

STUDIES IN THE ACENAPHTHENONE

AND

FLUORANTHENE SERIES

by

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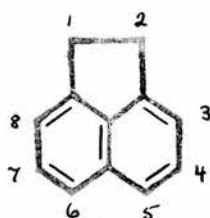
INTRODUCTION.

ACENAPHTHENE AND ITS DERIVATIVES.

Acenaphthene is obtained commercially from coal tar and as a byproduct in the vapour phase cracking of petroleum.

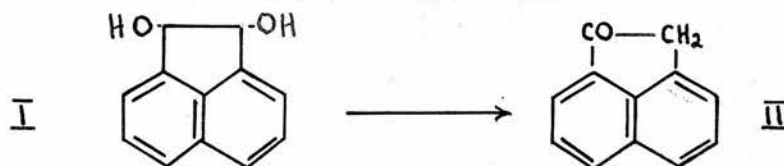
The presence of the ethylene bridge in acenaphthene was clearly demonstrated by Behr and van Dorp (1), when they isolated naphthalic acid as an oxidation product. The exact position, however, of the bridge in the molecule remained in doubt until Bamberger and Philip (2) synthesised naphthalic acid by an unequivocal route in 1887.

Several systems of numbering of the acenaphthene molecule have been employed in recent years.



Although suffering from the disadvantage that a change in numbering is required on passing to the naphthalene series, the system adopted throughout this work is the international system to be found in *Chemisches Zentralblatt*, the American Chemical Society Abstracts and Beilstein.

ACENAPHTHENONE-1.

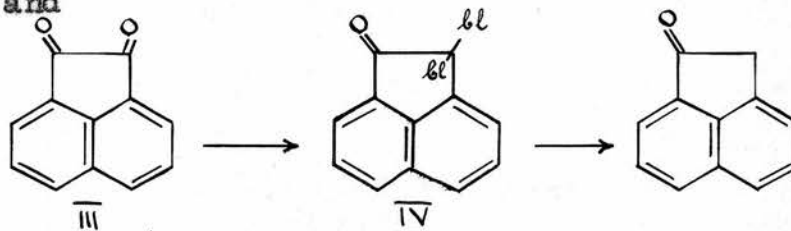


Acenaphthenone (II) represents an intermediate stage between the parent hydrocarbon and the fully oxidised acenaphthenequinone. It does not occur in any natural product and is solely a synthetic material.

Acenaphthenone was first isolated by Ewan and Cohen (3), from a reaction mixture containing acenaphthylene glycol (I), methyl iodide and sodium ethoxide.

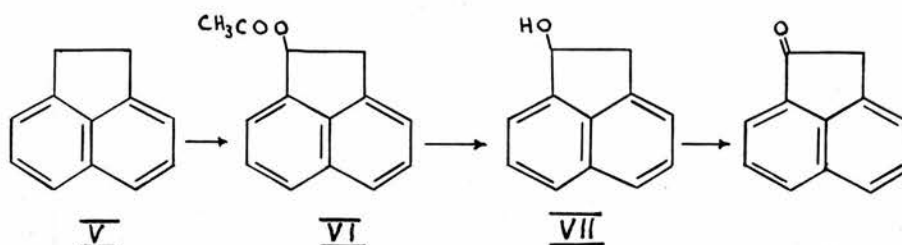
Dehydration instead of methylation took place and acenaphthenone (II), was formed.

For many years acenaphthenone was prepared by the method of Graebe and Jequier (4), in which acenaphthenequinone (III), is treated with phosphorus pentachloride. 2:2'- Dichloroacenaphthenone (IV) is formed and

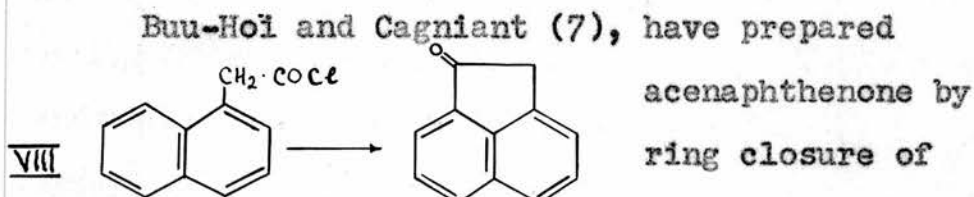


is reduced to acenaphthenone with zinc dust and acetic acid. The over-all yield is poor and it is this lack of a suitable method of preparation which has retarded the growth of acenaphthenone chemistry. Prior to 1940 the abstracts show that only a few workers were

engaged in acenaphthenone research. The situation however, has since altered due to the discovery of better methods of synthesis.



Marquis (5), observed that acenaphthenol is produced in the form of the acetate (VI), when acenaphthene (V) is oxidised with lead dioxide in acetic acid. Fieser and Cason (6), were able to improve the yield of acenaphthenyl acetate considerably by using a modified oxidation procedure. The acetate can readily be hydrolysed to acenaphthenol and the alcohol oxidised with chromic acid to give acenaphthenone, in an over-all yield of 47%.



Buu-Hoï and Cagniant (7), have prepared acenaphthenone by ring closure of 1-naphthylacetyl chloride (VIII), in the presence of aluminium chloride. A recent report by Ogata and Ishiguro (8), of an improvement in the preparation of naphthylacetic acid from naphthalene and chloracetic acid has added considerably to the significance of this reaction.

SUBSTITUTION AND CHEMICAL PROPERTIES OF ACENAPHTHENONE

The last decade has seen the number of known nuclear substituted acenaphthenones increase considerably.

3-, 5-, and 3:7 dimethyl acenaphthenone have been prepared from their respective naphthylacetic acids by ring closure, (Buu Hoï and Cagniant (7) and (9).

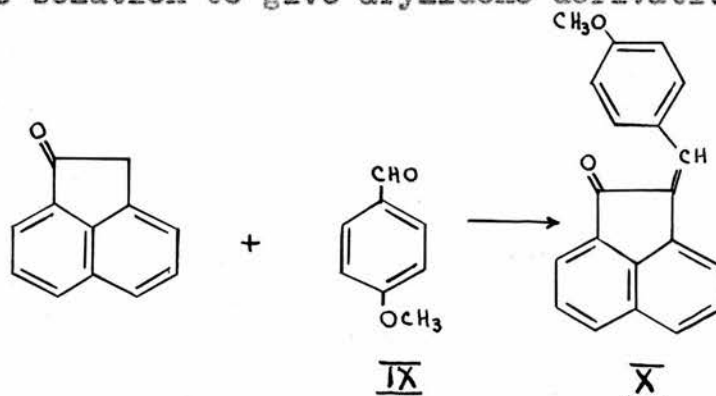
Direct halogenation of acenaphthenone results in substitution at the bridge methylene group. Graebe and Jequier (4), for example found that bromination with one molecule portion of bromine in carbon disulphide solution gives 2-bromo-acenaphthenone. With excess bromine, Rule and Thompson (10) showed that 2:2' dibromoacenaphthenone is formed.

At present, the only orientated nuclear halogen derivative known is 5-bromoacenaphthenone prepared in 1922 by Mayer and Sieglitz (11), by ring closure of 4-bromonaphthylacetic acid.

Although acenaphthenone behaves as a typical ketone in forming an oxime and a dinitrophenylhydrazone, the presence of an enolic form in alkaline solution has been demonstrated by coupling with diazonium salts (12). In cold, pyridine solution acenaphthenone with acetic anhydride forms a pyridyl acenaphthylene acetate due to acetylation of the enol, (13) and (14) . The free enolic form has yet to be isolated however.

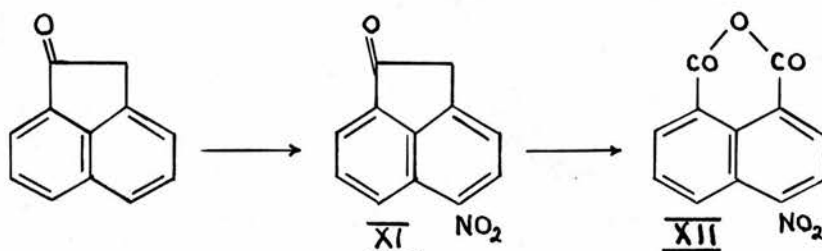
The presence of a reactive methylene group in acenaphthenone is illustrated by the formation of an iso-nitroso derivative with nitrous acid, (15) and (16).

Condensation with aromatic aldehydes also takes place in alkaline solution to give arylidene derivatives.

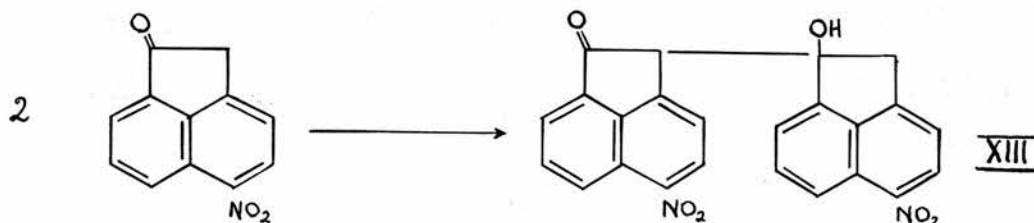


e.g. p-Anisalacenaphthenone (X) is formed when p-anisaldehyde (IX) is warmed with acenaphthenone in the presence of a little alkali, (17) and (18).

Direct nuclear substitution of acenaphthenone has been demonstrated in one case only. A mononitro derivative (XI) was prepared in 1935 by S.B. Thompson, (Thesis, Edinburgh) by the nitration of acenaphthenone with mixed acid. When the product is oxidised with sodium dichromate 4-nitronaphthalic anhydride (XII) is obtained, indicating that substitution has occurred in either the 5-, or 6- positions.

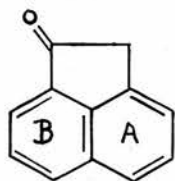


Thompson was unable to reconcile the high melting point (230°) with the fact that the unsubstituted material melts at 121° C. He was led to postulate the formation of a dimer (XIII) formed by an aldol type of condensation, but he did not attempt to substantiate this.



Later R. S. Gow (Thesis, Edinburgh 1948), established that the nitroacenaphthenone was monomolecular by preparing the phenylhydrazone and determining its nitrogen content.

Gow assumed that the ketone was, in fact, the 5-nitroacenaphthenone. The structure of the acenaphthenone molecule is such that one expects



nitro substituents to enter the ring to which the methylene group is attached. The $-\text{CH}_2-$ grouping will have an ortho and para directive effect on ring A while the carbonyl group will tend to deactivate ring B. By analogy with acenaphthene it is to be expected that the peri position of ring A is more likely to favour substitution than the ortho position, i.e. position 3-.

More detailed reference to this compound is to be found further on in the text.

FLUORANTHENE.

As in the case of acenaphthene, the chief source of fluoranthene is coal tar. The neutral fraction boiling between 370° and 390° C. is treated with sodium at 160° C. (19). Fluoranthene forms a benzene insoluble tetrasodio derivative while the other high-boiling hydrocarbons present, such as pyrene, remain unaltered.

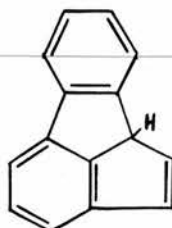
Washing the mixture with benzene leaves the sodium compound which is then decomposed with water to give tetrahydrofluoranthene.

The aromatic hydrocarbon is readily obtained by dehydrogenation.

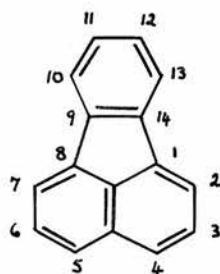
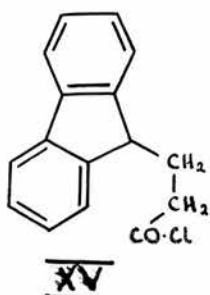
The first, though impure, specimen of fluoranthene was isolated by Bödecker (20), in 1844 from Stupp fat obtained in Italy as a byproduct from the treatment of mercury ores.

Fittig and Gebhard (21) and (22), were the first to isolate fluoranthene from coal tar. Because of its ready degradation to derivatives of fluorene they ascribed to it the name fluoranthene.

An erroneous structure for fluoranthene assigned by Fittig (XIV), went unchallenged until 1929 when von Braun and Anton (23) effected a synthesis from



9-fluorenyl- β -propionyl chloride (XV) and proposed the structure accepted today.

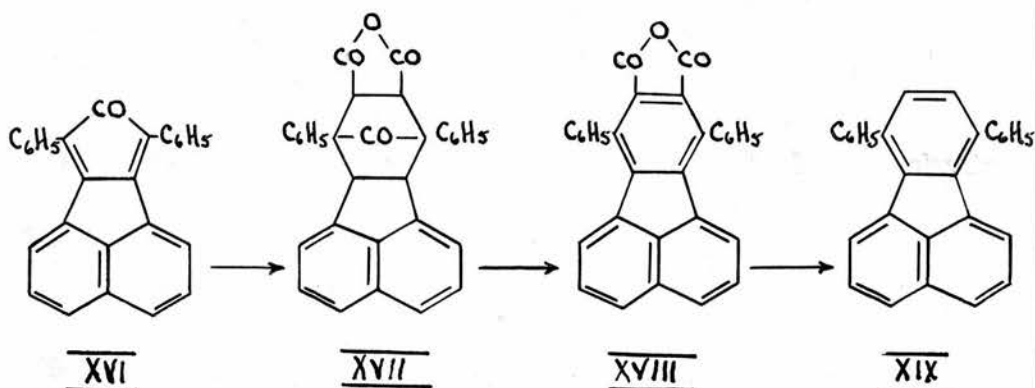


The numbering of the fluoranthene molecule is as used by von Braun. (24).

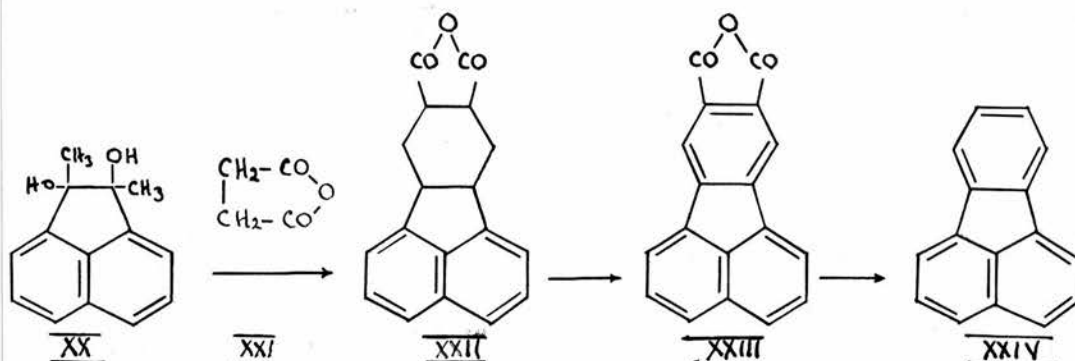
Because of the close relationship between fluorene and fluoranthene it is not surprising to find that most of the methods employed for the synthesis of substituted fluoranthenes started from fluorene derivatives.

The first synthesis from an acenaphthene derivative was devised by Dilthey and Henkels (25) and (26).

Acceyclone (XVI) was condensed with maleic anhydride in a

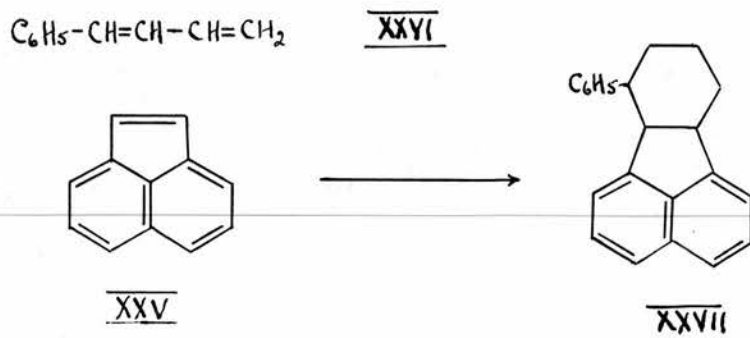


Diels-Alder reaction and 10 : 13 diphenylfluoranthene (XIX) obtained by removing the carbonyl bridge from the adduct (XVII) to give (XVIII) and decarboxylating over soda-lime.



Fluoranthene itself was first prepared from an acenaphthene nucleus by Campbell and Gow. (27). trans-1 : 2 Dimethylacenaphthene glycol (XX) condenses smoothly with maleic anhydride (XXI) if the reaction is carried out in a dehydrating solvent to prevent polymerisation. The resulting 10, 11, 12, 13 tetrahydrofluoranthene - 11 : 12 dicarboxylic anhydride (XXII) is dehydrogenated with chloranil to (XXIII) and fluoranthene (XXIV), obtained by subliming over calcium oxide.

Bergmann (28), working on the widely accepted theory that the formation of aromatic hydrocarbons in high temperature cracking processes is due to diene syntheses between butadiene and olefinic hydrocarbons, found that acenaphthylene (XXV) reacts easily with 1-phenyl-1:3 butadiene (XXVI) to give 10-phenyl-9,10,13,14 tetrahydrofluoranthene (XXVII).



Further investigations along these lines by Kloetzel and

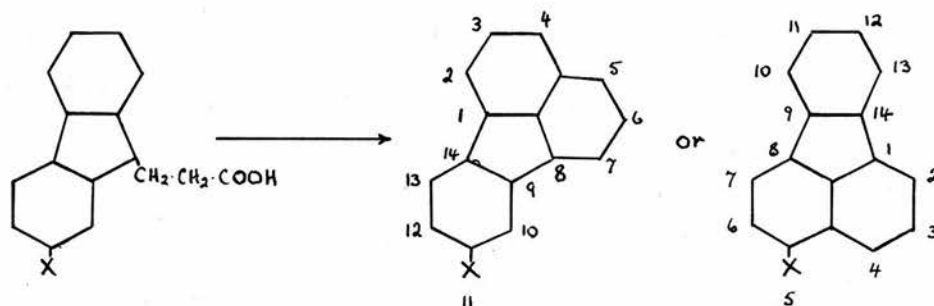
Mertel (29), have resulted in the synthesis of fluoranthene from acenaphthylene and butadiene followed by dehydrogenation of the adduct with palladium on a barium sulphate catalyst . The same authors also describe the syntheses of 10-methyl, 11-methyl and 11 : 12 dimethyl fluoranthenes from the corresponding 1 : 3 butadienes.

The synthesis of yet another derivative has recently been reported by Deno, (30). The diene employed was sorbic acid, $\text{CH}_3 \cdot \text{CH} : \text{CH} \cdot \text{CH} : \text{CH} \cdot \text{COOH}$, which condensed on heating with acenaphthylene to give 10,11,12,13 tetrahydro-10 methylfluoranthene-13- carboxylic acid. Dehydrogenation to the completely aromatic system has still to be carried out.

THE PURPOSE AND INITIAL PLAN OF RESEARCH.

Attention has already been drawn (c.f. introduction) to the recent trend in fluoranthene syntheses to commence the building up of the fluoranthene molecule from an acenaphthene foundation. The majority of the earlier fluoranthene syntheses started from a fluorene nucleus.

There is one great disadvantage in this line of approach, i.e. when a synthesis of a substituted fluoranthene derivative is undertaken.



It will immediately be seen that orientation of the product, or products, does not follow unequivocally from the synthesis.

A transition from the acenaphthene to the fluoranthene series based upon ring closure to form the 10,11,12,13 ring, would suffer from no such faults. Orientation would follow automatically from the position of substitution in the pre-ring-closed compound.

With this aim in view, acenaphthenone was chosen as the starting material, and it was hoped :-

(a) to complete the orientation of a

mononitroacenaphthenone prepared some time ago

in this department, and

(b) from it build by methods outlined in the sequel
a nitrofluoranthene of known structure..

SECTION A.

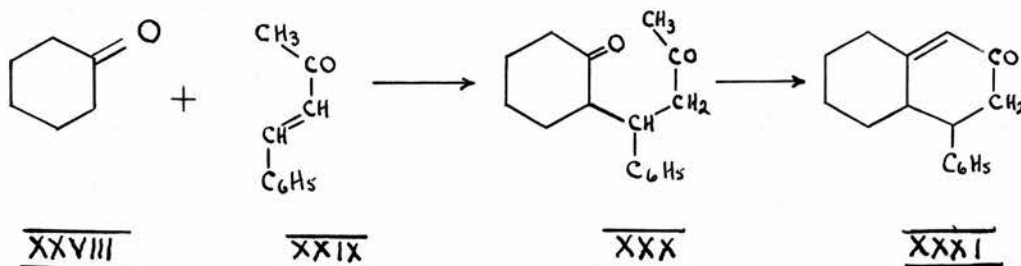
AN ATTEMPTED SYNTHESIS OF 13-PHENYLFLUORANTHENE
FROM ACENAPHTHENONE.

DISCUSSION.

The methylene group in acenaphthenone is extremely reactive and readily condenses with reactive compounds such as aldehydes with the formation of unsaturated condensation products.

The condensation of unsaturated ketones with ketones of the cyclopentanone and cyclohexanone series under the influence of alkaline reagents was reported by Stobbe. (31).

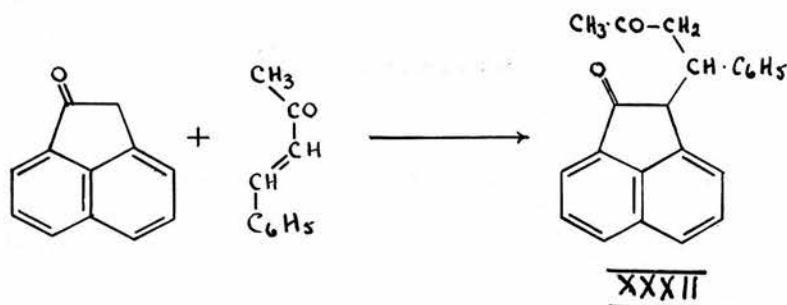
More recently Rapson and Robinson, (32), extended these studies to the condensation of cyclohexanone with α/β unsaturated methyl ketones. Cyclohexanone (XXVIII) for example, was successfully condensed



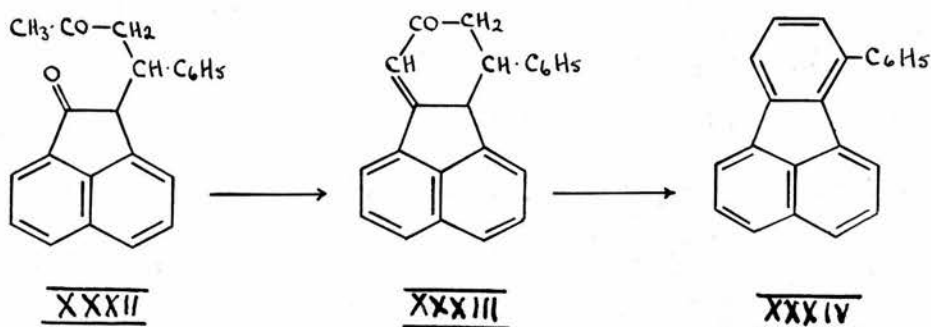
with benzal acetone (XXIX) to give 2-keto-4-phenyl- $\Delta^{1:9}$ octalin (XXXI). The work of Rapson and Robinson was repeated and the intermediate (XXX) not obtained by them, was isolated and dehydrated.

An attempt to extend Rapson and Robinson's work

work to the condensation of acenaphthenone with benzalacetone was made.



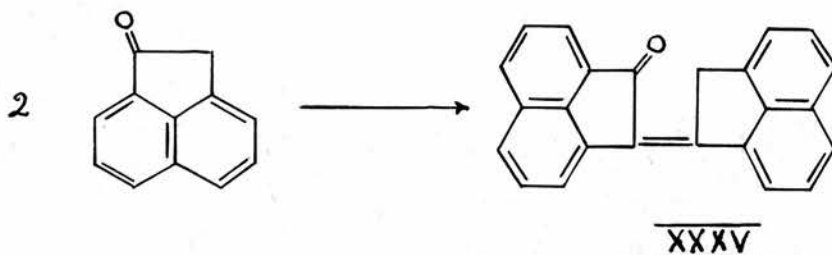
It was hoped to ring close (XXXII), and by reduction of (XXXII) followed by dehydrogenation, convert it to 13-phenylfluoranthene (XXXIV).



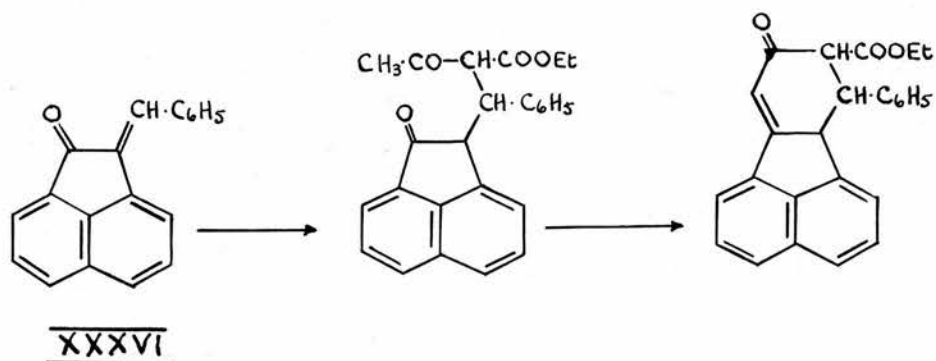
Attempts to achieve the initial condensation were unsuccessful; oily products were obtained which could not be purified.

From the results of experiments conducted in the course of later research it appears that in aqueous alkali, condensation of acenaphthenone with itself to the dinuclear compound occurs more readily than with other condensing reagents. Although the dimer was not isolated in this case it is suggested that the formation of biacenaphthylidene-one (XXXV) or its sodium salt

might account for the failure of the attempted condensation.



At this stage attention was focussed on the other problem, namely, the orientation of the nitroacenaphthenone. This proved to be more formidable than had been anticipated and occupied the remainder of the research. As a result, other acenaphthenone fluoranthene syntheses were not investigated, but it may be mentioned that one of these has proved promising, (Stafford, Thesis, Edinburgh 1951). This is based on a Michael condensation of



benzilideneacenaphthenone (XXXVI), and acetoacetic ester.

SECTION B.

NITROACENAPHTHENE.

The orientation problem has been attacked from several directions. Broadly speaking, these fall into four categories :-

- (i) attempts to achieve an unsymmetrical degradation of the acenaphthene molecule.
- (ii) an attempt to correlate the colour reaction given by nitroacenaphthene in acetone and alkali with the position of the nitro substituent.
- (iii) attempts to prepare 6-nitroacenaphthene.
- (iv) the nitration of the analogous 2-phenylacenaphthene and the orientation of the resulting mononitro derivative.

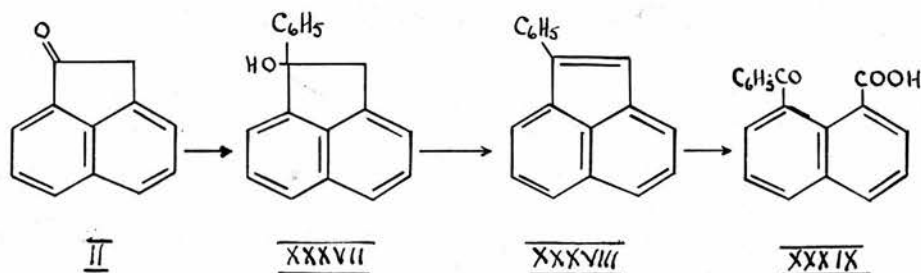
ATTEMPTS TO ACHIEVE AN UNSYMMETRICAL DEGRADATION
OF THE ACENAPHTHENE MOLECULE.

SECTION B (i) 1.

There are not many reactions recorded in the literature where the carbon bridge in acenaphthene is broken in such a way that the C₁ substituent differs from that attached to carbon atom-2. Several possibilities were investigated.

Elisa Ghigi, (33) describes the treatment of

acenaphthenone (II) with phenylmagnesium bromide to give 1-phenylacenaphthylene (XXXVII). Oxidation of the



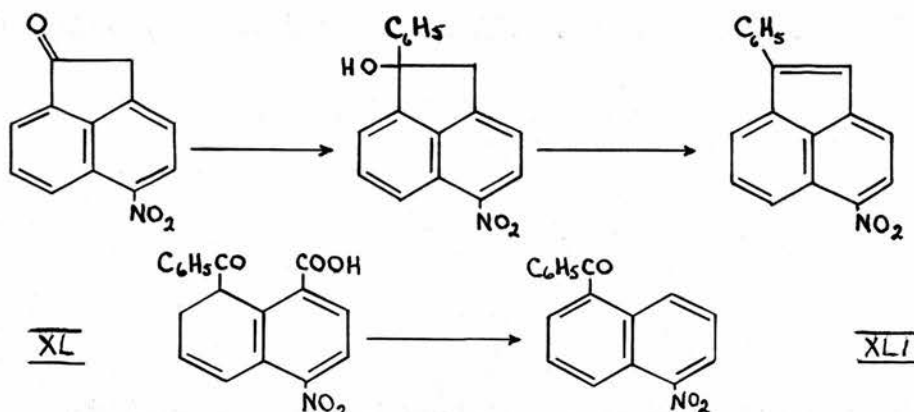
latter yielded a product which the author suggested was 1-benzoyl-8-naphthoic acid, (XXXIX).

It was considered that it might be possible to degrade nitroacenaphthenone by an analogous Grignard reaction, followed by oxidation. The above work was repeated and 1-phenylacenaphthylene was isolated fairly readily from the Grignard mixture. Along with it, however, a white crystalline product was also obtained, the analysis of which corresponded with the intermediate 1-phenylacenaphthene-1-ol, (XXXVII), containing one molecule of water. No mention is made of this product either by Ghigi or by Brown and Hammick (34) who prepared 1-phenylacenaphthylene in the course of the examination of some asymmetric naphthalene and acenaphthene derivatives.

The corresponding reaction with nitroacenaphthenone would be expected to yield 4-nitro-8-benzoylnaphthoic acid (XL), and this product would decarboxylate to give 1-benzoyl-5-nitronaphthalene (XLI).

The synthesis of this compound by another method

is described later in the text.

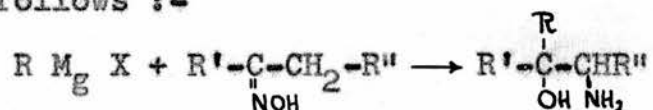


Treatment of the nitroacenaphthenone with phenylmagnesium bromide, however, resulted in a certain amount of decomposition and an oily product was obtained which could neither be crystallised nor purified chromatographically.

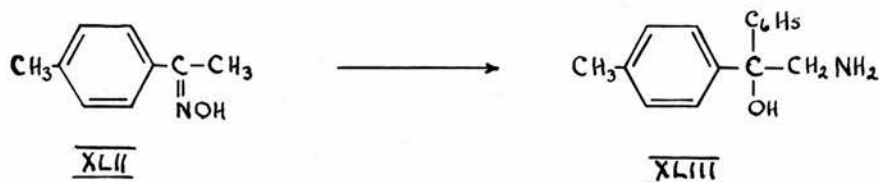
SECTION B (1) 2.

THE ACTION OF PHENYLMAGNESIUM BROMIDE
ON ACENAPHTHENONE OXIME

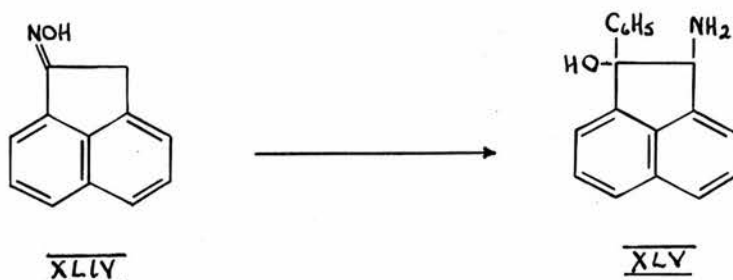
K. N. Campbell and co-workers, in two publications (35) and (36), describe investigations by them into the reaction between mixed ketoximes and Grignard reagents. They confirmed previous work by Professor Stieglitz showing that the general reaction is not as would be expected, i.e. $R M_g X + R' - \underset{\text{NOH}}{\underset{||}{C}} - CH_2 - R'' \rightarrow R' - \overset{R}{\underset{\text{NHOH}}{\underset{|}{C}}} - CH_2 R''$ but as follows :-



Instead of a hydroxylamine derivative being formed, a β -aminoalcohol results from the migration of a nitrogen atom from one carbon atom to another. The oxime of p-methylacetophenone (XLII), for example, yields 1-phenyl-1-(p)tolyl-1-hydroxy-2-aminoethane (XLIII).



The oxime of acenaphthenone (XLIV) was treated in a similar way in the hope that the reaction would yield 2-amino-1-phenyl-acenaphthen-1-ol (XLV).



A product was isolated as the hydrochloride but analysis indicated that it contained a higher percentage of nitrogen and chloride than was expected. (N 6.9%, Cl 14.8% as opposed to the expected N 4.7%, Cl 11.9%). As the material could not be recrystallised it is reasonable to assume that these values would be low. Since there can only be one atom of nitrogen in the molecule and thus only one of chlorine, the approximate molecular weight of the compound is :-

$$\frac{14 \times 100}{6.94} = 220 \text{ from the nitrogen analysis}$$

$$\text{and } \frac{35.5 \times 100}{14.8} = 240 \text{ from the chlorine analysis.}$$

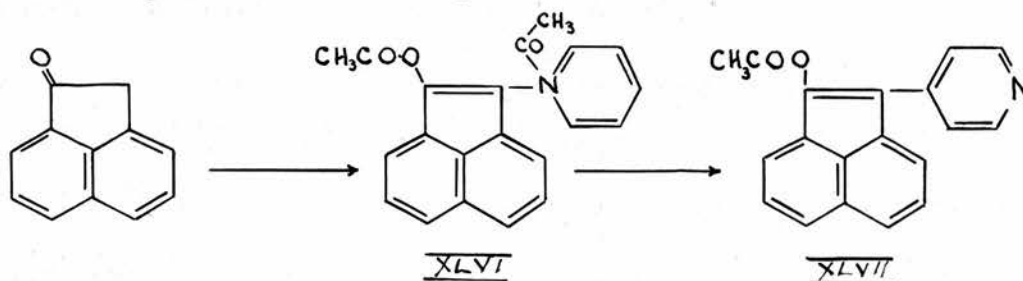
Thus the molecular weight is unlikely to exceed 240. Considering that there must be an acenaphthene nucleus + one atom of nitrogen + one atom of chlorine, i.e. $144+6+14+35 = 199$, it would appear that the product isolated did not contain the phenyl radical. Since oximes possess basic as well as acidic properties it is possible that the isolated product is acenaphthenone oxime hydrochloride (Requiring N 6.4% ; Cl 16%) in an impure form.

The reaction, however, not having proceeded along the desired line and the nature of the product being unknown, investigation in this direction was pursued no further.

SECTION B (i) 3.

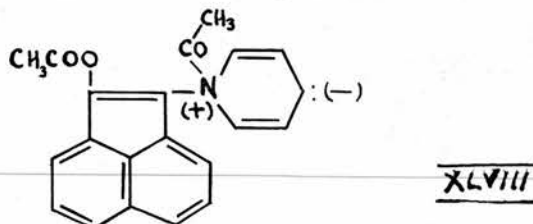
THE CONDENSATION OF NITROACENAPHTHENONE AND ACETIC ANHYDRIDE IN PYRIDINE SOLUTION.

The third method to be tried yielded more promising results than either of the first two, but unfortunately it could not be completed. The method was based on an acenaphthenone degradation by Ghigi (14). When acenaphthenone dissolved in pyridine is treated with acetic anhydride the main products are :-



1-acetoxy-2(N-acetylpyridino)acenaphthylene (XLVI), and the acetate of 1-hydroxy-2-(γ -pyridyl)acenaphthylene (XLVII).

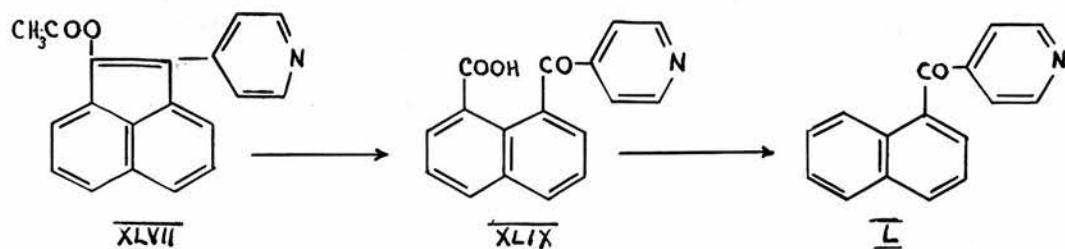
NOTE: The classical structure of (XLVI) is used for the sake of simplicity and because the fine structure (XLVII) as suggested by Ghigi (37) is viewed with reserve by other workers (38).



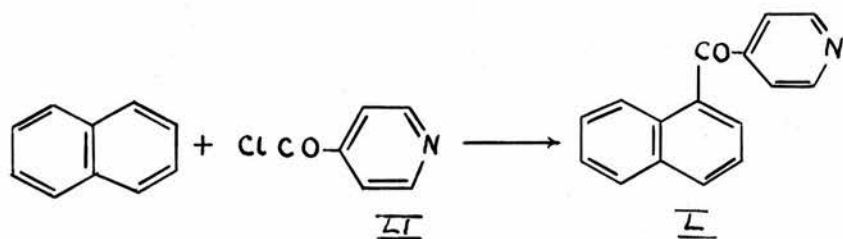
Treatment of (XLVI) with more acetic anhydride and pyridine resulted in the splitting off of one molecule of acetaldehyde to form 1-hydroxy-2-(γ -pyridyl)acenaphthylene

acetate (XLVII). Thus the longer the reaction mixture was allowed to stand the more of the latter was formed. The paper quoted (14) concerns itself primarily with the structure of the final product, while the configuration of the intermediate, which is more debatable, is discussed by the same author in a later publication.(37).

The pyridylacenaphthylene acetate (XLVII) was degraded by oxidation with alkaline permanganate to (XLIX) followed by decarboxylation as follows :-



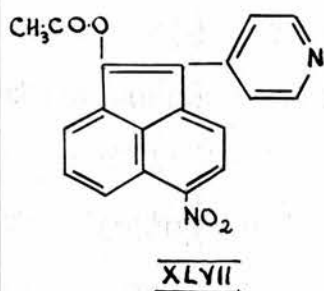
Synthesis of the δ -pyridyl-naphthyl ketone (L) was accomplished by a Friedel Crafts reaction with isonicotinyl chloride (LI) and naphthalene (44). An oily product was obtained which formed a picrate of the same melting point as that of the decarboxylation product and a mixed melting point showed no depression.



On treating a pyridine solution of 5-nitroacenaphthenone with acetic anhydride a colour change is observed from deep green (characteristic of the compound in all alkaline solutions), to a deep blood red. Deposition of a dark red, crystalline compound is complete within twenty-four

hours. No further deposit takes place after this time. This is rather striking when compared with the fact that the unsubstituted parent compound requires twenty days before deposition of the 1-hydroxy-2-(γ -pyridyl)-acenaphthylene acetate is complete. It is however, in keeping with the fact that the position of the nitro group would be expected to enhance the enolisation at the acenaphthene bridge and so increase the rate of condensation.

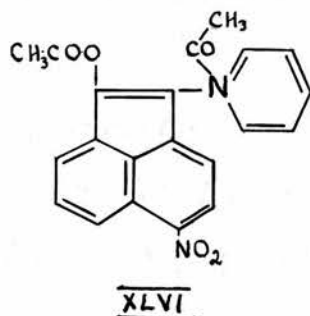
The dark red product was originally considered to be the simple 1-hydroxy-5nitro-2-(γ -pyridyl)acenaphthylene acetate (XLVII) because it separated from solution in the same manner as the unsubstituted parent compound. As expected it did not melt below 300° C. On the other hand, it was found that the analyses figures corresponded more closely with 1-acetoxy-2-(N-acetylpyridino)-5-nitro-acenaphthylene (XLVI).



$C_{19}H_{12}O_4N_2$

requires

C 68.7% ; H 3.6% ; N 8.4%



$C_{21}H_{16}O_5N_2$

requires

C 67.0% ; H 4.3% ; N 7.4%

cf. however
W. von E. Döhring &
W. D. McInnes,
J. Am. Chem. Soc., 1951, 73, 2104

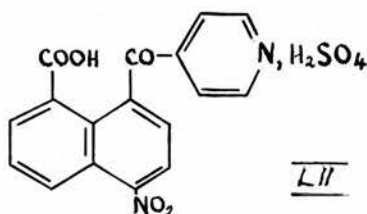
Analyses of the adduct obtained were :-

C 67.4% ; 68.0%

H 4.1% ; 4.6%

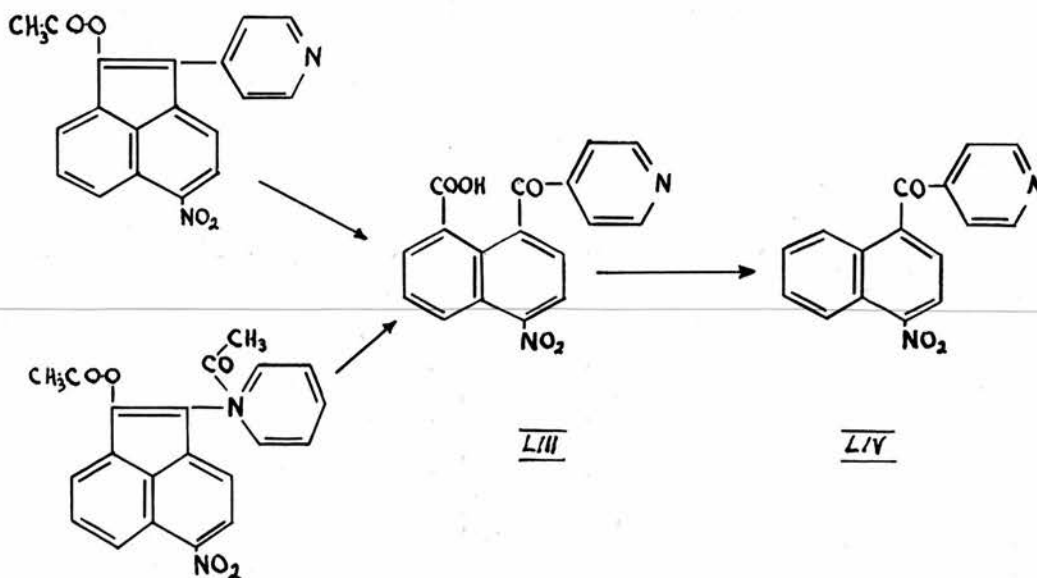
N 7.5% ; 7.2%

Oxidation with permanganate in dilute sulphuric acid gives a substance melting $269 - 271^{\circ} \text{C}$. A sample, on analysis, indicated that the carbon and hydrogen content was much lower than had been anticipated, (C 48.4% ; H 3.3% as compared with the expected C 63.3% ; H 3.1%). A Lassaigne test however, revealed the presence of sulphur presumably in the form of the amine sulphate. Comparison of the analysis quoted above and the theoretical value for the sulphate of 1-carboxy-2-(δ -pyridyl)-5 nitro -naphthalene (LII), indicated that the sample was almost completely in the form of the amine salt.



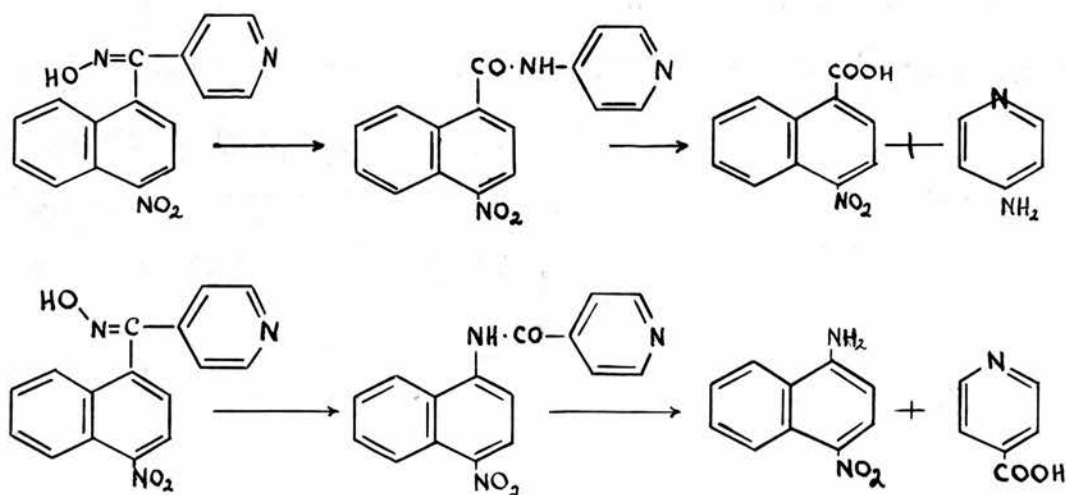
required C 48.6% ; H 2.9%

Treatment with a solution of sodium acetate effectively removed the sulphate and the resulting substance, though too insoluble to be recrystallised, gave a satisfactory analysis.



Despite the ambiguity as to the molecular composition of the material melting above 300° C, the same doubt cannot be entertained as to the structure of the pyridine nucleus in the oxidation product. It must be as shown (LIII) in order to explain the formation of the sulphate salt. Decarboxylation of this acid proved to be difficult and very small yields of an oil were obtained. The oil, however, formed a picrate which analysed to show that the removal of the carboxylic group had been effected to give 4-nitronaphthyl- δ -pyridyl ketone (LIV).

At the conception of this reaction series it was proposed to degrade the ketone further by means of a Beckmann rearrangement on its oxime.



The products would of course depend upon the amounts of the two oximes present. Both the possible naphthalene derivatives are well known compounds and could easily have been identified.

The very poor yields from the decarboxylation, however, ruled out the possibility of attaining this final stage.

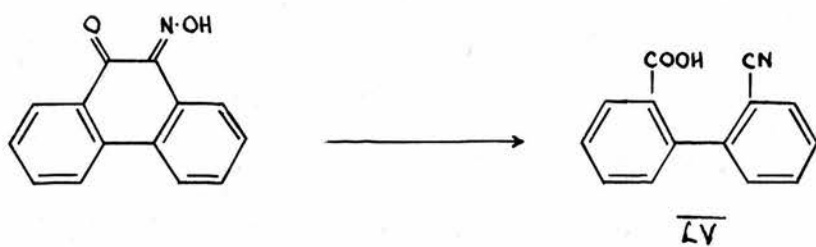
Mention has already been made that Ghigi (39) endeavoured to synthesise the unsubstituted γ -pyridyl-naphthyl ketone by means of a Friedel Crafts reaction using isonicotinyl chloride and naphthalene.

The ketone was isolated only in the form of the picrate. Attempts to repeat this work before trying the reaction with nitronaphthalene failed to give satisfactory results and not even a pure picrate could be isolated. An attempt to achieve the same synthesis by means of the Grignard reagent, naphthylmagnesium bromide, and 4-cyanopyridine also failed. This line of investigation was then abandoned.

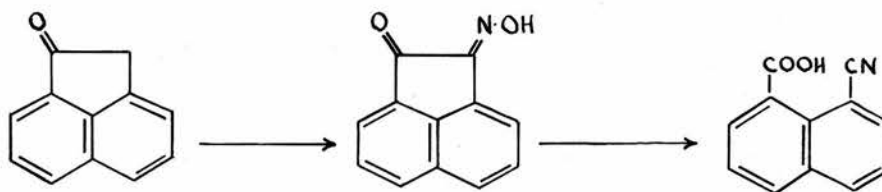
*Perhaps
by means
of Grignard
reagent.*

SECTION B (1) 4.

THE ATTEMPTED ENLARGEMENT OF THE FIVE MEMBERED
RING OF ACENAPHTHENONE TO FACILITATE THE
UNSYMMETRICAL FRACTURE OF THE
ETHYLENE BRIDGE.



The conversion of phenanthraquinone monoxime to 2-(2'-cyanophenyl) benzoic acid (LV) in the presence of benzenesulphonyl chloride and pyridine by Rapoport and Williams (42) suggested that a similar reaction might take place with an acenaphthene derivative.



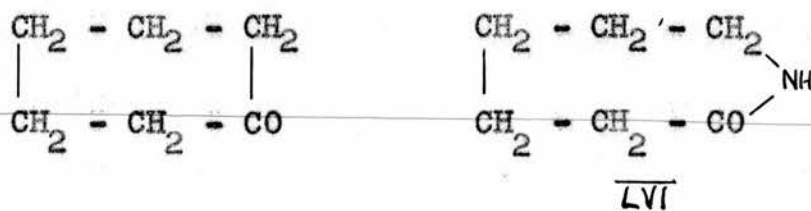
It was considered that acenaphthenequinone monoxime being an ortho diketone monoxime might also undergo the secondary Beckmann transformation. Since Raja Gopalan and Sircar (15), have shown that acenaphthenone gives acenaphthenequinone monoxime on treatment with boiling

amyl nitrite and hydrogen chloride, the degradation of a substituted acenaphthenone in the above manner would constitute a good method of orientating the substituent. Decarboxylation of the Beckmann product followed by hydrolysis to the corresponding derivative of naphthoic acid would give a product readily identifiable from the literature.

Reference to work performed as early as 1904 by Werner and Piguet (43), showed that the action of benzenesulphonylchloride on the monoxime of acenaphthenequinone had been examined and that naphthalimide not cyanonaphthoic acid was formed. Repetition of the work of Sircar and Raja Gopalan and Werner and Piguet confirmed their observations.

THE SCHMIDT REACTION ON ACENAPHTHENONE.

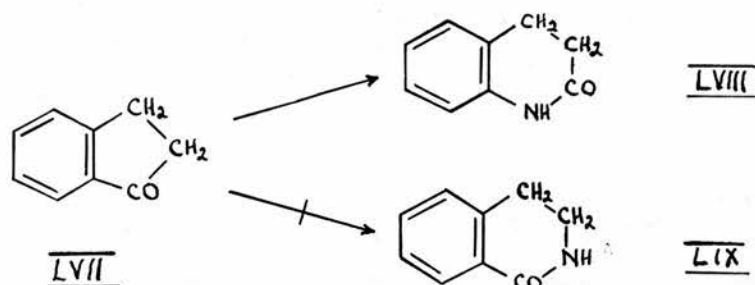
Karl Schmidt (40), found that hydrazoic acid reacted with cyclohexanone in the presence of concentrated sulphuric acid to give ϵ -leucine lactam (LVI) by the introduction of an imino group with consequent ring enlargement.



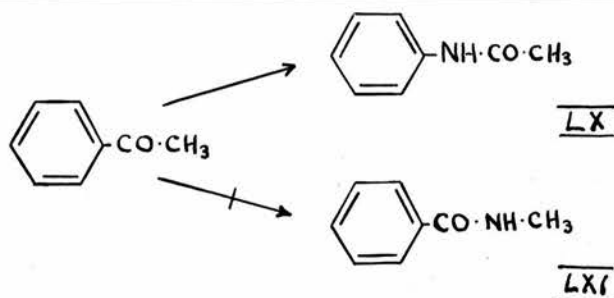
Investigations were extended to cyclic ketones annealed to a benzene nucleus by Briggs and De Ath (41),

and in particular to α hydrindone and α tetralone. The reaction of the former to hydrazoic acid is more apposite because of the close structural and chemical similarity between α hydrindone and acenaphthenone.

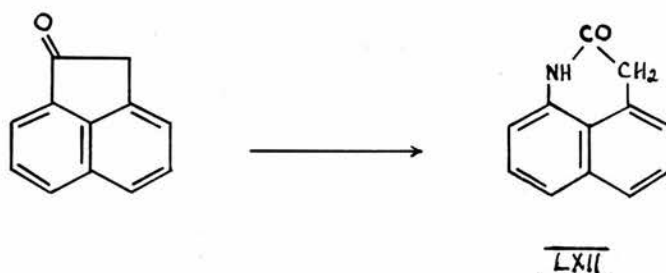
α Hydrindone (LVII) in the presence of hydrazoic acid and concentrated sulphuric acid shows alicyclic ring enlargement with the formation of dihydrocarbostyryl (LVIII). No dihydroisocarbostyryl (LIX), is formed in the course of the reaction.



The hydrocarbon residue apparently migrates more readily than the methylene group. This tendency of the imino group to separate the carbonyl group from an aromatic system can also be observed in α tetralone and acetophenone. The latter, for example gives (41) a 77% yield of acetanilide (LX) but no benzomethylamide (LXI).



The Schmidt reaction on acenaphthenone, seemed by analogy with α -hydrindone unlikely to give naphthalimide. If interposition of the imino grouping were to take place between the aromatic ring and the carbonyl group then a considerable advance in the attempts to procure an unsymmetrical degradation would have been made.



Dihydro-peri-naphthisatin

When the Schmidt reaction was carried out on acenaphthenone in benzene with sulphuric acid as catalyst at room temperature, it was found that the required naphthisatin LXII derivative was not formed. Instead a white, crystalline product was isolated, which on analysis seemed to be the hitherto unknown anil of acenaphthenone. The formation of such a compound, though entirely unexpected, is feasible since Schmidt as early as 1924 (44), had observed the formation of aniline from benzene and hydrazoic acid although a reaction time extending to several days was employed.

The results of later workers, e.g. Briggs and Lyttleton (45), suggest that such nuclear aminations do

not take place to any appreciable extent below 40° C.

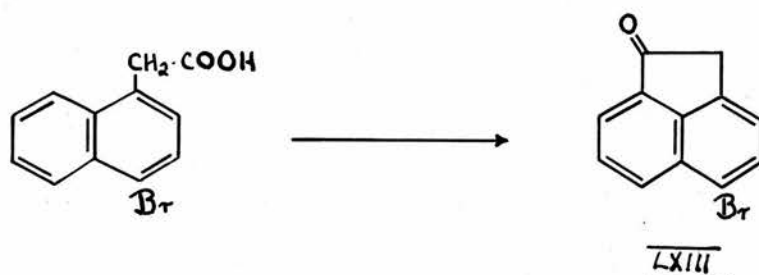
Attempts to prepare acenaphthenone-anil under similar conditions to those employed in the Schmidt reaction were unsuccessful, unchanged acenaphthenone and biacenaphthylidene-one being isolated. The condensation of acenaphthenone with itself to form the yellow dimer in acid solution is interesting as previously this has been reported in the presence of alkali only.

Nevertheless, it seems fairly certain that the product of the Schmidt reaction is acenaphthenone-anil. No other explanation for the complete lack of oxygen in the product appears reasonable.

SECTION B(1) 5.

THE REDUCTION OF NITROACENAPHTHENONE AND AN ATTEMPT
TO CONVERT THE PRODUCT TO 5-BROMOACENAPHTHENONE.

5-Bromoacenaphthenone (LXIII) has been known since 1922, when it was prepared (11) by ring closure of 4-bromonaphthyl acetic acid.



A method of reducing nitroacenaphthenone was sought which would attack the nitro group and leave the carbonyl grouping intact. A Sandmeyer reaction on the resulting amine if successful would reveal the position of the original nitro substituent since the bromoacenaphthenone thus obtained could be compared with that described in the literature.

A small scale reduction of nitroacenaphthenone with sodium sulphide and sulphur gave a product melting over a large temperature range. It did not give a positive diazo reaction or form an acetyl compound.

Simpson, Atkinson and co-workers have reported (46), that the use of acetic acid and iron filings as a

reducing agent, gives improved yields when compared with those obtained by some of the older methods. Several amino ketones can be prepared with this reagent where a preferential reduction of a nitro substituent is required.

It was found that boiling an acetic acid solution of nitroacenaphthenone with iron filings gives a compound which has a nitrogen content in agreement with that required for aminoacenaphthenone. From the result of a mixed melting point determination with the product of the catalytic hydrogenation, it was not possible to say with certainty whether the ketonic group had been reduced in this reduction.

Catalytic hydrogenation of nitroacenaphthenone results in the uptake of approximately three moles of hydrogen and a product can be isolated which dissolves on gentle warming in hydrochloric acid, gives a red wine colouration when diazotised and mixed with β -naphthol and which forms an acetyl derivative containing 6.1% nitrogen. N-acetyl-5-aminoacenaphthenone requires 6.2% nitrogen. If the ketonic grouping were reduced to a secondary alcohol, it is likely that on acetylation a diacetyl derivative would be obtained containing 5.2% nitrogen.

Although the amine could not be obtained pure, the evidence does suggest that an amino-ketone is obtained

when nitroacenaphthenone is hydrogenated under pressure with a platinum catalyst.

Two attempts to convert the amino compound to the corresponding bromoacenaphthenone by means of the Sandmeyer reaction were unsuccessful, the amine salt being recovered from the reactions. Investigations in this direction were discontinued.

SECTION B (11)

A COMPARISON OF THE COLOUR REACTIONS OF AROMATIC
NITRO COMPOUNDS CONTAINING A METHYLENE GROUP OR
A CARBONYL GROUP PARA TO THE NITRO SUBSTITUENT.

While working with compounds of the azobenzene series, Janovsky (47) observed that some nitro derivatives gave characteristically coloured solutions in the presence of acetone and caustic potash. In the following year, Bitto (48) devised a method of identifying aldehydes and ketones based on Janovsky's reaction in which the unknown aldehyde or ketone is treated with a dinitrocompound and caustic potash.

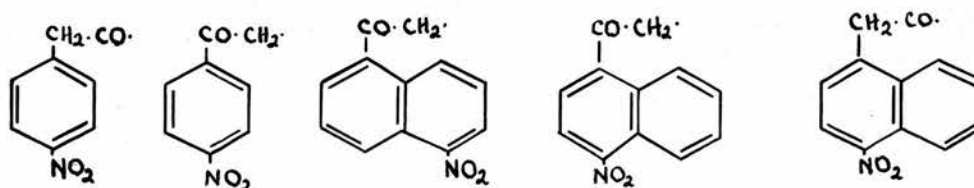
Colour formations were observed with a large variety of nitro compounds and two publications list these in detail. The first, (49), gives a list of nitro compounds and the colours they form with acetone and alkali. Variations in the colour reaction produced by the introduction of other substituents into the molecule such as amino, methyl, chloro and hydroxyl are also discussed.

The second communication appeared more recently, (50), and confined itself solely to compounds in the benzene series. Nevertheless a considerable number of compounds were investigated and the striking fact emerged that as a general rule dinitro and trinitro compounds give purplish-blue and blood-red colours respectively, while mononitro compounds give no colour.

Nitro ketones, however, were not examined.

Of the properties of nitroacenaphthenone, one of the first to be discovered was the consistent formation of green solutions in the presence of alkali. If acetone was added to a suspension of the ketone in caustic soda the depth and intensity of this green colouration were considerably enhanced.

It appeared that this phenomenon might be due to interaction between the methylene and nitro group in the molecule, and it was decided to test this by comparing the colours given by nitro compounds related to nitroacenaphthenone. Since no other substituted acenaphthenones were available analogous benzene and naphthalene compounds of the type shown below were prepared and examined.

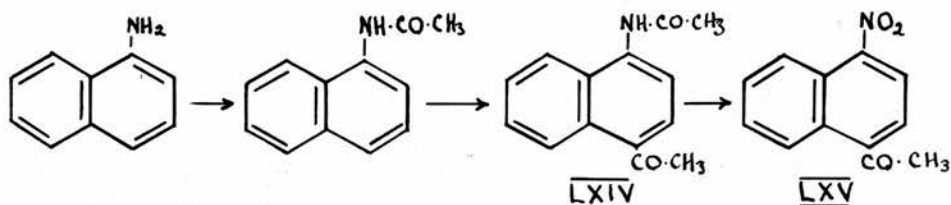


A search through the literature quickly revealed that nitronaphthyl ketones of the type required, i.e. 4- and 5- nitro derivatives, were unknown and several of these compounds were therefore synthesised.

One of the first compounds to be required was 1-acetyl-4-nitronaphthalene (LXV), and several methods of preparation were tried before success was achieved.

A simple Friedel-Crafts reaction with

1-nitronaphthalene and acetyl chloride was considered unlikely to yield the desired compound, since in all probability the nitro grouping would prevent further substitution in the same ring. An indirect method had, therefore, to be used and the first to be chosen was based on a general method for the replacement of the diazonium group by the nitro group (51).

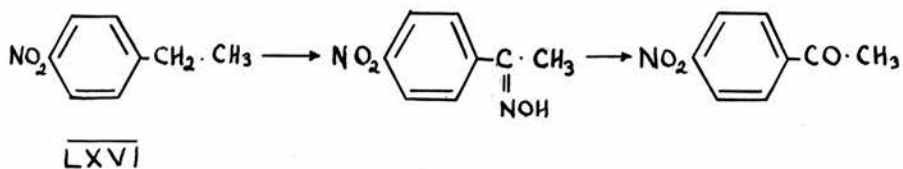


4-aceto-N-acetyl- α -naphthylamine (LXIV) was prepared by the acetylation of 1-naphthylamine in tetrachloro-ethane.

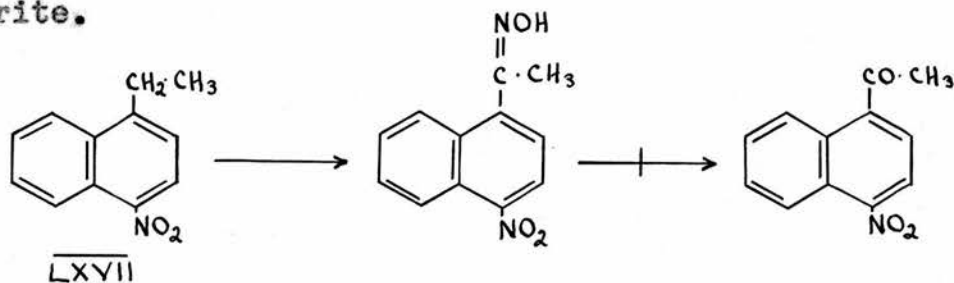
Hydrolysis of the product to the free amine was found to give a compound melting at the same temperature as 4-acetyl-1-naphthylamine subsequently prepared and conclusively orientated by Leonard and Hyson (52).

Diazotisation of the amine hydrochloride, however, gave no diazonium cobaltinitrite, thus bringing this line of investigation to a close.

A second attempt was made to procure the desired compound by the oximation of 1-ethyl-4-nitronaphthalene. The oximation of p-nitroethylbenzene (LXVI), has been reported by Hochst (53), and Ford-Moore and Rydon (54).



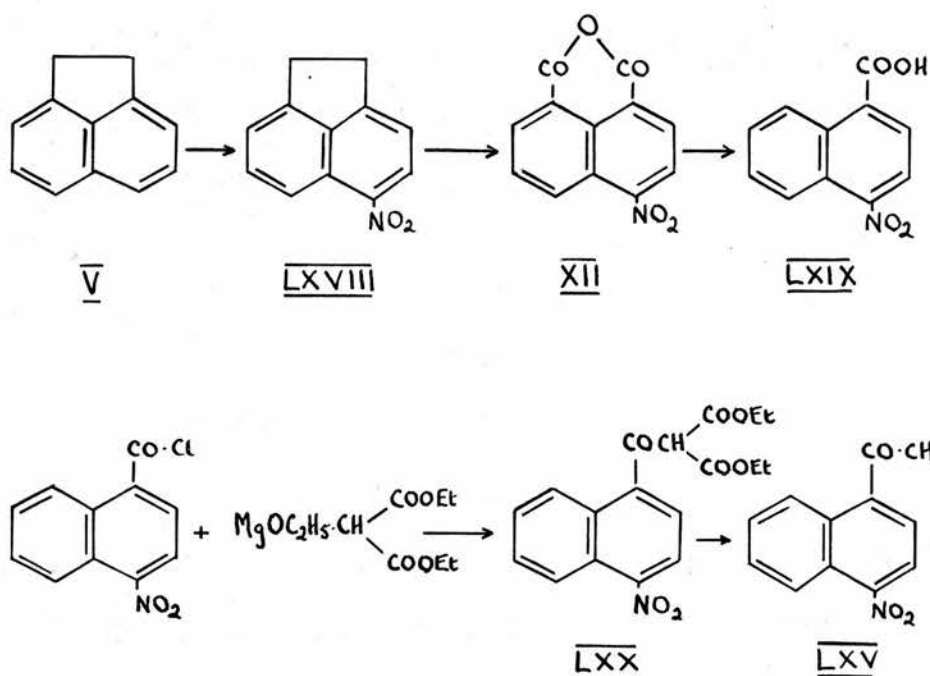
The reaction was found to proceed at room temperature when p-nitroethylbenzene was treated with alkali of the sodium methoxide or tertiary butoxide type and an organic nitrite such as amyl nitrite or tertiary butyl nitrite.



When 1-ethyl-4 nitronaphthalene (LXVII), was treated in a similar manner, a small amount of an alkali soluble product was obtained but it did not give a satisfactory analysis for the required oxime. (Required N 12.2% ; Found 9.4%). The yield was very poor and further investigation along these lines was not warranted.

In recent years considerable attention has been devoted to the preparation of methyl and substituted methyl ketones from the corresponding malonic esters. The Acyl malonic esters are in general high boiling liquids or low melting solids existing mainly in the enolic form. They are consequently readily soluble in aqueous alkalis in which they hydrolyse to give their progenitors. (55). In acid solution, on the other hand, hydrolysis and decarboxylation take place with the formation of methyl ketones. This type of degradation has been realised by several groups of workers, notably Walker and Hauser, (56), and Bowman (57).

The scheme of reactions was as follows :-



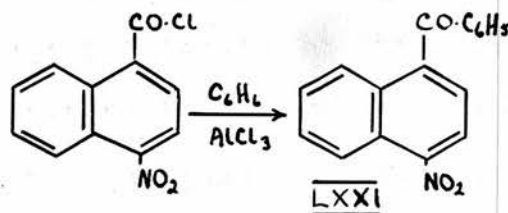
Direct nitration of 1-naphthoic acid gives a mixture of the 5- and 8- nitronaphthoic acids. The required 4-nitronaphthoic acid (LXIX) was prepared by the nitration of acenaphthene (V) to give 5-nitroacenaphthene (LXVIII), (58), which was oxidised by sodium dichromate and acetic acid to 4-nitronaphthalic anhydride (XII). Mercuration of this compound gave anhydro-4-nitro - 8 hydroxymercuri-1-naphthoic acid (59) which on hydrolysis with concentrated hydrochloric acid gave 4-nitronaphthoic acid. *mp. 225/6°.* It is interesting to note that 5-nitronaphthoic acid could not be isolated from the hydrolysed mixture.

Aroylation of diethyl magnesiummethoxy malonate (Walker & Hauser, loc. cit.) with 4-nitronaphthoyl chloride gave the aroyl malonate (LXX) in the form of an oil which crystallised after standing for some time. Simultaneous hydrolysis and decarboxylation of this ester was readily accomplished with a mixture of

dilute acetic and sulphuric acids to give 1-acetyl-4-nitronaphthalene (LXV).

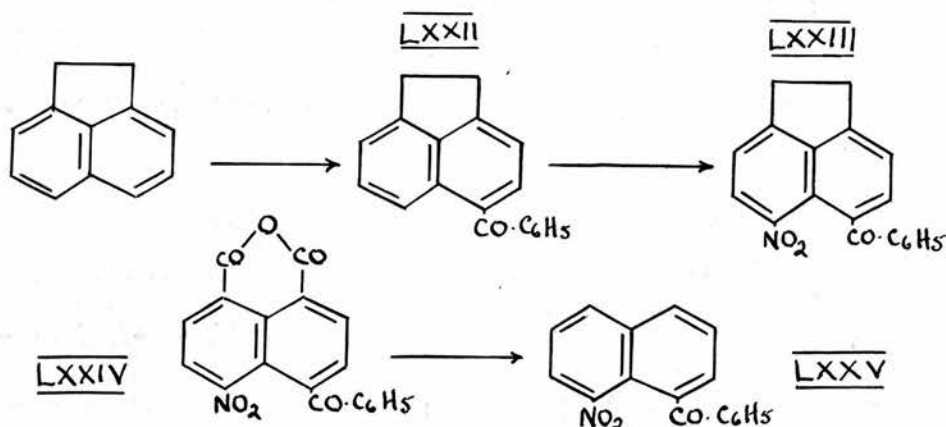
In a similar manner the corresponding 1-acetyl-5-nitronaphthalene has been prepared. As has already been stated, direct nitration of 1-naphthoic acid gives a mixture of 5- and 8-nitronaphthoic acids. These can be separated by fractional crystallisation by making use of the slightly greater solubility in alcohol of the 8-isomer. Some difficulty was experienced in forming the acid chloride of 5-nitronaphthoic acid. A suspension of phosphorus pentachloride in liquid phosphorus trichloride was found to be necessary after thionyl chloride and phosphorus trichloride had failed. Condensation with diethyl magnesium-ethoxy malonate followed by decarboxylation and hydrolysis gave the required methyl ketone.

From the acid chlorides of 4- and 5-nitronaphthoic acids, 1-benzoyl-4-nitronaphthalene (LXXI), and



1-benzoyl-5-nitronaphthalene respectively, were prepared by the Friedel Crafts reaction. The benzoylnitronaphthalenes were isolated from their respective reaction mixtures chromatographically.

The final member of the benzoyl nitronaphthalene series to be examined was 1-benzoyl-8-nitronaphthalene.

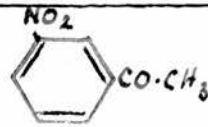
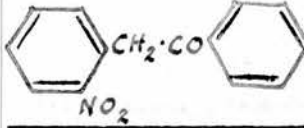
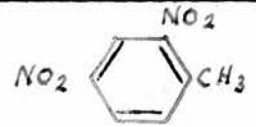
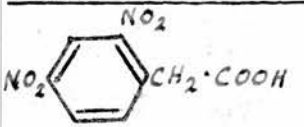
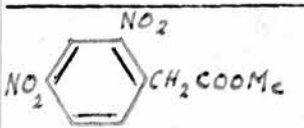


Acenaphthene was benzoylated by treatment with benzoyl chloride in the presence of aluminium chloride and phenyl acenaphthyl ketone (LXXII), isolated from the reaction mixture by distillation with superheated steam. (60). Nitration in acetic acid with nitric acid (S.G.1.48) gave a mononitro derivative considered to be 6-nitro-5-benzoyl acenaphthene (LXXIII) and oxidation with sodium dichromate furnished the corresponding naphthalic anhydride (LXXIV). Decarboxylation of the anhydride was achieved by employing the method of Dziewonski & Kahl (61) for the decarboxylation of peri-dicarboxylic acids and their anhydrides. After 4-benzoyl-5-nitronaphthalic anhydride had been heated in a sealed tube with a suspension of freshly prepared mercuric oxide for four hours at 230° C removal of the anhydride bridge was complete and 1-benzoyl-8 nitro-naphthalene (LXXV) was separated chromatographically from the reaction mass.

The compounds examined and their colour reactions are given overleaf in tabular form.

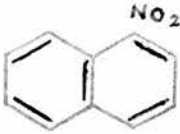
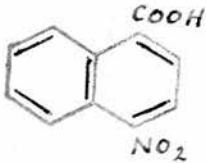
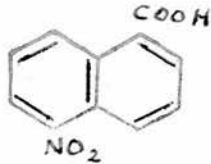
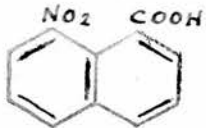
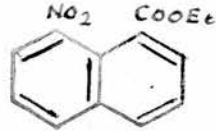
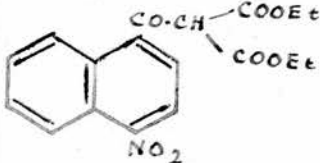
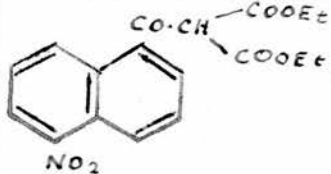
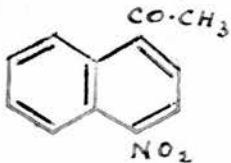
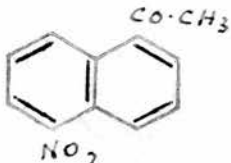
- 42 -
COMPOUNDS IN THE
BENZENE SERIES.

COLOUR REACTION
WITH ACETONE
AND
CAUSTIC SODA.

	p-Nitrotoluene	-----
	p-Nitrophenylacetonitrile	Violet
	p-Nitroacetophenone	Pale Yellow
	m-Nitroacetophenone	-----
	o-Nitrodesoxybenzoin	Magenta
	2:4 Dinitrotoluene	Deep Blue
	2:4 Dinitrophenylacetic acid	Deep Green
	Methyl 2:4 Dinitrophenyl- acetate	Very deep Magenta

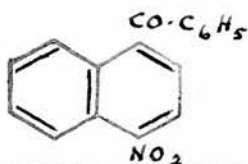
COMPOUNDS IN THE
NAPHTHALENE SERIES.

COLOUR REACTION
WITH ACETONE AND
DILUTE CAUSTIC
SODA.

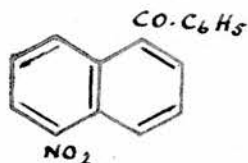
	1-nitro naphthalene	Reddish brown after several hours.
	4-nitro-1-naphthoic acid	-----
	5-nitro-1-naphthoic acid	Pink after standing for ten minutes.
	8-nitro-1-naphthoic acid	-----
	ethyl-8-nitro-1- naphthoate	Brown
	ethyl-4-nitro-1- naphthoylemalonate	Amber.
	ethyl-5-nitro-1- naphthoylemalonate	Yellow.
	1-acetyl-4-nitro- naphthalene	Amber, darken- ing to red on standing.
	1-acetyl-5-nitro- naphthalene	Pale pink on standing for fifteen min- utes.

COMPOUNDS IN THE
NAPHTHALENE SERIES.

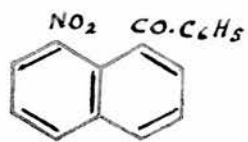
COLOUR REACTION
WITH ACETONE AND
DILUTE CAUSTIC
SODA.



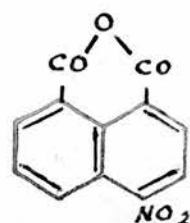
1-benzoyl-4-nitro
naphthalene



1-benzoyl-5-nitro
naphthalene

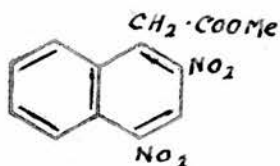


1-benzoyl-8-nitro
naphthalene



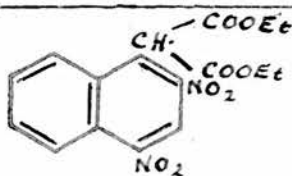
4-nitronaphthalic
anhydride

Pale yellow.



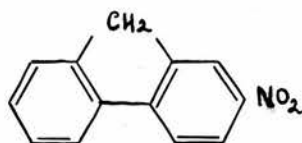
methyl-2:4-dinitro
naphthylacetate

Blood red.



ethyl 2:4 dinitro
naphthylmalonate

Blood red.



2-nitro fluorene

Pink.

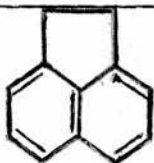


6-nitroacenaphthene

Green after
standing 1½
hours.

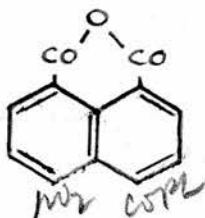
COMPOUNDS IN THE
NAPHTHALENE SERIES.

COLOUR REACTION
WITH ACETONE
AND DILUTE
CAUSTIC SODA.

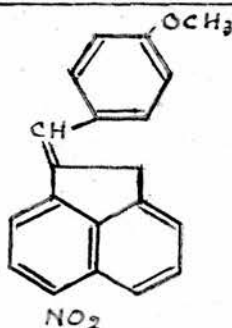


NO₂ CO-C₆H₅

5-benzoyl-6-nitro
acenaphthene

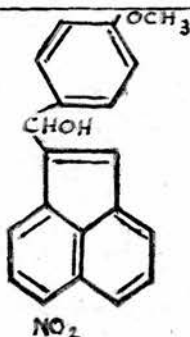


4-benzoyl-5-nitro
naphthalic anhydride



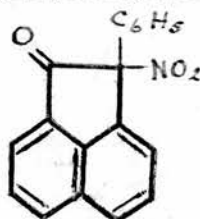
1-Anisyl-6-nitro
acenaphthene

Deep red.

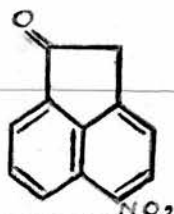


p-methoxyphenyl-
1-(6-nitroacenaphthyl-
ene)-carbinol

Ruby colour-
ation after
1½ hours.



2-phenyl-2'-nitro
acenaphthenone

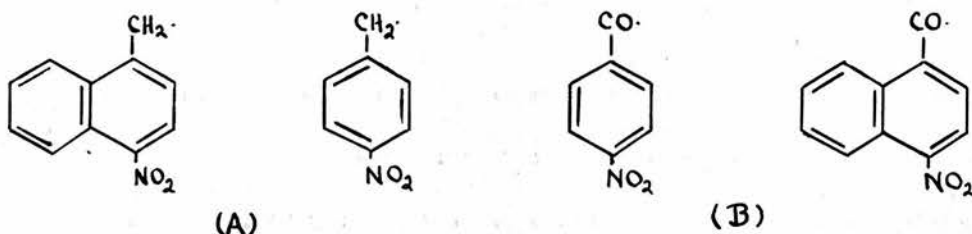


5-nitroacenaphthenone-1

Deep green.

It will be observed from the results that no general correlation is justified between the position of the nitro substituent and the particular colouration produced with alkali and acetone.

As the first experimental results were obtained it appeared that compounds of type (A) gave green colourations, while those of type (B) showed little or no colouration.



Subsequent results quickly showed that this was by no means a general rule. Compounds of type (A) proved to be capable of forming either green or red colourations.

SUMMARY :

Compounds of the benzene and naphthalene series tend to give a bright colouration if the nitro grouping is either ortho- or para- to a methylene group, p-nitrotoluene being a notable exception. In the benzene and naphthalene series, where the nitro group is para to a -CO- grouping no such colouration is formed.

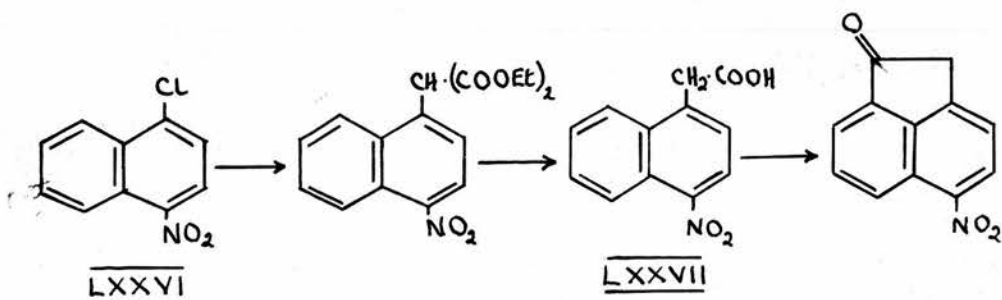
Although final conclusions are not justified, the evidence supports the view that the nitro substituent in nitroacenaphthenone is para to the methylene grouping.

SECTION B. (iii).

THE ATTEMPTED SYNTHESSES OF
5- and 6- NITROACENAPHTHENONES.

Since attempts to break down the nitroacenaphthenone molecule into identifiable fragments had met with little success it was logical that attention should be directed to synthetic methods.

In view of the achievements of Buu-Hoi and co-workers (7) and (9) in ring closing naphthylacetic acids to acenaphthenone derivatives it is not surprising to find that the first attempted synthesis of 5-nitroacenaphthenone (R.S.Gow, Thesis, Edinburgh 1948, 26), involved the preparation of 4-nitronaphthylacetic acid (LXXVII).



An attempt was made to synthesise this compound from 1-chloro-4-nitronaphthalene (LXXVI), and malonic ester as shown above. Gow, however, found that the halogen of chloronitronaphthalene was not sufficiently reactive and no condensation took place in the presence of sodium.

When the halogen was activated by the presence of two nitro groups, e.g. 1-chloro-2:4 dinitronaphthalene,

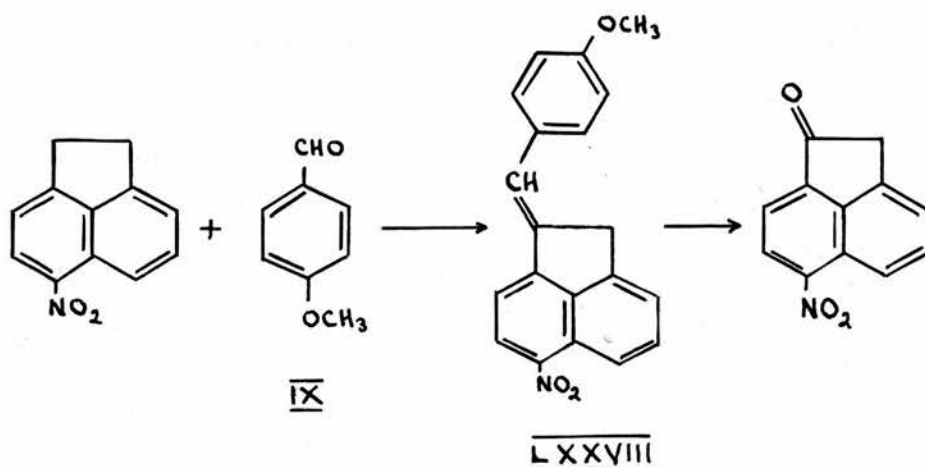
condensation with malonic ester did occur. After hydrolysis and decarboxylation Gow obtained 2:4 dinitronaphthylacetic acid but was unable to ring close the acid chloride, to dinitroacenaphthenone.

For many years it has been known that naphthylacetic acid may be prepared (62) from 1-acetylnaphthalene by heating the ketone in a sealed tube at 210° C. with ammonium polysulphide solution. Naphthylacetamide is formed which can be readily hydrolysed to naphthylacetic acid (Willgerodt's reaction). This technique has largely been superseded by the Kindler modification in which the ketone is heated with sulphur in the presence of an amine. Schwenk and Bloch (63) successfully reduced several aryl methyl ketones by boiling under reflux with a solution of sulphur in morpholine. The morpholides of the corresponding thioacetic acids are formed and are readily hydrolysed to the corresponding carboxylic acids.

As 4-nitronaphthyl methyl ketone had been synthesised for examination in a previous section (B.ii), an attempt to convert this compound to nitronaphthylacetic acid was made. Without quoting specific instances, Schwenk and Bloch have stated that the reaction with sulphur and morpholine seems inapplicable to substances containing a nitro substituent and thus the original ammonium polysulphide technique was employed with the modification that a little dioxan was added to increase the solubility of the organic material.

A brown tarry residue is obtained from the reaction. Prolonged extraction with boiling alkali gives a material which crystallises from benzene in yellow blades. This compound, however, proved to be other than the required nitronaphthylacetic acid. It contains sulphur in quantity and no nitrogen.

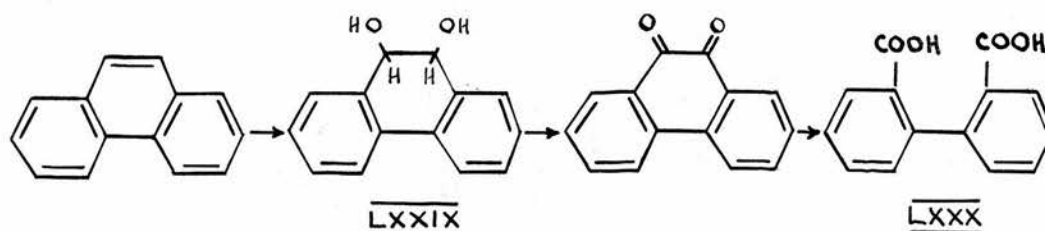
With the failure of this plan, attention was transferred to the possibility of synthesising 6-nitroacenaphthenone. The reported (64) condensation of anisaldehyde (IX) with 6 nitroacenaphthene



to (LXXVIII) gave rise to the hope that the product might be oxidised to yield 6-nitroacenaphthenone.

Milas's reagent (65) and (66) a tertiary butyl alcohol solution of hydrogen peroxide with an osmium tetroxide catalyst was chosen as the oxidising agent because of its selective reaction with double bonds. The normal products with this reagent are cis-glycols apparently formed by the dissociation of hydrogen peroxide in the presence of osmium tetroxide into two hydroxyl radicals which subsequently add on to the

carbon to carbon double bonds. When the glycols are unstable degradation may proceed further with the formation of ketones or acids. Cook and Schoental studying the oxidation effects of osmium catalysed solutions upon hydrocarbons (67) and (68), have for example, shown that phenanthrene gives a mixture of cis 9:10 dihydroxy-9:10 dihydrophenanthrene (LXXIX), phenanthraquinone and diphenic acid (LXXX).



Before attempting the oxidation of anisal-6-nitroacenaphthene it was decided to carry out a model reaction upon 2-p- anisalacenaphthenone-1,

When a suspension of anisalacenaphthenone in a ter. butyl alcohol solution of hydrogen peroxide and osmium tetroxide is allowed to stand for four days, acenaphthenequinone is obtained in 85% yield and the presence of anisaldehyde in the oxidation mixture established by the isolation of a 2:4 dinitrophenylhydrazone.

Under similar conditions it is found that no oxidation of anisal-6-nitroacenaphthene takes place owing to its marked insolubility in ter. butyl alcohol. The additions of small amounts of solvents such as ether, chloroform, dioxan and benzene cannot induce oxidation even after several days standing.

When anisal-6-nitroacenaphthene, the peroxide solution and catalyst are heated in boiling chloroform for three and a half hours the bright red starting material gradually dissolves and a dark reddish-brown solution is formed. If the volume of the solution is reduced by distillation, deposition of a brown product takes place and the presence of ~~p~~-anisaldehyde in the mother liquors can be demonstrated.

When a solution of the brown solid is chromatographed on alumina a small amount of an orange powder, melting $165^{\circ} - 170^{\circ} \text{ C.}$ can be isolated containing C 71.4% ; H 4.5%. This however does not agree with 6-nitroacenaphthenone which requires C 67.6% ; H 3.3%.

Since the greater part of the product adheres firmly to the alumina it appears that oxidation proceeds further than intended with the formation of an acid or anhydride. This is to some extent borne out by an analogous reaction with anisalacenaphthenone. The formation of the naphthalic anhydride along with acenaphthenequinone can be shown.

Because of the low solubility in *ter.* butyl alcohol Cook and Schoental (68) found that the addition of acetone was necessary to enable an osmium tetroxide-hydrogen peroxide oxidation of 1:2-5:6 dibenzanthracene to take place. The acetone appeared to have no significant influence on the course of the reaction although its trimeric peroxide was detected in the



reaction mixture.

When an acetone solution of anisal-6nitroacenaphthene, osmium tetroxide and peroxide reagent is boiled for three hours then distilled on a hot water bath under reduced pressure a clean dark brown oil is obtained. If the oil is dissolved in chloroform and chromatographed on alumina, as before, a bright orange band develops. Collection and evaporation of this band give a residue which recrystallises from acetic acid in golden-orange needles. M.Pt. 179° - 180° C. The yield of material is very poor - 600 mg. from five grammes of starting material.

Subsequent fractions from the column give oils.

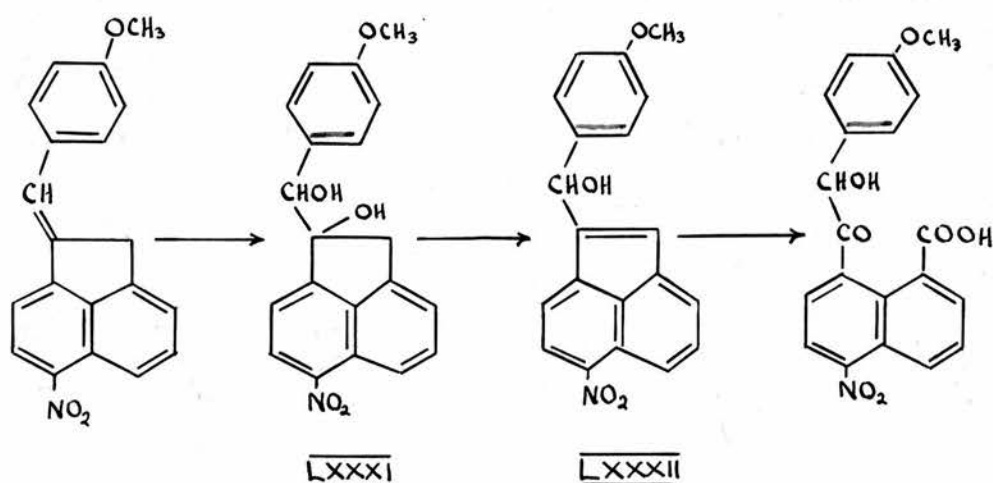
Although the orange material oxidises to give 4-nitronaphthalic anhydride and apparently forms a phenylhydrazone when heated with an acetic acid solution of phenylhydrazine it is not 6-nitroacenaphthenone. It appears to be a purer form of the product isolated from the chloroform oxidation.

The material contains C 71.7% ; H 3.8% ; N 4.3% showing little resemblance to the required C 67.6% ; H 3.3% ; N 6.6%. Molec. Weight 213.

The orange product gives a value of 347 for the molecular weight and the phenylhydrazone contains 8.6% N compared with the expected 13.9%.

From a critical review of the facts it is suggested that the orange oxidation product might be

p-methoxyphenyl-1-(6 nitroacenaphthylene) carbinol (LXXXI) formed by the dehydration of the glycol (LXXXI) in all probability unstable.

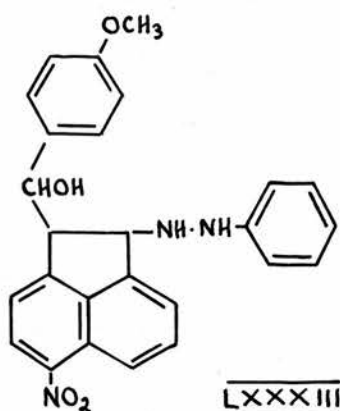


The small amount of material isolated from the alumina column is taken as indicating that degradation of the acenaphthylene derivative to the acid shown or even further to nitronaphthalic anhydride takes place. A comparison of the theoretical analysis figures for (LXXXI) and those actually found is given below :-

$C_{20}H_{15}O_4N$, M.Wt.333 required C 72.1% ; H 4.5% ; N 4.2%
found C 71.7% ; H 3.8% ; N 4.3%.

One would expect such an acenaphthylene derivative to be orange in colour. An acetyl derivative is formed when the orange product is warmed in acetic anhydride with a drop of pyridine, thus lending support to the proposed structure. The product gave an analysis agreeing reasonably well with that required by the monoacetyl derivative of LXXXI.

Finally it is possible that the 'phenylhydrazone' obtained is an addition of phenylhydrazine to the olefinic double bond giving an adduct (LXXXIII) requiring 9.5% nitrogen.



Attempts to oxidise the orange product with lead tetra-acetate and with periodic acid gave back unchanged material, thus adding weight to the supposition that the product isolated was not a diol.

It has already been mentioned that the greater part of the oxidation mixture adhered to the alumina when chromatographed. An endeavour to isolate the main component of the reaction mixture using a neutral adsorbent, cane-sugar, failed to give any purification. Extraction of the reaction mixture with different solvents also failed to furnish any improvement.

Although some doubt may exist as to the exact structure of the oxidation product obtained from anisal-nitroacenaphthene, it is obvious from the analyses results that the anisal residue survives the reaction. An attempt was made to bring about cleavage of the anisal residue from the acenaphthene nucleus by boiling with neutral permanganate. Some anisic acid is obtained from the reaction mixture but along with it no component other than starting material can be isolated.

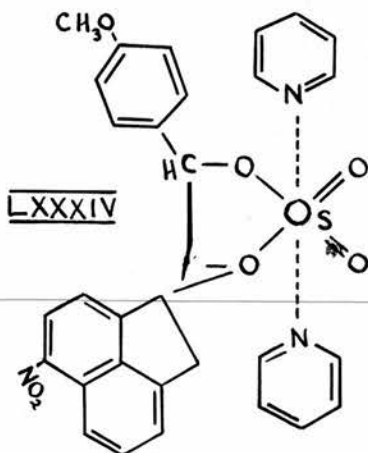
A similar oxidation with the model compound, anisal-acenaphthenone gives anisic acid, a little unchanged material and a product which is firmly adsorbed on alumina - presumably naphthalic acid or anhydride.

An attempt to prepare the glycol from anisal-6-nitroacenaphthene by shaking with mildly alkaline permanganate did not give oxidation.

Finally an endeavour was made to obtain the required glycol using the method of Criegee, Marchand and Wannowius (69). These authors found that the osmic ester formed by the addition of osmium tetroxide to olefinic double bonds could be isolated as a crystalline solid in the form of a pyridine complex.

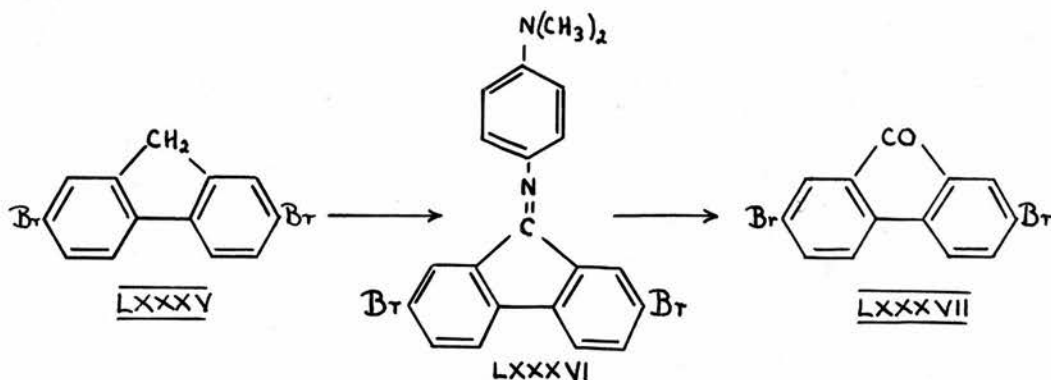
An almost quantitative yield (95%) of a product assumed to be the pyridine-osmic ester of anisal-6-nitroacenaphthene (LXXXIV) is obtained when the latter is treated with a dry benzene solution of osmium tetroxide and pure pyridine.

Hydrolysis of the ester in the conventional manner by shaking with a mildly alkaline solution of mannitol gives an orange product identical to that obtained by oxidation with hydrogen peroxide.



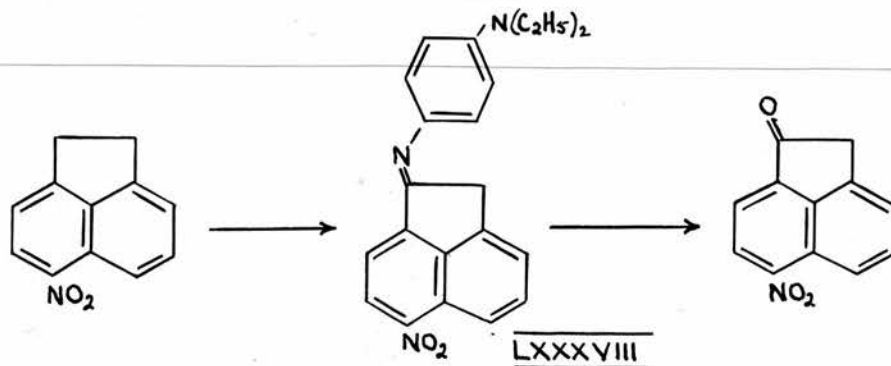
With the failure of the peroxide oxidations to give

the desired ketone another approach to the preparation of 6 nitroacenaphthenone was made. Novelli found that 2:7 dibromofluorene (LXXXV) condensed with p-nitrosodiethylaniline to give a condensation product referred to as an azomethine (LXXXVI).



Hydrolysis of (LXXXVI) gives the corresponding dibromofluorenone (LXXXVII). This method of oxidation has been extensively employed by Buu-Hoi and Cagniant (7) in the conversion of substituted acenaphthenones to acenaphthenequinones.

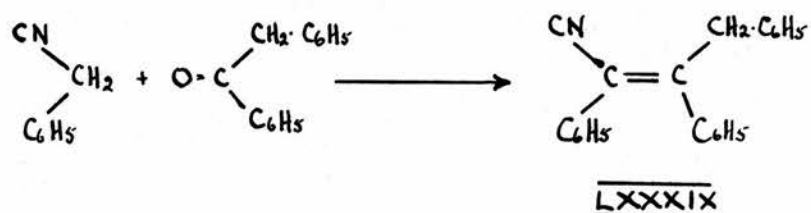
The methylene group on carbon atom-1 of 6 nitroacenaphthene is activated by the para nitro substituent, condensation with aromatic aldehydes being one manifestation of this reactivity. An attempt was made to condense p-nitrosodiethylaniline with 6-nitroacenaphthene with the intention of hydrolysing the azomethine so formed (LXXXVIII) to 6 nitroacenaphthenone.



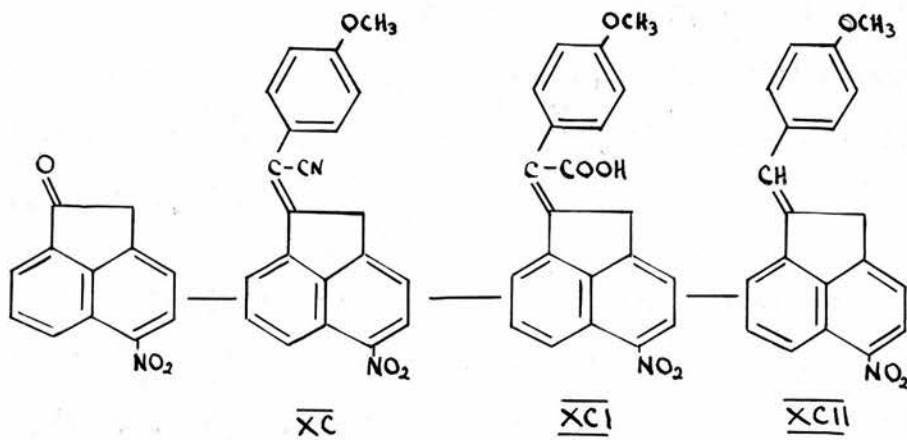
The product from this condensation, a dark powder with an indeterminate melting point, did not hydrolyse when boiled with acid and it was doubtful whether it was an azomethine.

As a final endeavour to obtain an absolute orientation of nitroacenaphthenone it was proposed to synthesise 1-anisal-5 nitroacenaphthene from the nitro ketone. 1-anisal-6-nitroacenaphthene had already been prepared in the course of previous work and was available for comparison with the synthetic product.

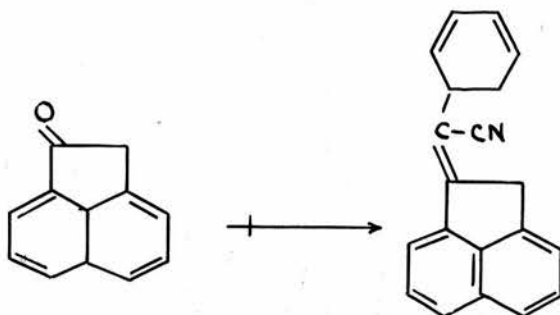
Riedel (71) has shown that condensation between benzyl cyanide and ketones occurs in the presence of sodium ethoxide. Desoxybenzoin, for example, condenses with benzyl cyanide to give cyano-1:2 diphenyl-benzylethylene (LXXXIX).



A similar condensation with nitroacenaphthenone, if successful would give a product (XC) which one might expect to hydrolyse to (XCI) and decarboxylate readily to anisal-5 nitroacenaphthene (XCII).



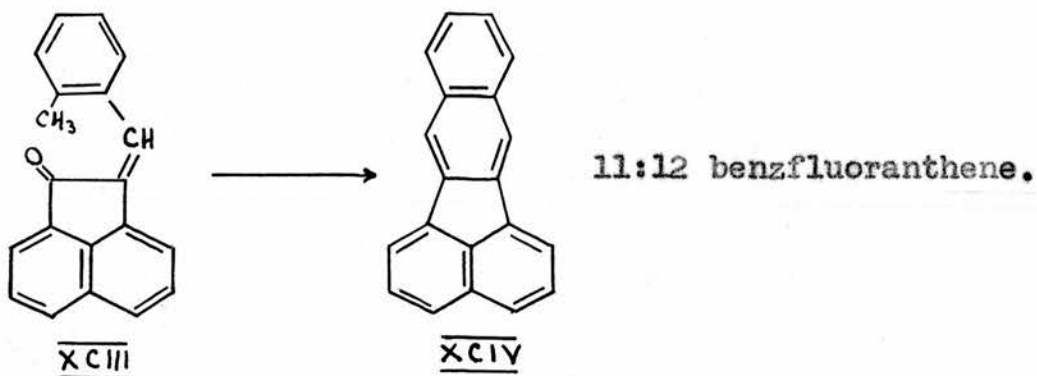
Preliminary condensation experiments were attempted with benzyl cyanide and acenaphthenone.



The results were discouraging, it being found that in the presence of an alkaline condensing reagent biacenaphthylidene-one is formed. With a dehydrating solvent such as acetic anhydride no condensation takes place but after standing for seven months a small amount of naphthalic anhydride is precipitated. On the basis of these results no further attempts to procure this type of condensation were carried out.

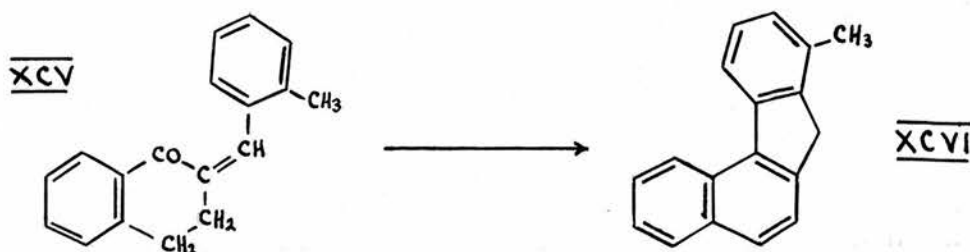
TWO ATTEMPTS TO SYNTHESISE HIGHER RING SYSTEMS FROM
ACENAPHTHENONE UNDERTAKEN IN THE COURSE OF SECTION B.

Throughout the preceding discussion stress has been laid on the reactivity of the methylene group in acenaphthenone. While studying the oxidation of arylidene derivatives of acenaphthenone, e.g. anisalacenaphthenone, it was decided to prepare the corresponding σ -tolualdehyde derivative (XCIII) and attempt the ring closure of the methyl and carbonyl groups to XCIV.

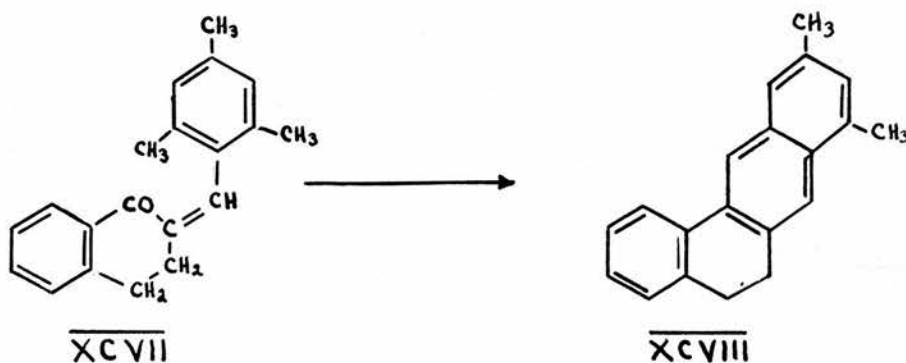


Although the journals of organic chemistry are deficient in work concerned with the ring closure of acenaphthenone derivatives this does not apply to compounds of similar structure. Substituted benzylidene derivatives of α -tetralone have been studied in some detail, notably by Rapson and Shuttleworth (72). These authors found that benzylidene- α -tetralone gives 3:4 benzfluorene on heating with phosphorus pentoxide and assumed that the product obtained by ring closure of σ -tolual- α -tetralone (XCV) is the corresponding

8 methyl-3:4 benzfluorene (XCVI).



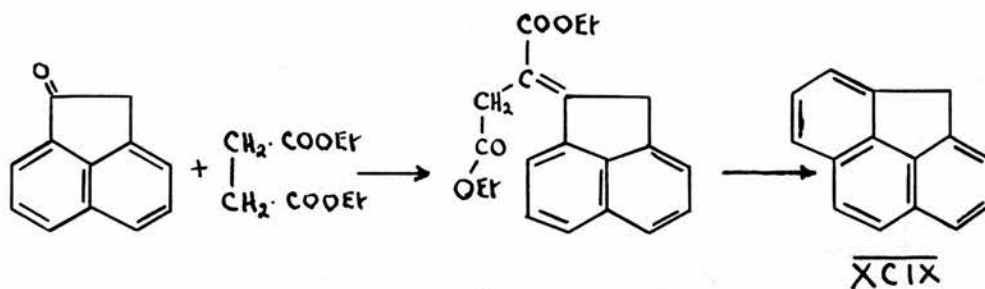
Dehydration involving the ortho-methyl group is only found when the other ortho position is blocked. Thus 2-(2':4':6' trimethyl-benzylidene)- α -tetralone (XCVII) gives a mixture of products of which the dihydrobenz-anthracene shown (XCVIII) is one possibility.



Considerable decomposition is observed when α -tolualacenaphthenone is heated in xylene with phosphorus pentoxide. A brown oil obtained from the eluate after chromatographing the product on alumina failed to form a picrate and it was assumed that 11:12 benzfluoranthene was not present.

α -Tolualacenaphthenone readily forms a dinitrophenyl-hydrazone and in the light of this it was considered that failure to effect dehydration was due to the extensive spacial separation of the methyl group and the oxygen atom.

THE ATTEMPTED STOBBE REACTION ON ACENAPHTHENONE.



The recent development of new condensing agents employed in the Stobbe reaction has added considerably to its value in synthetic work. When compared with sodium methoxide, the classical condensing agent, sodium hydride and potassium *tert.*butoxide have been shown (73) and (74) to give much improved yields in the condensation of ketones and esters of succinic acid.

It was hoped that such a condensation might lead from acenaphthenone to naphthindene (XCLX).

When, however, acenaphthenone is mixed with diethyl succinate in the presence of potassium *tert.*butoxide condensation between the ester and ketone does not take place. Preferential condensation between acenaphthenone molecules occurs and biacenaphthylidene-one along with some unchanged ketone is recovered. Sodium methoxide as the condensing agent gives a similar result.

It is interesting to note that the more strongly enolisable ketones do not condense readily to give the Stobbe reaction. Daub and Johnson, for example, found that desoxybenzoin gives only a 19% yield when condensed with succinic ester in the presence of sodium hydride.

Under similar conditions yields of more than 90% are recorded with benzophenone.

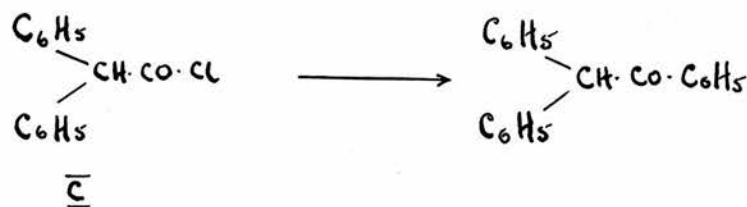
SECTION B (iv)

THE NITRATION OF PHENYL ACENAPHTHENONE.

The nitration of a compound analogous to acenaphthenone suggested itself as another way of attacking the problem, particularly if that compound could be readily degraded to a material of known configuration.

Such a material seemed to be 2-phenylacenaphthenone-1 which was first synthesised by MacKenzie and Tattersall (75), although they did not appreciate the true nature of their product.

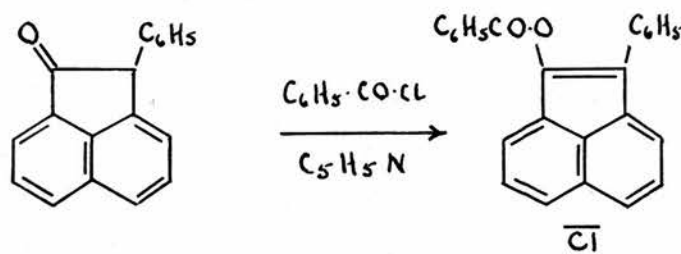
Diphenylacetyl chloride (C) reacts in the presence of aluminium chloride and benzene to give diphenylacetophenone (76).



MacKenzie and Tattersall trying to carry out a similar reaction with phenyl-1-naphthylacetyl chloride and benzene did not, however, obtain the expected phenyl-1-naphthylacetophenone but a compound $\text{C}_{18}\text{H}_{12}\text{O}$ formed by the abstraction of hydrogen chloride from the acid chloride.

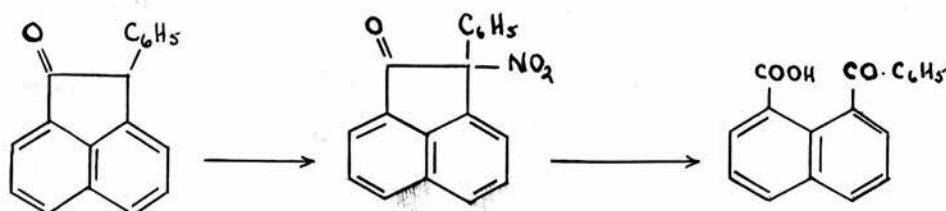
The actual structure was not established until

twelve years later when C.F. Koelsch and H.J. Richter (77), isolated 8-benzoylnaphthoic acid by oxidation with chromic anhydride and acetic acid. As with the parent compound, phenylacenaphthenone can also exist in the enolic form, as shown by the formation of an orange benzoate (Cl) in pyridine solution.



A nitration of 2-phenylacenaphthenone was carried out under similar conditions to those employed in the preparation of nitroacenaphthenone. The product of this nitration contains nitrogen, but is very insoluble in the commoner organic solvents. The weight of this product (0.65g.) is in excess of the theoretical yield for a mononitro-derivative (0.59g.) and a little less than that required for a dinitro derivative (0.69g.) It is also a mixture since it contains an acetic-acid soluble portion and an insoluble residue.

Milder conditions of nitration were sought and fuming nitric acid in glacial acetic acid was found to be satisfactory. This mixture gives a white crystalline mono-nitro derivative



An attempt was made to oxidise the nitro compound with chromic anhydride. Only a small amount of acid material was isolated from the oxidation mixture and this was found to contain no nitrogen.

Initially this was interpreted as indicating that the conditions of oxidation were too severe. A second oxidation in which sodium dichromate was employed gave a cleaner product. A carboxylic acid was isolated and its ethyl ester purified chromatographically. It was found to contain no nitrogen and was identified as ethyl 8-benzoylnaphthoate.

Substitution must therefore take place at the tertiary carbon atom of the ethylene bridge. This also accounts for the lack of either a yellow or an orange colour generally associated with aromatic nitro-substituted compounds. It may be noted that tertiary carbon atoms are very susceptible to attack by nitric acid in acetic acid, and other examples of this have recently been noted in this department. Mixed acids, however, attack aromatic rather than aliphatic systems.

CONCLUSION :

When 2-phenylacenaphthenone-1 is nitrated in acetic acid solution, 2-phenyl-2'-nitroacenaphthenone-1 is formed. The nitration is therefore not analogous to the nitration of acenaphthenone.

EXPERIMENTAL.

The melting points of all compounds, unless otherwise stated, were determined on the macro scale using the apparatus illustrated in "Qualitative Organic Chemistry" by Dr. N. Campbell, page 7, fig. 4. Where specifically stated, micro-melting point determinations were observed with the aid of a microscope equipped with an electrically heated stage. All melting points are uncorrected.

Purification of organic compounds chromatographically was performed with Brockmann standardised alumina and the formation of fluorescent bands in ultra-violet light was detected by the "Hanovia-Muir Analytic Lamp".

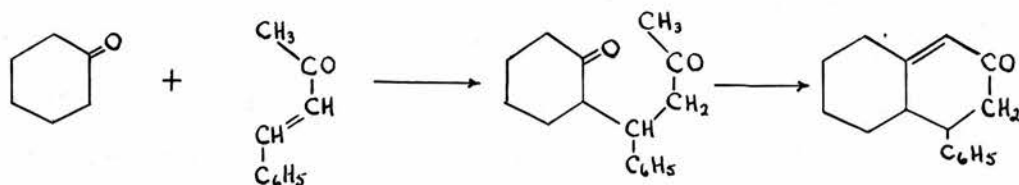
The analyses of organic compounds were carried out by Drs. Weiler and Strauss, Oxford.

SECTION A.

BENZALACETONE.

Benzalacetone was prepared using the method of Drake and Allen (Organic Syntheses, Vol 111, 17), from acetone and benzaldehyde. From benzaldehyde (420g.), benzalacetone (340 g.; (59%)) was obtained as a refractile, yellow oil boiling at 160° , 35 mm. pressure. It solidified rapidly on cooling.

CONDENSATION OF BENZALACETONE WITH CYCLOHEXANONE.



Ref. Rapson and Robinson J.C.S. 1935, 1286.

Cyclohexanone (15g.) was dissolved in dry ether (200 c.c.) and sodamide (6 g.) was added while a stream of hydrogen passed through the reaction vessel. Benzalacetone (22.5g.) dissolved in ether (20 c.c.) was added dropwise with shaking and cooling in ice water. After standing for some time at room temperature a white solid was precipitated from solution which did not dissolve on the addition of more ether. The precipitate (12 g.) was filtered off and the ethereal filtrate evaporated down. The oily residue distilled between 200° C. and 210° C. at 25 mm. pressure.

Trituration of the distillate with petrol ether gave a small amount of a pale yellow solid, M.Pt. 45-50° C. suspected to be impure 2-Keto-4-phenyl Δ 1:9 octalin.

There was insufficient material for further identification.

The white precipitate after being filtered off was recrystallised from ethanol giving white needles, M.Pt. 204° - 205° C. An analysis of this material indicated that it was the intermediate condensation product.

$C_{16}H_{20}O_2$ required C 78.7% ; H 8.2%
found C 78.9% ; H 8.1%

RING CLOSURE OF THE INTERMEDIATE TO 2-keto-4-phenyl Δ 1:9 OCTALIN.

(2 keto-4-phenyl-n-butyl) cyclohexane-2-one (3 g.) was dry distilled in a Claisen flask at a pressure of 50 mm. A small amount of a syrupy liquid distilled over at 252° C. which on trituration with 40-60° petrol ether yielded a white solid. M.Pt. 82 - 85° C. Repeated recrystallisation from petrol ether gave 2 keto-4-phenyl Δ 1:9 octalin as prisms. M.Pt. 88° C. (Lit. 90° C.)

$C_{16}H_{18}O$ required C 85.0% ; H 8.0%

found C 85.0% ; H 8.2%

The same product was obtained when the intermediate was heated for an hour in an oil bath at $220^{\circ} C$.

The fact that ring closure results when the intermediate is heated explains the failure of Rapson and Robinson to isolate this compound. On separating the ethereal layer from the reaction mixture they immediately distilled it 'in vacuo' thus causing dehydration.

ACENAPHTHENONE-1.

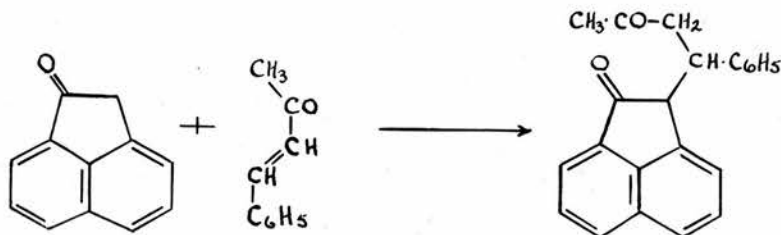
Acenaphthenone was prepared according to the method of Fieser and Cason, (J.A.C.S. 1940, 62, 434) by the lead tetra-acetate oxidation of acenaphthene. From 154 g. of acenaphthene a final yield of 60 g. of acenaphthenone was obtained giving an over-all yield of 36%. The steam distillation of the ketone from the oxidation mixture though tedious (average run 60 hours), gave a product which was sufficiently pure to dispense with recrystallisation. M.Pt. $118^{\circ} - 120^{\circ} C$. (Lit. $121^{\circ} C$.).

Acenaphthenone-2:4 dinitrophenylhydrazone was prepared in alcohol and recrystallised from xylene in fine maroon needles. M.Pt. $259^{\circ} - 260^{\circ} C$. (d).

Required 16.1% N.

Found 15.9% N.

ATTEMPTED CONDENSATION OF ACENAPHTHENONE
AND BENZALACETONE.



Acenaphthenone (2g.) was dissolved in dry ether (100 c.c.) and sodamide (0.5 g.) added. The blood red solution was heated to reflux temperature for eight hours. During this time the evolution of ammonia was detected at the top of the reflux condenser. Benzalacetone (1.8g.) dissolved in dry ether (20 c.c.) was added slowly to the ice-cooled acenaphthenone solution and the mixture was stirred at room temperature for twelve hours.

The addition of water to decompose the reaction mixture produced little reaction showing that only a small amount of sodamide remained unaltered. The reddish brown ether layer was separated and evaporated. A brown, oily residue gave a semi-solid (0.7g.) on trituration with alcohol. An attempt to purify the product chromatographically in benzene did not prove successful.

SECTION B (1) 1.

5-NITROACENAPHTHENONE-1.

Ref. S.B. Thompson Thesis, Edinburgh,
1935, 126.

Acenaphthenone (3.4g.) was dissolved in concentrated sulphuric acid (20 c.c.) and the deep green solution cooled in an ice bath. Fuming nitric acid (0.9 c.c. : S.G. 1.51) was dissolved in concentrated sulphuric acid (10 c.c.) and the nitration mixture dropped in gradually with constant stirring over a period of half an hour. Stirring in the ice bath was continued for a further half hour and then at room temperature for two hours. By this time the colour of the solution had changed from deep green to an intense blood red.

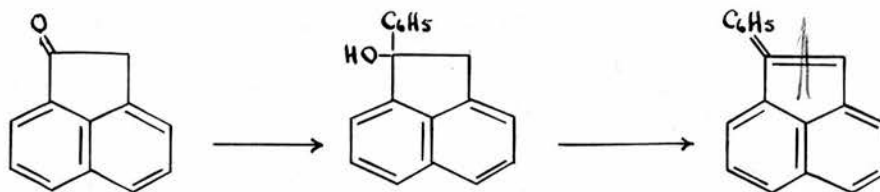
On pouring into ice water a buff coloured solid was precipitated and after allowing to stand for some time this was filtered off, washed well with water and dried. The dry solid was repeatedly extracted with boiling 100 - 120° petrol ether and concentration of the extracts under reduced pressure yielded orange-yellow feathery needles. The optimum conditions of extraction were found to be two litres of petrol per half gramme of crude product.

Though laborious, extraction with this solvent gave a cleaner product than that isolated with other

solvents such as benzene or nitrobenzene in which nitroacenaphthenone is more soluble. The material which crystallised on concentration of the extracts was sufficiently pure for all subsequent experiments. Weight 3.2g. (74)%. A small sample recrystallised from ethanol crystallised in feathery needles, M.Pt. 215° - 221° C., with steady decomposition above 200° C. Nitroacenaphthenone was very strongly adsorbed onto alumina to give deep green banding. Purification with this adsorbent was not possible.

THE ACTION OF GRIGNARD REAGENTS ON ACENAPHTHENONE.

Ref. Ghigi, Ber. 1940, 73, 700.



A solution of bromobenzene (8.3g.) in dry ether (15 c.c.) was added to magnesium (1.24 g.) covered by a little ether. Addition of a small amount of methylmagnesium iodide started the reaction and the rate of addition of bromobenzene adjusted so that a brisk reaction was maintained. The complete formation of phenyl magnesium bromide was ensured by heating on a warm water bath for half an hour.

The Grignard reagent was cooled and a solution of

acenaphthenone (2.95 g.) in dry benzene (20 c.c.) was added gradually and the contents of the flask were maintained at reflux temperature for four and a half hours. Decomposition of the Grignard complex was effected by pouring into saturated ammonium chloride solution (20 c.c.). The ether-benzene layer was separated, washed and dried and the solvents were distilled off. A yellow oil was obtained whose ethanolic solution deposited a crop of white crystals (0.5g.) after standing for an hour. Repeated recrystallisation from alcohol gave white needles, M.Pt. 200° - 201° C. 1-phenylacenaphthene-1-ol with one molecule of water of crystallisation,

$C_{18}H_{14}O \cdot H_2O$ required C 81.8% ; H 6.1%

found C 81.5% ; H 5.9%

*not isolated
by G. H. J.*

Evaporation of the alcoholic solution from which phenylacenaphthenol had deposited, gave a yellowish brown oil. This oil was dissolved in benzene and chromatographed on alumina (12" x 1 $\frac{1}{4}$ ").

A broad, orange band which passed rapidly down the column was collected and evaporated down. An orange crystalline residue (2 g. : 50%) was recrystallised from alcohol to give sparkling orange-yellow plates, M.Pt. 54° - 55° C.

(lit. 52-55°)

A crystal in concentrated sulphuric acid gave a violet coloured solution characteristic of phenylacenaphthylene. Lit. M.Pt. 57° - 58° C.

PHENYLMAGNESIUM BROMIDE AND NITROACENAPHTHENE.

Nitroacenaphthenone (0.6g.) was dissolved in dry benzene (15 c.c.) and the solution added to the Grignard reagent formed in ether by bromobenzene (2.3g.) and magnesium (0.3g.). The dark brown solution obtained was warmed under reflux for two hours and decomposed by pouring into saturated ammoniumchloride solution.

After separation of the benzene-ether layer the solvents were distilled off. A dark brown oil which remained could not be triturated and on chromatographing a benzene solution on alumina very strong adsorption took place.

Extraction of the alumina with several solvents failed to give anyproduct.

SECTION B (1) 2.

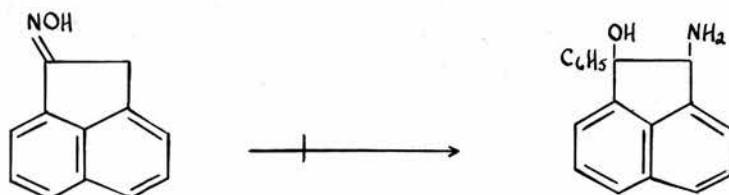
ACENAPHTHENONE OXIME.

To a solution of acenaphthenone (4 g.) in ethanol (15 c.c.) was added hydroxylamine hydrochloride (2.5g.) in water (4 c.c.) A strong solution of caustic potash (7.5g.) in water (9 c.c.) was poured in and the mixture boiled under reflux for two hours.

The reaction mixture was diluted with ice water and acidified with hydrochloric acid. The precipitated oxime was washed with water and crystallised several times from alcohol. Yield 2.5g. (58%), M.Pt. 178° - 179° C. (Lit. 175°)

$C_{12}H_9ON$ required N 7.6% ; found 7.8%

THE ATTEMPTED REACTION OF PHENYLMAGNESIUM BROMIDE
WITH ACENAPHTHENONE OXIME.



The Grignard reagent was prepared from magnesium (0.26g.) dry ether (8 c.c.) and bromobenzene (2 g.). When the magnesium had dissolved the ether was distilled

off by heating the reaction flask in an oil bath. When the bath temperature reached 120° C., dry toluene (3 c.c.) was added. The temperature was raised to 140° C. and acenaphthenone oxime (1 g.) in dry toluene (12 c.c.) dropped in.

A vigorous reaction took place and the reaction mixture took on a deep reddish colouration. Heating was continued for a further fifteen minutes, the mixture allowed to cool and finally poured into dilute hydrochloric acid. Any unchanged oxime was removed by extracting with ether and the acid solution then made alkaline with ammonium hydroxide. The red alkaline solution was extracted with ether and the extract refluxed for half an hour, to expel any dissolved ammonia.

Evaporation of the ether gave an oil which could not be crystallised and which did not form a picrate. When hydrogen chloride was passed through an ether solution of the oil, a bulky precipitation took place. The hydrochloride salt was filtered off. Attempts to crystallise it from alcohol-ether and ethyl acetate - petrol ether mixtures were unsuccessful.

M.Pt. of crude product 164° - 166° C.

Mixed melting point with acenaphthenone oxime softened and melted at 150° C..

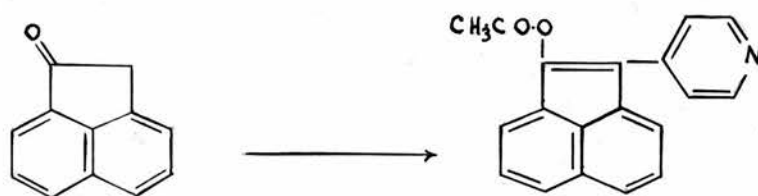
1-phenyl-1' hydroxy-2-aminoacenaphthene hydrochloride,
 $C_{18}H_{16}ONCl$ required Cl. 11.9% ; N 4.7%
found Cl. 14.8% ; N 6.9%.

SECTION B (1) 3.

CONDENSATION OF ACENAPHTHENONE WITH ACETIC ANHYDRIDE
AND PYRIDINE.

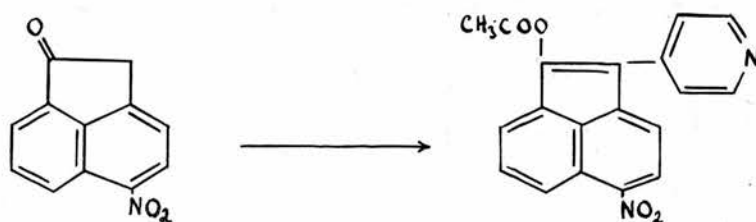
1-Hydroxy 2-(α -pyridyl) acenaphthylene acetate.

Ref. Ghigi Ber. 1942, 75, 768.



Acenaphthenone (10 g.) was dissolved in pyridine (100 c.c.) with slight warming and the pale brown solution cooled. Acetic anhydride (70 c.c.) was added slowly with gentle agitation and the mixture set aside. A red colouration developed slowly over a period of two to three days. After standing twenty days the mixture was deep red in colour and a red crystalline precipitate (3.6g.) was filtered off. Washing with ligroin and a recrystallisation from toluene gave prisms, M.Pt. $245^{\circ} - 246^{\circ}$ C. (Lit. $245^{\circ} - 247^{\circ}$ C.).

1-Hydroxy-2-(α -pyridyl)-5 nitroacenaphthylene acetate.



$C_{20}H_{12}N_2O_4$
18.7
3.6
14.3 8.4

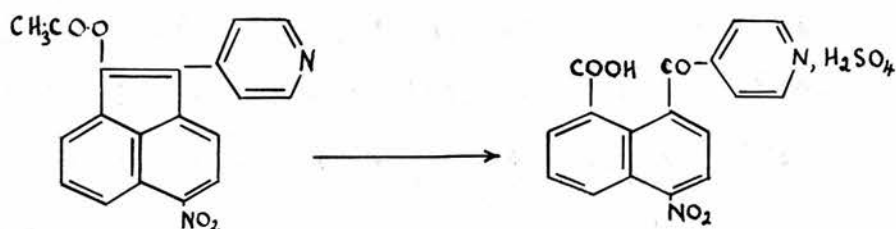
Nitroacenaphthenone (3.4g.) was dissolved with gentle warming in pyridine (29 c.c.) to give a deep green solution.

Acetic anhydride (19 c.c.) was added slowly with shaking, producing a rapid colour change to deep red.

The mixture was set aside for twenty-four hours and a dark red crystalline product filtered off (4.1g.). Recrystallisation from toluene gave deep red prisms which did not melt below 300° C.

Found C 67.4% ; 68.0%
H 4.1% ; 4.6%
N 7.5% ; 7.2%.

DEGRADATION OF 1-ACETOXY-2-(γ -PYRIDYL) 5-NITROACENAPHTHYLENE.



1-acetoxy-2-(γ -pyridyl)-5-nitroacenaphthylene (4 g.) was boiled gently with potassium permanganate (2.8 g.) in dilute sulphuric acid (100 c.c.) for five hours. The reaction mixture was filtered hot and a black filtration residue washed with hot, dilute sulphuric

acid. The acid filtrate on cooling deposited a flocculent, orange-buff precipitate which was filtered off and washed with water. It was found to be extremely insoluble in organic solvents and was purified by the extraction of unwanted organic material with acetone.

The insoluble residue was filtered off and dried. Weight 0.7 g. M.Pt. 269° - 271°C . Found C 48.4% ; H 3.3%.

The sulphate of 8-Carboxy-4 nitronaphthyl- δ -pyridyl ketone, $\text{C}_{17}\text{H}_{10}\text{O}_5\text{N}_2, \text{H}_2\text{SO}_4$ required C 48.6% ; H 2.9%.

An elements test showed the presence of sulphur, presumably as the pyridyl sulphate, and this was confirmed by shaking with a little barium chloride.

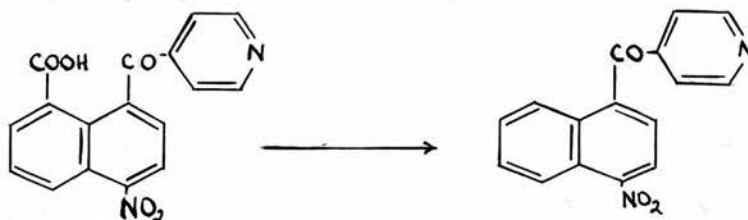
Treatment of the oxidation product with a boiling solution of sodium acetate (20 c.c.; 10%) effectively removed the sulphate. The free amine was filtered off as a dark green powder and found to melt 228° - 231°C . Considering that it could not be recrystallised, the analysis it gave was regarded as satisfactory.

As before $\text{C}_{17}\text{H}_{16}\text{O}_5\text{N}_2$ required C 63.3% ; H 3.1% ; N 8.7%.
found C 62.5% ; H 3.4% ; N 8.3%

A picrate prepared in acetone solution melted after recrystallisation from the same solvent at 227° - $230^{\circ}\text{C}.$ (d). The picrate admixed with the purified oxidation product showed a melting point depression of twelve degrees.

$C_{23}H_{13}O_{12}N_5$ required N 12.7%
found N 11.6%.

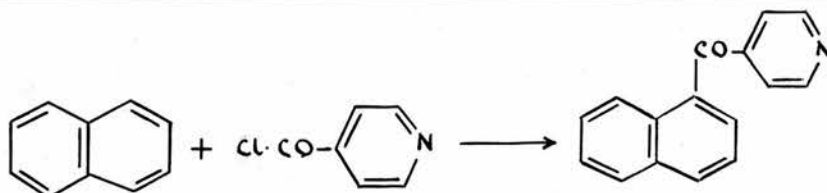
DECARBOXYLATION OF 8-CARBOXY-4-NITRONAPHTHYL-(δ) PYRIDYL
KETONE.



The acid (0.1 g.) was heated under reflux with copper bronze (0.02g.) and pyridine (3 c.c.) for three hours. The mixture was then filtered and poured into water (10 c.c.). An ether extract on evaporation gave a small quantity of an oil which formed a picrate in alcohol solution. There was insufficient material for recrystallisation. M.Pt. 201° - 203° C (d).

$C_{22}H_{13}O_{10}N_5$ required N 13.8%
found N 13.5%.

ATTEMPTED SYNTHESIS OF (α)NAPHTHYL-(δ) PYRIDYL KETONE.



ATTEMPTED PREPARATION OF ISONICOTINYL CHLORIDE.

Phosphorus pentachloride (7g.) was added to a suspension of isonicotinic acid (4g.) in dry benzene (25 c.c.). On heating the suspension the solids gradually dissolved over a period of two hours; gentle boiling under reflux was continued for a further fourteen hours. Benzene was recovered from the deep green solution by distilling from a water bath and an attempt made to fractionate the residue under vacuum. A sublimate of long white needles (M.Pt. 265° - 270°) was produced. These were scraped from the condenser (Weight 0.5g.) and used in a Friedel Crafts reaction with aluminium chloride and naphthalene.

*try prep. of
acid HCl
first: then
acid chloride*

The white sublimate (0.5g.) was added to a solution of naphthalene (1.8g.) in carbon disulphide (10 c.c.) on a warm water bath ($\approx 65^{\circ}\text{C.}$). Aluminium chloride (0.75g.) was added and the blood red solution boiled under reflux for four hours. The mixture was decomposed in ice-water and steam distilled to remove carbon disulphide and excess naphthalene. The residue was made alkaline and extracted with ether. The extract on evaporation gave a brown oily residue which was dissolved in benzene and chromatographed on a column of alumina (8" x $\frac{1}{2}$ ").

A band with a yellow fluorescence in ultra-violet light was collected and evaporated. A small, oily residue solidified on trituration with 40 - 60 petrol

ether. M.Pt. $86^{\circ} - 91^{\circ}$ C.

1:1-Dimethyl ?

The required ketone melts at $50^{\circ} - 51^{\circ}$ C. An elements test on the solid isolated failed to show the presence of nitrogen. The nature of this material was not established.

ATTEMPTED PREPARATION OF ISONICOTINYL CHLORIDE
WITH THIONYL CHLORIDE.

A decision to use the acid chloride 'in situ' was made after several attempts to isolate it proved unsuccessful.

Isonicotinic acid (4g.) was dissolved by heating in thionyl chloride (80 c.c.) and heating under reflux continued for four days. Excess thionyl chloride was distilled off under reduced pressure. A solution of naphthalene (11g.) in carbon disulphide (10 c.c.) was added with stirring and the temperature raised to reflux. Powdered aluminium chloride (24g.) was added in portions with vigorous stirring; the solution was then boiled for six hours and allowed to stand overnight. The mixture was decomposed by pouring into ice-water and was submitted to prolonged steam distillation in order to remove as much naphthalene as possible. The residue was made alkaline and ether extracted. The extract when dried and evaporated yielded 2 g. of a viscous brown oil. An attempt to form a picrate in

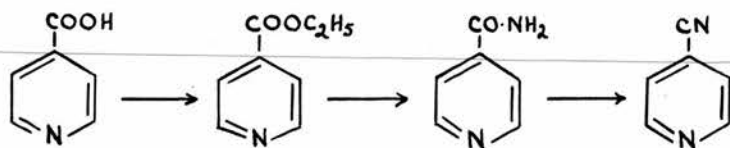
alcohol solution with a little of the oil, gave an oily product. Recrystallisation from a mixture of alcohol and acetic acid gave a small amount of an impure solid. M.Pt. 140° - 146° C.

A mixed melting point with an authentic sample of naphthalene picrate (M.Pt. 149° C.) showed a depression of twenty degrees.

The remainder of the oil from the ether extraction was dissolved in benzene and chromatographed on a column of alumina ($15'' \times 1\frac{1}{2}''$). A yellow band which moved down the column fairly rapidly was collected and evaporated. On triturating the residue with alcohol an oily solid was obtained, M.Pt. 71° - 76° C.

The column was finally washed through with a 50 : 50 mixture of alcohol and benzene and the dark brown oils obtained treated with an alcohol-acetic acid solution of picric acid. A crude product melting 136° - 140° C. was formed. No further attempts to identify this material were made.

ATTEMPTED PREPARATION OF α -NAPHTHYL- γ -PYRIDIYL KETONE
FROM 4-CYANOPYRIDINE.



Ethyl Isonicotinate.

Isonicotinic acid (10 g.) was dissolved by

warming in a solution of ethanol (21g.) and concentrated sulphuric acid (21g.) and the solution was heated for four hours on a boiling water bath. After cooling the mixture was poured onto ice and made alkaline by the addition of concentrated ammonia solution. The ester was extracted with ether, the extract washed with sodium bicarbonate solution then dried and distilled under reduced pressure. The fraction boiling 115° - 120° C. at 35 mm. pressure, was collected as a colourless oil. Yield 6.6g. (54%).

ISONICOTINAMIDE.

An attempt to prepare isonicotinamide by bubbling a continuous stream of ammonia through an alcoholic solution of the ester in the manner of Leis and Curran, (J.A.C.S. 1945, 67, 79) was unsuccessful. The unchanged ester was recovered and converted to the amide using a similar method to that described by LaForge, (J.A.C.S. 1928, 50, 2480).

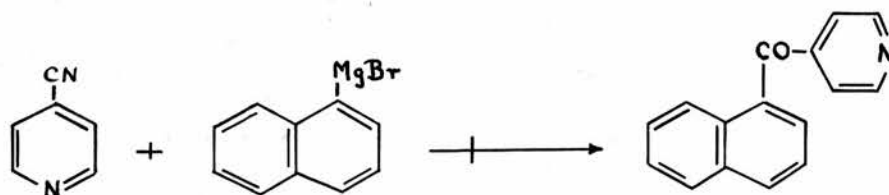
Ethyl isonicotinate (6g.) was covered with approximately 1.5 volumes of concentrated aqueous ammonia saturated at 0° C. The flask was kept loosely closed for approximately eighteen hours. Deposition of colourless crystals was observed after this time and the mixture was resaturated with gaseous ammonia and left for a further five hours. Evaporation to dryness on the steam bath and recrystallisation from benzene

gave 3.5g. (58%) of isonicotinamide. M.Pt. 154°C.
(Lit. 156°).

4-CYANOPYRIDINE.

Isonicotinamide (3.5g.) was dry distilled under vacuum with phosphorus pentoxide (5g.) in a 25 c.c. flask. The flask was immersed in an oil bath and the temperature raised to approximately 300° C. A liquid distillate was obtained but in insufficient quantity to keep the thermometer at a steady boiling point. The oil crystallised on cooling. Yield 1.6g. (54%). M.Pt. 70° - 72° C. (not recrystallised) (Lit 78° - 80°).

THE ATTEMPTED REACTION OF NAPHTHYL MAGNESIUM BROMIDE WITH 4 CYANOPYRIDINE.



The experimental conditions for this reaction were based upon those of LaForge (Loc. cit.) for 3-cyanopyridine and naphthyl magnesium bromide.

4-cyanopyridine (1.6g.) in dry ether (10 c.c.) was added to the Grignard reagent formed by magnesium (0.4g.) and 1-bromo-naphthalene (4.2g.) in ether (15 c.c.).

*Try 3 mols. of
Grignard*

A yellow precipitate formed immediately and the ether was distilled off and replaced by an equal quantity of dry benzene. The mixture was boiled under reflux for an hour and decomposed with ice-cold dilute sulphuric acid. Excess naphthalene was removed by steam distillation and the residual solution was made alkaline and extracted with benzene. Evaporation of the extract gave a little of a brown oil which was distilled in a small flask under reduced pressure. The distillate which crystallised on cooling proved to be naphthalene.

SECTION B (1) (4).

THE SCHMIDT REACTION ON ACENAPHTHENONE.

Preparation of hydrazoic acid reagent.

Ref. Organic Reactions Vol.111 p. 327.

In a three-necked, 100 c.c. flask fitted with a stirrer a paste was made with sodium azide (3.2g.) and a little warm water. Benzene (25 c.c.) was then added and the contents of the flask were cooled to 0° C. Concentrated sulphuric acid (2 c.c.) was added dropwise while cooling was maintained. The benzene solution of hydrazoic acid was separated and dried.

THE REACTION OF ACENAPHTHENONE AND HYDRAZOIC
ACID AT 40° C.

A method similar to that employed by Briggs and De Ath (J.C.S. 1937, 456), for α -hydrindone was used.

Acenaphthenone (2.5 g.) in benzene (20 c.c.) and concentrated sulphuric acid (4 c.c.) were heated to 40° C and the hydrazoic acid solution dropped in with stirring. After standing at room temperature for two days the sulphuric acid layer was run off into cold water. The separation of a brown tar was observed, the quantity of which was not augmented by neutralisation with ammonia. The precipitate was extracted with chloroform, the solvent evaporated off and the residual

oil boiled with charcoal in methylated spirits and hot filtered. On cooling a brown, amorphous solid was deposited melting $215^{\circ} - 221^{\circ} \text{ C.}$ which contained nitrogen. An attempt was made to purify this material chromatographically. The product was dissolved in chloroform and chromatographed on a column of alumina $8" \times \frac{3}{4}"$. A brown band was strongly adsorbed at the top of the column while a small yellow band washed through fairly quickly. Collection of this band and evaporation of the solvent left an oil which on trituration with methylated spirits yielded a small amount of a yellow solid. Micro-melting point $140 - 160^{\circ} \text{ C.}$ A Lassaigne test failed to show the presence of nitrogen and insufficient material prevented identification being carried further. Attempts to extract the brown band from the alumina using chloroform met with no success.

The benzene layer from the reaction mixture gave a yellow oil on boiling off the solvent which solidified when triturated with methylated spirits to form a bright yellow solid. Recrystallisation from a benzene-ligroin solvent gave a yellow product, M.Pt. $260 - 263^{\circ} \text{ C.}$ which showed no depression in melting point when mixed with biacenaphthylidene-one. (Lit. M.Pt. 262° C.).

The tarry nature of the product isolated from the sulphuric acid layer suggested that experimental conditions were too severe. A repetition of the experiment under modified conditions was carried out.

SCHMIDT REACTION ON ACENAPHTHENONE AT ROOM TEMPERATURE.

Hydrazoic acid solution prepared as previously described was added dropwise to a solution of acenaphthenone (2.5g.) in benzene (20 c.c.) and concentrated sulphuric acid (4 c.c.). Mechanical stirring at room temperature was employed during the period of addition (1 hour) and continued for a further hour. As before the sulphuric acid layer was run off into water forming a yellow solution from which a brown oil settled out on standing. The oil was extracted with chloroform and the solvent distilled from the extract to leave an oil which on trituration with methylated spirits gave a reddish brown solid. The product contained nitrogen but no way of purifying it could be found. When a chloroform solution was chromatographed on alumina it was held fast as previously.

The benzene layer from the reaction mixture was green in colour and possessed a strong blue fluorescence. When evaporated it gave a pale buff crystalline solid containing nitrogen.

Weight of crude product 0.7g. M.Pt. 89 - 91° C.

The solid redissolved in benzene was purified on a column of alumina 14" x $\frac{3}{4}$ ". In daylight the column appeared uniformly white but when examined in ultra-violet light a band with a pronounced blue fluorescence was observed. After passing through the column it was

collected and evaporated, giving a white solid M.Pt. 92 - 94° C. On recrystallisation from alcohol the melting point was raised to 93° C. White prisms.

$C_{12}H_9ON$ dihydronaphthisatin required C 78.7% ; H 5.0% ; N 7.7%
found C 89.1% ; H 5.6% ; N 5.5%

It will be seen that the Schmidt product contains no oxygen.

Acenaphthenone-anil $C_{18}H_{13}N$ required C 88.9% ; H 5.3% ; N 5.8%

AN ATTEMPT TO PREPARE ACENAPHTHENONE-ANIL UNDER THE SAME CONDITIONS AS EMPLOYED IN THE SCHMIDT REACTION.

Acenaphthenone (1.2g.) was dissolved in benzene (16 c.c.) and concentrated sulphuric acid (4 c.c.) added. On stirring, the sulphuric acid rapidly became dark green in colour while the benzene layer acquired a strong blue fluorescence. A solution of aniline (0.5g.) in benzene (25 c.c.) was added with vigorous stirring. Stirring was maintained for an hour and the sulphuric acid layer run off into cold water. A yellow precipitate formed and was filtered off. Extraction of this precipitate with alcohol and cooling of the extract gave crude acenaphthenone (0.5g.) confirmed by a mixed melting point determination.

The yellow, alcohol insoluble residue was resrystallised from benzene and identified as biacenaphthylidene-one.

Weight 0.2g. Yellow needles.

M.Pt. 259-261° C. (Lit. 262° C.).

The benzene layer from the reaction mixture yielded a very small quantity of a brown oil which was not investigated further.

ATTEMPTED DIRECT CONDENSATION OF ACENAPHTHENONE
AND ANILINE.

Acenaphthenone (0.5g.). aniline (0.5g.), zinc chloride (0.5g.) and methylated spirits (3 c.c.) were boiled together for five minutes in a test tube then poured into dilute sulphuric acid. A precipitate which formed was extracted with benzene and the extract dried and evaporated. The extract residue was dissolved in benzene and allowed to wash through a column of alumina (12" x $\frac{3}{4}$ "). A small amount of a reddish brown solid was obtained from a band of the same colour which travelled through the column. M.Pt. 113° - 119° C. It gave a green colour with concentrated sulphuric acid and no depression in melting point was observed when mixed with acenaphthenone. The material isolated was therefore acenaphthenone in an impure condition.

SECTION B (1) 5.

THE REDUCTION OF NITROACENAPHTHENONE.

ATTEMPTED REDUCTION WITH SODIUM DISULPHIDE.

Sulphur (2g.) was dissolved in a solution of sodium sulphide (8g.) in water (30 c.c.), and the mixture was boiled until a clear reddish-brown solution was obtained.

5 c.c. of this solution were added dropwise to a boiling ethanolic solution of nitroacenaphthenone (0.5g. in ethanol 30 c.c.). The nitroacenaphthenone solution immediately developed a green colouration. Heating under reflux was maintained for twenty minutes and water (20 c.c.) was added. Organic material was extracted with chloroform and the chloroform extract washed with dilute hydrochloric acid. By adding excess ammonium hydroxide to the acid washings 50 mg. of a crude product were precipitated. M.Pt. 120° - 140° C. This material dissolved in boiling alcohol and on cooling was precipitated as a brown, amorphous powder. M.Pt. 130° - 145° C. (d). An attempt to diazotise some of the product and couple it with β -Naphthol gave a negative result. When water was added to a boiled solution of the reduction product in acetic anhydride containing a trace of concentrated sulphuric acid no precipitate of an acetyl compound was obtained.

THE REDUCTION OF NITROACENAPHTHENONE WITH IRON FILINGS
IN ACETIC ACID SOLUTION.

Nitroacenaphthenone (0.5g.) was dissolved in glacial acetic acid (6 c.c.) and water (1 c.c.) and the solution heated on a water bath at 90° - 95° C. Iron filings (1g.) were added in small portions and the reduction mixture heated for one and three-quarter hours then filtered while hot into cold water (2 c.c.).

Extraction of the cold filtrate with ether gave a brick-red powder (80 mg.) melting 175° - 180° C. with signs of softening above 165° C. The product did not give a green colour with acetone and alkali and thus contained no unchanged starting material.

Crystallisation could not be effected.

A mixed melting point determination with the product from the catalytic hydrogenation, (M.Pt. 180° - 185° C.) softened at 174° C. and continued to melt slowly up to 182° with decomposition.

5-aminoacenaphthenone, $C_{12}H_9ON$ required 7.7% N
found 7.7% N.

THE CATALYTIC HYDROGENATION OF NITROACENAPHTHENONE.

CATALYST.

A platinum catalyst was employed and was prepared

from chloroplatinic acid according to the method given in *Organic Syntheses*, VIII, 92. The precipitate of platinum oxide was washed by decantation with water and water removed by centrifuging several times with absolute ethanol. The catalyst was used as a suspension in ethanol.

CALIBRATION OF HYDROGENATION APPARATUS.

Ref. Buck and Jenkins, *J.A.C.S.* 1929, 51, 2163.

As the hydrogenation apparatus gave readings in pressures only, a calibration with benzoin was carried out to establish a relationship between fall in pressure and the amount of hydrogen absorbed. It was found that the absorption of one molecular proportion of hydrogen by 0.01 mole of benzoin corresponded to a fall in pressure of $7\frac{1}{2}$ pounds per square inch, when the volume of the reduction mixture was 100 c.c.

HYDROGENATION OF NITROACENAPHTHENONE.

All hydrogenations were carried out at room temperature.

Nitroacenaphthenone (2.13g. ; 0.01 mole) was added to the catalyst obtained from chloroplatinic acid (0.5g.) suspended in absolute ethanol (100 c.c.).

The amount of hydrogen absorbed was equivalent to a fall in pressure of 21 pounds per square inch.

In a second hydrogenation with 0.01 mole of nitro-ketone a total fall in pressure of 23 pounds per square inch was observed.

Finally a third hydrogenation with nitroacenaphthenone (3.97g.) gave a reduction in pressure of 45 pounds per square inch.

Thus although rigorous consistency in experimental conditions could not be maintained the observed measurements suggested that only three moles of hydrogen were reacting with one mole of nitroacenaphthenone. This is consistent with the selective reduction of the nitro group, to leave the carbonyl group intact.

A typical extraction of the hydrogenated material was as follows :-

After the reduction of nitroacenaphthenone (3.97g.) was complete the hydrogenation mixture was filtered and the residue repeatedly washed with acetone. The filtrate and washings were poured into water (300 - 400 c.c.) and a green coloured precipitate filtered off and dried. Weight 1.2g. It was dissolved in acetone and chromatographed on a column (16" x $\frac{3}{4}$ ") of alumina. A brown and a green band were strongly absorbed at the top of the column while a bright orange band moved down through the column quickly and was collected.

Evaporation of the acetone solution under reduced pressure gave orange prisms, decomposing and melting $200^{\circ} - 204^{\circ} \text{ C.}$

5-aminoacenaphthenone, $\text{C}_{12}\text{H}_9\text{ON}$

required C 78.7% ; H 5.0% ; N 7.7%

found C 79.9% ; H 5.8% ; N 6.4%.

The orange compound in alcohol solution gave a copious precipitate with 2:4 dinitrophenylhydrazine which was very insoluble in the in the commoner organic solvents. The precipitate was filtered off, washed with boiling alcohol and dried. M.Pt. $230^{\circ} - 234^{\circ} \text{ C. (d).}$

5-aminoacenaphthenone -2:4 dinitrophenylhydrazone, $\text{C}_{18}\text{H}_{13}\text{O}_4\text{N}_5$

required N 19.3%

found N 15.8%

No conclusions were drawn as to the structure of this compound.

When the aqueous filtrate of the hydrogenation reaction mixture was concentrated under reduced pressure cocoa-coloured prisms crystallised out. Weight 1.1g. M.Pt. $180^{\circ} - 185^{\circ} \text{ C. (d).}$

An analysis for carbon and hydrogen gave C 77.1% ; H 5.0%.

A little of this material dissolved on boiling in benzene containing a few drops of acetic anhydride. Concentration of the solution gave a greyish white

powder which recrystallised from boiling water in small white prisms. M.Pt. 209° C.

N-acetyl-5-aminoacenaphthenone required N 6.2%

found N 6.1%.

ATTEMPTED SANDMEYER REACTION.

CUPROUS BROMIDE.

Ref. Practical Organic Chemistry by Cohen, p.189.

Crystalline copper sulphate (2g.) was dissolved in water (8 c.c.) and mixed with a solution containing potassium bromide (1g.) in water (4 c.c.). Sulphur dioxide was bubbled through the solution until precipitation of white cuprous bromide was complete. The white precipitate was filtered off and dissolved in concentrated hydrobromic acid solution, (5c.c. S.G. 1.31).

The cocoa-coloured hydrogenation product (0.74g.) was treated with concentrated hydrochloric acid (2 c.c.) and water (1.5 c.c.). Diazotisation was carried out by adding pulverised sodium nitrite (0.5g.) in small portions over a period of twenty minutes, while cooling the mixture on ice. At this stage the diazo mixture showed the presence of free nitrous acid on testing with starch-iodide paper and was also strongly acid to litmus.

A drop of the solution on mixing with a drop of an alkaline solution of β -naphthol did not give a

precipitate but developed a wine colouration, assumed to be a positive reaction.

The cuprous bromide solution was then cooled in ice and the diazotisation mixture added slowly. A brisk effervescence of a colourless gas took place. When the addition was complete the temperature of the reaction mixture was allowed to rise to room temperature and the mixture then warmed gradually on a hot water bath. After fifteen minutes in boiling water the mixture was diluted with water (25 c.c.) and extracted with chloroform.

Some solid material (0.30g.) which did not dissolve was filtered off, washed and dried. When some of this solid was boiled with dilute nitric acid and silver nitrate solution added, a white precipitate was formed which dissolved rapidly in dilute ammonium hydroxide. It was concluded that this material was the hydrochloride salt of the starting material.

The chloroform extract when evaporated under reduced pressure gave a solid (0.31g.) melting over a large range in temperature. An elements test showed the presence of nitrogen in quantity and a trace of chloride. Bromine was not detected.

The Sandmeyer reaction was therefore unsuccessful.

A second Sandmeyer reaction modelled on the preparation of p-bromotoluene from p-toluidine (Organic

Syntheses V, 21) gave a product showing the presence of nitrogen and some sulphur. No halogens were identified. As the reaction had been carried out in sulphuric acid it was concluded that the product isolated was the sulphate of the starting material.

COMPARISON OF THE COLOUR REACTIONS OF AROMATIC
NITROCOMPOUNDS CONTAINING A METHYLENE GROUP OR
A CARBONYL GROUP PARA TO THE NITRO GROUP.

Colour tests in acetone solution.

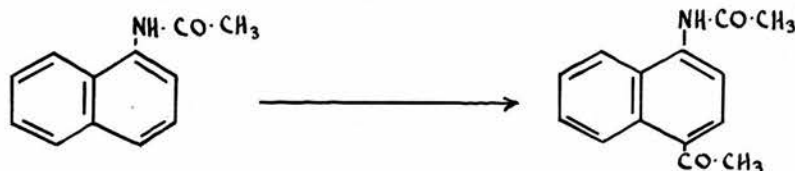
The nitro compound (20mg.) was dissolved in acetone (1 c.c.) and dilute caustic soda solution (1 c.c. 10%) added down the inside of the test tube to form a second liquid layer. Unless otherwise stated the colours formed within one minute of the alkali addition and invariably in the acetone layer.

N-acetyl-1-naphthylamine.

1-Naphthylamine was acetylated in benzene solution according to the general method of Kaufmann (Ber. 1909, 42, 3480).

Yield 61 g. (quantitative) M.Pt. 159° Lit (160°) from 48 g. of 1-naphthylamine.

The attempted acetylation of N-acetyl-1-naphthylamine
in carbon disulphide solution.



N-acetyl-1-naphthylamine (18.5g.), acetic anhydride (20.4g.) and carbon disulphide (200 c.c.) were mixed together in a litre flask fitted with a reflux condenser and stirrer. The contents of the flask

were warmed to approximately 50° C. in a water bath and aluminium chloride (107g.) added portionwise over a period of two hours. Heating was continued for a further two hours and the mixture was then allowed to stand at room temperature for three hours. Excess carbon disulphide was removed by distillation, and the aluminium chloride complex decomposed by pouring into cold, dilute hydrochloric acid. A precipitate was filtered off and recrystallised from methylated spirits, admixed with N-acetyl-1-naphthylamine it melted 155-157° C. Lit. 160° C.

The acetylation of N-acetyl-1-naphthylamine in tetrachloro-ethane.

N-acetyl-1-naphthylamine (18.5g.) was dissolved in tetrachloro-ethane (200 c.c.) and acetic anhydride (21 c.c.) with stirring and gentle warming.

Freshly powdered aluminium chloride (107g.) was added over a period of one hour while the temperature was maintained in the 50°-60° region on a water bath. Stirring was continued until the evolution of hydrochloric acid vapour had virtually ceased (approx. 7 hrs.), and the mixture was allowed to stand at room temperature for two days. The reaction complex was decomposed with cold, dilute hydrochloric acid and tetrachloro-ethane was removed by steam distillation. A brown tar was skimmed from the surface of the

residual solution and the latter, on cooling, deposited yellowish needles. Weight of crude product 7.8g. (34%).

Repeated recrystallisation from benzene gave small white needles. M.Pt. 160° - 161° C.

$C_{14}H_{13}O_2N$ requires 74.0% C ; 5.7% H ; 6.2% N.
found 73.3% C ; 5.2% H ; 6.4% N.

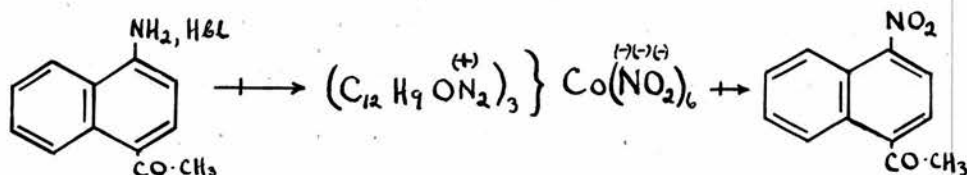
Hydrolysis of 4-aceto-N-acetyl-1-naphthylamine.

4-aceto-N-acetyl-1-naphthylamine (1g.) was boiled with dilute hydrochloric acid (25 c.c.) for forty-five minutes. On cooling the solution pale brown needles separated out and were filtered off. The crude hydrochloride melted with decomposition above 210° C. An aqueous suspension of the hydrochloride treated with concentrated ammonia formed a yellow precipitate. Recrystallisation of the free base from benzene-ligroin gave yellow prisms. M.Pt. 135 - 136° C. (Lit. 135.5° - 136.5°).

4-Aceto-1-naphthylamine hydrochloride.

4-aceto-N-acetyl-1-naphthylamine (5g.) was boiled with dilute hydrochloric acid (100 c.c.) for forty-five minutes. The solution on cooling deposited 4.5g. (92%) of the hydrochloride.

Attempted conversion of 4-aceto-1-naphthylamine hydrochloride to 4-aceto-1-nitronaphthalene.



Ref. Hodgson and Marsden (J.C.S. 1944, 22.)

4-aceto-1-naphthylamine hydrochloride (4.5g.) was suspended in concentrated hydrochloric acid (6 c.c.) and the suspension cooled in a freezing mixture. A solution of sodium nitrite (2g.) in water (7 c.c.) was added with stirring and the excess acid neutralised by the addition of calcium carbonate. The diazonium solution was filtered off and tested by the addition of a drop to an alkaline solution of β -naphthol. A bulky red precipitate was formed showing that diazotisation had taken place.

Sodium cobaltinitrite (4g.) was stirred in to the diazo solution and a maroon coloured precipitate filtered off. Weight 0.7g.

A small sample of the precipitate failed to give a coupling colour with β -naphthol; therefore it was not a diazonium cobaltinitrite.

p-Nitro-acetophenone oxime.



Ref. Höchst, D.R.-P, 109, 663.

Ford-Moore & Rydon, J.C.S. 1946, 679.

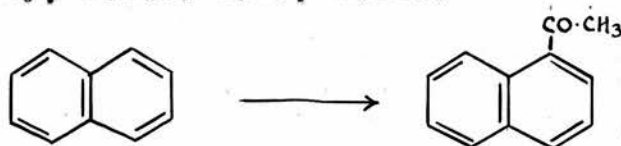
Sodium methoxide was prepared by dissolving sodium wire (2.5g.) in dry methanol (40 c.c.) and distilling off approximately 15 c.c. of the alcohol. The methoxide solution was cooled to room temperature and treated with a mixture of p-nitro-ethyl-benzene (15g.) and amyl nitrite (12g.), the addition being fairly slow with shaking. After being kept overnight the mixture was heated in a warm water bath (approx. 50°C.) for half an hour and excess methanol was removed by steam distillation. The residue was cooled and extracted with chloroform and the extract shaken with dilute caustic solution (10%). The alkaline washing was added to the aqueous layer separated from the first chloroform extraction and the combined solutions treated with carbon dioxide until precipitation was complete. The precipitate was filtered off and dried. Yield 8g.

p-Nitro-acetophenone.

The crude oxime (8g.), water (20 c.c.) and sulphuric acid (10 c.c.) were boiled for three hours with stirring. The mixture was allowed to cool and a chloroform extraction made. The chloroform layer was washed with dilute alkali, water, and finally dried over sodium sulphate. Distillation gave the pure ketone boiling point 181°C at 32mm. pressure. Yield 2g. (12%).

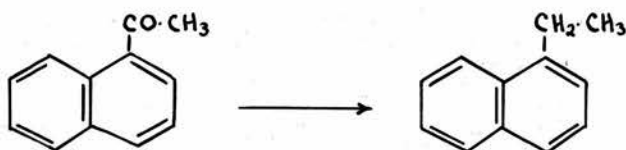
Methyl-1-naphthyl ketone.

Methyl-1-naphthyl ketone was prepared according to Baddeley, J.C.S. 1949, S.102.



With ethylene dichloride and double the quantities stated, a yield of 30g. (87%) of the ketone was obtained as a pale yellow oil, boiling point 166°C . at 15mm.

1-Ethynaphthalene.



Ref. Clemmensen Ber. 1913, 46, 1840

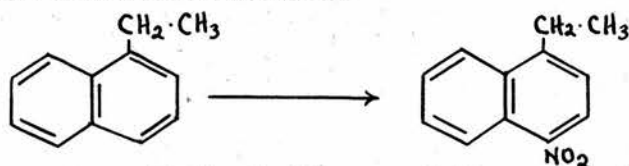
Fröshl and Harless Monatsch. 1932, 59, 280.

The Clemmensen reduction was effected in a two-phase system. The following is a typical experiment:-

Amalgamated zinc was prepared by shaking together granulated zinc (100g.), mercuric chloride (10g.), concentrated hydrochloric acid (5 c.c.) and water (125 c.c.). After five minutes the aqueous solution was decanted and the zinc amalgam covered with a solution of concentrated hydrochloric acid (175 c.c.) and water (100 c.c.). The methyl naphthyl ketone (16g.) was added as a solution in toluene (100 c.c.). During a reflux period of fifteen hours two 50 c.c. portions of concentrated hydrochloric acid were added. The toluene layer was separated,

washed with water, dried and the toluene distilled off. When the residual oil was fractionated in vacuum, a colourless oil was collected boiling 132° - 140° C. at 15mm. Yield 7g. (47%).

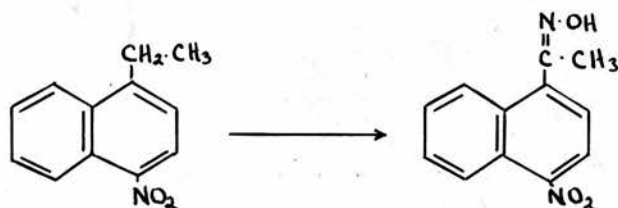
4-Nitro-1-ethylnaphthalene.



Ref. Baddar and Warren, J.C.S. 1938, 403.

A solution of 1-ethylnaphthalene (12g.) in glacial acetic acid (15 c.c.) was cooled to 0° C. and fuming nitric acid (5.5 c.c.) was added very slowly. The mixture was allowed to stand for four days in a refrigerator. Ice was then added and the oil precipitated extracted with benzene. The extract was washed with dilute sodium carbonate solution and dried. Evaporation of the benzene left a red oil which on distilling under reduced pressure gave 4-nitro-1-ethylnaphthalene as an orange oil, boiling point 190 - 200° C. at 15 mm. Yield 6.0g. (39%).

Attempted oximation of 4-nitro-1-ethylnaphthalene.

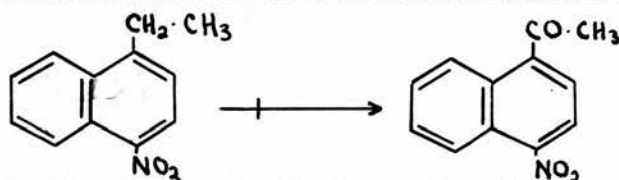


(See prep. of p-nitro acetophenone).

To sodium (0.25g.) dissolved in dry methanol (4 c.c.), was added a solution of 4-nitro-1-ethylnaphthalene (2.2g.) in amyl nitrite (1.5 c.c.)

and the mixture allowed to stand at room temperature for thirty-six hours. The formation of a buff coloured precipitate was observed. An equal volume of water was added and the aqueous solution extracted with chloroform. The chloroform extract was washed with dilute sodium hydroxide solution (5 c.c., 10%) and the alkaline washing was added to the original aqueous layer. Bubbling carbon dioxide through the solution gave a small yellow precipitate (0.2g.) which was filtered off and recrystallised from aqueous methylated spirits. M.Pt. 148-150° C. $C_{12}H_{10}O_3N_2$ requires 12.17% N ; found 9.4%.

Attempted oxidation of 4-nitro-1-ethylnaphthalene.

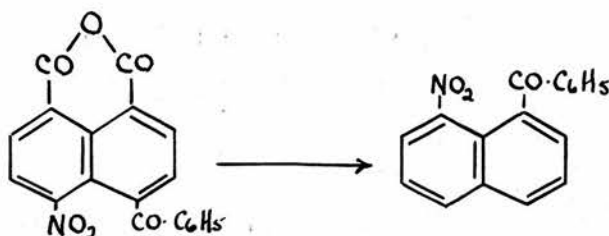


4-Nitro-1-ethylnaphthalene (1g.) was heated for an hour with a solution of Chromic anhydride (A.R. 1g.) dissolved in acetic acid (10 c.c.) and water (2 c.c.). The green solution was poured into water and the oil which deposited was extracted with ether. The extract was dried and the solvent evaporated off on the water bath. Attempts to obtain a 2:4 dinitrophenylhydrazone from the residual oil by means of either Allen's (J.A.C.S. 1930, 52, 2955) or Brady's (J.C.S. 1931, 756) method were unsuccessful.

The preparation of Benzoyl-8-Nitro-Naphthalene.

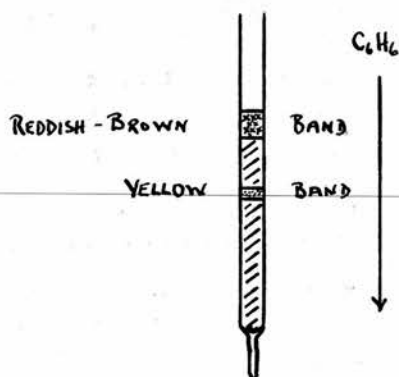
5-Benzoyl-6-nitroacenaphthene was prepared and oxidised to the corresponding anhydride in the manner described by Dziewonski and Rychlik, Ber. 1925, 58B, 2239.

Decarboxylation using the method of Dziewonski and Kahl,
Chem. Abstracts, 1935, 29, 2941.



Mercuric oxide was freshly prepared by precipitation from a solution of mercuric acetate (1.5g. in water, 15 c.c.) with dilute caustic soda. The bright yellow precipitate was filtered off and washed by decantation until neutral to litmus, care being taken to prevent the precipitate drying and coming in direct contact with the air.

The anhydride (1g.) was heated with a suspension of the HgO precipitate in water (20 c.c.) in a sealed tube at $230^{\circ}C$. for five hours. The solid was filtered off and boiled for half an hour with concentrated hydrochloric acid (15 c.c.) and benzene (25 c.c.). The benzene layer was separated, the acid layer shaken with more benzene (15 c.c.), and the extract added to the original benzene layer. The combined benzene extracts were washed with water, dried over anhydrous sodium sulphate and the solvent removed

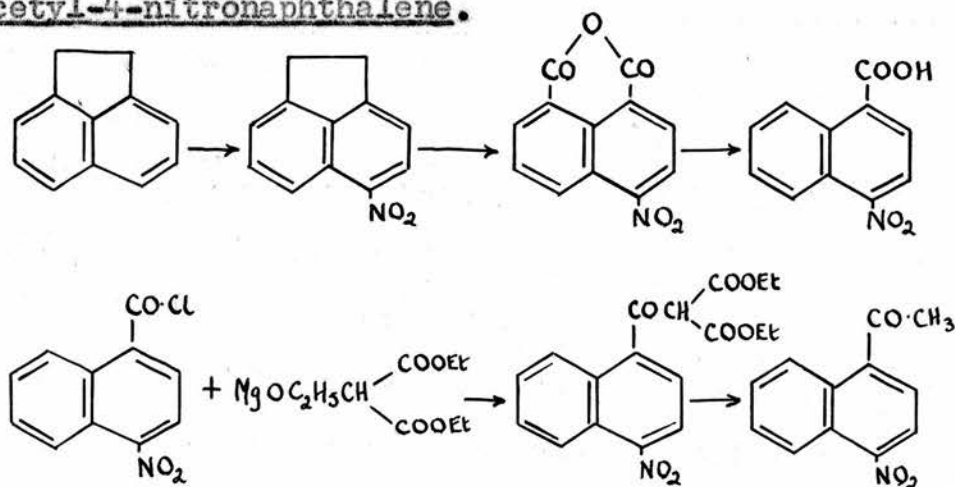


by evaporation. A reddish brown oil obtained was dissolved in benzene and chromatographed on a column of alumina $8'' \times \frac{1}{2}''$. A yellow band which separated, as shown, was collected and yielded a pale yellow solid.

Recrystallisation from alcohol gave colourless prisms

M.Pt. 122° C. Yield 100 mg. $C_{17}H_{11}O_3N$ requires N 5.1% ; found N 5.0%.

1-acetyl-4-nitronaphthalene.



5-nitroacenaphthene.

5-nitroacenaphthene was prepared in the manner described by Sachs and Mosebach (Ber. 1911, 44, 2854). Half quantities were employed and from 50 g. of acenaphthene, 32 g. (49%) of pure 5-nitroacenaphthene were obtained after the crude product had been crystallised from $80-100^{\circ}$ Pet Ether.

4-nitronaphthalic anhydride.

5-nitroacenaphthene (40 g.) was dissolved in glacial acetic acid (500 c.c.) and sodium dichromate (280 g.) was added in portions while the mixture was immersed in a warm water bath. When the addition of the dichromate was complete the temperature of the water bath was raised to the boiling-point and maintained there for three hours. The green solution was poured into dilute sulphuric acid and a precipitate filtered off. The latter, after being well washed with water was found to be orange in colour. The precipitate was digested in boiling sodium carbonate solution

(400 c.c.: 5%) and a small amount (1-2g.) of an orange, carbonate insoluble material filtered off. The filtrate was poured into dilute sulphuric acid and a white precipitate filtered off. Recrystallisation from glacial acetic acid gave needles of 4-nitronaphthalic anhydride. M.Pt. 230° C. (Lit. 230° C.). Yield 25g. (50%).

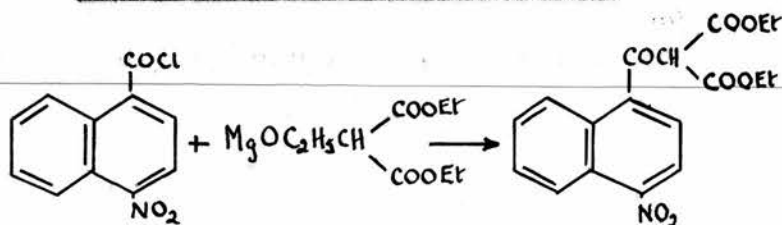
Mercuration of 4-nitronaphthalic anhydride.

Ref. Leuck, Perkins, Whitmore. J.A.C.S. 1929, 51, 1835. 4-Nitronaphthalic anhydride (25 g.) was dissolved in water (650 c.c.) containing caustic potash (17 g.). This solution was filtered and to it was added mercuric oxide (32 g.) previously dissolved in acetic acid (24 c.c.) and water (80 c.c.). A buff coloured precipitate was produced on mixing the two solutions.

The mixture was heated for fifty hours, cooled and filtered. The solid was washed with water and hydrolysed by boiling with excess concentrated hydrochloric acid for two hours over a small flame.

Crude, 4-nitronaphthoic acid (20 g.: 89%) was filtered off and recrystallised from acetic acid. Yellow needles M.Pt. $224-225^{\circ}$ C. (Lit. $225-226^{\circ}$ C.)

1-Acetyl-4-nitronaphthalene.



4-Nitronaphthoyl chloride.

4-Nitronaphthoic acid (20 g.) was mixed with

phosphorus pentachloride (16.9 g.) and phosphorus trichloride (40 c.c.) and the mixture heated over a small flame, for an hour. Excess phosphorus trichloride and oxychloride were removed by distilling under reduced pressure on a water bath. The residue was dissolved in dry benzene (45 c.c.) and the solution filtered.

Magnesium ethoxymalonic ester.

(Ref. Walker and Hauser J.A.C.S. (1946), 1387).

In a 250 c.c. flask were placed magnesium (3.3 g.), absolute ethanol (13 c.c.) and carbon tetrachloride (approx. 1 c.c.). A reflux condenser equipped with a calcium chloride tube was fitted to the flask. The reaction was started by gentle warming and allowed to continue for several minutes. Dry ether (45 c.c.) was then cautiously poured in and the mixture placed on the hot water bath, while a solution of diethyl malonate (20 c.c.) in absolute alcohol (13 c.c.) and dry ether (20 c.c.) was added drop by drop. The whole was refluxed for about one hour. The grey coloured solution was allowed to cool and the filtered benzene solution of the acid chloride added. During the addition a vigorous reaction was observed and a homogeneous liquid phase was formed. The contents of the flask were heated to reflux temperature for three-quarters of an hour and allowed to stand overnight.

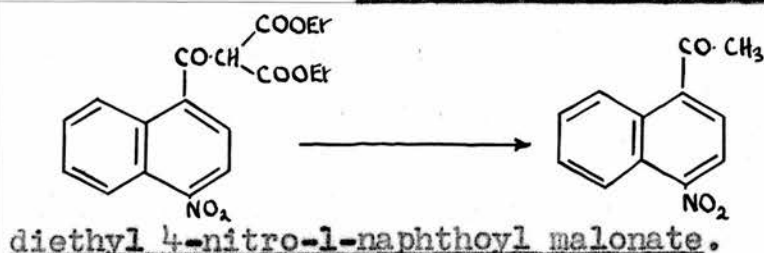
On the following day, the mixture was decomposed by pouring into ice-cold, dilute sulphuric acid and the benzene layer which formed was separated from the aqueous solution. This aqueous solution was further extracted

with benzene and the extract added to the original benzene layer. The combined benzene solutions were washed with water, dried, and the benzene distilled off. The brownish oil which remained had a characteristic ester-like smell. Trituration of the oil with methanol, ether, petroleum ether and benzene in each case gave solutions. Attempts to purify the oil by distillation under reduced pressure resulted in its decomposition to a dark brown tar. An attempt to purify the oil chromatographically was also unsuccessful. After two weeks standing, however, solidification took place and the buff coloured prisms formed were filtered off. The filtrate was a viscous, reddish-brown oil which did not solidify further.

Crystallisation of the crude product from methylated spirits gave buff coloured rhombic prisms melting over a considerable range of temperature, ($60^{\circ}\text{C} - 74^{\circ}\text{C}.$) Further purification was brought about by extraction with boiling $60 - 80^{\circ}$ Petroleum ether. On cooling the extracts, lemon-yellow prisms were formed which on recrystallisation from methylated spirits gave 5.8 g. of pale lemon-yellow prisms. M.Pt. $74 - 75^{\circ}\text{C}.$

$\text{C}_{18}\text{H}_{17}\text{O}_7\text{N}$ requires C 60.2% ; H 4.8% ; N 3.9%
found C 59.8% ; H 4.9% ; N 3.9% .

1-acetyl-4-nitronaphthalene.



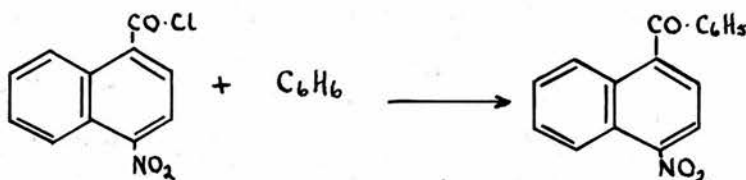
The aroyl malonate (1 g.) was boiled under reflux with a solution of glacial acetic acid, (3 c.c.), concentrated sulphuric acid (0.4 c.c.), and water (2 c.c.) for four hours. On cooling two liquid phases were observed to be present; one, the aqueous solution of acids and, the other, a small amount of a brown oil.

Sufficient caustic soda solution (20%) was added to make the reaction mixture alkaline and the oil was extracted with ether. A second ether extraction was also made. The extracts were combined, washed and dried. Evaporation of the solvent gave an oil which solidified rapidly and recrystallisation of this solid from alcohol gave pale yellow plates. Yield 0.4 g.; 67%. M.Pt. 90° C.

$C_{12}H_9O_3N$ requires C 67.0% ; H 4.2% ; N 6.5%

found C 67.4% ; H 4.4% ; N 6.4%

1-Benzoyl-4-nitronaphthalene.



4-Nitronaphthoic acid (2 g.) was added to a suspension of phosphorus pentachloride (2 g.) in phosphorus trichloride (8 c.c.). The acid dissolved on gentle warming with a vigorous evolution of hydrogen chloride. Heating was continued for half an hour and excess phosphorus chlorides were removed by distilling under reduced pressure. The residue was dissolved in dry benzene (10 c.c.) and powdered aluminium chloride (3.5 g.) was added with stirring. An instantaneous blood-red

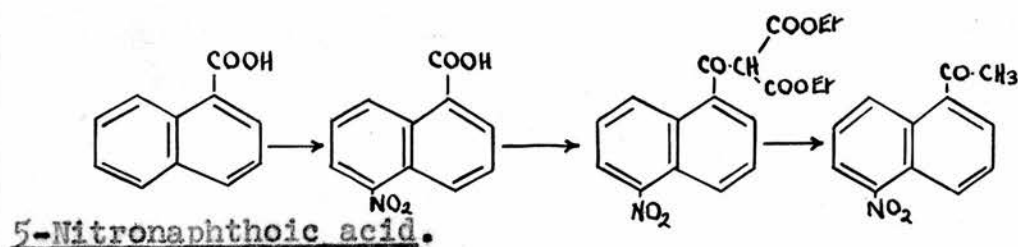
colouration was produced. Vigorous stirring was continued for half an hour and the reaction mass was decomposed by pouring into ice water. A brown oil which separated was extracted with benzene and the extract washed with sodium carbonate solution and finally dried. The solvent was removed by distillation and the residual oil taken up in benzene and chromatographed on a column of alumina (8" x $\frac{1}{2}$ "). Some brown impurities were strongly adsorbed to form a brown band at the top of the column but a yellow band descended rapidly and was collected. From this band an oil was obtained which solidified to give 0.9 g. (39%) of a yellow solid.

Pale yellow, rectangular plates of 4-nitro-1-benzoylnaphthalene were obtained when the crude product was recrystallised from methylated spirits. M.Pt. 97° C.

$C_{17}H_{11}O_3N$ requires C 73.6% ; H 4.3% ; N 5.1%

found C 73.7% ; H 3.7% ; N 5.0%

1-Acetyl-5-nitronaphthalene.



Ref. Eckstrand J. pr. Chemie 188, 38, 156.

Spence Thesis Edinburgh, 1925, 34.

The method described by Spence was employed at 5-Nitronaphthoic acid separated from the 8-isomer by fractional crystallisation from alcohol. From 40 g. of naphthoic acid 12 g. (24%) of the pure 5 nitro isomer

were obtained. M.Pt. 239° - 240° C. (Lit. 239°).

5-Nitronaphthoyl Chloride.

5-nitronaphthoic acid (1.5g.) was treated with phosphorus pentachloride (1.3g.) and phosphorus trichloride (8 c.c.) and the mixture boiled for half an hour. Phosphorus oxychloride and trichloride were distilled off 'in vacuo' and the residual acid chloride was dissolved in dry benzene (15 c.c.)

Magnesiumethoxymalonic ester.

Magnesium ethoxymalonic ester was prepared from magnesium (0.25g.), absolute alcohol (1 c.c.) and carbon tetrachloride (2 drops) in the manner described for 1-Acetyl-4-nitronaphthalene. Dry ether (3.5 c.c.) was added and the resulting mixture placed on the steam bath. Diethylmalonate (1.6 g.) in absolute alcohol (1 c.c.) and dry ether (1.5 c.c.) was added and the combined materials boiled under reflux for an hour. After cooling, the benzene solution of the acid chloride was added from the funnel and the temperature again raised to reflux for half an hour. The mixture was decomposed with dilute sulphuric acid and the product extracted with benzene. Recrystallisation of the product from alcohol gave 2 g. (80%) of buff coloured, rhombic plates. M.Pt. 85° - 86° C.

$C_{18}H_{17}O_7N$ requires N 3.9%

found N 3.7%

Hydrolysis of 5-nitronaphthoyl-diethylmalonate.

The Aroyl malonate (1g.) was boiled with glacial acetic acid (3 c.c.), concentrated sulphuric acid (0.4 c.c.) and water (2 c.c.) for six hours. Sufficient caustic soda solution (20%) was added to ensure that the mixture

was alkaline and an ether extraction made. A further ether extraction was made and the two extracts combined. After drying and evaporation, the resulting oil crystallised to form rosettes. Lemon-yellow rhombic prisms were obtained after recrystallising from alcohol. Yield 0.35 g. (58%). M.Pt. 108°-109° C.

$C_{12}H_9O_3N$ requires C 67.0% ; H 4.2% ; N 6.5%

found C 66.3% ; H 4.1% ; N 6.1%

SECTION B (iii).

THE ATTEMPTED WILLGERODT REACTION WITH

1-ACETYL-4-NITRONAPHTHALENE.

Ref. Organic Reactions, 111, p. 96.

Ammonium polysulphide was prepared by saturating concentrated ammonia solution with hydrogen sulphide for seventeen hours. Sulphur (10% by weight) was added and was found to dissolve with a fairly brisk reaction at room temperature. The reddish brown solution was employed in subsequent experiments.

1-Acetyl-4-nitronaphthalene (0.5g.) prepared according to Experimental Section B.(ii) was heated in a sealed tube with the ammonium polysulphide solution (7 c.c.) and dioxan (5 c.c.). The tube exploded after heating for half an hour at 150° C.

The presence of peroxide in the dioxan was detected by shaking a drop with a little 0.1N potassium iodide solution in the presence of acid. Addition of a drop of starch indicator showed that iodine had been liberated. Since it was considered that the peroxides had possibly caused the explosion, the dioxan was purified. Removal of peroxide was carried out by allowing the dioxan (10 c.c.) to diffuse through a column of alumina (12" x $\frac{1}{2}$ ") as suggested by Vogel in "A Textbook of Practical Organic Chemistry" p. 175 (1948 Ed.).

A test with potassium iodide solution on the eluate indicated that only a trace of peroxide was present.

The experiment was repeated with the same quantities as before and the purified dioxan. The tube was heated at 160° C. for fourteen hours and then opened. The contents after boiling with alkali gave on acidification a semi-solid product. Repeated extraction of this solid with benzene and concentration of the extracts gave a small amount of a solid which crystallised from benzene in yellow blades. Micro-M.Pt. 121° C.

An elements test indicated that the product contained sulphur in quantity and a analysis showed that the compound contained no nitrogen.

THE PREPARATION OF 2-p-ANISALACENAPHTHENONE-1.

Ref. de Fazi, Gazz. Chim.ital. 1924, 54, 664.

Sircar and Raja Gopalan, J.Indian C.S. 1932, 2, 639

also Chem. Abs. 1933, 27, 3930.

Acenaphthenone (1g.) and p-anisaldehyde (0.8 c.c.) were dissolved in ethanol (15 c.c.) by gentle warming. The solution was cooled to approximately 40° C. and caustic soda (2 c.c.; 10%) solution was added. On scratching vigorously with a glass rod, the reddish-purple solution deposited an oil which on continued trituration

was transformed to a yellow solid. This was filtered off and recrystallised from alcohol.

Yield 1.6g. (94%) Canary-yellow, rhombic prisms. M.Pt. 124° C. giving a blood-red colour with sulphuric acid.

$C_{20}H_{14}O_2$ required C 83.9% ; H 4.9%

found C 83.5% ; H 5.1%

DIMORPHISM OF 2-p-ANISALACENAPHTHENONE.

de Fazi described the condensation product as crystallising in needle form M.Pt. $95-98^{\circ}$ C. This was considerably below the melting point found above. Investigation showed that anisalacenaphthenone is capable of crystallising in two forms. A hot ethanolic solution deposited on cooling a mixture of fine, feathery needles and small compact prisms. Reheating the solution followed by cooling yielded prisms alone. Sometimes only needles were deposited which, on standing for several hours, reverted to the prismatic form. One of the prisms obtained by selection under a microscope melted at $117-123^{\circ}$ C. (micro). The feathery needles showed partial melting at 98° C, the material continuing to remain in the semi solid state until the temperature reached 120° C. It is suggested that this partial melting might account for the value given by de Fazi.

Sircar gives the melting point of his preparation of anisalacenaphthenone as $126.5 - 127^{\circ}$ C.

OXIDATIONS WITH HYDROGEN PEROXIDE AND OSMIUM TETROXIDE.

The preparation of an anhydrous solution of hydrogen peroxide in ter. butyl alcohol.

Ref. Milas, J.A.C.S. 1936, 58, 1302.

Milas, J.A.C.S. 1937, 59, 2343.

To hydrogen peroxide (50 c.c. 30%) was added tertiary butyl alcohol (200 c.c.) and the solution was treated with small portions of anhydrous sodium sulphate. Milas states that two liquid phases were formed but this was not observed although the reagent was prepared several times. Excess anhydrous sodium sulphate (30-40g.) was then added and the mixture allowed to stand overnight to ensure the maximum uptake of water. The solution of peroxide in butyl alcohol was filtered off and stored in a glass-stoppered flask.

Hereafter this solution is referred to as the 'peroxide solution'.

PREPARATION OF OSMIUM TETROXIDE CATALYST SOLUTION.

0.5% and 1% solutions of osmium tetroxide were prepared by dissolving 0.5g. or 1g. respectively of the tetroxide in ter. butyl alcohol (100 c.c.). Addition of a few drops of the peroxide solution was found to be necessary to prevent the reduction of the catalyst to metallic osmium by butylenes present in solution.

THE OXIDATION OF 2-p-ANISALACENAPHTHENE BY MILAS'S
REAGENT AT ROOM TEMPERATURE.

Anisalacénaphthenone (0.5g.), the peroxide solution (5 c.c.) and the solution of osmium tetroxide (5 c.c.; 0.5%) were shaken together in a glass stoppered tube for four days at room temperature. By this time the compact prisms had been completely replaced by short, yellow needles. The latter were filtered off and the filtrate concentrated to yield a little more solid. Weight of product 0.27g. (84%). M.Pt. 260° - 261° C. A sample admixed with a little acenaphthenequinone showed no depression.

The filtrate when treated with 2:4-dinitrophenylhydrazine in ethanol gave a derivative which was filtered off. Weight 0.13g. Recrystallisation from acetic acid gave scarlet needles M.Pt. 250° C. A mixed melting point with p-anisaldehyde-2:4 dinitrophenylhydrazone (M.Pt. 253° C.) was found to melt 251° - 252° C. The weight of the dinitrophenylhydrazone corresponded to a 25% yield of p-anisaldehyde.

THE PREPARATION OF 1-p-ANISAL-6-NITROACENAPHTHENE.

6-NITROACENAPHTHENE.

6-Nitroacenaphthene was prepared according to the method employed by Sachs and Mosebach, Ber. 1911, 44, 2854, by the direct nitration of acenaphthene. Before

proceeding to the following stage the product was recrystallised from 80°-100° petrol ether. M.Pt. 139° C. (Lit. 139° C.)

1-p-ANISAL-6 NITROACENAPHTHENE.

Condensation between p-anisaldehyde (8g.) and 6-nitroacenaphthene (10g.) was carried out using the method of Lohe, Chemische Ber. 1949, 82, 214. The product was ground up in a mortar with 80°-100° petrol ether and a little alcohol to remove unchanged anisaldehyde. The crushed material was then filtered off and washed repeatedly with dilute acid to remove all traces of piperidine. Failure to do this gave a product which darkened on exposure to air. Finally the product was washed with water and air dried.

Yield 14g. (88%). M.Pt. 215°-217° C. (Lit. 218° C.)

Subsequent preparations gave yields of the order claimed by Lohe, namely 94%.

Anisal-6 nitroacenaphthene gives a characteristic deep blue colouration with concentrated sulphuric acid.

THE ATTEMPTED OXIDATION OF 1-ANISAL-6-NITROACENAPHTHENE
WITH MILAS'S REAGENT AT ROOM TEMPERATURE.

1-Anisal-6-nitroacenaphthene was found to be completely insoluble in the ter.butyl alcohol solution. A suspension of anisal-6-nitroacenaphthene (0.5g.), the peroxide solution (5 c.c.) and 0.5% catalyst solution

(5 c.c.) remained unchanged after standing at room temperature for several days.

Similar oxidations were tried with the addition of other solvents in an endeavour to increase the solubility of an anisal-6-nitroacenaphthene. At room temperature however, no improvement was observed after addition of chloroform, ether, dioxan and benzene. With the exception of the latter, all gave back the starting material. The benzene mixture did yield unchanged material but in an oily, impure form, probably due to the oxidation of benzene itself. (Ref. Cook & Schoental, J.C.S. 1950, 47).

THE OXIDATION OF 1-ANISAL-6-NITROACENAPHTHENE IN BOILING CHLOROFORM SOLUTION WITH MILAS'S REAGENT.

1-Anisal-6-nitroacenaphthene (5 g.), peroxide reagent (50 c.c.), catalyst solution (30 c.c. ; 0.5%) and chloroform (25 c.c.) were heated together on a boiling water bath.

After three and a half hours, complete solution was attained suggesting that a reaction had taken place. The volume of the solution was reduced by distilling under vacuum and the solid material was filtered off and dried.

The filtrate when treated with an ethanolic suspension of 2:4 dinitrophenylhydrazine gave a

precipitate (1 g.) corresponding to a yield of anisaldehyde of 20%.

The solid material obtained by evaporation of the oxidation mixture was found to be a brown powder decomposing above 140° C. In concentrated sulphuric acid it gave a dark green-brown colour sufficiently intense to obscure any blue colouration due to the presence of starting material.

An attempt was made to purify the product by adsorption on alumina. The brown solid (0.5g.) was dissolved in chloroform (30-40 c.c.) and the solution developed on a column of alumina ($13'' \times \frac{3}{4}''$). An orange yellow band which developed rapidly on washing with chloroform gave a solid of the same colour when evaporated. M.Pt. $165-170^{\circ}$ C. (d).

6-nitroacenaphthenone, $C_{12}H_7O_3N$ required C 67.6% ; H 3.3%
found C 71.4% ; H 4.5%

THE OXIDATION OF 2-p-ANISALACENAPHTHENONE IN BOILING
CHLOROFORM SOLUTION WITH MILAS'S REAGENT.

Anisalacenaphthenone (0.5g.) peroxide reagent (4 c.c.), catalyst solution (3 c.c.; 1% soln.) and chloroform (5 c.c.) were refluxed on a water bath for half an hour. The yellow solution darkened rapidly to a deep orange colour and within twenty minutes fine yellow needles began to crystallise from the boiling solution. The mixture was concentrated under reduced

pressure and the precipitate filtered off. Weight 0.3g.
M.Pt. 260° - 268° C.

The orange filtrate gave a precipitate with an alcoholic suspension of 2:4 dinitrophenylhydrazine. After recrystallisation from acetic acid the dinitrophenylhydrazone melted at 251° C. Weight 60 mg. An authentic sample of p-anisaldehyde-2:4dinitrophenylhydrazone was prepared and found to melt at 252° C. (Lit. 253° C.), while a mixture of the two materials melted at 251 - 252° C. The filtrate of the oxidation mixture therefore contained anisaldehyde.

Some of the solid oxidation product M.Pt. 260 - 268° C. was mixed with a sample of acenaphthenequinone, M.Pt. 261° C. which had been freed from naphthalic anhydride impurity by extraction with hot sodium carbonate solution. The mixture melted at 252 - 255° C. In concentrated sulphuric acid the oxidation product gave a brown solution with a strong blue fluorescence. The pure sample of acenaphthenequinone gave a brown solution in sulphuric acid and naphthalic anhydride was found to give a yellow solution with a strong blue fluorescence.

When warmed with an acetic acid solution of σ -phenylenediamine, the oxidation product gave a yellow precipitate melting over the range 198° - 203° C. Acenaphthenequinone gave a white derivative with σ -phenylenediamine, M.Pt. 240° C., while naphthalic anhydride gave a yellow product M.Pt. 204° C. (Lit. 206° C.)

Naphthalic anhydride is thus one of the oxidation products of anisalacenaphthenone and is presumably formed along with acenaphthenequinone.

THE OXIDATION OF 1-p-ANISAL-6-NITROACENAPHTHENE IN
BOILING ACETONE SOLUTION WITH MILAS'S REAGENT.

It had previously been observed that in several attempted oxidations with the above reagent at room temperature anisal-6-nitroacenaphthene had been recovered as a bright scarlet powder as opposed to the darker, maroon starting material. Preliminary treatment of anisal-6-nitroacenaphthene at room temperature with some of the peroxide reagent was found to give slightly higher yields and cleaner products in the acetone oxidation.

Accordingly anisal-6-nitroacenaphthene (5g.) was mixed and allowed to stand for an hour with chloroform (25 c.c.), the peroxide solution (15 c.c.) and 1% catalyst solution (5 c.c.). Unchanged anisalnitroacenaphthene was recovered as a bright, brick-red powder (4.3g.) by filtration.

The oxidation was accomplished by heating the purified anisal-6-nitroacenaphthene (4.3g.) with peroxide solution (60 c.c.), 1% osmium tetroxide solution (12 c.c.) and acetone (100 c.c.) on a boiling water bath for three hours. Within this time all the solid had dissolved to give a reddish-brown solution which

was filtered hot and the filtrate evaporated under reduced pressure. The dark brown oil obtained was chromatographed on a column of alumina (9" x 1 $\frac{1}{4}$ ") in chloroform solution. Development was rapid and an orange band washed through the column after two hours development. Evaporation of the eluate gave a bright-orange solid. Yield 0.68 g. Recrystallisation from glacial acetic acid gave golden-orange needles with a pleasant smell. M.Pt. 179°-180° C.

Found C 71.7% ; H 3.8% ; N 4.3%.

Molecular weight 347.

p-methoxyphenyl-1-(6-nitroacenaphthylene)-carbinol

C₂₀H₁₅O₄N, required C 72.1% ; H 4.5% ; N 4.2%

Molecular weight 333.

Subsequent development of the alumina column gave oils.

THE FORMATION OF A DERIVATIVE WITH PHENYLHYDRAZINE.

The orange compound (0.2g.) phenylhydrazine (4 drops) and glacial acetic acid (3.4 c.c.) were heated together for two minutes over a small flame. The orange solution became blood red in colour and on cooling yielded a bulky precipitate of dark coloured needles. On filtering off the needles and washing with alcohol they were found to be purple in colour with an iridescent sheen. It was not found possible to recrystallise the derivative owing to its sparing

solubility. A sample was extracted with alcohol to remove any impurity and then dried. M.Pt. 195° - 197° C. (vigorous decomposition). The melting point was found to vary slightly depending upon the rate of heating. This material was found to contain 8.6% N.

An acetyl derivative of the orange product was prepared by warming an acetic acid solution of the compound with a few drops of acetic anhydride and one drop of pyridine. Recrystallisation from acetic acid gave reddish brown needles. M.Pt. 259° C.

Found C 71.6% ; H 3.7%

The acetyl derivative of p-methoxyphenyl-1-(6-nitroacenaphthylene)-carbinol

required C 70.5% ; H 4.5%

OXIDATION OF THE ORANGE COMPOUND TO 4-NITRONAPHTHALIC ANHYDRIDE.

The orange compound (0.3g.) was dissolved by warming in acetic acid (7.5 c.c.) and the flask containing the solution was placed in a water bath at 80° C. Potassium dichromate (1.7g.) was added in small portions and when the addition was complete the flask was heated over a small flame for five and a half hours. The mixture was then poured into dilute sulphuric acid and a yellowish-green precipitate was filtered off,

washed with water and digested in boiling sodium carbonate solution (50 c.c.; 2% soln.). The solution was filtered and the filtrate acidified with dilute sulphuric acid. A buff coloured precipitate was filtered off (weight 0.23g.), and recrystallised from acetic acid as pale buff needles. M.Pt. 230° C.

4-Nitronaphthalic anhydride is quoted (Rowe and Davis, J.C.S. 1920, 117, 1349), as having a melting point of 229° - 230° C.

An authentic specimen was prepared by the oxidation of 6-nitroacenaphthene and found to melt at 230° C.

Admixture of some of the oxidation product from the orange compound with some of this specimen did not depress its melting point.

THE ATTEMPTED OXIDATION OF THE ORANGE COMPOUND WITH
LEAD TETRA-ACETATE.

Lead tetra-acetate was prepared as described in "Organic Preparations" by Weygand, p.131.

The orange compound (0.25g.) and lead tetra-acetate (0.32g.) were suspended in acetic acid and stirred for six hours while the temperature was maintained at 65° C. in a water bath.

The mixture was concentrated under reduced

pressure and an orange crystalline material was precipitated. Yield 120 mg. Melting at 180° C and showing no depression in melting point when mixed with a little starting material.

Pouring the filtrate into water gave a precipitate of starting material contaminated with a lead impurity.

Similarly unchanged material was recovered from an attempted oxidation with periodic acid in an aqueous dioxan solution after the mixture had stood for ten days at room temperature.

As the main product of the osmium tetroxide oxidation appeared to be strongly adsorbed on alumina an endeavour was made to purify the reaction mixture without resorting to chromatography with this adsorbent. The oxidation of anisal-6-nitroacenaphthene in acetone was repeated on the five gramme scale and after heating for three hours the peroxide, catalyst and solvents were distilled off under reduced pressure. The residual viscous oil was triturated with methylated spirits and after standing overnight a brown powder was filtered off. Weight 2.4g. M.Pt. $80-90^{\circ}$ C. Repeated extraction of this powder with benzene followed by concentration of the extracts gave a brown oil. Further extraction of this oil with boiling water gave, on cooling, a few milligrammes of a yellow solid. M.Pt. $150^{\circ}-154^{\circ}$ C. Despite repeated extractions insufficient material was

obtained to identify this substance.

The benzene-insoluble residue failed to show any definite melting below 320° C. Decomposition began slowly above 100° C. and became more rapid as the temperature was increased. The material was, however, entirely organic since it ignited on a platinum foil to leave no residue. A Lassaigne test confirmed the presence of nitrogen.

The powder did not form a derivative with an acetic acid solution of σ -phenylenediamine and an attempt to chromatograph a chloroform solution of some of the powder on finely ground cane-sugar failed to give any purification.

THE OXIDATION OF 2-p-ANISALACENAPHTHENONE WITH
POTASSIUM PERMANGANATE.

Anisalacenaphthenone (0.5g.) powdered potassium permanganate (1.0g.) and water (30 c.c.) were heated together for three and a half hours on a boiling water bath. Sulphurous acid was added to dissolve manganese salts and a yellowish white solid was filtered off. The precipitate was washed with cold sodium carbonate solution and an attempt made to recrystallise it from alcohol. Crystallisation could not be effected and it appeared that the product was a mixture. A benzene solution of the product was chromatographed on a column of alumina (6" x $\frac{1}{2}$ "). An orange band remained firmly adsorbed

by the alumina while a yellow band washed through and was collected. The material from this band was identified as anisalacenaphthenone. The orange band did not yield any material on prolonged extraction with alcohol.

Acidification of the sodium carbonate washings gave a white precipitate (150 mg.; 57%) which was recrystallised and identified as anisic acid.

Acenaphthenequinone was not obtained and in view of the fact that part of the oxidation mixture was strongly adsorbed on alumina it was assumed that degradation had proceeded directly to naphthalic anhydride.

THE ATTEMPTED OXIDATION OF 1-ANISAL-6-NITROACENAPHTHENE
WITH NEUTRAL PERMANGANATE SOLUTION.

1-p-anisal-6-nitroacenaphthene (1g.) and finely powdered potassium permanganate (2g.) were heated in water (50 c.c.) on a steam bath. After two hours the mixture was filtered hot and on cooling the filtrate deposited a pale orange flocculent precipitate (70 mg.) M.Pt. 174° - 178° C. After a recrystallisation followed by a mixed melting point determination the material was identified as anisic acid.

On treating the filtration residue with sulphurous acid to remove manganese salts, a bright scarlet powder was revealed. M.Pt. 212° - 214° C. (d). Sodium

carbonate solution failed to extract any acidic material from this residue. When admixed with a little starting material melting took place between 213° - 216° C. The product gave the deep blue colouration with sulphuric acid characteristic of anisal-6-nitroacenaphthene.

THE ATTEMPTED OXIDATION OF ANISAL-6-NITROACENAPHTHENE
WITH MILDLY ALKALINE POTASSIUM PERMANGANATE SOLUTION.

Anisal-6-nitroacenaphthene (1g.) was shaken for forty-eight hours with finely ground potassium permanganate (2g.) dissolved in dilute sodium carbonate solution (100 c.c.; 1%). The solid suspension was filtered off and the filtrate acidified with sulphurous acid. A few milligrammes of anisic acid were precipitated.

Washing the brown filtration residue with sulphurous acid once again gave a bright red powder. Recrystallisation from toluene gave a pure sample of anisal-6-nitroacenaphthene, melting point 217° - 218° C.

THE PREPARATION OF THE OSMIUM TETROXIDE-PYRIDINE
COMPLEX OF ANISAL-6-NITROACENAPHTHENE.

The purified anisal-6-nitroacenaphthene (0.38g.) in dry benzene (7 c.c.) and dry pyridine (0.2g. A.R.) was treated with osmium tetroxide (0.32g.). The insoluble bright red anisal-nitroacenaphthene was gradually replaced by a deposit of fine brown needles. To

ensure complete reaction the mixture was allowed to stand for twenty-four hours and the coffee-coloured precipitate was filtered off and found to weigh 0.86 g. The theoretical yield was calculated as 0.87g.

The precipitate was found to be very soluble in water and on boiling with a little acid and adding a few milligrammes of thiourea a bright cherry red colour, characteristic of osmium, was formed.

HYDROLYSIS OF THE OSMIC ESTER.

Ref. Criegee, et alia, Annalen 1942, 550, 129.

The osmic ester (0.86g.) was shaken for eight hours with an alkaline solution of mannitol (caustic potash 0.25g.1 mannitol 2.5g. and water 25 c.c.) and methylene chloride (20 c.c.). Separation of the deep brown methylene chloride layer and evaporation at room temperature gave a dark green-brown, oily material.

In experiments recorded in the literature hydrolysis is shown by the gradual decolourisation of the methylene chloride layer accompanied by the appearance of a pink colouration in the aqueous solution due to the formation of potassium osmate. Both the liquid phases were observed to be deeply coloured in the experiment.

The residue from the methylene chloride layer was dissolved in benzene and chromatographed on a column of alumina (6" x $\frac{1}{2}$ "). A very dark green band was adsorbed strongly at the top of the column while an

orange band separated from it. This band was cut out and extracted with chloroform. Recrystallisation of the chloroform extracted material (50 mg.) from acetic acid gave small orange needles. M.Pt. 180-181° C.

Mixed melting point with orange product (M.Pt. 179°-180° C.) formed by hydrogen peroxide oxidation of anisal-6-nitroacenaphthene.

The orange product, as before, was found to possess a sweet, pleasant smell.

THE ATTEMPTED CONDENSATION OF 6-NITROACENAPHTHENE AND
p-NITROSO-DIETHYLANILINE.

p-Nitrosodiethylaniline (0.5g.) and 6-nitroacenaphthene (0.5g.) were melted together with sodium ethoxide (approximately 20 mg.) by gentle warming. Heating was maintained for five minutes, ethanol (4-5c.c.) was added and the mixture allowed to cool.

A semi-solid, reddish-brown material was filtered off and dried. On heating it decomposed steadily above 180° C. with the formation of a voluminous, carbonaceous ash. Ignition of some of the product on a piece of platinum foil indicated that the product was entirely organic.

0.23g. of this powder was heated for two hours with methylated spirit (5 c.c.) and concentrated hydrochloric acid (10 c.c.). The mixture was poured

into water and a precipitate filtered off. When dry it weighed 0.15 g. and from its appearance and the fact that it did not melt on heating, it was considered to be starting material.

An attempt to effect the condensation in alcohol gave the same infusible product. Chromatographing the oil obtained by evaporation of the mother liquors gave a small amount of impure 6-nitroacenaphthene and a trace of p-nitrosodiethylaniline. A black band adhering to the top of the column could not be extracted.

THE ATTEMPTED CONDENSATION OF BENZYL CYANIDE AND
ACENAPHTHENONE WITH SODIUM METHOXIDE.

Acenaphthenone (0.5g.) was dissolved in absolute ethanol (25 c.c.) and benzyl cyanide (0.35g.) added. Sodium methoxide (0.1g.) was rapidly weighed out and transferred to the mixture. After standing overnight a yellow precipitate was filtered off (0.2g.) and recrystallised from benzene in bright yellow needles. A mixed melting point determination and a violet colour with concentrated sulphuric acid characterised the product as biacenaphthylidene-one.

When the filtered reaction mixture was allowed to stand a further twenty-four hours a small buff coloured precipitate formed which recrystallised from acetic acid to melt at 270° C. It gave a brown solution with a blue fluorescence in sulphuric acid and did not contain nitrogen. The material was identified as

naphthalic anhydride.

ATTEMPTS TO OBTAIN CONDENSATION UNDER DIFFERENT
CONDITIONS.

(i) Acenaphthenone (0.3g.) was warmed gently over a small flame with benzyl cyanide (5 drops). The mixture was boiled for two minutes and allowed to cool. Crystallisation took place, the product was identified as acenaphthenone.

(ii) Acenaphthenone (0.3g.) was dissolved in absolute ethanol and a mixture of benzyl cyanide (5 drops) and piperidine (two drops) was added. Although the solution turned deep brown in colour no precipitation took place after standing seven months at room temperature.

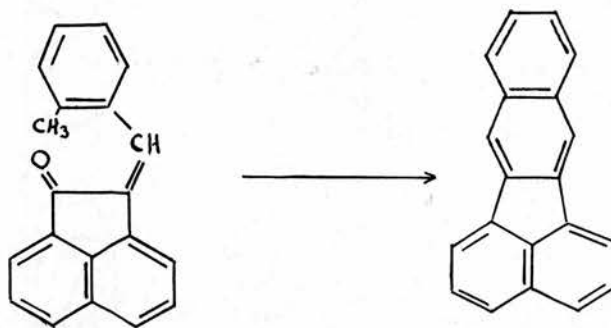
(iii) Acenaphthenone (0.3g.) was boiled gently for two minutes with benzyl cyanide (5 drops) and piperidine (2 drops). From this reaction mixture, biacenaphthylidene-one and acenaphthenone were recovered. As the dimer is insoluble in alcohol the two were readily separated and identified.

(iv) Acenaphthenone (0.3g.) was dissolved in absolute ethanol (15 c.c.) and benzyl cyanide (5 drops) and acetic anhydride (2 drops) were added. After standing for seven months at room temperature a small amount of

naphthalic anhydride was deposited.

(v) When the above (iv) reaction mixture without the alcohol was boiled for two minutes and cooled complete recovery of unchanged acenaphthenone was obtained.

THE ATTEMPTED SYNTHESIS OF 11:12 BENZFLUORANTHENE
FROM σ -TOLUALACENAPHTHENONE.



σ -TOLUALDEHYDE.

σ -Tolualdehyde was prepared by the Bodroux-Tschitschibabin Synthesis as described by Smith and Bayliss, J. Org. Chem. 1941, V1, 440.

The Grignard reagent from σ -bromotoluene (34g.) and magnesium (5g.) in ether was allowed to stand for fifteen hours with an ethereal solution of triethyl orthoformate (29.6g.).

Steam distillation of the mixture followed by fractionation gave σ -tolualdehyde as an almost colourless liquid, B.Pt. 190°-199° C. (Lit. 197° C).

Yield 10g. (42%). A forerun boiling between 180°-190° C. was discarded.

The fraction collected gave a dinitrophenylhydrazone melting at 194° C. (Lit. 193-194° C.)

2-o-Tolualacenaphthenone.

The preparation was similar to that previously described for the preparation of 2 -p-anisalacenaphthenone.

The condensation product crystallises from ethanol in yellow plates. M.Pt. 117° C.

$C_{20}H_{14}O$ required C 88.9% ; H 5.2%
found C 88.9% ; H 5.3%

As with benzal and anisalacenaphthenone the o-tolual compound gives a bright scarlet colour with concentrated sulphuric acid.

o-Tolualacenaphthenone formed a 2:4dinitrophenylhydrazone when warmed with a suspension of 2:4 dinitrophenylhydrazine in alcohol. Recrystallised from acetic acid it melted 250°-251° C. Red needles.

$C_{26}H_{18}O_4N_4$ required N 12.4%
found N 11.9%

ATTEMPTED DEHYDRATION OF 2-o-TOLUALACENAPHTHENONE.

Ref. Rapson and Shuttleworth J.C.S. 1940, 636.

o -Tolualacenaphthenone (0.6g.) was boiled in xylene (15 c.c.) for twenty-four hours with regular additions of small amounts of phosphorus pentoxide. The xylene was cooled and decanted and the residue extracted with two portions (10 c.c.) of benzene. The xylene and the benzene extracts were combined and concentrated and chromatographed on an alumina column (12" x $\frac{3}{4}$ "). On developing with benzene a uniform brown band moved down the column. The eluate was a brown solution which when evaporated gave an oil which did not solidify and which failed to form a picrate in benzene solution.

THE STOBBE CONDENSATION WITH ACENAPHTHENONE.

Acenaphthenone (1g.) was dissolved in diethyl succinate (1.5g.) and tertiary butyl alcohol (15 c.c.). On cooling the solution some of the acenaphthenone separated out. This suspension was added to an almost solid solution of potassium (0.25g.) in ter. butyl alcohol (5 c.c.). After standing overnight in the refrigerator the blood-red mixture was melted in a water bath and the temperature raised to boiling. After heating for half an hour the mixture was cooled and a yellow solid filtered off. The solid when washed with water and dried weighed 0.49 g.. It recrystallised from benzene in bright yellow needles and was identified as biacenaphthylidene-one.

The deep brown filtrate was poured into dilute hydrochloric acid and the reddish brown oil which separated was extracted with ether. The ether layer was washed with dilute caustic soda solution and dried. Evaporation of the ether gave an oil which crystallised on cooling. After recrystallising from ethanol the solid was proved by mixed melting point determination to be acenaphthenone (0.21g.)

When sodium methoxide was used as the condensing agent acenaphthenone and the dimer were again recovered from the reaction mixture.

SECTION B (iv).

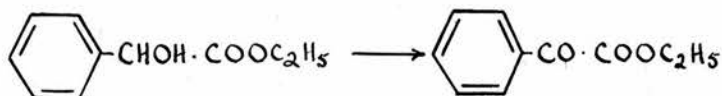
ETHYL MANDELATE.

Mandelic acid was esterified using the general method of Fischer and Speier. Ber. 1895, 28, 3254.

From 100g. of the acid, 83g. (70%) of ethyl mandelate were obtained, boiling 145° - 147° C. at 13 mm. pressure.

ETHYL BENZOYLFORMATE.

Ref. Astin, Moulds and Riley, J.C.S. 1935, 903.



Small scale preliminary experiments indicated that the yield of formic ester was improved if the selenium dioxide employed in the oxidation had previously been sublimed.



The sublimation was smoothly and efficiently carried out by heating in a porcelain basin under two inverted filter funnels. A plug of glass wool between the shoulders of the two funnels prevented any direct

losses due to convection currents.

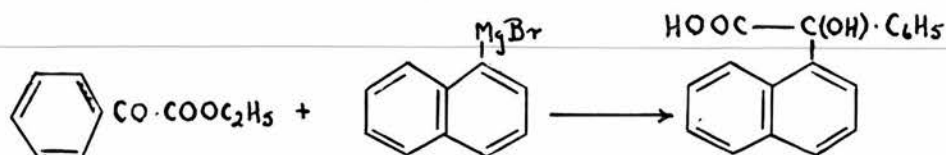
Ethyl mandelate (100g.) and sublimed selenium dioxide (24g.) were heated together with a reflux condenser for two and a half hours at 160°C. The amber liquid was decanted and distilled in vacuum. The fraction distilling between 140° C. and 155° C. at 11 mm. pressure, was collected as a refractile lemon-green oil. The distillate was shaken with sodium metabisulphite solution (60-70g. bisulphite in 100 c.c. water) and the pearly-white addition compound filtered off, washed with a little bisulphite solution and then with ether. The bisulphite compound was decomposed on a hot water bath (70° C.) with dilute sulphuric acid (50 c.c.; 20%) and benzene (200 c.c.) for half an hour.

Fractionation of the resulting liquid product gave ethyl benzoylformate boiling at 148° C. at 13 mm. Yield 38g. (38%).

Phenyl-1-naphthylglycollic acid.

Ref. McKenzie and Tattersall,

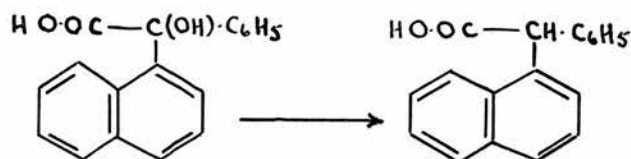
J.E.S. 1925, 127, 2525.



By following the method of McKenzie and Tattersall

80g. of benzoylformic ester were converted to 60g. (48%) of anhydrous phenyl-1-naphthylglycollic acid crystallising from benzene in colourless prisms. M.Pt. 146° - 147° C. (Lit. 147° C.)

Phenyl-1-naphthylacetic acid.



Ref. McKenzie and Tattersall,

J.C.S. 1925, 127, 2527.

Phenyl-1-naphthylglycollic acid was reduced with concentrated hydriodic acid solution (S.G. 1.94) and red phosphorus.

Some difficulty was experienced in obtaining an iodine-free product. A satisfactory answer to this problem was obtained by crushing the crude phenyl-naphthylacetic acid with a strong solution of potassium iodide followed by charcoal treatment and recrystallisation from aqueous acetic acid (70%). A final recrystallisation from aqueous methylated spirits (70%) gave a colourless crystalline product. M.Pt. 139° - 140° C. (Lit. 140° - 141° C.)

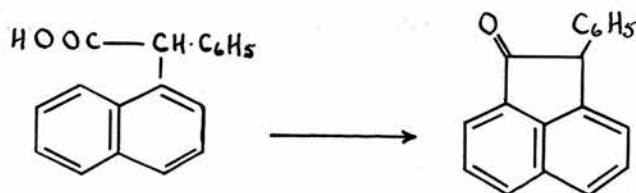
39g. of phenyl-naphthylglycollic acid gave 30g.

(82%) of phenyl-naphthylacetic acid.

2-PHENYLACENAPHTHENONE-1.

Ref. Koelsch and Richter,

J.A.C.S. 1937, 59, 2165.



A solution of phenyl-1-naphthylacetic acid (22g.) in dry benzene (220 c.c.) was treated with phosphorus pentachloride (18g.) added cautiously in small portions. The mixture was then boiled until the evolution of hydrogen chloride ceased (approx. 1 hour.).

Freshly powdered aluminium chloride (12.5g.) was slowly added. After standing overnight the mixture was heated under reflux for an hour and decomposed by pouring into ice-cold concentrated hydrochloric acid. The benzene layer was separated, washed with sodium bicarbonate solution and the benzene removed by steam distillation.

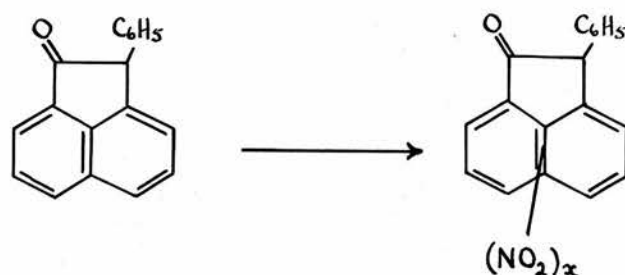
The residual oil was distilled under vacuum and a thick orange syrup was collected between 190°C . and 200°C . while the pressure was approximately 1 millimetre. Yield 10.12g.

Trituration of the syrup with methanol gave a cream

coloured solid which was filtered off and recrystallised from methanol. M.Pt. 107° - 112° C. Several recrystallisations were found to be necessary to bring the melting point up to the literature value of 115° C. Yield of purified ketone = 6.1g. (30%), white prisms. M.Pt. 115° C. (Lit. 115.5° - 116.5°).

An acetone solution of the product when treated with dilute caustic soda gave a brilliant purple colouration.

THE ATTEMPTED NITRATION OF 2-PHENYLACENAPHTHENONE-1
IN SULPHURIC ACID SOLUTION.



2-Phenylacenaphthenone-1 (0.5g.) was dissolved in concentrated sulphuric acid (2 c.c.; S.G. 1.84) and the solution cooled in ice. A mixture of fuming nitric acid (0.02 c.c.; S.G. 1.51) and concentrated sulphuric acid (2 c.c.) was dropped in with stirring, the agitation being maintained for a period of two hours. After this time the solution was poured onto ice and a reddish-brown precipitate was filtered off, washed with water and air dried at 80° C. It gave a strongly positive Lassaigne test for nitrogen. Weight of crude product 0.65g.; decomposing above 170° C. with frothing.

(Theoretical weight of product for mono-nitro derivative
= 0.6g.)

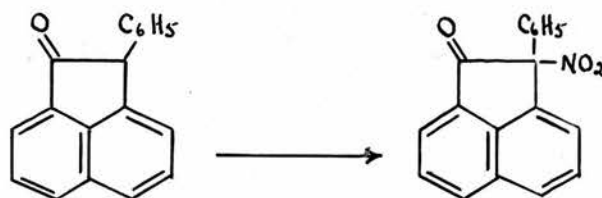
The product was insoluble in petroleum ether,
almost insoluble in alcohol and slightly soluble in
benzene. In the presence of acetic acid the product
seemed to consist of two components, one readily
soluble and the other almost completely insoluble
regardless of the amount of acetic acid used.

All attempts to recrystallise the material
failed.

A hot benzene extract when cooled and chromatographed
on alumina formed two contiguous bands, one deep red
and the other brown, which became strongly adsorbed at
the top of the column.

Extraction of the bands with hot alcohol failed
to give any appreciable amount of material.

THE NITRATION OF 2-PHENYLACENAPHTHENONE-1 IN
ACETIC ACID SOLUTION.



2-phenylacenaphthenone-1 (2g.) was dissolved in
glacial acetic acid (20 c.c.) and stirred vigorously
while kept in a water bath at 80° C. Fuming nitric

acid (0.3 c.c. ; S.G. 1.51) was dropped in and the vigorous stirring continued. After half-an-hour a further addition (0.3 c.c.) of nitric acid was made, stirring continued for thirty minutes and the whole poured into cold water. A semi-solid mass was precipitated and extracted with chloroform. The chloroform extract was washed with a little sodium bicarbonate solution and dried over anhydrous sodium sulphate. Removal of the solvent gave a brown oil which rapidly solidified when triturated with methanol. The crude product was filtered off and found to weigh 1.42 g. (60% of the theoretical yield of a mono-nitro derivative). M.Pt. of crude product 105° - 112° C. After several recrystallisations from methanol, 0.9g. (38% theoretical yield) of material was obtained as white needles melting sharply at 117° C.

The product was very soluble in acetic acid and also dissolved in boiling 100° - 120° C. petroleum ether.

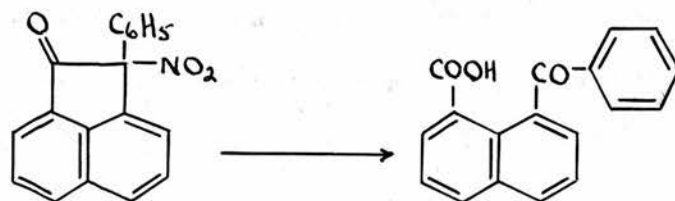
$C_{18}H_{11}O_3N$ requires C 74.7% ; H 3.8% ; N 4.8%
found C 74.8% ; H 4.4% ; N 5.1%

An acetone solution of the product treated with dilute caustic soda gave no colour reaction.

The product gave a brilliant, deep green colour with concentrated sulphuric acid.

An increase in the reaction time resulted in a product which was of a more oily nature than the above and consequently more difficult to purify.

THE ATTEMPTED OXIDATION OF
2-PHENYL-2'-NITROACENAPHTHENONE-1 USING CHROMIUM
TRIOXIDE.



The nitro compound (0.45g.), chromium trioxide (A.R., 1.0g.) and glacial acetic acid (4 c.c.) were heated together in a water bath at 80° C for half-an-hour. The mixture was poured into water and the aqueous solution reduced in volume to 3-4 c.c. by distilling under reduced pressure.

Concentrated hydrochloric acid was added to the residue and an extraction made with ether. The extract was shaken with concentrated sodium carbonate solution and the two layers separated. The ethereal solution, on evaporation, yielded a small amount of a brown solid, M.Pt. (micro) 105° - 109° C.; it gave a green colouration with concentrated sulphuric acid and was starting material in an impure form.

The sodium carbonate solution was acidified with concentrated hydrochloric acid, the latter producing an intense white turbidity with a brownish-white scum floating on the surface of the solution. The whole was shaken up with ether, the extract washed with water and dried over anhydrous sodium sulphate. A small

quantity of an oily solid melting below 80° C., remained after the ether had been allowed to evaporate off at room temperature. It gave an orange-brown colouration with concentrated sulphuric acid but the Lassaigne test failed to reveal the presence of nitrogen.

Chromic anhydride was thus too severe in its oxidising action and a milder reagent was sought.

THE OXIDATION OF 2-PHENYL-2'-NITROACENAPHTHENONE-1
WITH SODIUM DICHROMATE.

The nitro compound (1 g.), glacial acetic acid (20 c.c.) and sodium dichromate (7 g.) were heated together over a small flame for one hour. Approximately 11 c.c. of the acetic acid were removed by distillation under reduced pressure and the residue was poured into water. To allow the precipitate to settle out fully, the mixture was set aside for three hours.

The solid material was filtered off and the filtrate extracted with chloroform. The filtered solid was dissolved in the chloroform extract and shaken up with sodium carbonate solution. The two layers were separated.

The chloroform extract gave, on evaporation, a trace of an oil which dissolved in concentrated sulphuric acid to give an orange solution rapidly turning to brown.

The sodium carbonate extract when acidified with

concentrated hydrochloric acid gave a precipitate which was extracted from the acid solution with chloroform. The latter was dried over sodium sulphate and furnished, on evaporation, an oil which solidified rapidly when triturated with methanol. 420 mg. of a white product were filtered off. Recrystallisation from methylated spirits gave white needles, M.Pt. 108° - 109° C.

$C_{18}H_{11}O_5N$ requires C 67.3% ; H 3.5% ; N 4.4%
found C 75.0% ; H 4.7% ; N 2.2%

The product dissolved in cold, concentrated sulphuric acid to give a bright, orange solution; no colour was observed on treating an acetone solution of the product with dilute caustic soda solution.

THE ESTERIFICATION OF THE OXIDATION PRODUCT OF
2-PHENYL-2'-NITROACENAPHTHENE-1.

The general method for the preparation of esters described by E. Fischer and A. Speier, Ber. 1895, 28, 3254, was employed.

The acid (240 mg.) was dissolved in a mixture of absolute ethanol (400 mg.) and concentrated sulphuric acid (0.02 c.c.; S.G. 1.84), the solution being boiled under reflux for five hours. On pouring into water, a white, sticky solid precipitated. The latter was extracted with benzene and the extract washed with dilute sodium bicarbonate solution, water and finally dried

over anhydrous sodium sulphate. Evaporation of the solvent left an oil which solidified instantly on trituration with methanol to give a white solid, M.Pt. 114° - 117° C.; Yield 160 mg.

The product was dissolved in benzene and chromatographed on a short column ($5'' \times \frac{1}{2}''$) of aluminium oxide. In daylight no banding was observed but in ultra-violet light a region of bright blue fluorescence was observed to be moving down the column while a thin, yellow-green band remained firmly adsorbed at the top.

The descending band was collected and evaporated. A white solid remained and on recrystallisation from methanol short, white prisms were obtained. M.Pt. 167° - 168° C.

$C_{20}H_{15}O_5N$ requires N 4.0%

found no nitrogen present.

An authentic sample of ethyl-8-benzoyl-1-naphthoate was prepared by the oxidation of 2-phenylacenaphthenone with sodium dichromate and acetic acid and esterification of the 8-benzoyl-1-naphthoic acid produced using the above adaptation of the Fischer-Speier method. The ester was obtained in an impure form melting 124° - 128° C. (Lit. 164° - 166° C.) Purification was carried out by chromatographing a benzene solution of the ester on a ($6'' \times \frac{1}{2}''$) column of alumina. As before, a band with a bright blue fluorescence in ultra-violet light was observed moving down the column and was

collected. Recrystallisation from methanol gave white prisms. M.Pt. 167° C.

When mixed with the esterified oxidation product some softening around 160° C. was observed, but no depression in melting point took place.

Oxidation of the mononitrophenylacenaphthenone therefore gave 8-benzoyl-1-naphthoic acid as one of the products.

SUMMARY.

SECTION A.

Acenaphthenone does not condense with benzalacetone in the presence of an alkaline condensing agent. The apparent lack of reactivity is possibly due to the preferential formation of biacenaphthylidene-one.

SECTION B. (1).

Attempts to achieve an unsymmetrical degradation of the acenaphthenone molecule by a variety of methods met with little success. It had been intended to apply such methods as proved successful to the orientation of a nitro substituted acenaphthenone.

Of the different schemes examined, the most promising was the degradation of pyridylnitroacenaphthylene acetate to the corresponding pyridylnitronaphthyl ketone. Lack of a suitable means of synthesising this compound prevented the orientation from being completed.

When shaken in a hydrogenator with a platinum catalyst nitroacenaphthenone was reduced, but an attempt to convert the amine by means of a Sandmeyer reaction to 5-bromoacenaphthenone was unsuccessful.

The Schmidt reaction on acenaphthenone appears to form acenaphthenone-anil

SECTION B (ii).

By comparing the colour reaction given by the nitro-substituted acenaphthenone with those given by a series of similar compounds support was obtained for the view that substitution had taken place in the 5- position.

SECTION B (iii).

Attempts to prepare 6-nitroacenaphthenone by the osmium tetroxide-hydrogen peroxide oxidation of anisal-6-nitroacenaphthene did not furnish the ketone but a comparatively small amount of a compound considered to be p-methoxyphenyl-1-(6-nitroacenaphthylene) carbinol). The same product was obtained when the osmic ester-pyridine complex of anisal-6-nitroacenaphthene was hydrolysed with a mildly alkaline solution of mannitol.

SECTION B (iv).

Finally the nitration of 2-phenylacenaphthenone gave 2 phenyl-2'-nitroacenaphthenone-1 and not the expected product analogous to nitroacenaphthenone.

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POSTSCRIPT

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