SOME STUDIES
OF THE CHLORINATION OF AROMATIC HYDROCARBONS

A THESIS
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The products of chlorination of naphthalene and phenanthrene in acetic acid have been examined.

Analytical and chromatographic methods have been developed to determine and isolate the reaction products.

The work on naphthalene was of a preliminary nature. It was shown that chlorine addition products and acetoxy-chloroadducts were formed in the reaction.

The chlorination of phenanthrene was examined in greater detail. The effect of the presence of electrolytes on the product composition was investigated by volumetric analysis and isotope dilution.

One of the reaction products was shown to be 9-acetoxy-10-chloro-9,10-dihydrophenanthrene. One of the geometrical isomers of this compound was isolated. It is considered to be the trans-isomer, from the products of its reaction with silver acetate in acetic acid.

The significance of these observations is discussed in relation to the reaction paths involved in the chlorination, and to addition-elimination sequences leading to aromatic substitution.
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The author wishes to thank Professor P.B.D. de la Mare for his advice and encouragement throughout this work.

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The author wishes to take this opportunity to thank Mr. J. Lomas for many helpful discussions.
SECTION A.

INTRODUCTION
1. HISTORICAL PERSPECTIVE

In the nineteen twenties, Ingold and his school succeeded in relating the quantum mechanical description of the atom to the accumulated knowledge of chemical reactions. This initiated the systematic study of organic reaction mechanisms. "Structure and Mechanism in Organic Chemistry" by Ingold gives an account of the developments triggered off by these ideas.

The significance of this development must be gauged in the light of the history of ideas in the natural sciences. From the time of the Pythagoreans, physics developed as a theoretical science distinct from practical applications. The development of chemistry followed a very different path. Empirical knowledge accumulated from the earliest days of human civilisation, in connection with metallurgy, pottery, food preservation, medicine and the dyeing of cloth. The discipline of theoretical chemistry in the modern sense of the word did not develop till the 18th century. Since then theoretical chemistry has made progress in fitting the vast store of chemical knowledge into a coherent system.

Ingold's synthesis of the earlier chemical theories, with the findings of quantum theory, together with the work of Robinson, Pauling, Wheland, Hammett and many others, has given new power to this movement.

The new theoretical approach to the study of rates and
products of reactions coincided with the emergence of new analytical tools. Radioactive tracer techniques have made it possible to follow the fate of specific atoms in the course of a reaction. The development of spectrographic methods (mass spectrometry, nuclear magnetic resonance, electron spin resonance, as well as the older methods of measurements in the visible, ultra-violet, and infra-red range) has made it possible to identify pure compounds and determine their properties and concentrations; and the (re-) discovery of chromatography provides a technique of separation of unparalleled efficiency. The combination of such procedures has provided the theoretical chemist with a powerful set of tools to test his hypotheses.

The following study is an example of the use of such a combination for the clarification of the mechanism of the reaction between chlorine and aromatic hydrocarbons.
2. DEFINITION OF TERMS AND CONCEPTS

I. Atomic Structure

The quantum mechanical picture of the atom is derived largely from spectral measurements, i.e. from the observation of the interaction of matter and light, considerations of the relationship between matter and energy. The quantitative results obtained from the study of the simplest available atom, hydrogen, have been used as a model to provide generalisations applicable to other atoms, and extended to give a theoretical basis for the consideration of molecules and their interactions. It is proposed to give the definitions of the concepts used. Their derivation and detailed discussion is beyond the scope of this paper.

The atom is described as a positively charged nucleus surrounded by an equivalent number of electrons, whose position and velocity are subject to the laws of quantum mechanics. Chemical reactivity is expressed in terms of the behaviour of the outer electrons. A covalent bond is equivalent to the pairing of electrons with antiparallel spins.

Electrons in an atom are pictured as moving with a calculable probability distribution in the space about the nucleus. The energy of the electron associated with its most stable state is called its zero-point energy. The energy of the electron will decrease when its range of motion is increased.
When the structure of a molecule makes delocalisation possible, the energy of the system is reduced, and stability is gained.

II. Molecular Structure and Reactivity
a) Inductive Effects

The part which a group or molecule will play in a reaction depends on the distribution of bonds and charges among the constituent atoms, firstly, in a hypothetical state of isolation, the 'ground state' and, secondly, as affected by its surroundings. Because different atomic nuclei have different powers of attraction, electrons between unlike atoms will be unequally distributed. As a consequence, such bonds are dipolar. The influence of a substituent B on X in R-X arising from this is called the inductive effect, $^+I$. It is propagated along a chain of atoms by electrostatic induction, with loss of intensity. Its sign refers to the electron-attracting, $-I$, or repelling, $^+I$, power of the group compared with hydrogen.

TABLE 1 (see over)
TABLE 1

Inductive Effects of Substituent Groups

<table>
<thead>
<tr>
<th>+I GROUPS</th>
<th>-I GROUPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_3 )</td>
<td>( \text{NH}_3^+ )</td>
</tr>
<tr>
<td>( \text{CH}_2R )</td>
<td>( \text{NR}_3^+ )</td>
</tr>
<tr>
<td>( \text{CHR}_2 )</td>
<td>( \text{NO}_2 )</td>
</tr>
<tr>
<td>( \text{CR}_3 )</td>
<td>( \text{C}:\text{O} )</td>
</tr>
<tr>
<td>( \text{CO}_\text{O} )</td>
<td>( \text{C}:\text{O} )</td>
</tr>
<tr>
<td>( \text{O}_- )</td>
<td>( \text{CH}:\text{CH}_2 )</td>
</tr>
</tbody>
</table>

An analogous effect, the inductomeric effect, involves electronic shifts specific to the activated complex or transition state of a reaction and results from the polarising influence of one molecule on another. This effect is called into play by the mutual approach of the reactants, and can increase the rate of a reaction, but not retard it.

b) Conjugative Effects

Electrical effects in a conjugated system, where electrons are involved, will become distributed through the entire area of delocalisation of \( \pi \)-electrons.
The loss of intensity in transmission is less than the corresponding loss in inductive effects. Conjugation or mesomeric effects may be indicated by writing the possible resonance structures for a molecule and deducing the resulting changes in electron density,

or they may be represented by curved arrows.

| TABLE 2 |
| Mesomeric Effects of Substituent Groups |

+M Groups: -O⁻, -S⁻, -F, -Cl, -Br, -I
-OR, -OH, -NH₂, -CH₃, -NH₂

-M Groups: -NO₂, -C:N, -C:O, -C:O, -C:O, -C:O, -C:O, CH:CH₂

H R OH OR NH₂
As with inductive effects, conjugative effects may be permanent (i.e. dependent on ground-state properties \( \Phi_M \)) or time variable (i.e. determined by specific transition-state interactions, \( \Phi_E \)).

III. The Transition State

In the course of a chemical reaction, bonds are broken and formed. The reacting molecules pass through distorted and strained configurations to products.

The transition state theory describes reaction rates in terms of the work required to convert molecules of reactants into the most unstable configuration through which they must pass on their way to becoming products.

This configuration is called the activated complex; the energy required for its formation from the initial state is the energy of activation of the reaction. An intermediate formed in the reaction is represented by a dip in the energy profile diagram, and divides the reaction into stages. The stage with the highest activation energy will be the slowest, and constitutes the rate-determining step.

IV. Classification of Reagents

The description of a chemical bond in physical terms as the sharing of two electrons implies that bond breaking and bond making will consist of a redistribution of electrons between atoms.

It has been found possible to distinguish on chemical
grounds between two possible types of bond-breaking or making: homolytic, where the two bonding electrons are separated and form highly reactive but electrically neutral free radicals:

\[ A:B = A^* + B^* \]

and heterolytic, where the two bonding electrons remain with one fragment of the molecule which thus acquires one unit of negative charge, leaving the other more positively charged to an equivalent extent:

\[ A:B = A^- + B^+ \]

Only heterolytic reactions will be considered in detail. In the context of this work, homolytic reactions are of importance only as possible interfering side reactions, and in some cases provide analogies for mechanisms.

The definition of a heterolytic reaction leads to the classification of its participants into two types. Electrophilic reagents have a tendency to accept electrons or to attack positions of high electron density; examples are: NO\(_2^+\), AlCl\(_3\), halogens. Nucleophilic reagents, likely to donate electrons or attack positions of low electron density, are: OH\(^-\), OR, NH\(_3\).

In order to be able to classify a reaction, it is necessary to define arbitrarily which of its participants is the substrate and which the reagent. In this context halogen is considered to be the (electrophilic) reagent, and the organic compound the (nucleophilic) substrate.
V. Electrophilic Reagents

Halogenation and nitration are among the most important reactions of this type. Their part in aromatic substitution has been reviewed by de la Mare and Ridd.\(^{(1)}\) Nitration has also been reviewed by Hughes.\(^{(2)}\)

a) The Nitronium Ion

The fact that nitration of reactive aromatic compounds using excess of nitric acid in a suitable solvent (acetic acid or nitromethane) is of zero kinetic order, shows that the rate determining step involves only the nitrating agent.

The generally accepted mechanism involves the rapid protonation of nitric acid to form the nitric acidium ion, followed by its slow heterolysis to give the nitronium ion, which is considered to be the nitrating species.

\[
\begin{align*}
2\text{NO}_2\text{-OH} & \overset{fast}{\underset{slow}{\rightleftharpoons}} \text{NO}_2\text{-OH}_2^+ + \text{NO}_3^- \\
\text{NO}_2\text{-OH}_2^+ & \overset{slow}{\rightarrow} \text{NO}_2^+ + \text{H}_2\text{O} \\
\text{Ar-H} + \text{NO}_2^+ & \rightarrow \text{Ar-NO}_2^- + \text{H}^+
\end{align*}
\]

With relatively unreactive aromatic substrates the rate becomes dependent on the concentration of the

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(1) de la Mare and Ridd, Aromatic Substitution, London, 1959.
aromatic compound.

The existence of the nitronium ion has been established independently by cryoscopic measurements and the examination of Raman spectra, and by the isolation of nitronium salts (e.g. nitronium perchlorate).

b) Positive Halogenating Species

Reagents concerned in halogenation are classified as positively charged and neutral.

The reactions of fluorine are not relevant in this context, as they are predominantly homolytic.

Among the possible types of positively charged halogenating species are included the free halogenium cations, \( \text{X}^+ \); and their covalently solvated forms involving water (e.g. \( \text{XOH}_2^+ \)); a hydroxylic solvent (e.g. \( \text{XOHMe}^+ \), \( \text{XOHAc}^+ \)); or an amine (e.g. \( \text{XNH}_2^+ \)).

Evidence for the existence of the free halogenium cations has been reviewed by J. Arotsky and M.C.R. Symons. Spectral and magnetic evidence and thermodynamic calculations show that the order of stability is \( \text{I}^+ \), \( \text{Br}^+ \), \( \text{Cl}^+ \),

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(3) a) Bennett, Brand and Williams, J. chem. Soc., 1946, 69.
   b) Ingold, Millen and Poole, ibid. 1950, 2575.
as would be expected from the atomic structure. The existence of an iodinium cation is well documented, but the kinetic evidence for its part in iodination is ambiguous. (8) There is no independent physical evidence for either a chlorinium ion or a brominium ion; but the existence of the former has been inferred from kinetic evidence.

Reactivity of the substrate was found to affect the rate law of chlorination in acidic solutions of hypochlorous acid, in a manner analogous to nitration by the nitronium ion. (9) For very reactive substrates, rate = k(HOCl)(H⁺). The rate determining step was considered to be the formation of the active chlorinating species from the reagent. Of the two alternatives, ClOH₂ and Cl⁺, the latter was thought to be the more likely, as the protonation of HOCl is likely to be too fast.

The fact that methyl-para-tolyl ether is chlorinated faster in D₂O than in H₂O (10) was taken to confirm the view that the rate determining step is not a proton transfer, because D⁺ transfer would be expected to be

---

(9) de la Mare, Hughes and Vernon, Research, 1950, 2, 192, 242.
faster than $H^+$. These conclusions have, however, been subjected to criticism, and further work is desirable.

Bromination by acidified hypobromous acid involves a positively charged intermediate, $Br^+$ or $BrOH_2^+$. The rate of bromination of hexadeutero benzene was found to be approximately the same as that for benzene, indicating that proton loss is not rate determining to any important extent.

In aqueous acetic acid, bromination by hypobromous acid, and chlorination by hypochlorous acid, is subject to acid catalysis, consistent with an active species $XOH_2^+$, $X^+$, or $XOAcH^+$. In the case of hypochlorous acid, the variation of rate with solvent composition follows neither the change in carbonium ion formation from a triaryl methanol ($J_oCl^+$), nor the extent of protonation of a base ($H_oXOH_2^+$). It has therefore been suggested that the increase in the rate of chlorination by hypochlorous acid in 50% aqueous acetic acid over that in water indicates that the active species is $ClOAcH^+$.

   b) Derbyshire and Waters, J. chem. Soc., 1951, 73.
   c) de la Mare and Harvey, ibid., 1956, 36.
(12) de la Mare and Harvey, J. chem. Soc., 1957, 923.
(14) a) de la Mare, Hilton, and Vernon, J. chem. Soc., 1960, 4039.
   b) de la Mare, Hilton, and Varma, J. chem. Soc., 1960, 4044.
Few examples of amine co-ordination have been investigated. Kinetic evidence for a halogenating species of the type $R_2NHCl^+$ in the chlorination of phenols has been given for diethyl chloramine\(^{(15)}\) and the corresponding cation derived from morpholine.\(^{(16)}\) The catalytic action of pyridine in chlorination and bromination may be due to such co-ordination.

c) Neutral Halogenating Reagents

The neutral reagents include molecular halogens and interhalogen compounds.

The behaviour of halogens in substitution reactions has shown them to act as electrophiles. Electron donating substituents increase reactivity.

The relation between the structure of aromatic substrates and their reactivities towards halogenating agents has been discussed by de la Mare.\(^{(17)}\)

The importance of electron release through conjugative effects is illustrated by the comparison of the partial rate factors of halogenation in the para position of derivatives of benzene.\(^{(18)}\)(19)

\(^{(18)}\) de la Mare and Ridd, Aromatic Substitution, London, 1959.
\(^{(19)}\) Robertson, de la Mare, and Swedlund, J. chem. Soc., 1953, 782.
N,N Dimethylaniline $3 \times 10^{19}$
Anisole $7 \times 10^9$
Fluorobenzene 6.3

Comparisons of the partial rate factors for para-nitration and para-chlorination of aromatic compounds show that substituents contributing to conjugative electron release have a much more marked effect on molecular chlorination than on nitration.\(^{(20)}\)

<table>
<thead>
<tr>
<th>Substituent</th>
<th>MeO</th>
<th>Me</th>
<th>Ph</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Partial rate factor, $f_p$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) Nitration</td>
<td>280</td>
<td>58</td>
<td>11</td>
<td>0.79</td>
</tr>
<tr>
<td>(b) Molecular chlorination</td>
<td>$4 \times 10^7$</td>
<td>820</td>
<td>600</td>
<td>6.3</td>
</tr>
</tbody>
</table>

From the lack of retarding effect of Cl\(^{-}\) and HCl on chlorination and the positive catalytic effect of HBr on the bromination of mesitylene, Robertson concluded that the molecular halogens act as reactive species. This confirmed the conclusions of Bradfield and Orton.\(^{(20c)}\)

Bromine differs from chlorine in giving the kinetic form $-d(Br_2)/dt = k(ArH)(Br_2)^2$. The extra molecules of bromine are believed to assist in breaking the Br-Br bond in a complex of the form AHBBr\(_2\) by forming Br\(_3^-\).\(^{(20b)}\)


\(^{(20b)}\)Robertson, J. chem. Soc., 1943, 276.

\(^{(20c)}\)Bradfield and Orton, J. chem. Soc., 1927, 986.
Molecular iodine is too inactive to behave as an efficient iodinating agent except for the most active aromatic species; and, in general, it is necessary to remove hydrogen iodide as it is formed, in order to circumvent the unfavourable equilibrium which lies to the left in the equation $\frac{I^-}{\frac{3}{2}} \rightleftharpoons I_2 + I^-$. 

VI. Nucleophilic Substrates

a) Olefins

Covalent chemical bonds, which hold atoms together in a molecule, are considered to involve the sharing of electrons and electronic orbitals between atoms. The geometry of the orbitals determines the direction and magnitude of the forces. The carbon-carbon bond in a saturated organic compound is described as an $sp^3$-hybrid; carbon atoms share one of each of four tetrahedrally arranged $\sigma$-orbitals. In an olefinic compound, the bond is an $sp^2$-hybrid consisting of shared $\sigma$-orbitals in the same plane as the remaining bonds to the other substituents, and of $\pi$-orbitals situated above and below the plane of the molecule with a node in that plane. Overlap of adjoining $\pi$-orbitals prevents rotation about the $C=C$ bond.

b) Conjugated Olefins

The physical properties and chemical behaviour of compounds containing double bonds alternating with single bonds in general cannot be completely described by a single
conventional structure. For such compounds it is usually possible to write a number of structures which have the same positions of the skeletal atoms but differ from each other in the distributions of the electrons. These structures contribute to the configuration of the molecule in proportion to their stability.

Taking butadiene as an example, the formula can be written: $\text{CH}_2\text{CH}^+\text{CH}_2 \leftrightarrow \text{CH}_2\text{CH}^+\text{CH}^+\text{CH}_2$. Interaction between the $\pi$-orbitals of carbon atoms 2 and 3 as well as 1, 2 and 3, 4 allows delocalisation over the entire system. 1, 4 addition, which accompanies 1, 2 addition in the bromination of butadiene, can be described using this assumption:

$$\text{CH}_2\text{CH}^+\text{CH}^+\text{CH}_2 \rightarrow \text{BrCH}_2\text{CH}^+\text{CH}^+\text{CH}_2 \rightarrow \text{BrCH}_2\text{CH}^+\text{CH}^+\text{CH}_2 \rightarrow \text{BrCH}_2\text{CH}^+\text{CH}^+\text{CH}_2\text{Br}$$

The sharing of the double bond character is also apparent in the bond lengths: the C:C bonds in butadiene (1.37Å) are longer than those in ethylene (1.33Å), while the C:C distance (1.47Å) is shorter than that in ethane (1.55Å). (21)

According to the quantum mechanical picture of the atom, the energy of a particle is related to its motion; conjugation can be seen to make delocalisation of $\pi$-electrons possible.

and therefore reduce the energy of the molecule, that is increase its thermodynamic stability.

c) Aromatic Compounds

Benzene and related compounds have characteristic properties in common: chemical reactivity with many reagents which normally attack unsaturated compounds; a tendency to undergo substitution reactions rather than additions, and greater thermochemical stability.

Consideration of the chemical properties of these compounds, together with deductions from the application of quantum physics to the physical properties of atoms and molecules, have led to a description of aromatic compounds which gives a quantitative basis for the discussion of thermochemical stability and, indirectly, reactivity of aromatic compounds. The physiochemical approach has led to a wider concept of aromaticity, with benzenoid compounds a special case within a larger group, described as "alternant", whose carbon atoms can be divided into two sets in such a way that no two members of the same set are joined by a bond. In this type of molecule, delocalisation of the \( \pi \)-electrons will not be associated with the formation of terminal charges, and the resulting gain in stability will be greater than for ordinary conjugation.

The three most important properties of benzenoid compounds, stability, tendency to undergo substitution reactions,
and the orienting effects of substituents on subsequent reactions, can be explained by the electronic theory of organic chemistry in terms of electrostatic effects (induction) and 'electrodynamic' effects, (mesomerism or resonance).

Stability is accounted for by the great extent to which the $\pi$-orbitals are delocalised and by the symmetry of the system.

Substitution reactions are more likely to occur than additions because they cause less reduction of symmetry and extent of $\pi$-orbital delocalisation.

The orienting effect of substituent groups is shown to be the result of their electrostatic and conjugative effects on electron distribution in the molecule: substituents will change the electron density, and therefore the reactivity, at other carbon atoms in a benzene ring by their inductive and conjugative effects. The inductive effects of most substituents, such as halogens, OH, OR, 0.CO.R, SR, NH$_2$, are electron withdrawing (-I), but the conjugative effects can act in the opposite sense, and are often more powerful. The overall effect will vary with the position of the reaction centre in relation to the substituent. When the substituent is para to the reaction centre, conjugation will be less affected by the intervening four carbon atoms than induction, but when the meta position is substituted, the situation is reversed. The acidities of the hydroxybenzoic acids illustrate
this point: in para-hydroxybenzoic acid (pK 4.58) the OH group exerts a +M effect on the carboxyl group stronger than the -I effect, reducing the ease of ionisation of the proton compared with benzoic acid (pK 4.20), but in meta-hydroxybenzoic acid (pK 4.08) the inductive effect predominates, making it a stronger acid.

The changes in electron density brought about by the presence of a substituent in a benzene ring will determine the relative stability of possible transition states. An electron-donating substituent, e.g. a methoxy group, will increase the rate of reaction resulting from attack by an electrophilic reagent $E^+$ in the ortho and para positions by contributing to charge delocalisation in the transition state through the following structures:

With an electron-withdrawing substituent, e.g. a nitro group, the positive charge on the nitrogen atom near the nucleus does not allow an extension of delocalisation, and structures in which the carbon atom bonded to the nitrogen
carries a positive charge are excluded. Electrophilic attack at the meta position will lead to a transition state with greater scope for delocalisation than at the ortho or para position:

but the reactivity will be less than in the case of an electron-donating substituent.

d) Polycyclic Hydrocarbons

Compounds consisting of benzene rings fused through ortho-carbon atoms have characteristic aromatic thermodynamic stability. The interdependence of the benzenoid resonance of individual rings causes the total stabilisation energy of such a compound to be lower than that of the sum of an equal number of separate benzene rings. The loss of stabilisation energy due to addition across one double bond is, therefore, smaller than in the case of benzene, and addition takes place more readily. Molecular orbital calculations for alternant hydrocarbons suggest that the charge density of all the carbon atoms is unity. (22) In the ground state, all carbon atoms are, therefore, equivalent.

Different positions in polycyclic aromatic hydrocarbons show different reactivities towards electrophilic reagents. This was at one time attributed to 'localisation of double bonds' and this aspect has been reviewed by Badger. (23)

It is now considered that reactivity must be discussed in terms of polarisability, i.e. the charge distribution in the transition state.

Naphthalene undergoes electrophilic substitution preferentially at the 1-position; electrophilic attack at this position leads to a Wheland transition state with four possible structures in which the benzenoid nature of the ring is maintained:

```
\[
\begin{array}{c}
\text{H} & \text{Cl} \\
\text{+} \\
\end{array}
\quad
\begin{array}{c}
\text{H} & \text{Cl} \\
\text{+} \\
\end{array}
\quad
\begin{array}{c}
\text{H} & \text{Cl} \\
\text{+} \\
\end{array}
\quad
\begin{array}{c}
\text{H} & \text{Cl} \\
\text{+} \\
\end{array}
\]
```

Attack at the 2-position leads to only two such structures:

```
\[
\begin{array}{c}
\text{H} & \text{Cl} \\
\text{+} \\
\end{array}
\quad
\begin{array}{c}
\text{H} & \text{Cl} \\
\text{+} \\
\end{array}
\]
```

Substitution at the 1-position can thus be rationalised in terms of greater resonance stability of the transition state.

The transition state resulting from electrophilic attack has a positive charge, under favourable conditions the reaction

(23) Badger, Quart. Revs., 1951, 5, 147.
may be completed by combination with a nucleophile to give an addition product. Addition to these systems normally proceeds in such a way as to leave the greatest possibilities for resonance in the remaining system.

Phenanethrene readily gives 9,10 addition products, leaving the diphenyl structure of the two remaining rings available for $\pi$-electron delocalisation. Similarly, of all possible addition products of anthracene, the 9,10 adducts allow maximum resonance, and such products are known to be formed with ease.
3. INTERACTION BETWEEN AN ELECTROPHILE AND AN UNSATURATED CENTRE

I. General Outline

The reaction between an electrophile and an unsaturated compound acting as a nucleophile may give products of addition, substitution, or a competition between the two. It is generally considered that aromatic compounds give substitution products and aliphatic compounds give addition products, but exceptions to this rule are familiar. Thus addition is known to accompany substitution in polycyclic compounds; iso-butylene reacts with chlorine predominantly by substitution. (24)

\[
\begin{align*}
\text{Me}_2\text{C}:\text{CHCl} & \rightarrow 3\% \text{Me}_2\text{C}:\text{CHCl} \\
\text{Me}_2\text{C}:\text{CH}_2 & \rightarrow 87\% \text{ClCH}_2:\text{CMe}:\text{CH}_2 \\
\text{Me}_2\text{CCl}:\text{CH}_2:\text{Cl} & \rightarrow 6\% \text{Me}_2\text{CCl}:\text{CH}_2:\text{Cl} \\
\text{chlorides from secondary reactions.} & \rightarrow 3\%
\end{align*}
\]

Chem. Abs., 1940, 24, 3234.
Substitution accompanies addition in the chlorination of other olefins. (25)

<table>
<thead>
<tr>
<th>Olefin</th>
<th>% Subst.</th>
<th>Subst. Product</th>
<th>% Addition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>33</td>
<td>Cl H H . Ĉ : Ĉ . H</td>
<td>67</td>
</tr>
<tr>
<td>Butene-1</td>
<td>43</td>
<td>H H CH₃ . Ĉ : Ĉ . CH₂Cl</td>
<td>57</td>
</tr>
<tr>
<td>Butene-2</td>
<td>23</td>
<td>H₂C : Ĉ . Ĉ . CH₃ Cl</td>
<td>77</td>
</tr>
<tr>
<td>Tetraethyl-ethylenne</td>
<td>60</td>
<td>H₂C . Ĉ : Ĉ . Ĉ . Et Cl</td>
<td>40</td>
</tr>
<tr>
<td>Propylene</td>
<td>37</td>
<td>H₂C : Ĉ . CH₂Cl</td>
<td>63</td>
</tr>
<tr>
<td>Tetramethyl-ethylenne</td>
<td>90</td>
<td>H₂C : Ĉ . Ĉ . Me Cl</td>
<td></td>
</tr>
<tr>
<td>2-Methylbutene-1</td>
<td>70-75</td>
<td>H₂C : Ĉ . CH₂Cl</td>
<td>10</td>
</tr>
</tbody>
</table>

In discussing the interaction between halogen and a double bond we assume that the halogen is polarised and approaches the unsaturated compound with the positive end first:

$$\text{X-C=C-H + HX} \rightarrow \text{X-C=C-H + HX}$$

Both reactions require the transfer of a positive charge from the reagent to the aromatic substrate, and the breaking of the interhalogen bond to give a nucleophilic halide ion. In a substitution reaction, the substrate loses positive charge in the form of a proton which combines with the halide, and in an addition reaction the halide, or other nucleophile derived from the solvent, combines with the positively charged substrate.

The course of the reaction will be influenced by the conditions immediately surrounding the atoms involved: the nature of the solvent, the other substituents on the carbon atoms, and the temperature. Experimental evidence for the mechanism is derived from the observation of the effect of changes in these conditions on the rates and products of reactions.
The state of hybridisation of the neighbouring carbon controls the possibilities for delocalisation of the electrons and therefore the energy barrier to a change of configuration of the unsaturated centre.

The unsaturated centre may be:
- isolated, i.e. olefinic
- conjugated
- part of an aromatic system
- intermediate, e.g. in a polycyclic hydrocarbon.

II. Addition of Olefins

Addition of halogens to olefinic compounds has been reviewed by de la Mare. (26)

The two-step nature of the process was clearly recognised by Francis, (27) who related the formation of bromohydrins from olefinic compounds and bromine water to the formation of mixed halogen addition products from ethylene and bromine in the presence of chloride or nitrate ions.

---

(26) de la Mare, Quart. Revs., 1949, 2, 126.
Bartlett and Tarbell\textsuperscript{(28)} in their work on the bromination of stilbene in methanol, confirmed that such reactions are diverted additions and do not necessarily involve new electrophilic reagents such as MeOBr.

They proposed a 'Donor Theory of Halogenation' with a positively charged intermediate, and refuted the possibility of a negatively charged intermediate by showing that acids do not diminish the rate of formation of methoxybromide.

The two-stage mechanism was confirmed by showing that dimethylmaleic and dimethylfumaric acids gave the same lactone on halogenation, which is not formed from the dihalo acid.

Many other examples of solvent participation have been encountered, some are tabulated below:

<table>
<thead>
<tr>
<th>Hal:</th>
<th>Solvent</th>
<th>Substrate</th>
<th>Product</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl₂</td>
<td>H₂O</td>
<td>R.CH:CH.COOH</td>
<td>R.CH(OH).CHCl.COOH</td>
<td>(31)</td>
</tr>
<tr>
<td>Cl₂</td>
<td>HOAc</td>
<td>CH₂:CH.CH₂Cl</td>
<td>AcOCH₂.CHCl.CH₂Cl</td>
<td>(32)</td>
</tr>
<tr>
<td>Cl₂</td>
<td>MeOH</td>
<td>H₂C:CH₂</td>
<td>ClCH₂.CH₂(OCH₃)</td>
<td>(33)</td>
</tr>
<tr>
<td>Br₂</td>
<td>MeOH</td>
<td></td>
<td>[Diagram]</td>
<td>(34)</td>
</tr>
<tr>
<td>Br₂</td>
<td>HOAc</td>
<td>Cholest-2-ene</td>
<td>3β-cholestan-2-yl acetate</td>
<td>(35)</td>
</tr>
<tr>
<td>Br₂</td>
<td></td>
<td></td>
<td>[Diagram]</td>
<td>(36)</td>
</tr>
</tbody>
</table>

A mechanism of broadside-on single-stage addition leading to the formation of a cis-adduct is ruled out in such cases by this diversion of addition.

A two-stage mechanism leading to a cationic intermediate, a β-halocarbonium ion, on the other hand, should, assuming free rotation about a C-C bond, lead to mixtures

(36) Dinulescu et al. Chem. and Ind. 1964, 840.
of equal amounts of cis and trans adducts. In polar reactions, generally either cis or trans products predominate, forming about 80% of the product.

In order to account for the general predominance of trans addition in the reaction between halogens and olefins, it is necessary to account for the resistance of the C - C bond to free rotation.

Roberts and Kimball (37) provided an explanation which has been generally accepted. They suggested that the formation of a co-ordinate link between the halogen and the carbon possessing an unoccupied orbital forming a halogenonium ion, except where the two other substituents are similarly charged and cause rotation before the next step takes place.

This retention of configuration is equivalent to the action of halogen as a neighbouring group in nucleophilic substitution. A cyclic halogenonium ion is postulated to account for the retention of configuration in reactions such as the conversion of the diastereomeric 3-bromo-2-butanols to dibromobutanes (38) and the reaction of the 3-iodo-2-butanols with hydrochloric acid. (39)

$\text{CH}_3\text{HO-C-H}$

$\xrightarrow{+\text{H}^+}$

$\text{H}_2\text{O}^+\text{-C-H}$

$\xrightarrow{-\text{H}_2\text{O}}$

$\text{I-C-H}$

$L(\text{+})\text{erythro-3-iodo-2-butanol}$

$\xleftarrow{+\text{Cl}^-}$

$\text{CH}_3\text{I-C-H}$

$\text{H-C-I}$

$\text{H-C-Cl}$

$\text{opt.active}$

$\text{ret.config.}$

$\text{CH}_3\text{H-C-OH}$

$\text{I-C-H}$

$\text{CH}_3$

$\text{H-C-Cl}$

$\text{H-C-I}$

$\text{CH}_3$

$\text{activity lost}$

$\text{threeo-config. retained}$
As with the halogen cations, the formation of a chloronium ion is less likely than that of the corresponding bromonium or iodonium ion, but a suggestion by Winstein\(^{(40)}\) that a corresponding cyclic chloronium ion might exist was taken up by Lucas and Gould\(^{(41)}\) to account for trans addition of chlorine and hypochlorous acid to the 2-butenes.

The driving forces contributed by the participation of halogens and other neighbouring groups have been compared by measuring the rates of acetolysis of 2-substituted cyclohexyl \(\text{para-}\)bromobenzene sulphonates,\(^{(42)}\) and found to be in the order \(\text{I} > \text{Br} > \text{Cl}\).

The driving force of chlorine appeared insignificant.

Similarly, bromine and iodine participate readily in the product-forming stage of the acid-catalysed addition of hypochlorous acid to allyl bromide and iodide, whereas chlorine shows a much smaller tendency to participate.\(^{(43)}\)

Investigation of the products of addition of hypochlorous acid to allyl chloride\(^{(44)}\) labelled with \(^{36}\text{Cl}\) has given an indication of the configuration of the cationic intermediate.

\(^{(41)}\) Lucas and Gould, J. Amer. chem. Soc., 1941, 63, 2541.
\(^{(42)}\) Winstein, Grunwald, and Ingraham, J. Amer. chem. Soc., 1948, 70, 821.
\(^{(43)}\) de la Mare, Naylor and Williams, J. chem. Soc., 1962, 443.
\(^{(44)}\) de la Mare and Pritchard, J. chem. Soc., 1954, 3910, 3990.
The greater amount of the 2,3-dichloropropan-1-ol does not come from a symmetrical cation.

\[
\begin{align*}
\text{Cl} & \\
\text{CH}_2\text{-CH}-\text{CH}_2 & \quad 36\text{Cl}
\end{align*}
\]

It seems, therefore, that the entering chlorine substituent interacts more readily with the developing carbonium ionic centre than does the labelled \(^{36}\text{Cl}\) substituent already present. In support of this mechanism, it was found that the corresponding carbonium ion derived from 3-chloro-2-methylpropene was, as expected, stabilised by electron release from the methyl group, and gave an increased proportion of the product derived from the symmetrical intermediate.

**trans- Addition to compounds with restricted rotation.**

In compounds for which rotation about the attacked C - C bond is excluded, the two-stage carbonium-ion mechanism would lead one to expect halogen addition to result in products with a \textit{trans} configuration. The first halogen atom should prevent the second from coming in on the same side of the molecule, by steric hindrance or the formation of a cyclic ion. Halogen addition is known often to give such products. Addition of chlorine and bromine to cholest-2-
and -3-en gives as main products the diaxial dihalides.\(^{45}\)

An investigation of the stereochemistry of cholesterol\(^{46}\) dichlorides showed that cholesterol, on addition of chlorine, gives a dichloride to which a trans- configuration is assigned from the observation of its resistance to dehydrochlorination.\(^ {47}\)

A similar mechanism with an iodonium ion intermediate has been suggested for the stereospecific additions to cyclic olefins.\(^ {48}\) Cholest-2-en gives the diaxial product with iodine iso-cyanate.

cis- Addition to compounds with restricted rotation.

The reaction of cholesterol with iodobenzene dichloride\(^ {49}\) was found to lead to cis addition, and the following scheme was suggested:

\[
\begin{array}{c}
\text{Cl} \\
\leftarrow \leftarrow \\
\text{Cl} \\
\text{I} \\
\text{C}_6\text{H}_5 \\
\rightarrow \rightarrow \\
\text{Cl} \\
\text{Cl} \\
\text{C}_6\text{H}_5 \\
\rightarrow \rightarrow \\
\text{Cl} \\
\text{Cl} \\
+\text{C}_6\text{H}_5\text{I}
\end{array}
\]

From these results it appeared reasonable to generalise that chlorine addition by molecular chlorine should be trans, and with iodobenzene dichloride cis. In contrast, the chlorination of acenaphthylene was found to take place in

\(^{45}\) Ali and Barton, J. chem. Soc. 1954, 4284
\(^{46}\) Barton and Miller, J. Amer. chem. Soc., 1950, 72, 370.
\(^{48}\) Hassner and Heathcock, Tetrahedron Letters, 1964, 1125.
\(^{50}\) Barton and Miller, J. Amer. chem. Soc., 1950, 72, 370.
the opposite sense. (51) Chlorine in a non-polar solvent gave cis-dichloroacenaphthene, and iodobenzene dichloride gave trans-dichloroacenaphthene.

Similar behaviour was observed in the chlorination of para-dioxene; addition of chlorine by means of iodobenzene dichloride occurred in an almost exclusively trans manner, and with molecular chlorine the cis product was predominant. (52)

De la Mare and Klassen (53) found that addition of chlorine to phenanthrene resulted in the formation of a considerable amount of cis-9,10-dichloro-9,10-dihydrophenanthrene, and suggested that the formation of cis-isomers in such reactions is determined in a stage of chlorination prior to the formation of a β-halo-carbonium ion, and that part of the nucleophilic chlorine never gets entirely free but constitutes an ion pair leading to the cis-adduct.

A similar mechanism has been suggested for the addition of deuterium halides to acenaphthylene and indene (Dewar). (54)

III. Addition to Conjugated Olefins

The investigations by Burton and Ingold, (55) de la Mare (56)

(53) de la Mare and Klassen, Chem. and Ind., 1960, 498.
(56) de la Mare and Hughes and Ingold, J. chem. Soc., 1948, 910.
and others have been summarised by Ingold. (57) More recent work is discussed by de la Mare. (58) As with addition of halogens to olefins, the addition is a two-stage process involving a cationic intermediate. There are many parallels to the action of hydrogen halides on polyolefins. The first halogen atom which approaches the olefin is assumed to behave in a similar way to the proton of a hydrogen halide. In an unsymmetrical conjugated system, the end which is capable of giving the highest electron density will be attacked first. The second halogen atom will act as a nucleophile; in a diene there will be two alternative positions that it can attack.

\[
C : C . C : C \xrightarrow{H^+} CH . C^+ . C : C \leftrightarrow CH . C : C . C^+
\]

If the two possible products can undergo an anionotropic rearrangement, the predominating product will be the more stable of the two, and the reaction will be thermodynamically controlled. If such a re-arrangement is sufficiently slow under the reaction conditions, the product which is formed faster will predominate, and the reaction will be kinetically controlled.


controlled. In the addition of chlorine to butadiene at room temperature, the less stable 1,2-dichloride predominates, i.e. the reaction is kinetically controlled but, as the reaction temperature is raised, the proportion of the more stable 1,4-dichloride increases, the reaction is thermodynamically controlled. (59)

The trans configuration which has been found to occur in the product of the 1,4 addition of chlorine to butadiene (i)(ii) excludes the possibility of a 5 membered chloronium ion (ii).

\[
\begin{align*}
\text{(i)} & \quad \text{(ii)} \\
\text{ClCH}_2 & \quad \text{HC} \\
\text{CH} & \quad \text{CH} \\
\text{CH}_2\text{Cl} & \quad \text{Cl}^+ \\
\end{align*}
\]

or a one-step process, both of which would give cis-dichloride. The cation will, therefore, be a chlorinated carbonium ion (iii) or a chloronium ion (iv).

\[
\begin{align*}
\text{(iii)} & \quad \text{(iv)} \\
\text{(ClCH}_2 & \quad \text{H}_2\text{C} \\
\text{CH}...\text{CH}...\text{CH}_2) & \quad \text{CH} \\
\text{Cl}^+ & \quad \text{CH} \\
\end{align*}
\]

Such a cyclic transition state for the bromination of 1,3

(60) Mislow, and Hellmann, J. Amer. chem. Soc., 1951, 73, 244.
butadiene (61) has been inferred from the absence of the cis-1, 4 adduct.

On the other hand, Young, Hall and Winstein (62) propose a bromocarbonium bromide ion pair to account for

the presence of a cis-1,4 adduct, the 3,5 dibromide, as a major product of bromination of cyclopentadiene.

For an extended conjugated system, there will be a tendency to preserve conjugation as much as possible. The addition of bromine to hexatriene gives the 1,2 and 1,6 adducts, which have two double bonds in conjugation. (63)

\[
\begin{align*}
\text{BrCH}_2\cdot\text{CHBr}\cdot\text{CH}:\text{CH}&\cdot\text{CH}:\text{CH}_2 \\
\text{CH}_2\cdot\text{CH}:\text{CH}&\cdot\text{CH}:\text{CH}:\text{CH}_2 \quad \text{Br} \\
\text{BrCH}_2\cdot\text{CH}:\text{CH}&\cdot\text{CH}:\text{CH}:\text{CH}_2\text{Br}
\end{align*}
\]

The 1,4-adduct, (BrCH\_2.CH:CH.CHBr.CH:CH\_2), in which conjugation is broken, is apparently not formed.

**IV. Substitution in Aromatic Compounds**

It was at one time widely held that aromatic substitution

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(62) Young, Hall and Winstein, J. Amer. chem. Soc., 1956, 78,
takes place via an addition-elimination mechanism. The development of this view was reviewed by Fieser. An addition-elimination sequence had been suggested by Armstrong. Nitration of benzene was discussed by analogy with the reported nitration of styrene, isobutylene, cinnamic acid, and the products observed in the nitration of ethylene with fuming nitric and sulphuric acid. The formation of \( \beta \)-nitroethyl nitrate, \( \text{CH}_2(\text{NO}_2)\text{CH}_2\text{ONO}_2 \), was thought to result from the esterification of \( \beta \)-nitroethyl alcohol, formed as a primary addition product. The alcohol could be dehydrated to nitroethylene with phosphorous pentoxide, giving a substitution product through an addition-elimination sequence. Similarly, nitration of \( \alpha,\alpha \)-diphenylethylene in glacial acetic acid, gave a nitro-alcohol which could be converted to the corresponding unsaturated nitro compound.

\[
(C_6H_5)_2C : \text{CH}_2 \xrightarrow{\text{HONO}} 2 \rightarrow (C_6H_5)_2C : \text{CH}_2 \quad \text{H}_2\text{O}
\]

\[
(C_6H_5)_2C : \text{CH} \quad \text{NO}_2
\]

---

(68) Erdmann, Ber., 1884, 17, 412.
(70) Anschütz and Hilbert, Ber., 1921, 54, 1845.
A closer analogy was found in the study of the nitration of anthracene, (71)

\[
\text{\includegraphics[width=0.4\textwidth]{anthracene}}
\]
furan acetate, and the halogenation of phenanthrene and furan.

The bromination of ethyl-2-furyl acrylate gave an unstable dibromo-addition compound, which readily lost hydrobromic acid to give ethyl-5-bromofuryl acrylate. Isolation and analysis of the intermediate dibromo compound was taken as supplementary evidence for an addition-elimination sequence. (72)

This type of analogy for the mechanism of aromatic substitution was attacked by Michael (73) who showed that nitric and sulphuric acids do not add to ethylene as HO-NO₂ and HO-SO₂OH.

Although such routes to substitution are theoretically possible, and can be shown to operate in some aromatic systems, they are not now normally considered to be important.

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(71) Meisenheimer and Connerade, Ann., 1904, 330, 133.
Price, (74) in his examination of the bromination of phenanthrene, found that substitution products do not arise from the decomposition of the dibromide, which is stable under the conditions of the reaction. He states that addition and substitution are alternative fates of a common intermediate, and that addition is not a preliminary stage in substitution. He follows Pfeiffer and Wizinger (75) in describing substitution mechanisms via the formation of a complex.

Current theories of aromatic substitution involve an intermediate of carbonium ionic character, the so-called Wheland intermediate:

\[
\text{C}_6\text{H}_5\text{H} \rightarrow \text{C}_6\text{H}_5\text{H}^+ \rightarrow \text{C}_6\text{H}_5^+\text{CH}_2\text{H}
\]

An electrophile attacks an aromatic carbon atom which changes to an \(\text{sp}^3\)-hybridised tetrahedral configuration.

One of the \(\sigma\)-bonds uses two of the \(\pi\)-electrons of the aromatic system. The loss of stabilising energy of the residual pentadienate cationic system compared with the original benzene system is partly compensation by the formation of the \(\sigma\)-bond and hyperconjugation of hydrogen. Such an intermediate will be represented by a dip in the reaction.


(75) Pfeiffer and Wizinger, Ann., 1928, 461, 132.
co-ordinate profile. The second barrier represents the activation energy for the loss of a proton to give a substitution product.

An addition reaction requires the involvement of a second carbon atom, and therefore greater loss of stabilising energy of the residue. Its energy requirements compare unfavourably with those for substitution in monocyclic aromatic compounds. In the case of polycyclic compounds, there is relatively less loss of stabilising energy, and addition becomes a possible alternative reaction path.

V. Substitution in Olefins

Aromatic substitution has a parallel in electrophilic displacement at vinylic centres, which may accompany addition in olefins. The attack of an electrophilic reagent will result in a carbonium ion. The mechanism of this type of substitution has been examined by de la Mare, Salama and Ballinger, and an asymmetric configuration involving neighbouring group participation has been suggested for the transition state.

VI. Addition to Polycyclic Aromatic Hydrocarbons

The tendency of aromatic polycyclic hydrocarbons to give specific addition products has been discussed.

(76) de la Mare, Progress in Stereochemistry, II, London, 1958.
(77) a) de la Mare and Salama, J. chem. Soc., 1956, 3337.
     b) Ballinger and de la Mare, ibid., 1957, 1481; 1960, 2467.
Many examples of such reactions are known, but there have been few investigations of the reaction paths leading to these products.

**Addition to Anthracene and Naphthacene**

Products of addition of chlorine and of bromine have been described, and shown to decompose giving the corresponding acids. The products of nitration of anthracene gave 9-hydroxy-10-nitro-9,10-dihydro-anthracene, its acetyl derivative and its methyl ether. All these compounds were found to give 9-nitro-anthracene with water. (78)

Barnett and Cook prepared stable dibromides of alpha-haloanthracenes, and Meyer and Zahn characterised anthracene dichloride. (79)

The analogy in reactivity between naphthacene and anthracene is illustrated by the nitration of naphthacene in acetic acid. (80) On dilution with water it gave 5-nitro-12-hydroxy-5,12-dihydronaphthacene.

**Addition to Phenanthrene**

An addition product of chlorine and phenanthrene was found by Sandquist (81) and the addition of bromine to phenanthrene was studied by Price. (82) His mechanistic conclusions

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(78) a) Perkin, Chem. News, 1876, 34, 144.
b) Meisenheimer, *see Ref. 71.*
b) Barnett and Matthews, Rec. trav. chim., 1924, 43, 530.
(80) Bednyagina et al., Chem. Abs., 1958, 52, 13697g.
(81) Sandquist, Ann. 1918, 417, 17; Ber., 1918, 51, 1515.
have been discussed above. Van der Linde\(^{(83)}\) has attempted
to investigate the nature of the addition process of bromine
to phenanthrene in methanolic solution, by observing the
effects of steric hindrance on the ratio of dibromide to
methoxybromide for a series of 9,10-dialkyl phenanthrenes,
but was unsuccessful since only substitution and no addition
products were formed.

**Addition to Naphthalene**

Repeating the work of Laurent,\(^{(84a)}\) E. Fischer described
the preparation of naphthalene di- and tetrachlorides.\(^{(84b)}\)
Four stereoisomers of naphthalene tetrachloride have been
prepared, but not characterised (Mueller)\(^{(85)}\) and three such
tetrachlorides have been assigned configurations from the
study of their behaviour with alkali.\(^{(86)}\)

**Recent Investigations of Addition Accompanying Substitution.**

De la Mare and his co-workers have made a survey of
addition accompanying substitution in the chlorination of
aromatic compounds in acetic acid. The existence of chlorine
addition compounds was inferred from the fraction of chlorine
used which formed hydrochloric acid, and that of acetoxyl

\(^{(83)}\) Van der Linde, *Thesis*.
\(^{(84)}\) a) Laurent, *Ann.* 160, 65; *Zeitschr.*, 5, 705.
   b) Fischer, *E. Ber.* 1878, 11, 785.
adducts from the oxygen content of the reaction product and from the appearance of a characteristic peak in the infra-red spectrum. Unstable adducts, which might have been destroyed during the working up of the product, could be detected by these methods. In certain cases they were found to be isolable by chromatography.

The application of these methods showed that addition occurred not only with compounds which were expected to add readily, such as naphthalene, 2-methylnaphthalene, and phenanthrene, but also with biphenyl, fluorene, and 9,10-dihydrophenanthrene.

In the case of biphenyl, fluorene and, particularly, phenanthrene, acetoxy-adducts were shown to be present. Diversion of addition of halogens to olefins by participation of the solvent is a common phenomenon. It had been used in the discussion leading to the establishment of the two-stage mechanism for such additions (5.11).

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(87) V. Sanchez del Olmo, Unpublished Work.
(89) de la Mare and Klassen, Chem. and Ind., 1960, 498.
(90) de la Mare, Klassen and Koenigsberger, J. chem. Soc., 1961, 5285.
(91) Beaven, de la Mare, Hassan, Klassen and Johnson, J. chem. Soc., 1961, 2749.
(92) Beaven, de la Mare, Johnson and Klassen, J. chem. Soc., 1962, 988.
(93) de la Mare, Johnson and Lomas, J. chem. Soc., 1963, 5973.
AIMS OF THE INVESTIGATION

Addition and acetoxychloride formation had been observed in the chlorination of aromatic hydrocarbons.

For phenanthrene, the most reactive positions for addition are known to be at the 9 and 10 carbon atoms. The possible 9,10-addition products of phenanthrene in acetic acid are the cis- and trans-dichlorides and the cis- and trans-acetoxychlorides. Both cis- and trans-dichlorides have been found in the chlorination product of phenanthrene. (94, 95)

Trans- addition of halogen or halogen acetate in acetic acid can be visualised by analogy with halogen addition to olefins, but the formation of a cis-dichloride from phenanthrene cannot be explained in this way. An alternative mechanism, involving an intermediate or transition state, consisting of the aromatic compound and the chlorine molecule, was proposed by de la Mare. (96)

The evidence available for the existence of an acetoxy-adduct was not sufficient to allow conclusions as to its configuration.

No detailed investigation of the reaction products of naphthalene had been made.

It was considered that an investigation of the products of chlorination of phenanthrene and naphthalene might help

(94) de la Mare and Klassen, Chem. and Ind., 1960, 498.
(95) de la Mare, Klassen and Koenigsberger, J. chem. Soc., 1961, 5285.
(96) de la Mare and Klassen, Chem. and Ind., 1960, 498.
to clarify the mechanism of the reaction.

The work described here has been concerned with the separation and identification of the products of chlorination of phenanthrene and naphthalene, and with an attempt to investigate the effect of electrolytes on the course of the reaction.
SECTION B.

EXPERIMENTAL
1. PURIFICATION OF MATERIALS

Acetic Acid:

Glacial Acetic Acid (2.51) was treated with a drop of bromine and allowed to stand for 24 hours. It was then shaken with freshly prepared, alkaline free, silver oxide. The liquor was distilled over glass wool. Five per cent by volume of water and 250g. potassium dichromate were added to the distillate, the mixture was refluxed for eight hours over glass wool, using an isomantle, and distilled. The distillate was fractionated using a jacketed heated fractionating column. When the boiling point had reached 118°C, the freezing point of subsequent fractions was taken, using a Beckmann thermometer, and the fractions were collected after the freezing point showed no further rise. For large-scale preparations, glacial acetic acid was used without purification.

Alumina:

The alumina used was Hopkin and Williams' aluminium oxide "CAMAG M.F.C., 100 to 200 mesh, alkaline, Brockmann activity = 1. It was found necessary to deactivate this material by shaking with 3% water for four hours.

Silica Gel:

Hopkin and Williams' M.F.C. silica gel was used for column chromatography. For thin layer chromatography, silica gel (Merck) acc. to Stahl, containing about 13% plaster of Paris, was used.
**Chlorine:**

Chlorine was obtained from Imperial Chemical Industries Ltd. Before use it was passed through water to remove hydrogen chloride and then through concentrated sulphuric acid to dry it.

**Radioactive Chlorine:**

In the earlier experiments, aqueous hydrochloric acid containing H\(^{36}\)Cl was obtained from the Radiochemical Centre, Amersham. This was neutralised with sodium hydroxide and evaporated to dryness. The dry sodium chloride was shaken with a solution of chlorine in acetic acid. The radioactive chlorine was distilled at room temperature under reduced pressure, and kept as a solution in acetic acid in the dark until it was used.

Later radioactive chlorine gas became available and was used in solution in acetic acid.

**Phenanthrene:**

To remove any anthracene, Light's phenanthrene (100g) was refluxed with maleic anhydride (120g.) in xylene (800 ml.) for eight hours. A large excess of potassium hydroxide was added and refluxing continued for two hours. The xylene solution was washed with water and evaporated. The residue, dissolved in light petroleum, was passed through an alumina column and then repeatedly recrystallised from ethanol, m.p. 99.5°.
2. ANALYTICAL METHODS

I. Volumetric Analysis:

a) Chloride was determined by potentiometric titration against silver nitrate (N/50 or N/100) in acetone solution acidified with nitric acid.

b) Both hydrochloric and acetic acids are produced in the decomposition of the acetoxy-chloro-adduct. Titration in a non-aqueous solvent was found suitable for following this reaction. By following the method Yacubic, Safranski and Mitchell, (97) two well separated inflections were obtained for hydrochloric and acetic acid. The acids were titrated against 0.01N potassium methoxide in benzene-methanol using a glass electrode as reference. The alkali was standardised separately against hydrochloric acid and benzoic acid; slight differences in the normality factors were observed. Under the conditions described, the plots of e.m.f. against vol. of added alkali were S-shaped, not in the form of the first differential as described by the authors. (Fig. 1). The disadvantage of this method was the long time required by the electrode system to reach stability (up to 30 mins. per point).

Fig. 1

STANDARDISATION OF POTASSIUM METHOXIDE

1) 5ml Acetic Acid Solution
2) 10ml Benzoic Acid, 0.02N
3) 15ml Hydrochloric Acid, 0.02N
4) 5ml Hydrochloric Acid + 5ml Acetic Acid
5) 5ml Hydrochloric Acid + 10ml Acetic Acid
II. Isotope Dilution.

The concentrations of the reaction products under various conditions were estimated by the method of isotope dilution. The reaction was carried out using radioactive chlorine (Cl.36). The quantity used for each experiment was about 22 $\mu$ curie, 0.5 mM. The radioactive chlorine was diluted with a solution containing about 5 mM inactive chlorine, and made up to 100 ml in a graduated flask. Aliquots were used for analysis. Chlorine was estimated by titration against thiosulphate; the determination of specific activity is described below. After it had gone to completion, a weighed excess of the component under investigation was added to the reaction mixture; the diluted active material was then isolated, and purified by chromatography and re-crystallisation until subsequent samples had the same specific activity. The adducts under investigation were hydrolysed in alkali. The hydrolysate was partitioned between ether and water, and the aqueous extract was used for the determination of specific activity.

If $x$ = amount produced in the reaction  
$y$ = amount of inactive material added  
$S_x$ = specific activity of starting material  
$S_{x+y}$ = specific activity of final product

$$x = \frac{y}{S_x/S_{x+y} - 1}$$
Determination of Specific Activity:

It is important to determine the specific activity of the starting material and the final product under comparable conditions, i.e. in solutions of equal density. To avoid errors due to the presence of salts or solvents, the following procedure was adopted in the later experiments: an aliquot of the active chlorine solution was treated with excess aqueous bisulphate solution to convert it to chloride ion, and precipitated with silver nitrate. The silver chloride was reduced in a hot silica tube in a stream of hydrogen, and the HCl gas was collected in water. Chloride and count were determined for this solution of hydrochloric acid. The activity of the solution to be counted was kept between 200 and 800 c.p.m. and at least 10,000 counts were timed.

III. Thin Layer Chromatography

This technique was found very useful for detecting the presence of reaction products in column eluates and for identifying the products of reactions on a small scale.

A thin layer of a slurry of a suitable absorbent, e.g. silica gel G (Merck, containing about 13% plaster of Paris) is spread evenly on a glass plate, either by using a special spreading device, or by the method described by Lees and de Muria. (98) This method consists of sticking adhesive tape

(drafting tape) on two sides of a glass plate, and pushing (not rolling) a glass rod over the slurry poured on the plate. The plates are dried in an oven at $100^\circ$ to $120^\circ$ for about an hour, and allowed to cool at room temperature without any precautions to exclude moisture.

For analysis, drops of sample and corresponding marker solutions are applied with a capillary pipette (5 microl.) about 1cm from the bottom edge of the plate; the plate is put in a tank with a layer of solvent in the bottom, and the solvent is allowed to run upwards to the required height in the closed tank.

The positions of the spots after running are detected by applying a suitable spray reagent or by inspection.

**Spray Reagents:**

i) Silver nitrate - fluorescein in water. The sprayed plate was exposed to ultraviolet light from a Hanovia "Chromatolite" lamp. Phenanthrene and chlorophenanthrene showed a yellowish fluorescence. After irradiation the dichlorides appeared as yellow spots in visible light, and acetoxychloride as a yellow spot with a dark halo. Phenanthrol gave dark spots at once, while those of acetoxyphenanthrene developed slowly.

ii) Vanillin (3%), and concentrated sulphuric acid (0.5%) in absolute ethanol. After heating the sprayed plates to about $100^\circ$, the oxygen-containing compounds appeared as brown
spots. This spray was particularly useful for phenanthrene diacetates.

iii) Diazotised sulphanilic acid. This was effective for phenolic compounds. With light petroleum (60°-80°) as a solvent, chlorophenanthrene, phenanthrene and phenanthrene dichlorides were separated in that order, while the oxygen containing material remained at the origin. With benzene, as solvent, on the other hand, chlorophenanthrene, phenanthrene and phenanthrene dichlorides went to the solvent front, and the oxygen containing compounds were separated. Their approximate Rf values were:

- acetoxychloride: 0.7
- acetoxyphenanthrene: 0.6
- phenanthrol: 0.3
- phenanthrene diacetate: 0.2
- cis-hydroxy-acetoxy-phenanthrene: ---
(Fig. 2)

DIAGRAMMATIC REPRESENTATION OF CHROMATOGRAMS

Light Petroleum

1. Chlorophenanthrene
2. Phenanthrene
3. Phenanthrene dichlorides
4. Acetoxy chlorophenanthrene
5. Phenanthryl acetate
6. Phenanthrol
7. Phenanthrene diacetate
8. Phenanthrene hydroxyacetate

Benzene

Direction of Solvent flow
It may be possible to obtain better separations, particularly for the non-oxygen containing compounds, by using a more polar layer, in a partition system, e.g. cellulose acetate.

3. THE CHLORINATION OF NAPHTHALENE

Naphthalene, (12.8g, 100mM, m.p.80.5°), was dissolved in glacial acetic acid (100 ml.)(not specially purified). A solution of chlorine (25mM) in acetic acid (37 ml.) was added in the absence of light. The mixture was left in the dark over night, and extracted with ether and water. The ether extract was washed three times with water and distilled under reduced pressure; the residue was dissolved in light petroleum (40°-60°).

Chromatography of the Product of Chlorination of Naphthalene:

The solution of the total product in light petroleum, (40°-60°), was chromatographed on a column of silica gel (500g), and eluted successively with 3l light petroleum, (40°-60°), 750 ml. of benzene in light petroleum, 1:3,v/v, 750 ml. of benzene in light petroleum, 1:1,v/v, and solutions of increasing concentrations of ether in benzene. The separation of the components of the mixture is shown in the elution diagram (Fig.3). The three main peaks were shown to contain the following groups of compounds:- (The fractions were numbered consecutively, but were not of equal volumes).
CHROMATOGRAPHY OF CHLORINATION PRODUCTS OF NAPHTHALENE

![Graph showing the distribution of elution volumes and weights.]

- Weight of Eluate, g.
- Vol. of Eluate, L.
- Fraction No: 8, 14, 25, 50, 100% Benzene
Fraction Number:

1 - 8  chloronaphthalene and naphthalene  11.61g.
9 -19  naphthalene tetrachlorides  0.79g.
32 -35  naphthalene acetoxychloride  0.45g.

No solid material was eluted with ether.

Infra-red Spectra:

The spectra of fractions 2-8 corresponded to mixtures of naphthalene and 1-chloronaphthalene. The shape of the elution peak between fractions 9 and 19 suggests that more than one compound is present. The spectra of fractions 11-13 were identical with that of a sample labelled α-naphthalene tetrachloride. Those of fractions 15-18 were different, showing an increase in a component with a marked peak at 705 cm⁻¹. No change in spectrum could be seen in the subsequent fractions up to No.29. The spectra of fractions 32-35 differed from each other, but they all had a marked peak in the region of 1750 cm⁻¹, indicating the presence of an acetoxy group.

Reaction with Alkali:

Aliquots of the fractions were treated with alcoholic potassium hydroxide under reflux. The chloride liberated was determined by titration using ammonium thiocyanate. The "tetrachloride fraction" gave 26% inorganic chloride, the "acetoxychloride" fraction 23%.
Quantitative Analysis:

Microanalyses on fractions 19 and 32 were carried out by A. Bernhardt, Muelheim.

Sample 19: (BC 160, 20043, 44/60) found: C, 44.82; H, 3.06; O, 0.28; Cl, 51.58. Calculated for naphthalene tetrachloride: C, 44.50; H, 2.96; Cl, 52.60.

Sample 32: (BC 161, 10043, 44/60) found: C, 52.02; H, 3.99; O, 10.80; Cl, 32.57; calculated for acetoxytrichloride: C, 49.2; H, 3.76; O, 10.90; Cl, 36.2.

Melting Points:

Schütz and Hahnfeld (99) give the melting points for three isomers of naphthalene tetrachloride as $\alpha$: 182$^\circ$, $\delta$: 97$^\circ$, $\gamma$: 132$^\circ$. Fraction 12 had a m.pt. of 175$^\circ$-182$^\circ$, close to that of Schuetz and Hahnfeld's $\alpha$-compound, and fraction 16 of 87$^\circ$-97$^\circ$, near the $\delta$-compound.

4. CHLORINATION OF PHENANTHRENE

I. Separation of Reaction Products on Silica Gel:

The separation of the products of chlorination of phenanthrene on a silica gel column was investigated in the hope of getting quantitative recovery of some of the components.

A reaction mixture, produced by allowing chlorine, 12.4mM, to react with phenanthrene, 4.45g, 25mM, in the absence of light, was extracted with ether and water, the ethereal layer was evaporated to dryness in a weighed dish, and finally dried.

(99) Schuetz and Hahnfeld, Ber. 1952, 85, 131.
in a vacuum desiccator. The weight of the total product was 4.97g. The product was dissolved in acetone and made up to 250 ml. 65 ml. of the solution were used to analysis, the remaining 185 ml. were distilled to dryness under reduced pressure; the residue was taken up in light petroleum and chromatographed on 500g. silica gel (Hopkin and Williams, M.F.C.). The eluates were identified by their infra-red spectra. Mixtures of chlorophenanthrene and phenanthrene, 2.32g, were eluted in the first 1200 ml, followed by a mixture of 9-chlorophenanthrene and cis-dichlorodihydrophenanthrene, 0.76g. No further solid was eluted with another 500 ml. of light petroleum; on changing to benzene, an acetoxychloroadduct 0.203g, was eluted. On changing to acetone, 0.14g of an unidentified yellow material was eluted.

No trans-dichloride was isolated. Evidence for the decomposition of the trans-dichloride was indicated by calculating the approximate ratio of chlorophenanthrene to phenanthrene in the first five fractions from a comparison of their infra-red spectra. The ratios for the first five fractions are:

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.3</td>
<td>0.4</td>
<td>0.2</td>
<td>0.5</td>
<td>0.3</td>
</tr>
</tbody>
</table>

The comparatively high ratio in fraction 4 is likely to be due to chlorophenanthrene derived from the decomposition of trans-dichloride.
The destruction of trans-dichloride by silica gel chromatography was later confirmed by passing purified trans-dichloride, 0.1g, through a silica gel column (50g), chlorophenanthrene, 0.082g, equivalent to 96% of the trans-dichloride used, was recovered.

In order to test whether the chromatographic method is suitable for use in quantitative estimation, a sample rich in cis-dichloride was put through a column, and the concentration of cis-dichloride in the starting material and the eluate was estimated.

The results are shown in Table 1:

<table>
<thead>
<tr>
<th>TABLE 1</th>
<th>Chromatography of cis-Dichloride</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wt.g</td>
</tr>
<tr>
<td>Sample used</td>
<td>0.1555</td>
</tr>
<tr>
<td>chlorophenanthrene eluted</td>
<td>0.085</td>
</tr>
</tbody>
</table>

The cis-dichloride eluted corresponds to 70% of the starting material, indicating that the method is not suitable for quantitative analysis. The total weight recovered accounts for 96% of the starting material; the loss is therefore due to chemical decomposition, not physical technique.

II. Trans-9-Acetoxy-10-chloro-9,10-dihydrophenanthrene:

The acetoxy-chloro adduct of phenanthrene was first
isolated from the chlorination product of phenanthrene in acetic acid by chromatography on silica gel in petroleum ether followed by benzene. A purer compound was later obtained by chromatography of deactivated alumina in ether-petroleum ether mixtures. Chlorine in glacial acetic acid (40ml., about 1.7M, i.e. 50mM) was added to a solution of phenanthrene (10g., 56mM) in glacial acetic acid (400ml) in the dark. After the solution had been allowed to stand overnight, it was diluted with water, and the organic reaction product was extracted repeatedly with ether. The ethereal solution was washed with water until most of the acetic acid had been removed and then with bicarbonate and again with water. It was dried with sodium sulphate; the ether was evaporated off under reduced pressure, and most of the cis-dichloride and excess phenanthrene were removed by precipitation with petroleum ether.

The rest of the product was chromatographed on 500g. of alumina which had been deactivated by shaking with 15 ml. water for four hours.

It was difficult to transfer the product to the column without diluting it too much. To keep the volume low, the petroleum ether was removed by evaporation, the product was dissolved in the minimum volume of ether, diluted with nine times its volume of petroleum ether, and the resulting suspension was quickly poured on the column. On eluting with
10% ether in petroleum ether, the trans-dichloride, detected by thin layer chromatography, started to come out after 450 ml. had passed through, and was collected in the next 300 ml. After a further 500 ml. the concentration of ether in the solvent was increased to 20%, and the acetoxy-chloride, again detected by thin layer chromatography, was eluted after a further 300 ml. in the next 500 ml.

Yield: 0.75g, approximately 5 mole %. To purify it, the product was dissolved in ether and then precipitated by adding petroleum ether and evaporating some of the solvent; m.p., 101°. A small portion was recrystallised from methanol; m.p., 103°. Elementary Analysis: Found: BC 492 (13256/63); C,70.0; H,4.7; O,11.9; Cl,13.2. Calc. for C_{16}H_{13}O_2Cl:
C,70.5; H,4.8; O,11.8; Cl,13.0.

III. The Preparation of Model Compounds:
trans-9,10-dichloro-9,10-dihydrophenanthrene.

The compound could be isolated in sufficiently good yield from the product of chlorination of phenanthrene in acetic acid by chromatography on deactivated alumina as described in (II) above. It was recrystallised from chloroform solution by cooling from 30° to 50° m.p. To avoid decomposition during heating, the melting point was determined by inserting a freshly filled melting point tube into a block held at a steady temperature. Fusion in less than one minute was considered genuine and not due to decomposition.
The compound was stored at \(-78^\circ\).

**cis-9,10-dichloro-9,10-dihydrophenanthrene.**

The compound was prepared from the chlorination product of phenanthrene in acetic acid as described by de la Mare and Klassen.\(^{(100)}\) It was precipitated from the oily chlorination product by the addition of light petroleum (40\(^\circ\)-60\(^\circ\)), purified by chromatography on silica gel in light petroleum or benzene—light petroleum, and recrystallised from a solution in benzene by adding light petroleum. The melting point (101\(^\circ\)) was determined as described for the trans-dichloride. The compound was stored at \(-78^\circ\).

**9-Phenanthrol.**

9-Phenanthrol was prepared by brominating phenanthrene in methyl alcohol in the presence of sodium acetate, as described by Fieser.\(^{(101)}\)

A solution of phenanthrene (20g.) and anhydrous sodium acetate (6g.) in warm methyl alcohol (360ml.) was cooled quickly to about 35\(^\circ\) to 40\(^\circ\) and a solution of bromine (3 ml.) in cold methyl alcohol (40 ml.) was added all at once. The mixture was cooled rapidly in a salt-ice bath and the temperature was brought to \(-5^\circ\). A yellow solid, presumably the

\(^{(100)}\) de la Mare and Klassen, Chem. and Ind. 1960, 498.

molecular compound of phenanthrene methoxybromide and phenanthrene dibromide, was collected and washed with a solution of 5% sodium acetate in 70% aqueous methyl alcohol. The first filtrate was again treated with bromine in methyl alcohol to give a second crop of the complex. The crude, undried complex was debrominated by heating it to 50° to 60° in methyl alcohol containing potassium hydroxide and potassium acetate. The product, consisting of phenanthrene and 9-methoxyphenanthrene, was demethylated with hydrobromic acid in glacial acetic acid. It was extracted into alkali, reprecipitated by acidification and extracted with ether. The washed ethereal extract was diluted with benzene and hexane, dried over sodium sulphate, and filtered through a column of activated alumina. Evaporation of the filtered solution gave 9-phenanthrol, m.p. 153°C. (1.2g.). This yield, about 7% of the total phenanthrene used is considerably lower than that reported by the authors. Hunsberger reports a yield of 12% using this method.

In our experience, about 5g. of phenanthrene were recovered from the washed ethereal solution which remained after alkaline extraction.

9-Acetoxyphenanthrene.

9-Acetoxyphenanthrene was prepared by acetylation

9-phenanthrol with acetic anhydride in sodium hydroxide in the cold. The product was recrystallised from aqueous alcohol; m.p. 73°.

cis-9,10-diacetoxy-9,10-dihydrophenanthrene.

cis-9,10-diacetoxy-9,10-dihydrophenanthrene was obtained by acetylation in acetic anhydride of cis-9,10-dihydro-9,10-dihydroxyphenanthrene obtained from Professor Boyland, m.p. 108°.

trans-9,10-diacetoxy-9,10-dihydrophenanthrene.

The menthoxyacetate of trans-9,10-dihydroxy-9,10-dihydrophenanthrene was obtained from Professor Turner. After hydrolysis the diol was acetylated with acetic anhydride to give the diacetate, m.p.

IV. Reactions of the Acetoxy-chloride:

a) Decomposition by Heat:

Gas-chromatography of the acetoxy-chloride (br Dr. E.A. Johnson) showed a presence of two compounds. One was 9-chlorophenanthrene; the other was first suspected to be some other chloro-compound, but it was then proved to be acetoxyphenanthrene. A sample of the acetoxy-chloride was heated under reduced pressure in nitrogen. Thin-layer chromatography of the product showed that some


acetoxy-chloro adduct remained and that chlorophenan-
therene, acetoxy-phenanthrene and phenanthrol had been
produced in the approximate ratios 5:10:1.

(Fig. 4)

THIN LAYER CHROMATOGRAM OF ACETOXY-CHLORO ADDUCT
AFTER HEATING. SEMIQUANTITATIVE ESTIMATION OF
PHENANTHROL.

SOLVENT: Benzene        REAGENT: Silver Nitrate

STAT. PHASE: Si Gel G.

Weight per Spot

2, 4, 6 ≈ 600 μg Sample

1  12.5 μg Phenanthrol
2  25.0 " "
5  37.5 " "
7  50.0 " "

Not Identified
Acetoxychloride
Phenanthyln acetate

Phenanthrul
b) Reaction of Acetoxy-chloride with Alkali:

Titration in benzene/methanol was used to observe the liberation of acetic acid from the acetoxy adduct in the presence of alkali. It could be shown that when the liberation of chlorine had reached 94%, that of acetic acid had proceeded to no more than 2%. It is therefore possible to measure the rate of dehydrochlorination by estimating the chloride liberated without interference by the hydrolysis of the acetate group.

In a kinetic experiment at 0°, 0.2737g. (0.993 mM) of material obtained by chromatography on alumina were dissolved in ethanol (96%) and made up to 100ml. Aliquot portions (10 ml.) of this solution were mixed with 10 ml. of 0.0378 N potassium hydroxide in ethanol (96%); the chloride liberated was determined at intervals by titration against standard silver nitrate.

<table>
<thead>
<tr>
<th>Rate of Dehydrochlorination of the Acetoxychloride.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (min.)</td>
</tr>
<tr>
<td>HCl liberated, ml. 0.01080 N</td>
</tr>
<tr>
<td>k² (1.mole⁻¹.min⁻¹)</td>
</tr>
</tbody>
</table>
The titration with potassium hydroxide in benzene/methanol showed that the acetoxychloride will liberate hydrochloric acid before the acetoxy link is attacked. We did not, however, succeed in isolating phenanthryl acetate from the alkaline reaction mixture by extraction, but instead a small amount of material having the infra-red spectrum of phenanthroline was obtained. In order to clarify this point, the effect of water on the reaction of phenanthryl acetate with alkali was examined.

Three solutions of phenanthryl acetate (5ml, 0.01 M) were treated with potassium hydroxide (5ml, 0.02M) in the presence of 1, 3, and 5 ml. of water respectively. Titration against potassium hydroxide in benzene/methanol showed that the amount of acetic acid liberated depends on the presence of a large excess of water: (see Fig. 5).

<table>
<thead>
<tr>
<th>Vol. of Water, ml.</th>
<th>1</th>
<th>3</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic Acid liberated, %</td>
<td>12</td>
<td>77</td>
<td>93</td>
</tr>
</tbody>
</table>
TITRATION OF HYDROLYSATE OF PHENANTHROL ACETATE

(Fig. 5)

Water added

0  
1  1 ml
2  3 ml
3  5 ml
These results resolve the apparent contradiction between the observations that no acetic acid was liberated during the reaction of the acetoxychloride with alkali, but no phenanthryl acetate could be extracted from the reaction product. The extraction involved the partition of the product between ether and water, and phenanthryl acetate is hydrolysed during this process.

c) Solvolysis of the Chloroacetoxy-adduct in Acetic Acid containing Silver Acetate:

Solutions of silver acetate in acetic acid were prepared as described by Winstein. Silver acetate, prepared by adding excess potassium acetate to aqueous silver nitrate, was filtered and washed with glacial acetic acid, suspended in glacial acetic acid, and the water content was estimated from the depression of the freezing point. Excess acetic anhydride was added to remove the water.

Experiment 1.

Treatment with a large excess of silver acetate at 100-110°C.

The acetoxy-chloride (ca.2mM) was treated with a solution of silver acetate (25mM) in dry acetic acid (20 ml.) at 100-110°C for four hours. The product was filtered; acetic acid was removed from the filtrate by distillation under reduced pressure; and the residue was chromatographed on silica gel in benzene. The bulk of the eluate

(105) Winstein and Buckles, J.Amer. chem. Soc., 1942, 64, 2780.
was found to be 9-acetoxyphenanthrene, identified by its infra-red spectrum.
The final benzene eluates had an infra-red spectrum which closely resembled that of trans-9,10-diacetoxy-9, 10-dihydrophenanthrene, followed by a fraction which appeared from its infra-red spectrum to be mainly cis-9-acetoxy-10-hydroxy-9,10-dihydrophenanthrene, as identified later.

**Experiment 2.**

Treatment with a slight excess of silver acetate at 62$^\circ$. From a similar experiment in which 2.5mM silver acetate and 2.1mM acetoxy-chloride were heated to 62$^\circ$ for one hour, only phenanthrol acetate (40%) and cis-hydroxy-diacetoxy dihydro-phenanthrene (30%) were recovered.

**Experiment 3.**

Treatment with a slight excess of silver acetate at 30$^\circ$. The acetoxychloride (0.436g, 1.6mM) in dry acetic acid (50ml) was added to a nearly saturated solution of silver acetate (400ml, 0.0056N) and left for four days at 30$^\circ$C. The solution was filtered through a weighed sintered glass crucible and the precipitate was washed with glacial acetic acid. The precipitate was then washed with diluted nitric acid, dried at 120$^\circ$ and weighed; it was silver chloride, (0.2196g.) equivalent to 0.417g. (95%) of the adduct used.
Acetic acid was evaporated under reduced pressure from the bulk of the filtrate and the acetic acid washings. The residue was suspended in the minimum amount of light petroleum (40°-60°), and chromatographed on a column of 40g. silica gel (H+W, M.F.C.). Nothing was eluted with petroleum ether (30 ml, b.p. 40°-60°) and a mixture (1:1) of benzene and petroleum ether. On changing the solvent to benzene, 0.0598g. of a solid were obtained in the next 50 ml; it was shown to be phenanthrol acetate, and accounted for 16% of the adduct used. The column was further washed with benzene (200 ml.). A yellow band was eluted, and 6 mg. of an unidentified orange solid were obtained. The column was then eluted with ether. The ether eluate contained 0.3077g. (76%) of a white crystalline material which, after recrystallisation from a mixture of ether and petroleum ether, had a m.p. 115°. On acetylation it gave cis-9,10-diacetoxy-9,10-dihydrophenanthrene with infra-red spectrum identical with that of the authentic material. It was therefore considered to be cis-9-acetoxy-10-hydroxy-9,10-dihydrophenanthrene.

Elementary Analysis (BC495, 14441/63)

Found  C, 75.7;  H, 5.62;  O, 19.0.

C₁₆H₁₄O₃ requires  C, 75.6;  H, 5.51;  O, 18.9.
Experiment 4.

A similar experiment was carried out in the presence of 1% of water. Cis-9-acetoxy-10-hydroxy-9,10-dihydrophenanthrene, identified by its infra-red spectrum, was obtained from the reaction mixture in 74% yield. The remainder consisted of phenanthrol acetate, detected by thin-layer chromatography in the column eluate.

d) The Reaction of 9-acetoxy-10-chloro-9,10-dihydrophenanthrene with perchloric acid in acetic acid.

Samples of trans-dichloride and of the acetoxy chloride with 0.1M perchloric acid were left in dry acetic acid overnight. No change was observed in the absence of perchloric acid.

10 x 5 ml. of each sample, containing 2 - 4 g/1 were applied to a prepared plate of silica gel in a current of compressed air to remove acetic acid. Market spots of each of 9-chlorophenanthrene (4 g/1), phenanthrene (4.5 g/1) and cis-9-acetoxy-10-hydroxy-9,10-dihydrophenanthrene (1 g/1) were also applied to the starting line. The chromatogram was run in benzene and sprayed with fluorescein and silver nitrate. Inspection under untra-violet light showed that, in the presence of perchloric acid, the acetoxy adduct had all been converted to chlorophenanthrene; the trans-dichloride had not been changed.
e) Reaction of 9-Acetoxy-10-9,10-dihydrophenanthrene with hydrochloric acid in acetic acid.

The purified acetoxy chloride (0.49g.) was left in a solution of HCl in dry acetic acid (approx. 1N) for two weeks. The solution was extracted with water and ether. The ethereal solution (about 20ml.) was dried, and divided into two equal parts.

One part was evaporated to dryness in a dish containing 1g. suitably deactivated alumina, to absorb the product. This portion of alumina was then placed on the top of a column of 25g. deactivated alumina in 10% ether/light petroleum (40°-60°) and chromatographed. Plate chromatography showed that the first 20ml. contained 9-chlorophenanthrene (0.018g.) and the following 16ml. dichloride with chlorophenanthrene (0.028g.). The solid obtained from the latter was washed with light petroleum (b.p. 40°-60°) to remove 9-chlorophenanthrene, leaving a residue of 0.014g. The infra-red spectrum of this residue was characteristic for trans-dichloride contaminated with 9-chlorophenanthrene. The solids from the fraction rich in trans-dichloride accounted for about 6% and these fractions together accounted for about 20%; the remaining balance of 9-chlorophenanthrene being about 14% by weight of the starting material. Some allowance can be made for thermal decomposition of trans-dichloride to give 9-chlorophenanthrene.
The other half of the ethereal solution was treated similarly, using silica gel as an absorbent and light petroleum as solvent. No dichloride fraction could be isolated, and the 9-chlorophenanthrene amounted to about 20% of the weight of the starting material. Elution with benzene followed by ether gave no diacetate or hydroxy-acetate. It has been shown earlier that cis-dichloride can be eluted from silica gel columns in about 80% yield, and its absence from the column eluate indicates that it was also absent from the reaction mixture. No acetoxy-chloride was eluted from either column, but discolouration at the top of the columns indicated that some decomposition to give phenolic material had occurred. It can be concluded that in dry hydrochloric acid in acetic acid, about 10% of the acetoxy-chloride is converted to trans-dichloride and probably an equal amount to 9-chlorophenanthrene.

5. RATES OF SOLVOLYSIS OF ADDUCTS WITH SILVER ACETATE AT 30°.

Aliquots of solutions of silver acetate (20ml, @ 0.004 M) and adduct (10ml, @ 0.007 M) were mixed at 30° and allowed to stand in a thermostat in the dark. To stop the reaction, excess of aqueous hydrochloric acid (10 ml, @ 0.011 M) was added; the extent of solvolysis was determined by titrating the chloride against standard silver nitrate ( @ 0.011 M), and subtracting the corresponding value for the mixture of silver
acetate (20 ml.) and hydrochloric acid (10ml.). Determinations containing adduct without silver acetate did not give significant amounts of liberated chloride at the end of the reaction. The following are the results:

**TABLE 2**

<table>
<thead>
<tr>
<th>Adduct:</th>
<th>AgOAc Molarity</th>
<th>Time Min</th>
<th>Titr. -Blank ML.</th>
<th>AgNO₃ Molarity 1. Mole Min⁻¹⁻¹</th>
<th>k₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetoxychloride</td>
<td>0.00700 M</td>
<td>244</td>
<td>1.39</td>
<td>0.01090</td>
<td>0.43</td>
</tr>
<tr>
<td></td>
<td>1047</td>
<td>3.54</td>
<td></td>
<td></td>
<td>0.39</td>
</tr>
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<td></td>
<td>1133</td>
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<td>0.39</td>
</tr>
<tr>
<td></td>
<td>1376</td>
<td>4.06</td>
<td></td>
<td></td>
<td>0.41</td>
</tr>
<tr>
<td>trans-Dichloride</td>
<td>0.00751 M</td>
<td>1020</td>
<td>2.28</td>
<td>0.01093</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>1260</td>
<td>2.58</td>
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<td>0.17</td>
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<td></td>
<td>2400</td>
<td>3.52</td>
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<td>2640</td>
<td>3.74</td>
<td></td>
<td></td>
<td>0.16</td>
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<td></td>
<td>2820</td>
<td>3.84</td>
<td></td>
<td></td>
<td>0.16</td>
</tr>
<tr>
<td>cis-dichloride</td>
<td>0.00813 M</td>
<td>184</td>
<td>1.47</td>
<td>0.01089</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>3177</td>
<td>2.30</td>
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<td></td>
<td>0.40</td>
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<td>627</td>
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<td>0.39</td>
</tr>
<tr>
<td></td>
<td>995</td>
<td>4.13</td>
<td></td>
<td></td>
<td>0.41</td>
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<td></td>
<td>1072</td>
<td>3.99</td>
<td></td>
<td></td>
<td>0.37</td>
</tr>
</tbody>
</table>

6. **PRODUCTS FROM REACTIONS OF REFERENCE MATERIALS WITH SILVER ACETATE IN ACETIC ACID.**

a) **cis- and trans- diacetates:**

Samples of the cis- and trans- diacetates and acetoxychloride were treated with silver acetate under conditions equivalent to those of the kinetic experiment. The products were examined by thin-layer chromatography, together with an
untreated sample of the **cis**-acetoxy-hydroxy compound derived from an earlier experiment.

(Fig. 6)

Chromatogram of Products of Silver Acetate Treatment

Identified by comparison with earlier work:

1. Acetoxychloride
2. Phenanthryl Acetate
3. Phenanthrol.

The photograph of the chromatogram shows that the di-acetates are substantially stable under reaction conditions. On the original chromatogram it could be seen that the trans-diacetate gave a trace of hydroxyacetate, and the **cis**-isomer a trace of acetoxyphenanthrene.
b) cis- and trans-dichlorides:

The dichlorides were treated with the silver acetate under conditions equivalent to those of the kinetic experiment. Examination of the products by thin-layer chromatography, together with suitable markers, showed that the major product was chlorophenanthrene. Both dichlorides also produced a very small amount of phenanthryl acetate.

7. QUANTITATIVE ANALYSIS OF PRODUCTS

I. From the Determination of Hydrogen Chloride:

The overall reaction-scheme for the chlorination of phenanthrene allows for five main components: cis- and trans-dichlorides, cis- and trans-acetoxy chlorides, and the substitution product 9-chlorophenanthrene.

Both substitution and addition leading to acetoxychloride liberate one mole of hydrochloric acid per mole of chloride consumed. Measurement of the ratio of hydrochloric acid produced in the reaction to chlorine used therefore gives a figure equal to the sum of substitution and acetoxy-chloride formation. The dichlorides and acetoxychlorides will give inorganic chlorides on treatment with alkali, and the acetoxychlorides will also liberate acetic acid on hydrolysis.

It is, therefore, possible to estimate the proportion of substitution, addition leading to dichlorides, and addition leading to acetoxychlorides from the determination of (a) hydrogen chloride liberated in the reaction per mole of chlorine.
consumed and (b) hydrogen chloride liberated on alkaline dehydrochlorination of the product, per mole of chlorine consumed.

This scheme can be summarised as follows:

\[ X \text{ chlorophenanthrene } + X \text{ hydrochloric acid} \]
\[ 100 \text{ Cl}_2 \rightarrow Y \text{ phenanthrene dichlorides} \]
\[ Z \text{ acetoxychloride } + Z \text{ hydrochloric acid} \]

\[ X + Y + Z = 100 \]

hydrochloric acid liberated in the reaction = \( X + Z \)
chloride liberated in hydrolysis of product = \( Y + Z \)

\[ X + 2Z + Y - 100 = Z = \text{ acetoxychloride produced} \]

\[ X + Z - Z = X = \text{ chlorophenanthrene produced} \]
\[ Y + Z - Z = Y = \text{ dichlorides produced} \]

It was considered desirable to estimate the acetic acid liberated from the acetoxychloride directly, and not only by difference. A portion of the produce hydrolysate was therefore titrated against potassium methoxide in benzene-methanol. Investigation of the hydrolysis of phenanthryl acetate had shown that the presence of a large excess of water was essential for the hydrolysis of the acetate link, but water interfered with the titration. The following procedure was devised, in which the hydrolysis was carried out in a very small volume, so that the water concentration in the final titration was not greater than 5\%. 
Procedure:

Approximately 4mM of chlorine were allowed to react with 8mM of phenanthrene in 50ml. dry acetic acid in the dark and left overnight. The reaction mixture was extracted with ether and water in three separating funnels using about 300ml. water. The aqueous extract was concentrated to less than 250ml., cooled, and made up to 250ml. The distillate of the aqueous extract was checked and found to contain no significant amount of chloride. The ether extract was evaporated in a current of air and left overnight in a vacuum desiccator. The solid residue was made up to 50ml. in benzene. Aliquots of the solution (2 x 2ml.) were treated with an excess of alcoholic potassium hydroxide for three hours, acidified with nitric acid and titrated against silver nitrate (N/100).

Another two samples (2 x 20ml.) were treated with 5ml. aqueous potassium hydroxide (0.4 N), benzene was removed on a water bath in a stream of nitrogen to ensure the presence of a high enough concentration of water for acetate hydrolysis and the aqueous suspension was refluxed in a stream of nitrogen (using the gas to stir) for three to four hours. The solutions were cooled, acidified with 5ml. 0.2N hydrochloric acid, tested with lacmoid to ensure acidity, diluted to 150ml. with benzene:methanol (4:5) and titrated against N/50 potassium methoxide in benzene:methanol (4:1).
Preparation of electrolyte solutions:

a) Sodium acetate:
Anhydrous sodium acetate was dried in an oven at about 90° and dissolved in dry acetic acid.

b) Lithium chloride:
Chloride estimation showed that the lithium chloride available did not contain more than 0.5% of water. This was not considered sufficient to interfere in the reaction; the salt was dissolved in dry acetic acid.

c) Lithium perchlorate:
Lithium perchlorate was dried under vacuum, using a mercury diffusion pump, for 12 to 15 hours at 150°.

d) Perchloric acid:
The strength of the stock solution of perchloric acid was determined by titration of a weighed sample against standard alkali. A weighed amount of perchloric acid was dissolved in acetic acid. The calculated amount of acetic anhydride was added slowly to the perchloric acid solution with cooling.
### Table 3

**Quantitative Analysis of the Product of Chlorination of Phenanthrene**

<table>
<thead>
<tr>
<th>Additive</th>
<th>moles/l.</th>
<th>$\text{Cl}_2$ used</th>
<th>HCl</th>
<th>Cl$^-$ by $\text{ClP}$</th>
<th>POAcCl</th>
<th>POAcCl $\text{POCl}_2$</th>
<th>$\text{PCl}_2$</th>
<th>$\text{POAcCl}$</th>
<th>$\text{POCl}_2$</th>
<th>Hydrochloric acid liberated in the course of the reaction.</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>3.80</td>
<td>53.0</td>
<td>59.4</td>
<td>40.6</td>
<td>47.0</td>
<td>12.4</td>
<td>14.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>3.29</td>
<td>52.9</td>
<td>62.3</td>
<td>37.5</td>
<td>46.9</td>
<td>15.2</td>
<td>14.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaOAc</td>
<td>4.3</td>
<td>3.86</td>
<td>56.1</td>
<td>61.6</td>
<td>38.4</td>
<td>43.9</td>
<td>17.7</td>
<td>15.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaOAc</td>
<td>4.5</td>
<td>3.40</td>
<td>54.2</td>
<td>61.9</td>
<td>38.1</td>
<td>45.8</td>
<td>16.1</td>
<td>15.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiCl</td>
<td>1.21</td>
<td>3.94</td>
<td>53.5</td>
<td>61.7</td>
<td>38.8</td>
<td>46.7</td>
<td>15.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiClO$_4$</td>
<td>3.8</td>
<td>3.80</td>
<td>59.5</td>
<td>49.2</td>
<td>50.8</td>
<td>40.5</td>
<td>8.70</td>
<td>12.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiClO$_4$</td>
<td>3.1</td>
<td>3.99</td>
<td>57.8</td>
<td>52.4</td>
<td>47.6</td>
<td>42.2</td>
<td>10.2</td>
<td>10.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HClO$_4$</td>
<td>4.0</td>
<td>3.77</td>
<td>69.3</td>
<td>32.0</td>
<td>69.3</td>
<td>32.0</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HClO$_4$</td>
<td>4.0</td>
<td>3.69</td>
<td>69.0</td>
<td>31.2</td>
<td>69.0</td>
<td>31.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(1) Hydrochloric acid liberated in the course of the reaction.

(2) Chloride liberated from the reaction product by alkali.

(3) Chlorophenanthrene by difference

(4) Phenanthrene dichlorides

(5) Phenanthrene acetoxychlorides

(6) Phenanthrene acetoxychlorides by direct titration.
II. By Isotope Dilution:

The general procedure has been described above.

Experiments 1 and 2:

Inactive cis-dichloride was added to the product of the reaction of radioactive chlorine with excess phenanthrene. The reaction product was partitioned between water and ether. The ether layer was washed with bicarbonate, most of the ether was removed by distillation under reduced pressure, and the cis-dichloride was precipitated by addition of light petroleum ($40^\circ$-$60^\circ$), chromatographed on silica gel, and recrystallised three times from benzene solution by adding light petroleum. The specific activities of the successive crops was compared by counting acetone solutions of the dichloride. The change in specific activity between the second and third crops was less than 2%.

Experiment 3:

Inactive acetoxychloride was added to the reaction mixture and the product was isolated as described above. The ether was removed by distillation under reduced pressure in a flask containing glass wool, and the bulk of the reaction product was transferred to the top of a column containing deactivated alumina in 5% ether/light petroleum ($40^\circ$-$60^\circ$). The distillation flask was washed with the minimum amount of ether, light petroleum was added to make the ether concentration about 5%, and the product was chromatographed as described
for the preparation of the acetoxychloride.

A small fraction (0.07 g.) of the radioactive acetoxychloride isolated (0.47 g.) was hydrolysed and the specific activity of the hydrolysate was determined. The remainder of the product was rechromatographed and the specific activity was again determined. The two values agreed within 0.2%.

The quantities used and results obtained are shown below:

**TABLE 4**

**ANALYSIS BY ISOTOPE DILUTION**

<table>
<thead>
<tr>
<th>Experiment</th>
<th>DILUENT</th>
<th>(1) cis-dichl.</th>
<th>(2) cis-dichl.</th>
<th>(3) acetoxychloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>mM</td>
<td></td>
<td>2.805</td>
<td>3.74</td>
<td>2.80</td>
</tr>
<tr>
<td>Cl₂ used, mM</td>
<td></td>
<td>1.098</td>
<td>4.21</td>
<td>2.86</td>
</tr>
<tr>
<td>Phenanthrene, mM</td>
<td></td>
<td>11.2</td>
<td>8.4</td>
<td>8.8</td>
</tr>
<tr>
<td>Specific activity*</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Before dilution</td>
<td></td>
<td>1.03x10⁶</td>
<td>2.82x10⁵</td>
<td>8.04x10⁵</td>
</tr>
<tr>
<td>After dilution</td>
<td></td>
<td>1.30x10⁵</td>
<td>0.88x10⁵</td>
<td>1.06x10⁵</td>
</tr>
<tr>
<td>% in product</td>
<td></td>
<td>36.9</td>
<td>39.0</td>
<td>14.8</td>
</tr>
<tr>
<td>* Specific activity: Counts per minute/Molarity of the solution.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
In an earlier series of experiments, activities were determined by counting the aqueous solutions without the precipitation and reduction procedure. It was later found that such figures were subject to considerable errors, as illustrated in Table 5.

**TABLE 5**

EFFECT OF "PRECIPITATION-REDUCTION" ON ACTIVITY

<table>
<thead>
<tr>
<th>Solution</th>
<th>Specific Activity</th>
<th>Before Reduction</th>
<th>After Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bisulphite sol(^n).</td>
<td>6.54x10(^5)</td>
<td>6.68x10(^5)</td>
<td></td>
</tr>
<tr>
<td>Bisulphite sol(^n).</td>
<td>6.60x10(^5)</td>
<td>6.66x10(^5)</td>
<td></td>
</tr>
<tr>
<td>Dichloride hydrolysate</td>
<td>4.52x10(^4)</td>
<td>4.92x10(^4)</td>
<td></td>
</tr>
<tr>
<td>Acetoxychloride hydrolysate</td>
<td>1.09x10(^5)</td>
<td>1.14x10(^5)</td>
<td></td>
</tr>
</tbody>
</table>

The results of these experiments can, therefore, not be used for quantitative interpretation, but are included to illustrate trends observed on adding electrolytes to the reaction mixture. They are given in Table 6.
### TABLE 6

**ISOTOPE DILUTION IN THE PRESENCE OF ELECTROLYTES**

<table>
<thead>
<tr>
<th>Additive</th>
<th>LiCl</th>
<th>LiCl</th>
<th>NaOAc</th>
</tr>
</thead>
<tbody>
<tr>
<td>mM</td>
<td>4.00</td>
<td>5.00</td>
<td>6.40</td>
</tr>
<tr>
<td>Diluent</td>
<td>cis-phenanthrene dichloride</td>
<td></td>
<td></td>
</tr>
<tr>
<td>mM</td>
<td>1.04</td>
<td>2.52</td>
<td></td>
</tr>
<tr>
<td>Cl₂ used, mM</td>
<td>5.80</td>
<td>2.39</td>
<td></td>
</tr>
<tr>
<td>Specific Activity*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Before dilution</td>
<td>3.00x10⁵</td>
<td>5.63x10⁵</td>
<td>1.87x10⁵</td>
</tr>
<tr>
<td>After dilution</td>
<td>5.04x10⁴</td>
<td>6.95x10⁴</td>
<td>1.60x10⁴</td>
</tr>
<tr>
<td>% in Product</td>
<td>32.1</td>
<td>34.4</td>
<td>34.5</td>
</tr>
</tbody>
</table>

*See Table 4*
8. SOME RELEVANT INFRA-RED SPECTRA

Infra-red Absorption Bands (cm$^{-1}$; range 600-1800 cm$^{-1}$)

<table>
<thead>
<tr>
<th>trans-9-acetoxy-10-dihydrophenanthrene:</th>
<th>cis-9,10-diacetoxy-9,10-dihydrophenanthrene:</th>
<th>trans-9,10-diacetoxy-9,10-dihydrophenanthrene:</th>
</tr>
</thead>
<tbody>
<tr>
<td>696 sh</td>
<td>700 m</td>
<td>734 s</td>
</tr>
<tr>
<td>702 m</td>
<td>712 w</td>
<td>763 s</td>
</tr>
<tr>
<td>734 s</td>
<td>734 s</td>
<td>787 w</td>
</tr>
<tr>
<td>746 w</td>
<td>770 m</td>
<td></td>
</tr>
<tr>
<td>760 m</td>
<td>783 m</td>
<td></td>
</tr>
<tr>
<td>813 w</td>
<td>912 m</td>
<td>855 w</td>
</tr>
<tr>
<td>920 w</td>
<td>935 w</td>
<td></td>
</tr>
<tr>
<td>944 w</td>
<td>942 m</td>
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</tr>
<tr>
<td>954 m</td>
<td>1012 m</td>
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</tr>
<tr>
<td>1010 m</td>
<td>1031 m</td>
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</tr>
<tr>
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<td>1080 m</td>
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<td>1120 w</td>
<td>1129 w</td>
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<td>1163 w</td>
<td>1167 w</td>
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<td>1188 w</td>
<td>1204 m</td>
<td>1185 w</td>
</tr>
<tr>
<td>1219 sh</td>
<td>1211 m</td>
<td>1220 s</td>
</tr>
<tr>
<td>1230 s</td>
<td>1222 s</td>
<td>1235 s</td>
</tr>
<tr>
<td>1241 w</td>
<td>1345 w</td>
<td>1308 w</td>
</tr>
<tr>
<td>1310 w</td>
<td>1368 w</td>
<td>1350 w</td>
</tr>
<tr>
<td>1370 NJ</td>
<td>1450 NJ</td>
<td>1368 NJ</td>
</tr>
<tr>
<td>1450 NJ</td>
<td>1520 sh</td>
<td>1449 NJ</td>
</tr>
<tr>
<td>1733 s</td>
<td>1728 s</td>
<td>1739 s</td>
</tr>
</tbody>
</table>

s = strong; m = medium; w = weak; sh = shoulder;
NJ = Nujol bands.
Infra-red Absorption Bands (cm$^{-1}$; range 600-1800 cm$^{-1}$)

<table>
<thead>
<tr>
<th></th>
<th>cis-9-acetoxy-10-hydroxy-9,10-di-hydrophenanthrene:</th>
<th>9-acetoxyphenanthrene:</th>
<th>Phenanthr-9-ol:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>734 s</td>
<td>724 s</td>
<td>725 s</td>
<td></td>
</tr>
<tr>
<td>744 s</td>
<td>748 s</td>
<td>746 s</td>
<td></td>
</tr>
<tr>
<td>762 m</td>
<td>758 s</td>
<td>762 s</td>
<td></td>
</tr>
<tr>
<td>789 w</td>
<td>771 s</td>
<td>790 w</td>
<td></td>
</tr>
<tr>
<td>935 w</td>
<td>907 w</td>
<td>839 w</td>
<td></td>
</tr>
<tr>
<td>944 w</td>
<td>926 w</td>
<td>871 w</td>
<td></td>
</tr>
<tr>
<td>1021 m</td>
<td>1034 w</td>
<td>1031 w</td>
<td></td>
</tr>
<tr>
<td>1030 m</td>
<td>1065 s</td>
<td>1067 s</td>
<td></td>
</tr>
<tr>
<td>1050 m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1083 m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1097 m</td>
<td>1106 w</td>
<td>1107 w</td>
<td>NJ = 1144 w</td>
</tr>
<tr>
<td></td>
<td>1148 m</td>
<td>1144 w</td>
<td></td>
</tr>
<tr>
<td>1159 m</td>
<td>1168 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1202 w</td>
<td>1208 s</td>
<td>1221 w</td>
<td></td>
</tr>
<tr>
<td>1243 s</td>
<td>1227 s</td>
<td>1232 w</td>
<td></td>
</tr>
<tr>
<td>1250 sh</td>
<td></td>
<td>1277 w</td>
<td></td>
</tr>
<tr>
<td>1286 w</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1336 w</td>
<td>1305 m</td>
<td>1346 w</td>
<td></td>
</tr>
<tr>
<td>1373 NJ</td>
<td>1374 NJ</td>
<td>1374 NJ</td>
<td></td>
</tr>
<tr>
<td>1450 NJ</td>
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<td>1460 NJ</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1460 NJ</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1731 s</td>
<td>1751 s</td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

s = strong;  m = medium;  w = weak;  sh = shoulder;

NJ = Nujol bands.
SECTION C.

DISCUSSION
I. THE CHLORINATION OF PHENANTHRENE

I. The Separation of the Reaction Products by Chromatography:

The products of the chlorination of phenanthrene could be separated by chromatography, but the addition products were not sufficiently stable for quantitative recovery. Chlorophenanthrene, phenanthrene, cis-dichloride, and acetoxychloride could be separated on silica gel; but it was difficult to separate the acetoxychloride from its decomposition product, phenanthryl acetate. On deactivated alumina, chlorophenanthrene, phenanthrene, trans-dichloride, and acetoxychloride were separated.

The stability of the adducts under the conditions obtaining during chromatography will be discussed below.

Except for the cis- and trans-dichlorides, all components could be separated by thin-layer chromatography on silica gel. The time taken (1/2 to 1 hour) is so short that the trans-dichloride is not destroyed to an appreciable extent.

II. The Chemistry of the Dichlorides:

The cis- and trans-dichlorides produced in the chlorination of phenanthrene in acetic acid had been characterised earlier.\(^{(105)}\) The cis-dichloride, in which a hydrogen atom can be placed suitably for bimolecular trans-elimination,\(^{(106)}\)

\(^{(105)}\) de la Mare and Klassen, Chem. and Ind. 1960, 498.

\(^{(106)}\) Cristol, Hause and Meek, J. Amer. chem. Soc., 1951, 73, 674.
had been found to be very much more reactive with alkali
\( k_2 = \text{Ca} 160 \text{ l. mole}^{-1}\text{min.}^{-1} \text{at } 0^\circ \), than the \underline{\text{trans}}-dichloride
\( k_2 = \text{Ca} 0.02 \text{ l. mole}^{-1}\text{min.}^{-1} \text{at } 0^\circ \).(107)

The behaviour of the dichlorides with chromatographic
adsorbents followed a similar pattern; on "alkaline" alumina
the \underline{\text{cis}}-dichloride was destroyed, whereas the \underline{\text{trans}}-dichloride
could be recovered. On silica gel the \underline{\text{cis}}-dichloride could
be isolated, but the \underline{\text{trans}}-dichloride was destroyed.

Both compounds gave 9-chlorophenanthrene and titratable
chloride on treatment with hot alkali. It was observed that
the \underline{\text{trans}}-dichloride tended to give values for chloride
somewhat higher(by Ca.3- 10%) than those calculated from its
formula.

Both dichlorides appeared to be reasonably stable in
acetic acid at 30°, giving no titratable chloride in the
course of two days.

In a solution of silver acetate in dry acetic acid,
both chlorides reacted to give the elimination product,
9-chlorophenanthrene. The liberation of chloride followed
a second-order rate equation; the reaction of the \underline{\text{cis}}-
dichloride is faster \( (k_2 = 0.4 \text{ l.mole}^{-1}\text{min.}^{-1}) \) than that of
the \underline{\text{trans}}-dichloride \( (k_2 = 0.16 \text{ l.mole}^{-1}\text{min.}^{-1}) \), probably
due to synchronous removal of hydrogen and chlorine in the

(107) de la Mare, Klassen, and Koenigsberger, J. Chem. Soc.,
1961, 5285.
case of the former.

III. The Reactions and Structure of the Acetoxychloride:

The presence of an acetoxy-adduct in the chlorination of phenanthrene had been inferred from the oxygen content and the infra-red spectrum of the chlorination product. In the present work it has been found possible to isolate and identify an acetoxychloride of phenanthrene by chromatography.

a) Reactions which prove that it is 9-Acetoxy-10-chloro-9,10-dihydrophenanthrene.

The compound liberated inorganic chloride on treatment with alkali, and 9-chlorophenanthrene, identified by its melting point and infra-red spectrum, could be isolated from the reaction.

Pyrolysis and vapour phase chromatography of the adduct have been shown to give 9-acetoxyphenanthrene and 9-chlorophenanthrene, and treatment with perchloric acid in the absence of water gave 9-chlorophenanthrene. The adduct thus has two possible products of elimination which it can give by four different routes:
All these findings, and the results of elementary analysis, are in agreement with the proposed formula.

b) Stereochemical Configuration of the Acetoxychloride.

i) Reaction with Alkali.

In the absence of a difference in inductive effects of the chlorine and acetoxy groups, a hypothetical \textit{cis}-acetoxychloride would be expected to have a rate of elimination of hydrochloric acid about half that of the \textit{cis}-dichloride, of the order of 80 l.mole\textsuperscript{-1}min\textsuperscript{-1} at 0\textdegree. The value found, 2.6 l.mole\textsuperscript{-1}min\textsuperscript{-1} at 0\textdegree, makes it appear unlikely that the compound has the \textit{cis}-configuration, but allows no positive correlation with a \textit{trans} configuration.

ii) Behaviour on Chromatography.

The stability of the acetoxy fraction towards chromatographic adsorbents can be correlated with its tendency to undergo elimination in comparison with the dichlorides. Products with similar infra-red spectra were eluted from silica gel and alumina columns in yields of the same order. The eluates from silica gel columns were tacky syrups contaminated with acetoxyphenanthrene, and it was very difficult to remove the last traces of the solvent, benzene, without further decomposition of the sample.

Chromatography on deactivated alumina gave a white crystalline product, and no acetoxyphenanthrene.

A cis-acetoxychloride would be expected to undergo trans-elimination on alumina as readily as the cis-dichloride, but the adduct is eluted without its decomposition product.

The decomposition of the trans-dichloride indicates that adsorption on silica gel creates conditions favourable to cis-elimination. The formation of acetoxyphenanthrene from acetoxychloride in the course of chromatography on silica gel can be interpreted as due to such a reaction.

These facts point to a trans-configuration for the acetoxychloride.

iii) Stereochemistry from Solvolysis in Silver Acetate.

The assignment of configuration at the 9- and 10-carbon atoms is made particularly difficult by the fact that only one of the two possible isomers is available, and direct comparison of rates and products is not possible.

In order to determine the configuration of the compound, its reaction with silver acetate in acetic acid has been studied and compared with that of the 1-acetoxy-2-chloro-cyclohexanes. (109)

It was to be expected that the phenanthrene system would show greater reactivity towards the reagent than the cyclohexane adducts; the aryl group stabilises the development of the carbonium ionic character on the carbon atom from which the chlorine atom is heterolysed, leading to displacement or elimination. Elimination will be further favoured by the aromatic stability gained by forming the phenanthrene system.

The reaction could therefore be carried out in dilute solutions at $30^\circ$, much milder conditions than those required for the cyclohexane system ($100^\circ$, solid silver acetate).

The reaction of $9$-acetoxy-$10$-chloro-$9,10$-dihydrophenanthrene with dilute silver acetate in dry acetic acid gave about $76\%$ of $\text{cis}$-$9$-acetoxy-$10$-hydroxy-$9,10$-dihydrophenanthrene and some acetoxyphenanthrene at $30^\circ$ with dilute silver acetate; a small amount of $\text{trans}$-diacetate was isolated from a reaction carried out at high temperature with a large excess of silver acetate. The products of the reaction were not altered by the addition of water at low temperature and concentration.

Neither the $\text{cis}$- nor the $\text{trans}$-diacetate forms a hydroxyacetate under the reaction conditions.
The possible reaction paths for the reaction between a trans-acetoxychloride and silver acetate are represented as follows:
The formation of both the trans-diacetate (III) and the cis-hydroxyacetate (V) depends on the possibility of internal nucleophilic displacement by the acetoxy group which must be situated trans to the leaving chlorine. A cyclic transition state (II) is proposed which, in dry acetic acid, reacts with acetate to give the trans-diacetate (III) or in the presence of small amounts of water, through the formation of an ortho-ester (IV), gives a cis-acetoxy-hydroxy-compound (V).

A similar reaction in the opposite direction occurs in the stereospecific conversion of the monoacetate of cis-cyclohexanediol to trans-acetoxy-cyclohexylchloride. (110).

Cyclic intermediates of the type of the acetoxonium ion have been isolated. (111, 112, 113)

![Diagram](image)

By analogy with these systems it is concluded that the acetoxy-chloro-phenanthrene has the trans-configuration. In the presence of sufficient acetate, the trans-diacetate is formed, in dilute solution the acetoxonium ion survives to give the cis-hydroxy compound during the working up process, resulting in an overall inversion of configuration.

This conclusion was confirmed by the comparison of the rates of solvolysis of the acetoxychloride in acetic

(113) Meerwein, Ann. 1960, 632, 38; 635, 1.
acid containing silver acetate, with the corresponding figures for the dichlorides.

All three were catalysed by silver acetate, and gave satisfactory second-order rate-coefficients:

\[ k_2 \text{ (l.mole}^{-1}\text{min.}^{-1}) \]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Rate Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-dichloride</td>
<td>0.17</td>
</tr>
<tr>
<td>cis-dichloride</td>
<td>0.40</td>
</tr>
<tr>
<td>acetoxychloride</td>
<td>0.40</td>
</tr>
</tbody>
</table>

The dichlorides gave almost entirely products of elimination. The acetoxychloride, on the other hand, reacted almost entirely by displacement. The displacement reaction must therefore be considerably faster for the acetoxychloride than for the dichlorides. The inductive influences of chlorine and acetoxyl, as measured by the dissociation constants of substituted benzoic acids \( k_m = 0.37 \) and \( 0.39 \) respectively\(^{114}\) are nearly the same. In the absence of the neighbouring group effects they should have qualitatively similar effects.

The effect of a neighbouring group on the rate of a nucleophilic displacement has been demonstrated by comparing the rate of solvolysis in acetic acid of

cyclohexyltoluene-para-sulphonate and the cis- and trans-2-acetoxy-compounds. The electron withdrawing effect of the acetoxy group is apparent in the reduction of the solvolysis rate of the cis-compound. Due to the participation of the acetoxy group, the trans-compound reacts almost as rapidly as the cyclohexyl sulphonate.

The reactivity of the 9-acetoxy-10-chloro-9,10-di-hydrophenanthrene therefore indicates that the neighbouring acetoxy group is participating in the rate-determining stage of the solvolysis. This can happen only if the acetoxy group is trans to the departing chlorine.

iv) Stereochemistry from Acid-catalysed Reactions in Acetic Acid.

The elimination of acetic acid from the acetoxychloride, which has been observed in the presence of perchloric and hydrochloric acids, can be formulated as follows:

(115) Winstein, Hess and Buckles, J.A.C.S., 1942, 64, 2796.
The first part of the reaction resembles the hydrolysis of an ester undergoing alkyl-oxygen cleavage, forming a carbonium ion, as shown by e.g. the acid hydrolysis of \( t \)-butyl acetate in \( H_2O^{18} \), giving labelled \( t \)-butyl alcohol. (116)

\[
(\text{CH}_3)\text{C} = \text{O} + \text{H}_2\text{O}^{18} \xrightarrow{\text{H}^+} (\text{CH}_3)\text{C} = \text{O}^{18} + \text{CH}_2\text{COOH}
\]

and the racemization, on hydrolysis, in aqueous dioxan, of

\[
\text{Et} - \text{O} - \text{Et} \quad \xrightarrow{\text{H}^+} \quad \text{Me} - \text{O} - \text{Me}
\]

90% racemised.

The reaction must have proceeded through a carbonium ion and be unimolecular. A bimolecular reaction would have led to inversion. Similarly, the phenanthrene acetoxychloride can be envisaged to undergo protonation of the acetoxy group, followed by ionisation to form the carbonium ion. Being potentially part of an aromatic system, it will have a strong tendency to loosen.

a proton and undergo elimination to form chlorophenanthrene.

In the presence of a high concentration of chloride ion, i.e. concentrated HCl, it can also undergo addition to form phenanthrene trans-dichloride.

It will be of interest to investigate the effects of changing acid concentration on the rate and products of this acid catalysed elimination, to establish the mechanism on a more quantitative basis.

IV. The Formation of Substitution Products other than 9-Chlorophenanthrene.

The possibility of substitution at carbon atoms other than 9 in the phenanthrene molecule must be considered.

Gas chromatography of the chlorophenanthrene fraction of the chlorination product, using an electron capture detector, showed that a total of 1% of 3- and 4-chlorophenanthrene was present, probably divided in the ratio of 3-chlorophenanthrene = 0.4% to 4-chlorophenanthrene = 0.6%. 1-chlorophenanthrene could not be separated from 9-chlorophenanthrene by this method, and could therefore not be estimated.

An alternative method of estimation, comparison of the peak heights of infra-red spectra of samples and standards,

(118) E.A. Johnson, private communication.
(119) J. Lomas, private communication.
indicated that the chlorophenanthrene fraction contained 1% of 3-chlorophenanthrene and 2.5% of 1-chlorophenanthrene.

It appears that a total of 2 - 4% of chlorophenanthrene other than 9-chlorophenanthrene is produced in the chlorination of chlorophenanthrene, and that 1-chlorophenanthrene accounts for more than half of this. This figure is somewhat lower than the 10% suggested earlier, and shows an even greater contrast between the reactivity of corresponding sites in the molecule in chlorination and nitration. (120)

V. The Possible Presence of another Acetoxychloride.

It was of interest to ascertain whether more than one acetoxychloride was produced in the chlorination of phenanthrene in acetic acid. The methods used and the results obtained are tabulated below:

<table>
<thead>
<tr>
<th>Method of Analysis</th>
<th>% Acetoxychloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride Determination (by difference)</td>
<td>14-15%</td>
</tr>
<tr>
<td>Isotope Dilution (using the trans-compound)</td>
<td>15%</td>
</tr>
<tr>
<td>Titration of Acetic Acid liberated from product</td>
<td>14-15%</td>
</tr>
<tr>
<td>Colorimetric Estimation of Phenol liberated from product</td>
<td>14-15%</td>
</tr>
</tbody>
</table>

(120) de la Mare, Klassen and Koenigsberger, J. chem. Soc., 1961, 5285.
(121) Bavin and Dewar, J. chem. Soc., 1955, 4477; 1956, 164; Dewar and Warford, ibid. 1956, 3570.
(122) J. Lomas, private communication.
The agreement between these figures suggests the absence of an acetoxychloride other than the trans-acetoxychloride isolated earlier.

It is possible that such a compound could be produced, but not be sufficiently stable to survive in the product under the working up conditions used.

VI. The Effects of Added Electrolytes.

Product analyses of products of reactions with and without added electrolytes were carried out to clarify the details of the reaction paths. The results of these experiments are difficult to interpret. Isotope dilution was the only method available for the determination of the cis/trans ratio of the dichlorides, but it was not possible to obtain a sufficient number of accurate results. The unexpected instability of the acetoxychloride in an acid environment, which did not become apparent till the end of this investigation, may have contributed to the poor reproducibility of the volumetric determination when experiments were carried out at different concentrations.

One set of analyses was carried out under carefully controlled conditions; the molarity of chlorine used was kept between 0.07 and 0.08M and that of phenanthrene at about 0.14M.

The results are tabulated below:
The Effect of Added Sodium Acetate.

Sodium acetate is seen to cause an increase in the proportion of acetoxychloride and a slight decrease in the sum of the dichlorides, about 3%. Isotope dilution experiments indicated that the amount of cis-dichloride may be reduced by as much as 10%. It appears that the amount of trans-dichloride is increased.
Trans-dichloride, trans-acetoxychloride and 9-chlorophenanthrene are probably formed via a cationic intermediate or transition state. If the total of the products derived from such an intermediate is compared with cis addition in the presence and absence of sodium acetate, it can be seen that the ratio of products derived from the cationic intermediate to that derived from an ion pair is increased in the presence of sodium acetate.

The Effect of Added Chloride Ion.

It was expected that the addition of chloride ion would have a marked effect on the product ratios of the reaction, through a common ion effect. However, no change could be detected by comparing the products by chloride analysis or isotope dilution.

The Effect of Added Lithium Perchlorate.

The overall effect of the addition of lithium perchlorate is an increase in substitution (formation of chlorophenanthrene) over addition (formation of acetoxychloride and dichlorides). No figures for the trans/cis- ratio of the dichlorides under these conditions are as yet available. It is to be expected that this ratio will be decreased by addition of perchlorate.

The Effect of Added Perchloric Acid.

Perchloric acid addition results in the production of chlorophenanthrene and cis-dichloride only. The product
composition was found to vary with perchloric acid concentration. There is evidence that some acetoxychloride is formed and converted to chlorophenanthrene but, as trans-dichloride is stable in the presence of perchloric acid, its absence indicates that it is not formed under these conditions. Like lithium perchlorate, perchloric acid is seen to increase substitution at the expense of addition, but its effect on cis-addition is much less marked than that on trans-addition.\(^{(123)}\)

**General Conclusions.**

Halogen addition has been described as a two-step process, where the halide ion can act as a nucleophile in the second step of the reaction, or the second step may involve the solvent or another nucleophile present. The formation of an acetoxychloride is in accordance with such a mechanism.

It was to be expected that the addition of halide ion to such a system would lead to an increase in the formation of an addition product, which should have trans configuration.

In the chlorination of phenanthrene in acetic acid, this was not found to be so. A considerable proportion of the addition product was found to be cis-dichloride, and the presence of a common ion did not lead to an increase in addition.

These findings, together with the formation of the

\(^{(123)}\) A. Sexton, private communication.
Acetoxychloride were summarised in the following reaction scheme:

The effects of electrolyte addition confirm that at least two different intermediates are involved in the reaction; different electrolytes influence the relative importance of the various possible reaction paths.

The first transition state consists of the hydrocarbon and the halogen molecule. An intermediate of this type was first proposed by de la Mare and Robertson, (124) to account

for the effects of added electrolytes on the kinetics of the halogenation of aromatic compounds.

The formation of an intermediate of the type

\[
\begin{align*}
\text{H} & \\
\text{Ar} & \\
\text{Cl} & - \text{Cl}
\end{align*}
\]

has been used to rationalise the formation of the cis-di-chloride, via a transition state involving an ion pair, where the second chlorine atom never becomes entirely free. \(^{(125)}\)

An alternative route leads to the formation of a carbonium ion, which can give rise to an addition product by reaction with a nucleophile, chloride or acetate, or to a substitution product by loss of a proton.

Chloride ion does not affect the distribution of the reaction product between these alternative paths of ion pair or carbonium ion formation, but the addition of acetate and, in all likelihood, perchlorate reduces the proportion of cis-dichloride in the reaction product. This may be due to an increase in conductivity of the medium, which favours the development of a carbonium ion rather than the persistence of an ion pair.

The ratio of substitution over addition is increased slightly in the presence of sodium acetate and considerably

\(^{(125)}_{\text{de la Mare and Klassen, Chem. and Ind. 1960, 498.}}\)
in the presence of perchlorate and perchloric acid. The results so far obtained suggest that cis addition is not as strongly affected as the ratio of substitution to addition in the part of the reaction which goes through the carbonium ion.

2. THE CHLORINATION OF NAPHTHALENE

I. The Separation of the Reaction Products by Chromatography.

The present work, on naphthalene, though carried out before that on phenanthrene, is of preliminary character.

It has been shown that naphthalene tetrachlorides can be isolated from the chlorination product of naphthalene by chromatography in light petroleum on silica gel, and that an acetoxychloride fraction can be eluted with benzene. It has since been found possible to separate naphthalene chlor-ide isomers from each other by recrystallisation and repeated chromatography. This process is very laborious, and it may be advisable to investigate alternative systems. The use of a more polar adsorbent, such as alumina, or a form of magnesium silicate, may improve separation. Partition chromatography is generally more efficient than adsorption chromatography, and may offer some advantage. A nitromethane/cyclohexane system on silica has been used to separate benzene hexachlorides. (126)

A similar method may be applicable to the naphthalene tetrachlorides and acetoxychlorides.

II. The Naphthalene Chlorides.

The weight of the naphthalene tetrachloride fraction isolated in the preliminary experiment accounted for about 2% of the chlorine used in the reaction. Most of this fraction could be identified as the alpha-tetrachloride by its infra-red spectrum, but spectra of the later fractions indicated the presence of at least one other component.

A number of products of addition of chlorine to naphthalene have been reported in the literature, E. Fischer,\(^{(127)}\) repeating the work of Laurent,\(^{(128)}\) obtained a dichloride, two tetrachlorides, a chlorodichloride, and two chloro-tetrachlorides. Schütz and Hahnfeld\(^{(129)}\) obtained three naphthalene tetrachlorides, and investigated their reactions with nitric acid, and the rates and products of the reactions with alkali. They concluded that all three compounds have the four chlorine atoms in the same ring, and assigned the following configurations by comparing the behaviour with alkali with that reported for the benzene hexachlorides.\(^{(130)}\)

\(^{(127)}\) Fischer, E., Ber. 1878, 11, 785.
\(^{(128)}\) Laurent, Ann. 160, 65.
\(^{(129)}\) Schuetz and Hahnfeld, Ber., 1952, 85, 131.
Mueller\(^{(131)}\) described four naphthalene tetrachlorides, but used the Greek letters in a different order. Schuetz and Hahnfeld's notation is used here.

The configuration of the alpha isomer has been determined independently by X-ray crystallography; it was shown to have the (peep) conformation.\(^{(132)}\)

It is likely that addition to the naphthalene molecule is initiated by electrophilic attack at the 1 position.

The alpha tetrachloride could be obtained by any of the following sequences:

\(^{(131)}\) Mueller, Monatsh, 1953, 84, 640.
(a) cis-1,2-addition, followed by cis-3,4-addition.
(b) trans-1,4-addition, followed by trans-2,3-addition.
(c) trans-1,2-addition, followed by cis-S_Ni rearrangement, followed by trans-2,3-addition.

More recent work\(^\text{(133)}\) has shown that the amount of alpha tetrachloride is reduced by added electrolytes, including added halide ion. It is likely, therefore, that it is not formed through a "Wheland"-like intermediate, and in this respect addition to naphthalene appears to resemble addition to phenanthrene. Further work is in progress.\(^\text{(133)}\)

III. Naphthalene Acetoxychlorides.

Evidence for the existence of acetoxychlorides has been given in the experimental section. Thin-layer chromatography using diazotised para-nitroaniline showed that, on hydrolysis of the acetoxy fraction, a mixture of chloronaphthols was obtained. The major component of the chloronaphthol mixture could be isolated, and was found to have an infra-red spectrum identical with 4-chloro-naphth-1-ol, derived from 1-acetoxy-2,3,4-trichloro-1,2,3,4-tetrahydro-naphthalene.

Two routes could be envisaged for the formation of this compound:

Electrophilic attack of chlorine on naphthalene at the 1, followed by the addition of acetate at the 4-position.

\(^\text{(133)}\) V. Sanchez del Olmo, unpublished work.
or 1,2-addition of chlorine followed by attack of chlorine at the 3-, and addition of acetate at the 4- position.

B.

Greater possibility for delocalisation in the intermediate stage of B, compared with A, suggests that B is the more likely route.

3. ADDITION-ELIMINATION SEQUENCES IN AROMATIC SUBSTITUTION.

The experimental work described here has shown that substitution compounds of phenanthrene can be formed by an addition-elimination sequence, as well as by direct substitution. The adducts isolated were not very stable; it seems possible that such compounds could be missed in the analysis of reaction products, and the formation of addition products may be more common than is generally recognised. It seems also likely that familiar addition reactions are accompanied by the formation of unstable stereoisomers which have not
been detected.

The early attempts to describe aromatic substitution in terms of an addition-elimination sequence arose from the wish to reconcile the chemical properties of aromatic compounds with the olefinic cyclohexatriene formula for benzene. Addition reactions of olefins were studied and used as analogy for the mechanism of aromatic substitution. The evidence adduced in support of such a theory has been reviewed in the introduction.

An alternative mechanism, relating aromatic substitution to the formation of complexes of aromatic compounds with molecules and ions able to act as electron acceptors was proposed by Meerwein(134) and Pfeiffer and Wizinger.(135) Such a complex was considered to be the first phase in a substitution reaction involving a "saltlike" intermediate which is not necessarily an addition product. This mechanism could be used to explain the action of halogen carriers and the ease of halogenation of phenols and aromatic amines.

This view was strengthened by the demonstration that the analogy between nitration and sulphonation of ethylene and benzene is not valid,(136) and by the work of Price(137) who showed that in the bromination of phenanthrene, addition and

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(135) Pfeiffer and Wizinger, Ann. 1928, 461, 132.
substitution are alternative, not successive paths.

Additive and dissociation mechanisms were incorporated (138) in a generalised theory of substitution of Ingold and Hughes.

The interpretation of reactions in terms of wave mechanics led Wheland (139) to propose the following model for aromatic substitution:

An electrophile attacks an aromatic system to give a cationic intermediate, resulting in the formation of a carboxonium ion centre. The type of bond between the substrate and the reagent is not specified. Substitution is completed by proton loss.

Consideration of kinetic isotope effects (140) in the bromination of benzene and bromobenzene, and the nitration of benzene, toluene, bromobenzene, naphthalene and nitrobenzene show proton loss is not generally rate determining, i.e. the new bond is formed before the old bond breaks.

In compounds where the intermediate can be expected to be stabilised, like phenols and aromatic amines, hydrogen isotope effects have been observed, (141,142) and it has been concluded that the rate determining step includes the removal of the proton.

(138) Ingold and Hughes, J. chem. Soc., 1935, 244.
In the reaction sequence:

\[
\text{[Diagram]}
\]

the presence of an accompanying nucleophile is implied, though not explicitly stated. The importance of an intermediate or transition state incorporating the nucleophilic fragment of molecular halogen reagents has been emphasised in a discussion of reactivity and orientation in aromatic halogen substitution.\(^{(143)}\) An alternative role which can be played by the nucleophile is the completion of the reaction by combining with the carbonium ionic centre, giving an addition product. In such a case electrophilic attack is not balanced by proton loss but by combination with a nucleophile, where the nucleophile may be a fragment of the attacking halogen molecule or an anion derived from the solvent.

The formation of acetoxyphenanthrene in the chlorination of phenanthrene, as in the bromination\(^{(144)}\) must go through an addition-elimination sequence where the addition takes place as described.

---


The formation of chlorophenanthrene, on the other hand, can be visualised in four, or possibly five, ways: An intermediate of the type is followed either by cis-addition, or by the breaking of the interhalogen bond to give a carbonium ion which, in turn, can lead to trans-addition of chloride or acetate, or to proton loss, i.e., substitution. The formation of an unstable cis-acetoxy-chloride which eliminates acetic acid too quickly to be detected, is another possible path.

The cis- and trans-dichlorides and the trans-acetoxy-chloride can be considered as stable intermediates which can be converted to chlorophenanthrene under suitable conditions, providing alternative paths to direct substitution.

The proportion of cis-dichloride produced appears to be less easily affected by the presence of electrolytes, particularly chloride, than the other components. This suggests that the intermediate is common to all reaction products.

This discussion may be summed up as follows:

Olefinic addition was at one time viewed as a one-stage process, and aromatic substitution as an addition to both ends of a Kekule double bond, followed by elimination.
Considerations of chemical behaviour and physical structure have led to the replacement of these descriptions by more sophisticated theories. The results obtained in the present series of investigations indicate that reaction paths corresponding to the earlier views do occur, and that they can be included as special cases in the general theory.
THE KINETICS AND MECHANISMS
OF AROMATIC HALOGEN SUBSTITUTION.
PART XX. ACETOXYCHLORIDE ADDUCTS FROM
THE CHLORINATION OF PHENANTHRENE
IN ACETIC ACID

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The chlorination of phenanthrene by chlorine in acetic acid, or by chlorine acetate in acetic acid, is accompanied by the formation of 9-acetoxy-10-chloro-9,10-dihydrophenanthrene, one of the geometrical isomers of which has been isolated and characterised kinetically and by thin-layer chromatography. It decomposes on heating to acetoxyphenanthrene and chlorophenanthrene. It is considered to be the trans-isomer, from the products of its reaction with silver acetate in acetic acid. The presence also of its geometrical isomer is inferred. The significance of these observations is discussed in relation to the reaction-paths involved in chlorination and to addition-elimination sequences leading to aromatic substitution.

The reaction of chlorine with phenanthrene in acetic acid gives 9-chlorophenanthrene (ca. 34%), and cis- and trans-9,10-dichloro-9,10-dihydrophenanthrene (ca. 42%). It was considered also, from analytical evidence, that acetoxychlorides (ca. 14%) are formed, but these were not isolated or properly characterised, and the remainder of the chlorine consumed in the reaction was not accounted for. In reactions of halogens with olefins or aromatic compounds in acetic acid, the formation of acetoxychloride adducts, followed by elimination of hydrogen chloride, results in the introduction of an acetoxyl substituent:

\[
\begin{align*}
\text{AcO} & \quad \text{Cl} \\
\text{H} & \quad \text{H} \\
\text{Cl} & \quad \text{Cl} \\
\text{OAc} & \quad \text{OAc}
\end{align*}
\]

Various reports of acetoxylations and benzoyloxylations accompanying electrophilic substitution in aromatic systems focus attention on possible routes by which electrophilic acetoxylation can be effected. The above addition-elimination sequence is one such route, and the present work establishes conditions under which such a path accompanies chlorination of phenanthrene.

**Experimental**

Light petroleum had b. p. 40—60°. Some materials and methods have been described,¹² Phenanthr-9-yl methyl ether was prepared by Fieser, Jacobson, and Price's method,² through the reaction of bromine with phenanthrene in methanol containing sodium acetate; it was demethylated with hydrogen bromide to give phenanthr-9-ol, m. p. 153°. We were unsuccessful in obtaining the yields recorded by the original investigators. 9-Acetoxyphenanthrene was prepared by acetylation of phenanthrol with acetic anhydride. After recrystallisation from aqueous ethanol its m. p. was 78°. Its ultraviolet absorption spectrum with maxima at \(\lambda = 3500 \text{ Å} (e, 280), \lambda = 3410 \text{ Å}, \lambda = 3325 \text{ Å} (e, 320), \lambda = 3255 \text{ Å}, \lambda = 3175 \text{ Å}, \lambda = 2970 \text{ Å} (e, 10,000), \lambda = 2850 \text{ Å}, \lambda = 2765 \text{ Å}, \lambda = 2530 \text{ Å} (e, 57,000), \lambda = 2140 \text{ Å} (e, 32,000)
\), shows a marked resemblance to those of the known chlorophenanthrenes. The isomeric 9,10-dichloro-9,10-dihydrophenanthrenes were prepared for reference as before.² When reaction-mixtures containing the cis-isomer are chromatographed on silica gel, this compound is eluted by light petroleum after phenanthrene and 9-chlorophenanthrene. It is destroyed, however, by chromatography on alumina, whereas the trans-isomer is destroyed on silica gel, but can be recovered from alumina.

Thin-layer Chromatography.—Some of the products of chlorination of phenanthrene could be separated by thin-layer chromatography on silica gel ("G," Merck) by Stahl's technique.² For qualitative work the method described by Lees and de Muria,⁶ involving no elaborate apparatus, was adequate. The components could be seen under ultraviolet light (Hanovia
Chromatolite), or detected by spraying with diazotised p-nitroaniline, with silver nitrate sensitised with fluorescein, or with vanillin and sulphuric acid in absolute ethanol followed by heating to 120°. With light petroleum as solvent, chlorophenanthrene, phenanthrene, and dichlorodihydrophenanthrene were separated in that order, while the oxygenated material remained at the origin. With benzene, a component appeared as a characteristic spot (R<sub>p</sub>, 0·7) which appeared light yellow with the silver nitrate–fluorescein reagent; part of this was later identified (see below) as an acetoxychlorodihydrophenanthrene. 9-Acetoxyphenanthrene, (R<sub>p</sub>, 0·6) and phenanthrol (R<sub>p</sub>, 0·3) gave black spots; the latter appeared instantaneously, whereas the former developed slowly.

**trans-9-Acetoxy-10-chloro-9,10-dihydrophenanthrene.— (a) Isolation.** In early experiments, chromatography on silica gel in light petroleum followed by benzene was used to separate the products of chlorination of phenanthrene. A 9-acetoxy-10-chloro-9,10-dihydrophenanthrene was isolated as a tacky syrup, often contaminated with acetoxyphenanthrene. Adducts showing very similar infrared spectra were obtained from chlorinations in which molecular chlorine or hypochlorous acid in 80% acetic acid were used.

Later it was found that a white crystalline adduct with a similar infrared spectrum could be isolated from the reaction mixture by chromatography on suitably deactivated alumina. This method was used for the preparation of material for most of the quantitative work described below.

Chlorine (about 100 millimoles) in glacial acetic acid was added to phenanthrene (25 g.) in glacial acetic acid (total volume about 400 ml.) in the dark. The mixture was left overnight and was then added to ether. The solution was washed with water until the washings gave

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**Infrared absorption bands (cm.⁻¹; range 600—1800 cm.⁻¹) of 9-acetoxy-10-chloro-9,10-dihydrophenanthrene and derived materials.**

<table>
<thead>
<tr>
<th>trans-9-Acetoxy-10-chloro-9,10-dihydrophenanthrene</th>
<th>cis-9-Acetoxy-10-dihydrophenanthrene</th>
<th>trans-9-Acetoxy-10-dihydrophenanthrene</th>
<th>cis-9-Acetoxy-10-hydroxy-9,10-dihydrophenanthrene</th>
<th>9-Acetoxyphenanthrene</th>
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</table>

s = Strong; m = medium; w = weak; sh = shoulder; NJ = Nujol bands.
no turbidity with silver nitrate and were no longer acid to methyl orange. Free chloride was rapidly removed, but a large volume of water was needed to remove the last traces of acetic acid. Ether was removed from the solution containing the organic reaction product by distillation under reduced pressure. The pale yellow oily residue was suspended in a solution of 10% ether in light petroleum and chromatographed on alumina (M. & B. "for chromatography," ca. 500 g.) which had been shaken for 4 hr. with 3% by weight of water. It had been found that the required material was destroyed unless the alumina was sufficiently deactivated by water. The critical concentration of water is reached when, on packing the column, the alumina no longer adheres to the glass. The first 450 ml. of eluate contained chlorophenanthrene and phenanthrene; the following 300 ml. contained trans-dichloride, identified by thin-layer chromatography and by its infrared spectrum. The solvent was changed to 20% ether in light petroleum. No significant amount of adduct was found in the next 850 ml. The acetoxychloro-adduct was eluted in the following 450 ml. The solvent was distilled off under reduced pressure and the white crystalline material was recrystallised by dissolving it in the minimum of ether and adding light petroleum. There was obtained 0.9 g. (yield, 3%), m.p. 101°C (Kofler hot-stage apparatus). Further recrystallisation from ethanol gave a product of m. p. 104°C. (Found: C, 70.0; H, 4.6; Cl, 13.2; O, 11.9. C₁₉H₁₄ClO₂ requires C, 70.5; H, 4.8; Cl, 13.0; O, 11.7%). Its infrared spectrum and those of a number of related compounds are given in the Table. The spectra, which refer to mulls in Nujol, were recorded on a Grubb–Parsons DB1 recording spectrophotometer.

(b) Reaction with alkali. The reaction of 9-acetoxy-10-chloro-9,10-dihydrophenanthrene with alkali could be followed by titration in a mixture of benzene and methanol essentially as described by Yacubik, Safranski, and Mitchell. By using a glass electrode, with a silver electrode as reference, and 0.01N-potassium methoxide in benzene–methanol, two well-separated inflections were obtained for hydrochloric and acetic acid. Direct plots of e.m.f. against volume of added alkali were used; with our set-up the plots had the normal S-shape (cf. ref. 9). The alkali was standardised separately against hydrochloric acid and benzoic acid; slight differences in the normality factors were observed.

It could be shown that, when the liberation of chloride had reached 94%, that of acetic acid had proceeded to no more than 2%. It is therefore possible to measure the rate of dehydrochlorination by estimating the chloride liberated, without reference to the hydrolysis of the acetate group.

In a kinetic experiment at 0°C, the material obtained by chromatography on alumina (0.2737 g., 0.993 mM) was dissolved in ethanol (96%) and made up to 100 ml. Aliquot portions (10 ml.) of this solution were mixed with 10 ml. of 0.0378N-potassium hydroxide in ethanol (96%), and the chloride liberated was determined, as follows:

<table>
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<tr>
<th>Time (min.)</th>
<th>3</th>
<th>6</th>
<th>9</th>
<th>12</th>
<th>24</th>
<th>48</th>
<th>72</th>
<th>96</th>
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<tr>
<td>HCl liberated (ml. 0.01M KOH)</td>
<td>1.41</td>
<td>2.26</td>
<td>3.12</td>
<td>3.87</td>
<td>5.82</td>
<td>7.66</td>
<td>8.63</td>
<td>9.93</td>
</tr>
<tr>
<td>k₄ (l. mole⁻¹ min⁻¹)</td>
<td>2.87</td>
<td>2.69</td>
<td>2.66</td>
<td>2.64</td>
<td>2.45</td>
<td>2.31</td>
<td>2.77</td>
<td>—</td>
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</table>

By using samples of the syrup isolated by chromatography on silica gel, it was shown that liberation of chloride by alkali at 0°C, as determined by titration against silver nitrate, has a rate coefficient (k₄) decreasing from 3.6 l. mole⁻¹ min⁻¹ (37% reaction) to 2.8 l. mole⁻¹ min⁻¹ (92% reaction). This result suggests that such samples contain a small amount of a more reactive isomer. Further indications in the same direction have also been obtained; thus bulked fractions of the acetoxychloride, separated by relatively large-scale chromatography on silica gel, gave acetoxyphenanthrene and chlorophenanthrene in the ratio of 10:1 on vapour-phase chromatography; if these samples were allowed to stand at room temperature for some weeks, the value fell to ca. 4:1. This result indicates the presence of an isomer which decomposes on heating to give a much greater proportion of acetoxyphenanthrene than is given by the purified material.

(c) Decomposition by heat. A portion of the purified 9-acetoxy-10-chloro-9,10-dihydrophenanthrene was heated (30 min.) under nitrogen in vacuo at 180°C. The products were separated by chromatography on silica gel. Chlorophenanthrene, identified by its characteristic infrared spectrum, and 9-acetoxyphenanthrene, identified by its infrared spectrum and m. p. (78°C) after recrystallisation, were obtained in the ratio 1:2 by weight.

(d) Vapour-phase chromatography. 9-Acetoxyphenanthrene on vapour-phase chromatography under conditions suitable for separating mono- and di-chlorophenanthrenes etc. gave a
peak which fell between these groups of substances. Vapour-phase chromatography of either the crude product of chlorination of phenanthrene or fractions rich in 9-acetoxy-10-chloro-9,10-dihydrophenanthrene gave a peak corresponding with 9-acetoxyphenanthrene. The corresponding material was collected and identified as 9-acetoxyphenanthrene by its m. p. (77—78°) and its ultraviolet spectrum. The purified trans-9-acetoxy-10-chloro-9,10-dihydrophenanthrene under these conditions gave acetoxyphenanthrene and chlorophenanthrene in the ratio 4:1.

(e) Reaction with silver acetate in acetic acid. For characterisation of the products of solvolysis of 9-chloro-10-acetoxy-9,10-dihydrophenanthrene in acetic acid in the presence of silver acetate, we were fortunate to have, through the courtesy of Professor E. E. Turner, a sample of the menthoxyl-acetate of the relevant trans-diol, from which was prepared trans-9,10-diacetoxy-9,10-dihydrophenanthrene; and through the courtesy of Professor E. Boyland, of the cis-diol, from which was prepared cis-9,10-diacetoxy-9,10-dihydrophenanthrene. These compounds could be distinguished clearly by their infrared spectra, which are recorded in the Table.

A number of preliminary experiments were made to establish the best conditions for solvolysis of the acetoxychloro-adduct. In the first of these, by reaction in acetic acid with excess of solid silver acetate at 110°, both cis- and trans-9,10-diacetoxy-9,10-dihydrophenanthrene were detected in the product, but most of the reaction resulted in elimination. More satisfactory results were obtained at low temperature with dissolved silver acetate. The crystalline acetoxychloro-adduct, 0.4364 g. (1.6 millimoles) in dry, purified acetic acid (50 ml.), was added to a saturated solution of silver acetate (400 ml. 0.0056%) and left for 4 days at 30°. The solution was filtered through a weighed sintered glass crucible and the precipitate was washed with glacial acetic acid. The washings were added to the filtrate. The precipitate was then washed with dilute nitric acid, dried at 120°, and weighed; it was silver chloride, (0.2196 g.), equivalent to 0.417 g. (95%) of the adduct used. Acetic acid was evaporated from the filtrate under reduced pressure. The residue was suspended in the minimum amount of light petroleum and chromatographed on a column of 40 g. silica gel (Hopkin and Williams, M.F.C.). After being washed with light petroleum (30 ml.) and a mixture (1:1) of benzene and light petroleum, the solvent was changed to benzene. 9-Acetoxylphenanthrene (0.0598 g.; 16%) was quickly eluted, followed by a yellow band which yielded an unidentified orange solid (0.006 g.). The column was then eluted with ether. The ether eluate contained cis-9-acetoxy-10-hydroxy-9,10-dihydrophenanthrene (0.308 g., 76%), which after recrystallisation from a mixture of ether and light petroleum had m. p. 113° (Found: C, 75.7; H, 5.6; O, 19.0. C_{16}H_{14}O_4 requires C, 75.6; H, 5.6; O, 19.9%). On acetylation it gave cis-9,10-diacetoxy-9,10-dihydrophenanthrene, with infrared spectrum identical with that of authentic material.

A similar experiment was carried out, the acetylation being performed in a solvent containing 1% of water. cis-9-Acetoxyl-10-hydroxy-9,10-dihydrophenanthrene, identified by its infrared spectrum, was obtained from the reaction mixture in 74% yield. Most of the remainder consisted of 9-acetoxyphenanthrene, detected in the eluate by thin-layer chromatography.

The second-order rate-coefficients, $k_a$, for the acetylation of the acetochloride adduct, the cis-dichloride, and the trans-dichloride (0.0023, 0.0027, 0.00255 respectively) with silver acetate (0.0027, 0.0029, 0.00275 respectively) in acetic acid at 30° were 0.40, 0.49, and 0.171. mole^{-1} min^{-1} respectively.

The products of acetylation of the three adducts were compared by thin-layer chromatography on silica gel ("G," Merck) with benzene as solvent and vanillin–sulphuric acid as the spray-reagent. The acetochloride, after treatment with silver acetate in anhydrous acetic acid, evaporation to dryness under reduced pressure, and solution of the organic material in acetone, still contained some unchanged acetochloride, together with 9-acetoxyphenanthrene, phenanthrol, a trace of a 9,10-diacetoxy-9,10-dihydrophenanthrene (the isomers are not separated under these conditions) and 9-acetoxy-10-hydroxy-9,10-dihydrophenanthrene. The 9,10-diacetoxy-9,10-dihydrophenanthrenes, after the same treatment, were substantially unchanged; a trace of 9-acetoxyphenanthrene could be detected in the solution of the cis-, and a trace of the acetohydroxy-compound in that of the trans-isomer.

Analysis by Isotope D ilution.—The method of isotopic dilution was used to determine the amount of the crystalline 9-acetoxy-10-chloro-9,10-dihydrophenanthrene formed in the reaction of phenanthrene with chlorine in acetic acid. The general procedure has been described in earlier Papers. The specific activity of chloride solutions was determined by conversion into silver chloride and reduction in a stream of hydrogen at about 600°. The resulting hydro-
chloric acid was absorbed in water; its specific activity was determined as a ratio of counts per minute to normality, the latter being determined by potentiometric titration with silver nitrate. Appropriate correction was made for background. Solutions of molecular chlorine were converted into chloride with sodium metabisulphite. Phenanthrene (8.8 millimoles) was allowed to react with chlorine ($^{36}$Cl, 2.86 millimoles, specific activity of derived chloride, 8.03 x $10^4$ counts min.$^{-1}$ mole$^{-1}$) in acetic acid (90 ml.). After the reaction was complete, inactive trans-9-acetoxy-10-chloro-9,10-dihydrophenanthrene (0.7637 g., 2.80 millimoles) was added, and the total acetoxychloro-adduct was isolated as described above. The specific activity of the hydrolysate of this product was $1.056 \times 10^4$ counts min.$^{-1}$ mole$^{-1}$, unchanged within experimental error on re-chromatography. From this result it can be calculated that $14.9 \pm 0.3\%$ of the chlorine used in the reaction had been converted into the crystalline trans-9-acetoxy-10-chloro-9,10-dihydrophenanthrene; the limits given are those of statistical probable error of counting.

**Discussion**

*Structure of the Crystalline Acetoxychloride Adduct.*—It is clear that one of the components of the product of chlorination of phenanthrene by chlorine in acetic acid (where the electrophilic reagent is molecular chlorine$^{6,19}$) or by hypochlorous acid in aqueous acetic acid (where the electrophilic reagent is considered$^{14}$ to be chlorine acetate) is 9-acetoxy-10-chloro-9,10-dihydrophenanthrene. Part of this can be purified by chromatography, and when so purified is reasonably stable. It is hydrolysed by alkali very rapidly; second-order rate-coefficient, $k_a = ca. 2.5 \times 10^2$ mole$^{-1}$ min.$^{-1}$ in ethanol at $0^\circ$. This value is less than that for cis-9,10-dichloro-9,10-dihydrophenanthrene ($k_a = ca. 160 \times 10^2$ mole$^{-1}$ min.$^{-1}$ at $0^\circ$ in ethanol), but it is very much greater than that for trans-9,10-dichloro-9,10-dihydrophenanthrene, which reacts at a negligible speed at $0^\circ$ ($k_a = 0.02 \times 10^2$ mole$^{-1}$ min.$^{-1}$ at $58.7^\circ$)$^{2}$.

We have determined the configuration of this adduct by determining the steric course of its reaction with silver acetate in acetic acid. Winstein and his co-workers$^{15,16}$ have shown that trans-1-acetoxy-2-chlorocyclohexane (I) can react with silver acetate in acetic acid at ca. $100^\circ$ in various ways, the most important of which are: (a) in dry acetic acid, with overall retention of configuration, when the product is trans-1,2-diacetoxy-2-hydroxycyclohexane (IV); (b) in acetic acid containing a little water, with overall inversion of configuration, when the product is cis-1-acetoxy-2-hydroxycyclohexane (V). It was made probable that the ortho-ester (VI) is an intermediate, and its various alternative reactions were established; for example, when the solvolyses leading to (VI) are carried out in the absence of a base, a path from (VI) to cis-diacetoxy-cyclohexane is apparently available.

The essential feature of these reaction-sequences (Scheme I) depends on the possibility...
of internal nucleophilic displacement (neighbouring-group participation) by the acetoxy-
group, which must be trans to the leaving chlorine. The cis-isomer reacts more slowly, to
give predominantly products of elimination.

The conditions adopted in our experiments on 9-acetoxy-10-chloro-9,10-dihydrophen-
anthrene involved the use of much more dilute solutions than those available to Winstein
and his co-workers for the acetoxychlorocyclohexanes; for our reactions were much more
rapid, proceeding smoothly at 30°. The greater reactivity of our system is to be expected,
since the aryl group will stabilise the development of carbonium ionic character on the
carbon atom from which the chlorine atom is heterolysed. The driving force for elimination
must, however, be much increased also; not only because the adjacent electron-withdrawing
aryl groups facilitate proton-loss, but also because of the aromatic stability gained by
forming the phenanthrene system.

All our solvolyses were catalysed by silver acetate, and so (since silver chloride is
precipitated during the reaction and hence silver acetate is removed) gave satisfactory
second-order rate-coefficients. The reactions of cis- and of trans-9,10-dichloro-9,10-di-
hydrophenanthrene gave almost entirely products of elimination. The more rapid reaction
of the cis-isomer may involve synchronous removal of hydrogen and chlorine, but this is
unlikely for the trans-isomer. Displacement processes are negligible under these conditions
for the dichlorides.

By contrast, the reaction of 9-acetoxy-10-chloro-9,10-dihydrophenanthrene gives mainly
the product of displacement, and so this type of reaction must be considerably faster
for the acetoxychloride than for the dichlorides. Consideration of the effect expected for
chlorine and acetoxy on displacement of chlorine in the absence of neighbouring-group
participation suggests that these two groups should have qualitatively similar effects;
their inductive influences, as measured for example by the dissociation constants of
substituted benzoic acids (\(\sigma_m = 0.37\) and 0.39, respectively)\(^{17}\) are nearly the same. The
reactivity of 9-acetoxy-10-chloro-9,10-dihydrophenanthrene, therefore, requires for its
interpretation the postulate that the neighbouring acetoxy group is participating in the rate-
determining stage of the solvolysis. This can happen only if the acetoxy group is trans
to the departing chlorine (VII; Scheme 2).

This conclusion is supported by the nature of the products isolated from the solvolysis.
Under our conditions we obtained evidence for reaction to form diacetates (cf. path (a),
Scheme 1) only under forcing conditions similar to those adopted by Winstein and his
co-workers.\(^{15}\) Under the conditions of the kinetic experiments, the hydroxyacetate (X;
Scheme 2), was isolated in ca. 70% yield. In the experiment without deliberately added
water, it is possible that the ortho-ester (IX) was formed, and that the final product was
obtained only by decomposition of this when water was added in working up the reaction
mixture. The overall steric course of the reaction and the yield of the cis-hydroxyacetate
were not significantly altered by carrying out the reaction in the presence of deliberately
added water. The only other substantial component of the reaction-product was 9-acetoxy-
phenanthrene (XI), obtained no doubt by dehydrochlorination catalysed by silver acetate.

It was shown in independent experiments that the 9,10-diacetoxy-9,10-dihydrophen-
anthrenes were essentially stable under the conditions used for the acetolyses.\(^*\) The
only reasonable interpretation of the course of acetolysis of our acetoxychloride, therefore,
is that it is the trans-isomer (VII), which on solvolysis in acetic acid containing silver acetate
forms a cyclic intermediate (VIII) which ring-opens with water to give cis-9-acetoxy-
10-hydroxy-9,10-dihydrophenanthrene (X); inversion of configuration is therefore the
overall result.

Intermediates in the Electrophilic Chlorination of Phenanthrene.—In an earlier Paper\(^2\) we
reported from analytical data that chlorination of phenanthrene in acetic acid gives 14%
of an acetoxychloride. Analysis by isotopic dilution has now shown that 15% of *trans-*9-acetoxy-10-chloro-9,10-dihydrophenanthrene is formed; a substantial part of this can be isolated by careful chromatography of the product of reaction. The implication that the acetoxychloride adduct produced in the chlorination is wholly of the *trans*-configuration is not, however, certain. We believe that up to about 5% of the *cis*-isomer may also be formed, but if it is formed, that it is too labile for isolation by our methods. Our reasons are indicated in the experimental section; further work is in progress, and will be reported later, on the effects of added electrolytes on the proportions of the various components of the reaction mixtures, and these should help to throw further light on this problem. One important point that seems quite clearly established, however, is that the main acetoxychloride produced in chlorination in acetic acid contains a considerable excess of the *trans*-isomer. This is, of course, the stereochemistry expected for a two-stage addition in which the entering electrophilic chlorine protects the adjacent carbonium ionic centre from attack by the nucleophile on the same side of the double bond; the result, however, is in very marked contrast with that for the concomitant

Scheme 2. Some reactions of 9-acetoxy-10-chloro-9,10-dihydrophenanthrene.

Scheme 3. Possible reaction path in the chlorination of phenanthrene.
addition of chlorine, for which the cis-isomer predominates. The results are consistent with the view that the formation of the cis-dichloride is determined at an early stage in the reaction path, perhaps through the intermediate (XIV), whereas the trans-adducts are derived at a later stage, perhaps through a different intermediate (e.g., XV).

Pyrolysis of trans-9-Acetoxy-10-chloro-9,10-dihydrophenanthrene.—The thermal, gaseous, unimolecular decompositions of acetates are usually faster than those of chlorides. In the present system, however, hydrogen chloride is lost more readily than acetic acid, since acetoxyphenanthrene predominates over chlorophenanthrene in the product of pyrolysis. These reactions must both be cis-eliminations; it may be that the four-centre transition state for loss of hydrogen chloride is favoured by considerations of entropy over the six-centre transition state for loss of acetic acid.

It seems that the corresponding cis-isomer, with hydrogen atoms trans to both the chlorine and the acetoxyl substituent, gives an even greater proportion of 9-acetoxyphenanthrene on pyrolysis; since the oily acetoxychloride adduct isolated in early experiments almost certainly contained this isomer, and gave on pyrolysis acetoxyphenanthrene and chlorophenanthrene in a ratio greater than 10:1. The cis-isomer seemed also to be the more labile to acid-catalysed hydrolysis, probably giving first 9-chloro-10-hydroxy-9,10-di­hydrophenanthrene, which rapidly loses hydrogen chloride and gives phenanthrol.

Addition-elimination Sequences Associated with Electrophilic Attack on Aromatic Compounds.—The present experiments establish the importance, for chlorination of phenanthrene in acetic acid, of a reaction path of the addition-elimination type (eqn. 1), the adducts in this case being in part unstable even under the most cautious working-up procedures that we have been able to employ, and in part stable to these conditions, though unstable to heat. The amount of product appearing from this route depends critically on the method of working-up; from the results of vapour-phase chromatography, for example, one would deduce that about 20% of acetoxylation accompanies chlorination of phenanthrene in acetic acid.

Rates and products of electrophilic aromatic substitutions are commonly discussed in terms of intermediates (e.g., XVI) formed by attachment of an electrophil (E) to the aromatic system with consequent development of a carbonium-ionic centre. The substitution is then completed by proton-loss, and various degrees or types of bonding between the electrophil and the aromatic nucleus can be envisaged. Even this simple mechanism can lead to considerable complexities in the reaction path. Theoretical discussions often neglect the function of the associated nucleophil, probably because this usually, though not invariably, does not participate in the removal of the proton. There are various other ways, however, in which the nucleophil can play a vital role in the reaction. Elsewhere we have emphasised that the formation of intermediates with structures such as (XVII) may have important consequences in determining, inter alia, the response of the system to change in structure. Proton-loss from other parts of the molecule may lead to complicated reaction-sequences involving double-bond migrations.

The present work illustrates some further aspects of a third role of the nucleophil, whether derived directly from the reagent or from the environment; if, in competition with any of the processes already mentioned, it can complete addition to the aromatic system by combining with the developing carbonium ionic centre. The formation of predominantly cis-dichloride is most easily rationalised in terms of a very specific geometry for the transition state. The formation of acetoxychloride, of which the most
easily isolated component is the *trans*-isomer, comes about through diversion of an inter-
mediate by reaction with the solvent.

The chlorination of phenanthrene to form chlorophenanthrene, therefore, does not
necessarily proceed through an addition–elimination sequence, though it is possible to
choose conditions of working-up which ensure that part is formed in this way. The
accompanying acetoxylations, on the other hand, necessarily must go through such a path.

Corresponding conclusions have been reached for other reactions of phenanthrene with
electrophils. Thus Price has shown that the bromination of phenanthrene does not
necessarily involve 9,10-dibromo-9,10-dihydrophenanthrene; whereas methoxylation of
phenanthrene must involve 9-bromo-10-methoxy-9,10-dibromophenanthrene (XVIII), thus:

\[
\begin{align*}
\text{Br}_2 & \quad \text{MeOH} \quad \text{HBr} \\
\text{H} & \quad \text{H} \quad \text{OMe} \quad \text{OMe}
\end{align*}
\]

(XVIII)

It is difficult to assess from the data available whether the acetoxylations and benzoyl-
oxylations, which have been observed to accompany electrophilic nitrations and halogen-
ations of benzene derivatives could have arisen in a similar way. For derivatives of benzene
it would normally be expected that the cyclohexadienes (e.g., XIX) produced by 1,2-addition
initiated by electrophilic halogen would undergo rapid further reaction at the double bond,
so that addition–elimination sequences give di- or tri-substituted derivatives. This is
the situation for the chlorination of biphenyl; and we have shown recently that tetra-
chloride and acetoxylchloride adducts are formed in the reaction of naphthalene and of
2-methylnaphthalene with chlorine in acetic acid. It is by no means so clear, however,
what would be the situation for a 1,4-adduct (e.g., XX).

\[
\begin{align*}
\text{R} & \quad \text{Br} \\
\text{H} & \quad \text{H} \quad \\
\text{H} & \quad \text{H} \quad \\
\text{X} & \quad \text{X}
\end{align*}
\]

(XIX) (XX)

bonds are isolated and are deactivated by the adjacent substituents. The reversibility of
the whole addition process may for bromine and iodine make the diversion of the reaction
to products of elimination a reaction path more readily available than for chlorination;
1,4-elimination of HBr from such a structure as (XX) might well in some cases compete
with 1,2-elimination of HX from (XIX).

Analyses (C, H, O) are by A. Bernhardt. We thank Mr. R. Mitchell for technical assistance;
the Council of Bedford College for a Postgraduate Fellowship (to R. K.); Messrs. J. Lyons and
Co. for leave of absence (to R. K.); and Imperial Chemical Industries Limited, for a grant for
chemicals. We are greatly indebted to Dr. E. A. Johnson for vapour-phase chromatographic
measurements, and for helpful discussions and comment.

Bedford College, Regents Park, London N.W.1. [Received, January 23rd, 1964.]

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THE KINETICS AND MECHANISMS
OF AROMATIC HALOGEN SUBSTITUTION.
PART XX. ACETOXYCHLORIDE ADDUCTS FROM
THE CHLORINATION OF PHENANTHRENE
IN ACETIC ACID

BY

P. B. D. DE LA MARE
AND
R. KOENIGSBERGER

Preprinted from the
The Kinetics and Mechanisms of Aromatic Halogen Substitution. Part XI. Chlorination of Phenanthrene in Acetic Acid.

By P. B. D. de la Mare, N. V. Klassen, and R. Koenigsberger.

Phenanthrene and chlorine in acetic acid give 9-chlorophenanthrene as the main product of substitution, but the reaction is accompanied by addition which accounts for more than 40% of the chlorine consumed and gives mainly cis-9,10-dichloro-9,10-dihydrophenanthrene, which is much more reactive than the trans-isomer with alkali. About 10% of the reaction gives an acetoxychlorodihydrophenanthrene. No evidence of the participation of homolytic processes was obtained. The results are interpreted as further evidence that intermediates of the type ArHCl, involving halogen with an expanded octet, are important in aromatic substitution.

The discovery that a part of the reaction of chlorine with biphenyl in acetic acid involves addition to the aromatic nucleus led us to consider whether analogous processes would be found for other, chemically related compounds.

Phenanthrene is well known to undergo addition across the 9,10-positions accompanying substitution, and such processes have often been regarded as involving alternative fates of a common intermediate, although for chlorination no detailed study has been made to establish this matter. Sandqvist obtained 9-chlorophenanthrene, m. p. 53°, and a 9,10-dichloro-9,10-dihydrophenanthrene, m. p. 157°, as products of reaction of phenanthrene with one mol. of chlorine. A more detailed study of this reaction comprises the main part of the investigation now reported. A preliminary account has been given elsewhere.

Experimental

Some of the materials and methods have been described in previous Parts of this series. Phenanthrene was purified by treatment with maleic anhydride. 9-Chlorophenanthrene after repeated recrystallisation from aqueous ethanol had m. p. 53—53.5°. Sandqvist had previously reported the preparation of trans-9,10-dichloro-9,10-dihydrophenanthrene, m. p. 156—157°, as a compound of then unknown stereochemistry. We obtained it in very poor yield by treating phenanthrene with chlorine in chloroform. After removal of solvent, the product was dissolved in ethanol, and sodium ethoxide was added until no more was rapidly consumed (lactmoid as indicator). The organic product was precipitated with water, filtered off, and washed several times with light petroleum. It was then recrystallised many times from benzene—light petroleum; the infrared spectrum and chemical behaviour of specimens of m. p. 148° and upwards seemed to be little changed by further purification.

Chlorination in the presence of benzoyl peroxide gave a much purer product. To a solution of phenanthrene (100 g.) and benzoyl peroxide (1 g.) in dry chloroform (200 ml.) was added a slight deficiency of chlorine in chloroform. The solution was left overnight and then shaken with alcoholic sodium ethoxide to remove the cis-isomer. The solution was washed with dilute hydrochloric acid and with water, then passed through an alumina column to remove benzoyl peroxide. Most of the chloroform was removed in vacuo, and a solid product was precipitated from it by adding light petroleum and cooling the mixture to —78°. The sticky precipitate was washed repeatedly with light petroleum, and the residue was recrystallised several times by cooling; to 5°, a solution in chloroform saturated at 30°. The yield was 6.6 g.
The compound decomposes rapidly at or near the m. p. (157°), which was determined by holding the m. p. block at a steady temperature and inserting a freshly filled capillary. Fusion in less than 1 min. was considered genuine.

In the course of some days the compound decomposed at room temperature, but it could be stored for long periods at —80°; on being heated, it gave hydrogen chloride and 9-chlorophenanthrene.

The stereochemistry is indicated by its relatively small reactivity with alkali, and was proved by partial asymmetric decomposition with brucine—Cristol, Stermitz, and Ramey's method. The dichloride (0.39 g.) was heated in ethanol (50 ml.) with brucine (0.32 g., 0.5 equiv.) at 60° for 4 hrs, after which the chloride content of an aliquot part showed that 58% of the dichloride had reacted. The material was dissolved in ether, and brucine was removed by exhaustive extraction with aqueous sulphuric acid. The recovered material, which gave no colour reaction for brucine with concentrated nitric acid, had \( \alpha = -0.45° \) (0.25 g. in 5 ml. of CHCl₃; 1 dm. tube). Repeated washing with light petroleum gave a nearly pure specimen of the dichloride, m. p. 154°, \( \alpha = -1.67° \) (0.076 g. in 0.5 ml. of CHCl₃; 1 dm. tube). This corresponds to a specific rotation of ca. —11°. The recovery of optically active starting material indicates partial asymmetric decomposition of the dichloride, which must therefore be the racemic trans-9,10-dichloro-9,10-dihydrophenanthrene.

With ethanolic sodium hydroxide it gave 9-chlorophenanthrene, m. p. without further purification 47° (0.84 g. from 1 g.; 100% yield), identified also by its infrared spectrum. Its rate of dehydrochlorination with sodium ethoxide in ethanol was studied at 58.7°. The initial concentrations of organic compound and sodium ethoxide were 0.0340M and 0.1040M, respectively; 30 ml. portions were titrated with 0.01N-silver nitrate.

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>0</th>
<th>2</th>
<th>4</th>
<th>7</th>
<th>13</th>
<th>20</th>
<th>∞</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titre (ml.)</td>
<td>1.02</td>
<td>1.88</td>
<td>4.65</td>
<td>8.34</td>
<td>11.43</td>
<td>14.38</td>
<td>16.46</td>
</tr>
<tr>
<td>( k ) (l. mole⁻¹ min.⁻¹)</td>
<td>0.0228</td>
<td>0.0244</td>
<td>0.0238</td>
<td>0.0228</td>
<td>0.0220</td>
<td>—</td>
<td></td>
</tr>
</tbody>
</table>

* No NaOEt added. † These values correct an error in our preliminary communication.

**cis-9,10-Dichloro-9,10-dihydrophenanthrene**—This compound was present in the crude product obtained by treatment of phenanthrene with chlorine in a wide variety of solvents; it could be detected by its very great reactivity with alkali. Reaction in acetic acid gave material which was shaken with light petroleum (b. p. 40—60°); the compound began to separate and, when recrystallised from benzene-light petroleum, had m. p. 101° (Found: C, 67.9; H, 3.8; Cl, 28.5. C_{14}H_{10}Cl₂ requires C, 67.5; H, 4.0; Cl, 28.5%). Treatment of this material (0.16 g.) with brucine (0.12 g., 0.5 equiv.) in ethanol (50 ml.) for 19 hrs at room temperature (50° reaction) gave an organic product which within experimental error was optically inactive (0.143 g. in 1 ml. of CHCl₃ had a rotation of —0.005°; 1 dm. tube). So this isomer is the internally compensated, (meso-)*cis-9,10-dichloro-9,10-dihydrophenanthrene. Like its isomer, it can be stored at —80° but decomposes slowly at room temperature. It gave 9-chlorophenanthrene in almost quantitative yield when heated or when treated with alcoholic alkali. Its rate of reaction with sodium ethoxide in ethanol was determined. Solutions of *cis*-9,10-dichloro-9,10-dihydrophenanthrene (initially \( 5.00 \times 10^{-5} \)M) and sodium ethoxide (initially 20 \( \times 10^{-3} \)M) were mixed in a 1 cm. silica cell kept (thermostat) at 25°, and readings of the optical density were made at 3000 Å, at which wavelength *cis*-9,10-dichloro-9,10-dihydrophenanthrene has \( \varepsilon = 1600 \), and 9-chlorophenanthrene has \( \varepsilon = 13,960 \). The following are readings of optical density as a function of time, interpolated graphically (initial and final values are calculated from the observed spectra of the two compounds):

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>0</th>
<th>2</th>
<th>4</th>
<th>7</th>
<th>13</th>
<th>20</th>
<th>∞</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optical density</td>
<td>0.081</td>
<td>0.205</td>
<td>0.299</td>
<td>0.397</td>
<td>0.498</td>
<td>0.557</td>
<td>0.707</td>
</tr>
</tbody>
</table>

Values of the integrated second-order velocity-coefficients calculated from these data fall from 560 l. mole⁻¹ min.⁻¹ at the beginning of the reaction to about 540 l. mole⁻¹ min.⁻¹ at 50% reaction. The main features of the infrared and ultraviolet spectra of these substances are recorded below.

**Products of Reaction of Phenanthrene with Chlorine in Acetic Acid at 25°**—(i) **Hydrogen chloride.** After completion of the reaction, hydrogen chloride was determined in reaction mixtures by potentiometric titration with silver nitrate. End-points were stable and were not interfered with by other products. Great care was taken to avoid loss of hydrogen chloride by volatilis-
ation when the sealed vessels were opened. Initial concentrations of chlorine were determined by control measurements. The following are the results:

<table>
<thead>
<tr>
<th>Init. ArH</th>
<th>Init. Cl₂</th>
<th>Conditions</th>
<th>HCl produced</th>
<th>Init. ArH</th>
<th>Init. Cl₂</th>
<th>Conditions</th>
<th>HCl produced</th>
</tr>
</thead>
<tbody>
<tr>
<td>m</td>
<td>m</td>
<td></td>
<td>Cl₂ used up</td>
<td>m</td>
<td>m</td>
<td></td>
<td>Cl₂ used up</td>
</tr>
<tr>
<td>0-075</td>
<td>0-015</td>
<td>AcOH, 25°</td>
<td>0-59</td>
<td>0-10</td>
<td>0-01</td>
<td>AcOH, 35°</td>
<td>0-59</td>
</tr>
<tr>
<td>0-029</td>
<td>0-006</td>
<td>..</td>
<td>0-57</td>
<td>0-10</td>
<td>0-01</td>
<td>..</td>
<td>0-59</td>
</tr>
<tr>
<td>0-057</td>
<td>0-006</td>
<td>..</td>
<td>0-58</td>
<td>0-07</td>
<td>0-04</td>
<td>..</td>
<td>0-58</td>
</tr>
<tr>
<td>0-10</td>
<td>0-01</td>
<td>..</td>
<td>0-68</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(ii) 9-Chlorophenanthrene. 9-Chlorophenanthrene was determined directly in the reaction mixture by the method of isotopic dilution. To a mixture which contained initially 4-50 millimoles of phenanthrene and in which, by titration, it was established that 0-416 millimole of ³⁵Cl-labelled chlorine had been consumed, inactive 9-chlorophenanthrene (16-68 millimoles) was added. The mixture was then worked up quickly at as low a temperature as possible to avoid decomposition of the dichloride adducts. The molar radioactivity of the diluted 9-chlorophenanthrene after recrystallisation to constant radioactivity showed that 0-1438 millimole of 9-chlorophenanthrene had been produced. On this basis, 0-345 mole of 9-chlorophenanthrene is formed from each mole of chlorine. Repetition gave 0-334 mole.

In a separate experiment, in which 0-414 millimole of ³⁵Cl-labelled chlorine were used up in reaction with a similar excess of phenanthrene, and the reaction mixture was diluted with 11-59 millimoles of inactive 9-chlorophenanthrene, the bulked diluted organic products were refluxed with an excess of ethanolic alkali for 6 hr. The recovered 9-chlorophenanthrene, now derived in part from the dichloride adducts, had after purification radioactivity corresponding with the formation of 0-3229 millimole (i.e., of 0-78 mole from each mole of chlorine).

(iii) Acetoxy-chloride adducts. The crude product of reaction between chlorine and phenanthrene in acetic acid, isolated by ether extraction and carefully freed from acetic acid, contained oxygen [determined by direct analysis (by A. Bernhardt)] and had a strong infrared absorption band at 1745 cm⁻¹ together with an even stronger band with a main component at 1221 cm⁻¹ and shoulders at ca. 1235 and 1205 cm⁻¹. None of these bands appeared in the spectra of the starting material or the other known products; all are characteristic of acetates, and the group of bands in the region of 1220 cm⁻¹ appears to be characteristic of acetates in which the acetoxyl group is not restricted sterically to a single conformation about the C-O bond.

Acetoxy-chloride adducts can be formed by such a reaction as:

\[
\begin{align*}
\text{AcO} & + \text{HCl} \\
\text{Cl} & + \\
\text{HOAc} & \\
\text{Cl} & + \\
\text{HCl} & \\
\end{align*}
\]

Treatment of such adducts with alkali should give acetic acid, hydrogen chloride, and phenanthroly, thus:

\[
\begin{align*}
\text{AcO} & + 2\text{NaOH} \\
\text{HCl} & + \text{NaCl} + \text{NaOAc} + \text{H}_2\text{O} \\
\end{align*}
\]

Accordingly, the organic product of the reaction of phenanthrene (5 millimoles) with chlorine (2-32 millimoles) in acetic acid (50 ml.) was isolated quantitatively, acetic acid was removed by washing the ether solution with aqueous sodium hydrogen carbonate, and 10 ml. were treated with 10 ml. of 0-0435M-potassium ethoxide in 96% ethanol under reflux for 3 hr. After reaction was complete, aliquot parts were titrated potentiometrically (a) with 0-0151N-barium hydroxide, after addition of a known excess of 0-02M-hydrogen chloride, in a current of nitrogen; and (b) with silver nitrate. Both these volumetric solutions were standardised against the same standard 0-02M-hydrogen chloride. The results showed that the product liberated 1-62 millimoles (69-8%) of total acid (assumed to be a mixture of hydrogen chloride and acetic acid, as was consistent with the shape of the titration curve) and 1-31 millimoles (56-5%) of
chloride ions. 9-Chlorophenanthrene does not liberate chloride under these conditions. From the difference between the results it can be estimated that 0.31 millimole of acetic acid was liberated from the product by alkali; and hence, if a monoacetoxy-monochloride adduct is the main material responsible for the liberation of acetic acid from the product, that 13.4% of chlorine are used up in the reaction to form acetoxychlorodihydrophenanthrene.

The chloride content of the aqueous extract of the reaction mixture was determined by potentiometric titration of an aliquot part against silver nitrate and found to be equivalent to 1.35 millimoles (58.2%). The sum of this figure and the chloride liberated from the reaction product with alkali (1.31 + 1.35 = 2.66 millimoles) exceeds the total chloride (2.32 millimoles) by 0.34 millimole (14.7%). This value ought also to represent an estimate of the amount of acetoxy-chloride adduct calculated as acetoxychlorodihydrophenanthrene. The mean of the two estimates (14%) is used in the following discussion.

The acetoxy-chloride adducts are difficult to isolate in a pure state, as they, like the dichloride adducts, tend to decompose on such chromatographic columns as we have tried.

(iv) Materials dehydrochlorinated by alkali. The organic products were carefully freed from hydrogen chloride and acetic acid by washing them in ether solution with aqueous sodium hydrogen carbonate and with water. The residue contained (a) material which reacted completely with an excess of alcoholic sodium ethoxide in 10 min. at room temperature, and (b) material which reacted much more slowly with alcoholic sodium ethoxide but could be destroyed completely by boiling alcoholic sodium ethoxide in 3 hr. The ratio of rapidly reacting to slowly reacting material, determined by back-titration with acid to the end-point of Bromocresol Green-Methyl Red, was 3:9.

Infrared Spectra. These were recorded for Nujol mulls by using a Grubb-Parsons double-beam spectrophotometer. Some of the results are tabulated.

Ultraviolet Spectra. These were determined by using a Unicam S.P. 500 spectrophotometer, 95% ethanol being used as solvent. The spectra of the 9,10-dichloro-9,10-dihydrophenanthrenes are similar in general features to the spectrum of 9,10-dihydrophenanthrene. The broad absorption band in the region 2700 Å is somewhat reduced in intensity (particularly for the trans-compound) and shifted to longer wavelengths. The subsidiary absorption in the region of 3000 Å is reduced in intensity (particularly for the cis-compound) and hence is not clearly resolved. No significant absorption was detected in the region 3250—3500 Å, where

Infrared absorption bands (cm⁻¹) of phenanthrene and some of its derivatives (range, 650—1350 cm⁻¹).

<table>
<thead>
<tr>
<th>Phenanthrene</th>
<th>9-Chlorophenanthrene</th>
<th>9,10-Dichlorophenanthrene</th>
<th>cis-9,10-Dichloro-9,10-dihydrophenanthrene</th>
<th>trans-9,10-Dichloro-9,10-dihydrophenanthrene</th>
</tr>
</thead>
<tbody>
<tr>
<td>713m</td>
<td>722s</td>
<td>719m</td>
<td>690m</td>
<td>704w</td>
</tr>
<tr>
<td>733s</td>
<td>744s</td>
<td>753m</td>
<td>712w</td>
<td>717w,sh</td>
</tr>
<tr>
<td>810s</td>
<td>846w</td>
<td></td>
<td>740m</td>
<td>732s</td>
</tr>
<tr>
<td>861m</td>
<td>858w</td>
<td></td>
<td>759s</td>
<td>766m</td>
</tr>
<tr>
<td>871m</td>
<td>879m</td>
<td></td>
<td>800m</td>
<td>774w</td>
</tr>
<tr>
<td>946m</td>
<td>953m</td>
<td></td>
<td>840m</td>
<td>790w</td>
</tr>
<tr>
<td>971w</td>
<td>941w</td>
<td></td>
<td>870sh</td>
<td>855w</td>
</tr>
<tr>
<td>1000w</td>
<td>951w</td>
<td></td>
<td>874m</td>
<td></td>
</tr>
<tr>
<td>1030w</td>
<td>973w</td>
<td></td>
<td>941w</td>
<td></td>
</tr>
<tr>
<td>1080w</td>
<td>1042w</td>
<td></td>
<td>973w</td>
<td></td>
</tr>
<tr>
<td>1138w</td>
<td>1026w</td>
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<td>1031w</td>
<td></td>
</tr>
<tr>
<td>1147w</td>
<td>1045w</td>
<td></td>
<td>1053w</td>
<td></td>
</tr>
<tr>
<td>1196w</td>
<td>1143w</td>
<td></td>
<td>1125w</td>
<td></td>
</tr>
<tr>
<td>1242m</td>
<td>1126w</td>
<td></td>
<td>1126w</td>
<td></td>
</tr>
<tr>
<td>1290m</td>
<td>1205w</td>
<td></td>
<td>1176w</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1242w</td>
<td></td>
<td>1186m</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1290w</td>
<td></td>
<td>1219w</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1292w</td>
<td></td>
<td>1250w</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1305w</td>
<td></td>
<td>1287w</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1312w</td>
<td></td>
<td>1305w</td>
<td></td>
</tr>
</tbody>
</table>
phenanthrene, 9-chlorophenanthrene, and related compounds have a marked series of weak bands.

Values of the extinction coefficients at maxima and minima according to our measurements are as follows:

\[
\begin{align*}
\text{9,10-Dihydrophenanthrene, } & \varepsilon_{\text{min}} = 5000; \varepsilon_{\text{max}} = 19,300; \varepsilon_{\text{min}} = 4800; \varepsilon_{\text{max}} = 5050. \\
\text{cis-9,10-Dichloro-9,10-dihydrophenanthrene, } & \varepsilon_{\text{min}} = 5200; \varepsilon_{\text{max}} = 16,000. \\
\text{trans-9,10-Dichloro-9,10-dihydrophenanthrene, } & \varepsilon_{\text{min}} = 4350; \varepsilon_{\text{max}} = 12,850. \\
\text{9-Chlorophenanthrene, } & \varepsilon_{\text{min}} = 10,400; \varepsilon_{\text{max}} = 61,200; \varepsilon_{\text{min}} = 8850; \varepsilon_{\text{max}} = 11,200. \\
\end{align*}
\]

Rates of Reaction with Chlorine—These were measured in acetic acid (m. p. 16-55°) essentially by conventional methods. Precautions were taken to avoid loss of chlorine by volatility. For phenanthrene, the rate observed \(k_2 = 0.24 \text{ l. mole}^{-1} \text{ min}^{-1}\) at 25° for ca. 0.04M-ArH and ca. 0.01m-CI₂) is in good agreement with that recorded by Mason, but in poor agreement with the measurements recorded by Dewar and Mole. We believe that the present value is substantially correct; and we obtained the same value within experimental error when the reaction mixture was illuminated and when the solutions were previously saturated and the vessels flushed either with nitrogen or with oxygen.

9-Chlorophenanthrene, as expected, reacted much more slowly \(k_2 = 0.24 \text{ l. mole}^{-1} \text{ min}^{-1}\) at 25° for ca. 0.04M-ArH, and ca. 0.01m-CI₂). The isomeric 9,10-dichloro-9,10-dihydrophenanthrenes reacted still more slowly (cis-isomer, \(k_2 = 0.0015 \text{ l. mole}^{-1} \text{ min}^{-1}\); trans-isomer, \(k_2 = 0.0009 \text{ l. mole}^{-1} \text{ min}^{-1}\); both at 25°). These two reactions were followed for several days and ca. 10% reaction. So, in the time necessary for the reaction of phenanthrene and isolation of the product therefrom, these isomers do not decompose significantly to 9-chlorophenanthrene, which is more reactive than either by a factor of more than 100. This establishes that in the rapid reaction of phenanthrene in acetic acid no significant amount of 9-chlorophenanthrene is formed from either of the isomeric 9,10-dichloro-9,10-dihydrophenanthrenes.

**Discussion**

Detailed Course of the Reaction.—Cristol, Stermitz, and Ramey \(^8\) found that acenaphthylene with chlorine in a non-polar solvent (where the trans-adduct was expected) gave cis-dichloroacenaphthene, whereas with benzene iodochloride (where the cis-adduct was expected) trans-dichloroacenaphthene was obtained. They proved unambiguously the structures of their adducts and commented on the mechanistic implications. The present results for phenanthrene are clearly related to Cristol, Stermitz, and Ramey's findings. For reaction with chlorine in acetic acid in the absence of electrolytes, our results can be summarised by the annexed scheme.

Neither cis- nor trans-9,10-dichloro-9,10-dihydrophenanthrene decomposes to give significant amounts of 9-chlorophenanthrene under the conditions of the reaction or the working up of the products. Formally, all the indicated products can be considered to be derived from a common carbonium ionic intermediate, (I).
Since, in the presence of added chloride ions, no less hydrogen chloride is produced than in its absence, a scheme involving only the carbonium ionic intermediate cannot adequately represent the reaction.

\[
\text{[Diagram of reaction involving carbonium ion and chloride ion]}\]

It is suggested, therefore, that the observations require a more elaborate scheme; the one which we favour is that involving reactions (A)—(D).

Route B is considered to give mainly the cis-isomer; it is suggested that it involves partial ionisation of chloride ion, through a transition state which in this solvent resembles an ion-pair, followed [as an alternative to loss of chloride ion giving the carbonium ion, (I)] by the internal capture of chloride ion to give mainly the cis-product.

Analogy may be drawn between the reaction of the neutral intermediate (II) to give alternatively the cation (I) or the adducts (III, IV), and the reaction of 1,1-dimethylallyl chloride to give products either of solvolysis or of rearrangement.¹⁴

Those who believe that an ion-pair (V) is involved as an intermediate in the true sense (i.e., a minimum which is actually reached by the reacting system in the potential energy surface) in the rearrangement and solvolysis of 1,1-dimethylallyl chloride should be as easily convinced that such an intermediate is the initial product of reaction of the neutral intermediate (II).

The cationic intermediate (I) would be expected by analogy with aliphatic systems¹⁵ to give mainly the trans-isomer. In fact, the main products of addition are materials...
that react rapidly with alkali and must therefore have been formed by cis-addition (see below). Kinetic analysis of the reaction mixture is complicated by the fact that it seems that cis- and trans-isomers both of the dichloride adducts and of the acetoxy-chloride adducts are present. According to our analysis, the extreme assumption being made that all the acetoxy-chloride adduct might be cis-, not more than 11% of trans-dichloride, and hence not less than 31% of cis-dichloride, are produced in the reaction. Investigations leading to further details of the cis-trans ratio are in progress.

Route C, leading to acetoxy-chloride adducts, has not been elucidated in detail; it is possible that chloroacetates and dichlorides are in part produced also from the cationic intermediate (I; route D). It is intended to study in more detail the formation of acetoxy-chlorides as a function of the environment, but our analyses suggest that both cis- and trans-acetoxy-chlorides are formed.

P. W. Robertson and his co-workers first emphasised that intermediates, 
\[
\text{Ar-Hal}^+X, \text{involving expanded octets of halogen, were helpful in rationalising kinetic features of the halogénation of aromatic compounds. In the course of the present series, and elsewhere,}^{11,16} \text{the possible role of such intermediates in determining relative reactivities has been pointed out, and their probable importance in determining the relative effectiveness of reagents Cl-X has been discussed.}^{18} \text{The present results suggest that the products and stereochemistry of the addition which accompanies substitutions are also in part determined by their intervention in the complicated sequences involved in reaction.}
\]

Elsewhere we have stressed the structural analogy between the complexes, \[\text{Ar-H-Cl-X} \] (e.g., III), which we regard as concerned in these additions, and the trihalide ions (Cl-Cl-Cl)\). In such complexes the central halogen bears 5 electron-pairs (hybridisation \(sp^3d\)), which are disposed at the corners of a trigonal bipyramid.\(^{19}\) The favoured arrangement of the bonded groups in the trihalide ion places these so that the complex is linear. The alternative arrangements, with the Cl-Cl bond at right angles or at 120° to the Ar-Cl bond, illustrated in structure (VI) need, however, to be considered for the neutral complexes if our interpretation of cis-addition is correct. It seems likely that these particular electronic arrangements would not be very much less satisfactory than the linear alternative.

**Orientation and Reactivity.**—In the present investigation we have identified positively the conversion of 76% of the reacting chlorine into 9-chlorophenanthrene and 9,10-dichloro-9,10-dihydrophenanthrenes; and of 14% into material in which no chlorine remains in the organic nucleus after treatment of the product with alkali, i.e., into acetoxy-chloride adducts. The amount of other nuclear-substituted phenanthrenes which can have been formed may be as large as 10%, though this figure is subject to the combined uncertainties of isotope-dilution and acetoxyl determination, and could possibly be in error by two or three units %. The conclusion that such isomers are present is consistent with theoretical calculations.

For nitration, Dewar and his co-workers have recorded the partial rate factors indicated in the formula (VII). In this, the italicised numbers are reactivity numbers, \(N_x\), which should, according to simple theory, be related to the partial rate factors through the equation:

\[
\log_{10} f_x = \text{Const.} (N_0 - N_x) \quad (3)
\]
where $N_q$ is the reactivity number (2.31) for benzene. If we assume that the proportionality constant can be obtained from the partial rate factor for the most reactive position, this theory predicts the partial rate factors for nitration given in parentheses; they accord only qualitatively with the experimentally observed values. It has been suggested \(^{21}\) that the discrepancies arise in part because 1-, 4-, and 9-positions are partly sterically hindered for electrophilic substitution, but analysis of the non-bonded repulsions which might be concerned hardly supports this contention.\(^{3}\)

A similar analysis can be carried out in part for the chlorination of phenanthrene, by using the rate-ratio, phenanthrene : benzene = 1.02 x 10\(^6\), established in the present series of investigations.\(^{6}\) This value accords reasonably with an earlier estimate\(^{3}\) from the best literature values. If the whole of the observed relative rate of reaction is divided between the various positions according to equation (3), then attack at the 9- and the 1-position should occur in the ratio 84 : 15; less than 1% of reaction should occur at the other nuclear positions. According to this calculation, therefore, up to 15% of 1-chlorophenanthrene might be formed in the chlorination. If the discrepancy between found and calculated values were in the same direction as for nitration, then still more of the 1-chloro-isomer should be present.

The dichloride adducts seem to be derived almost entirely from 9,10-addition, since the amount estimated by converting them into 9-chlorophenanthrene (44%) is the same within

$$\text{(VIII)} \quad \begin{array}{c}
\text{H} \\
\text{Cl} \\
\text{Cl}
\end{array} \\
\text{Cl} \quad \text{H} \\
\text{Cl} \\
\text{Cl}
$$

$$\text{(IX)} \quad \begin{array}{c}
\text{H} \\
\text{Cl} \\
\text{Cl}
\end{array} \\
\text{Cl} \quad \text{H} \\
\text{Cl} \\
\text{Cl}
$$

experimental error as that (42%) derived from the ratio of hydrogen chloride produced to chlorine consumed. It is possible, however, that the acetoxy-chloride adducts are not produced so exclusively by this mode of addition.

**Chemistry of the 9,10-Dichloro-9,10-dihydrophenanthrenes.**—Both isomers of this compound undergo elimination to give 9-chlorophenanthrene. The base-catalysed reaction of the cis-isomer (VIII) is undoubtedly a bimolecular (E2) elimination; it is faster than that for cis-dichloroacenaphthene or for any of the isomers of benzene hexachloride.\(^{22}\) Examination of models shows that the dichloride (VIII) can exist in two equivalent nearly strainless conformations with about 20° between the planes of the aryl groups, in each of which one hydrogen is almost exactly conformationally trans to a chlorine atom, as is required for ready bimolecular elimination. This hydrogen atom is relatively accessible; it projects nearly at right angles to a plane drawn to approximate as nearly as possible to that of both rings.

The reactivity of the trans-isomer (IX) seems to be substantially less than that of \(\beta\)-benzene hexachloride,\(^ {22}\) which itself is less than that of trans-dichloroacenaphthene.\(^{8}\) Two nearly strainless conformations are possible for the trans-isomer: in neither has either chlorine atom an available conformationally trans-hydrogen atom.

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