for the synthesis. This lack has since been eliminated and work can proceed as planned.

ATTEMPTED OXIDATION OF ACENAPHTHENE BY SELENIUM DIOXIDE

Selenium dioxide (47.5 gm. C.P. grade) was added to fused acenaphthene (30 gm.) heated to 150-170°C. in a 500 ml. round bottom flask. The addition was made very slowly, and, after all of the selenium dioxide had been added, the mixture was heated for a half hour at the same temperatures. The mixture was then exhaustively extracted with hot ethyl alcohol. The alcohol was removed by distillation, and the residue was steam distilled. The distillate was extracted with ether, and the ether extract was dried over anhydrous calcium chloride. The ether was removed from the dried extract by evaporation, leaving a crystalline residue which had only a faint tinge of yellow color. No separation of acenaphthylene could be made, and only acenaphthene could be recovered.

The oxidation was repeated using commercial grade selenium dioxide, but no better results were obtained. Only unoxidized acenaphthene was recovered.

ACENAPHTHYLENE FROM 1-ACETOXYACENAPHTHENE

Preparation of 1-Acetoxyacenaphthene

1-Acetoxyacenaphthene was prepared by the method of Fieser and Cason (J. Amer. Chem. Soc. 62; 434.).

A solution of acenaphthene (154 gm.) in glacial acetic acid (1100 ml.), which had been distilled over potassium per--manganate, was raised to a temperature of 60-70°C. This temp--erature was maintained during the addition of red oxide of lead (820 gm.) in 50 gm. lots over a period of about 50 minutes. Each fresh addition of red oxide of lead was made upon the discharge of the red coloration of the solution. Shortly after the addition of the oxidizing agent the test for lead tetraacetate with moistened starch-iodide paper was negative. The red viscous liquid was poured into two litres of water, and the precipitated yellow oil was extracted with two portions of ether, 350 ml. and 250 ml. respectively. The ether extract was shaken with a saturated salt solution and then washed again with water. The ethereal solution was dried over anhydrous sodium sulphate. After removal of the ether, the residue was distilled under reduced pressure. The fraction distilling at 165-175°C. at 12 mm. was collected. The yield was 170 gm. of acetoxyacenaphthene, or 70%.

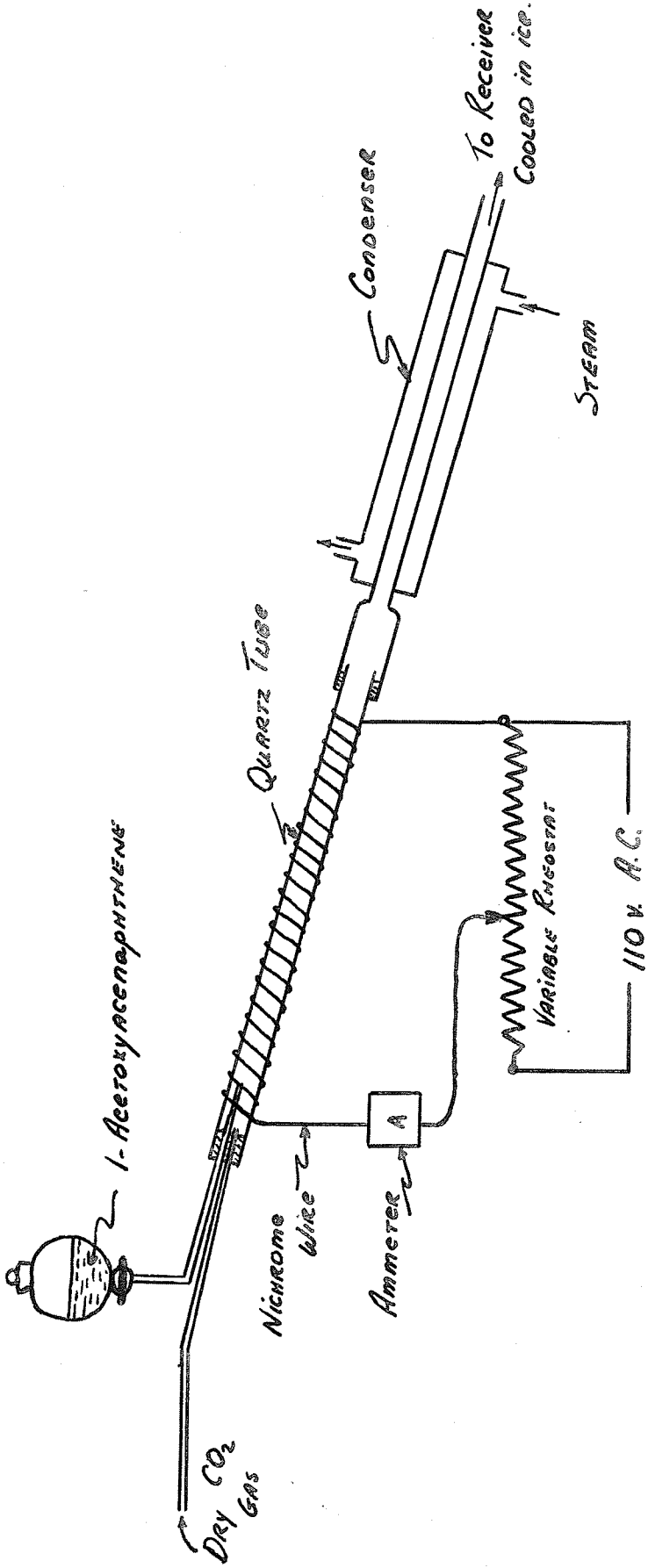
There was a considerable bulk of residue in the distill--ing flask, after the distillation of the 1-acetoxyacenaphthene was completed. It was a shiny, black vitreous mass, which was insoluble in all organic solvents, and only very slightly soluble in hot concentrated sulphuric acid.

Pyrolysis of 1-Acetoxyacenaphthene

A 5/8 inch quartz tube was wound with nichrome wire for about 8 inches, starting 2 inches from the top end of the tube and ending about 3 inches from the lower end of the tube. The wire windings were then covered with a half inch layer of an asbestos and water mixture, and finally covered with a few sheets of asbestos paper. The asbestos paper was held in place by three pieces of wire.

The ends of the nichrome wire heating coil were connected to a variable rheostat as in the diagram on page 50. The rheostat was in turn connected to a 110 volt A.C. source. An ammeter was inserted into the heating circuit to determine the current which must be maintained for a temperature of 520°C. inside the tube. The resistance of the heating coil was 12.5 ohms. To produce at least 100 watts of power a current of approximately 3 amperes was desired. Using a 110 volt A.C. source the total resistance of the heating circuit had to be around 40 ohms. The rheostat, therefore, had to have a resistance over 30 ohms and a current capacity of over 3 ohms.

A thermocouple, which read the temperature directly, was inserted into the end of the quartz tube until it was in the centre of the tube. The heating coil was connected to the 110 volt A.C. source, and the rheostat was adjusted until the temperature of the quartz tube registered at 520°C. on the thermocouple. Several trials were made, and the average current through the heating element required to produce the temperature of 520°C. was found to be 3.29 amperes.



Pyrolysis of 1-Acetoxyacenaphthene

The apparatus was set up as in the diagram on page 50. The reservoir for the 1-acetoxyacenaphthene was a small dropping funnel with the tip drawn out to a jet approximately ½ mm. in diameter. The tip of the jet extended at least 3 inches into the tube. 1-Acetoxyacenaphthene was passed through the heated tube at the rate of roughly 80 drops per minute. At the same time, dry carbon dioxide gas from a Kipp generator was passed through at the rate of two bubbles per second. The carbon dioxide gas served as a diluent and prevented the occurrence of side reactions. The hot vapours were passed through a steam heated glass condenser, and the condensate was collected in a large receiver cooled in ice. The product was a hard dark green mass. It was crushed and washed with water until entirely free from acetic acid. The crude residue was then recrystallized from ethyl alcohol to form large yellow plates, or fine yellow crystals of acenaphthylene, melting at 92-3°C.

A typical run, using 245 gm. of 1-acetoxyacenaphthene, produced 140 gm. of acenaphthylene, a yield of 80%. The total time of the run was seven hours.

The most efficient rate of flow of the acetoxyacenaph-
-thene was best judged by observation of the vapours as they left the heated quartz tube. They should not be thick and billowy, but should be thin and pale yellow in color. The color of the vapours as they condense on the upper part of the condenser should be very pale yellow or even colorless, but never a bright yellow. Acetic acid was a by-product of the pyrolysis reaction, and helped to carry the acenaphthylene through the condenser. The appearance

of a heavy yellow cloud of vapours issuing from the end of the heated tube indicated that the acetoxyacenaphthene was passing unreacted through the tube, and the rate of flow of the acetoxy--acenaphthene was cut down. This adjustment was very fine, and, at best, the rate of flow was quite slow. The rate of flow was judged after a time by experience.

After several runs of 1-acetoxyacenaphthene of several hundred grams each, the quartz tube was found to be coated on the inside with a thin layer of black carbonaceous material which cut down the efficiency of operation. This layer had to be scraped out of the tube in order to return to efficient operation.

Freshly recrystallized acenaphthylene could be kept for several weeks in a closed container without much oxidation. Upon exposure to air for several days, it appears to oxidize slightly and should be recrystallized before use.

ATTEMPTS TO PREPARE ACENAPHTHYLENE CHLOROHYDRIN

Preparation of Hypochlorous Acid Solutions

Urea (40 gm.), precipitated chalk (28 gm.), and water (30 gm.) were placed in a 250 ml. Erlenmeyer flask equipped with an inlet tube passing well below the surface of the mixture, and an outlet tube leading to the fume chamber to conduct off the carbon dioxide gas and any unreacted chlorine gas. Chlorine gas from a cylinder was added through the inlet tube until the weight of the tube and flask increased by 24 gm. All the time the

chlorine was being passed in, the solution was cooled in ice and was frequently agitated. After the chlorine had been added, the solution was filtered and diluted to 200 ml. with water. This solution was a fairly concentrated solution of monochlorourea.

The strength of the solution was determined by withdrawing a 1 ml. sample, diluting the sample with 25 ml. of water, adding excess 10% potassium iodide solution, and acidifying with glacial acetic acid. The solution darkened with the liberation of iodine, and this free iodine was titrated with N/10 sodium thiosulphate solution, using starch solution as the indicator.

Typical Data

Weight of chlorine -- 24 gm. Time -- 6 hours

Volume of solution -- 205 ml. 1 ml. = 39.6 ml. N/10 sodium thiosulphate solution

This was a 16% hypochlorous acid solution, and contained sufficient acid to react with 66 gm. of acenaphthylene, allowing 10% excess of acenaphthylene.

REACTION OF HYPOCHLOROUS ACID SOLUTION AND ACENAPHTHYLENE

Acenaphthylene (66 gm.) was added to 203 ml. of the monochlorourea solution (prepared above) in a 1 litre flask fitted with an efficient stirrer. Water (150 gm.) and glacial acetic acid (25 ml.) were added. The mixture was stirred until all of the hypochlorous acid was used up. The reaction took several days for completion at room temperature. A very thick brown mass settled to the bottom of the flask. The reaction mixture was then steam distilled until 3 litres of distillate

had been collected. The distillate was saturated with salt and extracted with ether. The ether extract was dried over anhydrous sodium sulphate, and then the ether was distilled off under reduced pressure. The distillation was continued and a yellow solid distilled over at 130-145°C. at 10 mm. pressure. The yield was 2 gm. The crude solid melted at 68-74°C., and when purified from ethyl alcohol it melted at 91-3°C. It was only recovered acenaphthylene. The brown residue in the steam distillation flask was insoluble in all organic solvents, and could not be identified.

Several trials resulted in the same negligible results. the brown inert mass was undoubtedly a condensation product of acenaphthylene, or a polymerized form of acenaphthylene.

MODIFIED ATTEMPTS TO PREPARE THE CHLOROHYDRIN OF ACENAPHTHYLENE

A second quantity of monochlorourea solution was prepared, using twice the previous quantities of reagents. The addition of 49.6 gm. of chlorine required 3 hours. A solution of 450 ml. was prepared, 1 ml. of which was equivalent to 39.8 ml. of N/10 sodium thiosulphate solution. This meant that the solution was 14% hypochlorous acid. The solution was divided into three 150 ml. portions, each of which contained 20 gm. of hypochlorous acid, which is sufficient to react with 60 gm. of acenaphthylene.

The three solutions were placed in 500 ml. round bottom flasks, and labelled I, II, and III respectively. To

each flask acenaphthylene (25 gm.) was added, as well as glacial acetic acid (20 ml.). To flask II, water (75 ml.) was added. To flask III, water (150 ml.) was added.

The flasks were shaken occasionally, and allowed to stand overnight at room temperature. The material in Flask I had almost completely liquefied, while in flasks II and III there were signs of liquid, but only to a limited extent. The flasks were then shaken for 60 hours, and then allowed to stand for 5 days in the dark.

Flask I was extracted with ether, and the extract was washed with dilute sodium hydroxide solution, then with water to remove the sodium hydroxide, and finally dried over anhydrous sodium sulphate. The dried extract was distilled in vacuo to yield 12 gm. of a yellow oil, which distilled at 175-190°C. at 29 mm. pressure. The chlorine content of the oil was determined as 19.93% chlorine. There appeared to be some slight decomposition during distillation with the evolution of hydrogen chloride gas. The residue in the flask appeared to be the same as that residue found in the distillation of 1-acetoxyacenaphthene.

Flask II was steam distilled to recover unreacted acenaphthylene. None was recovered. The residue in the steam distillation flask was extracted with ether. The ether extract was washed with dilute sodium bicarbonate solution, then with water, and finally dried over anhydrous sodium sulphate. The dried extract was distilled under reduced pressure to yield 5 gm. of a yellow oil, which distilled over at 170-180°C. at 25 mm. pressure. This appeared to be the same product that was obtained

in larger yield from flask I. Again there appeared to be some slight decomposition during distillation with the evolution of hydrogen chloride gas.

Flask III was accidentally broken.

ISOLATION OF A NEW DICHLOROACENAPHTHENE

A number of small runs were made according to the plan followed for flask I of the above experiment until about 30 gm. of the yellow oil were collected.

The oil was allowed to stand for several weeks, at the end of which time a crop of crystals had appeared in the oil. The crystals were filtered from the oil, washed with ether, and then recrystallized from ethyl alcohol to yield 1 gm. of fine white needles, which melted sharply at 64°C. The compound contained chlorine.

% chlorine found ---------- 31.83%

% chlorine for $C_{12}H_8Cl_2$ --- 31.79% (calculated)

The chlorine content was identical with that of a dichloroacenaphthene. It was most probable that the chlorine atoms were in the 1- and 2- positions. That means the compound would be 1,2-dichloroacenaphthene. A 1,2-dichloroacenaphthene had already been isolated by previous investigators, and had been found to melt at 115°C. The two dichloroacenaphthenes were assumed to be geometric isomers.

PREPARATION OF 1,2-DICHLOROACENAPHTHENE

According to B.A. Campbell. (J. Chem. Soc. 107; 918.)

Acenaphthylene (20 gm.) was dissolved in carbon tetrachloride (150 ml.) in a 200 ml. round bottom flask, which was equipped with an inlet tube passing well beneath the surface of the solution, and also an outlet tube to conduct excess chlorine vapours to the fume chamber. The flask and contents were cooled in ice, and chlorine, which had been saturated with carbon tetra--chloride vapours, was passed into the solution through the inlet tube until the weight of the flask had increased by 11.5 gm. The flask and contents were allowed to stand for several hours in an ice chest, after which time a crop of light green crystals was filtered from the solution. Repeated evaporation of the solvent, cooling, and filtration yielded considerable quantities of crystals until the mother liquor became too thick for further crystallization to occur. The crystals were washed with ligroin, and recrystallized from ethyl alcohol until the crystals melted sharply at 115°C. The yield was 9 gm. of fine white crystals of 1,2-dichloroacenaphthene.

PREPARATION OF 1-MONOCHLOROACENAPHTHYLENE

According to B.A. Campbell. (J. Chem. Soc. 107; 918.)

Dichloroacenaphthene (10 gm.) was placed in a 125 ml. round bottom flask equipped with a reflux condenser. Sodium (1.2 gm.) was dissolved in ethyl alcohol (70 ml. of absolute ethyl alcohol) and added to the dichloroacenaphthene in the

flask. The mixture was refluxed for one hour, and then thoroughly cooled. The solution was poured into 150 ml. of ice water. A bright orange precipitate formed, and, after settling, was filtered off. The precipitate liquefied upon standing at room temperature for a few minutes. The filtrate was extracted with ether, and the precipitate was added to the ether extract, which was washed with water and dried over anhydrous magnesium sulphate. The dried extract was distilled under reduced pressure to yield a yellow oil which distilled at 135-140°C. at a pressure of 6 mm. of mercury. A picrate derivative of the oil was made, and found to melt at 150-152°C.

IDENTIFICATION OF THE PRODUCT OF REACTION BETWEEN HYPOCHLOROUS ACID AND ACENAPHTHYLENE

The yellow oil produced by the reaction of hypochlorous acid upon acenaphthylene (page 54) was fractionated into three fractions under a reduced pressure of 6 mm. of mercury.

The three fractions were

Fraction 1 - 130-140°C.

Fraction 2 - 140-145°C.

Fraction 3 - 145-150°C.

When placed in an ice chest overnight, the three fractions each behaved differently. Fraction 1 remained liquid, fraction 2 became quite viscous, and fraction 3 became completely solid.

A solution of fraction 2 in ethyl alcohol was mixed with an equal volume of a saturated solution of picric acid in ethyl

alcohol. The mixture was heated to boiling, and then cooled in an ice chest until an orange picrate derivative precipitated from the solution. This picrate derivative melted at 151-3°C. A mixed melting point of this picrate and that of 1-monochloroace--naphthylene was found to be 149-151°C.

The first two fractions were analysed for chlorine. Fraction 1 contained 17.12% chlorine, and fraction 2 contained 22.24% chlorine. The calculated chlorine content of acenaphthylene chlorohydrin was 17.23% chlorine.

Fraction 1 was possibly the desired acenaphthylene chlorohydrin, and fractions 2 and 3 possibly contained some of the new dichloroacenaphthene as an impurity to account for the high chlorine content. A comprehensive study of the yellow oil should reveal its nature readily.

PERBENZOIC ACID OXIDATION OF ACENAPHTHYLENE

Perbenzoic acid solution was prepared by the method outlined on page 44. Acenaphthylene (10.5 gm.) was added to the chloroform solution (275 ml.) of perbenzoic acid, which contained 9.5 gm. of perbenzoic acid, in a 500 ml. round bottom flask. The flask was stoppered and allowed to stand at room temperature until reaction was complete, as shown by titration of a sample of the solution with sodium thiosulphate solution. The flask was shaken occasionally. The reaction was complete in 5 days. The chloroform solution was washed with dilute sodium hydroxide solution until the alkaline washing ceased to produce

benzoic acid upon acidification with hydrochloric acid. The solution was then washed free of alkali with water, and finally dried over anhydrous sodium sulphate. The chloroform was evaporated under reduced pressure, leaving a dark red viscous liquid. Upon standing for several days, crystals separated out of the liquid. They were filtered off and recrystallized from ethyl alcohol to yield light white flashing flakes, melting at 175-178°C. There was an insufficient quantity of these flakes to make a complete analysis.

Upon further standing, more crystals separated out. These were recrystallized from water to yield white crystals, melting at 121-122°C. A mixed melting point with benzoic acid was 121-122°C. These crystals were thus proved to be benzoic acid.

SUMMARY AND RECOMMENDATIONS FOR FUTURE WORK

(1) A survey and experimental trial of the methods of preparation of acenaphthylene was made. It was found that the best method of preparation was the pyrolysis of 1-acetoxyacenaph--thene. The acenaphthylene produced was quite pure and free from acenaphthene.

(2) Attempts to prepare acenaphthylene chlorohydrin by the action of hypochlorous acid upon acenaphthylene have met with little success. The yellow oil produced in the reaction was fractionated into three fractions under a reduced pressure of 6 mm. of mercury. The three fractions were (I) 130-140°C., (II) 140-145°C., (III) 145-150°C.

The middle fraction (II) was identified as 1-monochloro-acenaphthylene by means of its picrate derivative. It was believed that fraction (III) was also 1-monochloroacenaphthylene with a new dichloroacenaphthene mixed with it. Fraction (I) had a chlorine content approximately that of the chlorohydrin, and could be investigated further, especially the action of alcoholic alkali upon it. The methoxyl derivative of the fraction should be prepared by the action of methylating agents upon the oil, to establish the existence of the hydroxyl group in the molecule.

(3) A new dichloroacenaphthene was isolated from the yellow oil, prior to its fractionation. This dichloroacenaphthene melted sharply at 64°C., and was assumed to be a geometric isomer of 1,2-dichloroacenaphthene, which melted sharply at 115°C. These two dichloroacenaphthenes should be investigated further to

determine which form is the cis form and which one is the trans form. This may be accomplished by converting the dichlorocompound to the corresponding dihydroxyacenaphthenes, whose geometric forms are known. It may also be possible to replace one of the chlorine atoms of the dichloroacenaphthene by a hydroxyl group to form the chlorohydrin, using water and calcium carbonate.

(4) Acenaphthylene oxide has not been isolated through the chlorohydrin. The perbenzoic acid oxidation of acenaphthylene should be repeated, and the high melting white solid, melting at 175-178°C, identified.

BIBLIOGRAPHY

1. R.G. Flower and Miller. J. Amer. Chem. Soc. 69; 1388-89, 1947.
2. A. Detoeuf. Bull.soc.chim. Mem 31; Series 4, 102-8, 1922.
3. B.A. Campbell. J. Chem. Soc. 107; 918-21, 1915.
4. P.A. Hawkins and N. Bennett. Brit. Patent 571,265.
5. Berthelot and Bardy. Bull. soc. chim. (2), 18; 231, 1872.
6. McRae, Charlesworth, and Alexander. Can. J. Research. B,21; 1-12, 1943.
7. Charlesworth, McRae, and MacFarlane. Can. J. Research. B,21; 55-64, 1943.
8. McRae, Charlesworth, Archibald, and Alexander. Can. J. Research. B,21, 186-93, 1943.
9. Berthelot. Jahrsber; 594, 1867.
10. Berthelot. Bull. soc. chim. 9; 265, 1868.
11. Bamberger and Philipp. Ber. 20; 273, 1887.
12. Baly and Tuck. Proc. Roy. Soc. 24; 223, 1908.
    J. Chem. Soc. 93; 102, 1908.
13. C. Graebe. Ber. 20; 657, 1887.
14. F. Sachs and G. Mosebach. Ber. 44; 2852, 1911.
15. Blumenthal. Ber. 7; 1092, 1874.
16. Ann. 327; 77, 1903.
17. Buri-Hoi and P. Cagneant. Rev. sci. 80; 176-8, 1942.
    Chem. Zentr. I; 2608, 1943.
18. M.N. Goswami. Compt. rend. 179; 1269-70, 1924.
19. Blumenthal. Ber. 7; 1092, 1874.
20. J. T. Kebler. Amer. Chem. J. 10; 217, 1888.
21. E. Bamberger. Ber. 21; 836, 1888.
22. T. Ewan. J. Chem. Soc. 55; 591, 1889.
23. Ann. 327; 85, 1903.
24. H. Crompton. Proc. Chem. Soc. 24; 241, 1908.

25. J.E. Purvis. J. Chem. Soc. 11; 1315, 1912.

26. K. von Auwers. Ber. 45; 2988, 1913.

27. F. Sachs and G. Mosebach. Ber. 43; 2473, 1910.

28. H. Paillard and P. Favarger. Helv. Chim. Acta. 16; 614-23, 1933.

29. Dashevski and Karishin. Org. Chem. Ind. (U.S.S.R.) 4; 109-13, 406-10, 1937.

30. Dashevski and Karishin. Org. Chem. Ind. (U.S.S.R.) 6; 507-11, 1939.

31. Fieser and Cason. J. Amer. Chem. Soc. 63; 204, 1941.

32. F. Quincke. Ber. 20; 609, 1887 and Ber. 21; 1454, 1888.

33. E. Jandrier. Compt. rend. 104; 1858, 1887.

34. C. Graebe. Ann. 327; 80, 1903.

35. N. Briones. Bull. soc. chim. (3) 14; 116, 1895.

36. F. Sachs and G. Mosebach. Ber. 44; 2860, 1911.

37. Morgan and Sheasby. J. Soc. Chem. Ind. 44; 408-10T, 1925.

38. Morgan and Harrison. J. Soc. Chem. Ind. 49; 413-21T, 1930.

39. Morgan and Stanley. J. Soc. Chem. Ind. 45; 408T, 1926.

40. F. Quincke. Ber. 21; 1456, 1888.
C. Graebe. Ann. 327; 81, 1903.

41. F. Sachs and G. Mosebach. Ber. 43; 2852, 1911.
Rodionov and Mel'nik. Khim. Referat. Zhur. 2; 30, 1940.

42. G. Ampola and V. Recchi. Atti. accad. Lincei. 8; 209, 1899.

43. A. Cruto. Gazz. chim. ital. 45; II 324, 1915.

44. G. Charrier. Gazz. Chim. ital. 45; I 516, 1915.

45. L. Behrend. J. Prakt. Chem. (2) 60; 1, 1899.

46. J. Hermes. Dissertation, Kiel, 1898.

47. K. von Auwers. Ann. 378; 210, 1910.

48. F. Ullmann and E. Cassirer. Ber. 44; 439, 1910.

49. L. Fransconi and F. Pirazzoli. Gazz. chim. ital. 33; I 36, 1903.

50. E. Oliveri-Mandala. Atti. accad. Lincei. 21; I, 779, 1912.

51. K. Dziewonski and T. Stolyhwo. I^{szy} Zjazd Chemikow Polskich, 57, 1923.

52. K. Dziewonski and T. Stolyhwo. Ber. 57B; 1531-40, 1924.

53. Kalle and Co. D.R.P. 248,994 , 1910.

54. I.G. Farbenind A.-G. Ger. 669, 809 , 1939.

55. K.Dziewonski and T. Orzelski. Bull. Intern. acad. Polonaise. A; 347-59, 1911.

56. Elberfelder. (See Ber. 44; 2860, 1911.)

57. Berthelot. Bull. soc. chim. (2) 13; 391, 1870.

58. Gattermann. Ann. 244; 29, 1888.
E.P. Harris. Dissertation, Gottingen, 1888.

59. Liebermann. Ber. 44; 202, 1911.

60. Grignard. Ann. chim. phys. (9) 4; 28, 1915.

61. Imperial Chemical Industries Ltd. Fr. 783,091 , 1935.

62. C. Graebe. Ber. 20; 237, 657, 1887., Ber. 25; 652, 1892., Ann. 290; 195, 205, 1896., Ann. 276; 12, 1893., Ann. 327; 77, 1903.

63. Dashevski and Karishin. Org. Chem. Ind. (U.S.S.R.) 1; 729-31, 1936.

64. Ber. 43; 440, 1910.

65. T. Ewan and J. Cohen. J. Chem. Soc. 55; 580, 1889.

66. C. Graebe and J. Jequier. Ann. 290; 205, 1896.

67. L. Monti. Gazz. chim. ital. 68; 609-12, 1938.

68. T. Ewan and J. Cohen. J. Chem. Soc. 55; 580, 1889.

69. C. Graebe and J. Jequier. Ann. 290; 205, 1896.

70. R. Marquis. Compt. rend. 182; 7227-9, 1926.

71. Basler chemischen Fabrik. D.R.P. 230,237 , 1909.

72. Fr. Bayer and Co. D.R.P. 237,819 and D.R.P. 237,266.

73. Dashevski and Karishin. Org. Chem. Ind. (U.S.S.R.) 1; 729-31, 1936.

74. Ann. 276; 7, 1893.

75. A. Reissert. Ber. 44; 1749, 1911.

76. M. Zsuffa. Ber. 43; 2915, 1910.

77. A. Grob. Ber. 41; 3331, 1908.

78. Bezdrik and Friedlander. Montasch. 29; 359, 1908.

79. Behr and van Dorp. Ber. 6; 60, 1873., Ann. 172; 263, 1874.
Bamberger and Philipp. Ber. 20; 237, 1887.
C. Graebe. Ber. 20; 657, 1887., Ber. 25; 652, 1892.
T. Ewan and J. Cohen. J. Chem. Soc. 55; 578, 1889.

80. F. Ullmann. Ber. 43; 440, 1910.

81. C. Graebe. Ann. 290; 202, 1896., Ber. 25; 652, 1892.,
Ann 276; 18, 1892.

82. Kalle and Co. D.R.P. 243,536.

83. K. Dziewonski and J. Suszko. Ber. 58B; 723-32, 1925.

84. I.G. Farbenind. A.-G. Brit. 273,321 , 1926.

85. E. Clar. Reichsamtwirtschafsausbau, Chem. Ber. Pruf-Nr 015
(PB52017), 859-78, 1942.

86. I.G. Farbenind. A.-G. Fr. 702,612 , 1930.

87. E. Oliveri-Mandala. Gazz. chim. ital. 68; 324-7, 1938.
Oliveri-Mandala, Giacolone, and Deleo. Gazz. chim. ital. 69;
104-10, 1939.
Oliveri-Mandala and Deleo. Gazz. chim. ital. 70; 186-90, 1940.
E. Oliveri-Mandala. Atti. X° Congr. intern. chim. 4; 460-4, 1939.

88. Efremov, Fedormeer, and Prinkmann. Bull. acad. sci. U.R.S.S.,
Classe. sci. math. nat., Ser. chim. 1936, 515-31.

89. Remo de Fazi. Gazz. chim. ital. 51 I; 328-38, 1921.
Gazz. chim. ital. 46 I; 334-59, 1916.

90. K. Dziewonski. Ber. 53; 2173-92, 1920.

91. Bowen and Marsh. J. Chem. Soc. January, 1947, 109.

92. Fischer, Schrader, and Meyer. C. IV; 1039, 1922.

93. M. Goswami. Compt. rend. 179; 1269-70, 1924.

94. Marek and Hahn. "Catalytic Oxidation of Organic Compounds in the
Vapour Phase"; American Book Company.

95. I.G. Farbenind. A.-G. Fr. 762,672 , 1934.
Wulff, Nicodemus, and Treppenhauer. U.S. 2,004,884.

96. Mayer and Kaufmann. Ber. 53; 289-98, 1920.

97. K. Dziewonski and T. Stolyhwo. Ber. 57; 1535-7, 1924.
K. Dziewonski, Galitzerowna, and Kocwa. C. II; 2816, 1926.

98. E. Oliveri-Mandala. Atti. accad. Lincei. 21; I, 779, 1912.

99. Braun, Hahn, and Seemann. Ber. 55; 1687-1700, 1922.

100. L. Monti. Gazz. chim. ital. 68; 609-12, 1938.

101. L. Monti. Atti. X° Congr. intern. chim. 3; 256-7, 1939.

102. R. Marquis. Compt. rend. 182; 1227-29, 1927.

103. R.G. Flower and Miller. J. Amer. Chem. Soc. 69; 1388-89, 1947.

104. B.A. Campbell. J. Chem. Soc. 107; 918-21, 1915.

105. Dziewonski and Olesiowna. I^szy Zjazd Chemikow Polskich, 58, 1923.

106. Dziewonski and Rapalski. Ber. 45; 2491-5, 1912.

107. B.A. Campbell. J. Chem. Soc. 107; 918-21, 1915.