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The formation of phenanthridines, and other heterocyclic compounds, by the reaction of hydrazoic acid with cyclic compounds. The mechanism of such reactions.

being a thesis submitted to the University of London for the degree of Doctor of Philosophy in the Faculty of Science

by

Maurice Martin Coombs, B.Sc. (Lond.)

The work described in this Thesis was carried out in the laboratories of the Chemistry Department, Battersea Polytechnic, under the supervision of Dr. C. L. Arcus.

The writer wishes to express his sincere appreciation of the kindly help and encouragement received from Dr. C. L. Arcus, and to Dr. F. R. Goss and Mr. W. H. Gray, M.Sc., for their interest in the work.
The formation of phenanthridines, and other heterocyclic compounds, by the action of hydrazoic acid on cyclic compounds. The mechanism of such reactions.

Abstract of the Thesis

Eleven fluoren-9-ols, monosubstituted at positions 2, 3, or 9, have been submitted to reaction with hydrazoic acid in the presence of sulphuric acid, and the following have been obtained: 2-, 3-, 6-, and 7-nitro-, 7-amino-, 2- and 7-methoxy-, 2-, 3-, 7-, and 9-methyl, 9-phenyl, and 9-benzylphenanthridines. The last is also obtained by the action of hydrazoic and sulphuric acids upon 2-benzylidenefluorene. The pairs of isomeric phenanthridines from the unsymmetrically substituted fluorenols have been separated and the product ratios have been determined. It is found that the ratio of 2- and 7-methoxyphenanthridines from the reaction with 2-methoxyfluorene-9-ol is the same as that from the acid catalysed decomposition of 9-azo-2-methoxyfluorene. It is demonstrated that the above results support a reaction mechanism in which the carbonium ion derived from the fluorenol adds hydrazoic acid to form the protonated azide which undergoes intramolecular rearrangement,
the ease of migration of the substituted and unsubstituted rings being directly related to their capacity for electron release at the migration origin. Reactions of phenanthridine 6- and 7- dissonium sulphates, and of 7-hydroxyphenanthridine are reported, and new syntheses of 2- and 3-nitrophenanthridines and 2:7-dinitrophenanthridine have been carried out.

The Schmidt reaction with three unsymmetrically substituted fluorenones has been investigated. The literature of the Schmidt reaction with ketones has been surveyed critically, and a new proposal concerning the observed "geometrical effect" has been made.

The Schmidt reaction with 3-p-toluoylbenzoic acid has been found to yield 6-oxo-2-p-tolyl-4:5-benz-1:3-oxazine; the mechanism of this reaction is discussed.
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The Nature of the Schmidt Reaction.

The reaction between equimolecular quantities of carbonyl compounds and hydrazoic acid in the presence of strong acids is known as the Schmidt reaction. It is most familiar to organic chemists as a useful method for the preparation of primary amines, according to the equation

\[ \text{R-COH} + \text{HN}_3 = \text{R-NH}_2 + \text{CO}_2 + \text{N}_2. \]

It therefore offers an additional, and alternative, route to the Hofmann and Curtius degradations of carboxylic acids to amines having one less carbon atom, and it is more convenient than these older methods since it is a one-step reaction. The Schmidt reaction with ketones affords amides

\[ \text{R-CO-R} + \text{HN}_3 = \text{R-CO-NH-R} + \text{N}_2, \]

while aldehydes yield a mixture of the corresponding nitrile and formamide

\[ \text{R-CHO} + \text{HN}_3 \longrightarrow \text{R-CH} + \text{R-NH-CHO}. \]

With an excess of hydrazoic acid, aldehydes and ketones also
give 1:5-substituted tetraenes

\[ R\cdot CO\cdot R + 2\text{H}_2\text{N}_3 = R\cdot C\cdash N\cdot R + \text{N}_2 + H_2O \]

and tetraenes are also formed by the action of hydrazoic acid on several other classes of compounds, such as nitriles, and oximes. However, these reactions are not Schmidt reactions and they will not be considered here. Very similar to the Schmidt reaction with ketones is the formation of ketamines by the interaction of hydrazoic acid and certain olefines in the presence of strong acids (Ger. Pat., 563, 565),

\[ R_2C=CHR + \text{N}_3 = R_2C=N\cdot CH_2R + \text{N}_2 \]
The Mechanism of the Schmidt Reaction

In 1923 K. F. Schmidt (Asta Acad. Abcensia, math.
at phys., 1924, 2, 36 p.p.; Chem. Ab., 1925, 14, 3248; Ber.,
1924, 57, 704), in a study of the decomposition of hydrazinic acid, found that aniline was the main product when a solution of the acid in benzene was allowed to decompose at 60-70°C in contact with concentrated sulphuric acid. At room temperature the decomposition was slow and the main products were hydrazine and hydroxylamine; when, however, benzophenone was added, a vigorous reaction ensued with the formation of benzanilide in almost theoretical yield. To account for these results Schmidt postulated the cleavage of the $\text{HN}_3$ molecule by sulphuric acid to give the imine radical $[\text{NH}]$

$$\text{HN}_3 = [\text{NH}] + \text{H}_2$$

this radical was then supposed to react as follows

$$[\text{NH}] + \text{C}_6\text{H}_6 = \text{C}_6\text{H}_5\cdot\text{NH}_2$$

$$[\text{NH}] + \text{H}_2\text{O} = \text{NH}_2\cdot\text{OH}$$

$$4[\text{NH}] \rightarrow 2[\text{NH}_2\cdot\text{NH}] \rightarrow \text{NH}_2\cdot\text{NH}_2 + \text{H}_2$$

With benzophenone, Schmidt assumed that the imine radical added on to the carbonyl group, giving an oxime which then
underwent Beckmann rearrangement:

\[
\text{Ph}_2\text{C}=\text{O} + [\text{HN}] \rightarrow \text{Ph}_2\text{C}=\text{N} \cdot \text{OH} \rightarrow \text{Ph} \cdot \text{CO} \cdot \text{NH} \cdot \text{Ph}
\]

Subsequent work has confirmed the existence of the imine radical. Thus Tolmachev (J. Phys. Chem. U. S. S. R., 1940, 14, 615) has identified bands due to the \( \text{NH} \) radical in the spectrum of exploding hydrazoic acid, and Gleu (Ber., 1928, 61, 702) has demonstrated the formation of hydrazylamine when aqueous hydrazoic acid is irradiated with ultra-violet light. Keller and Smith (J. Amer. Chem. Soc., 1944, 66, 1122) found that the same products were formed on amination of aromatic nuclei with hydrazoic acid and by hydrazylamine-\( \text{O} \)-sulphonic acid, and they pointed out that these observations are best explained by the assumption of the intermediate formation of \([\text{NH}]\) or \([\text{NH}_2]^+\) radicals. On the other hand, many carbonyl compounds give oximes by the action of hydrazylamine-\( \text{O} \)-sulphonic acid, whereas with hydrazoic acid they yield amides. Moreover \( \alpha \)-hydrazonone oxime is stable to concentrated sulphuric acid at 100\(^\circ\) (Kipping, J. Chem. Soc., 1904, 65, 480), whilst the ketone is converted into hydrocarbostyril by the Schmidt reaction at 40\(^\circ\) (Briggs and deeth, J. Chem. Soc., 1937, 456). Keller and Smith (loc. cit.) have demonstrated that hydrazylamine-\( \text{O} \)-
sulphonic acid is not an intermediate in the Schmidt reaction, as suggested by Sanford, Blair, Arroyo, and Short (J. Amer. Chem. Soc. 1945, 67, 1641), for this compound does not react with ketones under conditions under which they are converted into amides by hydrazoic acid. Kollar and Smith also pointed out that while amination of aromatic nuclei proceeds only under conditions under which hydrazoic acid is known to be actively decomposing, the Schmidt reaction with ketones is vigorous even at 0°. It is therefore considered that the mechanisms of these two reactions are different.

As early as 1935 it was suggested by Oliveri-Mandala (Cass. chim. ital., 1925, 55, I, 271) that the first step in the Schmidt reaction with ketones was the addition of a molecule of hydrazoic acid (as opposed to an imine radical) to the carbonyl group, followed by the breakdown of the resultant azide

\[
\text{R}_2\text{C} = \text{O} + \text{HN}_3 \rightarrow \text{R}_2\text{C} \xrightarrow{\text{OH}} \text{R} \cdot \text{CO} \cdot \text{NH} \cdot \text{R} + \text{N}_2
\]

This idea was accepted by Hard (Gilman's "Organic Chemistry", John Wiley and Sons, New York, 1932, Vol. I, p. 699) who considered that the first step was the "activation" of the carbonyl compound and of the hydrazoic acid by the strongly
polar sulphuric acid. The activated molecules then combine to give the proton adduct of an amide, which, by loss of a molecule of nitrogen, gives an intermediate having a sextet of electrons. The final step is the Beckmann-type rearrangement of this intermediate to yield an amide:

When \( R = \text{OH} \) (i.e., a carboxylic acid), a carboxylic acid is formed which spontaneously loses carbon dioxide to yield a primary amine.

With the modifications discussed below this is essentially the mechanism accepted for the reaction today. It was pointed out by Newman and Gildenhorn (J. Amer. Chem. Soc., 1940, 72, 317) that the "activated" form of hydrosol acid postulated by Hard is merely one of the contributing resonance
structures and does not depend on a strongly polar environment for its existence. Ionisation of the carbonyl group occurs by the addition of a proton to the oxygen atom at the negative end of the permanent C=O dipole

\[ R_2C=O + H^+ \rightarrow R_2C^+OH \]

(see Hamnett, "Physical Organic Chemistry", McGraw-Hill Book Co., New York, 1940, p. 46), and they wrote for the Schmidt reaction with ketones

\[
\begin{align*}
\text{R'}-\text{C}^+ & \quad + \quad \text{H}-\text{N}=\text{N} \\
\text{R} & \quad \text{H} & \quad \rightarrow \\
\text{R'}-\text{C}=\text{N}=\text{N} & \quad + \\
\text{R} & \quad \text{H} & \quad \rightarrow & \quad \text{H'}-\text{C}=\text{N}=\text{R} \\
& \quad + \\
& \quad \text{H} & \quad \rightarrow \\
& \quad \text{R'}\cdot\text{CO}\cdot\text{NH}\cdot\text{R} & \quad + & \quad \text{H}^+ \\
\end{align*}
\]

They pointed out that if this mechanism is correct it is to be expected that in an unsymmetrical ketone the migratory aptitudes of the various groups during the Schmidt reaction would show some similarity to the migratory aptitudes of these groups in the pinacol rearrangement, the mechanism of which is very similar.
In general, carboxylic acids dissolve in sulphuric acid to give solutions with van't Hoff factors of 3, owing to ionisation according to the equation

\[ R\text{-CO(OH)} + H_2SO_4 \rightarrow R\text{-CO(OH)}_2^+ + HS_2O_6^- \]

The existence of a second type of ionisation was illustrated by the work of Troffors and Hammett (*J. Amer. Chem. Soc.*, 1937, **59**, 1759) with mesitoic acid. They found that a solution of this acid in sulphuric acid has a fourfold depression of the freezing-point, and on dilution with methanol affords methyl mesitoate. They interpreted these observations by the ionisation scheme

\[ (\text{CH}_3)_3\text{C}_6\text{H}_2\text{COOH} + 2H_2SO_4 = (\text{CH}_3)_3\text{C}_6\text{H}_2\text{CO} + H_2O + 2HSO_4^- \]

and this has been confirmed by Newman and Dono (*J. Amer. Chem. Soc.*, 1951, **73**, 3651) for certain other acids. Since mesitoic acid undergoes the Schmidt reaction readily at 0° whereas benzoic acid (which has an 1 factor of 2 in cold sulphuric acid) does not react below 40°, Newman and Gildenhorn (loc. cit.) concluded that only carbonium ions of the second type take part in the reaction, which they wrote as
The higher temperature required by benzoic acid and most carboxylic acids was considered to be due to the necessity for the occurrence of the second type of ionisation:

\[
\text{R-}\text{CO(OH)}^- + \text{H}^+ \rightarrow \text{R-}\text{CO(OH)}_{2}^+ + \text{H}^+ \rightarrow \text{R-}\text{CO}^+ + \text{H}_2\text{O}^+
\]

Evidence supporting this idea is their discovery that the decomposition of acyl azides (the Curtius reaction) is acid-catalysed: for the protonated azide (II), but not (III), may reasonably be postulated to be an intermediate in this reaction as well as in the Schmidt reaction

\[
\begin{align*}
\text{R-}\text{C-NH-N=NH}^- + \text{H}^+ \rightarrow \text{R-NH}_3^+ + \text{CO}_2
\end{align*}
\]

Simultaneously with the publication of these mechanisms, Smith (J. Amer. Chem. Soc., 1948, 70, 320) put
forward a similar mechanism for ketones, in which the protonated
amide (I) loses a molecule of water to give an oxime-like
structure (IV), which then undergoes rearrangement analogous
to the Beckmann rearrangement:

\[
\begin{align*}
R'-O^+ + :N-H-N=H &\rightarrow R'-C-NH-N=H &\rightarrow R'-C-R' + H_2O \\
\begin{array}{c}
\text{(I)} \\
\text{(IV)}
\end{array}
\end{align*}
\]

This mechanism differs from Newman and Gildenborn's in one
important respect. Since, with unsymmetrical ketones, the
intermediate (IV) could exist as two geometrical isomers, in
which the \(-N=H\) group is \textit{syn}- and \textit{anti}- to the group \(R\) (say),
then there should be a geometrical effect influencing the
migratory aptitudes of the groups during the rearrangement.
Presumably, by analogy with the Beckmann rearrangement, there
is \textit{trans}- migration in (IV).

McBreen and his coworkers have thrown considerable
light on the general question of the mechanism of the Schmidt
reaction. It was shown by Maclean, Gilliland, and Sparr (J. Amer. Chem. Soc., 1950, 72, 3812) that the reaction of 1:1-diphenylethylene with hydrochloric acid in the presence of sulphuric acid led to the formation of aniline and acetophenone. To account for these results the following mechanism, closely analogous to that of Newman and Gildenhorn for ketones, was proposed:

\[
\begin{align*}
\text{Ph} & \quad \text{C} = \text{CH}_2 \quad + \quad \text{H}^+ \quad \rightarrow \quad \text{Ph} \quad \text{C} = \text{CH}_3 \\
\text{Ph} & \quad \text{C} = \text{CH}_2 \quad + \quad \text{HN}^+ \text{N} = \text{N} \quad \rightarrow \quad \text{Ph} \quad \text{C} - \text{NH} - \text{N} = \text{N} \\
& \quad \text{Ph} \quad \text{C} = \text{CH}_2 \quad + \quad \text{H}_{2}\text{O} \quad \rightarrow \quad \text{Ph} \cdot \text{CO} \cdot \text{CH}_3 \quad + \quad \text{PhNH}_3^+ 
\end{align*}
\]

With unsymmetrical diarylethylenes there will result a mixture of products depending on the relative rates of migration of Ar and of Ar' to N

\[
\begin{align*}
\text{Ar'} & \quad \text{C} = \text{CH}_2 \quad \rightarrow \quad \text{Ar'} \cdot \text{CO} \cdot \text{CH}_3 \quad \text{and} \quad \text{Ar} \cdot \text{CO} \cdot \text{CH}_3 \\
\text{Ar} & \quad \text{C} = \text{CH}_2 \quad \rightarrow \quad + \quad \text{Ar} \cdot \text{NH}_3^+ \quad + \quad \text{Ar'} \cdot \text{NH}_3^+ 
\end{align*}
\]
In an extension of this work Meisen and Mehta (J. Amer. Chem. Soc., 1952, 74, 526) showed that with nine such diarylethlenes (in which Ar is phenyl, and Ar' is m- or p-substituted phenyl) that migration proceeds quantitatively as predicted by the electronic character of the substituents in the migrant groups by Hammett's σ values.

Hammett (op. cit., p.p. 184-199) has demonstrated that for many "side-chain reactions" of the type

\[ \text{m- or p-} \text{C}_6\text{H}_4 \ldots \text{A} + \text{B} \rightarrow \text{m- or p-} \text{C}_6\text{H}_4 \ldots \text{B} + \text{A} \]

and also for aromatic substitution, that the following simple expression is valid:

\[ \log \left( \frac{k}{k_0} \right) = \rho \sigma \]

where \( k \) is the rate constant or equilibrium constant of the reaction with the substituted compound;

\( k_0 \) is that with the unsubstituted compound;

\( \rho \) is a constant for the actual reaction

and \( \sigma \) is a constant for the substituent, \( X \).

This relationship applies only to reactions, the rates or equilibria of which are altered by the variation of the substituent, \( X \), in the m- or p-positions in a benzene ring.
No such simple correlation is observed with ρ-substituted systems or with aliphatic compounds; Hammett considers that in these cases reaction is accompanied by considerable changes in the kinetic energy of rotation and vibration in the molecule, in addition to changes in potential energy due primarily to the interaction of electrostatic charges. With m- and p-substituted benzene derivatives however, the rigidity of the ring and the remoteness of the substituents influencing the seat of reaction render changes in the kinetic energy terms unimportant, and the problem is reduced to one of comparing the potential energy terms for the reactants and products. Hence the physical significance of the substituent constant, σ', is that it is a measure of the influence of the substituent on the relative change in potential energy for a series of reactants; this is related to the electron availability influenced by the substituent, at the site of reaction. When there is no substituent, σ is unity; when the substituent has a positive σ value electrons are less available at the reaction centre than in the unsubstituted compound, and vice versa. The interpretation of the reaction constant, ρ, is that it measures the susceptibility of the reaction in question to changes in electron density. For purposes of comparison an arbitrary
standard must be adopted. By convention the accurately and extensively investigated "side-chain reaction", the dissociation of substituted benzoic acids, is chosen and ρ is arbitrarily assigned the value unity, when, if log (k/k₀) is plotted against σ the slope of the straight line is 45°. Incidentally, for this reaction log (k/k₀) = σ, and this offers the most direct way of calculating the value for σ for any given substituent if the ionisation constant for the correspondingly substituted benzoic acid is accurately known. If, for any reaction, log (k/k₀) is plotted against Hammett's σ values and a straight line is produced, then it follows that the reaction rate or equilibrium is dependent on the electronic character of the substituent groups, and further, that the extent of this dependence is indicated by the slope of the line, a steep slope implying marked dependence. A negative value of ρ shows that an increase in electron availability promotes the reaction in question. If the points are scattered, the implication is that simple dependence of this type is not a preponderating factor, and steric effects giving rise to large changes in the kinetic energy of the products are of importance.

For rearrangements of the type examined by McBean and Mehta (log. cit.) the ratio of the rates of migration is
obviously the same as the ratio in which the two sets of products are formed. Moreover, the fraction to which the unsubstituted ring migrates is equivalent to $k_0$ in the above reasoning. Hence Hammett's equation may be written as

$$\log \text{(product ratio)} = \rho \sigma$$

When McEwen and Mehta plotted the logarithms of their product ratios against Hammett's $\sigma$ values for the substituents in Ar, the linear relation

$$\log \text{(product ratio)} = -2.11 \sigma + 0.293$$

was found to hold with an average accuracy of $\pm 1\%$. The small intercept was considered to be due to some "systematic error" in the product ratios. It is reasonable to assume that the rate of evolution of nitrogen is directly proportional to the rate of migration of the aryl group in the Schmidt reaction with carboxylic acids. For a series of eleven substituted benzoic acids examined by Briggs and Lyttleton (J. Chem. Soc., 1948, 421), McEwen and Mehta plotted the ratio of the time for evolution of half the nitrogen with the substituted acid to that of benzoic acid itself against the corresponding Hammett $\sigma$ value. Again a good straight line resulted having a slope
\( \rho = -1.97 \), very similar to that for the reaction of unsymmetrical diaryl olefins with hydrazoic and sulphuric acids.

This is clear and conclusive proof that in both cases:

(i) the rates of migration are almost entirely dependent on the electron density at the point of attachment of the migrating group, and are favoured by a high electron density at this point, and (ii) that the rate-controlling step is the migration of the aryl group with the simultaneous loss of a molecule of nitrogen.

Inspection of the protonated azides (II, p. 9; V, p. 11) postulated as intermediates in these reactions shows at once that an oxime-like structure (IV, p. 10), suggested by Smith (loc. cit.) as an intermediate in the Schmidt reaction with ketones, is impossible in these cases simply because the necessary components for dehydration are not present in these systems. Also the work of McEwen and Mehta indicates very clearly that the reactions with carboxylic acids and olefins closely follow the mechanism proposed by Newman and Gildenhorn (loc. cit.) for ketones, and constitutes indirect evidence for the latter. The mechanism proposed by Smith therefore appears at first sight both arbitrary and unlikely, and it is therefore surprising to find that there is published work which supports Smith's view.
In a study of the Schmidt reaction with a series of seven p-substituted and p-p'-disubstituted benzenophenones which can, potentially, yield the two amides:

\[
\begin{align*}
R \text{C}_6\text{H}_4\text{C} & \rightarrow R \text{C}_6\text{H}_4\text{NH} \quad + \quad R \text{C}_6\text{H}_4\text{NH} \text{C} \\
\end{align*}
\]

(Smith and Howitz, J. Amer. Chem. Soc., 1950, 72, 3718; Smith and Ashby, ibid., p. 2503), the ratio of the two amides obtained was approximately 1:1 in all cases, including the extreme case, p-nitro-p'-methoxybenzenophene, in which migration of the methoxyphenyl group should be highly favoured if electronic effects are important. From these results Smith concluded that for ketones electronic effects are of little account in determining the migratory aptitudes and that a geometrical effect operates in the course of the reaction. For, since the substituents are in the p-position in the benzene rings, the latter are, from a steric point of view, practically equivalent, and the two doubly-bonded structures:

\[
\begin{align*}
\text{R-C}_6\text{H}_4\text{C} &= \text{C}_6\text{H}_4\text{R}' \\
\text{N} = \text{H} \\
\text{R'} &= \text{N} \quad \text{or} \quad \text{H} \\
\end{align*}
\]
are almost equally likely. If trans migration occurs in both cases, then an almost equal quantity of the two amides would result. In the series of alkylphenyl ketones, Ph·CO·R, the percentages of the amide Ph·CO·NH·R (from the migration of the alkyl group) in admixture with the isomer Ph·NH·CO·R were, when 
\[ R = \text{Me}, \text{5} ; \text{Et}, \text{15} ; \text{iso-Pr}, \text{49} ; \text{and tert.-Bu}, \text{100}\% . \]
The reason for this was considered to be that the -Ph group will tend to assume a configuration anti- to the alkyl group to an increasing extent in this series from methyl to tert.-butyl because of the increasing size of the alkyl groups in this order. A study of the Schmidt reaction with 2-substituted-cyclo-
heptanones and -pentanones by Schechter and Kirk (J. Amer. Chem. Soc., 1951, 73, 3067) corroborates Smith's idea. These authors found that in these cyclic ketones migration of the substituted carbon atom always occurs whether the substituent be electron releasing or electron withdrawing, as shown in the following diagrammatic abbreviation of their work:

![Diagram](attachment:diagram.png)

when \( n = 2 \); \( R = \text{Me, Et, n-Pr, iso-Pr, CB} \)

\( n = 3 \); \( R = \text{Me, Et, n-Pr, CB, NH·CO·Et} \). 
Only with 2-chloro-cyclohexanone was there an indication that the unsubstituted carbon atom migrates preferentially. If Smith's hypothesis, that the $\text{N=N}$ group will assume a configuration anti- to the larger group $R$ in the ketone $R\cdot\text{CO}\cdot R'$, is correct, one would expect that with $\beta$-substituted benzophenones the substituted ring would always migrate preferentially. However, this is not so, as may be seen from Table I which is a summary of the published data concerning this matter.
Table I

\[
\text{Ar-CO-Ph} \rightarrow \text{Ar-CO-NH-Ph} + \text{Ar-NH-CO-Ph}
\]

<table>
<thead>
<tr>
<th>group Ar</th>
<th>% migration of Ar</th>
<th>% migration of Ph</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{2-CH}_3\cdot\text{C}_6\text{H}_4)</td>
<td>12</td>
<td>88</td>
<td>Smith, (<em>J. Amer. Chem. Soc.</em> 1954, 76, 431)</td>
</tr>
<tr>
<td>(\text{2-(COOH)}\cdot\text{C}_6\text{H}_4)</td>
<td>98</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>(\text{2-Cl}\cdot\text{C}_6\text{H}_4)</td>
<td>30 ; 21</td>
<td>70 ; 79</td>
<td></td>
</tr>
<tr>
<td>(\text{2-Br}\cdot\text{C}_6\text{H}_4)</td>
<td>19 ; 17</td>
<td>81 ; 83</td>
<td></td>
</tr>
<tr>
<td>(\text{2-CH}_3\cdot\text{C}_6\text{H}_4)</td>
<td>50</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>(\text{2-NO}_2\cdot\text{C}_6\text{H}_4)</td>
<td>70 ; 98</td>
<td>30 ; 12</td>
<td></td>
</tr>
<tr>
<td>(\text{2-Ph}\cdot\text{C}_6\text{H}_4)</td>
<td>95 ; 70</td>
<td>5 ; 30</td>
<td></td>
</tr>
<tr>
<td>(2:4:6-(\text{CH}_3)_3\cdot\text{C}_6\text{H}_2)</td>
<td>95</td>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>


- **1-phenanthryl** predominates Dice and Smith, (*J. Org. Chem.* 1964, 14, 179)
The two sets of values quoted in certain instances in Table I are due to the use of two independent methods for assessing the ratio of the isomeric amides in the reaction product. The result for o-benzoylbenzoic acid cannot properly appear in this list because it has been shown by Arcus and the writer (J. Chem. Soc., 1953, 3698) that the mechanism of the Schmidt reaction with this compound is not that of a simple ketone (see also p. 108). Table I and the question of the mechanism of the Schmidt reaction with ketones are discussed more fully in connection with the present work on p. 101.
The Reaction of Arylmethanols with Hydroscopic and Sulphuric Acids.

In contrast to aliphatic alcohols which dissolve in sulphuric acid to give alkyl hydrogen sulphates (see Gillespie and Leisteen, Quart. Reviews, 1954, VIII, 47), many di- and tri-arylmethanols dissolve in this acid with the formation of carbonium ions of various degrees of stability. Thus it has long been known that triphenylmethanol gives a stable, yellow, sulphuric acid solution which has a van't Hoff 1 factor of four, ascribed by Newman (J. Amer. Chem. Soc., 1941, 63, 2431) to ionisation according to the equation:

\[
\text{Ph}_3\text{C} \cdot \text{OH} + 2\text{H}_2\text{SO}_4 = \text{Ph}_3\text{C}^+ + \text{H}_3\text{O}^+ + 2\text{H}_2\text{SO}_4^- .
\]

The adsorption spectrum of this solution is very similar to that of the electrically conducting solution of triphenylmethyl chloride in liquid sulphur dioxide. There is also considerable chemical evidence for the existence of the triphenylmethyl carbonium ion: for example, if a solution of triphenylmethanol in sulphuric acid is diluted with water, the alcohol is recovered, whereas addition of the solution to methanol affords the methyl ether:

\[
\text{Ph}_3\text{C}^+ + \text{CH}_3\cdot\text{OH} = \text{Ph}_3\text{C} \cdot \text{OCH}_3 + \text{H}^+ .
\]

It was pointed out by Arens and Wesley (*J. Chem. Soc.*, 1953, 173) that, in view of the carbonium ion mechanisms which have been proposed (above) for the Schmidt reaction, it was probable that arylmethanols would react with hydrazoic acid in the presence of sulphuric acid. These authors investigated the reaction with di- and triphenylmethanols and with fluorenone-9-ol from which were obtained, respectively, the following products:— aniline, benzaldehyde, and diphenylmethyl aside; triphenylmethyl aside; and phenanthridine and 9-acidofluorene. In order to account for these results they proposed the following reaction mechanism similar to the mechanisms proposed
by Newman and Gildenhorn (see p. 7) for ketones and by Holmen, Gilliland, and Sparr (see p. 11) for olefins.

(1) \[ RR'H^+C=CH + 2H_2SO_4 \rightarrow RR'H^+C^+ + H_3O^+ + 2HSO_4^- \]

(11) \[ RR'H^+C^+ + HN-N=N \rightarrow RR'H^+C-HN-N=N \] (VI)

(iii) \[ RR'H^+C-NH-N=N \] alternatively \[ RR'H^+C-N_3 + H^+ \]

(iv) \[ RR'C=NH_2^- \] \[ RR'C=NH_2^- + N_3 \]

(v) \[ RR'C=NH_2^- + H_2O \rightarrow RR'C=O + H^+NH_3^+ \]

In steps (i) and (ii) the carboxonium ion is released and reacts with hydrazine acid giving the protonated amide (VI). The latter can either, (iii), lose a proton to give a neutral amide or, (iv), eliminate a molecule of nitrogen with the simultaneous migration of a group from bonding to carbon to bonding with nitrogen, with the formation of the proton adduct of a Schiffs base. Acid hydrolysis of the latter yields a carbonyl compound and a primary amine.

With triphenylmethanol the amide was the sole product; this is understandable, taking into account the great resistance to decomposition exhibited by this compound (Wieland, Rep.,
The protonated oxides from diphenylmethanol and from fluoren-9-ol decomposed according to both (iii) and (iv): in the rearrangement of the protonated oxide from fluoren-9-ol the proton adduct of the Schiff's base is resistant to hydrolysis because it is the stable, cyclic, phenanthridinium ion.

The rearrangement (iv) was considered to proceed by the simultaneous loss of a molecule of nitrogen and intramolecular migration of the aryl group, the four electrons originally constituting the nitrogen lone pair and the C-aryl bond finally appearing as the N-aryl bond and the \( \pi \) electrons of the C=\( \text{NH} \) bond. The fact that substantial quantities of azide can be isolated (in favourable cases) is an indication that the decomposition of the protonated azide is the rate determining step in this reaction, as it was proved to be for the reactions with carboxylic acids and olefins by Nicholson and Mehta (see p. 16).

If the group \( R \) (say) in the carbonium ion \( R^+R'\text{NC}^+ \) has a methylene group \( \alpha \) to the central carbon atom, then this
ion may also arise by the addition of a proton to the requisite olefin. Thus it was shown by Kuhn and DiDomenico (J. Amer. Chem. Soc., 1950, 72, 5777) that both 1:1-diphenylethylene and α-α'-diphenylethanol gave the same products, acetophenone and aniline, on reaction with hydrazoic and sulphuric acids:

\[
\text{Ph}_2\text{C}=\text{CH}_2 + \text{H}^+ \rightarrow \text{Ph}_2\text{C}^+\text{CH}_3 \leftarrow \text{Ph}_2\text{C(OH)}\cdot\text{CH}_3
\]

Now since Hammett's equation is applicable in this case, there is strong reason for supposing that with alcohols in general there will be a simple dependence of the migratory aptitudes of the groups R, R', and R'', upon their capacity for electron release at the migration origin, as implied by the mechanism of Aronson and Wexley.
The Objects of the Present Work.

Consideration of the protonated amide 
RR'H'C-NH^+ shows that three sets of products may arise from 
the alcohol RR'H'C-OH depending on which of the groups, R, R', 
or R'', migrates. With the substituted fluoren-9-ol (VII), as 
is explained elsewhere (see p. 82), it is very unlikely that 
the group R will migrate in preference to one of the rings, A 
or B. Further experimental simplification results by virtue 
of the fact that the products, (VIII) and (IX), from these 
migrations are stable heterocyclic bases which do not break 
down further and which are readily separated from neutral 
materials, e.g. acids.

\[
\begin{align*}
\text{(VII)} & \quad \rightarrow \quad \text{(VIII)} + \quad \text{(IX)}
\end{align*}
\]

It was therefore decided to submit a series of 2- 
and 3-substituted fluoren-9-ols (i.e. m- and p-substituted with 
respect to the migration origin) to the reaction with hydrasol
and sulphuric acids, and to determine the ratios in which (VIII) and (IX) were formed. The primary object was to ascertain whether the relative migratory aptitudes of rings A and B were simply related to the electronic characteristics of the substituents, X, in accordance with the implications of the mechanism proposed by Arcus and Wesley. A secondary object of the present work was to investigate the utility of the reaction as a new method of synthesis in the phenanthridine field.

A search of the literature in 1951 revealed the surprising fact that of the large number of monosubstituted phenanthridines only eleven are known in which the substituent is not in the 9-position (VIII and IX, R=H). The reason for this appears to be twofold. The discovery that certain 9-substituted phenanthridines possess trypanocidal properties stimulated the preparation of large numbers of these compounds for pharmacological reasons; also it so happens that phenanthridines monosubstituted at positions other than 9 are difficult to prepare. For the synthesis of the phenanthridine system the only method which has been used in more than one or two isolated cases is the cyclisation of 3-acylaminodiphenyls, usually by phosphorus oxychloride:
This reaction is not successful when $R = H$; in order to overcome this difficulty a method for eliminating the methyl group in 9-methylphenanthridines has been developed by Ritchie (J. Proc. Roy. Soc. N. S. W., 1945, 79, 164). It consists of the following series of reactions:-

\[
\begin{align*}
\text{CH}_3 & \quad \text{CHO} & \quad \text{CH(NO\text{(CH}_2\text{OH})_2} & \quad \text{COOH} & \quad \text{H} \\
\rightarrow & \quad \rightarrow & \quad \rightarrow & \quad \rightarrow & \\
\text{C} = \text{N} & \quad \text{C} = \text{N} & \quad \text{C} = \text{N} & \quad \text{C} = \text{H} & \quad \text{C} = \text{H}
\end{align*}
\]

but it is not a good preparative route because the overall yield is poor. Therefore, at the inception of the present work, a new method to permit of the exploration of this field appeared desirable. It was, of course, realised that the fluorenol $\rightarrow$ phenanthridine reaction had one serious disadvantage from the synthetic point of view — a monosubstituted fluorenol would, in general, give a mixture of two isomeric phenanthridines.

Since 1961 interest in phenanthridine chemistry has
revived; several new syntheses of the parent base have been reported and a notable advance has been made by Caldwell and Walls (J. Chem. Soc., 1952, 2156). These authors succeeded in preparing all the nine possible mono aminophenanthridines, some by very laborious syntheses, and by means of these they were able to orientate the six mono nitrophenanthridines which they isolated from the complex mixture obtained on nitration of the base. However, there still remains the need for a more accessible means for the preparation of the majority of these compounds.
The Reaction of Some Derivatives of Fluorene with
Hydroxyl and Sulphuric Acids.

The Preparation of Substituted Fluorenes.

The preparations of the derivatives of fluorene used in this work fall into two classes: (i) the preparations of derivatives from fluorene itself, and (ii) the synthesis of fluorene derivatives by ring-closure of appropriate diphenyle and benzophenone. These preparations are summarised in diagrams I and II; literature references are given in the appropriate places in the Experimental Section.

In the course of carrying out these preparations the following new observations were made:-

A new form of 9-phenylfluoren-9-ol, m.p. 88°, was encountered when this compound was prepared by the interaction of phenyl magnesium bromide and fluorenone added (i) in benzene-ether solution, and (ii) as powdered solid according to the original method of Ullmann and von Buratemberger (Ber., 1904, 37, 73). These authors, also Williamson, Anderson, and Watts (J. Amer. Chem. Soc., 1943, 65, 49) record m.p. 107°, but this m.p. was never obtained during the present work. Like the
Diagram I
Diagram II
higher-melting fluorenol, the compound, m.p. 28°, showed a
marked tendency to form solvated crystals when crystallised
from benzene or from carbon tetrachloride. The structure of
this compound follows from the facts that (i) it yielded
3-chloro-3-phenylfluorenol having m.p. 78°, a value identical
with that recorded for this compound prepared from the higher-
melting fluorenol by both Ullmann et al. and by Williamson
et al., and that (ii) it gave an almost theoretical yield of
3-phenylphenanthridine by interaction with a hydrosulphuric acid mixture.

Reduction of 2-nitrofluorenone with a slight excess
of stannous chloride in an acid medium gave 2-aminofluorenone
in 79% yield; similarly 3-nitrofluorenone gave 3-aminofluorenone (74%). This is a more convenient method than that,
described in the literature, involving the use of ammonium
sulphide.

Nitration of 2-p-tolylsulphonamidodiphenyl by the
method of Bay and Barrick (J. Amer. Chem. Soc., 1948, 70, 1493)
led to a reaction of explosive violence, from the product of
which the 5-nitro derivative could not be isolated. Contrary
to the statement by these authors, nitration with 6% nitric
acid as described by Bell (J. Chem. Soc., 1928, 2774) proved
quite satisfactory. Much tar and poor yields of 3-nitrodiphenyl-2-carboxylic acid resulted when the nitrile was hydrolysed with 50% sulphuric acid according to the directions of Ray and Barrick; the method of Jones and Braker (U. S. P., 1, 976, 960), employing a homogeneous solution in aqueous sulphuric-acetic acid, was satisfactory.

The amide of 2-p-tolnoylibenzoic acid, prepared according to Kippenberg (Ber., 1904, 30, 1128), melted at 165-169° after crystallisations from water and from chloroform; these authors reported m.p. 175-178°. The Hofmann reaction with this low-melting amide gave a poor yield of 2-amino-4'-methylbenzophenone; this compound was therefore prepared by the alternative route shown in diagram II. The Schmidt reaction with 2-p-tolnoylibenzoic acid did not yield 2-amino-4'-methylbenzophenone, but 6-oxo-2-p-toly1-4:5-benz-1:3-oxazine was obtained in good yield; this reaction is discussed on p. 108.

2-Nitro-, 3-nitro-, 2-methoxy-, 3-methoxy-, 2-hydroxy-, 2-amino-, 2-methyl-, and 3-methylfluoren-9-ols were prepared by reducing the corresponding fluorenone with aluminium-isopropoxide in hot isopropenol; the respective yields were approximately as follows: 65, 85, 70, 70, 50,
70, 80, 85%. 2:7-Dinitrofluorenone could not be reduced to the carbinal by this method, possibly owing to the almost total insolubility of this ketone in isopropanol. The new carbinols have been characterised by the preparation of the corresponding 9-acetoxyfluorenes. 9-Chloro-2-methoxy-, 9-chloro-2-nitro-, and 9-chloro-3-nitrofluorene have been prepared by the action of thioisul chloride on the corresponding fluoren-9-oIes.
General Remarks concerning the Hydrazoic - Sulphuric Acid Reaction.

In his original work (Ger. Pat., 500, 435; 1928), F. F. Schmidt used a solution of hydrazoic acid in an inert solvent such as benzene or chloroform, which was added with stirring to a solution of the organic acid in sulphuric acid at 40°. Many modifications of this procedure have been made by other workers, but these modifications are of three main types.

The most straightforward way of carrying out the reaction is to add an excess of sodium azide to a solution of the organic compound in sulphuric acid at such a rate that the temperature does not rise unduly. This method was employed by Walls (J. Chem. Soc., 1935, 1407) and has been used in this work for the reactions with fluorenone, 2-nitro-, 3-nitro-, and 2:7-dinitrofluorenone, all of which give, in this way, almost theoretical yields of the corresponding phenanthridones. The method is of limited applicability however, for many compounds are not sufficiently stable to sulphuric acid to permit of its use. Thus 2-nitrofluoren-9-ol, which gave an excellent yield of 2- and 7-nitrophenanthridines by the third method discussed below, when dissolved in sulphuric acid and
treated with sodium aside, yielded an amorphous solid containing sulphur, from which no nitrophenanthridines were isolated.

Trichloroacetic acid has been used to dilute the sulphuric acid in the Schmidt reaction (Smith, J. Amer. Chem. Soc., 1946, 70, 392) and so decrease the chance of sulphonation and other side reactions attendant upon the use of sulphuric acid alone. However this method has the disadvantage that, since mixtures of sulphuric and trichloroacetic acids are not liquid below about 45-60°, the reaction must be carried out above this temperature. Further, since hydrosoio acid boils at 87° it is necessary to add an excess of sodium aside gradually to a solution of the compound in the trichloroacetic-sulphuric acid mixture; the "inverted" method (adding the compound to the pre-formed hydrosoio-sulphuric acid mixture) cannot be employed. The trichloroacetic acid method was not used in the present work except in the Schmidt reactions with g-acyl bensoic acids. Of other solvents miscible with sulphuric acid, reference has been found only to the use of diozen (Briggs, deAth, and Ellis, J. Chem. Soc., 1946, 81).

Solutions of hydrosoio acid in inert solvents immiscible with sulphuric acid have found wide application in the Schmidt reaction (see "Organic Reactions", John Wiley
The solvent usually employed is chloroform, which has the advantages of being a good solvent for many types of organic compounds and of being completely inert towards hydrosolcic and sulphuric acids; various other solvents have been utilised (cf. cit., p. 329). At the beginning of this work a number of experiments with 2-methoxyfluoren-9-ol were carried out to determine the best conditions for the reaction of this compound with hydrosolcic acid in the presence of sulphuric acid; these experiments are discussed in detail in the section on this compound below. However, the conclusion was reached that the best conditions (i.e. the conditions giving the optimum yield of methoxyphenanthridines) were similar to those employed by Arcus and Macleod (J. Chem. Soc., 1963, 173) for the reaction with fluorenol, and by MacEwen, Gilliland, and Sparr (J. Amer. Chem. Soc., 1950, 72, 3212) for the reaction with olefins.

In this method a solution of hydrosolcic acid is prepared by adding sulphuric acid to a suspension of sodium azide in chloroform, and the organic compound under investigation is gradually added to the vigorously stirred mixture at 25°C. In such an "inverted" method the organic compound is in contact with the sulphuric acid for the minimum time; this seems
essential with compounds sensitive to sulphuric acid, such as the fluoronols. It is to be noticed that since an excess of sulphuric acid is present throughout, this procedure is probably unsuitable to general use with ketones, from which 1:3-disubstituted tetrasoles may be formed by the action of an excess of hydroxide acid.

Several other acid catalysts have been employed in the Schmidt reaction (op. cit., p. 320), but there is no evidence that any of these is as good as concentrated sulphuric acid. In this work no attempt was made to investigate the use of acid catalysts other than 98% Analar sulphuric acid.
The Hydrazole - Sulphuric Acid Reaction with 2-Methoxyfluoren-9-ol.

Since the first step in this reaction (the ionisation of the carbinol) must occur in the sulphuric acid, while most of the hydrazole acid is present in the chloroform solution, the second step (the addition of hydrazole acid to form the protonated amide) must presumably occur largely at the sulphuric acid - chloroform solution interface.

(i) \[ R\text{•OH} + 2H_2SO_4 = R^+ + H_3O^+ + 2HSO_4^- \] 

(in sulphuric acid).

(ii) \[ R^+ + HS = R\text{•NH} \] 

(at sulphuric acid - chloroform interface).

Hence it is to be expected that the greater the surface area of the interface the faster, within limits, the formation of the protonated amide will occur, and therefore the less chance there will be of the occurrence of side-reactions leading to lower yields of base. (The situation in this particular case is further complicated by the fact that part of the non-basic reaction product appears to be formed by a side reaction.)
involving the protonated amide, and not simply by one involving the carbonium ion derived from the carbinol; see p. 49). It might therefore be expected that rates, and yields of amide, and hence of base, would be susceptible to factors, such as rate of stirring and viscosity of the reaction mixture, which have an effect on the degree of mixing of the two layers.

Right experiments with 2-methoxyfluoren-9-ol were carried out. When equal volumes of sulphuric acid and chloroform were used in relatively large amount (15 ml. of each to 2.5 g. of carbinol), no base was obtained (Experiment VI). On the other hand, when only a catalytically small amount of sulphuric acid was employed, the carbinol was largely recovered (VII). The best results were given when 7 ml. of sulphuric acid was used for 5 g. of the carbinol and the ratio of the volumes of sulphuric acid to total chloroform was 1:3 (I-III). Arcus and Beasley (J. Chem. Soc., 1953, 178) found difficulty in obtaining reproducible yields of phenanthridine in the reaction of fluoren-9-ol with hydrazoic - sulphuric acid. This trouble was again experienced in the present work; for example, the identical experiments (I) and (II) yielded 40 and 26.5% of base respectively.

An experiment (IV), with slightly less sulphuric acid
and increased chloroform, gave a yield similar to that form (II) and (III). In contrast to this result no base was isolated when the quantities in (IV) were employed, but the sulphuric acid was added dropwise to a suspension of the carbinol and sodium azide in chloroform. Reaction under essentially milder conditions than (IV) — at 0°, a further increase in the volume of chloroform, and a shorter time, (V), — gave a definitely lower yield of base.

The essential conditions appear to be, qualitatively:

(i) the use of sufficient, but not excessive, sulphuric acid;
(ii) the use of a considerable volume of chloroform;
(iii) the addition of the carbinol in chloroform to a pre-formed mixture of hydrazoic acid, sulphuric acid, and chloroform;
(iv) vigorous stirring, at 25°.

In addition to the basic mixture of 2- and 7-methoxyphenanthridines, two neutral fractions were obtained from the reaction of 2-methoxyfluoren-9-ol with hydrazoic - sulphuric acid. From the chloroform solutions, after extraction with acid, were obtained neutral brown oils which could not be induced to crystallise. In all experiments there were also obtained brown, chloroform-insoluble solids. These neutral products are discussed in more detail in connection
with the products from the acid-catalyzed decomposition of 9-azido-9-methoxyfluorene (p. 49).

The basic mixtures obtained from all the experiments contained the same ratio of 2- and 7-methoxyphenanthridines since they all melted at 55-75°. This is further supported by the fact that two separate fractional crystallizations of the base gave practically identical ratios of the methoxyphenanthridines. Thus the base from experiments II to V (4.45 g.) yielded 7-methoxyphenanthridine (2.5 g.), m.p. 86-88° and 2-methoxyphenanthridine (1.2 g.), m.p. 56-58°, while the base from experiment I (2.0 g.) yielded 0.7 g., m.p. 89° and 0.35 g., m.p. 57-59°. These are in the ratios 67.8:32.4 and 66.7:33.3 respectively, based on the weights of the methoxyphenanthridines isolated. Such a method of estimating the relative proportions of two isomers in a mixture is not precise, but the ratio 67:33 is probably a fair approximation to the true value.

Orientation of the two methoxyphenanthridines, m.p. 90° and m.p. 58°, proved troublesome. It was hoped that oxidation of these compounds by permanganate in acid solution, a method by which nitrophenanthridines are converted into nitrophenanthridones in 50-60% yield, would lead to the known
2- and 7-methoxyphenanthridines. However, oxidation did not take this course with the isomer, m.p. 90°. Complete breakdown of the molecule appeared to occur, and besides unchanged methoxyphenanthridine only a trace of a solid which may have been a methoxyphenanthridone was obtained; when the amount of permanganate was so limited as to provide one atom of oxygen per molecule of methoxyphenanthridine, 90% of the latter was recovered. Several attempts to prepare 7-methoxyphenanthridine (i) by methylation of 7-hydroxyphenanthridine, and (ii) directly from 7-anilinophenanthridine were unsuccessful. When 7-hydroxyphenanthridine was shaken with dimethylsulphate, the product was an acidic substance which contained sulphur; it was probably 7-hydroxy-10-methylphenanthridinium sulphate. 7-Hydroxyphenanthridine was recovered after standing 24 hours in contact with a solution of an excess of diazomethane in diethylether; failure in this case may have been due to the almost total insolubility of the compound in this solvent.

When solid phenanthridine-7-diazonium sulphate was boiled with methanol, reduction of the former occurred and phenanthridine was the only product isolated. This was not unexpected for the phenanthridinium ion is strongly deactivated by the highly electron-attracting heterocyclic nitrogen atom, and it has
been shown (Hodgson and Foster, J. Chem. Soc., 1942, 581; Houben-Weyl, "Die Methoden der Organischen Chemie", Georg Thieme, Leipzig, 1924, Vol. IV, p. 613) that replacement by hydrogen rather than by methoxyl generally occurs with diazonium salts deactivated by electron-attracting substituents. The problem of orientation was finally solved by demethylation of the two methoxyphenanthridines with hydrobromic acid. The isomer, m.p. 580, yielded a hydroxyphenanthridine, m.p. 2450, while the isomer, m.p. 900, gave an isomeric phenol, m.p. 2880, identical with 7-hydroxyphenanthridine which was prepared from the known 7-amine compound. Hence the hydroxy- and methoxyphenanthridines, m.p.s 2450 and 580, must be the 2-isomers.

The preparation of 7-hydroxyphenanthridine, by heating a diazotised solution of 7-aminophenanthridine, gave only a small yield. The major product was a neutral, deep red solid, which after several recrystallisations gave analytical data approximating to those required by the aso-dye, C39H160N4, formed by coupling the phenanthridine-7-diazonium ion with 7-hydroxyphenanthridine. Such a coupling in acid solution is unusual and indicates that the phenol is susceptible to electrophilic attack (K. H. Saunders, "The
Aromatic Diazo Compounds", Edward Arnold and Co., London, 1949, p.p. 195, 196, and 230). 6-Aminophenanthridine did not behave abnormally in this repeat, and 6-hydroxyphenanthridine was obtained from it in good yield. An unexpected reaction of 7-hydroxyphenanthridine was that it formed a mono-iodo derivative, C_{13}H_{9}O_{2}I, when it was heated with constant-boiling hydriodic acid containing some free iodine. This again indicates susceptibility to electrophilic attack, for a recent study of the kinetics of the iodination of aniline in aqueous solution by Berliner (J. Amer. Chem. Soc., 1950, 72, 4003) has shown that this is an electrophilic reaction (see also C. K. Ingold, "Structure and Mechanism in Organic Chemistry", G. Bell and Sons, London, 1963, p.p. 290, 291). The reason for the reactivity of 7-hydroxyphenanthridine may lie in the possibility of a quinoid form (II), as well as the normal forms such as (I), contributing to the total resonance of the structure. Such a para-quinoid form cannot be written for 6-hydroxyphenanthridine (III)

![Chemical structures](image-url)
If this is so, the 8-position in 7-hydroxyphenanthridine would be especially prone to electrophilic substitution, and we may provisionally assign formulae (IV) and (V) to the azo-dye and the iodo compound described above.
The Preparation and Acid-Catalysed Decomposition of 9-Asido-2-methoxyfluorene.

9-Asidofluorene (VI) was shown by Arens and Mosley (loc. cit.) to suffer loss of nitrogen and rearrangement to form phenanthridine by the action of sulphuric acid at 35°. This asido was also obtained, in one experiment, in the hydroxo-sulphuric acid reaction with fluorene-9-ol, and it was therefore concluded that it is the proton adduct of the asido (VII) which is the entity that undergoes rearrangement.

![Diagram of compounds VI and VII](image)

9-Asido-2-methoxyfluorene was readily prepared from 9-chloro-2-methoxyfluorene and sodium asido: it appears to be trimorphic, and exists in three forms melting at 44°, 56-58°, and 63-65°. It was of interest to study the acid-catalysed decomposition of this asido, and in particular to compare the yield of methoxyphenanthridines and the ratio of the two
Isomers obtained in this reaction with the data obtained from the hydrazoic-sulphuric acid reaction with 2-methoxyfluoren-9-ol.

When 9-azoide-2-methoxyfluorene was treated with sulphuric acid under conditions simulating the hydrazoic-sulphuric acid reaction, there were obtained, from two experiments, basic mixtures of 2- and 7-methoxyphenanthridines (i), m.p. 58-75° (57%), and (ii), m.p. 60-74° (50%); the only other products were neutral, chloroform-insoluble solids. The melting-points of the basic mixtures show that the two isomers are present in essentially the same ratio as in the mixtures obtained from the hydrazoic-sulphuric acid reaction with 2-methoxyfluoren-9-ol. This was confirmed by fractional crystallisation of (i) which gave a ratio of 7- to 2-methoxyphenanthridine of 65.7:34.3, if these figures are based on the weights of the methoxyphenanthridines isolated.

Hence it is the proton adduct of the azide, formed either (i) by attack of hydrazoic acid on the carbonium ion, or (ii) by protonation of the azide, which rearranges with simultaneous loss of nitrogen.
If this was not so the ratio of the isomeric methoxyphenanthridines from (i) the carbinol, and (ii) the azide, would not necessarily be the same.

The neutral solids obtained in the acid-catalysed decomposition of 9-azido-2-methoxyfluorene and in the hydrochloric-sulphuric acid reaction with 2-methoxyfluoren-9-ol were identical in the following properties. They were brown, amorphous and infusible solids containing nitrogen and sulphur, and were unaffected by and insoluble in dilute acids, alkalis, and all the common organic solvents. The facts that this material is formed from the azide as well as from the carbinol, and that it contains nitrogen, indicate that it is formed in a side reaction subsequent to the formation of the protonated azide. Finally, the yields of base from the azide were somewhat higher (57, 50%) than those obtained from the carbinol (40, 20%); possibly this discrepancy gives a measure of the extent to which side reactions leading to neutral, chloroform-
soluble products occur with the carbinol, or with the cation derived from it, before reaction of the latter with hydrosol acid can take place.
The hydrazoic-Sulphuric Acid Reactions with 2-hydroxy- and 
and 3-Methoxyfluoren-9-ol and with 2-Methoxyfluorenone.

In two experiments with 3-methoxyfluoren-9-ol, closely 
following the optimum conditions established for the 2-isomer, 
the yields of base were about 5%. After molecular distillation, 
a technique which was found to be extremely useful for the 
purification of small quantities of phenanthridines, this base 
melted at 70-78° and analysed fairly satisfactorily for 
methoxyphenanthridine. It is therefore probably a mixture of 
3- and 6-methoxyphenanthridines, but unfortunately the total 
quantity was too small to permit a quantitative separation of 
these isomers. In addition to this base two neutral fractions 
were obtained. The chloroform solutions, on evaporation, gave 
brown oils which, when kept, solidified without crystallising; 
there was also obtained an infusible brown solid similar in 
its properties to the material from the reaction with 
2-methoxyfluoren-9-ol.

No yield of the expected basic mixture of 
hydroxyphenanthridines was given by the hydrazoic-sulphuric 
acid reaction with 2-hydroxyfluoren-9-ol. The entire reaction 
product was an infusible solid with all the properties of the 
similar materials from the methoxy compounds, except that it
retained its phenolic character, being reprecipitated (apparently unchanged) when a solution of it in alkali was saturated with carbon dioxide. The formation of these infusible solids seems to be connected with the presence of oxygen bonded to the aromatic ring, for this behaviour was not shown by fluorenols which were otherwise substituted. It is relevant to point out that Belfe, Kenyon, et al. (J. Chem. Soc., 1942-1962) have demonstrated that in the benzhydrol series the presence of substituent methoxy groups greatly increases the tendency to alkyl-oxygen fission owing to tautomeric electron release by the oxygen atom, and hence to various types of alkylation reactions.

\[ \text{It is therefore probable that a similar situation arises with the methoxy- and hydroxyfluoren-9-ols.} \]

Wells (J. Chem. Soc., 1935, 1407) found that when solutions of 2-hydroxy- and 2-methoxyfluorenones in sulphuric acid were treated with sodium azide, small yields of the corresponding phenanthridones could be isolated. It was therefore decided to see whether the reaction with 2-methoxyfluorenone could be improved by employing a chloroform
solution of hydrazoic acid in the "inverted" method, and to attempt a quantitative separation of the two isomeric methoxyphenanthridones. There was obtained by vacuum sublimation of the product from this reaction, a mixture of 2- and 7-methoxyphenanthridones in 36% yield; the non-volatile residue was an infusible solid containing sulphur and nitrogen. Thus the "inverted" procedure improves the yield from the ketone, as it does with the corresponding carbinal. In order to separate the two isomers the mixture was treated with phosphorus oxychloride to convert these to the corresponding 8-chlorophenanthridines:

![Chemical structure](image)

This reaction is a general one in the phenanthridine series: since the yield was almost quantitative, the ratio of 8-chloro-7-methoxy- to 8-chloro-8-methoxyphenanthridine in the product must be substantially the same as the ratio of the two methoxyphenanthridones in the original mixture. Separation of the two isomeric chloro compounds was easily accomplished by fractional crystallisation from light petrolatum, from which
they were obtained in almost exactly equal amounts. Hence it is concluded that the ratio of 7-methoxyphenanthridone to 2-methoxyphenanthridone in the original reaction product is approximately 50:50.

This result, which is considerably different from the ratio of 7- to 2-methoxyphenanthridine (67:33) obtained from the corresponding carbinol, was unexpected. Nevertheless, even more striking differences were observed in the two other cases where the carbinol and corresponding ketone were studied cooperatively (p. p. 62, 69). The theoretical implications of these results are discussed elsewhere (p. 101).
The Hydrosol-Sulphuric Acid Reaction with 2-Nitrofluoren-9-ol, 2-Nitrofluorenone, and 2-Aminofluoren-9-ol.

It has already been mentioned that the reaction of a solution of 2-nitrofluoren-9-ol in sulphuric acid with sodium aside gave an infusible, amorphous, brown material, insoluble in organic solvents and containing sulphur. However, when the carbinol was added to a solution of hydrosol acid in chloroform stirred with a limited amount of sulphuric acid, there was formed a mixture of 2- and 7-nitrophenanthridines in 90% yield.

Fractional crystallisation of this mixture from benzene gave, as principle product, a nitrophenanthridine of m.p. 180°, and another, m.p. 158°, was also isolated in small amount. Nitrophenanthridines having either of these melting-points are described in the literature as the 7-isomer:

Ritchie (J. Proc. Roy. Soc. N. S. W., 1945, 78, 164) nitrated 10-acetyl-9:10-dihydrophenanthridine (I), and by "oxidative hydrolysis" of the 7-nitro derivative (II) obtained 7-nitrophenanthridine having m.p. 178°. Caldwell and Wells (J. Chem. Soc., 1952, 2156) isolated a nitrophenanthridine having m.p. 158° from the mixture of isomers obtained in the nitration of phenanthridine. Ritchie had no definite proof of the orientation of his compound, m.p. 178°, but argued that
it was probably the 7-isomer because 2-acetamidodiphenyl, under the same conditions of nitration, yields 2-acetamido-4'-nitrodiphenyl (III).

\[
\text{(I) } \quad \text{(II) } \quad \text{(III)}
\]

On the other hand, Caldwell and Wells, in addition to showing that their substance gave 7-nitrophenanthridone on oxidation with acid permanganate, were able to isolate, from its reduction product, 7-aminophenanthridine identical with the compound obtained by an unambiguous route. Nevertheless, the results described below show that the substance m.p. 158\(^\circ\), is actually a 1:1 complex of 2- and 7-nitrophenanthridines, and that the compound having m.p. 180\(^\circ\) is 7-nitrophenanthridine. It is concluded that Caldwell and Wells' procedures for oxidation and reduction (together with the subsequent purifications) result in the preferential separation of, respectively, 7-nitrophenanthridone and 7-aminophenanthridine.

1. Oxidation of the compound, m.p. 180\(^\circ\), with alkaline permanganate gave no phthalic acid, the product being a
nitrogenous acid of unknown constitution. Huntress and Moore (J. Am. Chem. Soc., 1927, 49, 1324) showed that 2-nitrophananthridone yields phthalic acid under these conditions.

(ii) Oxidation of the compound, m.p. 180°, with acid permanganate gave almost pure 7-nitrophananthridone, m.p. 329° (for references to the orientation of 2- and 7-nitrophananthridones see p. 62), in 60% yield. The material obtained by Caldwell and Walls on oxidation of the substance, m.p. 158°, melted between 285-305° (i.e. approximately at the m.p. of the complex of 2- and 7-nitrophananthridones) and 7-nitrophananthridone was obtained from it, in unstated yield, only upon chromatographic purification.

(iii) Reduction of the substance, m.p. 180°, gave 7-aminophananthridine, m.p. 202-203°, in 83% yield, and this formed an ethoxycarbonyl derivative, m.p. 206-207°. Caldwell and Walls report 205-204° and 205-206° for the melting-points of these two substances; these authors do not state the yield in which 7-aminophananthridine was obtained by reduction of the substance, m.p. 158°.
Diagram III

showing the relationship between some phenanthridines formed in the hydrazoic-sulphuric acid reaction with 2-substituted fluorenes
(iv) 2-Nitrophenanthridine was synthesised as follows:-

2-nitrophenanthridone (see p. 61), on reaction with phosphorus oxychloride, gave 9-chloro-2-nitrophenanthridine, which was then condensed with p-tolylsulphonhydrazine. The resulting sulphonhydrazide, when treated with hot sodium hydroxide solution, formed 2-nitrophenanthridine of m.p. 196-197° (this synthesis is discussed on p. 63; Caldwell and Walls, loc. cit., record a m.p. 196-197° for this compound obtained from the nitration of phenanthridine). When equal weights of this compound and of the compound, m.p. 180°, were allowed to crystallise together from ethanol, the substance, m.p. 158°, was obtained.

It is therefore established that the nitrophenanthridine, m.p. 180°, is 7-nitrophenanthridine, and that of m.p. 158° is a 1:1 complex of 2- and 7-nitrophenanthridines. Diagram III summarises these relationships.

From the original fractional crystallisation of the mixture of nitrophenanthridines (26.0 g.) there were obtained 7-nitrophenanthridine (19.7 g.) and the complex (1.45 g.); i.e. 7-nitro- (20.42 g.) and 2-nitrophenanthridine (0.73 g.). Hence the ratio of 7-nitro to 2-nitrophenanthridine in the
reaction product is 96:4.

An attempt was made finally to confirm the structure of the nitrophenanthridine, m.p. 180°, by synthesis. It is known that the cyclisation of 2-azylaminodiphenyls (IV) by heating with phosphorus oxychloride fails when \( R = \text{H} \) (Schofield, *Chem. Rev.*, 1950, 171), but Cockenden and Schofield (J. Chem. Soc., 1953, 717) have recently discovered that addition of a small quantity of stannic chloride to the reaction mixture affords phenanthridine (from 2-formamidodiphenyl) in 90% yield.

Accordingly, 2-amino-4'-nitrodiphenyl was prepared by nitration of 2-acetamidodiphenyl, and converted into its formyl derivative. However, when the latter was heated in nitrobenzene solution with phosphorus oxychloride and stannic chloride, the main product was an amorphous material, and the only basic compound recovered was a small quantity of 2-amino-4'-nitrodiphenyl.

There is evidence that the mechanism of the cyclisation reaction involves electrophilic attack of the carbonium ion (V) on the aromatic ring (Schofield, *loc. cit.*; p.p. 178-179):

\[
\begin{align*}
\text{(IV)} & \quad \text{\rightarrow} \quad \text{(V)} & \quad \text{\rightarrow}
\end{align*}
\]
Therefore the failure of 2-formamido-4'-nitrodiphenyl to
cyclise under these conditions is probably due to the strong
deactivation of the ring (by its substituent nitro group)
towards electrophilic reagents. The reaction is in fact
similar to the Friedel-Crafts reaction, in which nitrobensene
can be used as a solvent because it is resistant to attack by
the carbonium ions liberated in the course of the reaction.

An attempt was also made to synthesis
3-nitrophenanthridine from 2-formamido-5-nitrodiphenyl. The
latter was obtained by formylation of the corresponding amine,
prepared by the nitration of 2-p-tolylsulphonamidodiphenyl and
subsequent hydrolysis of the product; when this formyl compound
was heated with a phosphorus oxychloride-stannic chloride
mixture, 3-nitrophenanthridine was produced, but in only 10% yield.
Thus a nitro group in the same ring as the formamido
residue also hinders the cyclisation reaction with a diphenyl;
the ring which suffers electrophilic attack does not contain a
nitro group, but suffers deactivation by its nitrophenyl
substituent. The m.p. of 3-nitrophenanthridine synthesised
in this way was 268°, in agreement with the figure (266–267°)
reported by Caldwell and Walls (J. Chem. Soc., 1952, 2156) for
this compound isolated from the nitration products of
phenanthridine.
It is stated, in British Patent 333, 175, that 2-nitrophenanthridone is the only product when a solution of 2-nitrofluorenone in sulphuric acid is allowed to react with a solution of hydrazide acid in benzene. Walls (J. Chem. Soc., 1935, 1407) found that treatment of a solution of 2-nitrofluorenone in sulphuric acid with sodium azide yielded a mixture of 2- and 7-nitrophenanthridones, but he did not separate these isomers. In view of this discrepancy and the fact that, if 2-nitrophenanthridone is the main product, the interesting situation arises that the ketone rearranges in the opposite direction (giving 2-) to the carbinol (giving 7-), it was decided to repeat Walls' work.

The mixture of nitrophenanthridones was obtained in theoretical yield by Walls' method, and a separation on 0.50 g. was attempted by fractional sublimation in vacuo. The more volatile fractions (0.03 g.) melted at 282-308°, and therefore correspond roughly to the 1:2 complex of 2- and 7-nitrophenanthridones, m.p. 266-267°, discovered by Nunn, Schofield, and Theobald (J. Chem. Soc., 1932, 2797). This was confirmed by conversion of this substance to the 9-chloro derivatives by the action of phosphorus oxychloride. The product melted at 165-180°; a synthetic mixture of 9-chloro-7-nitrophenanthridine, m.p. 200°, and 9-chloro-2-nitrophenanthridine, m.p. 207-209°, melted over a
similar range. The less volatile fractions (0.39 g.) were substantially 2-nitrophenanthridone for they yielded this compound, m.p. 360° (350° uncorrected) on one crystallisation from pyridine. The melting points of 2- and 7-nitrophenanthridones were established, for the first time unambiguously, by the above authors as 326-7° and 350° respectively. From the weights mentioned above it is evident that the ratio of 7-nitrophenanthridone to 2-nitrophenanthridone present in the reaction product is approximately 5:96.

Thus the situation initially inferred, above, is confirmed. Further evidence on the difference in migratory tendency between the carbinal and the ketone is supplied by the following observations: the nitrophananthridine, m.p. 180°, obtained as principal product from the carbinal, yielded on oxidation, a nitrophananthridone, m.p. 329°, while that obtained as main product from the ketone had m.p. 360°. Further, the nitrophananthridone, m.p. 360°, was reduced to a nitrophananthridine, m.p. 196-197°, not identical with that obtained from the carbinal.

A discussion of the methods available for passing from the phenanthridone to the phenanthridine series is set out by Albert (J. Chem. Soc., 1948, 1287) who showed that
reductive dehalogenation of 9-bromophenanthrindine with Raney nickel gives phenanthridine in almost theoretical yield. This method is not suitable when nitro groups are present because of the tendency for the latter to be reduced first, and this author developed a method involving cleavage of the tolylsulphonhydrazide by hot alkali for the reduction of 4-chloro-3-nitro-6:7-benzoquinoline to 3-nitro-6:7-benzoquinoline. This new method has since been used once in the phenanthridine series, by Badger, Seidler, and Thomson (J. Chem. Soc., 1951, 3210) who converted 9-chlorophenanthridine into phenanthridine in 30% yield. It was utilized in the present work for the reduction of 2-nitrophenanthridone to 2-nitrophenanthonidine; the former (I), on reaction with phosphorus oxychloride, yielded 9-chloro-2-nitrophenanthridine (II), which was then condensed with p-tolylsulphonhydrazine in chloroform solution at the boil. The 9-p-tolylsulphonhydrazide (III) underwent cleavage with evolution of nitrogen on heating with dilute aqueous alkali to give 2-nitrophenanthridine (IV) in 22% yield.
The reaction was also used to prepare the hitherto unknown 2:7-dinitrophenanthridine, which was formed in 25\% yield from 9-chloro-2:7-dinitrophenanthridine (prepared by literature methods). The precise mechanism of this reaction does not appear to be known.

It was intended to investigate the acid-catalyzed decomposition of 9-asido-2-nitrofluorene, but this compound could not be isolated, due probably to its low thermal stability. When 9-chloro-2-nitrofluorene was heated with sodium azide in methanol, a method successful for the preparation of the 2-methoxy-compound, 9-imino-2-nitrofluorene was isolated in high yield: the structure of the latter compound was established by hydrolysis, which gave 2-nitrofluorenone. Arcus and Mealey (J. Chem. Soc., 1953, 178) found that 9-asidofluorene, on storage or on heating above its m.p. (45\°), yielded 9-iminofluorene, and the formation of 9-imino-2-nitrofluorene is attributed to a similar breakdown of the initially-formed 9-asido compound under the conditions employed for its preparation.

The product from the hydrosolic-sulphuric acid
reaction with 2-aminofluorene-9-ol was a basic, resinous substance, from which there was obtained, by a careful fractional crystallisation from benzene, a small amount of unchanged carbinol, and 7-aminophenanthridine in 30% yield. The latter compound, after purification, was identical with this compound obtained by reduction 7-nitrophenanthridine. No more crystalline material could be isolated from the mother-liquors. There was no indication of the presence of 2-aminophenanthridine.
The Hydrosolic-Sulphuric Acid Reaction with 3-Nitrofluoren-9-ol and 3-Nitrofluorenone.

3-Nitrofluoren-9-ol behaved like the 2-nitro-compound in the hydrosolic-sulphuric acid reaction. There were obtained, in two experiments, mixtures of 3- and 6-nitrophenanthridines in 80 and 96% yields. Fractional crystallisation of this mixture from benzene gave, as principal product, a nitrophenanthridine of m.p. 194°, and a small amount of 3-nitrophenanthridine which after recrystallisation melted at 255-259° alone, and at 262-264° when mixed with an authentic specimen of this substance, m.p. 268°, synthesised by cyclisation of 2-formamido-5-nitrodiphenyl (see p.60). The nitrophenanthridine obtained as the major product did not correspond in m.p. to the 1-, 2-, 3-, 4-, 5-, or 7-isomers (for a table of the known nitrophenanthridines and nitrophenanthridones see Caldwell and Wells, J. Chem. Soc., 1932, 2160; the m.p. quoted for 7-nitrophenanthridine is, as described above, incorrect). It is 6-nitrophenanthridine since on reduction it gave 6-aminophenanthridine, m.p. 194-195° in agreement with the figure (192-194°) reported by Caldwell and Wells for this compound synthesised from 6-amino-9-methylphenanthridine. 6-Aminophenanthridine was converted into
6-hydroxyphenanthridine, m.p. 271-272°, via the diazonium sulphate, in excellent yield. 6-Nitrophenanthridine was oxidised by acid permanganate to 6-nitrophenanthridone which formed bright yellow needles, m.p. 369°, quite different in appearance from 3-nitrophenanthridone, m.p. 378°, which was prepared by nitration of phenanthridone by the method of Moore and Huntress (J. Amer. Chem. Soc., 1927, 49, 1332). Equal weights of this compound and of 6-nitrophenanthridone formed an eutectic mixture melting at 333-335° (see below). The 6-nitro compound was further characterised by conversion to 9-chloro-6-nitrophenanthridine, m.p. 218°.

From the original mixture of nitrophenanthridines (9.5 g.), there were obtained, on fractional crystallisation, 6-nitrophenanthridine (7.5 g.) and 3-nitrophenanthridine (0.45 g.) these are in the ratio 94:4:5:6. Since the 0.45 g. was not quite pure 3-nitrophenanthridine (see above), the ratio is probably more in favour of the 6-isomer, and the approximation 95:5 will be assumed.

It was of interest, in view of the unexpected behaviour of 3-nitrofluorenone, to determine whether 3-nitrofluorenone would give largely 3-nitro-, and not
6-nitro-, phenanthenridone.

The hydrazoic-sulphuric acid reaction was carried out by dissolving the ketone in sulphuric acid and adding sodium azide, and provided a theoretical yield of a mixture of nitrophenanthridones. Separation of this mixture was attempted by vacuum sublimation; twenty-two fractions were collected, and from the least volatile of these there was obtained a small quantity of 3-nitrophenanthridone, which, after one crystallisation, was identical with this compound prepared by the nitration of phenanthenridone. It was not found possible to isolate 6-nitrophanthridone from the most volatile fractions, and it later became evident that the reason for this was that these fractions consisted of practically equal quantities of the two isomers. Since a complete separation could not be achieved, recourse was made to the construction of a melting-point vs. percentage composition curve of mixtures of 3- and 6-nitrophanthridones, pure specimens of which were prepared as described above. The construction of this curve is fully described in the Experimental Section; it showed a simple form, with an eutectic at an approximately 50:50 mixture. Calculation of the percentage composition of the reaction product was conducted by summation of the
individual compositions of the 22 fractions, read off from the curve. In this way the ratio of 3-nitrophenanthridone to 6-nitrophenanthridone was found to be 70:30. Therefore, although 3-nitrofluorenone and 3-nitrofluoroneol show a qualitative similarity in behaviour to the 2-nitro-isomers, there is a definite quantitative difference.
The Hydrosulphuric Acid Reactions with 2- and 3-Methylfluoren-9-ols.

By analogy with the reactions of the methoxy compounds, which bear electron-releasing groups, it was expected that low yields might be encountered in the hydrosulphuric acid reactions with 2- and 3-methylfluoren-9-ols, which also contain groups capable of electron release. However, these expectations proved unjustified. The optimum conditions found for the reaction with 2-methylfluoren-9-ol were used, and both methylfluorenenols gave good yields of the basic mixtures of methylphenanthridines. In two experiments, 2-methylfluoren-9-ol gave yields of 82 and 78%; in two experiments with 3-methylfluoren-9-ol yields of 87 and 47% were obtained. The reason for the low yield in the second experiment with 3-methylfluoren-9-ol is not apparent; the two experiments with this compound were identical except that, (i) the latter was on thrice the scale of the former, and (ii) the carbinal was added to the hydrosulphuric acid mixture during twice the time taken in the first experiment. The neutral products from these reactions were chloroform soluble syrups from which no crystalline material was obtained.

Fractional crystallisation of the mixture (4.5 g.) of
methylphenanthridines from the reaction with 3-methylfluoron-9-ol, gave 3-methylphenanthridine (3.55 g.) which after further crystallisations melted at 80-80.5° and yielded a picrate, m.p. 270-271°. These figures agree with those (80° and 266° respectively) reported by Kemmer, Ritchie, and Stetham (J. Chem. Soc., 1937, 1169) for this compound synthesised by the dehydrogenation of 3-methyl-5:6:7:8-tetrahydrophenanthridine. (In general the picrates prepared in this work were found to melt a little higher than those given in the literature). Although 6-methylphenanthridine, together with more 3-methyl-, was probably present in the mother-liquor from the fractional crystallisation, it was not found possible to isolate the compound by further fractional crystallisations of the base or of the picrate prepared from it. It is therefore not possible to give a ratio of 6-methylphenanthridine to 3-methylphenanthridine formed in this reaction, but it may be stated with certainty that 3-methylphenanthridine is present to an extent greater than 70% in the basic reaction product.

The separation of the mixture of 2- and 7-methylphenanthridines, from the reaction with 2-methylfluoron-9-ol, proved more difficult. The least soluble material from a fractional crystallisation of this mixture gave, after further
recrystallisations, 7-methylphenanthridine melting at 87.5-88° which formed a picro, m.p. 240-241°. The melting-points of this compound and its picro, prepared by Kenner et al. (loc. cit.) by the dehydrogenation of 7-methyl-5:6:7:8-tetrahydrophenanthridine, are 86° and 236-237° respectively. It was not found possible to isolate the other isomer by fractional crystallisation of the more soluble fractions. However, this separation was achieved by converting these to the picro (m.p. 236-236°) and crystallising this repeatedly from dioxan until the m.p. was 230°. The base was then recovered and recrystallised several times to yield 2-methylphenanthridine, m.p. 80°, from which the picro, m.p. 253-254°, was prepared. 2-Methylphenanthridine was obtained by Ritchie (J. Proc. Roy. Soc., N. E. E., 1945, 78, 164) by distillation of 2-methylphenanthridone with zinc dust, and melted at 81° (picro, m.p. 251°). Since the actual quantities of the pure methylphenanthridines obtained were only a small fraction of the total mixture, it was not possible to estimate the ratio of these two isomers by employing the relative weights in which they were isolated. This ratio was obtained as follows:— a melting-point vs. percentage composition curve was constructed with the pure specimens of
2- and 7-methylphenanthridines isolated as described above; this curve was of a simple form with an eutectic at the 50:50 mixture. Mixtures of 2- and 7-methylphenanthridines were recovered in three fractions from the various mother-liquors from the above crystallisations, and the m.p. s of these fractions were determined. Their compositions were then read off from the curve, and, knowing their weights and the weights of the crops of the pure isomers, the percentage composition of the original reaction product was calculated. In this way the ratio of 7-methylphenanthridine to 2-methylphenanthridine was found to be 47:53.
The fluorenols discussed previously are all secondary carbinals; reference to the reaction with a tertiary carbinal is made by Arous and Mealey (J. Chem. Soc., 1953, 178), who studied triphenylmethanol (I). These authors found that this carbinal gave a high yield of triphenylmethyl aside (IV) by the action of hydrazoic acid in the presence of sulphuric acid, and attributed the formation of this compound to the tendency of the proton adduct of the aside (III) to lose a proton rather than to undergo rearrangement.

\[
\begin{align*}
\text{Ph}_3\text{C} - \text{OH} & \rightarrow \text{Ph}_3\text{C}^+ & \rightarrow \text{Ph}_3\text{C} \cdot \text{NH} \cdot \text{H} = \text{N} & \rightarrow \text{Ph}_3\text{C} \cdot \text{H}_5 + \text{H}^+ \\
(\text{I}) & & (\text{II}) & & (\text{III}) & & (\text{IV})
\end{align*}
\]

It was therefore of interest to investigate the tertiary carbinals, the 9-substituted fluoren-9-ols, and in particular to determine whether 9-phenylfluoren-9-ol, which is ostensibly similar to triphenylmethanol, would yield a stable aside, or an aside which rearranges with ring expansion like those from the secondary carbinals.
The result with 9-phenylfluoren-9-ol was unequivocal: it gave 9-phenylphenanthridine, in two experiments, in 96 and 90% yields. This compound melted at 106° and formed a picrate, m.p. 251°, in agreement with 9-phenylphenanthridine, m.p. 109° (picrate, 242°) prepared by Pictet and Hubert (Bcr., 1896, 28, 1184), by ring-closure of 2-benzamidodiphenyl. The high yield of 9-phenylphenanthridine probably reflects the ease and completeness of ionisation, and the absence of a tendency by the resultant carbonium ion to undergo side-reactions, to be expected by analogy with triphenylmethanol. (Gillespie and Leistern, Quart. Reviews, Vol. VIII, 1964, 51, point out that the stability of the triphenylmethyl carbonium ion is to be attributed to the relative instability of the precursor, Ph₃C·OH₂, due to the large steric repulsions between the phenyl groups and the OH₂ group, rather than to resonance stabilisation; these conditions apply equally to 9-phenylfluoren-9-ol). The fact that the intermediate protonated azide undergoes rearrangement, rather than loss of a proton to yield the azide, is a measure of the tendency for ring enlargement to occur in the fluorene series.

The hydrosol-sulphuric acid reactions with 9-benzyl- and 9-methylfluoren-9-ols gave the corresponding
phenanthridines, but the yields were not so high as that from the phenylfluorenol. 9-Benzylphenanthridine, m.p. 112°, was obtained in 40% yield from 9-benzylfluoren-9-ol, and formed a pierate, m.p. 200-202°. This compound was prepared by Ritchie (*J. Proc. Roy. Soc., New Zealand*, 1945, 78, 154) by the cyclisation of 3-phenylacetamidodiphenyl and melted at 112°; a pierate, m.p. 190°, is also described but no analysis is recorded.

9-Methylfluoren-9-ol gave, in three experiments,
9-methylphenanthridine in 34, 44, and 56% yields; this compound melted at 85°, and gave a pierate, m.p. 249°.
9-Methylphenanthridine has been synthesised, by cyclisation of 2-acetamidodiphenyl, by Pictet and Hubert (loc. cit.), who report m.p. a of 85° and 233° for the base and its pierate respectively. The rather low yields of 9-methylphenanthridine are anomalous, for it has been demonstrated (A. E. Lucken, unpublished work) that the higher homologues, 9-ethyl; 9-iso-propyl-, and 9-tert.-butylfluoren-9-ols, give higher (and more consistent) yields of the corresponding 9-alkylphenanthridines. The reason for this discrepancy appears to be that 9-methylfluoren-9-ol condenses with 9-methylphenanthridine, under the conditions of the reaction, with the elimination of a molecule of water, because a neutral,
nitrogenous compound was isolated from the chloroform solution from the third experiment in 26% yield. This compound had analytical figures agreeing with the empirical formula C_{28}H_{21}N, and this is probably also its molecular formula since it gave a mono picrate. This formula is correct for a (9-methylfluorenyl)-9-methylphenanthridine:

\[ C_{14}H_{12}O + C_{14}H_{11}N = C_{28}H_{21}N + H_2O \]

The structure of this compound is not known, but condensation involving the methyl group in 9-methylphenanthridine is suspected in view of the known reactivity of this group (Caldwell, J. Chem. Soc., 1952, 2035); however, the lack of basicity of the compound is puzzling.

It has been shown by Heisen, Gilliland, and Sparrow (J. Amer. Chem. Soc., 1950, 72, 3212) that 1:1-diarylethylenes (V) react with hydrazine in the presence of sulphuric acid, and these authors proposed a mechanism in which the carbonium ion (VI) is the essential intermediate.

\[ \text{ArgC=CH}_2 + H^+ \rightarrow \text{Arg}^+\text{-CH}_3 \]

(V) \hspace{2cm} (VI)

It was therefore considered that the carbonium ion (VII) might
be derived not only from 9-benzyfluoren-9-ol in the customary way, but also from 9-benzylidenefluorene by addition of a proton to the double bond:

$$\text{HO-CH}_2\cdot\text{Ph} \quad \text{C}^+ \quad \text{CH} \cdot \text{Ph}$$

(VII)

This proved to be so, for 9-benzylidenefluorene gave, in two experiments with hydrazoic and sulphuric acids, yields of 47 and 53% of 9-benzylphenanthridine identical with that from 9-benzyfluoren-9-ol. These yields do not differ substantially from that obtained in the reaction with the latter compound. The formation of the phenanthridine from the olefin constitutes evidence for carbon cation formation during the first step in the present series of reactions.

The neutral, chloroform soluble, materials from the hydrazoic-sulphuric acid reactions with both 9-benzylidenefluorene and 9-benzylfluoren-9-ol were amber oils, which could not be induced to crystallise. Presumably, since these materials are similar, and are obtained in similar yields, they are derived from a side reaction involving the common intermediary carbonium ion (VII).
9-Benzylidene-2-nitrofluorone, which was expected to yield 9-benzy1-2- and -7-nitrophenanthridines by reaction with hydrochloric acid in the presence of sulphuric acid, was recovered after treatment with these reagents in chloroform solution in the usual way. When the compound was dissolved in sulphuric acid and sodium azide was added, extensive sulphonation occurred and no base was isolated. Failure of the reaction with this compound is presumably due to the strong electron attraction of the nitro group, which so constrains the \( \pi \) electrons of the \( C_9 \) double bond that electrophilic attack on the latter by a proton is rendered impossible, and hence a carbonium ion analogous to (VII) cannot be formed.
Table II: A Summary of the Hydrazoic-Sulphuric Acid Reactions with Fluorene Derivatives.

In Table II are summarised the gross yields and the ratios of the isomeric phenanthridines and phenanthridones formed in the hydrazoic-sulphuric acid reactions with various fluorene derivatives, described in the previous sections.
<table>
<thead>
<tr>
<th>Fluorene Deriv.</th>
<th>Gross Yield %</th>
<th>Phenanthridine(s) formed: ratio as percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>$	ext{CH}_3\text{OH}$</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>$	ext{Ph}\cdot\text{CH}_2\cdot\text{OH}$</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>$	ext{Ph}\cdot\text{CH}$</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>$	ext{Ph}\cdot\text{OH}$</td>
<td>93</td>
<td></td>
</tr>
<tr>
<td>$	ext{H}\cdot\text{OH}\cdot\text{OCH}_3$</td>
<td>35</td>
<td>67, 33</td>
</tr>
<tr>
<td>$	ext{H}\cdot\text{OH}\cdot\text{OCH}_3$</td>
<td>5</td>
<td>mixture not separated</td>
</tr>
<tr>
<td>$	ext{H}\cdot\text{OH}\cdot\text{NO}_2$</td>
<td>90</td>
<td>96, 4</td>
</tr>
<tr>
<td>Fluorene Deriv.</td>
<td>Gross Yield %</td>
<td>Phenanthridine formed: ratio as percentage</td>
</tr>
<tr>
<td>----------------</td>
<td>---------------</td>
<td>------------------------------------------</td>
</tr>
<tr>
<td><img src="image1" alt="Image" /></td>
<td>88</td>
<td><img src="image2" alt="Image" /> 95</td>
</tr>
<tr>
<td><img src="image3" alt="Image" /></td>
<td>30</td>
<td><img src="image4" alt="Image" /> 100</td>
</tr>
<tr>
<td><img src="image5" alt="Image" /></td>
<td>80</td>
<td><img src="image6" alt="Image" /> 46</td>
</tr>
<tr>
<td><img src="image7" alt="Image" /></td>
<td>67</td>
<td><img src="image8" alt="Image" /> 54</td>
</tr>
<tr>
<td><img src="image9" alt="Image" /></td>
<td>67</td>
<td><img src="image10" alt="Image" /> &gt; 79</td>
</tr>
<tr>
<td><img src="image11" alt="Image" /></td>
<td>100</td>
<td><img src="image12" alt="Image" /> 5</td>
</tr>
<tr>
<td><img src="image13" alt="Image" /></td>
<td>100</td>
<td><img src="image14" alt="Image" /> 30</td>
</tr>
<tr>
<td><img src="image15" alt="Image" /></td>
<td>30</td>
<td><img src="image16" alt="Image" /> 50</td>
</tr>
</tbody>
</table>
The Relation between the Course and Mechanism of the Hydrazoic-Sulphuric Acid Reaction and the Steric and Electronic Properties of Substituents.

1. The Carbinols.

The Schmidt reaction is now generally agreed to proceed by an ionic mechanism. The first step is the formation of a cation, followed by nucleophilic attack by hydrazoic acid to give a proton adduct of an acid (which will be called the "protonated acid" in the following discussion). While, therefore it is unnecessary to stress further that the present work supports this view, it is relevant to point out that the fact that both 9-benzylfluoren-9-ol and 9-benzylidenefluorene give similar yields of the same compound, 9-benzylphenanthridine, constitutes proof that an ionic mechanism is operative.

The evidence, discussed on p. 48, that it is the protonated acid which is the entity which undergoes rearrangement, appears to be conclusive. It is therefore the exact mechanism of this rearrangement with which we are now concerned. This discussion will be devoted to a demonstration of how the results of the present work, and in particular the correlation found between the migratory aptitudes and the electronic nature
of the migrant groups, substantiate the mechanism put forward by Arcus and Nealey (see p. 24) for the reaction of carbamates with hydrosulphuric acid in the presence of sulphuric acid.

It is apparent that there are, theoretically, two paths open to the rearrangement of the protonated azide (I). As the $\text{N}_2$ molecule is released bearing the electrons of the $\text{N}$$\text{=N}_2$ bond either of the following may occur:

(i) migration of a phenyl group to nitrogen, resulting in ring enlargement with the formation of the phenanthridinium ion (II);

(ii) migration of the group R to nitrogen giving an intermediate which, by loss of a proton, yields the R-substituted-9-iminofluorene (III).

![Chemical Structures](image)

In actual fact (i) always occurs and (ii) has not been observed during the hydrosulphuric acid reaction, nor during the acid-catalysed decomposition of 9-azidofluorene or
of 9-azido-2-methoxyfluorene. On the other hand, thermal
decomposition of 9-azidofluorene and of 9-azido-2-nitrofluorene
results in the formation of the corresponding imines. As the
N₂ molecule recedes from the protonated azide, the formal
transition state (IV) arises in which the nitrogen is positively
charged. Therefore the group having the greatest electron
release will tend to migrate, in this case leading to ring
enlargement.

\[ R \text{WH}_2 \rightarrow R \text{N} \rightarrow \]

(IV)

The formal transition state (V), from an azide on release of the
N₂ molecule, has a neutral nitrogen atom with a sextet of
electrons. It appears that when \( R = H \), migration of the
hydrogen atom, rather than migration of the larger phenyl group,
offers a more facile route to a product having a nitrogen atom
with a stable octet. Nevertheless, this is the exception
rather than the rule, for ring enlargement is greatly favoured
since it releases the strained condition of the five-membered
ring, and results in a more stable system due to the relatively
large increase in resonance energy associated with the creation
of a third aromatic ring. Thus it has been found that thermal
decomposition of 9-azido-9-\(\text{α}\)-naphthylfluorene yields the
corresponding phenanthridine, as do the fluorenes (VI)

\[
\begin{align*}
\text{R} & \quad \text{NCl} \\
\quad & \quad \text{(VI)}
\end{align*}
\]

on treatment with pyridine (Pinck and Hilbert, J. Amer. Chem. Soc., 1937, 59, 8). That 9-phenylfluoren-9-ol gives 9-
phenylphenanthridine while the similar system,
triphenylmethanol, yields the stable azide on interaction with
hydrochloric and sulphuric acids is a measure of the tendency for
ring expansion to occur in the fluorene series, as is
mentioned on p. 75. There are many references in the literature
to ring enlargement with fluorene derivatives by various
reactions (see, for example, Rieveschl and Ray, Chem. Rev.,
1936, 23, 303). It is thought that a strong tendency to ring
expansion is an important factor in the formation of
1:3-oxazines in the Schmidt reaction with 9-arylsulphonic acids
(p. 113).

From a fluorenone substituted in positions 2- or 3-
there can arise, potentially, a pair of phenanthridines (VIII,
IX) substituted in positions 2- and 7-, or 3- and 6-,
respectively. Since each of these isomers follows from a common precursor, the protonated amide (VII), the relative rates with which the substituted and unsubstituted rings migrate from bonding with C_9 to bonding with N is given directly by the ratio of the yields of the two isomeric phenanthridines.

For the Schmidt reaction with ketones Smith and his coworkers have proposed an oxime-like intermediate (X), in which the $-\text{N}≡\text{N}^\dagger$ group is anti- to the larger group $R$: a $\text{H}_2$ molecule is released and $R$ migrates to $N$

\[
\text{H}-\text{N}≡\text{N}^\dagger
\]

\[
\vdash R-C-R^\dagger\quad (X)
\]
It was pointed out on p. 16 that such an intermediate cannot be postulated for the carbinol and olefin reactions. Furthermore, the protonated azide (VII) cannot have a similar structure in which the $-\text{N}^+\text{N}^-$ group is firmly held anti- to the larger group, for since the migrant group becomes bonded to the nitrogen atom at the face remote from that from which the $\text{H}_2$ molecule departs, this would imply that the larger group always migrates. Table II shows at once that this is not so; with 2-nitro, 3-nitro, 2-methoxy, and 2-aminofluorenols it is largely the unsubstituted ring that migrates. Also scale models show that with these substituents in positions 2- or 3- there is no steric hindrance of the $-\text{NH}^+\text{N}^-$ group about the $\text{C}_9\text{N}$ bond. Hence it is concluded that there is substantially free rotation and that the $-\text{N}^+\text{N}^-$ group is readily able to take up a configuration anti-to the migrant group.

It has been shown by Campbell and Kenyon (J. Chem. Soc., 1946, 25) that the Schmidt reaction with (+)-$\alpha$-phenylpropionic acid proceeds with a high retention of asymmetry, and, probably, of configuration, indicating intramolecular exchange of bonding at one face of the carbon atom. It is therefore highly probable that the rearrangement of the protonated azide is also an intramolecular process; it is
visualized as occurring in the following manner:

As the \( \text{N}_2 \) molecule recedes, ring A is continuously bonded to the CH-\( \text{NH} \) fragment, the four electrons originally constituting the nitrogen lone pair and the A-CH bond finally appearing as the A-\( \text{NH} \) bond and the \( \pi \) electrons of the CH-\( \text{NH} \) bond. Thus the migrant group (ring A) behaves as an electron donor, and hence it is concluded that the most important factor influencing the migratory aptitude of the ring is its capacity for electron release at the point of attachment to \( \text{C}_9 \).

The substituents, \( X \), in the protonated acid (VII) exhibit their permanent inductive and mesomeric (I, M) electron displacements; in addition they may exert the +E (electromeric) effect during the rearrangement, but the -E effect does not take part since the reaction is one requiring electron release. Position 3- is para to the point of attachment of ring A to \( \text{C}_9 \) (this is abbreviated to the symbol A-\( \text{C}_9 \) hereafter). Hence both inductive and tautomeric (T=E and/or M) electron displacements in substituents in position 3- are strongly
relayed to A-C$_9$ by the conjugated system of ring A. Position 2- is *meta* to A-C$_9$; hence only the I effects of substituents in position 2- are relayed, by induction through the carbon atoms of the ring, to A-C$_9$ since there is no conjugative route to this position. There is, however, such a route (XI) to the point of attachment of ring B to C$_9$ and it is considered that this route is important in relaying T effects of substituents in the 2-position to ring B.

\[ \text{(VII)} \quad \text{(XI)} \]

It is well established that T effects of *para* substituents in diphenyls are relayed to the $p'$ position of the other ring by a mechanism of this kind (Berliner and Bloxam, *J. Am. Chem. Soc.*, 1951, 73, 1479).

Table III shows the strengths of some $m$- and $p$-substituted benzoic acids as measured by their dissociation constants (Mippy, *Chem. Rev.*, 1939, 25, 151). Since the strengths of these acids give a quantitative measure of the
polarity of the O-H bond, they likewise show quantitatively the various capacities for electron release by the substituents to the point of attachment of the carboxyl group to the benzene ring. Acids having groups capable of electron release are weaker acids than benzoic acid whilst those having groups capable of electron withdrawal are stronger.

Table III

<table>
<thead>
<tr>
<th>Acid</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzoic</td>
<td>6.37 x 10^{-5}</td>
</tr>
<tr>
<td>p-methylbenzoic</td>
<td>5.35</td>
</tr>
<tr>
<td>p-methyl</td>
<td>5.24</td>
</tr>
<tr>
<td>p-methoxy</td>
<td>4.17</td>
</tr>
<tr>
<td>p-methoxy</td>
<td>3.39</td>
</tr>
<tr>
<td>m-nitro</td>
<td>32.1</td>
</tr>
<tr>
<td>p-nitro</td>
<td>37.6</td>
</tr>
</tbody>
</table>

The inductive and hyperconjugative electron release of the methyl group in 3-methylfluoren-9-ol is relayed to A-C⁹, and in accordance with the postulate that it is the ring...
with the greater electron release that migrates from $C_9$ to $N$.

migration of the substituted ring giving 5-methylphenanthridine
is found to occur to an extent greater than 70%.

A nitro group in the 3-position, by virtue of its
very strong $-$I effect, causes a strong electron withdrawal at
$A-C_9$ and therefore it is expected that the unsubstituted ring
will migrate almost exclusively. It is found that this
occurs, with the formation of 6-nitrophenanthridine, to the
extent of 98%.

Since $p$-methoxybenzoic acid is a weaker acid than
benzoic, while $m$-methoxybenzoic acid is stronger, it is
concluded that the $+$M effect outweighs the $-$I effect of the
methoxy group in the former. Hence 3-methoxyfluoren-9-ol
was expected to show electron release at $A-C_9$ with the form-
ation of more 3- than 6-methoxyphenanthridine. Unfortunately
the gross yield of methoxyphenanthridines from this reaction
was so small that not enough material was obtained to make a
quantitative separation practicable.

In considering the effects of substituents in the
3-position it is necessary to remember that inductive effects
control electron release or withdrawal at $A-C_9$ whilst
tautomeric effects are relayed by the conjugative route (XI) to
E-C\(_9\)._ Since \(\pi\)-nitrobenzoic acid is a very much stronger acid than benzoic, the nitro group must exert a very strong \(-I\) effect. Further, since \(\pi\)-nitrobenzoic acid is rather stronger than the \(\pi\)-acid, the nitro group must also possess a \(-X\) effect. The extent to which the latter is relayed to E-C\(_9\) would be expected, from the relative magnitude of these two effects, to be small in comparison with the inductive electron withdrawal at A-C\(_9\). In accordance with this view it is the unsubstituted ring that migrates, yielding 7-nitrophenanthridine (96\%).

In the presence of concentrated sulphuric acid the amino group in 2-aminofluoren-9-ol will exist almost entirely in the form of the ammonium ion which, due to its positive charge, exerts its considerable \(-I\) effect at A-C\(_9\). Hence the unsubstituted ring will again migrate, as is illustrated by the sole formation of 7-aminophenanthridine from this compound.

The strength of \(\pi\)-toluic acid indicates that the methyl group in 2-methylfluoren-9-ol is capable of \(+I\) release at A-C\(_9\). But since \(\pi\)-toluic acid is weaker than the \(\pi\)-acid the methyl group also possesses the property of hypoconjugative electron displacement which, being relayed by route (XI), causes electron release at B-C\(_9\). It is inferred that these two effects are about equal, since the unsubstituted
and substituted rings migrate to approximately the same extent, and 2-methylphenanthridine and 7-methylphenanthridine are formed in the ratio 47:53.

It has already been deduced that the methoxy group exhibits a weak -I effect and a stronger +E displacement. In 2-methoxyfluoren-9-ol the former will cause a slight electron withdrawal at A-C₉ and the latter effect, relayed by route (XI), will give rise to a slight electron release at A-C₉. The unsubstituted group would therefore be expected to migrate preferentially. The actual ratio in which 7-methoxyphenanthridine and 2-methoxyphenanthridine are formed, 67:33, indicates that the unsubstituted ring migrates about twice as readily as the substituted ring.

To sum up, there can be no doubt that the results with 3-nitro- and 3-methylfluoren-9-ols support the hypothesis that electronic effects are the most important factors in determining the migratory aptitudes of groups in this reaction, and that this reaction is one in which the migratory aptitudes of groups increase in the order of their capacity for electron release at the migration centre. The results of the reactions with 2-substituted-fluoren-9-ols, however, are less conclusive for, when the two routes for the relay of, respectively, I and T
effects act in opposition, the deductions drawn have necessarily
to be somewhat arbitrary. It is therefore satisfactory to find
that it is possible to correlate all the above results in an
adequate semi-quantitative manner using the Hammett equation
The Application of Hammett's Equation to the Carbinal Reaction.

Berliner and Blommers (J. Amer. Chem. Soc., 1951, 73, 2479) have shown that the \( pK \) values of diphenyl-4-carboxylic acids, substituted in positions 4' and 3', bear a linear relation to the Hammett \( \sigma \) values of these substituents; the slope of the straight line is \( \rho = 0.37 \). It is reasonable to assume that the strengths of diphenyl-3-carboxylic acids will be influenced in the same way and to the same extent by substituents in the 4' and 3' positions. Further, to a first approximation substituents at the 4 and 5 positions will influence the strengths of diphenyl-3-carboxylic acids in the same way and to the same extent as they do the corresponding benzoic acids. Hence we may employ Hammett's equation to calculate the strengths of these substituted diphenyl-3-carboxylic acids; no data concerning this matter have been published, except the value for diphenyl-3-carboxylic acid itself (Dippy and Lewis, J. Chem. Soc., 1937, 1486). Writing Hammett's equation (see p.p. 12, 13) for the dissociation of these acids we have
\[
\log \left( \frac{K'}{K''_0} \right) = \rho \sigma
\]

where \( \sigma = \log \left( \frac{K}{K_0} \right) \); since \( pK = -\log_{10}K \)

this equation may be written as
\[
pK' = pK''_0 - \rho (pK_0 - pK),
\]

where:

- \( K' \) is the dissociation constant for the substituted diphenyl-2-carboxylic acid;
- \( K''_0 \) is that for diphenyl-2-carboxylic acid itself
  \( (pK''_0 = 3.4507; \text{ Dippy and Lewis, loc. cit.}) \)
- \( K \) is that for the substituted benzoic acid (values are taken from Dippy, Chem. Rev., 1930, 25, 151);
- \( K_0 \) is that for benzoic acid \( (pK_0 = 4.2027; \text{ Dippy, loc. cit.}) \);
- \( \rho \) is a constant which is unity for 4- and 5-substituted diphenyl-2-carboxylic acids and which equals 0.37 for 4'- and 3'-substituted diphenyl-2-carboxylic acids.

Table IV shows values for \( pK' \) calculated by means of this equation.
Table IV

<table>
<thead>
<tr>
<th>Corresponding benzene acid</th>
<th>pK</th>
<th>Diphenyl-2-carboxylic acid</th>
<th>pK'</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-NO₂</td>
<td>3.4248</td>
<td>5-NO₂</td>
<td>2.6818</td>
</tr>
<tr>
<td>3-NO₂</td>
<td>3.4855</td>
<td>4-NO₂</td>
<td>2.7506</td>
</tr>
<tr>
<td>4-Me</td>
<td>4.3726</td>
<td>5-Me</td>
<td>3.6206</td>
</tr>
<tr>
<td>3-Me</td>
<td>4.2710</td>
<td>4-Me</td>
<td>3.5286</td>
</tr>
<tr>
<td>3-OH</td>
<td>4.0678</td>
<td>4'-OH</td>
<td>3.3448</td>
</tr>
<tr>
<td>4-NO₂</td>
<td>as above</td>
<td>4'-NO₂</td>
<td>3.1719</td>
</tr>
<tr>
<td>3-NO₂</td>
<td>&quot; &quot;</td>
<td>3'-NO₂</td>
<td>3.1974</td>
</tr>
<tr>
<td>4-Me</td>
<td>&quot; &quot;</td>
<td>4'-Me</td>
<td>3.5286</td>
</tr>
<tr>
<td>3-Me</td>
<td>&quot; &quot;</td>
<td>3'-Me</td>
<td>3.4952</td>
</tr>
<tr>
<td>4-OH</td>
<td>4.4711</td>
<td>4'-OH</td>
<td>3.5590</td>
</tr>
</tbody>
</table>

It should be noticed that the values of pK' give a quantitative measure of the calculated electron densities at the 2-position, rather than the actual pK values to be expected for these acids. For since the 2-position is an ortho position,
deviations from these values are likely to occur (see p-p. 13, 14): however it is the theoretical electron densities at the 3-position with which we are concerned (see below).

Consider the reaction of a 2- (or 3-) substituted fluoren-9-ol, yielding a mixture of 2- (or 3-) and 7- (or 6-) substituted phenanthridines:

\[
\begin{align*}
\text{Migration of ring A involves rupture of the } C_9-A \text{ bond; the} \\
\text{electron density at the point of attachment of ring A to } C_9 \text{ is} \\
\text{measured approximately by the dissociation constant of the} \\
\text{correspondingly 4- (or 5-) substituted diphenyl-2-carboxylic} \\
\text{acid. Similarly the electron density at the point of attach-} \\
\text{ment of ring B to } C_9, \text{ which is concerned with the migration of} \\
\text{ring B, is given by the dissociation constant of the} \\
\text{correspondingly 4′- (or 3′-) substituted diphenyl-2-carboxylic} \\
\text{acid.}
\end{align*}
\]
The "substituent constant" in the Hammett equation is, in essence, the difference between the logarithms of the electron density at the reaction centre in the substituted and unsubstituted compounds. Therefore migration of ring A is expressed by the equation:

$$\log \left( \frac{k_A}{k_o} \right) = a \log \left( \frac{k_A}{k_o} \right)$$

where $a$ is a constant.

Similarly for ring B:

$$\log \left( \frac{k_B}{k_o} \right) = a \log \left( \frac{k_B}{k_o} \right)$$

whence the unknown rate constant ($k_o$) and dissociation constant ($k_o$) for the "unsubstituted system" may be eliminated by subtraction giving:

$$\log \left( \frac{k_A}{k_B} \right) = a \log k_A - a \log k_B$$

But the ratio of the rate constants ($k_A/k_B$) is the same as the ratio in which the products are formed, hence

$$\log \left( \frac{\text{percentage of product from migration of } A}{\text{percentage of product from migration of } B} \right) = a \left( pK_B - pK_A \right)$$
Table V shows the logarithms of the product ratios and the differences in the $pK$ values for the corresponding diphenyl-3-carboxylic acids derived for the hydrosolic-sulphuric acid reactions with five 2- and 3-substituted fluoren-9-ols. These values are plotted against one another in Diagram IV; the best straight line calculated for the five points by the method of "least squares", has a slope $-2.317$ and an intercept $-0.113$. In view of the number of assumptions which have been made and the semi-quantitative nature of the product ratios, it is considered that this agreement is adequate to establish the simple correlation between the migratory aptitude of a group and its capacity for electron release at the migration origin in the reaction of fluorenols with hydrosolic acid in the presence of sulphuric acid.
<table>
<thead>
<tr>
<th>Corresponding compound</th>
<th>pH value</th>
<th>Difference in pH values</th>
<th>% formed (product)</th>
<th>log_{10} ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-nitrophenol</td>
<td>3.00</td>
<td>0.0156</td>
<td>-1.7949</td>
<td>0.0135</td>
</tr>
<tr>
<td>2-nitrophenol</td>
<td>3.1074</td>
<td>0.0014</td>
<td>-1.7811</td>
<td>0.0125</td>
</tr>
<tr>
<td>2-nitrophenol</td>
<td>3.1710</td>
<td>0.0014</td>
<td>-1.7439</td>
<td>0.0125</td>
</tr>
<tr>
<td>2-nitrophenol</td>
<td>3.4832</td>
<td>0.0014</td>
<td>-1.6867</td>
<td>0.0125</td>
</tr>
<tr>
<td>2-nitrophenol</td>
<td>3.5800</td>
<td>0.0014</td>
<td>-1.6549</td>
<td>0.0125</td>
</tr>
<tr>
<td>2-nitrophenol</td>
<td>3.5900</td>
<td>0.0014</td>
<td>-1.6486</td>
<td>0.0125</td>
</tr>
<tr>
<td>Fluoren-9-one</td>
<td>3.1949</td>
<td>0.95</td>
<td>95</td>
<td>0.0538</td>
</tr>
<tr>
<td>Fluoren-9-one</td>
<td>3.1802</td>
<td>0.96</td>
<td>96</td>
<td>0.0538</td>
</tr>
<tr>
<td>Fluoren-9-one</td>
<td>0.5754</td>
<td>0.53</td>
<td>53</td>
<td>0.0538</td>
</tr>
<tr>
<td>Fluoren-9-one</td>
<td>-0.0060</td>
<td>0.35</td>
<td>35</td>
<td>0.0538</td>
</tr>
<tr>
<td>Fluoren-9-one</td>
<td>-0.2142</td>
<td>0.67</td>
<td>67</td>
<td>0.0538</td>
</tr>
</tbody>
</table>
II The Ketones: a New Proposal Concerning the Nature of the Observed "Geometrical Effect".

Consent has already been made on the unexpected behaviour of 2-nitrofluorenone (p. 62), 3-nitrofluorenone (p. 69), and 2-methoxyfluorenone (p. 54; also see Table II) in the Schmidt reaction. It is most striking that in these nitrofluorenones the substituted ring migrates preferentially whereas just the reverse is true for the nitrofluorenols; this seems to be established beyond doubt in both cases. The fact that with these two nitrofluorenones it is the "sterically larger" group which migrates cannot be considered to confirm Smith's mechanism (p. 10) for the Schmidt reaction with ketones, for scale models show that free rotation of the \(-\text{CH}_2\) group about the \(C_\text{g}^-\text{H}\) bond is in no way hindered by a group of moderate size, such as a nitro group, in the 2- or 3- positions. Indeed Smith has found that with \(n\)-substituted benzophenones, which are comparable to 3-substituted fluorenones, the presence of the substituent has no affect on the relative extent to which the rings migrate, almost equal quantities of the two isomeric amides being formed whatever the nature of the substituent. Moreover, this was also found to be true of the
Schmidt reaction with 2-methoxyfluoronone in which the substituent group is about the same size as a nitro group. On the other hand, simple dependence of the migratory aptitudes of the rings on the electronic character of the substituents is also ruled out since this would lead to the prediction of migration of the unsubstituted ring, as in the case of the corresponding fluorenones.

In order to account for his results, Smith considers that a "geometrical effect" is of primary importance in deciding the relative migratory aptitudes of groups in the Schmidt reaction with ketones (see p.p. 7, 10, and 16–21). In detail this effect is envisaged as occurring by dehydration of the protonated oxime (I) to give two doubly bonded "oxime-like" structures, (II) and (III), which then undergo trans migration (similar to the Beckmann rearrangement with oximes). Hydration of the rearranged products then yields the precursors of the corresponding amides:
Dehydration is presumably affected by the sulphuric acid; it appears, therefore, most improbable that hydration of the rearranged products occurs in the same medium, whence we are led to conclude that this step occurs on dilution of the sulphuric acid solution with water at the end of the reaction. This offers a direct means for testing the validity of Smith's mechanism; for if the sulphuric acid solution is, at the end of the reaction, diluted with a nucleophilic solvent other than water, e.g. methanol, then one would expect the formation of, not the amide, but, in this case, the methyl ether (V) (from the intermediate IV):

\[
\text{R-N=CH}_3 + \text{CH}_3\text{OH} \rightarrow \text{R-N=CH}_2\text{OH} + \text{H}^+
\]  

(V)
For this purpose, the Schmidt reaction with 2-nitrofluorenone was carried out in the usual way, by adding sodium azide to a solution of the ketone in sulphuric acid; at the end of the reaction part of the solution was added to thoroughly dried methanol at 0° and part was added to ice and water. The two products were identical mixtures of 2- and 7-nitrophenanthridones, and no trace of the expected methyl ether was detected in the methanol-treated material. Hence it is deduced that either dehydration and rehydration both occur in the sulphuric acid solution, or, more probably, dehydration of the protonated azide does not in fact take place. The latter conclusion is also favoured from a theoretical point of view: for Smith's mechanism implies that the Schmidt reaction with ketones differs from the very similar reactions with carboxylic acids, olefins, and arylcarbinols, in so far as the rearrangement of the "oxime-like" structure is analogous to the Bechmann rearrangement. Rearrangement of the protonated azide in the ketone reaction as well as in these other reactions, i.e., on the contrary, analogous to the pinaisol and allied rearrangements. Nevertheless Smith's assertion, that a geometrical effect is operative in the course of the ketone reaction, is still true, for his work with p-substituted
bensoprones will allow of no other interpretation.

Inspection of a model of the protonated amide (I) reveals that the hydrogen atom bonded to nitrogen closely approaches the oxygen atom of the -OH group when the -NH-N=N group is pointing towards either of the groups R or R'. It is now suggested that the geometrical effect observed with ketones arises, not out of dehydration to give a rigid doubly-bonded structure, but within the protonated amide itself owing to hydrogen bonding between these hydrogen and oxygen atoms. If the four-membered ring so formed is sufficiently rigid to prevent free rotation of the -NH-N=N group about the C-N bond, then two geometrical isomers are possible:

\[
\begin{align*}
\text{H} & \quad \text{O} \\
\text{N} & \quad \text{N} \quad \text{N} \quad \text{N} \\
\text{R} & \quad \text{C} \quad \text{R'} \\
\text{H} & \quad \text{O} \\
\end{align*}
\]

Trans migration in these two acids leads to separate products, \( R'\cdot CO\cdot NH\cdot R \) and \( R\cdot CO\cdot NH\cdot R' \) respectively; steric considerations concerning the relative stability of the two forms apply in the same way as they do to Smith's oxime-like structures.

Thus the suggestion of a geometrical effect related to rigidity conferred by hydrogen-bonding within the protonated amide provides an alternative explanation for Smith's and for
Sehechter and Kirr's observations on the Schmidt reaction with unsymmetrical ketones, while it avoids the inconsistencies introduced by Smith's mechanism.

Application of this idea to the Schmidt reaction with 2- and 3-nitrofluorenone does not, however, lead to any simple explanation of the results observed with these compounds. If a simple geometrical effect was operative one would expect equal quantities of 2- and 7-, and of 3- and 6-nitrophananthridones; in this respect 3-methoxyfluorenone behaves normally. It is noteworthy that the electrostatic field set up by a nitro group is many times greater in intensity than that of a methoxy group, as may be readily appreciated by comparison of the strengths of the nitro and methoxybenzole acids in Table III (p. 89). Perhaps, therefore, the electrostatic field due to the nitro group in 2- and 3-nitrofluorenone acts in such a way as to stabilise the hydrogen-bonded form of the protonated amide in which the $\text{-N}^+\text{H}=\text{H}$ group is directed away from the substituted ring. The precise details of such a process are not clear; also it might be objected that preferential stabilisation does not occur in $\text{p}$-nitrobenzophenone which was studied by Smith. There are, however, two important differences between the benzophenone and fluorenone systems.
In the latter there is, by virtue of the linkage of the two rings in the $g-g'$ positions, a direct route for the relay of electronic effects from one ring to the other: moreover, the rigidity of the molecule prohibits rotation of the rings about their bonds to the $C_9$ atom. Neither of these considerations applies to the benzosphenone system. Possibly blockage of free rotation of the rings by $g$-substituents in benzosphenone partly accounts for the anomalous behaviour of these ketones in the Schmidt reaction (see p. 19). However, there is no simple or obvious correlation.
The Mechanism of the Schmidt Reaction
with o-Aroylbensoic Acids.

It was mentioned on p. 33 that o-toluoylbensoic acid gave 6-oxo-2-p-tolyl-4:5-benz-1:3-oxazine on reaction, in chloroform solution, with hydrazoic acid in the presence of sulphuric acid. The oxazine was obtained in 88% yield and melted at 155°, in agreement with the melting point (154.5°) recorded by Zentmeyer and Wagner (J. Org. Chem., 1949, 14, 967) for this compound prepared by heating N-toluoylanthranilic acid with acetic anhydride. Its structure was established, in the first instance, by hydrolysis, from the products of which o-toluic acid was obtained in theoretical yield.

Similarly o-benzooylbensoic acid gave 6-oxo-2-phenyl-4:5-benz-1:3-oxazine, of m.p. 123°, in 78% yield: this compound was reported by Zentmeyer and Wagner to melt at 123-124°.

Badger, Howard, and Simons (J. Chem. Soc., 1932, 2649) allowed o-benzooylbensoic acid to react in (i) trichloroacetic acid, and (ii) chloroform solution with hydrazoic acid in the presence of sulphuric acid; the reaction mixtures were finally poured into water. From the reaction in trichloroacetic acid solution N-benzooylanthranilic acid was obtained in 91% yield,
and this result was confirmed by Smith (J. Amer. Chem. Soc., 1954, 76, 431): N-benzoyleanthranilic acid (31%) was also obtained from the reaction in chloroform solution but here the main product was 6-oxo-2-phenyl-4:5-benz-1:3-oxazine (67%). Both Badger et al. and Smith consider that N-benzoyleanthranilic acid arises by the reaction of N-benzoylebenzoinic acid as a substituted benzophenone according to the mechanism proposed for the Schmidt reaction with ketones by Smith (p. 10). They further consider that this result supports this mechanism because it is the larger (o-carboxyphenyl) group which migrates, and they envisage the oxazine as resulting by the subsequent internal dehydration of the acid under the conditions of the reaction.

However, Newman, Kuivila, and Garrett (J. Amer. Chem. Soc., 1945, 67, 704) found that N-benzoylebenzoinic acid in solution in sulphuric acid has a van't Hoff factor of 3.8, in agreement with ionization according to the equation (I)

\[
\text{OCH}_2\text{CO} - \text{Ph}^+ \\
\text{OCH}_2\text{CO} \\
\text{(II)}
\]
Chemical evidence favours the cyclic cation (I) over the alternative ion (II) which would also require a van't Hoff factor of 4. Thos Newman (J. Amer. Chem. Soc., 1942, 64, 2324) observed that considerable methylpseud o-o-benzoyle benzoate (III) is formed when a solution of o-benzoyle benzoic acid in sulphuric acid is poured into methanol: moreover the interaction of (II) with hydrazic acid would lead to 2-aminobenzophenone and not o-benzoyleanthranilic acid as is observed.

It is therefore proposed that the Schmidt reaction with o-benzoyle benzoic acid proceeds via the cation (I) as follows:
This mechanism requires the oxazine (V) to be the initial product of the reaction, whereas N-benzoylanthranilic acid should be formed first according to Badger et al. Attempts were therefore made to confirm that the oxazine is the actual product of the Schmidt reaction.

The Schmidt reaction with o-benzoylbenzoic acid in trichloroacetic acid solution (Badger's method) was repeated, and N-benzoylanthranilic acid was obtained in 78% yield. If, however, the trichloroacetic-sulphuric acid reaction mixture was diluted with chloroform before addition of water, the product was the oxazine (91%). Moreover, the oxazine, submitted to the conditions of the Schmidt reaction in
trichloracetic acid but with the omission of hydrosol acid, gave N-benzoylantrenilic acid (92.5%) whereas the oxazine (93%) was recovered if the trichloracetic-sulphuric acid reaction mixture was diluted with chloroform before addition of water. These last two experiments were repeated, but the mixtures were heated only sufficiently long (one minute at 50°) to ensure homogeneous solutions of the oxazine in the trichloracetic-sulphuric acid mixtures: N-benzoylantrenilic acid (90%) was obtained when the solution was poured into water, but the oxazine (83%) was recovered when the solution was diluted with chloroform before it was shaken with water. The oxazine (90%) was recovered after being allowed to stand overnight with aqueous trichloracetic and sulphuric acids.

These experiments show clearly that the oxazine is the entity present in solution at the end of the Schmidt reaction, and that it becomes hydrolysed on subsequent treatment. Further, this hydrolysis may be largely avoided if the reaction mixture is diluted with chloroform before treatment with water. A possible explanation for this curious fact is that the proton adduct of the oxazine (IV), which is probably the precursor of acid hydrolysis, loses its proton when the dielectric constant of the medium is reduced by the
addition of chloroform, for the oxazine is a very weak base. On the other hand, addition to water of the solution in which the oxazine is largely present as the proton adduct (V) causes rapid hydrolysis of the latter to N-benzoxylanthrenilic acid.

When N-benzoxylanthrenilic acid, dissolved in chloroform or trichloracetic acid, was treated with sulphuric acid, as in the Schmidt reaction procedures, ring closure occurred; the oxazine was obtained from the former solution in 80% yield, and from the latter solvent (68%) provided that chloroform was added as a diluent. Thus the possibility cannot be excluded that N-benzoxylanthrenilic acid is initially formed in the Schmidt reaction as presumed by Badger et al. and by Smith and is followed by ring closure of the acid under the conditions of the reaction. However in view of the evidence of Newman et al. for the cyclic structure of the cation (I) it is concluded that the mechanism now proposed is the more likely.

If this mechanism is correct, o-arylsulphonic acids do not behave like simple ketones in the Schmidt reaction, and the steric considerations presumably do not apply. Also if electron release were important, migration of the aryl group would be preferred. It is therefore thought that a strong tendency to ring expansion is the deciding factor in these reactions.
Summary and Conclusions.

The following eleven fluorenols have been prepared by reduction of the corresponding ketones or by the Grignard reaction with fluorenones: 3- and 2-methyl-, 3- and 2-methoxy-, 2-hydroxy-, 5- and 2-nitro-, 3-amino-, 9-methyl-, 9-benzyl-, and 9-phenylfluoren-9-ols. The first six of these are new and have been characterised by the preparation of their 9-acetoxy derivatives; a new form of 9-phenylfluoren-9-ol of m.p. 85° (literature 107°) has been obtained. 9-Chloro-2-methoxy-, 9-chloro-9- and 3-nitrofluorenes have been prepared, and on reaction with sodium azide the first two give, respectively, 9-azido-2-methoxy- and 9-imino-2-nitrofluorenes. The synthesis of 3-nitrofluorenone due to Ray and Barrick has been revised.

The reactions of these carbincols, of 2- and 3-nitro- and 2-methoxyfluorenes, and of 9-benzylidenefluorene with hydroscopic sulphuric acid, also the acid-catalysed decomposition of 9-azido-2-methoxyfluorene, have been studied.

Both 9-benzylfluoren-9-ol and 9-benzylidenefluorene give 9-benzylphenanthridine in similar yields; this is further proof of the ionic mechanism of the hydroscopic sulphuric acid reaction. The fact, that the ratios of 2- and 7-methoxyphenanthridines from both the reaction with
2-methoxyfluoren-9-ol and from the acid-catalysed decomposition of 9-azido-2-methoxyfluoren are identical, constitutes evidence that it is the intermediary proton adduct of the azide which undergoes rearrangement. The isomeric phenanthridines from the reactions with the 2- and 3-substituted fluorenols have been separated and the product ratios have been determined. It is demonstrated that these ratios, which give the relative rates of migration of the substituted and unsubstituted rings from bonding to carbon to bonding with nitrogen, are simply related, in a semi-quantitative manner by Hammett's equation, to the capacities of the substituents for electron release, the migration being favoured by increased electron availability. These observations conform with the mechanism proposed by Arons and Wealoy.

On demethylation, 2- and 7-methoxyphenanthridines give the 2- and 7-hydroxy compounds, the latter being identical with that obtained by heating an aqueous solution of phenanthridine-7-diazonium sulphate. 7-Nitrophenanthridine of m.p. 180° is obtained from 2-nitrofluoren-9-ol, and it has been orientated by conversion into the known 7-amino-, 7-ethoxycarbonylamino-, and 6-chloro-7-nitrophenanthridines, and 7-nitrophenanthridone: the nitrophenanthridine, m.p. 158°, reported as the 7-isomer
by Caldwell and Walla has been shown to be a 1:1 complex of the 2- and 7-isomers. 3-Nitrofluoren-9-ol gives 6-nitrophenanthridine, which has been orientated by reduction to the known 6-amino compound; 6-hydroxy- and 9-chloro-6-nitrophenanthridines, and 6-nitrophenanthridone have been prepared from it. The following syntheses have been effected: - 2-nitro- and 2:7-dinitrophenanthridines from the corresponding 9-chloro compounds via the tolylsulphonhydrazides, and 5-nitrophenanthridine by the cyclisation of 2-formamido-5-nitrodiphenyl.

The isomeric phenanthridones from the hydrazoic-sulphuric acid reaction with the fluorenones have also been separated, but here no simple correlation between product ratios and the electronic or steric influences of substituents is evident. The literature of the Schmidt reaction with ketones has been examined critically, and it is suggested that the observed "geometrical effect" is better accounted for by the postulation of hydrogen bonding within the amide than by dehydration to give a doubly bonded structure, as proposed by Smith.

The Schmidt reaction with p-toluylbenzoic acid yields 6-oxo-2-p-tolyl-4:5-benz-1:3-oxazine, and p-benzoylbenzoic acid gives the 2-phenyl analogue. It has been shown that the
mechanism of this reaction is not that of a simple ketone, as supposed by Badger et al., but probably involves ring expansion of a cyclic cation. Evidence, both experimental and theoretical, for this view is presented.
Experimental Section.

Preparations taken directly from the literature without modification are headed with the name of the compound followed by the literature reference. In all other cases relevant references are placed in the text.

All melting-points are corrected and were determined with an electrically heated block.
The Preparation of Substituted Fluorenes.

I. The preparation of derivatives from fluorene.


Fluorene (60 g.), dissolved in glacial acetic acid (500 ml.), was nitrated with concentrated nitric acid (90 ml.) during 15 minutes at 50°. The reaction mixture was then heated to 75° during 40 minutes, and allowed to cool to room temperature (2 hours); the solid was collected and recrystallised from glacial acetic acid (300 ml.). 2-Nitrofluorene separated as cream-coloured needles (48 g.), m.p. 157-158°. (Idem, loc. cit., m.p. 157°)

2-Nitrofluorenone. (Diels, Ber., 1901, 34, 1760).

2-Nitrofluorenone (30 g.), powdered sodium dichromate (100 g.), and glacial acetic acid (300 ml.) were heated together under reflux for one hour. The reaction mixture was cooled, the solid was filtered off, washed with water and dried. Crystallisation from boiling xylene (300 ml.) gave the ketone in yellow leaflets (27 g.), m.p. 220-221°. (Idem, loc. cit., m.p. 222-223°).

Aluminium turnings (9 g.) were dissolved in dry isopropanol (110 ml.) by heating under reflux for several hours with traces of mercuric chloride and iodine. To this solution were added dry benzene (225 ml.) and 2-nitrofluorenone (22.4 g.); the ketone gradually dissolved on boiling, and after about 30 minutes the orange solution was poured into ice-cold 3N-sulphuric acid (500 ml.). After thorough shaking of the mixture the benzene layer was separated, washed with sodium hydrogen carbonate solution, dried over anhydrous sodium sulphate, and evaporated. Crystallisation of the crude brown solid from a mixture of benzene (150 ml.) and light petroleum (b.p. 60-80°C, 75 ml.) yielded large yellow prisms of 2-nitrofluoren-9-ol (18.7 g.), m.p. 128-129°C. (Idem, loc. cit., m.p. 128-129°C).

2,7-Dinitrofluorene. (Courtois, Ann. Chim., 1936 [10], 14, 83).

Fluorene (100 g.) was added in small portions to a mixture of fuming nitric acid (d 1.5, 500 ml.) and glacial acetic acid (500 ml.) during 65 minutes, so that the temperature did not rise above 50°C; the yellow suspension was left 13 hours at room temperature. The precipitate was collected,
washed with water, and extracted by boiling with glacial acetic acid (1.2 l.). The product which separated from the acetic acid gave, after recrystallisation from hot nitrobenzene (500 ml.), 2:7-dinitrofluorene (55 g.) as buff needles which decomposed but did not melt sharply below 340°. (Idem, loc. cit., m.p. 334°).

2:7-Dinitrofluorenone.

2:7-Dinitrofluorene (45 g.), glacial acetic acid (1.5 l.), and chromium trioxide (36 g.) were heated together under reflux for 75 minutes and allowed to cool. The solid which separated was collected, washed with water, and crystallised from hot pyridine (700 ml.), yielding pale yellow needles of 2:7-dinitrofluorenone (30 g.), m.p. 295-296°. (Schultz, Annalen, 1880, 205, 104, records m.p. 291-292°, but gives no experimental details).

2:7-Dinitrofluorenone (1.75 g.) was recovered after boiling for one hour with a solution of aluminium isopropanoxide (from aluminium turnings (0.5 g.) and 30 ml. of isopropanol). In a second experiment, in which pyridine was added, the product was very dark but consisted largely of the dinitrofluorenone.
2-Aminofluorenone.

2-Nitrofluorenone (100 g.), hydrated stannous chloride (400 g.), concentrated hydrochloric acid (400 ml.), and ethanol (96%, 800 ml.) were boiled together under reflux for six hours, and then cooled. The insoluble tin complex was collected, and decomposed with an excess of 2N-sodium hydroxide. Crystallisation of the base from hot xylene gave permanganate-coloured needles of 2-aminofluorenone (68 g.), m.p. 156°.

Diels (loc. cit.) who used ammonium sulphide as the reducing agent, records m.p. 180°.

2-Hydroxyfluorenone. (Diels, Ber., 1901, 34, 1760).

The clear solution of 2-aminofluorenone hydrochloride, formed by boiling the base (66 g.) with water (2.3 l.) containing concentrated hydrochloric acid (170 ml.), was rapidly cooled to 50° with vigorous stirring, and the yellow suspension dianisodised at this temperature with a solution of sodium nitrite (26.4 g.) in water (100 ml.) during 15 minutes. After filtration from a small amount of tar, the solution was cooled to 0° and kept in the refrigerator overnight. Fluorenone-2-diacsonium chloride, which separated in yellow leaflets, was collected,
washed with a little cold water and divided into three equal portions, each of which was treated as follows. The salt was suspended in water (1.5 l.) which was then boiled gently for 45 minutes; nitrogen was evolved and flocculent red solid separated. These solids were collected together on the same filter, washed with water, and dried, yielding 2-hydroxyfluorenone (61 g.), m.p. 206-208°. (Idem, loc. cit., m.p. 206-207°).

2-Methoxyfluorenone. (Werner and Gross, Annalen, 1902, 322, 169).

The deep red solution of 2-hydroxyfluorenone (55 g.) in 2.5N-sodium hydroxide (200 ml.) was shaken for five hours with dimethyl sulphate (50 ml.). The colour was discharged with the separation of an orange solid which was filtered off and washed with water. It was dried and gave 2-methoxyfluorenone (53.5 g.), m.p. 75-76°; this m.p. was raised only one degree, with considerable loss of material, by recrystallisation from ethanol. (Idem, loc. cit., m.p. 77-78° after recrystallisation from ethanol).
2-Aminofluoren-9-ol.

The deep red coloration formed on the addition of 2-aminofluorenone (16 g.) to a solution of aluminium turnings (6 g.) in dry iso-propanol (225 ml.) at 70° was completely discharged after boiling for five minutes. The colourless solution gave, on pouring into ice-cold 2.5N-sodium hydroxide (1 l.), a pale yellow solid which was purified by reprecipitation from a filtered solution in N-hydrochloric acid and by subsequent crystallisation of the base from ethanol (600 ml.). 2-Aminofluoren-9-ol formed silvery leaflets (11 g.), m.p. 197-198°. Diels (Ber., 1901, 34, 1767) obtained this compound, m.p. 196°, by reduction of 2-nitrofluorenone with zinc dust.

2-Hydroxyfluoren-9-ol.

2-Hydroxyfluorenone (2.0 g.) was heated under reflux with a solution of aluminium iso-propoxide, from aluminium turnings (0.85 g.) and iso-propanol (25 ml.); after 45 minutes the solution, originally red, had become yellow, and was poured into ice-cold N-sulphuric acid (200 ml.). The precipitate, after reprecipitation from a filtered solution in 2N-sodium hydroxide, and subsequent crystallisation from glacial acetic acid, gave golden-yellow needles of 2-hydroxyfluoren-9-ol (1.0 g.)
m.p. 188-189°. (Found: C, 78.5; H, 5.15. C₁₃H₁₀O₂ requires C, 78.75; H, 5.1%).

2:9-Diacetoxyfluorene.

2-Hydroxyfluoren-9-ol (0.15 g.), dry pyridine (2.5 ml.), and acetic anhydride (0.5 ml.) were heated together on the steam-bath for 4 hours and left overnight. On pouring the solution into water there separated a pale buff solid which was collected and recrystallised from 50% aqueous ethanol (4 ml.).

2:9-Diacetoxyfluorene formed almost colourless prisms (0.1 g.), m.p. 106°. (Found: C, 72.35; H, 4.95. C₁₇H₁₄O₄ requires C, 72.35; H, 5.0%).

2-Methoxyfluoren-9-ol.

2-Methoxyfluorenone (40 g., m.p. 76-78°) was boiled under reflux for two hours with a solution of aluminium iso-propoxide, from aluminium turnings (15 g.) and iso-propanol (450 ml.), and poured into ice-cold H₂SO₄ acid (3 l.). The buff precipitate was collected, dried, dissolved in hot benzene (400 ml.), and the solution boiled with activated charcoal (1 g.). After filtration the hot solution deposited large, pale buff prisms of
2-methoxyfluoren-9-ol (28.5 g.), m.p. 160°. (Found: C, 79.4; H, 5.95. \(\text{C}_{14}\text{H}_{12}\text{O}\) requires C, 79.25; H, 5.7%).

9-Acetoxy-2-methoxyfluorene.

2-Methoxyfluoren-9-ol (1.5 g.), acetic anhydride (1 ml.), and dry pyridine (5 ml.) were heated on the steam bath for 90 minutes, cooled, and poured into water. The precipitate was crystallized from ethanol yielding 9-acetoxy-2-methoxyfluorene (1.6 g.) as large orange tablets, m.p. 82-83°. (Found: C, 75.75; H, 5.8. \(\text{C}_{16}\text{H}_{14}\text{O}\) requires C, 75.6; H, 5.65%).

9-Chloro-2-methoxyfluorene.

2-Methoxyfluoren-9-ol (10 g.) was warmed with thionyl chloride (50 ml.). When evolution of hydrogen chloride was complete, the excess of thionyl chloride was removed by distillation in vacuo. The residue, on crystallization from light petroleum (b.p. 40-60°) gave yellow platelets of 9-chloro-2-methoxyfluorene (8.0 g.), m.p. 98.5-99.5°. (Found: C, 72.6; H, 4.85; Cl, 15.25. \(\text{C}_{14}\text{H}_{11}\text{OCl}\) requires C, 72.9; H, 4.8; Cl, 15.4%).
9-Chloro-2-nitrofluorene.

9-Nitrofluoren-9-ol (15.2 g.) was warmed with thiouyl chloride until evolution of hydrogen chloride was complete. After the removal of the excess of thiouyl chloride by distillation in vacuo, the crude material was crystallised from benzene, giving 9-chloro-2-nitrofluorene (10.5 g.) as yellow columns, m.p. 141°. (Found: C, 65.6; H, 3.25; N, 5.4; Cl, 14.45. C₁₅H₁₀N₂Cl requires C, 65.55; H, 3.3; N, 5.7; Cl, 14.45%)

9-Methylfluoren-9-ol.

A solution of methyl magnesium iodide was prepared by allowing methyl iodide (3.7 ml.) to react with magnesium turnings (1.4 g.) under absolute diethyl ether (40 ml.). To this solution was added, with stirring, a solution of fluorenone (8 g.) in a mixture of ether (20 ml.) and benzene (20 ml.) at such a rate that gentle refluxing was maintained (30 minutes). After a further hour on the steam bath, the cooled reaction mixture was decomposed with a mixture of ice (200 g.) and ammonium chloride (30 g.), more benzene being added to dissolve the solid that separated. From the organic layer was obtained, on concentration to 50 ml. and cooling, colourless needles of
9-methylfluoren-9-ol (7.2 g.), m.p. 175°. Ullmann (Ber., 1903, 36, 4107) obtained this compound, m.p. 174.5°, by a similar method, in which the ketone was added as a solid.

9-Benzylfluoren-9-ol.

To a stirred solution of benzyl magnesium chloride, from magnesium turnings (0.54 g.), benzyl chloride (3.8 ml.), and ether (25 ml.), was added, dropwise, a solution of fluorenone (8 g.) in a mixture of benzene (20 ml.) and ether (15 ml.). A vigorous reaction ensued with the separation of a brown solid which, after a further 30 minutes on the steam bath, was filtered off and decomposed by gradual addition to ice-cold 0.25N-hydrochloric acid (300 ml.). The yellow gum was dissolved in benzene, the solution was dried over anhydrous sodium sulphate, and concentrated to 20 ml. After the addition of light petroleum (b.p. 40-60°, 40 ml.) large colourless tablets of 9-benzylfluoren-9-ol (2.7 g.), m.p. 140-141°, separated slowly on standing. (Ibid. loc. cit., m.p. 139°).

9-Phenylfluoren-9-ol.

(i) Modified method.—To a stirred solution of phenyl magnesium bromide, from magnesium turnings (1.5 g.),
bromobenzene (6.6 ml.), and ether (40 ml.), was added a solution of fluorenone (10 g.) in a mixture of benzene (20 ml.) and ether (20 ml.) during 30 minutes; the solution became green and a grey solid separated. After a further hour on the steam bath the reaction mixture was added to a mixture of ice (200 g.) and ammonium chloride (50 g.). The benzene-ether solution was dried over anhydrous sodium sulphate and concentrated to 30 ml. Light petroleum (b.p. 40-60°, 100 ml.) was added and after an interval there separated colourless rhombs (11.1 g.), m.p. 73-75°. This compound (2.00 g.) lost solvent when kept at 120°, constant weight (1.74 g.) being attained after 30 minutes; the resulting colourless melt solidified on cooling, yielding a crystalline mass of 9-phenylfluoren-9-ol, m.p. 85°. (Found: C, 88.0; H, 5.4. Calc. for C_{19}H_{14}: C, 88.35; H, 5.45%).

This compound, on recrystallisation from benzene, gave rhombs, m.p. 74-75°, alone or when mixed with the substance, m.p. 73-75°, above. On recrystallisation from carbon tetrachloride, the compound, m.p. 85°, gave large prisms m.p. 80-84°, which effloresced on standing in the air; after 24 hours the white powder again melted at 85°, alone or in admixture with the analysed specimen.
(11) Using the method of Ullmann and v. Wursterberger (Ber., 1904, 37, 75).—To the stirred Grignard reagent, from magnesium turnings (2 g.), bromobenzene (11.6 ml.), and ether (28 ml.), was added finely powdered fluorenone (10 g.) in small portions during one hour. The green liquid, containing grey solid, was stirred 30 minutes at room temperature, and a further 30 minutes on the steam bath. After cooling, the solid was collected, washed with dry ether and decomposed by addition to cold H-sulphuric acid (300 ml.). The oily suspension was raised to the boil, then kept at room temperature overnight, yielding a white crystalline solid which was collected, washed with water, and dried in the air. Recrystallisation from light petroleum (b.p. 60-80°, 100 ml.) containing a little benzene gave rhombs (9.9 g.), m.p. 75° alone or when mixed with the compound of this melting point obtained by the modified method above. A specimen of this substance (9.9 g., m.p. 75°) after complete removal of solvent by heating at 120° for one hour melted at 85-86° alone or when mixed with the analysed specimen.

Ullmann and v. Wursterberger (loc. cit.) obtained 9-phenylfluoren-9-ol, m.p. 107°, which, recrystallised from carbon tetrachloride, formed solvated crystals, m.p. 85-88°;
they also obtained a similar solvated substance from benzene (m.p. unstated).

9-Chloro-9-phenylfluorene.

Phosphorus pentachloride (2.2 g.) was added to a solution of 9-phenylfluoren-9-ol (2.6 g., m.p. 85°) in dry benzene (25 ml.): after 10 minutes the solution was boiled under reflux for 5 minutes. The cooled, red solution was shaken with ice and water (100 g.), the benzene layer washed with ice water, dried over anhydrous sodium sulphate, and evaporated to dryness. The residual oil gave, on cooling, a waxy crystalline mass (2.8 g.), m.p. ca. 70°, which, on recrystallisation from a small volume of light petroleum (b.p. 40-60°), yielded large colourless tablets of 9-chloro-9-phenylfluorene (0.5 g., 18%), m.p. 79°.

Ullmann and v. Wurstemberger (loc. cit.) obtained 9-chloro-9-phenylfluorene, m.p. 78-79°, by this method from the carbinal, m.p. 107°, in unstated, but apparently poor, yield. Williamson, Anderson, and Watts (J. Amer. Chem. Soc., 1943, 65, 49) obtained this chloro-compound (38%), m.p. 78.2-78.7°, by the action of thiocynyl chloride on an ethereal solution of the carbinal of m.p. 107°.
9-Benzyldienefluorene. (Thiele, Ber., 1900, 33, 652).

Sodium (4 g.) was dissolved in absolute ethanol (200 ml.) and a hot solution of fluorene (20 g.) and bensaldehyde (12 ml.) in absolute ethanol (300 ml.) was added. After filtration from a little solid that separated on cooling, the solution was set aside in an air-tight flask. After about three weeks at room temperature the crude material was filtered off and recrystallised from ethanol, yielding 9-benzyldienefluorene (6.5 g.) as compact yellow prisms, m.p. 75°. (Idem, loc. cit., m.p. 75°).


Sodium (2 g.) was dissolved in absolute ethanol (250 ml.) and the solution was heated under reflux for 30 minutes with a solution of 2-nitrofluorene (10.5 g.) and bensaldehyde (5 ml.) also in absolute ethanol (600 ml.). The solution became red, and after standing at room temperature overnight the dark orange crystalline precipitate was collected and recrystallised from hot glacial acetic acid (100 ml.). 9-Benzyldiene-2-nitrofluorene separated as orange needles (6.5 g.), m.p. 147-149°. (Idem, loc. cit., m.p. 148.5-149.5°).
II. The preparation of 3-nitrofluoren-2-ol.


2-Aminodiphenyl (86 g.) was treated with p-tolylsulphonyl chloride (100 g.) in dry pyridine (300 ml.) at 100° during 30 minutes. The crude compound obtained on pouring the reaction mixture into cold dilute sulphuric acid gave, after recrystallisation from ethanol, colourless prisms of 2-p-tolylsulphonamidodiphenyl (140 g., 87%), m.p. 98-100°. (Idem, loc. cit., 84%, m.p. 98-99°).


A suspension of 2-p-tolylsulphonamidodiphenyl (200 g.) in water (2 l.) and concentrated nitric acid (200 ml.) was stirred at 100° for 9 hours, the yellow oil becoming converted into a floeculent orange solid after several hours. This solid was collected and crystallised from glacial acetic acid (750 ml.), yielding pale orange needles of 5-nitro-2-p-tolylsulphonamidodiphenyl (160 g., 79%), m.p. 168-169°. (Idem, loc. cit., m.p. 160°).
The procedure of Ray and Barrick (loc. cit.) was also tried. A suspension of the sulphonamide (78 g.) in glacial acetic acid (156 ml.) was stirred with fuming nitric acid (1.5, 19.5 ml.) while the temperature was gradually raised. When the temperature of the mixture reached 70°C a reaction of explosive violence occurred. In a second experiment on one-third the scale, the reaction was again violent, as it also was in a third experiment in which the following quantities were used: sulphonamide (20 g.), fuming nitric acid (1.5, 2.5 ml.), concentrated nitric acid (1.42, 2.5 ml.), and glacial acetic acid (40 ml.). The products from these last two experiments were solids, m.p. 150-180°C, from which no pure compound was isolated.

2-Amino-5-nitrodiphenyl. (Ray and Barrick, loc. cit.)

5-Nitro-2-p-tolylsulphonamidodiphenyl (570 g.) was added with stirring to concentrated sulphuric acid (1.4 l.) at room temperature. After one hour the red solution was added dropwise to ice (3 kg.), the yellowish brown precipitate was collected, washed, dried, and recrystallised from ethanol (1.5 l.); it yielded 2-amino-5-nitrodiphenyl (240 g., 72.5%), m.p. 123-124°C. A second recrystallisation gave large brown
needles, bright yellow when powdered, m.p. 125° (Idem, loc. cit., m.p. 125°).

2-Cyano-5-nitrodiphenyl. (Idem, loc. cit.).

Finely divided 2-amino-5-nitrodiphenyl (120 g.) formed a grey suspension in concentrated hydrochloric acid (600 ml.). This suspension was diazotised at -15° to -5° during two hours with a solution of sodium nitrite (48 g.) in water (180 ml.), the excess of nitrous acid being subsequently decomposed by the portionwise addition of urea (5 g.). Meanwhile a solution of sodium cuprocyanide was prepared as follows.——To a solution of hydrated cupric sulphate (240 g.) and sodium chloride (62.6 g.) in water (700 ml.) was added a solution of sodium metabisulphite (50.4 g.) and sodium hydroxide (33.5 g.) in water (370 ml.) and the white precipitate was allowed to settle. This precipitate was washed free from cupric ions by repeated decantation with water; it was suspended in water (400 ml.) and a solution of sodium cyanide (125 g.) in water (250 ml.) was added with stirring and cooling, giving an almost colourless solution. Addition of the diazotised solution was made at 5° to 10° during 3 hours with efficient stirring, sodium carbonate (350 g.) being added in seven equal portions at regular
intervals to keep the reaction mixture alkaline throughout. It was heated to 90° during one hour, and maintained at this temperature two hours longer; the fawn solid which separated was collected, washed, dried, and crystallised from benzene.

From this preparation and an exactly similar one using 100 g. of the amino-compound, was obtained 2-cyano-5-nitrodiphenyl (120 g., 52%), brown needles, m.p. 133-135°. (Idem. loc. cit., m.p. 134°).

5-Nitrodiphenyl-2-carboxylic acid. (Jones and Breker, U. S. P., 1, 975, 940).

2-Cyano-5-nitrodiphenyl (45.5 g.), dissolved in a mixture of concentrated sulphuric acid (540 ml.), glacial acetic acid (670 ml.), and water (450 ml.), was heated under reflux for 6 hours. The brown crystalline precipitate, formed on diluting the solution with water (2 l.) and cooling, was filtered off and dissolved in N-sodium hydroxide (300 ml.). The solution was boiled with charcoal, filtered and acidified, and the precipitate collected and dried. From a total of 117.5 g. of the nitrile was obtained, by this procedure, impure 5-nitrodiphenyl-2-carboxylic acid (99.5 g.) which after two recrystallisations from 50% aqueous ethanol (500 ml.) formed
pale buff leaflets (89 g., 70%), m.p. 180°. (Method of Jones and Breker, loc. cit.; Ray and Barrick, J. Amer. Chem. Soc., 1948, 70, 1463 record m.p. 180°).

3-Nitrofluorenone. (Ray and Barrick, loc. cit.).

5-Nitrodiphenyl-2-carboxylic acid (44.5 g.) was added to concentrated sulphuric acid at 95° with stirring, and after heating at 100° for 15 minutes the crimson solution was poured on to ice (2.5 kg.). The slimy yellow solid from this and a similar preparation was suspended in 2N-sodium hydroxide, filtered off, washed with water, and dried. Extraction with boiling glacial acetic acid (4 l.) left an insoluble yellow substance (17 g.), m.p. above 230°, and from the solution was recovered small yellow needles of 3-nitrofluorenone (60.6 g., 72%), m.p. 235°. Recrystallisation of a specimen from glacial acetic acid, from pyridine, and from ethanol, did not raise this m.p. (Idem, loc. cit., m.p. 235–236°, 239–240° corrected; see also Rum, Schofield and Theobald, J., 1952, 2797, m.p. 239–235° uncorrected).
3-Nitrofluoren-9-ol.

To a solution of aluminium iso-propanol, formed by dissolving aluminium turnings (8 g.) in dry iso-propanol (100 ml.), was added a suspension of 3-nitrofluorenone (20 g.) in dry benzene (200 ml.) and the mixture was boiled under reflux for 30 minutes. The ketone dissolved giving a pink solution, which, after cooling, was poured into 3N-sulphuric acid (300 ml.) containing ice (300 g.) and shaken vigorously. A solid separated; from it and the benzene solution there was obtained 3-nitrofluoren-9-ol as colourless, silky needles (17.3 g., 88%), m.p. 154-155°. (Found: C, 68.45; H, 4.1; N, 6.2.

C13H9O3N requires C, 68.7; H, 4.0; N, 6.2%.

9-Acetoxy-3-nitrofluorenene.

3-Nitrofluoren-9-ol (1.0 g.) was heated under reflux for 5 hours with a mixture of acetic anhydride (20 ml.) and glacial acetic acid (20 ml.). Next day the yellow solution was poured into water, and the precipitate was collected and crystallised from ethanol (30 ml.). 9-Acetoxy-3-nitrofluorenene separated as pale yellow needles (0.9 g.), m.p. 130°. (Found: C, 66.95; H, 3.85; N, 5.45. C15H11O4N requires, C, 66.9; H, 4.1; N, 5.2%).
3-Chloro-5-nitrofluorene.

3-Nitrofluoren-9-ol (1.8 g.) was warmed with thionyl chloride until gas evolution was complete. The excess of thionyl chloride was removed by distillation in vacuo and the crude product was crystallized from benzene, yielding colourless needles of 3-chloro-5-nitrofluorene (0.55 g.), m.p. 150-151°. (Found: C, 63.6; H, 3.3; Cl, 14.9. \( C_{13}H_{9}Cl_{2}O \) requires C, 63.55; H, 3.3; Cl, 14.46%).

3-Aminofluorenone.

3-Nitrofluorenone (5 g.), hydrated stannous chloride (20 g.), concentrated hydrochloric acid (30 ml.), and ethanol (15 ml.) were boiled together under reflux for 3 hours, and then cooled. The yellow insoluble tin complex was collected and decomposed by suspending it in an excess of 2N-sodium hydroxide. Crystallisation of the base (4.8 g.) from benzene (200 ml.) yielded 3-aminofluorenone (3.2 g.), m.p. 158-159°, as bright yellow, felted needles.

Bardout (Anales assoc. quím. Argentina, 19, 117), who used sodium sulphide as the reducing agent, records m.p. 159°.
III. The preparation of 2-methylfluoren-2-ol.


A mixture of p-toluidine (100 g.), benzoin (50 g.), and concentrated hydrochloric acid (12 ml.) was heated for one hour in a flask fitted with a short air-condenser so that most of the water evolved boiled off, but the amine was returned. After being cooled, the pasty mass was mixed with ether (500 ml.) and shaken twice with 8-hydrochloric acid and once with N-sodium hydroxide; the yellow solution was washed with water and dried over anhydrous sodium sulphate. The crude yellow solid obtained on evaporation of the ether was recrystallised from ethanol, from which separated almost colourless needles of 5-methyl-2:3-diphenylindole (49.5 g.), m.p. 155-156°. (Idem, loc. cit., m.p. 156°).

1-Acetyl-5-methyl-2:3-diphenylindole. (Idem, loc. cit.).

5-Methyl-2:3-diphenylindole (40.5 g.) was heated under reflux with fused potassium acetate (50 g.) and acetic anhydride (250 ml.) for four hours, and the dark brown liquid was added to cold water (1.7 l.) with good stirring. Next day
the brown solid was collected, and recrystallised from glacial acetic acid (350 ml.); 1-acetyl-5-methyl-2:3-diphenylindole (46 g.) formed pale buff needles, m.p. 175-177°. (Idem, loc. cit., m.p. 176°).

2-Amino-5-methylbenzenophene. (Idem, loc. cit.)

Oxidation.—To a stirred suspension of 1-acetyl-5-methyl-2:3-diphenylindole (46 g.) in glacial acetic acid (460 ml.) was added a solution of chromium trioxide (18.5 g.) in water (15 ml.) during 20 minutes with cooling so that the temperature did not rise above 25°. After being stirred for 3 hours at room temperature, and then in a boiling water bath for 30 minutes, the dark green solution was poured into water (1.5 l.) and the grey gum that separated was extracted with ether (one l.). The ethereal solution was washed with sodium carbonate solution until carbon dioxide was no longer evolved, dried over anhydrous sodium sulphate, and evaporated to dryness. The oxidation product remained as a yellow semi-solid which was not further purified.

Hydrolysis.—The oxidation product was stirred and heated under reflux with a mixture of concentrated sulphuric acid (250 ml.) and water (250 ml.) for 5 hours. The cooled acidic
solution, containing a small amount of crystalline material, was decanted from a black residue into concentrated ammonia solution (q 0.68, 600 ml.) containing ice (one kg.). When the mixture was cold, the orange oil which had separated was extracted with ether. The oil, remaining after the evaporation of the solvent, was thrice boiled with 4N-hydrochloric acid (200 ml. portions) and the extracts were decanted from a small amount of insoluble brown tar. The acidic solution was neutralised with concentrated ammonia solution, the oil was extracted with ether, the ethereal solution was washed with water, and was dried over anhydrous sodium sulphate. Removal of the ether by distillation left an oil which crystallised to give a yellow mass of 2-amino-5-methylbensophenone (32 g.), m.p. 60-61°. (Ibid. loc. cit., m.p. 63°).

2-Methylfluorenone. (Ibid. loc. cit.).

A solution of 2-amino-5-methylbensophenone (32 g.) in water (250 ml.) containing concentrated sulphuric acid (50 ml.) was stirred at 5° while a solution of sodium nitrite (8 g.) in water (10 ml.) was added during 30 minutes. Stirring was continued at 5-10° for 20 minutes longer, the dissoctised solution was raised to the boil during 30 minutes and kept
boiling gently for 15 minutes, when evolution of nitrogen was complete. The red oil which separated was cooled and extracted with ether; the ethereal solution was washed three times with 3N-potassium hydroxide (70 ml. portions) and with water, dried, and evaporated to dryness. The residual red oil, which solidified on cooling, was boiled repeatedly with small quantities of light petroleum (b.p. 40-60°, total volume 450 ml.) and the extracts were decanted from some amorphous red solid (0.7 g.). Concentration of the yellow solution to 200 ml. yielded large yellow needles of 2-methylfluorenone (9.2 g.), m.p. 91-92°. (Idem, loc. cit., m.p. 92°).

2-Methylfluoren-9-ol.

To a solution of aluminium isoproponide, from aluminium turnings (2 g.) and isopropanol (60 ml.), was added 2-methylfluorenone (5.0 g.) and the orange solution was boiled under reflux for 3 hours. The solution, now almost colourless, was poured into ice cold N-sulphuric acid (400 ml.); the precipitate was collected, dried, and crystallised from light petroleum (b.p. 60-80°, 350 ml.) containing some benzene. There was obtained colourless, silky needles of 2-methylfluoren-9-ol (4.0 g.), m.p. 143-144°. (Found: C, 85.65; H, 6.25.
2-Methylfluoren-9-ol (1.0 g.), acetic anhydride (1 ml.), and dry pyridine (5 ml.) were heated together on the steam-bath for 3 hours. The precipitate formed on pouring the solution into water was crystallised from ethanol, from which separated small colourless needles of 2-acetoxymethylfluorene (1.0 g.), m.p. 114-115°. (Found: C, 80.95; H, 6.2. C_{16}H_{14}O requires C, 80.65; H, 5.9%).
IV. The preparation of 3-methylfluoren-2-ol.

2-p-Toluoylbenzoic acid. (Org. Synth., Coll. Vol. 1, 519). Crashed aluminium chloride (100 g.) was added, in one lot with good stirring, to a suspension of phthalic anhydride (50 g.) in dry, sulphur-free toluene (230 ml.). After the initial reaction had slackened, the temperature was raised to 90° and there maintained for two hours, after which the brown solution no longer evolved hydrogen chloride.

About an equal quantity of ice was introduced cautiously, followed by concentrated hydrochloric acid (75 ml.), and the toluene was removed by distillation in steam. The acidic solution was decanted from the solidified brown oil, which was heated with a solution of sodium carbonate (33 g.) in water (500 ml.) and this solution was filtered from some insoluble material. The sodium carbonate extract gave, on acidification with concentrated hydrochloric acid, a white solid which was collected, washed, dried, and recrystallised twice from toluene. 2-p-Toluoylbenzoic acid formed clusters of pearly plates (38 g.), m.p. 138-139°. (Idem, loc. cit., m.p. 138-139°).
2-Amino-4′-methylbenezophenone (from 2-p-tolnoylbenzoic acid).

Preparation of the amide.——Phosphorus pentachloride (4.5 g.) was added to a solution of 2-p-tolnoylbenzoic acid (4.8 g.) in benzene (30 ml.); the mixture was stirred for a few minutes and then boiled gently under reflux for 20 minutes. The olive-green solution was cooled in ice and dry ammonia gas passed in for 30 minutes. Water (100 ml.) was added to the white suspension, the benzene was removed by distillation in steam, and the solid was collected, washed with water, and dried. The product (4.6 g.) had m.p. 164-167°; it was dissolved in ethanol (30 ml.) and added to boiling water (700 ml.). After filtration from a little brown gum, the cooled solution deposited copious white floccs (3.8 g.), m.p. 165-169°. This m.p. was not appreciably altered by further recrystallisations from water or from chloroform.

Kippenberg (Ber., 1904, 30, 1138) records m.p. 175-176° for the amide, prepared as described above, and crystallised from hot water.

Hofmann reaction with the amide.——A suspension of the amide, m.p. 165-169°, (3.8 g.) in 2.5N sodium hydroxide (11 ml.) was added during 10 minutes to a solution of sodium hypobromite (from bromine (5.5 g.), sodium hydroxide (5.5 g.), and water
(10 ml.) containing 25 g. of ice); the temperature did not rise above 10°. The deep yellow solution was boiled for a few minutes; the brown precipitate, which solidified on cooling, was collected, dissolved in concentrated hydrochloric acid (30 ml.), and the solution was clarified by filtration. Dilution of the solution with water (150 ml.) caused the separation of a brown tar from which the yellow solution was decanted into an excess of 2N-sodium hydroxide. 2-Amino-4'-methylbenzophenone separated as a yellow crystalline solid (1.4 g.), m.p. 94-95°. (Iadem, loc. cit., m.p. 96°).

2-Amino-4'-methylbenzophenone (from N-p-tolylsulphosylanthranilic acid. (Org. Synth., 1952, 32, 8).  

N-p-Tolylsulphosylanthranilic acid (48 g.) was stirred at 50° with sulphur-free toluene (490 ml.) and phosphorus pentachloride (30 g.) for 45 minutes, and the brown solution was cooled to 20° while aluminium chloride (94 g.) was added in four portions during 10 minutes. When the initial reaction had subsided the mixture was heated at 65° for 4 hours. After cooling, ice (200 g.) and concentrated hydrochloric acid (15 ml.) were added cautiously and the toluene was removed by distillation in steam. The residual
brown oil, which mostly crystallised on cooling, was filtered off at the pump, washed with dilute hydrochloric acid, dilute sodium carbonate solution, and water, and sucked as dry as possible.

The crude 4'-methyl-2-p-tolylsulphonamidobenzophenone so obtained was dissolved in concentrated sulphuric acid (400 ml.) and the red solution heated on the steam-bath for 30 minutes. The cooled solution was diluted by the cautious addition of ice (800 g.), and the grey suspension was stirred at 40° with charcoal (5 g.). The pale orange, filtered solution was added to ice (2 kg.) and on making alkaline with concentrated ammonia solution (3 0.98, one l.) a yellow crystalline precipitate of 2-amino-4'-methylbenzophenone (0.6 g.), m.p. 92°, separated. (Idem. loc. cit., m.p. 92-93°).

3-Methylfluoranone. (Ullmann and Mallet, Ber., 1898, 31, 1694).

A solution of 2-amino-4'-methylbenzophenone (10.7 g.) in water (125 ml.) containing concentrated sulphuric acid (25 ml.) was diazotised at 5° with a solution of sodium nitrite (3.5 g.) in water (5 ml.), and the solution was boiled for 15 minutes after standing for a short time. The orange oil that separated was extracted with ether, the etheral
solution was washed three times with 3N-potassium hydroxide and with water, and dried over anhydrous sodium sulphate.

Removal of the ether and crystallisation of the oil from light petroleum (b.p. 40-60°, 100 ml.) gave yellow prisms of 3-methylfluorenene (4.5 g.), m.p. 68°. (Ident. loc. cit., m.p. 66.5°).

3-Methylfluorenene-9-ol.

3-Methylfluorenene (4.5 g.) was heated under reflux with a solution of aluminium iso-propanoxide, from aluminium turnings (2 g.) and iso-propanol (60 ml.), for two hours, and the colourless solution was poured into ice-cold H-sulphuric acid (400 ml.). The white precipitate was collected, dried, and crystallised from light petroleum (b.p. 60-80°), yielding silky needles of 3-methylfluorenene-9-ol (3.8 g.), m.p. 144-146° (admixture with 2-methylfluorenene-9-ol depressed the m.p. by 20°). (Found: C, 85.8; H, 6.0. C_{14}H_{12}O requires, C, 85.7; H, 6.2%).

9-Acetoxy-3-methylfluorenene.

3-Methylfluorenene-9-ol (1.0 g.), acetic anhydride (1 ml.), and dry pyridine (5 ml.) were heated on the steam-bath
for 3 hours. The white solid, obtained on pouring the solution into water, crystallised from ethanol, yielding rosettes of hexagonal plates of 3-acetoxy-3-methylfluorone (0.75 g.), m.p. 90°. (Found: C, 80.6; H, 6.1. C₁₆H₁₄O₂ requires C, 80.65; H, 5.9%).
V. The preparation of 3-methoxyfluoren-2-ol.

2-p-Tolylsulphonylamido-4'-methoxybenzophenone. (Ullmann and Bleier, Ber., 1929, 62, 4275).

To a stirred suspension of N-p-tolylsulphonyl-anthranilic acid (45 g.) in carbon disulphide (900 ml.) was added phosphorus pentachloride (36 g.) and the mixture was boiled gently under reflux for 40 minutes, after which the clear brown solution no longer evolved hydrogen chloride. The solution was cooled and anisole (50 g.) was added, followed by aluminium chloride (20 g.); a red gum slowly separated in the cold and the reaction was accelerated by warming gently for a few minutes. When the initial reaction slackened, a second portion of aluminium chloride (20 g.) was added and after ten minutes the reaction mixture was heated under reflux for 30 minutes longer. The carbon disulphide was decanted off, and the residual red gum was decomposed by cautiously warming with 0.5M-hydrochloric acid (one l.): 2-p-tolylsulphonamido-4'-methoxybenzophenone separated as a pink solid which was collected, washed with dilute hydrochloric acid, with water, and dried. It weighed 57 g., m.p. 133-137°, and was not purified further.
3-Methoxyfluorenone. (Idem, loc. cit.).

Hydrolysis.—2-p-Tolylsulphonamido-4'-methoxybensophenone (57 g.), was dissolved in a mixture of concentrated sulphuric acid (100 ml.) and glacial acetic acid (100 ml.) and the red solution was heated on the water-bath for one hour. The turbid yellow solution formed on addition of this solution to water (one l.) was stirred with charcoal (5 g.) and filtered, yielding a clear solution of 2-amino-4'-methoxybensophenone sulphate.

Ring-closure.—The yellow solution was cooled to 5° and diazotised with a solution of sodium nitrite (11 g.) in water (100 ml.) during 20 minutes. The excess of nitrous acid was decomposed by the addition of urea (5 g.); copper-bronze powder (5 g.) was added, and the intensely yellow solution was boiled for 30 minutes. The orange oil that separated was extracted with ether, the ethereal solution was thrice washed with N-sodium hydroxide (200 ml. portions) and with water, dried over anhydrous sodium sulphate, and evaporated. The residual yellow oil was crystallised from a mixture of benzene (30 ml.) and light petroleum (b.p. 60-80°, 60 ml.) giving 3-methoxyfluorenone as clusters of yellow prisms (11.1 g.), m.p. 99-100°.


In a similar preparation of 3-methoxyfluorenol, on the same scale, the addition of the copper was omitted and the yield of pure ketone, m.p. 90-100°, was 9.5 g. (Idem, loc. cit., m.p. 99°).

3-Methoxyfluoren-9-ol.

3-Methoxyfluorenone (7.7 g.) was heated under reflux with a solution of aluminium iso-propoxide from aluminium turnings (3 g.) and iso-propanol (90 ml.) for 3 hours, and the solution poured into cold H-sulphuric acid (600 ml.). The oil that separated soon solidified, and the buff solid was collected, washed and dried. Crystallisation from light petroleum (b.p. 100-110°, 500 ml.) yielded 3-methoxyfluoren-9-ol (5.5 g.), m.p. 119°; a further crystallisation from the same solvent gave very pale yellow rosettes of leaflets, m.p. 120°. (Found: C, 79.6, 78.6; H, 5.75, 5.6.

C_{14}H_{12}O_2 requires C, 79.25; H, 5.7%).

9-Acetoxy-3-methoxyfluoren.  

3-Methoxyfluoren-9-ol (0.5 g.), dry pyridine (6 ml.), and acetic anhydride (1 ml.) were heated together on the steam bath for 3 hours. The solid formed on pouring the solution
into cold water was collected and twice recrystallised from ethanol. There separated pale yellow leaflets of 2-octoxy-3-naphoxyfluorone (0.4 g.), m.p. 126-127°. (Found: C, 75.55; H, 3.7. \( \text{C}_{16}\text{H}_{14}\text{O}_3 \) requires C, 75.6; H, 3.55%).
The Hydrosol-Sulphuric Acid Reaction.

Unless otherwise stated, the hydrosol-sulphuric acid reactions described on the following pages were carried out by the following general procedure.

In a three-necked flask of 150 ml. capacity, fitted with a stirrer, a short air condenser, and a small dropping funnel, a suspension of sodium azide in redistilled chloroform was cooled in an ice-bath during the dropwise addition of sulphuric acid (98%, Analar). Stirring was continued at 0° for 10 minutes, the temperature of the mixture was raised to 25° and the compound under investigation was gradually introduced, as a solid or as a suspension or solution in chloroform, into the vigorously stirred mixture; the reaction mixture was ultimately poured on ice.

The reaction of 9-methylfluoren-9-ol with hydrosol-sulphuric acid.

To a vigorously stirred hydrosol-sulphuric acid mixture from sodium azide (2.5 g.), sulphuric acid (10 ml.), and chloroform (40 ml.), was added 9-methylfluoren-9-ol
(4.9 g.) in small portions during one hour. After stirring for a further hour the deep red mixture was poured into ice and water (400 g.), and shaken thoroughly. From the acid solution and the base sulphate which separated, a brown solid was obtained on decomposition with 3N-ammonium hydroxide. This was collected, dried and extracted with boiling light petroleum (b.p. 60–80°); a small amount of dark solid remained undissolved. The solution yielded 9-methylphenanthridine (1.86 g., 34%), m.p. 83–85°, which after one recrystallisation from light petroleum formed colourless rosettes of needles, m.p. 85° (Found: C, 86.9; H, 5.9; N, 7.2. Calc. for C_{14}H_{11}N: C, 87.0; H, 5.75; N, 7.28%).

A repetition of this experiment gave 9-methylphenanthridine (44%), m.p. 80°, raised to 84° by two recrystallisations from light petroleum. In a third experiment on seven times the scale there was obtained 9-methylphenanthridine (7.75 g., 56%), m.p. 81–84°, raised to 84° by one recrystallisation from p-hexane.

Addition of an ethanolic solution of picric acid to 9-methylphenanthridine, also dissolved in ethanol, gave a precipitate of the picrate which, on recrystallisation from diisopropanol, formed small yellow needles m.p. 240° (decomp.).
(Found: N, 12.9. Calc. for $C_{20}H_{14}O_7N_4$: N, 13.2%).

9-Methylphenanthridine, m.p. 85°, and its picrate, m.p. 233° (decomp.), were prepared by Pictet and Hubert (Ber., 1896, 29, 1184) by heating 9-acetamidodiphenyl with zinc chloride.

The chloroform solution from the third experiment was washed successively with 3N-hydrochloric acid, sodium hydrogen carbonate solution, and water, was dried over anhydrous sodium sulphate, and was evaporated to dryness. The residual amber oil readily crystallised to give a brown solid (3.48 g., 26% based on the formula given below), m.p. 148-153°. This solid was dissolved in ethanol (160 ml.) and the solution was boiled with charcoal; from the filtered and cooled solution separated pale brown needles (3.27 g.), m.p. 157°. After two more recrystallisations using charcoal this substance was obtained in almost colourless needles, m.p. 157°. (Found: C, 90.3; H, 5.9; N, 4.0. $C_{28}H_{21}N$ requires C, 90.5; H, 5.7; N, 3.8%). The substance gave a picrate which formed yellow needles from ethanol, m.p. 226-228°. (Found: N, 9.55. $C_{34}H_{24}O_7N_4$ requires N, 9.35%).
The reaction of 9-benzylfluoren-9-ol with hydrazine-sulphuric acid.

To a hydrazine-sulphuric acid mixture, from sodium azide (0.7 g.), sulphuric acid (5 ml.), and chloroform (6 ml.), was added a solution of 9-benzylfluoren-9-ol (2.0 g.) in chloroform (90 ml.) during 30 minutes with vigorous stirring; after one hour longer the orange-coloured mixture was poured on ice (200 g.). From the acidic solution and the base sulphate which separated, was obtained, on decomposition with 3N-ammonium hydroxide, crude 9-benzylphenanthridine (0.8 g., 40%), m.p. 108-107°. Several recrystallisations from ethanal gave straw-coloured needles, m.p. 110-111°; a more satisfactory method of purification was by molecular distillation at 150°/0.4 mm., when colourless needles, m.p. 112°, were obtained. (Found: C, 86.7; H, 5.7; N, 5.15. Calc. for \( \text{C}_{20}\text{H}_{15}\text{N} \): C, 89.2; H, 5.6; N, 5.2%). The picrate, prepared by precipitation from ethanolic solution, formed yellow needles, m.p. 200-202° (decomp.), on recrystallisation from n-butanol. (Found: N, 11.1. \( \text{C}_{26}\text{H}_{18}\text{O}_{7}\text{N}_4 \) requires N, 11.95%).

obtained 9-benzylphenanthridine, m.p. 112°, by cyclisation of 2-phenylacetimidodiphenyl. A picrate, m.p. 190° (decomp.) is also described, but no analysis is recorded.

The original chloroform solution, on evaporation, yielded a neutral yellow oil (0.9 g.) which contained neither nitrogen nor sulphur.
The reaction of 9-benzylidenefluorene with hydrazoic-sulphuric acid.

A hydrazoic-sulphuric acid mixture, from sodium azide (1.5 g.), sulphuric acid (6 ml.), and chloroform (23 ml.), was vigorously stirred during the addition of 9-benzylidene-fluorene (3.8 g.) in small portions during one hour. The reaction mixture was stirred one hour longer and poured on ice. Isolation of the products as described for the reaction with 9-benzylfluoren-9-ol yielded crude 9-benzylphenanthridine (2.1 g., 53%), m.p. 102-105°, which after purification melted at 112° alone or when mixed with the analysed specimen above.

A repetition of this experiment gave a yield of 47% of base, m.p. 100-105°, raised to 110° by two recrystallisations from ethanol.

The original chloroform solution gave, on evaporation, a golden-yellow oil (1.2 g.) containing nitrogen but no sulphur.
The reaction of 9-phenylfluoren-9-ol with hydrosie-sulphuric acid.

A solution of 9-phenylfluoren-9-ol (2.6 g., m.p. 65°) in chloroform (10 ml.) was added, during one hour, to a vigorously stirred hydrosie-sulphuric acid mixture, from sodium acetate (1.0 g.), sulphuric acid (4 ml.) and chloroform (15 ml.), and the mixture was stirred for two hours longer. A deep red coloration developed on each fresh addition of the carbinoi, but this colour soon disappeared, leaving the sulphuric acid layer aseam-coloured with a violet fluorescence. The reaction mixture was poured on ice (100 g.), the mixture was shaken thoroughly, and the acidic and chloroform solutions were separated. The latter was extracted twice with 10N-sulphuric acid (50 ml. portions), the extracts were added to the original acidic solution, and the whole was made alkaline with 3N-ammonium hydroxide. 9-Phenylphenanthridine (2.5 g., 96%), m.p. 105-106°, separated; it formed colourless leaflets, m.p. 106°, on recrystallisation from ethanol or from light petroleum. This m.p. was unaltered by repeated recrystallisations of the compound from ethanol. (Found: C, 89.8; H, 5.2; N, 5.6. Calc. for C_{10}H_{15}N: C, 89.35; H, 5.15; N, 5.8%).
A repetition of this experiment gave 9-phenylphenanthridine (90%), m.p. 104-106°.

The picrate, prepared by precipitation from an ethanolic solution, on recrystallisation from glacial acetic acid formed yellow needles m.p. 251° (decomp.). (Found: N, 11.5. Calc. for C26H16O7N4: N, 11.5%).

9-Phenylphenanthridine, m.p. 109°, and its picrate, m.p. 242° (decomp.) were prepared by Pictet and Hubert (loc. cit.).
The reaction of 9-benzylidene-2-nitrofluorene

with hydrosol-sulphuric acid.

(i) 9-Benzylidene-2-nitrofluorene (3.0 g.) was added in small portions, during one hour, to a vigorously stirred hydrosol-sulphuric acid mixture, from sodium azide (1.0 g.), sulphuric acid (5 ml.), and chloroform (20 ml.); the sulphuric acid layer became deep red. The reaction mixture was stirred for two hours longer, without change in appearance, and was then poured into ice and water. After thorough shaking of the mixture, the acidic solution was separated and made alkaline with 3M-ammonium hydroxide; the precipitate was negligible. The chloroform solution, on evaporation at 30° in vacuo, yielded unchanged 9-benzylidene-2-nitrofluorene (2.5 g.), m.p. 147-149° alone or when mixed with an authentic specimen.

(ii) 9-Benzylidene-2-nitrofluorene (3.0 g.) formed a deep red solution in sulphuric acid (30 ml.). To this solution was added sodium azide (1.3 g.) in small portions during 30 minutes at 0°. The temperature was raised to 25° and after being stirred at this temperature for 6 hours, the reaction mixture was poured on ice (300 g.). The yellow
precipitate was collected. On being washed with water it became red and gelatinous, and it was found to be fairly soluble in cold water and easily soluble in 2N-sodium hydroxide; it was precipitated from these solutions, by the addition of dilute acids, as a yellow solid. The original aqueous sulphuric acid solution gave no precipitate when made alkaline with 2N-sodium hydroxide.
The reaction of 2-methoxyfluoren-9-ol with hydrozoic-sulphuric acid.

Eight experiments were carried out with this compound in order to discover the best conditions for the hydrozoic-sulphuric acid reaction. In experiments I to VI the procedure was as follows:-

To a vigorously stirred hydrozoic-sulphuric acid mixture, from sodium azide (a g.), sulphuric acid (b ml.), and chloroform (c ml.), 2-methoxyfluoren-9-ol (d g.) dissolved in chloroform (e ml.) was added at 25° during x hours. The almost black reaction mixture was stirred for y hours longer, poured on ice, and the mixture shaken thoroughly. The brown solid (f g.) was collected, washed with dilute hydrochloric acid and with water, and dried. The acidic and chloroform solutions were separated: the former was made alkaline with 2N-sodium hydroxide, the basic oil was extracted with ether, the ethereal solution was washed with water, and dried over anhydrous sodium sulphate. The amber oil, remaining on evaporation of the ether, crystallised on cooling, giving a mixture of 2- and 7-methoxyphenanthridines, m.p. 55-75° (in all experiments). On evaporation, the chloroform solutions
gave brown syrups.

Table VI summarises these six experiments.

Experiment VII was as follows:—

A solution of hydrazine acid in chloroform was prepared from sodium azide (3.0 g.), sulphuric acid (3 ml.), and chloroform (20 ml.) in the usual way, and decanted from the sulphuric acid layer. To this chloroform solution was added a solution of 2-methoxyfluoren-9-ol (5.0 g.) in chloroform (20 ml.), and sulphuric acid (0.5 ml.) was added dropwise with stirring at 85° during 45 minutes. On working up the reaction mixture as already described no basic material was obtained and the carbinol (4.9 g.), m.p. 154-156°, was recovered.

In experiment VIII sulphuric acid (5 ml.) was added drop by drop to a vigorously stirred mixture of 2-methoxyfluoren-9-ol (5.0 g.), sodium azide (2.3 g.) and chloroform (40 ml.) at 25° during 2 hours. After ½ hour longer the black reaction mixture was added to ice (200 g.) and the mixture was shaken thoroughly. No base was isolated from the acidic solution; the product consisted of an amorphous pink solid which tenaciously retained the chloroform.
### Table VI.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Hydrazine-Sulphuric Acid</th>
<th>Reactant Solution</th>
<th>Time (hours)</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NaN₃</td>
<td>H₂SO₄</td>
<td>CHCl₃</td>
<td>Carbinol</td>
</tr>
<tr>
<td>I</td>
<td>2.7</td>
<td>7</td>
<td>10</td>
<td>6.0</td>
</tr>
<tr>
<td>II</td>
<td>2.7</td>
<td>7</td>
<td>10</td>
<td>5.0</td>
</tr>
<tr>
<td>III</td>
<td>5.4</td>
<td>14</td>
<td>20</td>
<td>10.0</td>
</tr>
<tr>
<td>IV</td>
<td>2.3</td>
<td>5</td>
<td>20</td>
<td>5.0</td>
</tr>
<tr>
<td>V</td>
<td>3.0</td>
<td>5</td>
<td>30</td>
<td>5.0</td>
</tr>
<tr>
<td>VI</td>
<td>1.35</td>
<td>15</td>
<td>18</td>
<td>2.5 g. added as solid</td>
</tr>
</tbody>
</table>

† Reaction carried out at 0°.
Yields of the non-basic brown solid varied greatly (e.g., experiments I - IV). The solid from experiment III (7.06 g.) was finely ground and extracted by boiling with several lots of dilute hydrochloric acid; finally it was shaken mechanically for three hours with 5N-sodium hydroxide (100 ml.) and ether (100 ml.). The solid was collected, washed with water, and dried; it then weighed 6.85 g. It was an amorphous, fusible, fawn-coloured solid, containing nitrogen and sulphur, and insoluble in all the usual organic solvents.

The yields of the basic mixture of 2- and 7-methoxyphenanthridines also varied (e.g., identical experiments I and II, and III which is a repetition on twice the scale). Similar variations were observed in the yields of phenanthridine from fluoreneol, by Arous and Mealey (J. Chem. Soc., 1953, 178); variation is possibly due to the difficulty of obtaining uniform mixing, owing to the gummy nature that the relatively small sulphuric acid layer soon acquires during the addition of the carbinal. In an attempt to overcome this difficulty equal volumes of sulphuric acid and of chloroform were employed (experiment VI), but this experiment gave no base. On the other hand, no base was isolated from experiment
VII in which only a catalytically-small amount of sulphuric acid was used.

Separation of the two methoxysymprenaline. The combined basic fractions (6.2 g.) from experiments II - V were converted to their acid oxalate. To the solution of the basic material in ethanol (10 ml.) was added a solution of oxalic acid dihydrate (3.75 g.) also in ethanol (20 ml.); on cooling there separated buff needles (7.2 g.), m.p. 160-167°.

Fractional crystallisation of this derivative from ethanol (250 ml.) did not lead to a separation of the isomers: the five crops (totalling 6.7 g.) melted irregularly within the range 160-169°. The first crop was crystallised twice from ethanol yielding cream-coloured rosettes of feathery needles of 2- and 7-methoxysymprenaline hydrogen oxalate, m.p. 169° (decomp.). (Found: C, 64.35; H, 4.5; N, 4.65.

The rest of the acid oxalate (6.35 g.) was reconverted to the base (4.45 g.) by shaking with ether and 2N-sodium hydroxide, and this was fractionally crystallised from light petroleum (b.p. 100-110°, 150 ml.). The first crop (2.5 g.) formed pale pink leaflets, m.p. 86-88°, which after two recrystallisations from this solvent gave
7-methoxyphenanthridine (1.95 g.), m.p. 90°. (Found: C, 80.6; H, 5.5; N, 6.7%). From the original light petroleum mother-liquor were obtained, on concentration, three crops, (1.2 g.), m.p. 56-58°, which after two crystallizations from the same solvent formed pink rosettes of plates of 2-methoxyphenanthridine (0.34 g.) m.p. 57-59°. (Found: C, 80.8; H, 5.2; N, 6.6%).

The base from experiment I (2.0 g.) yielded, on fractional crystallisation as described above,

7-methoxyphenanthridine (0.7 g.), m.p. 90° (from a first crop, 0.9 g., m.p. 90-95°) and 2-methoxyphenanthridine (0.35 g.), m.p. 57-59°, (from the second and third crops, 0.65 g., m.p. 53-56°).

Demethylation of 7-methoxyphenanthridine. A solution of 7-methoxyphenanthridine (0.5 g.) in colourless, constant-boiling hydrobromic acid (25 ml.) was heated under reflux for three hours in a current of carbon dioxide. The yellow solution was made alkaline with 2N-sodium hydroxide, then just acidified with acetic acid; there separated a buff precipitate which was collected, washed with water, and dried.

Recrystallisation of this substance (0.48 g.), m.p. 272-277°.
from ethanol (50 ml.) yielded small buff prisms of 7-hydroxyphenanthridine (0.3 g.) which melted at 281-282° alone, and at 280-282° when mixed with an authentic specimen of this compound (see p. 191).

7-Methoxyphenanthridine was recovered unchanged after being boiled for six hours with constant-boiling hydrochloric acid.

When 7-methoxyphenanthridine (0.5 g.) was heated for three hours under reflux with constant-boiling hydriodic acid (25 ml., freshly distilled but containing some free iodine), a deep violet crystalline solid formed and tended to float on the surface of the liquid. The mixture was allowed to cool, and this solid was collected: it dissolved readily in very dilute sodium hydroxide solution from which was isolated, by the method described above, a pale yellow solid (0.64 g.), m.p. 230-235°. Two recrystallisations of this substance from dioden yielded small, dense, pale yellow tablets of 7-hydroxy-(2)-iodophenanthridine (0.25 g.), m.p. 235°. (Found: I, 39.2. C_{13}H_{10}INO requires I, 39.5%).

This compound dissolved in warm dilute hydrochloric acid from which there separated, on cooling, silky, bright yellow needles of the hydrochloride. The deep violet hydriodicide was
very sparingly soluble in boiling water. The base was freely soluble in 0.5 N-sodium hydroxide, but at concentrations above this the sodium salt tended to separate.

7-Hydroxy-(2)-iodophenanthridine (0.40 g., m.p. 229°) was also obtained when 7-hydroxyphenanthridine (0.25 g.) was boiled for three hours with the same specimen of hydriodic acid (10 ml.), and the product worked up as described above.

Demethylation of 2-methoxyphenanthridine. 2-Methoxyphenanthridine (0.50 g.) was treated with hydrobromic acid (25 ml.) and the phenol isolated just as described above for the 7-methoxy compound. Crystallisation from aqueous ethanol yielded small buff leaflets (0.20 g.) of 2-hydroxyphenanthridine, m.p. 245°. (Found: C, 79.6; H, 4.9; N, 7.1. \(C_{13}H_{10}O\) requires C, 79.05; H, 4.65, N, 7.2%).

The oxidation of 7-methoxyphenanthridine with acid permanganate. (1) 7-Methoxyphenanthridine (0.50 g.) was dissolved in N-sulphuric acid (30 ml.) at 60° and a solution of potassium permanganate (0.16 g., i.e. equivalent to one atom of oxygen per molecule) in water (6 ml.) added drop by
drop during 10 minutes. Decolorisation of the permanganate was rapid, a brown solid separated, and a smell of formaldehyde was detected. After a further 10 minutes at 60°, the solution was filtered, and from the filtrate was recovered the methoxyphenanthridine (0.46 g.), m.p. 90° alone and when mixed with the authentic specimen.

(ii) A solution of 7-methoxypenicillidine (0.46 g.) in 2N-sulphuric acid (15 ml.) was treated with potassium permanganate (1.00 g.) in small portions at 60-70° during 10 minutes. After a further 10 minutes at this temperature, the suspension was filtered and the brown solid was washed with a little water. From the acidic solution was recovered the methoxyphenanthridine (0.21 g.), m.p. 85-90°. The brown solid was extracted with boiling pyridine (20 ml.), the filtrate was concentrated to 5 ml. and poured into cold water (100 ml.). There separated a buff solid (0.04 g.), m.p. 235-260°.
The reaction of 2-methoxyfluorenone with hydrosol-sulphuric acid.

To a hydrosol-sulphuric acid mixture, from sodium azide (7.35 g.), sulphuric acid (22 ml.), and chloroform (75 ml.), was added 2-methoxyfluorenone (15.6 g.) in small portions during two hours. The reaction mixture, consisting of an almost black gum and an orange chloroform solution, was stirred for one hour longer, ice and water (500 g.) were added, and the mixture was transferred to a bottle and shaken mechanically for two hours. The brown suspension so formed was filtered with difficulty at the pump, a brown solid (12.4 g.), m.p. 195-215° being collected. In order to remove any unchanged ketone this solid was boiled with ethanol (500 ml.) and the brown solid collected. Purification was effected, and the separation of the 2- and 7-methoxypheneathridiones was attempted, by fractional sublimation at 200°/0.001 m.m. There was obtained a microcrystalline, cream-coloured solid (5.93 g.) in eight crops, all of which melted within the range 229-241°; the non-volatile residue, a dark brown solid (4.0 g.), was infusible and contained nitrogen and sulphur. One of these crops (0.50 g.), m.p. 237-241°, was recrystallised from pyridine (6 ml.) and gave
coloursless needles of 2- and 7-methoxyphenanthridones (0.35 g.), m.p. 239-242°. (Found: C, 74.4; H, 4.95; N, 6.4. Calcd. for C_{14}H_{11}O_{2}N: C, 74.6; H, 4.9; N, 6.2%).


It was therefore concluded that, while sublimation was successful in the purification of the reaction product, it was not effective in separating the two isomeric compounds. Fractional crystallisation was impracticable because of the low solubility of these compounds in most organic solvents.

The preparation and separation of 9-chloro-2-methoxy- and 9-chloro-7-methoxyphenanthridines. The original cream-coloured sublimate of 2- and 7-methoxyphenanthridones (5.25 g.) was heated under reflux with phosphorus oxychloride (25 ml.) for 4½ hours; the red solution was cooled and poured on ice (400 g.). The aqueous layer was decanted from the greenish-yellow oil, which had not solidified after one hour, and the oil was stirred with ice-cold water; it was slowly transformed to a grey solid (5.55 g.), m.p. 104-112°, which was collected and dried in vacuo.
Fractional crystallisation of this solid from light petroleum (b.p. 60-80°, 500 ml.) gave, as the first crop, buff needles (2.4 g.), m.p. 133-135°; recrystallisation of this material yielded pale yellow rosettes of stout needles of 9-chloro-2-methoxyphenanthridine (1.7 g.), m.p. 136-137°.

On concentration of the original mother-liquor there were obtained three crops: 0.75 g., m.p. 100-104°; 1.05 g., m.p. 100-102°; and 0.8 g., m.p. 94-99°. These were combined (total 2.6 g.) and recrystallised from the same solvent (100 ml.), giving almost colourless rosettes of needles of 9-chloro-7-methoxyphenanthridine (1.85 g.), m.p. 101-103°, raised to 104° by a second recrystallisation. (Ibid. loc. cit., 9-chloro-2-methoxy-, m.p. 137.5°, and 9-chloro-7-methoxyphenanthridine, m.p. 107°).
The reaction of 2-hydroxyfluoren-9-ol with hydracetic-sulphuric acid.

A hydracetic-sulphuric acid mixture, from sodium azide (2.5 g.), sulphuric acid (6.4 ml.), and chloroform (15 ml.), was vigorously stirred during the addition of 2-hydroxyfluoren-9-ol (4.35 g.) suspended in chloroform (10 ml.) during 40 minutes. The reaction mixture, consisting of a black gum and a colourless chloroform layer, was stirred for one hour longer, was added to ice (100 g.) contained in a bottle and the mixture was shaken mechanically, giving a brown suspension. The solid was collected and extracted by boiling with H-hydrochloric acid. The acid extracts were added to the original diluted sulphuric acid solution, which had been separated from the chloroform layer, and carefully neutralised to litmus with 3N-ammonium hydroxide: there was no precipitate or turbidity. The insoluble brown solid was washed with water and dried; it amounted to 4.6 g. It was amorphous, inflammable up to 350°, contained nitrogen and sulphur, and was insoluble in the usual organic solvents and in dilute acids. It differed, however, from the similar material formed in the reaction of 2-methoxyfluoren-9-ol with
hydrazoic-sulphuric acid in that it mostly dissolved in N
sodium hydroxide (200 ml.) giving a deep red solution. From
this solution, after filtration from a little insoluble black
material, was obtained, on saturation with carbon dioxide, a
reddish brown solid (3.8 g.), identical in its properties
with the original solid.
The reaction of 3-methoxyfluoren-9-ol with

**Hydrazine-sulphuric acid.**

A suspension of 3-methoxyfluoren-9-ol (4.25 g.) in chloroform (15 ml.) was added to a vigorously stirred hydrazine-sulphuric acid mixture (from sodium azide (2.3 g.), sulphuric acid (6 ml.), and 15 ml. of chloroform) in small portions during one hour at 25°. The almost black reaction-mixture became sticky and difficult to stir efficiently; after one hour longer it was added to cold water (200 ml.), and the mixture was shaken. The brown solid was filtered off, extracted by thrice boiling with N-hydrochloric acid (100 ml. portions), and was washed with water and dried; it weighed 0.90 g. The acidic extracts were added to the aqueous sulphuric acid - chloroform mixture; the chloroform layer was separated, washed with 3N-hydrochloric acid (100 ml.), with water, and allowed to evaporate to dryness, giving a friable brown solid (2.10 g.) containing nitrogen and sulphur. The hydrochloric and sulphuric acid solutions were together made alkaline with 2N-sodium hydroxide, and the dark oil was extracted with ether. On evaporation of the ethereal solution, which had been dried over anhydrous sodium sulphate, there
was obtained a deep red oil (0.65 g.) which was, however, no longer completely acid-soluble. It was extracted by thrice boiling with N-hydrochloric acid (total 100 ml.) and the base was recovered as before; it now formed an orange oil (0.26 g.). This oil was extracted with boiling light petroleum (b.p. 60-80°, total 100 ml.), and the solution, after being decanted from some red insoluble gum, was evaporated yielding an amber oil (0.20 g.) which partially crystallised after several days.

In a second experiment on the same scale there were obtained the brown, chloroform-insoluble solid (0.65 g.), the brown chloroform soluble solid (2.0 g.), and the petroleum soluble base (0.23 g.).

Molecular distillation of the combined bases (total 0.43 g.) at 150°/0.1 m.m. yielded pale yellow needles of 3- and 6-methoxyphenanthridines, (not quite pure) m.p. 70-78° (Found: C, 78.8; H, 5.15; N, 6.35. C_{14}H_{11}ON requires C, 80.4; H, 5.3; N, 6.7%).

The brown, chloroform insoluble material was infusible, contained nitrogen and sulphur, and was unaffected by and insoluble in dilute acids, alkalis, and all the common organic solvents. It is therefore similar to the material formed in the reaction of 3-methoxyfluoren-9-ol with hydrosulphuric acid (p. 167).
The reaction of 2-nitrofluorenone with hydrosol-sulphuric acid.

To the deep red solution of 2-nitrofluorenone (5.0 g.) in sulphuric acid (28 ml.) was added sodium azide (2.8 g.) in small portions during one hour with stirring at 0°. The resulting dark blue solution was poured on ice after a further 30 minutes and the yellow solid was collected, washed with water until the washings were no longer acid to litmus, and dried; it weighed 5.3 g., m.p. 326-338°. This substance (0.50 g.) was sublimed at 210°/0.5 m.m. in eleven portions: the first four (totalling 0.05 g.) melted at 282-308° and after crystallisation from pyridine formed a microcrystalline yellow powder (0.03 g.), m.p. 296-303°. The last seven fractions (totalling 0.39 g.) melted at 335-342° and after crystallisation from pyridine gave a yellow solid (0.23 g.) m.p. 360°.

Re-crystallisation from pyridine (700 ml.) of the crude material (25 g., m.p. 325-336°) from a second experiment (employing 25 g. of 2-nitrofluorenone), yielded 2-nitrophenanthridone (15 g.) m.p. 358-359°.

In a third experiment the solution was poured into absolute methanol instead of ice.
Methanol (700 ml.) was heated under reflux with freshly ignited quicklime for four hours and distilled off in a dry apparatus. About 50 ml. of this methanol was placed in a flask containing magnesium turnings (3 g.) and fitted with an efficient reflux condenser, and the reaction was initiated by the addition of a crystal of iodine. The vigorous reaction was soon complete and to the clear solution was added the rest of the lime-dried methanol; the whole was heated under reflux for one hour. The absolute methanol was distilled from the milky liquid in a thoroughly dried, all-glass apparatus, in which the receiver was a litre three-necked flask equipped with a mercury-sealed stirrer and tap funnel.

Meanwhile the reaction between 2-nitrofluorenone (5.0 g.), sodium azide, and sulphuric acid was carried out precisely as described above. Most of the deep blue solution was added dropwise via the tap funnel to the well stirred methanol, cooled in an ice and salt freezing mixture. There separated a yellowish-brown, finely-divided solid which was collected, washed several times with absolute ethanol, then with dried light petroleum, and was finally dried in the oven. There was obtained a brown solid (4.4 g.), m.p. 325-329°.

The rest of the deep blue solution was added to ice
in the usual way, yielding a brown solid, m.p. 321-325°.
The mixed m.p. with the 4.4 g. above was 322-326°.

2-Chloro-2-nitrophenanthridine.

2-Nitrophenanthridone (10.0 g.) was heated under reflux with phosphorus oxychloride (100 ml.) for four hours. Excess oxychloride was decomposed with ice and the 2-chloro-2-nitrophenanthridine (9.55 g., 95%) was crystallised from benzene, forming pale yellow needles of m.p. 206°. (Found: C, 50.8; H, 2.4; N, 10.3; Cl, 14.0. Calc. for C_{15}H_{9}Cl_{2}: C, 50.35; H, 2.75; N, 10.85; Cl, 15.7%).

The mixture of nitrophenanthridones, m.p. 206-303° (1.5 g.), obtained from the mother-liquor from the large recrystallisation above, treated in the same way yielded a mixture of 9-chloro-2-nitro- and 9-chloro-7-nitrophenanthridines (1.4 g.), m.p. 165-180°. A mixture of 2-chloro-2-nitrophenanthridine, m.p. 209°, and 2-chloro-7-nitrophenanthridine, m.p. 207-208° (see below), melted between 150° and 190°.
p-Tolylsulphohydrazine. (Freundberg and Blummel, Annalen, 1924, 440, 45).

Hydrazine hydrate (100%, 15 g.), diluted with water (5 ml.), was added to a cold solution of p-tolylsulphonyl chloride (25 g.), in benzene (100 ml.); the mixture was shaken and cooled. The colourless solid which separated was collected and recrystallised from benzene, yielding needles of p-tolylsulphonhydrazine (15 g.), m.p. 112°. (Idem. loc. cit., m.p. 112°).

2-Nitrophenanthridine (from 2-chloro-2-nitrophenanthridine).

2-Chloro-2-nitrophenanthridine (8.6 g.), p-tolylsulphonylhydrazine (2.0 g.), and chloroform (135 ml.) were heated under reflux. After 3 days (21 hours boiling) the cream-coloured crystalline precipitate (3.4 g.) was collected, was dissolved in 0.5N-sodium hydroxide (400 ml.), and the red solution was heated at 80° with stirring for 1 ½ hours. The colour was discharged with evolution of nitrogen and the separation of a brown solid. The latter was filtered off, extracted with boiling 5N-hydrochloric acid, and the extract was poured into an excess of 5N-sodium hydroxide. The yellow precipitate, after crystallisation
from benzene, yielded pale orange needles of
2-nitrophenanthridine (0.5 g.), m.p. 196-197°. (Found:
C, 69.6; H, 3.7; N, 12.4. Calc. for C₁₃₂₃₂₂: C, 69.66;
H, 3.6; N, 12.5%).


To the orange solution of 2:7-dinitrofluorenone
(15.0 g.) in sulphuric acid (85 ml.) was added sodium azide
(8.5 g.) in small portions at 0° during one hour. The brown
solution was stirred one hour longer, was poured into ice and
water (500 g.), and the straw-coloured precipitate of
2:7-dinitrophenanthridine (15.65 g.) was collected and dried.
It did not melt below 330°.

1949, 1284).

2:7-Dinitrophenanthridine (15.65 g.) was heated
under reflux with phosphorus oxychloride (150 ml.) for seven
hours. When cold, the pale brown crystalline paste was
gradually added to ice (500 g.), and 3N-ammonium hydroxide was
also added in small portions so that the mixture remained
alkaline throughout. The solid, after crystallisation from


A solution of 9-chloro-2:7-dinitrophenanthridine (10.5 g.) and p-tolylsulphonhydrazine (10.0 g.) in chloroform (850 ml.) was boiled under reflux for 60 hours in the course of 5 days, and the pale yellow crystalline precipitate (14.8 g.), m.p. 200° (decomp.), was collected. It gave an almost black suspension in cold 0.5N-sodium hydroxide (1.5 l.) which on stirring at 80° evolved nitrogen, becoming brown. After 80 minutes at this temperature the suspension was cooled, the brown solid was collected, extracted by boiling with 5N-hydrochloric acid (total, 200 ml.), and the extracts were poured into an excess of 5N-sodium hydroxide. There separated a flocculent orange solid (3.0 g.), m.p. 290-300°, which was best purified by sublimation followed by crystallisation of the sublimate from chlorobenzene.

2:7-Dinitrophenanthridine formed silky, pale yellow needles, m.p. 302°. (Found: C, 58.2; H, 2.6; N, 15.3. C_{15}H_{7}O_{2}N_{3} requires C, 58.0; H, 2.6; N, 15.6%).
The reaction of 2-nitrofluoren-9-ol with hydric-acetic acid.

To a vigorously stirred hydric-sulphuric acid mixture, from sodium acetate (4.3 g.), sulphuric acid (15 ml.), and chloroform (60 ml.), was added 2-nitrofluoren-9-ol (10.0 g.) in small portions during two hours; the mixture became orange and nitrogen was evolved. After being stirred for one hour longer, the reaction mixture was poured into ice-cold water (600 ml.), shaken thoroughly, the buff precipitate of the base sulphate was filtered off, and the aqueous and chloroform layers were separated. Decomposition of the precipitate, suspended in the aqueous layer, by shaking with 3N-ammonium hydroxide gave the mixture of nitrophenanthridines as a brown solid.

In three experiments, 2-nitrofluoren-9-ol (28.7 g.), treated in this way, gave the base (26.0 g.), m.p. 145-170°. Fractional crystallisation of this material from benzene (450 ml.) gave impure 7-nitrophenanthridine (19.7 g.), m.p. 171-176°, in several crops, and one crop of the impure complex of 2- and 7-nitrophenanthridines (1.45 g.), m.p. 155-160°. The former gave, on recrystallisation from benzene or from
ethyl acetate, orange leaflets of 7-nitrophenanthridine (11.0 g.), m.p. 180°. (Found: C, 70.1; H, 3.6; N, 12.8.
Calc. for C_{15}H_{8}O_{2}N: C, 69.65; H, 3.6; N, 12.5%). The complex, after recrystallisation from ethanol, formed small pale yellow needles (1.1 g.), m.p. 158-160°. (Found: C, 69.6; H, 3.7; N, 12.2%).

When 2-nitrophenanthridine, m.p. 196-107° (0.60 g.), and 7-nitrophenanthridine, m.p. 180° (0.60 g.), were together fractionally crystallised from ethanol (100 ml.), the first crop (A; 0.30 g.) melted at 161-162°, and the second and third crops (B, C; 0.75 g.) at 166-168°. The melting-point of a mixture of (A) with (B + C), or of a mixture of either with the analysed complex, m.p. 158-160° above, was 159-160°.

In a preliminary experiment the procedure was as follows.—To the deep red suspension of 2-nitrofluoron-9-ol (5.0 g.) in sulphuric acid (50 ml.) was added sodium azide (2.2 g.) during one hour with stirring at 0°. After two hours longer the suspension was added to ice-cold water (500 ml.) and the brown precipitate was filtered off; no base was liberated when the acid filtrate was made alkaline with 2N-sodium hydroxide. The solid, on grinding with 2N-sodium
hydroxide, became green. This suspension was filtered and the solid was washed with water until the washings were no longer alkaline, and dried, yielding a dark brown solid (4.75 g.). This substance was infusible, contained sulphur, was insoluble in the usual organic solvents and in dilute acids, and gave a green surface coloration with dilute alkalis.

7-Nitrophenanthridone.

7-Nitrophenanthridine (1.0 g.), dissolved in boiling 35%-sulphuric acid (60 ml.) was treated with potassium permanganate (2.0 g.) during 15 minutes. The brown precipitate was collected, washed with water, and extracted with boiling pyridine (40 ml.). Dilution of the extract with water gave a yellow solid (0.6 g.), m.p. 325—328°, which on crystallisation from pyridine or from glacial acetic acid yielded yellow needles of 7-nitrophenanthridone, m.p. 329° alone or when mixed with an authentic specimen of m.p. 328° kindly supplied by Dr. E. Schofield. (Found: C, 65.0; H, 3.8. Calc. for C₁₉H₁₂O₇: C, 65.0; H, 3.35%).
O-Chloro-7-nitrophenanthridine.

7-Nitrophenanthridine (0.3 g.), treated as described above for the 3- isomer, yielded colourless needles of 9-chloro-7-nitrophenanthridine (0.2 g.), m.p. 207-208°.

Oxidation of 7-nitrophenanthridine with alkaline permanganate.

7-Nitrophenanthridine (1.0 g.), potassium permanganate (8.5 g.), and water (50 ml.) were heated together cautiously. After the initial vigorous reaction had subsided, the mixture was boiled under reflux until the permanganate colour had disappeared (3 hours), and then filtered. The filtrate was concentrated to 10 ml. and acidified with 10N-hydrochloric acid: there separated, after several days, small brown crystals (0.4 g.), m.p. 255° (decomp.). This substance was acidic, contained nitrogen, and was readily soluble in hot water but insoluble in non-polar solvents.

7-Aminophenanthridine.

A suspension of 7-nitrophenanthridine (5.0 g.) and iron powder (10.0 g.) in 3N-acetic acid (5 ml.) and water (250 ml.) was heated under reflux for five hours. The black solid was collected, dried, and extracted with hot benzene,
yielding 7-aminophenanthridine (3.6 g., 83%), m.p. 301-303°C.
Reinstillation from aqueous methanol gave pale yellow
needles, m.p. 302-303°C. (Found: C, 80.2; H, 5.0; N, 14.8.
Calc. for C_{15}H_{10}N_2: C, 80.35; H, 5.25; N, 14.45%).

7-Ethoxycarbonylaminophenanthridine.

Ethyl chloroformate (1.5 ml.) was added drop by drop
to a solution of 7-aminophenanthridine (2.5 g.) in diethyl-

earnine (3 ml.) and boiling absolute ethanol (40 ml.), and the
red solution was heated under reflux for 30 minutes. From
the solution there separated 7-ethoxycarbonylamino-

phenanthridine, which after crystallisation from methanol
formed buff needles (0.75 g.), m.p. 305-307°C. (Found:
C, 72.5; H, 5.35; N, 10.8. Calc. for C_{16}H_{14}O_2N_2: C, 72.2; H, 5.3; N, 10.5%).

The mother-liquor on further keeping deposited a
substance which crystallised as felted needles (1.4 g.), m.p.
158-153°C (Found: C, 71.0; H, 5.3; N, 9.25%).

7-Hydroxyphenanthridine.

A hot solution of 7-aminophenanthridine (1.8 g.)
in water (20 ml.) containing sulphuric acid (0.75 ml.) was
cooled with stirring, and the suspension of orange flocculent solid dissolved at 0° with a solution of sodium nitrite (0.70 g.) in water (3 ml.) during 5 minutes. After 15 minutes at 0°, the orange solution was clarified by filtration and heated on the steam-bath. Nitrogen was evolved with the separation of a dark red solid; after 30 minutes the solution was cooled, made alkaline with 2N-sodium hydroxide, and filtered from the insoluble red substance. The latter, on drying, weighed 1.06 g. Neutralisation of the alkaline filtrate with H-sulphuric acid gave a pale pink precipitate (0.65 g.), m.p. 250-260°, which was purified via its hydrochloride; the base was dissolved in hot 3N-hydrochloric acid (35 ml.) and the solution was cooled to 0°, giving large, flat, orange needles (0.65 g.). The base, obtained from this hydrochloride by decomposition with one equivalent of sodium hydroxide solution, melted at 270-281° and yielded, on crystallisation from ethanol (60 ml.), a pale pink micro-crystalline powder of 7-hydroxyacridone (0.3 g.), m.p. 282-283°. (Found: C, 70.55; H, 4.9; N, 7.3. \( \text{C}_{15}\text{H}_{10}\text{N} \) requires C, 70.35; H, 4.65; N, 7.2%).

The insoluble red substance dissolved in much hot glacial acetic acid from which separated bright red, silky
needles which become reddish-brown on washing with water. This solid had m.p. 290-295° (decomp.) and after two recrystallisations from the above solvent melted at ca. 295° (decomp.). (Found: C, 76.65; H, 4.05; N, 13.0. C26H16O4N4 requires C, 78.0; H, 4.05; N, 14.0%).

Attempts to methylate 7-hydroxyphenanthridine.

(i) Using dimethyl sulphate.—A solution of 7-hydroxyphenanthridine (0.24 g.) in water (5 ml.) containing sodium hydroxide (0.15 g.) was shaken for two hours with dimethyl sulphate (0.15 ml.). No solid separated, and after diluting the solution with water (30 ml.) dilute sulphuric acid was added until the solution was just neutral to litmus, giving a pale yellow precipitate which was collected washed with water, and dried in vacuo. This solid (0.16 g.), m.p. 96-106°, contained nitrogen and sulphur.

(ii) Using diisocyanate.—A solution of diisocyanate was prepared by cooling a mixture of ether (15 ml.) and water (1.5 ml.) containing sodium hydroxide (1.0 g.) with stirring while N-nitrosomethylurea (1.0 g.) was added during 15 minutes; the bright yellow ethereal solution was decanted off. 7-Hydroxyphenanthridine (0.16 g.) was added to this solution,
and the whole was allowed to stand with occasional shaking for 24 hours at room temperature. The colour of the solution disappeared but the solid remained unchanged; 0.18 g., m.p. 262°C, was recovered.

The reaction of phenanthridine-7-diaxonium sulphate with methanol.

Freshly redistilled amyl nitrite (2.0 g., b.p. 96–98°C) was added to the buff suspension of 7-amino-phenanthridine sulphate, formed by the dropwise addition of concentrated sulphuric acid (3 ml.) to a solution of the base (2.0 g.) in absolute ethanol (40 ml.). The suspension was kept at 25°C with frequent shaking for 24 hours without much apparent change, except in the colour which became pink. At the end of this time the solid was collected, washed with absolute ethanol and with dry ether, and was suspended in absolute methanol (100 ml.) which was then raised to the boil. After one hour nitrogen evolution had ceased and the dark red solution was evaporated to ca. 10 ml. Addition of this solution to N-hydrochloric acid (150 ml.) gave a small amount of tar and a deep red solution; the latter was made alkaline with 3N-sodium hydroxide and the pink oil was thrice extracted.
with ether (100 ml. portions); some more tar remained undissolved. After being dried over anhydrous sodium sulphate, the ethereal solution was evaporated, yielding a red semi-solid. Extraction of this material with several lots of boiling light petroleum (b.p. 40-60°, 200 ml. in all) left a poppy-red solid (0.65 g.) undissolved, and from the extract was recovered crude phenanthridine (0.55 g.), m.p. 85-86°, which, after purification by molecular distillation at 120°/2 m.m., yielded colourless needles (0.45 g.), m.p. 103-104°. It formed a pierate which separated from much ethanol as silky yellow needles, m.p. 244-245°.


2-Acetamidodiphenyl (15.0 g.) was dissolved with cooling in glacial acetic acid (15 ml.) and concentrated sulphuric acid (30 ml.) and the solution cooled in a freezing mixture while a mixture of glacial acetic acid (14 ml.) and
fuming nitric acid (q 1.5, 6 ml.) was added drop by drop during one hour, so that the temperature did not rise above 5°. The precipitate obtained on pouring the product into ice and water (400 g.) was crystallised from ethanol (300 ml.) yielding 2-acetamido-4'-nitrodiphenyl (11.0 g.), m.p. 196-197°.

This acetamido compound was dissolved in ethanol (150 ml.) and hydrogen chloride was passed in until the increase in weight was 15 g. The orange solution was boiled under reflux for four hours, then poured into water (500 ml.); the crystalline precipitate obtained on making alkaline with 2N-sodium hydroxide was collected and dried. It yielded 2-amino-4'-nitrodiphenyl (0.3 g.), m.p. 157-158°. (Idem. loc. cit., m.p. 158°).

2-Formamido-4'-nitrodiphenyl.

2-Amino-4'-nitrodiphenyl (0.3 g.) was heated under reflux with formic acid (96%, 100 ml.) for one hour. The pale yellow precipitate obtained on pouring the solution into water (500 ml.) was collected and crystallised from ethanol (250 ml.) giving colourless silky needles of 2-formamido-4'-nitrodiphenyl (6.9 g.), m.p. 176°. (Found:
Attempt to synthesise 7-nitrophenanthridine by the cyclisation of 2-formamido-4'-nitrodiphenyl.

To a solution of 2-formamido-4'-nitrodiphenyl (5.9 g.) in nitrobenzene (60 ml.), phosphorus oxychloride (30 ml.) and stannic chloride (5 ml.) were added; the deep red solution was boiled under reflux for four hours, was cooled, and was poured on ice (one kg.). The mixture was shaken mechanically for two hours to decompose the excess of phosphorus oxychloride, and the nitrobenzene was distilled off in steam; there remained a yellow solution containing a brown non-basic solid which was filtered off, and extracted with hot 5N-hydrochloric acid (300 ml.). The combined acidic solutions were made alkaline with 5N-sodium hydroxide giving an orange crystalline precipitate (1.4 g.) from which 2-amino-4'-nitrodiphenyl (0.8 g.), m.p. 156-158° was recovered by crystallisation from benzene. No other basic material was isolated.
The reaction of 2-aminofluoren-9-ol with hydrazoic-sulphuric acid.

To a vigorously stirred hydrazoic-sulphuric acid mixture, from sodium azide (5.55 g.), sulphuric acid (14 ml.), and chloroform (20 ml.) was added a suspension of 2-aminofluoren-9-ol (9.25 g.) in chloroform (40 ml.) in twenty portions during one hour. The greyish-brown reaction mixture was stirred for one hour longer, then added to ice and water (200 g.) and shaken well. From the deep orange, acidic solution there separated, on making alkaline with 2N-sodium hydroxide, a red gum which gave a resinous solid (8.9 g.) on standing. After two extractions of this solid with boiling benzene (300 ml. portions) there remained a sticky red tar (1.65 g.); on cooling there separated from the combined solutions pale orange needles of impure 2-aminofluoren-9-ol (1.9 g.), m.p. 188-193° (the mixed m.p. with authentic 2-aminofluoren-9-ol was 193-195°). Concentration of the mother-liquor to 200 ml., and further concentrations, yielded six crops of reddish crystalline solid: 0.9 g., m.p. 183-190°; 0.45 g., m.p. 182-195°; 0.6 g., m.p. 193-197°; 0.15 g., m.p. 189-191°; 0.55 g., m.p. ca. 170°; and 0.35 g., m.p. ca. 165°. Further concentration of the mother-liquor yielded a red gum, from
which no more crystalline solid could be isolated. These six crops were combined (total 3.0 g.) and recrystallised from aqueous methanol, giving pale yellow needles of 7-aminophenanthridine, m.p. 202° alone and when mixed with an authentic specimen of m.p. 202-203°.
The reaction of 3-nitrofluoren-9-ol with hydrazoic-sulphuric acid.

To a vigorously stirred hydrazoic-sulphuric acid mixture, from sodium azide (2.15 g.), sulphuric acid (7.5 ml.), and chloroform (30 ml.), was added 3-nitrofluoren-9-ol (5.0 g.) in small portions during one hour. After being stirred for one hour longer, the orange reaction mixture was poured into ice and water (250 g.), shaken, the buff solid was filtered off, and the aqueous and chloroform layers were separated. The solid, suspended in the aqueous solution, yielded, on decomposition with 2N-sodium hydroxide, the crude base (1.6 g.), m.p. 185-190°; a further quantity (2.35 g.), m.p. 180-190°, was obtained from the chloroform solution. This material (total 3.95 g.), on fractional crystallisation from benzene (120 ml.) gave 6-nitrochryseneanthridine (3.3 g.), m.p. 192-194°, golden-yellow needles, m.p. 194° after further recrystallisations from benzene. (Found: C, 69.75; H, 3.65; N, 12.4. C_{13}H_{6}O.N requires C, 69.65; H, 3.6; N, 12.5%). A second substance obtained in small amount (0.25 g.) in the fractional crystallisation formed buff rosettes of needles, m.p. 225-245°; after two crystallisations from benzene it yielded pale orange
needles of 3-nitrophenanthridine, m.p. 256-259° alone, and
262-264° when mixed with an authentic specimen of this
substance, m.p. 268° (p. 203).

In a second experiment on twice the scale the total
yield of crude base was 9.5 g., m.p. 184-188°, which on
fractional crystallisation gave 6-nitrophenanthridine (7.5 g.),
m.p. 191-193°, and the buff solid (0.45 g.), m.p. 225-235°.

6-Nitrophenanthridone.

To a solution of 6-nitrophenanthridine (1.0 g.) in
boiling 3N-sulphuric acid (60 ml.) was added potassium
permanganate (2.0 g.) in small portions during 15 minutes.
Extraction of the brown precipitate with much boiling pyridine
and dilution of the extract with water gave a yellow solid
which, on recrystallisation from pyridine, yielded bright
yellow needles of 6-nitrophenanthridone (0.6 g.), m.p. 369°
(uncorrected). (Found: C, 65.2; H, 3.3; N, 11.6.
C_{15}H_{9}O_{3}N_{2} requires C, 65.0; H, 3.35; N, 11.65%).

2-Chloro-6-nitrophenanthridine.

6-Nitrophenanthridone (1.0 g.) was heated under
reflux with phosphorus oxychloride (10 ml.) for five hours.
The pale yellow precipitate obtained on pouring the product into water was collected, dried, and crystallised from benzene (40 ml.) yielding pale yellow needles of 2-chloro-6-nitrophenanthridine (0.7 g.), m.p. 218°. (Found: C, 60.95; H, 2.85; N, 10.75; Cl, 13.35. C₁₃H₇O₂N₂Cl requires C, 60.35; H, 2.75; N, 10.65; Cl, 13.7%).

**6-Aminophenanthridine.**

6-Nitrophenanthridine (1.0 g.), iron powder (2.0 g.), 3N-aetic acid (1 ml.), and water (50 ml.) were boiled together under reflux for five hours. The black solid was collected, dried, and extracted with boiling benzene; concentration of the solution yielded pale yellow rosettes of needles of 6-aminophenanthridine (0.75 g.), m.p. 194-195°. (Found: C, 80.45; H, 5.4; N, 14.35. Calc. for C₁₅H₁₀N₂: C, 80.35; H, 5.25; N, 14.45%).

**6-Hydroxyphenanthridine.**

A hot solution of 6-aminophenanthridine (1.7 g.) in water (50 ml.) containing sulphuric acid (5 ml.) was cooled to 3° with rapid stirring and the pale yellow suspension was diazotised by the dropwise addition of a solution of sodium
nitrite (0.7 g.) in water (3 ml.) during five minutes. After
a further 15 minutes urea was added and the orange solution
was boiled gently, for ten minutes, until the brisk evolution
of nitrogen had ceased. The yellow solution was cooled, made
alkaline with 2N-sodium hydroxide, and filtered from a trace
of insoluble red solid. The very pale pink precipitate which
formed on making the solution just acid with acetic acid was
collected, washed with water and dried: it weighed 1.55 g.,
m.p. 264-267°. Recrystallisation from ethanol yielded pale
pink leaflets of 6-hydroxyphenanthridine (0.9 g.), m.p.
272-273°. (Found: C, 80.3; H, 4.7; N, 7.2. C_{13}H_{9}ON
requires C, 79.85; H, 4.65; N, 7.2%).

2-Formamido-5-nitrodiphenyl.

2-Amino-5-nitrodiphenyl (5.0 g.) was heated under
reflux with formic acid (90%, 50 ml.) for one hour. The
brown precipitate formed on pouring into cold water (300 ml.)
was crystallised from ethanol, yielding buff, feathery needles
of 2-formamido-5-nitrodiphenyl (3.7 g.), m.p. 145-146°.
(Found: C, 64.25; H, 4.15; N, 11.6. C_{13}H_{10}O_{3}N_{2} requires
C, 64.45; H, 4.15; N, 11.85%).
The synthesis of 3-nitrophenanthridine by the acylation of 2-formamido-5-nitrodiphenyl.

The deep violet solution formed by the addition of stannic chloride (0.9 g.) to a solution of 2-formamido-5-nitrodiphenyl (8.0 g.) in nitrobenzene (30 ml.) and phosphorus oxychloride (10 ml.) was heated under reflux for four hours, and the basic material was isolated as described for the similar reaction with 2-formamido-4'-nitrodiphenyl (p. 196).

There was obtained, on crystallisation from benzene, pale orange needles of 3-nitrophenanthridine (0.8 g.), m.p. 263°. (Found: C, 69.5; H, 3.6; N, 12.6. Calc. for C_{15}H_{9}O_{2}N_{2}: C, 69.65; H, 3.6; N, 12.5%).
The reaction of 3-nitrofluorenone with hydrazoic-sulphuric acid.

(All melting-points in this section are uncorrected.)

The deep red solution of 3-nitrofluorenone (5.0 g.) in sulphuric acid (28 ml.) was stirred at 0° while sodium azide (2.8 g.) was added during one hour. After 30 minutes longer, the mauve solution was poured on ice (400 g.) giving a greenish-brown precipitate which was collected, washed with water until neutral, and dried. The brown solid weighed 5.2 g., m.p. ca. 340°: this material (4.7 g.) was purified by fractional sublimation at 220°/0.1 mm., but separation of the two isomeric nitrophenanthridones was not efficient. 19 crops were obtained (see Table VII) as yellow powders totalling 3.7 g.; the non-volatile residue was a black, infusible solid. Crop (d) gave the following analysis:

(found: C, 64.7; H, 3.55. Calcd. for C_{13}H_{11}NO,H: C, 68.0; H, 3.36%). Crop (n), originally 0.252 g., m.p. 344-355°, was carefully resublimed in four fractions, (n_1), (n_2), (n_3), and (n_4); the last, on recrystallisation from pyridine (5 ml.), gave small green coloured needles of 3-nitrophenanthridone (0.035 g.), m.p. 373-374°. Crop (a) was recrystallised from pyridine (3.5 ml.), yielding yellow needles (0.041 g.), m.p. 333-335°.
<table>
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<th>melting-point, (°C)</th>
<th>% of 3-nitro from diag. V.</th>
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<td>(l)</td>
<td>0.274</td>
<td>(339) - 350</td>
<td>69</td>
<td>0.186</td>
</tr>
<tr>
<td>(n)</td>
<td></td>
<td></td>
<td></td>
<td>0.581</td>
</tr>
<tr>
<td>(n₁)</td>
<td>(n₂) (n₃) (n₄)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(p)</td>
<td>0.082</td>
<td>(335) - 345</td>
<td>64</td>
<td>0.039</td>
</tr>
<tr>
<td>(q)</td>
<td>0.039</td>
<td>(346) - 354</td>
<td>74</td>
<td>0.039</td>
</tr>
<tr>
<td>(r)</td>
<td>0.016</td>
<td>(356) - 360</td>
<td>62</td>
<td>0.013</td>
</tr>
<tr>
<td>(s)</td>
<td>0.056</td>
<td>(365) - 367</td>
<td>92</td>
<td>0.051</td>
</tr>
<tr>
<td>(t)</td>
<td>0.182</td>
<td>(350) - 356</td>
<td>77</td>
<td>0.140</td>
</tr>
<tr>
<td></td>
<td>0.100</td>
<td>(347) - 355</td>
<td>75</td>
<td>0.075</td>
</tr>
<tr>
<td></td>
<td>0.059</td>
<td>(351) - 356</td>
<td>77</td>
<td>0.045</td>
</tr>
<tr>
<td></td>
<td>0.005</td>
<td>(353) - 357</td>
<td>73</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td>0.042</td>
<td>(340) - 347</td>
<td>67</td>
<td>0.023</td>
</tr>
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</table>

**Table VII.**

<table>
<thead>
<tr>
<th>crop</th>
<th>weight of crop, (g.)</th>
<th>melting-point, (°C)</th>
<th>% of 3-nitro from diag. V.</th>
<th>weight of 3-nitro in crop, (g.)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>total = 3.528 g.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>total of 3-nitrophenanthridone = 2.428 g.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
A melting point-composition curve for mixtures of 3- and 6-nitrophenanthridones, obtained from unambiguous sources (see p.p. 208 and 200), was constructed. Small quantities of the two compounds were accurately weighed out and intimately mixed together by grinding. The melting-points of these mixtures were determined as follows: the substance, in a melting-point tube 2 mm. in diameter, was immersed in an electrically heated block preheated to 320° and heated at the rate of one degree per minute. The temperature (in brackets) at which liquid first appeared and that at which the last trace of solid disappeared were recorded (see table VIII). Since some darkening occurred on fusion and this might have introduced decomposition errors, the mixtures were not fused before determining their melting-points. Diagram V shows melting-point plotted against percentage composition of the mixture; in the construction of this curve only the upper melting-points were used.
Table VIII.

<table>
<thead>
<tr>
<th>weight of 6-nitro (g.)</th>
<th>weight of 3-nitro (g.)</th>
<th>% 6-nitro</th>
<th>melting-point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0360</td>
<td>0.0140</td>
<td>60</td>
<td>(348) - 355</td>
</tr>
<tr>
<td>0.0420</td>
<td>0.0230</td>
<td>60</td>
<td>(334) - 344</td>
</tr>
<tr>
<td>0.0360</td>
<td>0.0230</td>
<td>50</td>
<td>(333) - 337</td>
</tr>
<tr>
<td>0.0280</td>
<td>0.0420</td>
<td>40</td>
<td>(334) - 348</td>
</tr>
<tr>
<td>0.0140</td>
<td>0.0660</td>
<td>20</td>
<td>(350) - 360</td>
</tr>
</tbody>
</table>

pure 6-nitrophenanthridone
368°
pure 3-nitrophenanthridone
378°

The fact that crop (a), which had m.p. 332-334°, raised to 335-338° after one recrystallisation from pyridine, is very near the eutectic mixture, while 3-nitrophenanthridone was obtained on recrystallisation of (n₁), shows that all the mixtures in Table VII lie on the left-hand branch of the curve. This is confirmed by the fact that (n₁) (20 mg.) mixed with 3-nitrophenanthridone (20 mg.) melted at (348) - 364°; if (n₁) is 66% 5-nitro, then the mixture is 82% 3-nitro, and
should melt at 360°. Similarly \( n_1 \) (20 mg.) mixed with 6-nitrophenanthridone (20 mg.) melted at (331) - 345° (calculated: 68% 6-nitro, m.p. 349°).

The percentage of 3-nitrophenanthridone in each crop was read off from the diagram, again using only the upper figures, and the actual weight of this compound was calculated (see table VII). Hence the percentage of 3-nitrophenanthridone in the reaction mixture is \( 100 \times \frac{2.428}{3.528} \) or 69.6%.


A solution of fluoranthene (4.5 g.) in sulphuric acid (30 ml.) was stirred at 0° during the addition of sodium azide (3.25 g.) during 1½ hours. After one hour further the green solution was poured on ice (200 g.); the buff precipitate was collected, washed with water, and crystallised from glacial acetic acid (150 ml.). There separated colourless crystals of phenanthridone (3.2 g.), m.p. 292-293°.


Phenanthridone (3.2 g.) was dissolved in cold concentrated nitric acid (4 l.42, 40 ml.), and the solution
was warmed gently: after a few minutes the solution became
red and solidified with the evolution of much heat. Water
was added, and the solid was collected and crystallised from
glacial acetic acid (500 ml.) giving small cream-coloured
needles of 3-nitrophenanthridone (1.06 g.), m.p. 372°
The reaction of 2-methylfluoren-9-ol with hydrazoic-sulphuric acid.

To a vigorously stirred hydrazoic-sulphuric acid mixture, from sodium aside (1.0 g.), sulphuric acid (4 ml.), and chloroform (15 ml.), was added 2-methylfluoren-9-ol (1.06 g.) in small portions during one hour. The deep red reaction mixture was stirred one hour longer and poured into cold water (100 ml.); the mixture was shaken, and the aqueous and chloroform solutions separated. The aqueous solution was made alkaline with 3N-ammonium hydroxide, the pale yellow oil was extracted with ether, the ethereal solution was dried over anhydrous sodium sulphate, and evaporated. The residual oil (1.75 g.) was extracted with boiling light petroleum (b.p. 40-60°, 100 ml.), the extract was decanted from a small amount of sticky red gum and was evaporated, yielding an amber oil (1.6 g.) which on standing at room temperature crystallised in large, dense rosettes of tablets, m.p. 42-53°.

In a similar experiment on twice the scale the yield of petroleum-soluble base was 3.05 g., m.p. 45-55°.

The combined basic fractions (4.65 g.) from these two experiments were fractionally crystallised from light
petroleum (b.p. 40–60°, initially 150 ml.), eight crops being obtained. The first four (totalling 0.95 g.) melted within the range 72–80°, and after three recrystallisations from this solvent gave pale pink needles of 7-methylphenanthridine (0.4 g.), m.p. 87.5–89°. (Found: C, 87.2; H, 5.75; N, 7.15. Calc. for C18H11N: C, 87.0; H, 5.75; N, 7.23%). It yielded a picrate, small yellow needles from dioxan, m.p. 240–241°.

The last four crops from the original fractional crystallisation weighed 3.35 g. and melted within the range 45–64°. They were converted to the picrate, by precipitation from alcoholic solution, and yielded a yellow solid (6.95 g.), m.p. 228–235°; this was then recrystallised from dioxan six times. The yellow, crystalline solid (4.15 g.), m.p. 248–250°, so obtained was recoverted to base by shaking with ether and 2N-sodium hydroxide giving a colourless solid (1.75 g.), m.p. 70–75°, which after four recrystallisations from light petroleum yielded colourless needles of 2-methylphenanthridine (0.7 g.), m.p. 80°. (Found: C, 85.9; H, 5.35; N, 6.9%).

The picrate formed yellow needles (from dioxan), m.p. 253–254°.

From the various filtrates were recovered three crops of base as follow:
(a) material derived from mother-liquors from 7-methylphenanthridine, (0.55 g.) m.p. 63-72°;
(b) material derived from mother-liquors from 2-methylphenanthridine, (0.50 g.) m.p. 67-73°;
(c) material derived from intermediate mother-liquors, (1.40 g.) m.p. 54-67°.

Thermal analysis of the mixtures of 2- and 7-methylphenanthridines (a, b, c, above) was carried out exactly as described for the 3- and 6-nitrophenanthridones (p. 206; also table IX).

<table>
<thead>
<tr>
<th>weight of 2-methyl (g.)</th>
<th>weight of 7-methyl (g.)</th>
<th>% 2-methyl</th>
<th>melting-point (°C)</th>
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<tbody>
<tr>
<td>0.056</td>
<td>0.014</td>
<td>80</td>
<td>(56) - 73</td>
</tr>
<tr>
<td>0.022</td>
<td>0.028</td>
<td>60</td>
<td>(54) - 64</td>
</tr>
<tr>
<td>0.025</td>
<td>0.025</td>
<td>50</td>
<td>(55) - 59</td>
</tr>
<tr>
<td>0.028</td>
<td>0.042</td>
<td>40</td>
<td>(55) - 69</td>
</tr>
<tr>
<td>0.014</td>
<td>0.056</td>
<td>20</td>
<td>(58) - 80</td>
</tr>
</tbody>
</table>

pure 2-methylphenanthridine

pure 7-methylphenanthridine

80°

88°
Diagram VI

- 2-methylphenanthridine
- 7-methylphenanthridine

Temperature: 65 °C
Diagram VI was constructed and the percentages of 2-methylphenanthridine in crops (a), (b), and (e) were read off (table X).

<table>
<thead>
<tr>
<th>crop</th>
<th>weight of crop (g.)</th>
<th>melting-point °C</th>
<th>% of 2-Methyl</th>
<th>weight of 2-Methyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>0.58</td>
<td>(63) - 72</td>
<td>35</td>
<td>0.19</td>
</tr>
<tr>
<td>(b)</td>
<td>0.50</td>
<td>(67) - 75</td>
<td>80</td>
<td>0.40</td>
</tr>
<tr>
<td>(c)</td>
<td>1.40</td>
<td>(54) - 67</td>
<td>42</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>0.38</td>
<td>87.5 - 89</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0.70</td>
<td>80</td>
<td>100</td>
<td>0.70</td>
</tr>
<tr>
<td>total = 3.53</td>
<td>total of 2-methyl = 1.88</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

That crop (c) is on the right-hand branch of the curve is shown by the fact that the melting-point of (c) was lowered (50–61°) by the addition of a little 2-methylphenanthridine, and raised (55–75°) by the addition of 7-methylphenanthridine.
The percentage of 2-methylphenanthridine in each crop was read off from the diagram, and the actual weight of this compound in the mixture was calculated. Hence the percentage of 2-methylphenanthridine in the reaction mixture is $100 \times \frac{1.86}{3.53}$ or 53%. 
The reaction of 3-methylfluoren-2-ol with hydrasie-sulphuric acid.

3-Methylfluoren-2-ol (1.95 g.) was treated with a hydrasie-sulphuric acid mixture, and the basic, petroleum-soluble fraction was isolated, precisely as described for the reaction with the 3-methyl isomer (p. 210). The yield of basic oil was 1.7 g.; it crystallised fairly readily to give a pale pink mass, m.p. 65-76°.

The basic, petroleum-soluble solid, from a second similar experiment on thrice the scale, weighed 2.75 g., m.p. 62-76°.

The combined base (4.5 g.) was crystallised from light petroleum (b.p. 40-60°, initially 70 ml.) in twelve fractions. The first eight (3.3 g.), melting within the range 72-86°, gave, after four recrystallisations from this solvent, large rosettes of pale pink leaflets of 3-methylphenanthridine (0.45 g.), m.p. 89-89.5°. (Found: C, 86.9; H, 5.7; N, 7.25. Calc. for C₁₄H₁₁N : C, 87.0; H, 5.75; N, 7.25%). It formed a picrate, pale yellow needles from dioxan, m.p. 271-272°. (Found: N, 13.15. Calc. for C₁₀H₁₀N₂O : N, 13.26%).
The last four crops from the original fractional crystallisation (0.42 g., m.p. 69-75°; 0.13 g., m.p. 55-60°; 0.03 g., m.p. 57-65°; and 0.40 g., m.p. 45-60°; total 0.98 g.) consisted largely of 3-methylphenanthridine, since this compound (0.25 g.), m.p. 84-86° (the m.p. when mixed with the pure compound was 86-89°) was obtained on recrystallising the combined crops three times from light petroleum. No other base was isolated.
Asido-Fluorenes

The reaction of 9-chloro-2-nitrofluorene with sodium asido.

A suspension of 9-chloro-2-nitrofluorene (2.0 g.) and sodium asido (1.0 g.) in methanol (40 ml.) was heated under reflux for four hours, and gave a voluminous orange solid which filled the liquid. When cold, this solid was collected, washed with water, dried, and crystallised from benzene; it yielded orange needles of 2-imino-2-nitrofluorene (1.4 g.), m.p. 209°. (Found: C, 69.75; H, 3.58; N, 12.3. C₁₃H₈O₂N₂ requires C, 69.65; H, 3.6; N, 12.5%)

Frequently on crystallisation from benzene, or from n-butanol 2-imino-2-nitrofluorene separated in two crystalline forms, orange needles and small, dark orange rosettes of leaflets; however both of these forms melted at 209°, as did a mixture of the two.

2-Imino-2-nitrofluorene (0.5 g.), when boiled with 12N-sulphuric acid (15 ml.) for 45 minutes, yielded yellow flocks of 2-nitrofluorenone (0.5 g.), m.p. 222° alone and when mixed with authentic material.

Attempts to carry out the reaction between 9-chloro-2-nitrofluorene and sodium asido under milder
conditions than those described above led to lower melting mixtures which always contained chlorine. For example, when 9-chloro-2-nitrofluorene (2.0 g.) was dissolved in acetone (20 ml.) and shaken with a solution of sodium azide (1.0 g.) in water (5 ml.) for six hours at room temperature, there was formed a deep orange solution which, on pouring into water, gave an orange solid (0.9 g.), m.p. 113-135°, containing chlorine.


9-Chloro-2-methoxyfluorene (2.0 g.), sodium azide (1.0 g.), and methanol (15 ml.) were heated together under reflux for three hours, and the yellow solution was poured into water (150 ml.). The orange oil which separated solidified giving a crystalline mass (1.9 g.), m.p. 36-38°. It yielded, after two crystallisations from light petroleum (b.p. 40-60°), pale yellow needles of 9-acido-2-methoxyfluorene. (Found: C, 71.1; H, 4.65; N, 17.45. C₁₄H₁₁O₂ requires C, 70.9; H, 4.65; N, 17.7%). The analysed specimen melted at 43.5-44.5° and it then recrystallised and remelted at 56-58°. When the melt was chilled, the crystalline solid obtained
usually had m.p. 65-66°, but one such specimen had the
original m.p. 44°. In a second preparation the crude solid
melted at 36-39°, and after one recrystallisation from light
petroleum it formed pale yellow needles, m.p. 55-56°.

The acid-catalysed decomposition of 2-amido-2-methoxyfluorene.

A mixture of sulphuric acid (2 ml.) and chloroform
(10 ml.) was vigorously stirred at 25° during the dropwise
addition (30 minutes) of a solution of 2-amido-2-
methoxyfluorene (1.0 g., m.p. 43.5-44.5°) in chloroform (5 ml.).
The almost black reaction mixture was stirred for an hour
longer at 25°, and then poured into water (100 ml.). The
whole was shaken thoroughly and a brown solid was filtered
off; the latter, after extraction by thrice boiling with
2N-hydrochloric acid (total, 150 ml.), weighed 0.37 g. The
acidic extract was combined with the aqueous sulphuric acid
solution (which had been separated from the chloroform layer),
made alkaline with 2N-sodium hydroxide, and the free base
extracted with ether. The ethereal solution, after drying
over anhydrous sodium sulphate, was evaporated, yielding a
pale amber oil which crystallised on cooling to pale yellow
rosettes of needles (0.50 g.), m.p. 59-75°. Fractional
crystallisation of this base from light petroleum (b.p. 100–110°C, 25 ml.) gave, as first crop, 0.23 g. of 7-methoxyphenanthridine (still containing a little of the 2-isomer), m.p. 85–88°; the mixed m.p. with pure 7-methoxyphenanthridine (m.p. 90°) was 87–89°. From the mother-liquor was recovered 0.12 g. of 2-methoxyphenanthridine (still containing a little of the 7-isomer), m.p. 55–57°; the mixed m.p. with pure 2-methoxyphenanthridine (m.p. 58°) was 56–58°.

In a second experiment, 9-acido-2-methoxyfluorene (0.90 g., m.p. 55–56°) yielded the basic mixture (0.40 g.), m.p. 60–74°, and the brown solid (0.30 g.).

The brown solids obtained in these two experiments were infusible but burnt completely; they contained nitrogen and sulphur, and were insoluble in and unaffected by mineral acids, alkalis, and all the common organic solvents. They therefore closely resemble the similar material obtained in the reaction between 2-methoxyfluoren-9-ol and hydrochloric-sulphuric acid (p. 167).
The Schmidt Reaction with α-Aroylbenzoic Acids.

With α-tolnoylbenzolic acid.

A solution of α-tolnoylbenzolic acid (4.6 g.) in chloroform (15 ml.) was added dropwise with vigorous stirring during one hour at 30°C to a hydroxo-sulphuric acid mixture, from sodium oxide (2.6 g.), sulphuric acid (15 ml.), and chloroform (15 ml.). Stirring was continued for two hours longer, and the reaction mixture was then poured into cold water (250 ml.). The chloroform layer was separated, was washed with sodium carbonate solution and with water, was dried over anhydrous sodium sulphate, and was evaporated. The product, on recrystallisation from ethanol, yielded α-oxo-2-p-tolyl-4:5-benz-1:3-oxazine (4.15 g., 88%), m.p. 155°C.

(Found: C, 76.1; H, 4.7; N, 6.1. Calc. for C₁₅H₁₁O₂N : C, 76.0; H, 4.7; N, 5.9%).

This oxazine (0.25 g.) was heated in a sealed tube at 160-170°C for four hours with concentrated hydrochloric acid (4 ml.). The almost colourless needles were collected and washed with water; they amounted to 0.11 g., m.p. 177-178°C alone or when mixed with authentic p-toluic acid.
With o-benzoxybenzoic acid.

(1) Chloroform Method. o-Benzoylbenzoic acid
(4.52 g.) yielded, by the above procedure, 6-axo-3-phenyl-
4:5-benz-1:3-oxazine (3.55 g., 60%), m.p. 122.5°. (Found:
C, 75.5; H, 4.4; N, 6.3. Calc. for C_{14}H_{9}O_{2}N: C, 75.3;
H, 4.1; N, 6.3%).

(11) Trichloroacetic acid method. (Badger, Howard,
o-Benzoylbenzoic acid (4.52 g.) was dissolved in a
mixture of trichloroacetic acid (40 g.) and sulphuric acid
(15 ml.) at 50°. To the stirred solution was added sodium
oxide (2.6 g.) in small portions during one hour; the solution
became yellow and nitrogen was evolved. After being stirred
three hours longer at this temperature the warm solution was
poured into cold water (300 ml.), giving a white precipitate
which was collected, washed, and dissolved in aqueous sodium
carbonate. After clarification of this solution by
filtration, the free acid was liberated by the addition of
3N-hydrochloric acid, and was collected, washed with water,
and dried; it gave 5-benzoxyanthranilic acid (3.75 g., 73%),
m.p. 176-179°.
(iii) Trichloracetic acid method, using chloroform as a diluent.

The Schmidt reaction with \(O\)-benzoylbenzoic acid was repeated as in (ii), but the warm reaction mixture was poured into chloroform (200 ml.). The cooled solution was washed with water, with aqueous sodium carbonate, and again with water, dried over anhydrous sodium sulphate, and evaporated. There remained 6-oxo-2-phenyl-4:5-benz-1:3-oxazine (4.05 g., 90%), m.p. 120°; after recrystallisation from ethanol, it (2.8 g.) had m.p. 123°.

Experiments on the hydrolysis of 6-oxo-2-phenyl-4:5-benz-1:3-oxazine.

(a) The oxazine (3.05 g.) was stirred at 50° for 4 hours with trichloracetic acid (20 g.) and sulphuric acid (7.5 ml.), and then treated as in the Schmidt reaction (ii). 3-Benzoylanthrenilic acid (3.05 g., 93%), m.p. 177°, was obtained.

(b) The oxazine (0.30 g.) was heated with trichloracetic acid (2.0 g.) and sulphuric acid (0.8 ml.) for one minute to 50° and the solution was poured into water. The
precipitate was filtered off, washed, and dried; it yielded N-benzoylanthranilic acid (0.26 g., 80%), m.p. 177°.

(a) The oxazime (0.30 g.), finely ground, was allowed to stand in contact with a mixture of trichloroacetic acid (2.0 g.), sulphuric acid (0.75 ml.), and water (30 ml.) for 24 hours in the refrigerator. The solid was collected, washed with aqueous sodium carbonate and with water, and dried. The oxazime (0.27 g.), m.p. 121°, was recovered.

(d) A solution of the oxazime (0.30 g.), prepared and heated as in (b), was poured into chloroform (25 ml.). From the chloroform solution, treated as described for the Schmidt reaction (iii), the oxazime (0.25 g., 83%) was recovered. From a similar experiment, but with heating for 4 hours at 50°, the oxazime (0.28 g., 93%), m.p. 121°, was recovered.
Experiments on the ring-closure of 4-benzoyleanthranilic acid 
under the Schmidt reaction conditions.

(e) A mixture of 4-benzoyleanthranilic acid (2.25 g.),
sulphuric acid (7.5 ml.), and chloroform (17.5 ml.) was 
stirred at 30° for three hours, and then treated as in 
the Schmidt reaction (1). There was obtained 
6-oxo-2-phenyl-4:5-benz-1:3-oxazine (1.85 g., 89%), 
m.p. 123°.

(f) A solution of 4-benzoyleanthranilic acid (0.5 g.) in 
trichloroacetic acid (4.0 g.) and sulphuric acid (0.75 ml.) 
was heated at 50° for four hours, and the brown solution 
was poured into chloroform (25 ml.). On treatment as in 
(d), the chloroform solution yielded 6-oxo-2-phenyl-4:5- 
benz-1:3-oxazine (0.38 g., 82%), m.p. 121°.
# Index to the Experimental Section

## General remarks

- Page 117

## The Preparation of Substituted Fluorenes

### 1. The preparation of derivatives from fluorene

<table>
<thead>
<tr>
<th>Compound</th>
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<td>2-Nitrofluorenol</td>
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<td>9-Benzyfluoren-9-ol</td>
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