A STUDY OF THE CHLORINATION OF SOME UNSATURATED COMPOUNDS

A THESIS

SUBMITTED FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN THE FACULTY OF SCIENCE OF THE

UNIVERSITY OF LONDON

by

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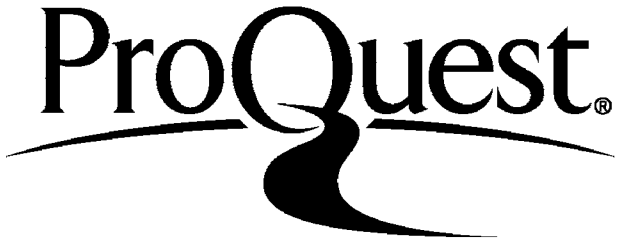
December, 1966



ABSTRACT

The products of chlorination of crotonic acid have been characterised. The reaction has been studied in a number of solvents; the reaction products are in general those expected from a conventional, heterolytic addition mechanism in which chlorine is an electrophile. Strong circumstantial evidence has been found for the formation of α-chloro-β-butyrolactone in many of the chlorination reactions investigated.

The chlorination of crotonaldehyde has also been studied in a number of solvents, and its reaction products have been incompletely identified, due to experimental difficulties. A mechanism of this reaction has been proposed.

The chlorination of phenanthrene has been studied in acetic acid, and the effects of added electrolytes upon the rate and products of the reaction have been investigated. A new adduct, cis-9-acetoxy-10-chloro-dihydrophenanthrene, has been found; to accomodate the formation of this compound, an amended reaction mechanism has been proposed.

ACKNOWLEDGEMENTS

The author wishes to thank Professor P.B.D. de la Mare for his advice and encouragement throughout this work.

The author expresses her thanks to the Department of Scientific and Industrial Research for a maintenance grant from September 1962 until September 1965.

Thanks are also due to Dr. M.D. Johnson, of University College, London, for measuring and interpreting the n.m.r. spectra described in this work, and to Drs. R. Koenigsberger, G. Cum, and J.S. Lomas for many helpful discussions.

The author also wishes to thank Dr. R. Bolton for assistance in the production of this thesis.

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INTRODUCTION

INTRODUCTION

With an increased interest in organic chemistry during the latter half of the 19th century there came a rapid expansion of the knowledge of both the structures and the reactions of many organic compounds. However, since the structural considerations did not go beyond those of the carbon skeleton and the functional groups bonded to it, the knowledge was far from systematic. There were empirical rules, like Markownikoff's, which could predict the products of a reaction but which had no rational explanation.

It became necessary to systematise the description of the behaviour of organic substances as far as possible. The development of the wave-mechanical picture of the atom and of bonds between atoms made it possible to relate behaviour with molecular structure.[1] The description of the reactivities of organic compounds, developed in the main by Lapworth, Robinson, Ingold, and Hughes, has played a large part in modern physical organic chemistry. The concepts of the inductive, conjugative, mesomeric, tautomeric, and hyperconjugative effects as

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1. See, for example, C.K. Ingold, "Structure and Mechanism in Organic Chemistry", Bell, London, 1953.

defined by Ingold play an important part in this electronic theory of organic chemistry.

Reactions of unsaturated compounds

The addition of halogens across double bonds is a reaction which has been known for many years. From experimental observations it was concluded that aromatic compounds and olefinic compounds could be readily distinguished by their invariant substitution and addition reactions respectively.[2]

However, it was soon realised that the generalisation is limited; even benzene itself shows olefinic character in its reaction with ozone or with diazoacetic ester. In particular, the higher condensed hydrocarbons are generally more reactive than their lower homologues and show a greater tendency to form addition compounds. There is considerable evidence, especially in regard to these polyannular hydrocarbons, that some of the bonds in the aromatic system may have "double-bond character". The chemical behaviour of some of the larger aromatic hydrocarbons bears out the theoretical calculations; simple resonance theory treatment, which weights equally the possible Kekule structures of a compound and neglects the higher energy Dewar structures, and the molecular

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2. The addition-elimination mechanism of aromatic substitution has been discredited as a general theory; for a review, see L.F. Fieser, "Organic Chemistry", p. 601 (Heath, Boston, 1950)

orbital treatment, which is more rigorous and detailed, can be used to predict accurately which bonds are most likely to be attacked to form addition compounds. The 9,10-bond of phenanthrene, the 1,2-bond of anthracene, and the 4,5-bond of pyrene are broken by attack of ozone (a reagent which is known to attack olefinic bonds[3]) in agreement with theoretical predictions.[4]

Correspondingly it was found that olefins may undergo substitution rather than addition. While allylic substitution as a result of a free-radical process has been widely known, as in the formation of allyl chloride from the high-temperature chlorination of propylene and the reaction of N-bromosuccinimide with olefins, there is evidence of substitution taking place in heterolytic halogenation reactions.[5]

Classification of reagents

Polar reagents are classified as nucleophiles or electrophiles according to their role in reactions. Nucleophiles include negatively charged ions, molecules possessing atoms with unshared electrons, and molecules containing highly polarised or polarisable bonds:

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3. G.M. Badger, Quart.Revs., 1951, 5, 147.
4. "Chemistry of Carbon Compounds", ed. E.H. Rodd, Amsterdam, Elsevier, Vol. IIIB
5. P.B.D. de la Mare and A. Salama, J.Chem.Soc., 1956, 3337.

e.g. I^-, OH^-, OR^-, CN^-, H_2O, NH_3, $R\text{-}M \leftrightarrow R^-M^+$

If a reagent functions by accepting electrons from carbon in an organic reaction it is said to be an electrophile. Electrophiles can be positively charged ions, molecules containing atoms without full octets (Lewis acids), or molecules with highly polarised or polarisable bonds:

e.g. NO_2^+, H_3O^+, H_4N^+, ROH_2^+, $R_2C{=}\overset{+}{O}H$, BF_3, I_2, $R_2C{=}O \leftrightarrow R_2\overset{+}{C}\text{-}\overset{-}{O}$

Classification of reagents in chlorination

In order to be able to classify a reaction, it is necessary to define arbitrarily which of the participants is the substrate and which the reagent. In organic reactions it is natural to consider an organic molecule as the substrate; hence in halogenation, the halogen molecule is considered to be the reagent.

Electrophilic reagents

The study of mechanisms of electrophilic aromatic substitutions has played a large part in the elucidation of reaction mechanisms, especially the various effects of substituents. De la Mare and Ridd[6] have reviewed the extensive work done on the nitration and halogenation of aromatic compounds. Nitration by nitric acid in

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6. P.B.D. de la Mare and J.H. Ridd, "Aromatic Substitution - Nitration and Halogenation", Butterworths, London, 1959.

various solvents involves the nitronium ion, NO_2^+, and has been reviewed by Hughes.[7] Reagents concerned in halogenation are classified as positively charged or neutral species. The reactions of fluorine are, in general, homolytic and are therefore not relevant here.

Positive halogenating species

The positively charged halogenating species include the free halogenium ions X^+, and their covalently solvated forms involving water (XOH_2^+), a hydroxylic solvent ($XOHMe^+$; $XOHAc^+$), or an amine (XNH_2R^+).

The existence of a free halogenium ion X^+ was first suggested by Noyes and by Stieglitz.[8] Support for the existence of the iodinium ion, I^+, was adduced when Lewis showed that liquid iodine possesses a considerable electric conductance.[9] Such direct evidence however has not been forthcoming for the other halogens. Kinetic evidence points to bromination in aqueous solution involving either Br^+ or $BrOH_2^+$, but cannot distinguish between these possibilities.

De la Mare, Hughes, and Vernon[10] showed that aqueous solutions of hypochlorous acid acidified with

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7. E.D. Hughes, Kekule Symposium, Butterworths, London, 1959.
8. W.A. Noyes, J.Amer.Chem.Soc., 1901, 23, 460; J. Stieglitz, J.Amer.Chem.Soc., 1901, 23, 797.
9. G.N. Lewis, J.Amer.Chem.Soc., 1916, 38, 762.
10. P.B.D. de la Mare, E.D. Hughes, and C.A. Vernon, Research, 1950, 3, 192, 242.

a strong acid (e.g. H_2SO_4, $HClO_4$), but free from elemental chlorine, contains a strong chlorinating agent. The kinetics showed the active chlorinating agent to be Cl^+ or $ClOH_2^+$, since the rate equation was

$$dx/dt = k[ArH][ClOH][H^+].$$

When the reactivity of the aromatic compound was increased, the term [ArH] vanished; i.e.

$$dx/dt = k'[ClOH][H^+],$$

and for suitable chlorinating solutions containing acidified hypochlorous acid the rate of reaction was found to be independent of the nature of the aromatic compound; anisole, p-dimethoxybenzene, and phenol all reacted at the same rate. It was also found that the same chlorinating solution could be used to effect addition reactions with olefins to give chlorohydrins, and that suitably reactive olefins, such as allyl ethyl ether and allyl fluoride, underwent reaction at a common rate independent of the concentration and nature of the olefin. Furthermore, the rate of the additions to the olefins were identical with the rate of the substitution of the aromatic compounds.

These investigations were similar to those made of the kinetics of nitration, and the results are like those

obtained for nitration by the nitronium ion formed from nitric acid in sulphuric acid, water, or nitromethane. The results of de la Mare, Hughes, and Vernon show that the measured rate is that of the splitting of the hypochlorous acidium ion ($ClOH_2^+$) to give the free chlorinium ion, Cl^+. This must be the electrophilic reagent because the protonation of hypochlorous acid should occur too rapidly to measure and could not be the rate-determining stage.

$$ClOH + H_3O^+ \xrightarrow{\text{fast}} ClOH_2^+ + H_2O$$
$$ClOH_2^+ \xrightarrow{\text{slow}} Cl^+ + H_2O$$

With a sufficiently reactive compound, the chlorinium ion is taken up rapidly; so rapidly, in fact, that its production is the rate-determining stage. Hughes, Ingold, and Reed[11] found that the rate of nitration is similarly controlled by the rate of formation of nitronium ions in suitable conditions:

$$HNO_3 + HNO_3 \rightleftharpoons H_2\overset{+}{O}NO_2 + NO_3^-$$
$$H_2\overset{+}{O}NO_2 \rightleftharpoons NO_2^+ + H_2O$$

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11. E.D. Hughes, C.K. Ingold, and R.I. Reed, J.Chem.Soc., 1950, 2400.

Aromatic compounds of considerably lower reactivity, such as the benzylsulphonate ion, are also chlorinated by the chlorinium ion. Because such compounds take up Cl^+ sufficiently slowly that a small stationary concentration can be built up, the term [ArH] appears in the rate equation. This parallels the results obtained for the nitration of suitably less reactive aromatic compounds in organic solvents when nitric acid is in constant excess,[12] where $dx/dt = k[ArH]$.

De la Mare, Hughes, and Vernon have found that the term [ArH] reappears in the rate equation when highly reactive compounds are being chlorinated by acidified hypochlorous acid solutions. This was interpreted to show that such compounds were taking chlorine directly from $ClOH_2^+$; such a situation is found with highly reactive compounds such as isobutylene.

In the case of chlorination by acidified hypochlorous acid, the variation of reaction rate with the solvent composition of aqueous acetic acid solutions follows neither the acidity function J_o (which would indicate Cl^+) nor H_o (which would indicate $ClOH_2^+$). Therefore it has been suggested that the increase in the rate of chlorination

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12. C.K. Ingold, "Structure and Mechanism in Organic Chemistry", p. 276. Bell and Son, London, 1953.

by hypochlorous acid in 50% aqueous acetic acid over that in water indicates the formation of the active species $ClOHAc^+$, although it has not been proved that this is the attacking species.

With molecular chlorine in acetic acid the reagent could be the free cation Cl^+, a solvated derivative of this $ClOHAc^+$ or perhaps a secondary reagent formed by interaction of the halogen with the solvent (e.g. ClOAc), apart from the dipolar molecule Cl-Cl. If the reacting species are postulated as arising from the following reversible reactions:

$$Cl_2 \rightleftharpoons Cl^+ + Cl^-$$

$$HOAc + Cl_2 \rightleftharpoons ClOHAc^+ + Cl^-$$

$$HOAc + Cl_2 \rightleftharpoons ClOAc + H^+ + Cl^-$$

then added salts such as sodium acetate, hydrogen chloride, or sodium chloride would have a profound effect upon the reaction rate. The addition of such compounds has little effect upon the rate of reaction of chlorine with various olefins apart from a normal salt effect. It follows that the electrophile responsible for chlorination in acetic acid solutions must be chlorine itself.

The fact that pyridine and other tertiary amines act as powerful catalysts for chlorination and bromination suggests that ions such as $PyCl^+$ may be effective halogenating agents. Brown and Soper[13] and Carr and England[14] have investigated the kinetics of some chlorinations of phenol, and have shown that cations of the type R_2NHCl^+ derived from diethylchloramine and from morpholine respectively may be effective in attacking the free phenol molecule.

Neutral halogenating agents

The neutral halogenating agents include the molecular halogens and the interhalogens. These generally behave as electrophiles in substitution reactions; electron-donating substituents increase the reactivity and electron-withdrawing substituents decrease the reactivity of the organic compound.

From the absence of retarding effects of chloride ion or of hydrogen chloride in the chlorination of mesitylene, and the positive catalytic effect of hydrogen bromide upon its bromination, Robertson and his co-workers concluded that the molecular halogens are the

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13. L.O. Brown and F.G. Soper, J.Chem.Soc., 1953, 3576.
14. M.D. Carr and B.D. England, Proc.chem.soc., 1958, 350.

effective electrophiles.[15] This confirmed previous conclusions of Bradfield and Orton.[16]

Bromine and iodine differ from chlorine in giving also the kinetic form

$$dx/dt = k_3[ArH][X_2]^2$$

The extra molecule of halogen is believed to assist in breaking the X-X bond in the complex $[ArH,X_2]$ by forming the relatively stable ion X_3^-.[17] Molecular iodine is too inactive to behave as an iodinating agent except for the most reactive substrates (e.g. amines, phenols). In general it is also necessary to remove the hydrogen iodide as it is formed in order to prevent reversibility of the halogenation reaction and to minimise the reaction

$$I_2 + I^- = I_3^-$$

since the equilibrium lies sufficiently far to the right that the stationary concentration of free iodine is small.

Nucleophilic halogenation

Although it has been shown that chlorination generally proceeds through electrophilic attack by the

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15. P.W. Robertson, J.E. Allan, K.N. Haldane, and M.G. Simmers, J.Chem.Soc., 1949, 933.
16. K.J.P. Orton and A.E. Bradfield, J.Chem.Soc., 1927, 986.
17. P.W. Robertson, P.B.D. de la Mare, W.T.G. Johnston, J.Chem.Soc., 1943, 276.

molecular halogen upon the olefins, in some cases chlorine and bromine can act as nucleophiles towards olefins. Ingold and Ingold[18] envisaged that if there were sufficiently powerful electron-withdrawal from the double bond a partial positive charge could arise in the unsaturated system and thus make nucleophilic attack energetically preferred. Nucleophilic attack by chlorine and by bromine was revealed through structural effects and acid catalysis in the reaction with the αβ-unsaturated aldehydes and acids. Although chloride ion is a weak nucleophile, in such a situation the reaction can occur more easily through a nucleophilic rather than an electrophilic attack by a strong electrophile at a centre which has been highly deactivated by electron-withdrawing groups such as -COOH and -CHO. In the case of crotonic and acrylic acids, the rates of addition of chlorine or of bromine are appreciably higher than those of crotonaldehyde and acraldehyde provided that the halogenation of the aldehydes is carried out in the presence of added base.[19] However, in the

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18. C.K. Ingold and E.H. Ingold, J.Chem.Soc., 1931, 2354.
19. P.W. Robertson and P.B.D. de la Mare, J.Chem.Soc., 1945, 888.

absence of base or in the presence of mineral acids both aldehydes add halogen at rates far greater than those of the corresponding acids, and far faster than most other slightly deactivated olefins such as cinnamic acid. The effect is specific to the αβ-unsaturated aldehydes and it has been proposed that there is prior protonation of the aldehyde group and a subsequent nucleophilic attack by chlorine upon the carbonium ion thus formed:

$$CH_2{=}CH.CHO + H^{\oplus} \rightleftharpoons \left[CH_2{=}CH.\overset{+}{C}HOH \;\leftrightarrow\; \overset{+}{C}H_2.CH{=}CH.OH \right] \xrightarrow{Cl_2} \text{Products}$$

The case is well known for bromination but has not been so extensively studied for chlorination.

The catalytic effect of hydrogen chloride and bromide on bromination was unusually great and quite out of proportion to their strengths as acids in acetic acid.[19] It was suggested that co-ordination of the attacking halogen with these anions resulted in the formation of Br_3^- and Br_2Cl^- which act as halogen carriers. Since the stabilities of the corresponding ions Cl_3^- and Cl_2Br^- (Cl-Cl-Br) are far less, because expansion of the octet

of chlorine is not easy, the same effect may not be apparent in the case of the addition of chlorine.

Olefins

Single covalent bonds, σ bonds, consist of shared pairs of electrons with their greatest electron density mainly between one pair of atoms. Double bonds, which consist of two pairs of shared electrons, present a different picture. Besides the σ bond, there is interaction between the p-electrons on adjacent atoms to form a π-bond. The σ bond orbital is in the same plane as the bonds to the other substituents. The π orbitals are situated above and below the plane of the molecule; in particular the π-bond has a node along the internuclear line where the charge of the σ bond is concentrated. Thus the two electron pairs are very unequally placed, the π electrons of the double bond being the more easily detached or excited and the more easily brought into chemical reaction. Overlap of the adjoining π orbitals prevents rotation around the C=C bond, and so affects the stereochemistry of reactions at this centre.

Conjugated olefins

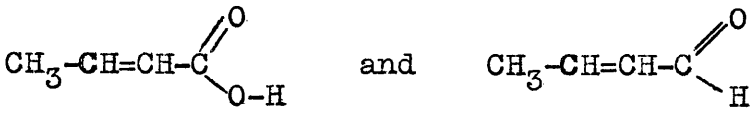
Molecules with double bonds alternating with single bonds belong to a special class. The π electrons of the

double bonds are not strongly localised and will spread themselves as a group over a large section of the molecule. A single structure is not sufficient to describe the molecule completely. For such compounds it is usually necessary to write a number of structures; these structures contribute to the configuration of the molecule in proportion to their stability. Buta-1,3-diene, for example, has the molecular formula C_4H_6; it can be written

$$\underset{(A)}{CH_2{=}CH.CH{=}CH_2} \longleftrightarrow \underset{(B)}{CH_2{=}CH.\overset{+}{C}H{-}\overset{-}{C}H_2} \longleftrightarrow \underset{(C)}{\overset{+}{C}H_2{-}CH{=}CH{-}\overset{-}{C}H_2}$$

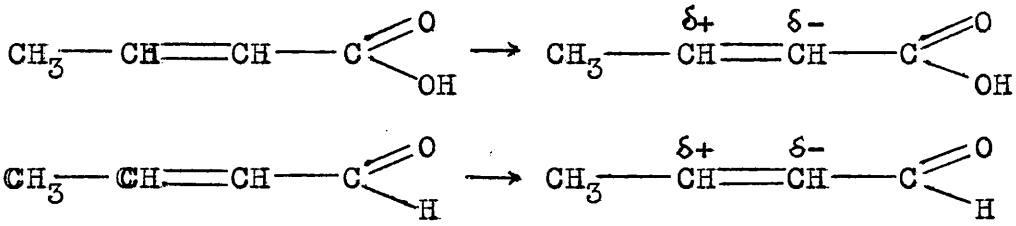
The π electrons of the molecule are partly delocalised over the whole system. This is born out by the lengths of the bonds in the molecule. The double bonds in butadiene (r = 1.37Å) are longer than that in ethylene (1.33Å) whilst the C-C single bonds (r = 1.47Å) are shorter than that in ethane (1.55Å). The conjugation, which makes the delocalisation of electrons possible, reduces the energy of the molecule and increases its thermodynamic stability. Structures such as (C) account for some of the chemical behaviour of buta-1,3-diene which cannot be fully explained if the molecule is represented by structures (A) and (B) only.

Crotonaldehyde and crotonic acid



crotonic acid and crotonaldehyde

Because the electron-withdrawing carbonyl group is conjugated with the double bond, the π electrons of the C=C bond are partially displaced. The positive inductive effect of the methyl group is in the same direction and can therefore help the polarisation of the olefinic bond.



This means that electrophilic attack will take place at the α-carbon atom. However, the electron-withdrawing effect of the carbonyl group is large and the result is that the C=C bond is deactivated towards attack by an electrophile; thus the rates of addition of bromine or chlorine to crotonic acid are vastly less than the rates of the same reactions with propylene.[20]

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20. P.B.D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems" p. 84 (Elsevier, Amsterdam, 1966)

Nucleophilic addition of chlorine and bromine has been observed in conditions where crotonaldehyde and acraldehyde become protonated.[19]

Structure of the aromatic system

Benzene is known to consist of six carbon atoms symmetrically arranged in a flat hexagon, each carbon atom being bonded to one hydrogen atom. The formula C_6H_6, however, suggests unsaturation and instability, whereas in fact aromatic compounds are characterised by thermal stability and the tendency to undergo substitution rather than addition reactions. The Kekule formulation of two 'oscillating' cyclohexatriene structures was one of the more successful early attempts to reconcile the stability of benzene with the formally unsaturated structure. Since then, the flat annular structure of benzene has been proved by X-ray crystallography.[21] Aromaticity has often been associated with a sextet of electrons in a cyclic, formally unsaturated, system; this explained the unusual stabilities of the cyclopentadienyl anion and the tropylium cation. Molecular-orbital and valence-bond treatments explained aromaticity in terms of the delocalisation of π electrons over a flat system.

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21. J.M. Robertson and J.G. White, Proc.Roy.Soc., 1947, A190, 329.

The stability is accounted for by the symmetry of the benzenoid system. In the valence-bond method it was found necessary to consider not only the Kekule structures but also the Dewar structures in defining the mobility of the bonds.

Because substitution reactions cause less reduction in aromatic resonance energy, they are more likely than addition reactions in aromatic systems. The orienting effects of substituents is the result of their electrostatic and conjugative effects upon the distribution of π electrons in the molecule. Substituents will change the electron density at, and therefore the reactivity of, the other carbon atoms in the system.

Condensed aromatic systems

On passing from benzene to naphthalene the molecule, and the π electron cloud, lose much of their symmetry. In general the formation of polyannular compounds by fusion of two or more benzene rings gives compounds which, although still obviously aromatic rather than olefinic, possess more tendency to undergo additions than does benzene itself. As a rule, increased size gives greater reactivity. This is particularly shown in the linearly

fused polyannular hydrocarbons, naphthalene being more stable to addition than anthracene, which readily forms derivatives of 9,10-dihydroanthracene.

This behaviour is also reflected in the resonance energies derived from the heats of hydrogenation. This energy is approximately a measure of the stabilisation that the aromatic compound receives through delocalisation of the π electrons, and represents the difference between the observed heat of hydrogenation and that calculated for a compound corresponding to one of the classical canonical structures. Thus benzene has a resonance energy of 36 kcal.mole^{-1}, but the fusion of another ring does not give rise to a doubling of the resonance energy, and in general the stabilisation energy increases by 20-30 kcal. mole^{-1} for each additional aromatic ring.

The greater reactivities of the higher polyannular aromatics can be explained by these differences in the resonance energies. Benzene has a stabilisation energy of 36 kcal.mole^{-1}, but its 1,2-adduct with one molecular equivalent of chlorine, if it is considered to be analogous to buta-1,3-diene, has a stabilisation energy of only 3 kcal.mole^{-1}. Hence in forming the latter from the former,

some 33 kcal.mole^{-1} of stabilisation is lost. The corresponding process with naphthalene involves a loss of only 23.5 kcal.mole^{-1}, and in the formation of 9,10-dihydroanthracenes only 11.5 kcal.mole^{-1} of stabilisation energy is lost.[6] Thus the formation of adducts becomes thermodynamically more favourable for the higher polycyclic hydrocarbons. Both substitution and addition take place in such a way as to involve the smallest loss of stabilisation energy; in general, addition occurs to form isolated, fully benzenoid residues, or to leave ring systems with the highest remaining stabilisation energies. Thus pentacene adds hydrogen to give 6,13-dihydropentacene (leaving two intact naphthalene systems) rather than 5,14-dihydropentacene (leaving one benzene and one anthracene system).

Simple resonance theory and molecular orbital theory predict essentially similar reactivities at certain bonds of the various hydrocarbons. The very simplified resonance treatment may be used successfully to predict and explain some reactions.

Naphthalene

The 1,2-bond of naphthalene is found to have a multiplicity of 5/3, which is greater than that of the other bonds, all of which have multiplicity 4/3.

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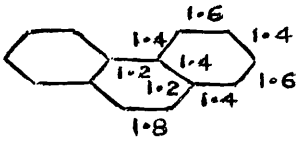
6. P.B.D. de la Mare and J.H. Ridd, "Aromatic Substitution -- Nitration and Halogenation" (Butterworths, London, 1959)

This suggests that the 1,2-bond of naphthalene should be more like a double bond than any of the bonds in benzene, and also that the -CH:CH.CH:CH- system in naphthalene should be similar to buta-1,3-diene, or 1,4-diphenylbuta-1,3-diene. These conclusions are borne out by general chemical experience. Naphthalene does not add chlorine as easily as an olefin, but more readily than benzene; the addition reaction is easily arrested after the addition of two molecules of halogen to give a 1,2,3,4-tetrachloro-1,2,3,4-tetrahydronaphthalene in which the benzene ring is left. Naphthalene is also reduced by sodium in alcohol to give 1,4-dialin (dihydronaphthalene) in which a benzene ring and an isolated double bond remain. Analogous reduction of 1,4-diphenylbuta-1,3-diene gives 1,4-diphenylbut-2-ene by a similar 1,4-addition of hydrogen.

Phenanthrene



Phenanthrene is another example in which the simple resonance theory leads to chemically reasonable results. There are five Kekule structures of phenanthrene; these

are of four different types, two differing only in orientation. If all five are equally weighted, the bond multiplicities which result are shown above (p. 21). The 9,10-bond should be closely similar to a double bond (multiplicity of 9/5), in agreement with its ready attack by double-bond reagents (H_2O_2; O_3) and the ready formation of 9,10-dihydrophenanthrene derivatives with bromine or chlorine.

Mechanisms of Halogenation

A. Olefins

The attack of chlorine and of bromine upon an unsaturated compound has, in general, two stages; one is the initial electrophilic attack by Cl^+ or some similar entity. The evidence for the electrophilic attack involves structural effects and orientation effects. The two-step nature of the addition to olefins was demonstrated by Francis[22] who showed that bromination of ethylene in aqueous solution yields bromohydrin as well as dibromide, and that in the presence of chloride or nitrate ions some β-bromoethyl chloride or β-bromoethyl nitrate was found in the product mixture.

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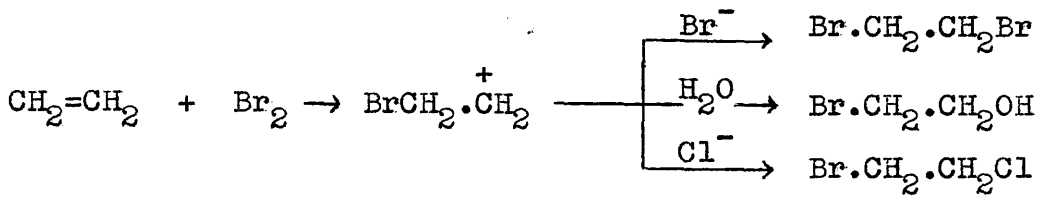
22. A.W. Francis, J.Amer.Chem.Soc., 1925, 47, 2340.



Structural effects

Robertson and his co-workers[23] have prepared a large number of olefins and have studied their rates of chlorination and bromination. The reaction rates in acetic acid were shown to vary according to the structure of the olefin and especially to the variations in the electronic effects of the substituents attached to the olefinic carbonatoms. Electron-withdrawing groups (NO_2, COOH) decrease the rate of addition while electron-donating groups (Me, Et) increase the rate of addition. For example, crotonic acid reacts fifty times as fast as acrylic acid, but five thousand times as fast as maleic acid, although the kinetic form of the reactions is that of the simple second-order equation

$$-d[Cl_2]/dt = k_2[Cl_2][Olefin].$$

A similar investigation of substituent effects at the β-position of styrene showed that at 25° k_2 for the addition reaction with chlorine in acetic acid decreases

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23. This work is summarised in the Table quoted in ref. 20. (p. 16 of this thesis)

from 61 (Ph.CH:CH.CO.Ph) through 49 (Ph.CH:CH.COOH) and 1.8 (Ph.CH:CH.CHO) to 0.002 (Ph.CH:CH.NO_2). These observations support the idea that addition of chlorine involves an electrophilic attack in the rate-determining stage.

Orientation effects

In an electrophilic addition it would be expected that the direction of addition of an unsymmetrical reagent across the double bond would be determined by which of the two olefinic carbon atoms has the greater nucleophilicity. Such considerations are the basis of the Markownikoff rule, for although this was originally formulated to explain the direction of addition of hydrogen halide to olefins[24] and despite the fact that the rule draws attention to the hydrogen atoms rather than to the electron-repelling alkyl groups attached to the olefinic carbon atoms, its mechanistic interpretation is grounded in the assumption that the addition of hydrogen halide involves attack by H^+ and that this attack will proceed with the greater ease at the carbon atom possessing the fewer alkyl groups, thus determining the orientation of addition of the molecule H-X

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24. W.W. Markownikoff, Ann., 1870, 153, 256.

The alkyl groups stabilise the carbonium ion formed

Chlorine is not unsymmetrical; it is therefore impossible to tell which atom attacks the olefin first. However, the addition of salts assists in giving a picture of the reaction involving prior electrophilic attack of chlorine at the position of higher nucleophilicity. In the presence of added anions in aqueous solutions, the chlorination of an unsymmetrical olefin $R.CH{:}CH_2$ produces mainly $R.CHCl.CH_2Cl$, $R.CHX.CH_2Cl$, and $R.CHOH.CH_2Cl$ (where X^- is the added anion and R is an alkyl or aryl group). These observations are best explained by assuming the formation of an intermediate carbonium ion such as

$$R.\overset{+}{C}H.CH_2Cl$$

which can then react with chloride ion, with foreign anions, or with the solvent. Electrophilic attack by chlorine in the sense $\overset{\delta+}{Cl}\text{-}\overset{\delta-}{Cl}$ is the only explanation of the results; nucleophilic attack by the chlorine molecule, initiated by Cl^-, would not explain the incorporation of other anions, nor would the formation

of other species such as BrCl which are precluded by the direction of the addition. Further evidence that chlorine adds electrophilically is derived from a study of the series Cl_2, ClOH, ClOAc. In each case the addition takes place in the manner expected from ionisation in the sense $\overset{+}{Cl}-\overset{-}{X}$, taking into account the structure of the olefin undergoing reaction. Also the effects of change in structure show that deactivation of the ethylenic double bond occurs with electron-withdrawing groups, which reduce the rate of addition and show that the rate-determining reaction involves electrophilic attack.

Kinetics of addition of halogens

The kinetics of halogen addition take their simplest form in the case of the addition of chlorine to olefins in solvents not less polar than acetic acid. These reactions are of the second order, as has been established by Robertson and his co-workers[23]* for a wide range of olefins, mainly using acetic acid as solvent.

$$dx/dt = k_2[\text{Olefin}][\text{Halogen}]$$

The kinetics indicate that it is molecular halogen which attacks the olefin. The addition of water and of ionised salts increases the rate of the reaction, in

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*p. 23 of this thesis.

agreement with the picture of a heterolytic process having a polar transition state. The effects of changes in the structure of the olefin on the rate of addition show that the halogen is acting as an electrophile.

The addition of bromine to olefins follows the same kinetics when the solvent is water, methanol, or aqueous acetic acid; but in anhydrous acetic acid it will only do so at low concentrations of bromine (ca. 0.001M). In a certain range of concentration (ca 0.025M) the addition of bromine to olefins in acetic acid proceeds according to a third-order kinetic equation,

$$dx/dt = k_3[\text{Olefin}][Br_2]^2.$$

Dilution, increase of temperature, or the addition of water to the solvent tend to break down the order from three towards two. The effect of constitutional changes in the structure of the olefin upon the third-order rate coefficient is strikingly similar to their effect on the rate of the second-order chlorine addition in acetic acid; this suggests that there is no fundamental change of mechanism between the two kinetic forms of reaction. In solution in acetic acid the addition of iodine follows the same third-order kinetic expression; so does the addition of bromine monochloride, iodine monochloride,

and iodine monobromide. The order of reactivity

$$I_2 < IBr < Br_2 < ICl < BrCl$$

suggests that addition starts with an electrophilic attack by the more electropositive halogen atom.

Chlorine does not show the third-order reaction, which suggests that this third-order process involves the use of higher co-ordination numbers which are more easily reached by the heavier halogen atoms. It is usually accepted that the halogen molecule adds reversibly by an octet expansion in one of its atoms, thereby forming a small stationary concentration of an adduct which cannot of itself eject its second halogen atom as the anion and only does so when another halogen molecule arrives and assists by forming the trihalide ion:

$$\text{Olefin} + X_2 \longrightarrow [\text{Olefin}, X_2] \xrightarrow{X_2} \text{Products}$$

For some olefins, notably vinyl and allyl halides, the addition of bromine in acetic acid is catalysed by bromide and by chloride ions. The catalysed processes have the following kinetic forms:

$$dx/dt = k[\text{Olefin}][\text{Bromine}][\text{Halide ion}]$$

It appears that the catalysed reactions are still electrophilic processes and therefore probably do not

depend upon preformed polyhalide ions such as Br_3^-. One interpretation of these reactions is that they are simply variants of the uncatalysed third-order process which arise when a halide ion is more effective than a halogen molecule in completing the second stage of the reaction.[23*]

$$\text{Olefin} + Br_2 \longrightarrow [\text{Olefin}, Br_2] \xrightarrow{X^-} \text{Products}$$

Nature of the intermediate in halogenation

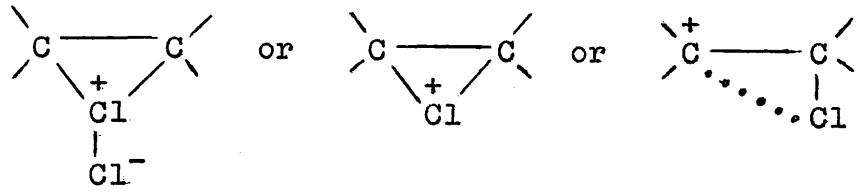
The intermediate is thought to have a structure similar to (I).

$$(R.\overset{+}{C}H.CH_2Cl)\ \ Cl^-$$

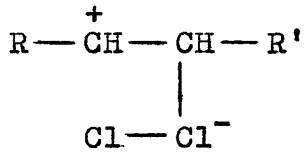
(I)

Such a structure will explain the effect of Lewis acids, which are capable of co-ordinating with chloride ion and which are known to catalyse the addition of chlorine to olefins, and it will also explain the incorporation of foreign anions. The attack of the incipient carbonium ion centre by solvent is also readily understood, since the partial positive charge located upon C_β is similar in type to the charge upon the α-carbon atom of a solvolysing alkyl halide.

An alternative structure is a chloronium ion, in which there is a strained three-membered ring:



Such a structure has been suggested to account for trans-addition of bromine and of chlorine, because the attack of the nucleophile would have to come from the side opposite to the halogen bridge, which is broken during the nucleophilic attack. The formation of this chloronium ion may be regarded as an extreme case of neighbouring group participation. Due to the partial charges on C_β and on one of the chlorine atoms in the ion (II)



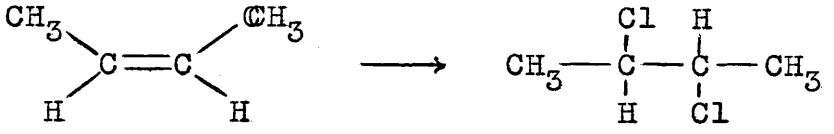
(II)

there will be electrostatic attraction which, in an extreme case, could be regarded as a chemical bond in the normal sense of the word. From spatial factors it seems unlikely that such an intermediate would be very long-lived; however, chlorine is one of the groups known to migrate during neighbouring-group participation (which involves a similar

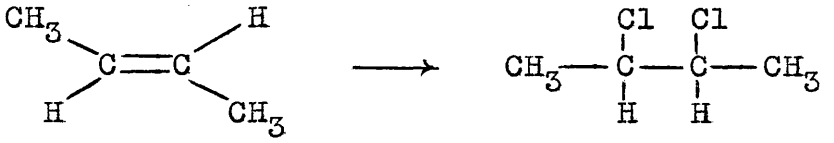
transition state) and doubtless a similar structure can be involved as an intermediate in chlorination.

Stereochemistry of addition

With few exceptions, the addition of chlorine and of bromine to olefins has been shown to be stereospecifically trans. For example, chlorine adds trans to both cis- and trans-but-2-ene; no evidence of cis-addition was found.[25]

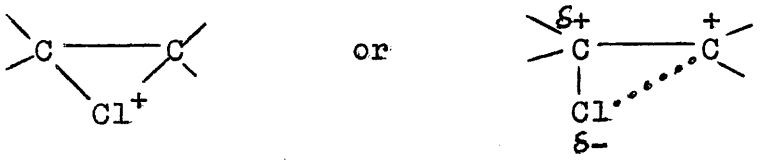


dl-2,3-Dichlorobutane



meso-2,3-Dichlorobutane

Fahey and Schubert[26] suggest that the intermediate might be either



In the latter structure, the interactions must be sufficiently strong to preclude collapse to form a

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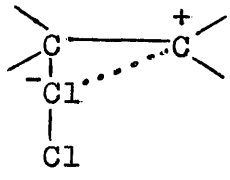
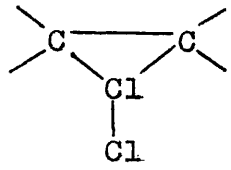
25. H.J. Lucas and C.W. Gould, J.Amer.Chem.Soc., 1941, 63, 2541.
26. R.C. Fahey and C. Schubert, J.Amer.Chem.Soc., 1965, 87, 5172.

cis-adduct. Intermediates of the type



and



are ruled out by these authors in the case of the but-2-enes since they believe that such interactions do not fit with the stereochemistry and the kinetics of the reaction.

Although trans-addition has been established in a large number of cases of addition of halogens, there are exceptions. Stilbene[27] and acenaphthylene[28] give significant amounts of cis-adducts when chlorinated in non-polar solvents. Another notable set of exceptions has been found in the case of additions to the anions of αβ-unsaturated dibasic acids; thus for the reaction of bromine with maleate and fumarate ions in polar solvents, both olefins yield the same meso-dibromosuccinate.[29] Similar results for the dimethylmaleate and dimethylfumarate ions are discussed below (p.). Still more recently, Fahey and Schubert[26] found that the chlorination of phenylpropenes in polar solvents gives substitution and addition,

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27. S.J. Cristol and F.H. Bly, J.Amer.Chem.Soc., 1960, 82, 142.
28. S.J. Cristol, F.R. Stermitz, and P.S. Ramey, J.Amer. Chem. Soc., 1956, 78, 4939.
29. R. Kuhn and T. Wagner-Jauregg, Ber., 1928, 61, 483, 504.

in most cases the cis-dichloride being formed in the larger amount. They proposed that the reaction went through an ion-pair type of intermediate, since the lack of stereospecificity indicates an open rather than a bridged structure for the intermediate ion.

Chlorine as a bridging atom in intermediates

The evidence suggests that chlorine is quite effective in bridging to a secondary carbonium ion centre, but that such bridging is often reduced or eliminated when the carbonium ion centre is conjugated with an aromatic system. Cyclohexene has been shown to add molecular chlorine to give exclusively trans-addition products[30]; this was explained by assuming the formation of an intermediate with chlorine as a bridging atom. A similar explanation has been given for the steric course of reaction of the stilbene dichlorides with silver acetate[31] and for the stereochemistry of addition of chlorine to cyclohexene and to stilbene by iodobenzene dichloride.[32] As the chlorine atom does not seem to bridge very effectively to a phenyl-substituted carbonium ion centre, one might expect that a bridge between chlorine and a tertiary carbonium ionic centre would also be less firmly bonded.

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30. M.L. Poutsma, J.Amer.Chem.Soc., 1965, 87, 2161.
31. S. Winstein and D. Seymour, J.Amer.Chem.Soc., 1946, 68, 119.
32. J.L. Cotter, L.J. Andrews, and R.M. Keefer, J.Amer. Chem.Soc., 1962, 84, 793.

However, there is some evidence that chlorine participation is important in such cases.[33] Just how strong this interaction is remains unclear and further evidence is needed to decided the point.

Neighbouring-group participation

This phenomenon was first observed in the uncatalysed solvolysis of the α-bromopropionate anion, when it was found that the rate of reaction was considerably higher than that expected, and of remarkable stereochemistry; replacement proceeded with retention of absolute configuration. The explanation of this was that electrostatic interaction took place between the oxygen atom of the carboxyl group and the incipient carbonium ionic centre, the COO^- group providing "built-in" solvation, since it assists both the formation of charge and the expulsion of the bromine atom as the ion. The exact nature of the intermediate has been debated, the argument being mainly concerned with the type of bonding in the "α-lactone" structure formed as an intermediate in the reaction.[34]

The evidence pointing to neighbouring-group participation is of three principal types. First, if

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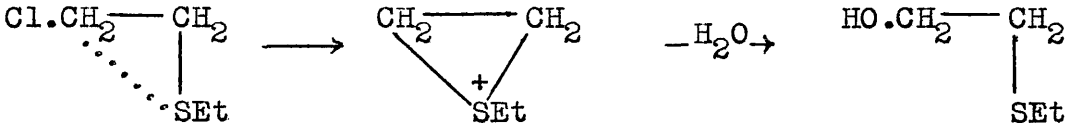
33. P. Ballinger and P.B.D. de la Mare, J.Chem.Soc., 1957, 1481; J.G. Traynham and O.S. Pascual, Tetrahedron, 1959, 7, 165.
34. W.A. Cowdrey, E.D. Hughes, and C.K. Ingold, J.Chem.Soc., 1937, 1208; S. Winstein and R.B. Henderson, J.Amer. Chem.Soc., 1943, 65, 2196.

the participation occurs during the rate-determining stage, the reaction is almost certain to be significantly faster than in its absence. The β-chlorosulphide, $Cl.CH_2.CH_2.S.Et$, is hydrolysed over 10,000 times as rapidly as the corresponding ether in aqueous dioxan.[35] Such a difference in rate is far too great to be explicable on considerations of inductive, conjugative, or steric effects; it is suggested that hydrolysis of the sulphide, but not the ether, proceeds through a cyclic ion. The intermediate, because of steric strain, is readily hydrolysed to the observed products.



A reaction which is accelerated by neighbouring group participation is sometimes said to be anchimerically assisted[34], since interaction between the neighbouring group and the carbonium ionic centre helps to lower the activation energy.

The stereochemistry of a reaction may suggest neighbouring-group participation. Hydrolysis of the

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35. H. Bohme and F. Sell, Ber., 1948, 81, 123.

α-bromopropionate anion in water yields the lactate ion with overall retention of configuration, which must involve two displacements iwithve two inversions; the first corresponds to the displacement of bromide ion by the carboxylate ion, and the second involving cleavage of the lactone-like structure. (Note that a full bond between the carboxylate group and the carbonium ion centre need not be formed.)

Further evidence of such participation has been found in a number of reactions involving the addition of halogens. One striking example is the chlorination of the dimethyl-maleate and -fumarate anions.[36] In each of these compounds the olefinic group, and therefore the attacked carbon atom, is adjacent to the $-COO^-$ group. Neighbouring-group participation would be expected to occur in this situation; but remarkably a chloro-lactone, which arises from ring-closure of the carboxylate group, can be isolated in these instances. This β-lactone is not the result of an S_Ni reaction from a previously formed αβ-dichlorosuccinate ion, since this dichloride will form neither this β-lactone nor the product of its hydrolysis, the α-chloro-β-hydroxysuccinate ion, under the

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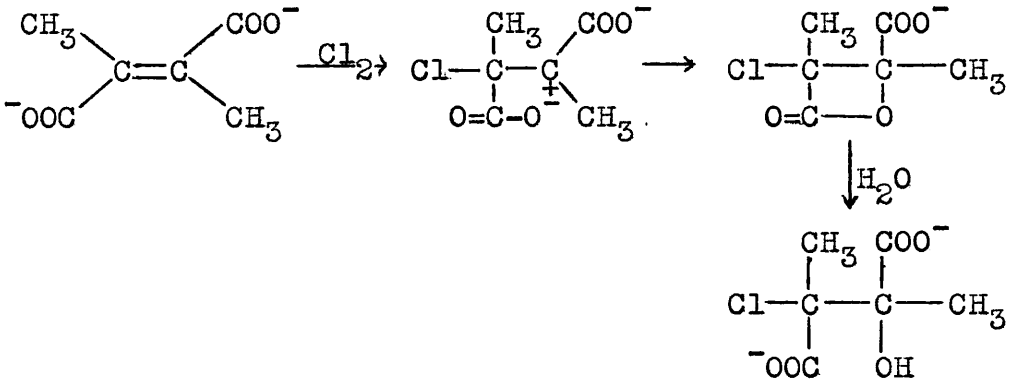
36. D.S. Tarbell and P.D. Bartlett, J.Amer.Chem.Soc., 1937, 59, 407.

experimental conditions.



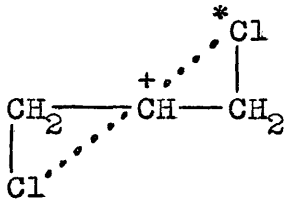
Since the β-lactone structure could be proved to be an intermediate (by isolation), this chlorination must have proceeded in two stages, one of which involved neighbouring group participation by the carboxylate ion.

Finally, neighbouring group participation may lead to molecular rearrangement when the group remains bonded to the reaction centre but breaks away from the atom to which it was originally attached.

$$CH_2{:}CH.CH_2^{*}Cl + HOCl \longrightarrow Cl.CH_2.CH^{*}Cl.CH_2OH \quad (^{*}Cl = {}^{36}Cl)$$

In the reaction of allyl chloride labelled with ^{36}Cl with hypochlorous acid in aqueous solution and added silver perchlorate the major product (2,3-dichloropropanol; 70%) shows some migration (ca. 12%) of the labelled chlorine atom to the second carbon atom. An intermediate

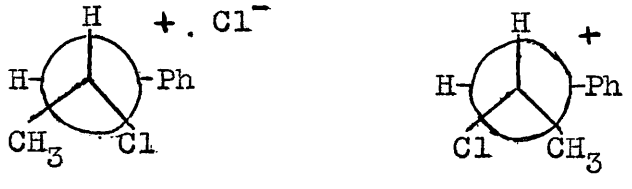
such as (III) must be involved.



(III)

Substitution accompanying addition

We have already noted the generalisation that olefins react with electrophiles by addition, whereas aromatic compounds react by substitution. In certain cases of chlorine attack, however, heterolytic substitution reactions can become the predominant mode of reaction for an olefin. Thus de la Mare and Salama[36] studied the reaction of isobutene with aqueous hypochlorous acid, when the main substitution product was 2-methylallyl chloride. Fahey and Schubert[26] found that the chlorination of 1-phenylpropene gives substitution, and suggested the formation of ion-pair intermediates:



36. P.B.D. de la Mare, A. Salama, J.Chem.Soc., 1956, 3337.

*For ref. 26, see p. 31 of this thesis.

from which the main substitution products could be formed by cis-elimination of hydrogen chloride.

Taft[37] studied the percentage of substitution which occurred in the reactions of a number of olefins, and assumed that both addition and substitution involved a common carbonium ionic intermediate. He suggested that the more reactive olefins were prone to substitution reactions; however, it has been realised recently that the problem is complex and needs further investigation.

The crotonic acid system

Most of the work on the chlorination of crotonic acid was carried out at the turn of the century, and the main interest was in the reaction products and not the mechanism. "Lower-melting" (l.m.) αβ-dichlorobutyric acid (m.p. 63°) was the only product isolated from chlorinations in chloroform or in carbon tetrachloride. This acid was reported to be the product of chlorination of either the cis- or the trans-crotonic acid. The αβ-dichlorobutyric acid, m.p. 63°, would be expected from the trans addition of chlorine to trans-crotonic acid. However, its formation from cis-crotonic acid might be attributed to isomerisation during the reaction, since

37. R.W. Taft, J.Amer.Chem.Soc., 1948, 70, 3364.

the trans compound is the more stable. The isomeric "higher-melting" (h.m.) αβ-dichlorobutyric acid, m.p. 78°, was prepared by the addition of hydrogen chloride to α-chlorocrotonic acid, or by the reaction of hydrogen chloride with α-chloro-β-hydroxybutyric acid, both of which reaction require vigorous conditions.[38,39]

These dichlorobutyric acids can be dehydrohalogenated by alkali; without temperature-control, a mixture of the cis- and trans-α-chlorocrotonic acids results from either isomer. However, the predominant product in each case is that expected from a trans-elimination: trans-α-chlorocrotonic acid results from the dichlorobutyric acid, m.p. 78°, and cis-α-chlorocrotonic acid (α-chloroisocrotonic acid) from the dichlorobutyric acid of m.p. 63°. If the temperature is carefully held to below 5°, the dichlorobutyric acid, m.p. 63°, yields the cis-α-chlorocrotonic acid almost entirely.[40]

The chlorination of crotonaldehyde gives αβ-dichlorobutyraldehyde; if this is warmed to 50° in aqueous solution with more chlorine, butyl chloral hydrate [$CH_3.CHCl.CCl_2.CH(OH)_2$] is formed.[41,42]

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38. A. Michael and O.D.E. Bunge, Ber., 1908, 40, 2907.
39. W. Melikoff and V. Petrenko-Kriskchenko, Ann., 1891, 266, 371.
40. J. Wislicenus, Ann., 1888, 248, 288, 290.
41. G.A. Ropp, W.E. Craig, and V. Raaen, Org.Synth., Coll. Vol. IV, p. 130 (Wiley, N.Y., 1963)
42. S. Zeisel, Monats., 1886, 7, 359.

On the other hand, the product of an excess of chlorine and liquid crotonaldehyde has been reported to be an αβ-dichlorobutyroyl chloride.[42]

Kinetics of halogenation

Robertson and his co-workers[43] studied the chlorination and bromination of crotonic acid and of crotonaldehyde in acetic acid. It was found that the rate of chlorination of crotonic acid was unaltered by the presence of added sodium acetate or hydrogen chloride, showed second-order kinetics, and seemed to involve electrophilic attack by the chlorine molecule. In contrast, the addition of bromine is accelerated by hydrogen bromide and by adding strong acids such as sulphuric acid. It was believed to be evidence of nucleophilic addition by HBr_3 with the subsequent elimination of HBr. The substituent effects indicate such a mechanism, since the addition of bromine to various unsaturated acids shows substituent effects opposite to those shown in chlorine, i.e.

$CH_2{=}CH.CO_2H$ > $Me.CH{=}CH.CO_2H$ > $Me_2C{=}CH.CO_2H$

for nucleophilic bromination.

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43. E.P. White and P.W. Robertson, J.Chem.Soc., 1939, 1509; I.D. Morton and P.W. Robertson, J.Chem.Soc., 1945, 129.

The results for αβ-unsaturated aldehydes show that bromine addition is catalysed by hydrogen bromide, since the kinetics show autocatalysis due to hydrogen bromide formed by side-reactions. In acetic acid, crotonaldehyde is chlorinated and brominated by a nucleophilic mechanism, since the reaction rate is much faster than that of crotonic acid and is increased by the addition of strong acid. The presence of acetate ion greatly reduces the rate of halogenation, in keeping with the suggestion that the addition reaction proceeds through prior protonation of the aldehyde followed by nucleophilic addition of halogen. These additions generally have the kinetic form

$$-d[X_2]/dt = k[\text{Olefin}][H^+][X_2].$$

Aromatic Substitution

It was once thought[44] that all aromatic substitutions took place through an addition-elimination mechanism. This concept was strengthened by the ease with which the addition products of polyannular aromatic compounds (e.g. phenanthrene, anthracene) lost hydrogen halide, or water, to give substitution products. Further evidence for this mechanism was found in the substitution of olefins

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44. H.E. Armstrong, J.Chem.Soc., 1887, 258.

by acetyl chloride in the presence of aluminium chloride (Friedel-Crafts conditions) to give an unsaturated ketone.[45] This reaction proceeds through an unstable α-chloro-β-acetyl adduct which loses hydrogen chloride readily:

$$R.CH{:}CH.R + CH_3.CO.Cl \longrightarrow R.CHCl.CHR.CO.CH_3 \longrightarrow R.CH{:}CR.CO.CH_3$$

and it was proposed that the Friedel-Crafts acylations of aromatic systems proceeded analogously. The development of this idea has been reviewed by Fieser.[46]

More recently it has been shown that the addition - elimination sequence is not normally important. Michael showed that nitric acid and sulphuric acid do not add to ethylene in the sense NO_2-OH and HO-SO_3H.[47] It was also shown that the formation of 9-bromophenanthrene results from the direct attack of bromine upon phenanthrene, and not through the formation and decomposition of 9,10-dibromo-9,10-dihydrophenanthrenes.[48]

When the addition-elimination mechanism of aromatic substitution was first discredited as a general theory, it was proposed that olefins undergo attack exclusively through addition reactions, and aromatic compounds react solely by substitution reactions; the addition reactions

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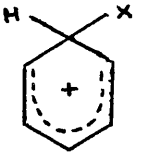
45. G. Darzens, Compt.rend., 1910, 150, 707.
46. L.F. Fieser, "Organic Chemistry", Vol. 1, 174 (Ed. H. Gilman, Wiley, N.Y., 1943)
47. See L. Melander, Arkiv.Kemi, 1950, 2, 211.
48. C.C. Price, J.Amer.Chem.Soc., 1936, 58, 1834, 2101.

of anthracene and phenanthrene were regarded as anomalous effects caused by especial reactivity. The discovery that isobutene reacts with chlorine under heterolytic conditions to give predominantly a substitution product suggests that the generalisation is not valid, and the isolation of polychloro adducts from the chlorination of naphthalene, fluorene, and biphenyl shows that addition reactions are not insignificant in aromatic chemistry.[49]

Modern theories of electronic organic chemistry offer a qualitative explanation of the observed effects of reactivity and orientation in electrophilic substitution reactions in aromatic systems. According to the transition state theory, the reactivity depends upon the differences in free energy between the reactants and the transition state. A Wheland-type intermediate[50] such as the following:



is assumed to be formed. The transition state for the reaction will, in general, be more like this intermediate than like the reactants. It is therefore

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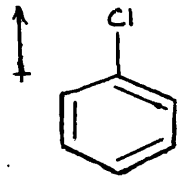
49. P.B.D. de la Mare and A. Salama, J.Chem.Soc., 1956, 3337; G.H. Beaven, P.B.D. de la Mare, M. Hassan, E.A. Johnson, and N.V. Klassen, J.Chem.Soc., 1961, 2749; P.B.D. de la Mare, E.A. Johnson, and J.S. Lomas, J.Chem.Soc., 1963, 5973 and refs. quoted therein.
50. P. Pfeiffer and R. Wizinger, Ann., 1928, 461, 132.

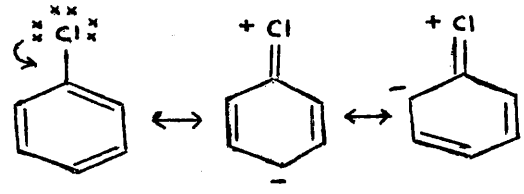
useful to discuss the orientation and reactivity in terms of the stability of the intermediate. Since electron donation by inductive or conjugative effects should stabilise the positively-charged ring of the intermediate and electron-withdrawal should destabilise a positive charge and raise the free energy difference, we expect electron-donating substituents should increase reactivity and electron with-drawing substituents should decrease reactivity. The inductive effect affects all positions of the ring, whereas conjugative effects will affect positions ortho and para to the substituent. Positions of relatively high electron density will be involved in electrophilic substitutions, and positions of low electron density will be involved in nucleophilic substitutions. Among substituents which increase reactivity towards electrophilic attack are alkyl groups, OR, OH, NH_2, O^-, S^-, and $NH.CO.CH_3$; and those which decrease reactivity to electrophiles will include the halogens, NO_2, CO_2H, CN, CO_2R, $CO.NH_2$, and $CH{:}CH_2$.

Generally there will be meta-substitution in a ring deactivated by conjugative effects because this position is the least deactivated by the substituent. However,

the same substituent may show both inductive and conjugative effects, and these need not necessarily act in the same direction. The halogens have a -I effect and a +M effect, the former being stronger so that the ring is deactivated, but least so at the positions ortho and para to the halogen substituent.



-I effect
Ring deactivated



+M effect
o- and p-positions activated towards electrophilic attack.

Mechanism of electrophilic aromatic halogenation

The halogenating agent in heterolytic substitutions is generally the halogenium ion, X^+, or the positive part of the polarised halogen derivative $\overset{+}{X}-\overset{-}{Y}$; where molecular halogen is the reagent, the attacking group is the positive part of the $\overset{+}{X}-\overset{-}{X}$ dipole. The first step is the formation of the Wheland-type intermediate by attack of the reagent, the second part being the expulsion of the proton to give a substituted compound.[51] Since the rate of bromination of hexadeuterobenzene is approximately the same as that of benzene, proton-loss is not the

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51. P.B.D. de la Mare, T.M. Dunn, and J.T. Harvey, J.Chem.Soc., 1957, 923.

rate-determining stage to any important extent. Thus as with nitration the attack of the electrophile is the critical step in aromatic halogenation.

Addition

An addition to an aromatic system involves a greater loss of stabilisation energy than a substitution, as a rule; substitution involves a disturbance of the π-electron cloud because of the electrical differences between hydrogen and the substituent, but addition involves the removal of two π-electrons from the system, with a resulting destruction of symmetry. For monocyclic compounds, the loss of resonance energy on undergoing an addition reaction is relatively large, and hence substitutions are favoured; in polyannular aromatic systems the loss of energy is relatively less and hence addition becomes more likely. Even so, addition takes place so that there is the least loss of resonance energy; this usually means that the product contains two smaller aromatic structures rather than a larger system, for in the former case the difference in resonance energies between the products and the starting material is minimised. For example, anthracene undergoes addition at the 9,10-positions rather than at the 1,2-positions since in the

former case two benzenoid entities are left.

Addition to naphthalene, anthracene, and phenanthrene

The halogenation of these compounds has been shown to yield both substitution and addition products. These adducts can decompose to form substitution products by the loss of hydrogen halide. The naphthalene tetrachlorides, which consist of one benzene ring fused to a tetrachloro-cyclohexene system, are fairly stable, as are the adducts of acenaphthylene, but the 9,10-dichloro-9,10-dihydro-anthracenes have been found to decompose readily to give the 9-halogenoanthracene. Cristol and his co-workers[52] have shown that chlorination of acenaphthylene in polar solvents give a *cis* adduct rather than a *trans* adduct.

Addition to phenanthrene

Sandqvist[53] found a single product of addition in the chlorination of phenanthrene; a similar dibromo-adduct has also been isolated. Price[54] and Mayo and Hardy[55] studied the bromination of phenanthrene and of naphthalene, and from their results concluded that substitution and addition took place concurrently and independently; from a study of the effects of catalysts and of change of solvent on the proportions of substitution and addition products they inferred a common carbonium ionic intermediate.

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52. S.J. Cristol, F.R. Stermitz and P.S. Ramey, J.Amer.Chem. Soc., 1956, 78, 4939.
53. H. Sandqvist, Ann., 1918, 417, 17.
54. C.C. Price, Chem.Revs., 1941, 29, 37.
55. F.R. Mayo and W.B. Hardy, J.Amer.Chem.Soc., 1952, 74, 911.

Identification of addition reactions

De la Mare and his co-workers[56] have made a study of addition reactions accompanying substitution in the chlorination of aromatic compounds in acetic acid. The isolation of the adducts is usually more difficult since they are generally less stable and are decomposed to some extent during the normal isolation processes. They can be detected by various means: chloroacetoxy adducts can be proved to be present by examination of the infra-red spectrum of the crude reaction product (C-O) and by analysis of the reaction product for oxygen. The estimation of the hydrogen chloride produced during the chlorination gives a measure of the extent of substitution unless solvent intervention takes place, since the formation of a chloroacetoxy adduct also involves the liberation of hydrogen chloride. Integrated n.m.r. spectroscopy gives a good picture of the presence of non-aromatic ring systems resulting from addition. For example, the ten aromatic protons of naphthalene are reduced to six when tetralin derivatives are formed, with the production of four aliphatic protons whose positions in the spectrum are different from those of the aromatic protons. Finally, it is often possible to isolate and

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56. Summarised in P.B.D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems" p. 241ff. (Elsevier, Amsterdam, 1966)

identify some addition products.

Additions were found not only in the expected systems, such as naphthalene, phenanthrene, and anthracene, but also in biphenyl, fluorene, and even toluene. When the chlorinations were carried out in acetic acid, chloroacetoxy adducts were formed in addition to polychloro adducts. Such solvent participation is well known in additions to olefins and is indicative of the two steps in such reactions. The additions studied took place in heterolytic conditions; in contrast, free-radical reagents are well known to add to aromatic systems, even to benzene, although in general more than one double bond is attacked.

Aims of the present work

Aromatic compounds are known to form some adducts in chlorination, along with the usual substitution products. Phenanthrene has been shown to add chlorine across the 9,10-bond and to form an acetoxychloride in acetic acid solution. There was evidence that the acetoxychloride isolated by Konigsberger was the *trans* adduct; it was believed that a *cis*-acetoxychloride was also formed but was too unstable to permit isolation or identification

directly, although its presence could be inferred from its decomposition products. This work set about to find evidence of this more labile isomer and to study the effects of salts upon the rates and products of the reaction of phenanthrene with chlorine in an attempt to define more closely the mechanism of the reaction.

In the case of the deactivated crotonic acid system and its analogues, it was intended to continue the work of Bailey[57] and to identify some of the uncharacterised products which were obtained. Most of the work is intended to set more close limits upon the conditions under which nucleophilic halogenation of αβ-unsaturated carbonyl and carboxyl derivatives might occur, and to attempt to define more clearly the mechanism of chlorination, with particular reference to the possibility of double-bond migration such as has been found in the chlorination of isobutene.

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57. J.E. Bailey, M.Sc. Thesis, University of London, 1963.

EXPERIMENTAL

EXPERIMENTAL.

A. Purification of materials

Acetic acid Glacial acetic acid (2,5 l.) was treated with a drop of bromine and was left to stand overnight. It was then shaken with freshly prepared silver oxide until all the bromine and bromide ion had been removed. The acid was distilled from glass wool, and the distillate was boiled under reflux for eight hours with powdered potassium dichromate (250 g.) and water (100 ml.). The acid was distilled from the inorganic residue, and the distillate was then fractionally distilled, using a heated column. When the boiling point of the acid reached 118°, the freezing points of subsequent fractions were taken and when a constant value (16.5-16.6°) was reached the pure dry acid was collected.

Chloroform The commercial material contains ethanol as a stabiliser; this was removed by washing with running water for three hours, followed by shaking with distilled water. The dried ($CaCl_2$) solvent was distilled and the clear fraction, b.p. 61°, was collected.

On account of the rapid decomposition of the purified solvent, it was used the same day.

Nitromethane Commercial nitromethane was passed through a column of activated alumina and was then dried by fractional distillation. The product, b.p. 101.5°, m.p. -29.0 to -30.4°, gave stable yellow solutions with chlorine. In commercial nitromethane, chlorine gives an unstable solution which tends to have a green-blue colour.

Carbon tetrachloride The commercial material was washed and purified by distillation in the same way as chloroform was purified. The purified material had b.p. 76.8°, m.p. -23.0 to -23.4°.

Methylene chloride The commercial material was purified by the same method which was used for chloroform and carbon tetrachloride. The material used had b.p. 42.4°, and readily decomposed to give hydrogen chloride.

Chlorine Chlorine from a cylinder of the liquified gas was passed through Dreschel bottles containing water, sulphuric acid, and glass wool to remove hydrogen chloride and water. The purified gas was passed into a darkened vessel containing the appropriate solvent, and the resulting solution was standardised

by pipetting samples into an excess of potassium iodide solution and titrating the liberated iodine with standard thiosulphate solution.

Crotonic acid The commercial material was purified either by distillation and then crystallising the fraction b.p. 180-184°/760 mm. from light petroleum (b.p. 60-80°) or by repeated crystallisation from light petroleum (b.p. 60-80°). The purified material had m.p. 71-72° and was completely colourless.

Crotonaldehyde The commcercial material was first distilled, with considerable loss. The fraction, b.p. 100-105°/760 mm. was fractionally distilled, and the material b.p. 104°/760 mm. was collected. The aldehyde could be stored at 0° for a few days, but it was usually used immediately after purification.

Phenanthrene The commercial product was treated with maleic anhydride to remove anthracene[58] and was then purified on an alumina column. Crystallisation from 95% ethanol gave a product, m.p. 100-100.5°, which contained less than 0.4% anthracene.[59]

Alumina The commercially available material (Hopkins and Williams, CAMAG M.F.C., 100-200 mesh,

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58. E. Clar, Ber., 1932, 65, 852.
59. I. Feldmann, P. Pantages, and M. Orchin, J.Amer. Chem.Soc., 1951, 73, 4341.

alkaline, Brockmann activity = 1) was generally used. For the isolation of 9-acetoxy-10-chloro-9,10-dihydrophenanthrene, this material was deactivated by shaking it with 3% water.

Silica gel For column chromatography, Hopkins and Williams' product, M.F.C., was used without further treatment. Merck's silica gel, according to Stahl and containing 13% plaster of Paris, was used for thin-layer chromatography.

B. Reference compounds

"lower-melting"-αβ-Dichlorobutyric acid This compound was obtained in the best yields (ca. 40%) by adding slightly more than one molecular proportion of chlorine in carbon tetrachloride to a solution of crotonic acid in the same solvent, using a trace of iodine as catalyst. The solution became almost colourless after a few hours at room temperature. The solvent was removed by distillation, and the residual oil was purified either by distillation under reduced pressure (water pump) or by chromatography on silica gel. Recrystallisation from light petroleum (b.p. 60-80°) gave white crystals, m.p. 62-63°.

"higher-melting"-αβ-Dichlorobutyric acid Hydrogen chloride was passed, in a slow stream, into a thick-walled tube containing α-chlorocrotonic acid (2 g.) dissolved in hydrochloric acid (12N; 50 ml.). The tube was cooled in ice and, when the solution was saturated with hydrogen chloride, was sealed at this temperature in order to minimise the loss of hydrogen chloride. The sealed tube was heated at 100° for fifty hours, after which the contents of the tube were almost neutralised ($NaHCO_3$) and the resulting solution was extracted with ether. The combined ether extracts were washed with water, dried (Na_2SO_4), and then concentrated. The residual oil was purified by chromatography upon silica gel. Apart from a little unchanged α-chlorocrotonic acid, the product was a mixture of the isomeric αβ-dichlorobutyric acids. The required isomer, m.p. 78°, was obtained by crystallisation of the appropriate fraction from light petroleum (b.p. 40-60°).

α-Chlorocrotonic acid The material used was supplied by J.E. Bailey[57], who prepared it from butyl chloral hydrate by Roberts' method.[60] It could also be obtained by the dehydrohalogenation of the αβ-dichlorobutyric acid, m.p. 78°, with alkali. α-Chlorocrotonic acid was purified by crystallisation from water or by

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60. J.C. Roberts, J.Chem.Soc., 1938, 779.

vacuum sublimation, m.p. 98-99°.

α-Chloroisocrotonic acid This was prepared from αβ-dichlorobutyric acid, m.p. 63°, by dissolving this in a minimum of water and adding sodium hydroxide (30%; 3 moles) at below 5°. The reaction mixture was left at 0° overnight and was then acidified with hydrochloric acid (12N) and left for a further three hours at 0°. A mixture of sodium chloride and α-chloroisocrotonic acid separated. The reaction mixture with suspended solids was extracted with ether, the extracts were washed with water and then dried (Na_2SO_4). Removal of the solvent left an oil which, on crystallisation from light petroleum (b.p. 60-80°) gave white crystals of α-chloroisocrotonic acid, m.p. 66-67°, in 50-70% yield.

α-Chlorovinylacetic acid This was prepared from acrolein through its cyanhydrin which was solvolysed in methanol to give methyl vinylglycollate. Esterification with thionyl chloride gave methyl α-chlorovinylacetate, from which the parent acid was obtained by acid hydrolysis.

(a) Acrolein cyanhydrin[61] Potassium cyanide (166 g.) was dried for two hours at 160-180°, and was then pulverised in a large mortar while still hot, and kept in a desiccator.

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61. J.W.E. Glattfeld and R.E. Hoen, J.Amer.Chem.Soc., 1935, 57, 1406.

The cooled, powdered cyanide was placed in a 5 l. flask fitted with two dropping funnels and a powerful mechanical stirrer. Ether (2.5 l.) was added, and the mixture was stirred vigorously to keep the cyanide in suspension while water (2.5 ml.) was added to promote the condensation. Acrolein (100 ml.) and acetic acid (150 ml.) were added dropwise and simultaneously from the two dropping funnels. In order to minimise polymerisation, some of the acetic acid (15 ml.) was added before the acrolein was introduced. The rates of addition were controlled so that the reagents were added over 1.5 hours, and the temperature of the well-stirred slurry was held at 20-22° by a water bath. The reaction mixture was then worked up by Rambaud's method[62] to give acrolein cyanhydrin in 70% yield.
Water was essential for this condensation[cf. 61, 62, 63] and it was found that sodium cyanide may not be substituted for the potassium salt, since the thick suspension of sodium acetate which results makes efficient stirring impossible and drastically reduces the yield.

(b) Methyl vinylglycollate Rambaud's method[62] gave poor yields, and so another method[63] of acid-catalysed methanolysis of the cyanhydrin was employed. In this

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62. R. Rambaud, Bull.soc.chim.[5], 1934, 1, 1317.
63. J. Van der Sleen, Rec.trav.chim., 1902, 21, 211.

way the required ester was prepared in 60% yield, b.p. 76-80°/30 mm.

(c) Methyl α-chlorovinylacetate

Methyl vinylglycollate (61 g.) dissolved in dry pyridine (42 ml.) was treated with freshly distilled thionyl chloride (62 ml.) as described by Rambaud.[62] After distillation, methyl α-chlorovinylacetate, b.p. 58-60°/18 mm., was obtained in 75% yield.

(d) α-Chlorovinylacetic acid Methyl α-chlorovinylacetate (10 g.), hydrochloric acid (12N, 10 ml.), and water (100 ml.) were heated together under reflux on a boiling water bath until the lower organic layer had completely dissolved (five hours). Extraction of the cooled solution with ether, and distillation of the solution after drying (Na_2SO_4) gave α-chlorovinylacetic acid, b.p. 114°/20 mm. (5 g., 55%).[62]

Υ-Chlorocrotonic acid Methyl Υ-chlorocrotonate was prepared by rearrangement of methyl α-chlorovinylacetate using cuprous chloride as catalyst. Ferric chloride, aluminium chloride, and hydrogen chloride each failed as catalysts in this reaction, and it was also found that when the solvent and the catalyst were scrupulously dry, no rearrangement took place until water

was added (0.5 ml.).

Methyl α-chlorovinylacetate (2 g.) was dissolved in benzene (5 ml.), and this solution was added to a suspension of cuprous chloride (freshly prepared, slightly moist; 2 g.) in benzene (10 ml.). The mixture was either heated under reflux for six hours on the steam bath, or left with occasional shaking for some days at room temperature. After this time, the catalyst was filtered off and the solvent was removed. The residue was methyl γ-chlorocrotonate. The course of the rearrangement could be followed by v.p.c., the reaction mixture being worked up when all the original ester was destroyed. The identity of the methyl γ-chlorocrotonate, which was shown to be distinct from methyl α-chlorovinylacetate by v.p.c. and by i.r. spectroscopy, was confirmed by n.m.r. spectroscopy. No attempt was made to hydrolyse the ester to the parent acid.

<u>α-Chloro-β-hydroxybutyric acid.</u> The chlorination of crotonic acid in water was used to prepared this acid.[57] A slow stream of chlorine was passed into an aqueous solution of crotonic acid (2%) over two hours. The mixture was left in a stoppered flask over three days, and was then extracted many times with ether after the

aqueous layer had been saturated with salt. The residue after distillation of the dried (Na_2SO_4) ether solution on the steam bath was purified by chromatography on silica gel to give, after a little αβ-dichlorobutyric acid, a thick oil which had the infra-red spectrum of the lower-melting isomer of α-chloro-β-hydroxybutyric acid[57] but which slowly crystallised to give the isomer, m.p. 85-86°. The n.m.r. spectrum of both compounds was the same, but the infra-red spectra differed.

General note

It should be stressed that many of the derivatives of crotonic acid, especially those of considerable acidity or containing other hydroxylic groups, are highly soluble in almost every solvent. Their partition ratios between aqueous and organic phases are usually quite small, and in preparations where the product has to be extracted from aqueous solutions many extractions are needed to ensure even moderate yields of these compounds.

It should also be pointed out that the chloro acids can cause painful blisters in contact with the skin, even over very short periods of time.

C. Phenanthrene derivatives

cis-9,10-Dichloro-9,10-dihydrophenanthrene This was isolated from the products of chlorination of phenanthrene in acetic acid.[64] It was obtained by adding light petroleum (b.p. 60-80°) to the oily mixture of chlorination products which resulted after removal of the acetic acid by distillation under reduced pressure. Recrystallisation of the precipitated material from benzene - light petroleum (b.p. 40-60°), keeping the temperature below 30° at all times, gave a pure product. The m.p., 101°, was determined using a pre-heated block by the method already described.[65] Due to the ease of decomposition, the adduct was stored at -70°.

trans-9,10-Dichloro-9,10-dihydrophenanthrene This was isolated from the residue from the products of chlorination of phenanthrene after the cis-isomer had been removed. The light petroleum solution was concentrated, and the resulting oil was purified by chromatography upon deactivated alumina. The trans-dichloride was recrystallised from chloroform solution by cooling from 50° to 20°. The product, m.p. 157° (using a pre-heated block[65]), was also stored at -70°.

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64. R. Koenigsberger, Ph.D. Thesis, London, 1965.
65. P.B.D. de la Mare and R. Koenigsberger, J.Chem.Soc., 1964, 5327.

trans-9-Acetoxy-10-chloro-9,10-dihydrophenanthrene

This compound represents 10% of the products of chlorination of phenanthrene in acetic acid; the yield may be doubled by carrying out the reaction in 1M-sodium acetate in acetic acid. The acetoxychloride may be isolated from the reaction mixture by chromatography upon deactivated alumina.[65] After removal of the trans-dichloride by light petroleum (b.p. 40-60°), the eluent was changed to ether - light petroleum (1:4) to remove the acetoxychloride. Pure trans-9-acetoxy-10-chloro-9,10-dihydrophenanthrene, m.p. 101°, was obtained by recrystallisation from methanol.

D. Analytical methods

Chloride ion was determined by potentiometric titration with 0.01N-silver nitrate; the end-point was best when the titrations were carried out in acetone solution and were acidified with nitric acid (6M). Volhard's method was used to estimate larger quantities of chloride ion.

Solutions of chlorine were standardised by pipetting samples into an excess of aqueous potassium iodide and estimating the liberated iodine with standard sodium

thiosulphate (0.1N or 0.05N). However, when samples from a reaction mixture were being estimated this method may not always be used, since the liberated iodine may catalyse the chlorination and give a spurious value. When chlorinations were studied in carbon tetrachloride or in chloroform the samples were withdrawn and were pipetted into a mixture of potassium iodide and alkaline standard sodium arsenite; the excess of arsenite was then titrated against standard iodine.

Kinetic methods of analysis

A rough measure of the extent of substitution in the chlorination reactions could be made by titration of the hydrogen chloride formed in the reaction. The chlorination was carried out either in a blackened iodine flask or in a blackened flask fitted with a rubber collar. When the reaction was complete, water was added around the lip of the flask and the stopper was gently eased out in such a way as to trap all the gaseous hydrogen chloride. More water was added, and the aqueous layer was separated and titrated for chloride ion. When the chlorination solvent was miscible with water, the organic products were extracted by ether. Although this technique gave a measure of the extent of substitution, it was complicated in the case of

acetic acid solutions, since hydrogen chloride also results from the formation of acetoxychloride adducts.

In the chlorination of phenanthrene, the extent of formation of the cis- and trans-dichlorodihydrophenanthrenes could be estimated by using their different rates of elimination in the presence of ethoxide ion.[64] After one hour at room temperature in the presence of an excess of sodium ethoxide, the cis-isomer is completely dehydrohalogenated, forming an equivalent amount of chloride ion; the trans-isomer was not significantly attacked under these conditions, and required refluxing for three hours with an excess of ethoxide ion before dehydrohalogenation was complete. The chloroacetoxy-adduct is dehydrohalogenated slowly at room temperature, and is not a source of error since only slight decomposition takes place after one hour. In this way estimates may be made of the proportions of each dichloride adduct in the reaction mixture.

Thin-layer chromatography (t.l.c.) The plates for thin-layer chromatography were prepared by Koenigsberger's method[64], using silica gel nach Stahl containing 13% plaster of Paris as a binding agent. The plates, which were eluted with light petroleum (b.p. 40-60°) or with benzene after spotting with samples and reference compounds as dilute

solutions in the same solvent, were developed by spraying the plate with an aqueous solution of silver nitrate and fluorescein. After irradiation with ultra-violet light from a Hanovia 'Chromatolite' lamp, the compounds with labile halogen appeared as yellow spots seen in visible light, phenanthrene and 9-chlorophenanthrene appeared as yellowish marks, but with a distinct fluorescence, and the acetoxychloride was seen as a yellow spot with a dark perimeter. The R_f values of the identified reaction products were:

(a) Light petroleum as eluent;

	R_f =
9-chlorophenanthrene	0.9
phenanthrene	0.8
dichlorodihydrophenanthrenes	0.4
chloroacetoxyphenanthrene adduct	0.0

(b) Benzene as eluent;

All substituted phenanthrenes and both dichlorodihydrophenanthrenes moved to the solvent front.

chloroacetoxydihydrophenanthrene	0.7

Vapour-phase chromatography (v.p.c.) A Griffin and George machine with a katharometer detector was used; the carrier gas was nitrogen (flow rate *ca.* 1 $l.hr^{-1}$).

Although it was hoped to separate the crotonic acid chlorination products themselves by gas chromatography[cf. 66] this method was abandoned because even the parent acid adhered to the column packing tenaciously excepting at temperatures (ca. 200°) high enough to decompose many of the chlorination products. The chlorination mixtures were therefore converted to their methyl esters, which could be satisfactorily separated using 6 ft. 25% polypropylene sebacate on Celite 540 at temperatures of 125-140°. Either diazomethane or methanolic hydrogen chloride gave quantitative and easy esterification of the acid mixture.

In order to be able to compare chromatograms obtained under slightly differing conditions, methyl crotonate was used as internal marker; all retention times are given relative to that of methyl crotonate.

Retention times of some methyl esters

Methyl crotonate	1.00
Methyl α-chlorovinylacetate	2.40
Methyl α-chloro-β-methoxybutyrate	2.44
Methyl α-chloroisocrotonate	2.6
Methyl α-chlorocrotonate	3.2
Methyl αβ-dichlorobutyrate*	5.2
Methyl γ-chlorocrotonate	6.7
Methyl αβ-dichlorobutyrate**	7.5

66. G. Raupp, Angew.Chem., 1959, 71, 284
* From acid m.p. 63° ** From acid m.p. 78°

Due to the greater sharpness of the peaks of compounds with lower retention times, the variations in these values of retention time increases from ±2% up to ca. ±4%.

The samples were introduced onto the column with a hypodermic needle, using one or two drops of pure ester, mixture of esters, or concentrated solution of ester in a volatile solvent (ether, methanol). Mixtures of products of chlorination of crotonic acid were esterified by removing the solvent under reduced pressure and then (i) adding a solution of diazomethane in ether or (ii) dissolving the crude mixture in methanol, passing in hydrogen chloride until the mixture was saturated, and then heating the solution under reflux on the steam bath for two hours. The sample could be injected onto the column after the bulk of the ether or methanol had been removed under reduced pressure. Both methods of esterification were quantitative; neither caused rearrangement.

Infrared Spectra These were measured on a Unicam SP200 twin beam grating instrument. Solids were examined as a mull in Nujol.

N.m.r. spectra Compounds were examined in solution in deuterochloroform or in carbon tetrachloride, using

tetramethylsilane as internal standard. The author is indebted to Dr. M.D. Johnson of University College for determining and interpreting the n.m.r. spectra.

Kinetic measurements.

Since it has been shown[67] that the reaction of chlorine with phenanthrene in acetic acid is a bimolecular process, and follows second-order kinetics, the rate coefficient, k_2, is given by the equation:

$$k_2 = \frac{2.303}{(a-b).t} \log_{10} \frac{b(a-x)}{a(b-x)}$$

where a = [Phenanthrene], b = [Halogen], and x = moles of reactant consumed at the time t. In all determinations of the reaction rate, the concentration of phenanthrene was kept at least 50% greater than that of the chlorine in order to minimise side-reactions. Salts were dried by heating under reduced pressure in a vacuum oven, the temperature being determined by the ease of decomposition and of sublimation of the salt. Solution of perchloric acid in acetic acid was effected by using pure acetic acid containing enough acetic anhydride to react with the water present in the commercial, 70%, AnalaR perchloric acid used.

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67. N.V. Klassen, Ph.D. Thesis, University of London, 1961

Solutions of perchloric acid prepared in this way decompose slowly at room temperature; a stock solution of perchloric acid in acetic acid (2M) was used to provide solutions of other concentrations, and was discarded when it became coloured.[68]

Measurements of the rates of chlorination were made in general by using a divided flask, one section of which was charged with standard hydrocarbon solution and the other containing standardised chlorine solution in the same solvent. After the vessel had been kept in the thermostat for fifteen minutes, it was shaken so that each solution was thoroughly mixed with the other, and the reaction was quenched after an appropriate interval by adding an excess of potassium iodide in water. The liberated iodine was then titrated with standard sodium thiosulphate.

In the case where the chlorination was carried out in a solvent immiscible with water, the sodium arsenite modification (p. 64) was used.

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68. See "Perchlorates; their properties, manufacture and uses", p. 193 ff. (Ed. J.C. Schumacher; A.C.S. Monograph No. 146, Reinhold, N.Y., 1960)

Chlorination of Crotonic Acid and Related Compounds

A. Chlorination of crotonic acid in chloroform

Crotonic acid (50 g., 0.582 moles) was dissolved in chloroform (350 ml.) and was treated with a solution of iodine (0.1 g.) in chloroform (25 ml.) followed by a solution of chlorine (0.414 moles) in chloroform (450 ml.). After the mixture had been left in the dark for two days all the chlorine had reacted. The clear solution was washed with water, was dried (Na_2SO_4), and was concentrated on the steam bath. The residual oil was esterified by boiling it for ten minutes with methanol which had been saturated with hydrogen chloride at 0° (50 ml.), and the cooled reaction mixture was extracted with ether and with water. The dried (Na_2SO_4) ether solution was concentrated on the steam bath, and the mixture of methyl esters was fractionally distilled under reduced pressure. The following fractions were obtained:

1.	B.p.	$20\text{-}25^\circ/28$mm.	$n^{20} = 1.4266$
2.		$25\text{-}35^\circ/28$ mm.	1.4456
3.		$35\text{-}45^\circ/28$ mm.	1.4484
4.		$45\text{-}60^\circ/28$ mm.	1.4484
5.		$85\text{-}90^\circ/19$ mm.	1.4991
6.		$92\text{-}95^\circ/20$ mm.	1.4991
7.		$93^\circ/19$ mm.	1.4995

The literature values for some of the expected products are: Methyl crotonate, b.p. 121°/760 mm., n^{20} = 1.425; Methyl α-chlorovinylacetate, b.p. 55°/28 mm., n^{20} = 1.440 Methyl αβ-dichlorobutyrate, b.p. 83-86°/28 mm., n^{20} = 1.499.

On the basis of the refractive index, fractions (2)-(4) were apparently rich in methyl α-chlorovinylacetate. These fractions (total yield, 1 g.) were analysed in an attempt to obtain derivatives of the α-chlorovinylacetic ester.

Hydrolysis of some of the ester mixture with cold 2N-sodium hydroxide gave an acid, m.p. 50-100°, whose S-benzylthiouronium salt had m.p. 190°. Mixed m.p. with the corresponding derivative of α-chlorocrotonic acid showed no depression, and hence identified the acid.

An attempt to hydrolyse the methyl ester with dilute hydrochloric acid (cf. p. 59) was unsuccessful.

V.p.c. examination of the ester mixture showed a component with the same retention time as that of synthetic methyl α-chlorovinylacetate. Several further attempts were made to obtain a pure sample of the compound thought to be this compound.

A solution of chlorine (1.28 moles) in chloroform (710 ml.) was added to a solution of crotonic acid (125 g., 1.47 moles) in chloroform (250 ml.). After eight days a

clear, colourless, chlorine-free (starch-iodide paper) solution resulted. As the stopper was removed, much hydrogen chloride was evolved. The solvent was removed under reduced pressure, the residue was dissolved in methanol (250 ml.) and saturated with hydrogen chloride at 0°, and the resulting solution was boiled for three hours. Most of the methanol was removed under slightly reduced pressure, and the mixture of methyl esters was then fractionally distilled under reduced pressure, using a large heated column packed with glass helices. The fractions which were obtained are listed on the next page; their compositions were determined by v.p.c., making the approximation that the areas under each chromatogram peak were directly proportional to the molecular proportions of the constituents.

Fractions (5)-(9) contained much of this unknown ester, and these were used in an attempt to characterise this compound.

The n.m.r. spectrum of fraction (6) showed the absence of methyl α-chlorovinylacetate. It was suggested from the spectrum that the compound might be methyl γ-chlorocrotonate, but this was disproved by comparison with an authentic sample.

Fractions of methyl esters from crotonic acid chlorination products

No.	B.p.	Crotonate	α-Chloro-crotonate	Unknown	αβ-Dichloro-butyrate	Other products*
1	30°/30mm.	93.2%	small	small	-	-
2	26°/30mm.	93.0%	small	small	-	-
3	26-43°/30mm.	68.4%	small	6.8%	small	-
4	43-60°/30mm.	20.3%	4.2%	27.4%	-	-
5	60-66°/30mm.	10.6%	4.9%	73.1%	1.7%	-
6	66-68.5°/30mm.	2.7%	6.1%	75.8%	3.0%	-
7	68.5-71°/30mm.	1.3%	5.3%	79.9%	8.4%	2.7, 1.1%
8	71-73.5°/30mm.	0,1%	5.0%	73.1%	17.9%	1.1, 1.5%
9	73.5-83°/46mm.	0.1%	4.2%	63.7%	29.3%	1.8, 1.0%
10	76-77.5°/32mm.	0.0%	2.7%	44.5%	49.1%	1.1, 2.5%
11	79-80°/32mm.	-	2.1%	37.3%	58.4%	1.0, 1,0%
12	79.5-81°/28mm.	-	1.5%	26.5%	71.6%	0.4%
13	83-83.5°/30mm.	-	0.6%	18.0%	80.5%	0.8%
14	83-83.5°/30mm.	-	0.8%	11.7%	86.9%	0.5%
15	83-83.5°/30mm.	-	0.3%	9.8%	89.5%	0.3%
16	83.5-84°/30mm.	-	0.3%	7.1%	92.3%	0.2%
17	83.5-84/30mm.	-	0.2%	4.8%	94.9%	-
18	83.5-84°/30mm.					
19	83.5-84°/30mm.					
20	83.5-84°/30mm.					
21-26	56-60°/8mm.	-	small	small	Almost entirely	-
27-32	60°/6mm. – 75°/3mm.	Tarry fractions; not analysed.				

*Two unknown compounds, with retention times greater than eight times that of methyl crotonate, were identified. Neither was characterised.

Fraction (8) was completely hydrolysed after boiling it with hydrochloric acid (1.2N; 10 ml.) for eight hours[cf. 62]. Ether extraction of the cooled and diluted reaction mixture gave an oil which provided an S-benzylthiouronium salt whose m.p. was different to that of S-benzylthiouronium α-chlorovinylacetate.

Fraction (7) was hydrolysed with dilute hydrochloric acid as above. The infra-red spectrum of the derived organic acid was quite different to that of authentic α-chlorovinylacetic acid. On treatment with diazomethane, the hydrolysis product gave the same mixture of esters, as shown by v.p.c., and by infra-red spectroscopy, as the original fraction. Hydrolysis therefore does not cause rearrangement of the organic acids.

Vapour-phase chromatography and identification of products

Although the areas of the v.p.c. peaks do not correspond accurately to the amounts of each reaction product, their positions enable identification of at least some of the constituents. It was also shown that the same mixture of products resulted, in similar amounts, regardless of whether the esterification process was carried out using methanolic hydrogen chloride or ethereal diazomethane containing a trace of boron trifluoride.

The chlorination of crotonic acid gave two main products, one of which proved to be the αβ-dichlorobutyric acid, m.p. 63°. The other was thought to be a substitution product from its position in the chromatogram; it was earlier thought to be α-chlorovinylacetic acid. This has now been disproved.

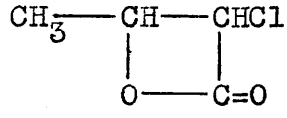
V.p.c. also showed that slightly more than one mole of chlorine was required to react with one mole of crotonic acid; equimolecular amounts of each reactant gave methyl crotonate in the chromatogram of the methyl esters of the chlorination products. When two moles of chlorine were used per mole of acid, only methyl αβ-dichlorobutyrate (from the acid, m.p. 63°) could be found in the ester mixture. The unknown product was decreased in amount when iodine was added to the chlorination reaction, but in the absence of iodine this unidentified product and αβ-dichlorobutyric acid were formed in approximately equal amounts.

The chlorination of methyl crotonate showed the main product to be the same methyl αβ-dichlorobutyrate. There was a trace of the unidentified product, corresponding to about 10% of the amount of methyl αβ-dichlorobutyrate; added iodine decreased the amount of this

unknown product.

N.m.r. identification of products

When equimolecular amounts of chlorine and crotonic acid were reacted together in chloroform, some of the acid remained unattacked. The products were αβ-dichlorobutyric acid, m.p. 63°, and about half this amount of the unidentified compound. The latter was not any of the reference acids. It was thought that it might be a polymeric compound formed from the lactone



If the ratio of chlorine to crotonic acid was increased to 2:1, and iodine was added as a catalyst, the major product was the αβ-dichlorobutyric acid, m.p. 63°, together with about 15% of the polymer. No crotonic acid was present.

Attempts to isolate the β-lactone

(a) Crotonic acid (10 g.) in chloroform (200 ml.) was stirred with calcium carbonate (25 g.) while a slow stream of chlorine was passed into the solution for three hours. The mixture was left overnight, when some of the chlorine was unreacted. The inorganic salts were removed

by filtration, and the chloroform and unreacted halogen were removed under reduced pressure. The remaining solution was pumped off at 25°/1mm., collecting the evolved compounds at -20° (one trap) and -70° (two traps). Although pumping was continued over several hours, no monomeric lactone was obtained; the flask residue contained a mixture of αβ-dichlorobutyric acid and the sticky polymeric product. It seems that hydrogen chloride need not be present to cause the polymerisation of the lactone.

(b) This reaction was carried out using solutions which had been flushed with nitrogen; so far as possible, a nitrogen atmosphere was maintained throughout the chlorination, and all operations were carried out either in the dark or in dim red light.

A solution of chlorine in chloroform (1.5M; 340 ml.) was added to a solution of crotonic acid (21.53 g., 0.25 mole) in chloroform (50 ml.), and the mixture was left in the dark for three days, after which it was divided into seven portions. (i) The solvent and the excess of chlorine were removed under reduced pressure (ii) the solvent and the chlorine were removed under reduced pressure, and the residue was left overnight with methanol (50 ml.) (iii) the residue after the solvent had been removed was left

overnight with acetic acid (50 ml.); (iv) the chloroform solution was washed several times with water, and the resulting organic solution was dried (Na_2SO_4) and concentrated under reduced pressure; (v), (vi), and (vii) were similarly treated but the organic layer was washed with buffer of pH 5.9 (0.05M-NaH_2PO_4), buffer of pH 8.2 (0.05M-Na_2HPO_4), and saturated potassium carbonate respectively before evaporation.

It was shown that treatment with methanol or with acetic acid under these conditions did not add any new compounds to the reaction mixture. Washing the organic solution with various buffers removed some or all of the acidic chlorination products; two hours washing with buffer of pH 5.9 removed all acids and left an oil which was probably the polyester formed from the chlorolactone.

Molecular weight of the polymer

The molecular weight was determined using a Mechrolab osmometer. This was calibrated using benzene (AnalaR) and solutions of purified benzil in benzene; a stock solution of the polymer (1.1683 g.) in benzene (25 ml.) was then diluted appropriately and used; the concentrations of these dilute solutions was then derived from the calibration curve found with benzil.

Dilution	dT	Derived Molarity
1:2	15.25, 15.28, 15.32	0.0310
1:5	9.73, 9.68, 9.67	0.020
1:10	5.02, 5.00, 4.90	0.010

Hence M.W. of polymer = 502 ± 2

This value was checked using a solution of polymer (0.2007 g.) in benzene (25 ml.), which was found to be 0.016M, from which the molecular weight of the polymer is 500.

Estimation of the hydrogen chloride produced during the chlorination of crotonic acid and methyl crotonate in $CHCl_3$

Crotonic acid (moles)	Chlorine (moles)	Iodine (g.)	HCl (moles)	HCl/Cl_2
0.058	0.0327	-	0.01047	0.320
0.058	0.0327	0.0108	0.00949	0.290
0.058	0.0327	0.0216	0.00790	0.244
Methyl crotonate (moles)				
0.050	0.03356	-	0.00397	0.118
0.050	0.03356	0.0215	0.00328	0.098

B. Chlorination of crotonic acid in nitromethane

Crotonic acid (15 g., 0.174 mole) was dissolved in nitromethane (75 ml.) and treated with a solution of chlorine (1.0M; 210 ml.) in the same solvent. On mixing the solutions a deep Prussian-blue colour developed, the temperature rose to 60°, and hydrogen chloride was evolved copiously. After thirty minutes the reaction mixture was distilled at 25°/1mm., collecting the volatile products in traps cooled at -20° and -70°. No lactone was found in either trap. The remaining solvent was then removed and the crude reaction mixture was examined by n.m.r. spectroscopy.

According to this, 50-60% of the crotonic acid had not reacted, and the polymer and αβ-dichlorobutyric acid, m.p. 63°, were present in a ratio of approximately 2:1. The spectrum of the polymer was poorly defined, and there was also a trace of a methyl peak which might have been due to nitromethane.

C. Chlorination of crotonic acid in water

Chlorination of crotonic acid in water gave only α-chloro-β-hydroxybutyric acid as an oil. It finally crystallised to give the isomer, m.p. 85-86°, but the

oil had the infra-red spectrum of the isomer, m.p. 59-60°, derived from trans-addition of Cl-OH to crotonic acid. In the presence of sodium chloride (saturated solution) almost equal weights of the same α-chloro-β-hydroxybutyric acid and the αβ-dichlorobutyric acid, m.p. 63°, were formed. These could be separated by chromatography on silica-gel.

D. Chlorination of crotonic acid in acetic acid.

The chlorination of methyl crotonate in acetic acid gave a mixture of three or four components which could be separated on v.p.c.; one was the ester of αβ-dichlorobutyric acid, m.p. 63°. There were also two peaks, one of relative retention time 2.41, and a major peak with relative retention time 4.48.* The latter peak was ill-defined and was thought to consist of one, or perhaps two, chloroacetoxy adducts. Chlorination in the presence of lithium chloride resulted in the almost exclusive formation of the ester of the αβ-dichlorobutyric acid. In a determination of the hydrogen chloride produced in this reaction (in the absence of added salts), methyl crotonate (2 g.) in acetic acid (25 ml.) reacted with chlorine (0.0125 mole) to give hydrogen chloride (0.0078 mole, 62.8%).

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*See p. 67 for table of relative retention times.

N.m.r. analysis of the products of chlorination of crotonic acid in acetic acid showed that a chloro-acetoxy adduct, probably $CH_3.CH(OAc).CHCl.CO_2H$, comprised 75% of the product mixture, together with about 15% of the dichlorobutyric acid, m.p. 63°; the isomeric dichlorobutyric acid was absent. Crotonic acid remained when equimolecular amounts of chlorine and acid were used.

The presence of lithium chloride increased the extent of formation of αβ-dichlorobutyric acid, m.p. 63°, which was then the main product together with two acetoxychlorides in about 4:1 ratio and an unidentified product which could have been a rearrangement product or a hydroxychloro adduct. The αβ-dichlorobutyric acid, m.p. 78°, was absent.

Chlorination of crotonic acid in perchloric acid and acetic acid (0.5M-$HClO_4$) reduced the amount of acetoxychloride adducts. The dichlorobutyric acid, m.p. 63°, was again the major product, and when two moles of chlorine were used per mole of crotonic acid it was formed almost exclusively.

Extent of decarboxylation during chlorination

Johnson[69] has found some evidence of decarboxylation during the halogenation of cinnamic acid. As the normal working-up procedures would have removed any comparable products from the chlorination of crotonic acid (since the isomeric chloropropenes have b.p. 30-50°/760 mm.), the following experiment was carried out. A solution of crotonic acid (25 g., 0.29 mole) in acetic acid (70 ml.) was treated with a solution of chlorine (0.30 mole) in the same solvent (250 ml.). The solution became warm and lost some hydrogen chloride before the reaction flask could be stoppered; however, it was two hours before all the chlorine had reacted. The solution was then evaporated at 25°, gradually reducing the pressure with a vacuum pump and collecting the distillate in two traps at -70°. Only acetic acid, m.p. 16.5-16.6°, collected in the traps. On adding water to the reaction mixture and to the trapped product completely clear solutions were obtained.

Repeating the experiment with added sodium acetate (0.20 mole) did not give any evidence of decarboxylation products. If any volatile products were formed, they were either lost during the time the chlorine solution was added, or were too volatile to be retained by the traps.

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69. M.D. Johnson, personal communication and forthcoming communication in J.Chem.Soc.

E. Chlorination of crotonaldehyde in acetic acid

Because of the instability of αβ-unsaturated aldehydes towards atmospheric oxidation and polymerisation, several attempts were made to oxidise the products of chlorination of crotonaldehyde to the corresponding acids. In no case was it possible to produce unsaturated carboxylic acids quantitatively, since the available reagents either displace chlorine from the compounds (e.g. ammoniacal silver nitrate, Fehling's solution), attacked the double bond (e.g. permanganate, dichromate), or gave very low yields of any oxidised product (Ag_2O, HgO). The crude chlorination product of crotonaldehyde was so unstable that it became a black tar on leaving for one hour in a sealed ampoule; for this reason, no n.m.r. spectra could be determined.

The acid-catalysed chlorination of crotonaldehyde in acetic acid is so rapid that it is possible to titrate chlorine against crotonaldehyde.

Crotonaldehyde (1.947 g., 0.0278 mole) was dissolved in 0.05M-sulphuric acid in acetic acid (25 ml.), and was titrated using a solution of chlorine in acetic acid (1.084M). The end-point could be determined either by using starch -

iodide paper or by observing the colour of the free halogen. When 24.96 ml. of chlorine solution had been added, the rapid reaction ceased. This corresponded to 0.0271 moles of chlorine; the whole titration took 55 seconds.

Hydrogen chloride produced during chlorination

During the 'fast' reaction, 1.00 moles of crotonaldehyde react with 0.98 moles of chlorine. Because of the speed of the reaction, crotonaldehyde was weighed out in a fragile glass bulb which was placed in an iodine flask containing the chlorine solution. The reaction was initiated by shaking the flask, whereupon the bulb broke and reaction occurred almost immediately.

In this way, crotonaldehyde (4.0597 g., 0.0577 moles) was treated with a solution of chlorine (40 ml., 1.38M) diluted with 0.03M-sulphuric acid in acetic acid (100 ml.) when 0.00514 moles (9.32%) of hydrogen chloride was formed.

Attempted characterisation of the reaction products

Crotonaldehyde (5 g., 0.07 mole) was dissolved in 0.05M-sulphuric acid in acetic acid (25 ml.) and treated with chlorine solution (1.2M, 50 ml.). The mixture was left for one hour, and then poured into a hot solution of potassium permanganate (30 g.) in water (500 ml.). This mixture was heated for three hours on the steam bath, and

the cooled reaction product was extracted with ether. The residue from the evaporation of solvent from the dried organic layer was chromatographed on a silica gel column. Both isomers of αβ-dichlorobutyric acid were isolated in approximately equal yield, but as there was some overlapping of the fractions a quantitative separation could not be achieved.

Despite a previous report[42]*, aqueous chlorine is not a satisfactory oxidising agent. Crotonaldehyde (1.947 g., 0.0278 mole) in 0.05M-sulphuric acid in acetic acid was titrated with chlorine solution (1.084M). After the fast reaction, a further molecular equivalent of chlorine was added and the mixture was left overnight, when a large excess of water was added and the solution was heated under reflux for three hours on the steam bath, using a dry-ice/acetone condenser. The cooled solution was extracted with ether, and the ether extract was washed with water, was dried (Na_2SO_4), and the solvent was removed.

The residue, m.p. 62-63°, was butyl chloral hydrate $CH_3.CHCl.CCl_2.CH(OH)_2$ (2.344 g., 41% yield based on crotonaldehyde).

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*See p. 40 of this thesis.

Chlorination of Phenanthrene

A. Stabilities of some of the chlorination products

9-Chlorophenanthrene is stable at room temperature and is unaffected by alkali; it is formed by the thermal decomposition and by the alkaline dehydrohalogenation of the 9,10-dichloro-9,10-dihydrophenanthrenes.

trans-9,10-Dichloro-9,10-dihydrophenanthrene slowly loses hydrogen chloride at room temperature. It was found to be stable to sodium acetate (1.5M) in acetic acid and to perchloric acid (2M) in acetic acid over one day, but it decomposed partly after a week at room temperature in the perchloric acid solution.

cis-9,10-Dichloro-9,10-dihydrophenanthrene must be stored at -70° because it also is unstable at room temperature. After one day it did not appreciably decompose either in 1.5M-sodium acetate in acetic acid or in 2M-perchloric acid in the same solvent, but after a week in the perchloric acid solution it had almost completely decomposed to form 9-chlorophenanthrene.

trans-9-Acetoxy-10-chloro-9,10-dihydrophenanthrene was completely decomposed into 9-chlorophenanthrene after one day in 2M-perchloric acid in acetic acid. After some weeks in saturated hydrogen chloride solution in

acetic acid it was completely converted to a dichlorodihydrophenanthrene, the stereochemistry of which was not determined.[70]

Estimation of the reaction products

In the chlorination of phenanthrene in acetic acid or in some other participating solvent, the hydrogen chloride which is evolved during the reaction results from substitution and from the formation of acetoxychlorides (or analogous compounds in other solvents). In the organic reaction products, chloride ion liberated by treatment of the mixture with alkali at room temperature over one hour results only from the dehydrohalogenation of the cis-dichlorodihydrophenanthrene; the further quantities of chloride ion which result on boiling the reaction product with more alkali are due to the dehydrohalogenation of the trans-dichlorides and of the trans - acetoxychloride, which yields only 9-acetoxyphenanthrene under these conditions.[70]

In the present work, the saponification of the organic chlorination products was carried out by dissolving the residue from removal of the solvent under reduced pressure at below 30° in equal volumes

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70. R. Koenigsberger, Ph.D. Thesis, University of London, 1965.

of benzene and 95% ethanol, and treating aliquot amounts of the solution with alkali.

Hence HCl formed ≡ 9-chlorophenanthrene + acetoxychloride adduct

= A + B;

Cl^- formed in 'cold' hydrolysis ≡ cis-dichloride adduct

= C;

Cl^- formed in 'hot' hydrolysis ≡ cis- and trans-dichloride adducts + trans-acetoxychloride adduct

= B + C + D;

A + B + C + D = 100%

From these values, A, B, C, and D can all be estimated.

B. Effect of perchloric acid upon the chlorination products

The table on p. 91 shows that in low concentration perchloric acid increases the extent of substitution, and decreases the extent of addition, especially trans addition. The acetoxychlorides are destroyed when the reaction mixture is left overnight. When larger concentrations of perchloric acid are used, the acetoxychlorides are either not formed or else are destroyed rapidly.

Effect of perchloric acid upon the chlorination products of phenanthrene

$[HClO_4]$	HCl evolved / Cl_2	Cold hydrolysis	Hot* hydrolysis	Total
0.00M	52-55%	34-36%	56-61%	108-116%
0.05	65.7	30.2	33.7	99.4(a)
0.05	68.5	40.5	44.2	112.7(b)
0.05	70.1	39.3	43.2	113.2(b)
0.2	76.7	21.3	22.4	99.1(a)
0.2	76.5	23.4	29.2	105.7(b)
0.2	75.5	28.3	30.8	106.3(b)
0.4	81.2	18.9	21.2	102.4(a)
0.5	80.2	16.1	19.1	99.3(a)
0.5	79.5	18.4	22.1	101.6(b)
1.2	85.5	12.7	13.9	99.4(a)

*Hot hydrolysis measures the amount of both dichlorides and the acetoxychlorides
(a) Reaction mixture left overnight before working up.
(b) Reaction mixture left 1-2 hours before working up.

C. Effects of added salts on the chlorination products

There was some evidence for the formation of a cis - acetoxychloride adduct which was too unstable to be isolated by column chromatography. Because of this, and because the differences in rates of dehydrohalogenation of the adducts does not give a very accurate measure of the amounts present, the crude mixtures of reaction products

were examined by n.m.r.. spectroscopy.

Phenanthrene was dissolved in acetic acid or in a solution of an electrolyte in acetic acid and then a solution of chlorine in acetic acid was added. After the solution had been left overnight it was evaporated under a pressure of *ca.* 5 mm.. Benzene was added to remove the last traces of acetic acid, and the oily reaction mixture was examined in carbon tetrachloride solution. When the reaction had been carried out in the presence of an electrolyte, the chlorination product mixture was dissolved in benzene and filtered from the salt, which was washed repeatedly with benzene to remove all organic materials.

Chlorination products of phenanthrene in the presence of salts

Electrolyte:	None	1M-LiCl	1M-NaOAc
cis-Dichloride adduct	59-60%	48%	47-51%
trans-Dichloride adduct	13-16%	34%	4-8%
cis-Acetoxychloride adduct	7.5%	3.8%	7.8%
trans-Acetoxychloride adduct	17%	14%	38.8%

*All values are expressed as percentages of total adducts

Koenigsberger[70] found that the amount of substitution remained reasonably constant (*ca.* 40%) when 0.1M-lithium

chloride and 0.1M-sodium acetate were added. Assuming that this is still true for 1M-solutions of these salts, the amounts of each adduct may be expressed as percentages of the total chlorine consumed:

Electrolyte:	None	1M-LiCl	1M-NaOAc
cis-Dichloride adduct	36.2%	29.6%	29.9%
trans-Dichloride adduct	9.1%	21.0%	3.6%
cis-Acetoxychloride adduct	4.6%	2.4%	4.8%
trans-Acetoxychloride adduct	10.3%	8.6%	23.5%

Kinetics of chlorination of phenanthrene in acetic acid

$[\text{Phenanthrene}]_o$	$[\text{Chlorine}]_o$	[Salt]	$k_2(M^{-1}.min^{-1})$
0.0160-0.0152M	0.0064-0.0044M	None	25.8
0.0161M	0.0050-0.0045M	0.08M-NaOAc	25.2
0.0161M	0.0046M	0.24M-NaOAc	29.3
0.0161M	0.0045M	0.60M-NaOAc	38.6
0.0161M	0.0050-0.0046M	0.08M-LiCl	33.9
0.0161M	0.0045-0.0040M	0.19M-LiCl	55.6
0.0161M	0.0051-0.0050M	0.40M-LiCl	133.5
0.0154M	0.0047-0.0044M	0.004M-$LiClO_4$	32.2
0.0161M	0.0064-0.0038M	0.08M-$LiClO_4$	42.6
0.0161M	0.0070-0.0020M	0.16M-$LiClO_4$	85

$[Phenanthrene]_o$	$[Chlorine]_o$	[Salt]	$k_2(M^{-1}.min^{-1})$
0.0161M	0.0053-0.0036M	0.40M-$LiClO_4$	186
0.0161M	0.0039-0.0033M	0.80M-$LiClO_4$	730
0.0161M	0.0054-0.0050M	0.75M-$HClO_4$ + 1% water	940
0.019M	0.0035-0.0030M	0.15M-$HClO_4$	123
0.0127M	0.0036-0.0041M	0.33M-$HClO_4$	258
0.0190-0.0160M	0.0045-0.0027M	0.48M-$HClO_4$	344
0.0161M	0.0020-0.0010M	0.80M-$HClO_4$	730

B. Chlorination of phenanthrene in solvents other than acetic acid

(a) Chloroform

$[Phenanthrene]_o$	$[Chlorine]_o$	[Added reagent]	$k_2(M^{-1}.min^{-1})$
0.0465M	0.0164M	None	0.73 ± 0.04
0.0440M	0.0160M	0.0047M-HCl	1.14 ± 0.16
0.0493M	0.0172M	0.0493M-HCl	2.43 ± 0.44
0.0297M	0.0166M	0.0505M-HCl	2.85 ± 0.48
0.0465M	0.0157M	$2.1x10^{-6}$M-I_2	6.3 ± 1.3
0.0290M	0.0083M	$9.8x10^{-6}$M-I_2	10.8 ± 1.5

It is evident from the large errors in k_2 that this system is not particularly suitable for kinetic study. Light, oxygen, and adventitious catalysts all contributed to the lack of reproducibility of the results, and it is

probable that the mechanism of the chlorination is rather more complex than the simple bimolecular rate coefficient would imply. The results definitely indicate catalysis both by hydrogen chloride and, to a greater extent, by iodine; some of the variation in k_2 of the chlorination carried out in the absence of added compounds is undoubtedly due to autocatalysis by hydrogen chloride.

The reaction products, which were estimated in a similar way to those used for the products of chlorination in acetic acid are described in the following table:

Added reagent:	None	HCl	Iodine
HCl formed	41.5%	Not detd.(c)	41.1%
Cl^- from cold hydrolysis(a)	41.0%	40.5%	45.0%
Cl^- from hot hydrolysis(b)	58.5%	60.7%	57.7%
Total	100.0%	-	98.8%

(a) Due to cis-dichloride adduct
(b) Due to both cis and trans-dichloride adducts
(c) Calculated to be 39.3%

(b) Nitromethane

Although nitromethane is only slightly soluble in water, reaction kinetics were studied by pipetting samples into a solution of standard sodium thiosulphate containing an excess of potassium iodide and back -

titrating with standard iodine solution. Alkaline sodium arsenite could not be used in these cases because of the alkali-catalysed reaction of nitromethane with iodine, which caused considerable drifting of the endpoint.

The results of the kinetic studies are tabulated:

$[\text{Phenanthrene}]_o$	$[\text{Chlorine}]_o$	k_2 ($\underline{M}^{-1}.\text{min}^{-1}$)
0.01036$\underline{M}$	0.00284$\underline{M}$	140 ± 1
0.01036$\underline{M}$	0.00248$\underline{M}$	133 ± 3
0.00921$\underline{M}$	0.00216$\underline{M}$	137 ± 15

Mean k_2: 137 ± 10 $\underline{M}^{-1}.\text{min}^{-1}$

These results indicate that the reaction is faster in nitromethane than in acetic acid (k_2 = 26$\underline{M}^{-1}.\text{min}^{-1}$) or in chloroform ($k_2$ = 0.7) but that the reaction is still first order with respect to each reactant.

In the same way as before, measurements of the chloride ion formed directly and during saponification gave a measure of the extents of substitution and of addition:

HCl formed from substitution:	64.8%
Cold hydrolysis (<u>cis</u>-dichloride):	22.6%
Hot hydrolysis (<u>trans</u>-dichloride + <u>cis</u> isomer):	33.8%
Total:	98.6%

DISCUSSION

DISCUSSION

A. Chlorination of crotonic acid

The chlorination of crotonic acid and some of its derivatives was studied at the beginning of the gentury[71]. At this time neither the absolute stereochemistry of the two crotonic acids nor the stereochemistry of addition had been well delineated; although Michael[71] showed that 96% of the αβ-dichlorobutyric acids formed from the chlorination of crotonic acid was the isomer, m.p. 63°, the evidence of the structure of this compound rested upon its dehydrohalogenation to give α-chloroisocrotonic acid. This could be explained by postulating that both addition and elimination took place in a cis or a trans sense, but could not differentiate between these.[72]

The final evidence came when the stereochemistry of the crotonic acid, m.p. 72°, was linked with that of fumaric acid[72], whose stereochemistry was evident from the fact that maleic acid, its isomer, readily forms an anhydride and hence must have both carboxylic acid groups on the same side of the olefinic bond.

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71. A. Michael and co-workers, J.prakt.Chem., 1895, 52 [2], 344; 1907, 75 [2], 112; 1892, 46 [2], 238, 258; Ber., 1908, 41, 2907; Am.Chem.J., 1887, 9, 281.
72. K. v. Auwers, Ber., 1923, 56, 721.

In this way, crotonic acid, m.p. 72°, was shown to be the trans-isomer; similarly, isocrotonic acid of m.p. 15° was the cis-isomer.

Since this early work on the chlorination of the crotonic acids there has been little definitive work on the reaction products, although yields of 88% have been claimed in the synthesis of αβ-dichlorobutyric acid, m.p. 63°, from the chlorination of crotonic acid in carbon tetrachloride. Bailey[73] has reinvestigated the products of chlorination of crotonic acid, methyl crotonate, and crotonaldehyde in various solvents. The reaction products were separated by column chromatography, which was not invariably effective, and they were characterised by comparison with authentic samples, by infra-red spectroscopy, and by degradation reactions.

The product of the chlorination of crotonic acid in water was, predictably, α-chloro-β-hydroxybutyric acid; in saturated salt solution, however, the products were equal weights of α-chloro-β-hydroxybutyric acid and the αβ-dichlorobutyric acid, m.p. 63°; each of these compounds resulted from trans addition across

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73. J.E. Bailey, M.Sc. Thesis, University of London, 1963.

the double bond. Using Bailey's results, it can be shown that chloride ion is seven times as powerful as water towards the initially formed carbonium ion (IV)

$$CH_3.\overset{+}{C}H.CHCl.COOH$$

(IV)

In other solvents the products of chlorination were not so easily predicted. Reactions were carried out with chloroform, carbon tetrachloride, methylene chloride, and nitromethane as solvent. In most cases some of the "normal" addition product, αβ-dichlorobutyric acid of m.p. 63°, was part of the reaction product, and unusual results were only obtained in the following instances:

(a) Chlorination in chloroform With crotonic acid the reaction seemed to take place in two stages; a "fast" reaction in which one mole of chlorine was consumed per mole of crotonic acid consumed, and a slower reaction, at the end of which two moles of chlorine had been taken up. In either case, 35% of the crotonic acid was unattacked.[73] At the end of the slow reaction an oily product was isolated. It was not

a simple product of addition or of substitution and was not identified. At the end of the 'fast' reaction, another oil ('Y') was isolated; infra-red analysis of the two oils was consistent with Bailey's deduction that 'Y' (an unsaturated acid) would add chlorine to form 'X'.

The compound 'Y' was believed to be α-chlorovinylacetic acid, since its infra-red spectrum differed from that of α-chlorocrotonic acid, α-chloroisocrotonic acid, or a mixture of the two, and the position on the chromatogram indicated that the compound was a product of substitution. It was identified by esterification of the oil with methanolic hydrogen chloride, followed by treatment of the ester with N-sodium hydroxide at room temperature, when chromatography of the acidic product gave α-chlorocrotonic acid in 50% yield by weight. This compound was thought to be formed by isomerisation of the chlorovinylacetic acid; the alternative possibility of a base-catalysed dehydrohalogenation, or of the isomerisation of some other substitution product, was not considered.

(b) Chlorination in nitromethane

The reaction of crotonic acid with chlorine in nitromethane gave large amounts (ca. 75% by weight) of α-chloro-β-hydroxybutyric acid, together with an unidentified oil ('A') and a solid ('B'), m.p. 105-6°. Neither of these compounds could be satisfactorily identified; the formation of the hydroxychloro-acid was explained by postulating the formation of α-chloro-β-butyrolactone, which subsequently hydrolysed during chromatography. The compound 'B' was only obtained in the presence of hydrogen chloride; the oil 'A' was not obtained pure, but was contaminated with αβ-dichlorobutyric acid.

This was the state of knowledge when the present work was begun. Vapour-phase chromatography was first used to identify other products of the reaction of chlorine with crotonic acid in chloroform, since one of the disadvantages of the previous work was that it could give a false picture of the products of reaction. The reasons for this were that the reaction products were all quite soluble in water and held to the chromatography column tenaciously; it was rare to be able to account for more than 50% of the reactants by

considering the weights of products in the eluent, and the more polar compounds might well be retained under these conditions.

In the case of v.p.c., the methyl esters of the reaction products were separated[74] ; this procedure lessened the chances of being unable to identify a constituent because of its adherence to the column. The methyl esters of the constituent acids were also capable of separation by fractional distillation; this gave a means of concentrating some of the reaction products and being able to identify them more satisfactorily. The compounds which were identified, by comparison with authentic compounds, were methyl α-chlorocrotonate, methyl αβ-dichlorobutyrate (from the acid, m.p. 63°), and a compound with the same retention time as methyl α-chlorovinylacetate. However, this was not methyl α-chlorovinylacetate, since neither the infrared nor the n.m.r. spectrum agreed with that of an authentic sample.

The richest fraction of this unidentified compound contained 80% of the product, by v.p.c. analysis; it was definitely not methyl α-chlorocrotonate, methyl α-chloro-isocrotonate, or methyl γ-chlorocrotonate. Hydrolysis of

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74. For a further discussion, see p. 67.

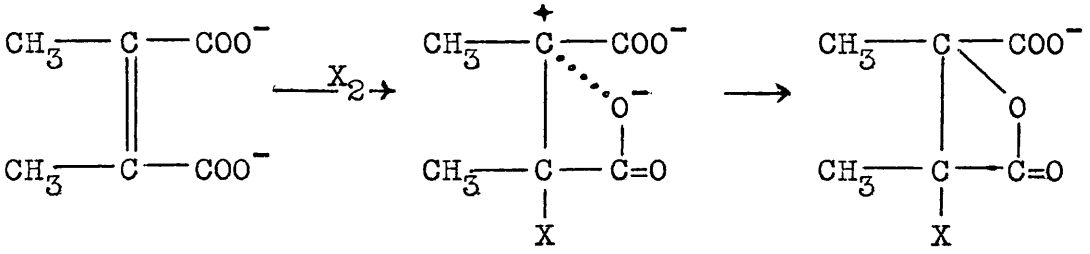
this fraction gave a liquid acid which was not α-chlorovinylacetic acid (i.r. spectrum), and which provided an S-benzylthiouronium salt, m.p. 135.5-137°, which was not identical with that of α-chlorovinylacetic acid (m.p. of S-benzylthiouronium derivative, 120-1°). It is believed that this compound is methyl α-chloro-β-methoxybutyrate (b.p. 72°/20mm.; relative retention time = 2.44) whose parent acid, a liquid, gives an S-benzylthiouronium salt, m.p. 138-9°. The significance of this result is discussed later in this thesis (p. 109).

Chlorination of crotonic acid in acetic acid

As well as the addition of chlorine and substitution by chlorine, a further reaction can take place. The solvent can divert some of the addition product to form α-chloro-β-acetoxybutyric acid, probably by reaction of the solvent with the initially formed chlorocarbonium ion. While the attempts to synthesise such compounds, whether by acetylating α-chloro-β-hydroxybutyric acid or by chlorinating crotonic acid in acetic acid with t-butyl hypochlorite, were unsuccessful, evidence for the formation of such acetoxychlorides was found in the n.m.r spectra of the reaction mixtures, and similar evidence of these compounds

was found in the reaction mixture when molecular chlorine was the reagent.

The chlorination of crotonic acid would also be expected to involve the formation of a β-lactone. An instance of the formation of such a compound occurs in the chlorination and bromination of dimethylmaleic and dimethylfumaric acids.[75] In aqueous solution, the sodium salts of these acids give, on halogenation, a β-lactone; this apparently results from an internal attack by the carboxylate group upon the incipient carbonium ionic centre, which is formed in the first stage of the addition reaction:



The evidence for such a β-lactone structure comes from the formation of a halohydrin adduct as well as from the direct isolation of the lactone intermediate; it was also shown that, under the experimental conditions, the dihalogenosuccinic acids formed neither the lactone nor the chlorohydroxysuccinic acid.

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75. P.D. Bartlett and D.S. Tarbell, J.Amer.Chem.Soc., 1937, 59, 407.

Formally, there is no reason why such an internal cyclisation could not occur in the crotonic acid system, and although it was not possible to isolate the monomeric lactone, the polyester derived from it could be obtained. Its identity was established by n.m.r. spectroscopy; its molecular formula is believed to be

$$CH_3.CH(OH).CHCl.CO.[O.CH(CH_3).CHCl.CO]_3.OH$$

in agreement with the derived molecular weight (Found, 501 ± 1. $C_{16}H_{22}Cl_4O_9$ requires 500).

The role of a β-lactone structure

Many of the unusual products of chlorination of crotonic acid may be rationalised by postulating the formation of an unstable β-lactone which may then polymerise to form a poly-ester.

The chlorination of crotonic acid in chloroform has been reported to give 45.8% substitution (Bailey)[73]. Since a maximum of 2% of the reaction product can be α-chlorocrotonic acid or its precursors (including α-chlorovinylacetic acid)[76], ca. 44% of the reaction product must result from substitution or from a reaction

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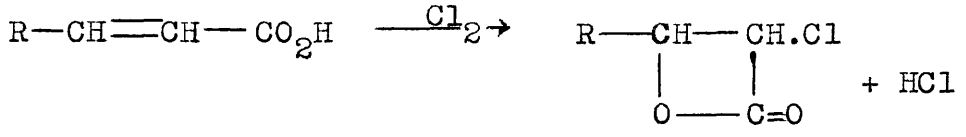
76. In an isotopic dilution experiment, the amount of αβ-dichlorobutyric acid, m.p. 78°, present was determined by measuring the amount of α-chlorocrotonic acid formed by dehydrohalogenation with alkali. A value of 2% was found (ref. 73).

in which one mole of chlorine gives one mole of hydrogen chloride. The present work has shown that substitution does not involve the formation of α-chloroisocrotonic acid or of γ-chlorocrotonic acid; nor is α-chlorovinyl-acetic acid formed. A β-lactone, formed by the equation



would also be formed with the liberation of hydrogen chloride. Since no attempts to isolate it have been successful, it is evidently less stable towards polymerisation than β-propiolactone itself, but the postulation of a β-lactone intermediate can explain the following observations:

(a) The distillation of the products of chlorination of crotonic acid in chloroform, whether at atmospheric pressure or under reduced pressure (20 mm.), gives two main fractions. The lower-boiling fraction is the αβ-dichlorobutyric acid, m.p. 63°; after this has distilled an exothermic reaction takes place and α-chlorocrotonic acid distils. There is no reason to suppose that the chlorocrotonic acid results from thermal decomposition of the αβ-dichlorobutyric acid, since the αβ-dichloro-butyric acid distills, unchanged, at a lower temperature.

The temperature (150-200°) at which the α-chlorocrotonic acid distils is almost independent of the pressure within the system, and suggests that the most reasonable explanation is the decomposition either of α-chloro-β-hydroxybutyric acid or of a polymer derived from α-chloro-β-butyrolactone. Under anhydrous conditions it is unlikely that the chlorohydroxybutyric acid could be formed in bulk; however, the behaviour of the still-pot residue upon attempted distillation is very similar to that of β-propiolactone polymer, which decomposes at about 200° to form acrylic acid in high yield.[77]

(b) The component of relative retention time 2.4, which occurs in the esterified products of chlorination of crotonic acid, does not occur to any appreciable extent in the products of chlorination of methyl crotonate. This compound must arise from some intermediate formed only by crotonic acid, and not by the ester; the only obvious choice would be a β-lactone, since the formation of this intermediate formally requires loss of an acidic proton from crotonic acid but the far less probable removal of a methyl group from the ester. In keeping with this premise, the

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77. See L.F. Fieser and M. Fieser, "Organic Chemistry", p. 319 (Heath, Boston, 1950).

amount of hydrogen chloride produced in the chlorination of crotonic acid is 46% of the chlorine consumed[73]*, whereas for methyl crotonate the value is only 11%. It is suggested that the compound taken by Bailey[73] to be α-chlorovinylacetic acid was in fact a polymeric form of the β-lactone. By analogy with β-propiolactone[77], this would be expected to form a mixture of methyl α-chlorocrotonate and methyl α-chloro-β-methoxybutyrate upon treatment with methanolic hydrogen chloride. The latter compound has been synthesised[78] and the evidence whereby it might be confused with methyl α-chlorovinylacetate has been presented (p. 103); saponification would give a mixture of α-chlorocrotonic acid and α-chloro-β-methoxybutyric acid from the mixture of methyl esters formed from the β-lactone or its polymer. Of these two acids, α-chlorocrotonic acid is a solid and hence readily separated by crystallisation from the liquid chloromethoxybutyric acid. Finally, the parent lactone polymer would show, in the infra-red spectrum, C=O, O-H, and C-Cl bands which would also be shown by a simple unsaturated chloro-acid.

(c) The chlorination of crotonic acid in nitromethane proceeds rapidly and exothermically; slightly more than

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*See p. 98.

78. R. Bolton, personal communication.

two moles of chlorine are consumed and slightly more than two moles of hydrogen chloride are produced per mole of acid.[73] The main organic product is α-chloro-β-hydroxybutyric acid. This may result from adventitious water in the solvent; it may also result from the hydrolysis of a β-lactone during column chromatography. The latter explanation was favoured by previous workers[73]; however, as methyl crotonate was also reported to show the same large amount of hydrogen chloride evolved (although the products of the reaction were not identified) it seems likely that a small amount of water in the solvent, together with much hydrogen chloride and a good solvating solvent, might be sufficient either to hydrolyse the ester and to open an initially-formed β-lactone system or, alternatively, to react with a chlorocarbonium ion. Since it is difficult to dry nitromethane, and since in most cases the reaction was worked up by pouring the mixture into water and then extracting the products with ether, the intervention of adventitious water seems the most likely explanation of the results. It is certain, however, that the β-lactone polymer is the major product of reaction in the chlorination of crotonic acid in nitromethane (p. 81).

It is unlikely that a β-lactone intermediate is formed in water when crotonic acid is treated with chlorine. In this reaction it has been found (p. 99) that the relative nucleophilicity of chloride, compared with water, is about 7. If β-propiolactone is taken as a model, Swain's equation[79]

$$\log k/k_o = s.n$$

indicates that the relative amounts of αβ-dichloride and α-chloro-β-hydroxy derivatives should be 200:1 when crotonic acid is chlorinated in saturated salt solution. Similarly, the reaction of β-propiolactone with saturated salt solution gives 91% yields of β-chloropropionic acid[77]. The low value of the relative nucleophilicity of chloride ion seems to indicate a carbonium ionic intermediate rather than a lactone; values of the same order are found in the competition between chloride ion and water in some S_N1 heterolyses.[80]

Reaction products from the chlorination of crotonic acid

In chloroform solution, crotonic acid reacts with one mole of chlorine to give αβ-dichlorobutyric acid, m.p. 63° (48%), and two unidentified products, one of which was believed to be α-chlorovinylacetic acid[73].

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79. C.G. Swain, J.Amer.Chem.Soc., 1948, 70, 1119.
80. C.K. Ingold, E.D. Hughes, and co-workers, J.Chem.Soc., 1940, 979 and successive papers.

In the present work, we have identified the same αβ-dichlorobutyric acid, α-chlorocrotonic acid, and have strong evidence for the formation of α-chloro-β-butyrolactone. An unidentified product, with a relative retention time of 1.87, was also found in the methyl esters of the chlorination product; it was not the ester of α-, β-, or γ-chlorocrotonic acid, nor of α- or β-chloroisocrotonic acid; it has not been possible to assign a structure to the compound. α-Chloroisocrotonic acid and γ-chlorocrotonic acid have not been found; α-chlorovinylacetic acid may be present, but in small amount.

Bailey[73] found that αβ-dichlorobutyric acid, m.p. 63°, accounted for 48.9% of the chlorine consumed, and that 45.8% of the chlorine gave hydrogen chloride in the reaction. She also showed that treatment of the chlorination product with alkali gave no more than 2% α-chlorocrotonic acid, and found that 5.4% of the chlorine was present in the aqueous washings of the chlorination reaction mixture as organic chloro-acids.

The present work has shown that a β-lactone or its polymer is formed, together with about twice as much αβ-dichlorobutyric acid (n.m.r.; p. 77), and that the

other possible substitution and addition products are not formed to any great extent (v.p.c., p. 74). The αβ-dichlorobutyric acid can be washed out of a chloroform solution of the reaction products, leaving the polymeric compound (p. 78). From this results, it seems likely that the compound washed out of the organic solution in Bailey's determination of the reaction products was αβ-dichlorobutyric acid, m.p. 63°. Combining these results, the best distribution of the reaction product composition seems to be:

αβ-Dichlorobutyric acid, m.p. 63°	53%
αβ-Dichlorobutyric acid, m.p. 78°	~ 1%
α-Chlorocrotonic acid	2%
α-Chloro-β-butyrolactone	44%*

*This value is taken from Bailey's determination of the hydrogen chloride formed, and from v.p.c. measurements. N.m.r. spectroscopy, which gives a lower value, was discarded because ths spectrum of the polymer was not well defined. Although no decarboxylation products were found, this may be due to their volatility and not to their absence from the reaction mixture. If chloro-decarboxylation does occur, the amount of the β-lactone would be correspondingly decreased.

Chlorination of crotonic acid in acetic acid

In acetic acid, solvent intervention to give acetoxychloride adducts comprises the major mode of reaction. The estimation of the reaction products was generally made by n.m.r. spectroscopy. It was found that substitution accounted for less than 2% of the total product; addition to form α-chloro-β-acetoxybutyric acid comprised 70% of the reaction when equimolecular amounts of chlorine and crotonic acid were reacted together; the only other identifiable product was the αβ-dichlorobutyric acid, m.p. 63°. In the presence of an excess of chlorine these two addition products were formed, together with 10-15% of a new, unidentified compound which might have arisen either by rearrangement or by oxidation.

The course of the reaction can be described simply as the competition of solvent and chloride ion for the first-formed chlorocarbonium ion:

$$\mathrm{Me.CH{:}CH.CO_2H} \xrightarrow{Cl} \mathrm{Me.\overset{+}{C}H.CHCl.CO_2H} \begin{cases} \rightarrow \mathrm{Me.CHCl.CHCl.CO_2H} \\ \rightarrow \mathrm{Me.CH(OAc).CHCl.CO_2H} \end{cases}$$

in the same way the reactions of crotonic acid with aqueous solutions of chlorine were explained.

Added lithium chloride gave again the dichlorobutyric acid, m.p. 63°, but in this instance two acetoxychlorides were found. One was the α-chloro-β-acetoxy adduct which was found when chlorination was carried out in the absence of added electrolyte; the other isomer, which was present in small amount and could not be positively identified, could possibly have been the stereoisomer resulting from a formally cis addition of ClOAc. It has already been pointed out that deactivated olefins such as crotonic acid are susceptible to nucleophilic attack, and it is possible that this other adduct results from such a reaction.

In the reaction of chlorine and crotonic acid in the presence of perchloric acid it was again found that two acetoxychloride adducts were present, but that the only other identifiable product, the major component of the mixture, was αβ-dichlorobutyric acid, m.p. 63°. In the phenanthrene system, perchloric acid has the effect of increasing the extent of substitution and also destroys acetoxychlorides to form substitution products (p. 91). If the addition across the 9,10-bond of phenanthrene is quantitatively similar to that across the double bond of crotonic acid, chlorination in the presence of perchloric

acid should give rise to α-chlorocrotonic acid; but in fact neither this, α-chloroisocrotonic acid, nor γ-chlorocrotonic acid were present above 2% concentration. Perchloric acid would also be expected to favour the nucleophilic addition of chlorine since partial protonation of the substrate could occur:

$$\mathrm{Me.CH{:}CH.CO_2H} \xrightarrow{H^+} \mathrm{Me.CH{:}CH.\overset{+}{C}(OH)_2} \longleftrightarrow \mathrm{Me.\overset{+}{C}H.CH{:}C(OH)_2}$$

$$\downarrow$$

$$\mathrm{Me.CHCl.CH{:}C(OH)_2}$$

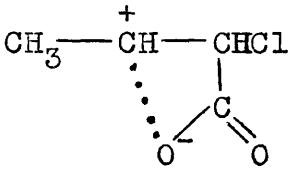
$$\downarrow$$

$$\mathrm{Me.CHCl.CHCl.CO_2H}$$

The favouring of the formation of αβ-dichlorobutyric acid may be due to such a sequence, since in acidic acetic acid the only nucleophiles present would be chloride ion and acetic acid, of which the halide ion would probably be the more reactive. However, the difference in reactivity is not great; it is also possible that the addition of chlorine is taking place at an ion-pair with the result that the proton transfers and the ionisation of the chlorine molecule are taking place in a momentarily highly polar environment:

$$\mathrm{Me.CH{:}CH.\underset{Cl\text{-}Cl}{\overset{+}{C}}(OH)_2 \quad ClO_4^-}$$

The formation of two acetoxychloride adducts when the chlorination is carried out in the presence of lithium chloride may be due to the basicity of chloride ion in this solvent.[88] Under such conditions crotonic acid would exist partly as the anion, and the intermediate zwitterion



would be shielded from attack at one side; solvolysis of this ion would be espected to give the stereoisomeric α-chloro-β-acetoxy adduct.

Although this ion might also be thought to give rise to the αβ-dichlorobutyric acid, m.p. 78°, by attack of chloride ion, the competition for the carbonium ion now involves acetate ion (from the equilibrium Cl^- + HOAc = HCl + OAc^-) as well as chloride ion and acetic acid. Of these, acetate ion is the strongest nucleophile.

B. Chlorination of crotonaldehyde

There is no evidence that crotonaldehyde contains more than a small proportion of the cis compound. Only trans-crotonic acid has been found as the product of oxidation of crotonaldehyde[82], and although the higher solubility and lower melting point of the cis-acid might make its estimation difficult, the yields of trans-acid are close to quantitative when oxidation is carried out using heavy metal oxides[82] at low temperatures, which implies that crotonaldehyde exists predominantly as the trans-isomer.

Bailey[73] found that the chlorination of crotonaldehyde in chloroform gives only 1.5% substitution, and that the products of the reaction, after oxidation with potassium permanganate in dilute sulphuric acid solution, consisted of both isomers of αβ-dichlorobutyric acid. The acid, m.p. 63°, comprised 70% of the dichlorobutyric acids isolated by chromatography; this isomer would result from the product of trans-addition of chlorine to trans - crotonaldehyde. In the presence of a deficiency of chlorine another, unidentified product was formed. This

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82. J.E. Young, J.Amer.Chem.Soc., 1932, 54, 2498.

was thought to arise from reaction of the crotonaldehyde with the oxidising agent.[73]

The chlorination of crotonaldehyde without a solvent has been used to prepared α-chlorocrotonaldehyde or butyl chloral hydrate; since good yields of each product are claimed, addition and substitution, but not rearrangement, appear to be the major modes of reaction. Other reports state that the chlorination of crotonaldehyde yields first αβ-dichlorobutyraldehyde which subsequently undergoes substitution to yield αβ-dichlorobutyroyl chloride. Finally, the use of an excess of chlorine in aqueous solution is claimed to give butyl chloral hydrate.[83]

Crotonaldehyde reacts with chlorine in acetic acid to give 9% hydrogen chloride. This may result from substitution, or from the formation of acetoxychloride adducts. In either case, it was necessary to try to identify the product. Bailey's method of converting the crude aldehyde mixtures to identifiable acids could not be quantitative, since the olefinic acids are in turn oxidised by the reagent. A considerable amount of work was directed towards finding a reagent which

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83. G.A. Ropp, W.E. Craig, and V. Raaen, Org.Synth., Coll. Vol. IV, p. 130 (Wiley, N.Y., 1963); S. Zeisel, Monats., 1886, 7, 359.

would convert the aldehyde to the acid without attacking the olefinic double bond. No suitable reagent was found. Permanganate and dichromate solutions oxidised the unsaturated acids; milder reagents either did not completely attack the aldehyde grouping before some reaction occurred at the olefinic fragment, or else only gave low yields of any acidic product. The search for a suitable reagent was also limited by the lability of the chlorine atoms; ammoniacal silver nitrate solution and Fehling's reagent were both rejected for this reason.

Finally, dilute (2%) permanganate was selected. With one mole of chlorine, crotonaldehyde in acetic acid yields, after oxidation, a mixture of αβ-dichlorobutyric acids. This mixture was separated by column chromatography and consisted roughly of equal weights of each stereo-isomer. The same product-mixture was obtained when sulphuric acid had been used as a catalyst for the chlorination. When two moles of chlorine were used, and the reaction mixture was warmed with water (when it was hoped to oxidise the aldehydes to the acid chlorides, which would then be hydrolysed), butyl chloral hydrate was isolated. This could arise either from the addition

of chlorine across the ethylenic system of α-chloro-crotonaldehyde or from the substitution of the αβ-dichlorobutyraldehydes by chlorine. It is more likely that the second explanation is correct. α-Chlorocrotonaldehyde could only arise from the (unlikely) dehydrohalogenation of the dichlorobutyraldehydes since less than 10% of the reaction of chlorine with crotonaldehyde gives rise to substitution products and the isomeric αβ-dichlorobutyraldehydes appear to be the major products of the reaction. In the reaction of chlorine and water upon this product from the reaction of equimolecular amounts of chlorine and crotonaldehyde, it is unlikely that an unsaturated aldehyde would add the elements of chlorine predominantly (cf. crotonic acid, p. 60); it would instead give rise to a chlorohydrin by solvent intervention. This would have the probable formula $CH_3.CHOH.CCl_2.CH(OH)_2$ and would be unlikely to be esterified by hydrogen chloride under such mild conditions. In contrast, substitution by chlorine to give butyl chloral from a αβ-dichlorobutyraldehyde would proceed readily, in the same way as α-halogenation of ketones, aldehydes, and acids takes place easily.

The isolation of the αβ-dichlorobutyric acid, m.p. 78°, from the oxidation products indicates one of two possible situations. This stereoisomer of αβ-dichlorobutyric acid is formed by the trans addition of chlorine to cis-crotonic acid; in this case, it could be formed from trans addition of chlorine to cis-crotonaldehyde or from cis addition of chlorine to trans-crotonaldehyde.

Bailey[73] explained the isolation of this αβ-dichlorobutyric acid, and the formation of the corresponding aldehyde, through a nucleophilic addition mechanism. Following the observation that stereochemically pure β-chlorocrotonic esters gave stereoisomeric mixtures upon reaction with sulphur-containing nucleophiles (SPh^-, SEt^-)[84] she proposed the following mechanism:

trans-Crotonaldehyde undergoes nucleophilic attack at the β-carbon atom of the ethylenic linkage by chloride ion. The resulting chlorocarbanion, in which the negative charge is situated upon the α-carbon atom, is capable of some degree of rotation about the C_α-C_β bond, as a result of which attack by the residual chlorinium ion (Cl^+) could take place to give either of

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84. C.A. Vernon and co-workers, J.Chem.Soc., 1960, 2349.

the two stereoisomeric addition products. If rotation could take place freely before this attack occurred and if the chlorinium ion could attack at either side of the carbanionic centre with equal facility, the result would be an equimolecular mixture of each dichlorobutyraldehyde. Although this mechanism does explain the products isolated from chlorination in acetic acid and, with the postulate that a less solvating medium (chloroform) would not permit equilibration before the addition was completed, explains the observed smaller quantity of the second isomer, it is open to some criticism.

In the first place, it involves attack by chloride ion upon an uncharged species. While nucleophilic additions to olefins are well known, they generally involve a very powerful nucleophile such as SR^- (as in the addition of thiols to olefins, and in Vernon's work[84]) or AlH_4^- (as in the addition of lithium aluminium hydride to ethylene[85]). Chloride ion is a weak nucleophile; the system is not strongly electrophilic, and the resulting attack, as written, seems unlikely.

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85. K. Ziegler, Angew.Chem., 1952, 64, 323.

In the second place, it involves the formation of a solvated chlorinium ion which moves away from the carbanion sufficiently to allow free rotation before returning to complete the addition reaction. The chlorinium ion is a very reactive electrophile even towards uncharged entities; towards a negatively charged carbanion its reaction would be expected to be instantaneous. Furthermore, such behaviour is contrary to experience, for it requires a more reactive system to be removed from a site of attack which finally reacts with a less reactive system (the solvated chlorinium ion).

De la Mare and Robertson, commenting upon the nucleophilic attack of crotonaldehyde by bromine in the presence of hydrogen bromide, suggested a mechanism[86] in which crotonaldehyde was in equilibrium with its conjugate acid ($CH_3.CH:CH.\overset{+}{C}(OH)_2$) and that the effect of this protonation of the carbonyl group was to bring bromine, as the tribromide ion, in suitable proximity to the ethylenic system. When this was accomplished, a proton and a bromide ion were lost, leaving the bromine molecule lying close to the ethylenic bond.

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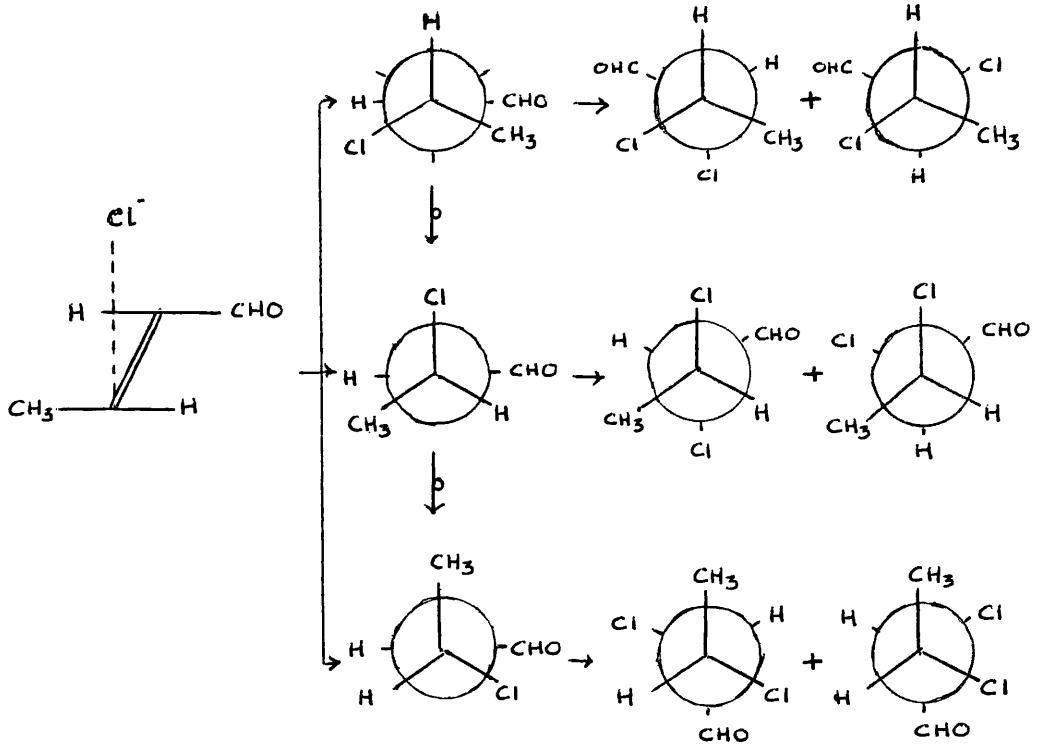
86. P.B.D. de la Mare and P.W. Robertson, J.Chem.Soc., 1945, 888.

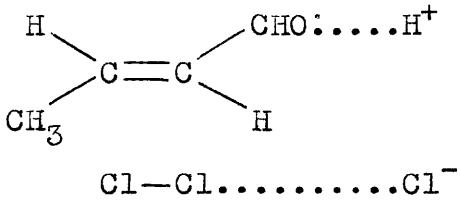
Bailey's mechanism for the chlorination of crotonaldehyde



This suggestion is plausible; in the present system, however, it is necessary to assume that the trichloride ion, a far less stable species, is the vehicle by which molecular chlorine and crotonaldehyde are brought together.

There seem to be two possible explanations of the cis addition of chlorine to crotonaldehyde. The trichloride ion may bring molecular chlorine close

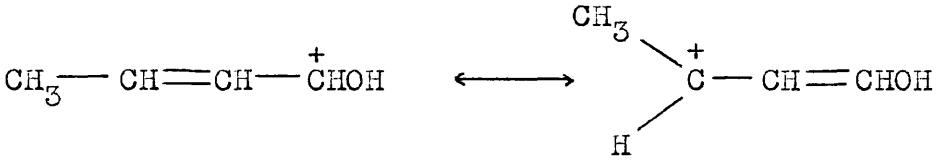
to the double bond of the protonated crotonaldehyde molecule. In leaving these two reagents together it also ensures that cis addition would occur preferentially.



Evidence for this can be found in the relatively small amount of acetoxychloride adducts which were formed (less than 10%, as compared with 75% for crotonic acid) since chlorine is in a favourable position not only to provide the chlorinium ion but also the chloride ion; it seems that the chlorocarbonium ion in this reaction is by no means as free as its analogue in the crotonic acid system.

The second possible mechanism involves a consideration of the conjugate acid of crotonaldehyde. The carbonium ion which results from protonation of the aldehyde has some formal resemblance to the allyl cation. In particular, the ethylenic linkage would not have such rigidity as a normal olefinic bond, and rotation of the groups around their central axis would be less encumbered.

It would then be a matter of probability which stereo-isomer of crotonaldehyde resulted at the moment when the proton left the carbonyl oxygen and the full ethylenic bond was reformed.

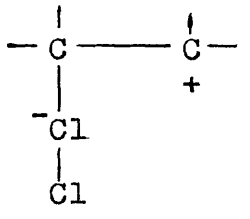


A "normal" trans addition of chlorine could occur with either isomer of crotonaldehyde which resulted, so that either isomer of αβ-dichlorobutyraldehyde could be formed.

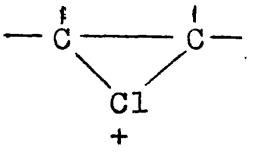
None of these mechanisms satisfactorily explains why the halogenation of crotonaldehyde is so much faster than that of crotonic acid. De la Mare and Robertson's theory suggests a means whereby molecular chloride can be brought to the ethylenic system, but it does not indicate how the site becomes so much activated.

A halogen molecule in the proximity of the olefinic system should form some sort of complex; a π-complex has been suggested, although this has been thought to involve little activation of the bond towards addition,

and various chlorocarbonium ionic intermediates have been put forward. These vary from structures such as the adduct

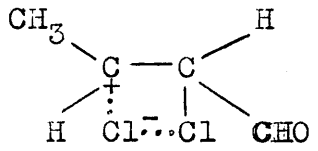


to the three-membered ring system



but all have the common background that they are intended to depict the stereospecificity of the addition (predominantly trans). Activation such as has been found in the crotonaldehyde system might result from the proximity of a bare chlorine molecule, as opposed to one surrounded by a solvent sheath. Probably this represents the most satisfactory way of explaining both the increased rate of the reaction (the first molecule of chlorine reacts as rapidly as the solutions of halogen and aldehyde can be mixed) and the lack of stereospecificity of the addition.

The resulting ion-pair



could be capable of some restricted rotation about the C_α-C_β bond; the fact that solvent attack upon the carbonium ion fragment is only a minor mode of reaction indicates that such a carbonium ion is not long-lived.

This mechanism assumes that the trichloride ion exists in a significant concentration. In aqueous solutions, the equilibrium constant for the formation of trichloride ion, $K = [Cl_3^-]/[Cl_2][Cl^-]$, is 0.01; in order to allow the formation of trichloride ion there must be a considerable amount of halide ion present.[87] In the reaction of crotonaldehyde with chlorine, however, there is no initial concentration of chloride ion; hydrogen chloride arises from side reactions such as the formation of acetoxychloride adducts or of substitution products. Also the reaction is taking place in acetic acid, in which hydrogen chloride is a weak electrolyte[88] and even in a saturated solution of the gas (ca. 3M) there

87. R.S. Halford, J.Amer.Chem.Soc., 1940, 62, 3233.
88. I.M. Kolthoff and A. Willman, J.Amer.Chem.Soc., 1934, 56, 1007.

would be little free chloride ion. A further point against the mechanism is the low basicity of αβ-unsaturated aldehydes, although this does not seem of great importance since the acid-catalysed hydration of such olefins is well known.[89]

The kinetic results of de la Mare and Robertson[86*] make the trihalide ion hypothesis very attractive; only by invoking the formation of such ions can the unusually great catalytic effects of hydrogen bromide and hydrogen chloride be explained. However, the trihalide ion should not be considered as the attacking species in this reaction; there is no evidence that X_3^- is a more powerful nucleophile than X^-, and it seems more likely that trihalide ion, when it can be formed (i.e. after the adventitious formation of hydrogen chloride in the halogenation of crotonaldehyde), acts more as a vehicle for bringing halogen to the double bond rather than as an attacking agent in its own right. It has already been pointed out that the presence of ionic clusters in acetic acid solutions makes it more probable that an intermediate (p. 130) can have a real, if transient

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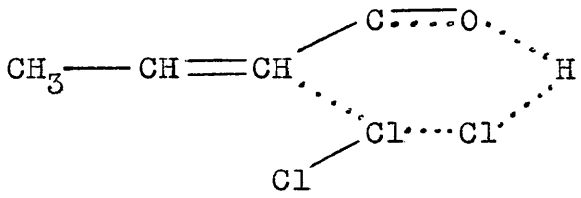
*See p. 123.

89. S. Winstein and H.J. Lucas, J.Amer.Chem.Soc., 1937, 59, 1461; D. Pressman, L. Brewer, and H.J. Lucas, J.Amer.Chem.Soc., 1942, 64, 1122; H.J. Lucas, W.T. Stewart, and D. Pressman, J.Amer.Chem.Soc., 1944, 66 1818.

existence in this solvent.



The explanation of the isolation of both stereo-isomers of αβ-dichlorobutyric acid from the oxidation products can only be made by postulating a highly arbitrary degree of rotation about the C_α-C_β bond; the product of <u>trans</u>-addition must result from a similar intermediate to those suggested (above, and p. 128), since it is isolated in sufficiently high yield to preclude its formation from the normal (slower) electrophilic attack of chlorine upon the unprotonated aldehyde.

C. Chlorination of phenanthrene

Phenanthrene reacts with chlorine to give both the products of addition and those of substitution. In chlorination in acetic acid as solvent, the main substitution product is 9-chlorophenanthrene; isomeric chlorophenanthrenes do not represent more than 1% of the reaction product.[90] However, 9-chlorophenanthrene comprises only 38-40% of the total reaction product; two isomeric 9,10-dichloro-9,10-dihydrophenanthrenes are also formed and a 9-acetoxy-10-chloro-9,10-dihydrophenanthrene was also isolated.[90]

These results indicate attack at C_9 of the phenanthrene nucleus; this is the most reactive site[91] and the absence of appreciable amounts of other chlorophenanthrenes is further evidence of the great sensitivity of the reagent towards changes in electron availability.

Existence of another acetoxychloride adduct

Koenigsberger[90, 92] isolated an acetoxychloride adduct from the chlorination of phenanthrene in acetic

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90. P.B.D. de la Mare and R. Koenigsberger, J.Chem.Soc., 1964, 5327.
91. "Chemistry of Carbon Compounds", Vol IIIB (Ed., E.H. Rodd. Elsevier, Amsterdam)
92. R. Koenigsberger, Ph.D. Thesis, University of London, 1965.

acid. Since this compound decomposed upon heating to form 9-acetoxy- and 9-chloro-phenanthrene, and other decompositions of the adduct also gave 9-substituted phenanthrenes or mixtures of 9,10-dihydrophenanthrene derivatives, it was evident that the adduct was derived from addition across the 9,10-bond of phenanthrene. No stereospecific reactions could be carried out with this adduct; for example, the reaction with silver acetate gave a mixture of 9-acetoxyphenanthrene and *cis*- and *trans*-9,10-diacetoxy-9,10-dihydrophenanthrene. The rate of dehydrohalogenation by alkoxide ion of the acetoxychloride (k_2 = 2.6 $M^{-1}.min.^{-1}$) was intermediate between that of the *trans*-9,10-dichloro-9,10-dihydrophenanthrene (k_2 = 0.02 $M^{-1}.min.^{-1}$) and that of the *cis* isomer (k_2 = 160 $M^{-1}.min.^{-1}$); a hypothetical *cis*-acetoxychloride adduct was considered to react at about half the rate of the corresponding dichloride adduct. The rate of dehydrohalogenation did not give proof of the configuration of the acetoxychloride, but suggested that it was not the *cis* isomer.[90]

Evidence that the compound was the *trans* adduct was obtained from chromatography and by correlating the

reaction products of the acetoxychloride with silver acetate with those obtained from the isomeric 2-acetoxychlorocyclohexanes.[93]

No definite evidence of a cis-acetoxychloride adduct was found in the earlier work[92] but its presence in the reaction mixture has been suspected.[90] It was noticed that the crude acetoxychloride fraction contained 9-acetoxyphenanthrene, which could have arisen from the decomposition of a cis-acetoxychloride during column chromatography; on v.p.c. the ratio of 9-acetoxyphenanthrene to 9-chlorophenanthrene formed upon pyrolysis of the crude fraction was 10:1, whereas from the pure acetoxychloride the value was 4:1.[94] The crude, syrupy acetoxychloride fraction was also found to have a different rate of alkaline dehydrohalogenation at 0°; k_2 decreased from 3.6 (37% reaction) to 2.8$\underline{M}^{-1}$.min.$^{-1}$ (92% reaction). This indicated that the crude samples contained a small amount of a more reactive entity, probably cis-9-acetoxy-10-chloro-9,10-dihydrophenanthrene. It was obviously desirable to obtain further evidence; if both isomers were isolated it would be easier to prove the trans configuration of

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93. S. Winstein and R.E. Buckles, J.Amer.Chem.Soc., 1942, 64, 2780, 2787, 2796.
94. E.A. Johnson, reported in ref. 90.

Koenigsberger's acetoxychloride.

The present work has confirmed that a cis-acetoxychloride adduct is formed during the chlorination of phenanthrene in acetic acid; it has also been confirmed that Koenigsberger's adduct is the trans isomer. N.m.r. spectroscopy of the reaction product and of the crude acetoxychloride fraction showed the presence of two acetoxychloride adducts. One was the known trans-adduct; the other appears to be the cis isomer.

It is fairly certain that this new compound results from addition across the 9,10-bond of phenanthrene, since no decomposition products other than 9-substituted phenanthrenes were found in the pyrolysis products of the crude acetoxychloride fraction. Furthermore, the n.m.r. spectrum indicated only one new compound; addition across any other bond in the phenanthrene system would be expected to give at least two, and probably four, new compounds (e.g. attack at the 1,2-bond would give two isomeric dichlorides and two isomeric acetoxychlorides). N.m.r. spectroscopy also indicated that a total of 15% of the reaction product was due to the acetoxychlorides; this agrees with Koenigsberger's figure of 13-15%.

The chlorination of phenanthrene in 1M-sodium acetate in acetic acid gives an increase in the amount of the trans-acetoxychloride from 10% to 24%, but does not alter the amount of the new acetoxychloride (4.6%). Similarly, a chlorination carried out in 1M-lithium chloride in acetic acid does not greatly affect the ratio of the two acetoxychloride adducts, but increases the amount of the trans-9,10-dichloro-9,10-dihydrophenanthrene from 9% to 21%, mostly at the expense of the cis-dichloride.

From these results, it seems certain that the new compound is cis-9-acetoxy-10-chloro-9,10-dihydrophenanthrene.

Chlorination of phenanthrene in the presence of salts

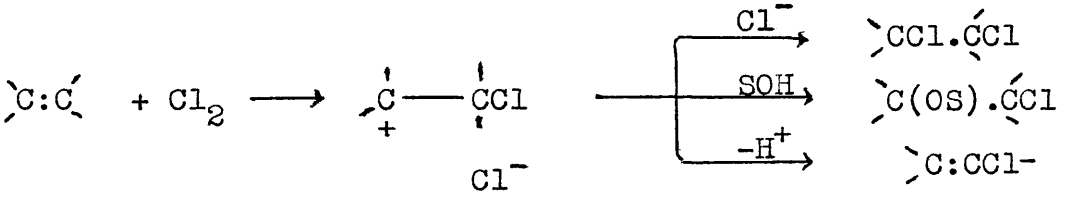
The reaction of phenanthrene with chlorine in acetic acid is modified, both in rate and in reaction products, by the presence of electrolytes.

Adducts formed in chlorination of phenanthrene in acetic acid

Added electrolyte:	None	1M-LiCl	1M-NaOAc
cis-Dichloride (%)*:	36.2	29.6	29.9
trans-Dichloride (%):	9.1	21.0	3.6
cis-Acetoxychloride (%):	4.6	2.4	4.8
trans-Acetoxychloride (%):	10.3	8.6	23.7

In the table, the amounts of each product are expressed as percentages of the total reaction product. The alterations of the amounts of the reaction products is paralleled by a change in the observed rate of reaction.

In the classical addition mechanism of chlorine to olefins the amount of trans addition to form the dichloride is increased by added chloride ions, which can compete with the solvent for the incipient carbonium ion formed during the first stage of the addition:



Thus the addition of lithium chloride expectedly favours the formation of trans-9,10-dichloro-9,10-dihydrophenanthrene; n.m.r. spectroscopy* gives values of the composition of such reaction mixtures which show that this compound is formed at the expense of all the other adducts (see p. 135). It is also noteworthy that the ratio of cis- and trans-acetoxychlorides changes slightly under these conditions; the cis/trans ratio being 0.28 in the presence of lithium chloride, and 0.40 in the absence of electrolytes.

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* Representative n.m.r spectra are shown in the Appendix.

In the same way as lithium chloride increases the formation of the trans-dichloride adduct, the chlorination of phenanthrene in the presence of sodium acetate increases the extent of formation of trans-acetoxychloro-dihydrophenanthrene. In the presence of 1M-sodium acetate, the cis/trans ratio of acetoxychlorides falls to nearly 0.20.

General effects of electrolytes

Each of the electrolytes studied in the present work accelerates the rate of chlorination of phenanthrene in acetic acid; with the exception of perchloric acid, all of these effects may be rationalised in terms of the simple classical addition mechanism depicted on p. 136 if it is remembered that lithium chloride behaves as a weak base in acetic acid and will also increase the extent of formation of trans-9-acetoxy-10-chloro-9,10-dihydrophenanthrene by providing acetate ions.

Rates of chlorination of phenanthrene in NaOAc - HOAc

[NaOAc]	0.00M	0.08M	0.24M	0.60M
k_2 ($M^{-1}.min.^{-1}$):	26.4	25.2	29.3	38.6

There is a stage in which added acetate ion slightly retards, rather than increases, the rate of

chlorination of phenanthrene in acetic acid. This may be compared with the characteristic behaviour of the lyate ion in a solvent; such retardations have been found for hydroxide ion in aqueous solvent mixtures and for ethoxide ion in ethanol. It is also possible that some of the effect is due to the removal of the hydrogen chloride formed during the substitution reaction, but these two effects must antagonise each other, since it is shown that chloride ion has a greater accelerating effect than has acetate ion.

Rates of chlorination of phenanthrene in LiCl - HOAc

[LiCl]	0.00M	0.08M	0.19M	0.40M
k_2 ($M^{-1}.min.^{-1}$):	26.4	33.9	55.6	134

Effect of lithium perchlorate

Lithium perchlorate has been described as a "super salt" since it has a much greater effect upon ionic reactions than other salts and it is obvious that the same effect is being seen in the present work:

Rates of chlorination of phenanthrene in $LiClO_4$ - HOAc

[$LiClO_4$]	0.00M	0.004M	0.077M	0.160M	0.40M
k_2 ($M^{-1}.min.^{-1}$):	26.4	32.2	42.6	85	186

Effect of perchloric acid

In the presence of perchloric acid, the rate of reaction is enormously increased, and when water (1%) is added to 0.75M-perchloric acid in acetic acid, the rate of chlorination in the solvent is even further accelerated -- k_2 = 940 $M^{-1}.min.^{-1}$

Rate of chlorination of phenanthrene in $HClO_4$ - HOAc

$[HClO_4]$	0.00M	0.148M	0.323M	0.485M	0.80M
k_2 ($M^{-1}.min.^{-1}$):	26.4	123	260	344	730

The effects of electrolytes agree with the simple concept of a salt behaving as an "ionising solvent" and enhancing the rate of reactions in which charge is developed, as a change to a more ionising solvent will do.

The presence of these electrolytes also has an effect upon the products of the chlorination reaction. Koenigsberger[92] has shown that added perchloric acid decreases the amount of trans adducts formed. She also found that solutions of perchloric acid in acetic acid destroy the acetoxychlorides to form 9-chlorophenanthrene, but that the dichlorides were much more stable to this reagent: trans-9,10-dichloro-9,10-dihydrophenanthrene was only attacked appreciably after one day in 0.1M-

perchloric acid in acetic acid.

The following table shows the variation of the reaction product composition with various concentrations of perchloric acid in acetic acid.

Products formed from chlorination of phenanthrene in $HClO_4$ - HOAc

$[HClO_4]$	9-Chlorophenanthrene (%)	cis-Dihydrodichlorophenanthrene (%)	trans-Dihydrodichlorophenanthrene (%)	Total*
1.2M	85.5	12.7	1.2	99.4%
00.5M	77.5-80.2	16.1-18.4	2-3	99±3%
0.4M	81.2	18.9	2.3	102.3%
0.2M	74.7-77.5	23.4-28.6	1.2-3.8	104±5%
0.08M	69.2	Total chlorides: 31.6		100.8%
0.05M	65.7-70.0	34-35	3-4	106±3%
0.00M	37-40	36.2	9.1	82-85%

The trans-dichloride only represents a few percentage of the reaction product, and increasing the concentration of perchloric acid in the solvent decreases the amount of the cis-dichloride and correspondingly increases the amount of the substitution product. It seems that in low concentrations of perchloric acid some of the acetoxy-

*All percentages were determined by titration (cf. p. 90-1); divergences in values resulted when the chlorination mixture was left over half an hour, or over twenty-four hours, before estimating the products.

chloride is formed, and is subsequently destroyed, when the reaction mixture is left overnight; in this way some variations were found in the amount of cis-dichloride detected by saponification with alkali at room temperature, depending on how rapidly the reaction mixture was analysed after completion of the chlorination reaction. N.m.r. spectroscopy also indicated the formation of small amounts of acetoxychlorides in the reaction mixture initially, but which disappeared on standing. At greater concentrations of perchloric acid, either the destruction of the acetoxychlorides proceeds too rapidly or else they are never formed. The trans-dichloride, however, is not destroyed under the experimental conditions and so the small amount formed when chlorination takes place in perchloric acid solution means that the course of the reaction is changed by added perchloric acid.

Lithium chloride and sodium acetate affect the proportions of the reaction products in the expected way. The added ions divert a carbonium ionic intermediate and increase the amount of the appropriate trans adduct. It seems that salts have very little effect upon the proportion of the substitution product. cf. [92] Lithium perchlorate, however, increases the amount of substitution

product (47.6% with 0.60M-$LiClO_4$; 50.8% with 0.76M-$LiClO_4$) to the detriment of every adduct.

Mechanism of chlorination of phenanthrene in acetic acid

The simple addition mechanism discussed on pp. 136ff. involves the formation of a carbonium ion intermediate in which there is interaction between the chlorine substituent and the carbonium ionic centre. Various degrees of interaction have been postulated, and the appropriate intermediates have been discussed earlier in this thesis. However, addition through such an intermediate in which such interaction occurs usually gives rise to a trans adduct because of hindrance of approach on the same side of the olefinic bond as the entrant chlorine atom; indeed, such an intermediate was postulated in order to explain the predominantly trans addition of reagents to olefins.

Chlorination of phenanthrene in acetic acid gives both cis- and trans-9,10-dichloro-9,10-dihydrophenanthrenes in a ratio of approximately 4:1. Some modification of the simple scheme is evidently needed in this case.

The previous results[90,92] have led to the proposition of the following mechanism:

Chlorine first attacks the 9,10-bond to form a zwitterion in which the two chlorine atoms are in a similar environment to that of the trichloride ion[90]; collapse of this intermediate would give rise to the cis-dichloride, presumably through an ion-pair. The loss of chloride ion from this intermediate gives the true carbonium ion which could give the trans-dichloride and the trans-acetoxychloride by attack of the appropriate nucleophile, or eliminate a proton to give 9-chlorophenanthrene. An intermediate similar to the zwitterion would also explain the formation of cis-7,8-dichloroacenaphthene from the addition of chlorine to acenaphthylene in chloroform.[95]

The formation of a cis-acetoxychloride adduct must cause some modification of this scheme, or at least some sharpening of the definition of the mode of formation and decomposition of the intermediates. The cis-acetoxychloride could arise from either the zwitterion or the carbonium ion intermediate, but the interaction between the chlorine atom and the carbonium ionic centre would make attack on the same side as the chlorine atom unlikely.

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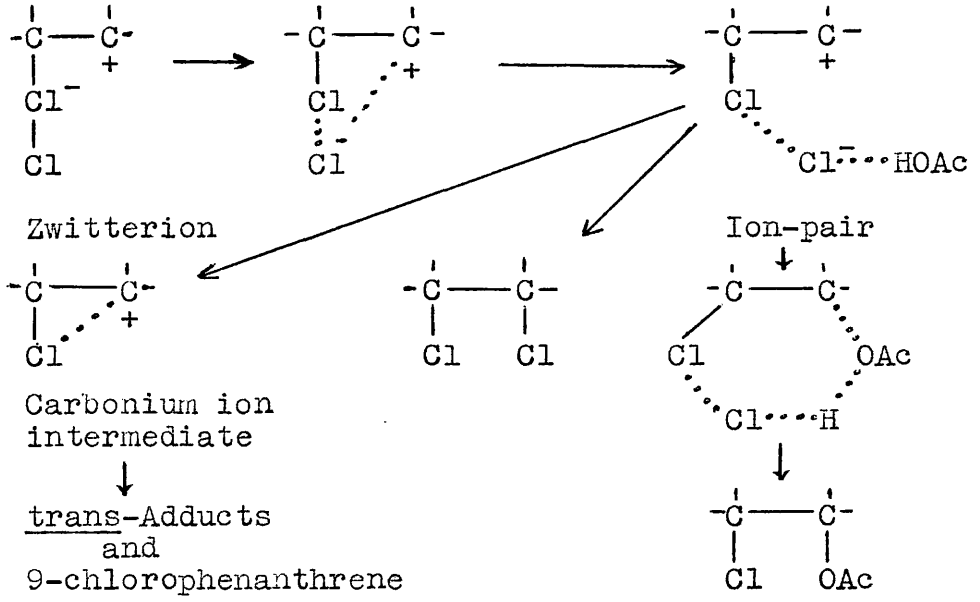
95. S.J. Cristol, F.R. Stermitz, and P.S. Ramey, J.Amer. Chem.Soc., 1956, 78, 4939.

In the stages between the zwitterion and the carbonium ion intermediate, there is an ion-pair which could explain the formation of cis-adducts.



This ion-pair breaks down under the influence of the solvent to give (i) the cis-dichloride, through a four-centre transition state in which the incipient chloride ion attacks the carbonium ionic centre (ii) the cis-acetoxychloride through a six-centre transition state or (iii) the carbonium ionic intermediate. The degree to which these three modes of reaction occur will be determined by the ability of the reaction solvent to assist in the formation and stabilisation of ions.

Application of this scheme

In the proposed modification of the reaction mechanism, the critical intermediate is the partially solvated ion-pair. Partial breakage of the Cl-Cl bond will give rise to the cis-dichloride or to the cis-acetoxychloride which, as it requires especial orientation of the solvent molecule which assists in removal of the chloride ion, would be less favoured. It can also lead to the formation of the conventional carbonium ionic intermediate, from which trans-adducts and products of elimination can arise. This proposed mechanism may also be used to explain the observed salt effects and the effect of changes of the reaction solvent.

Salt effects

The effects of lithium chloride and of sodium acetate upon the reaction products are those expected from any reaction scheme incorporating the formation of a carbonium ionic intermediate; there is no need to complicate the mechanism by a consideration of any other intermediates. In the same way, the kinetic effects of these two salts, and that of lithium perchlorate, may simply result from increasing the "ionising power" of the solvent; with added electrolytes, the formation of an

ionic transition state (in which charge is formed) would be aided by grouping ion-clusters* around the centres at which charge is forming. The greater magnitude of effect of lithium perchlorate may be due to an increased ionisation into Li^+ and ClO_4^-.

The effect of perchloric acid, however, cannot be dismissed so simply. Perchloric acid, even in very small amount, increases the extent of substitution by 20-25%, to the detriment of all the adducts. trans-9-Acetoxy-10-chloro-9,10-dihydrophenanthrene is completely removed; the amount of both trans- and cis-dichlorides is reduced. It could be assumed that with increasing perchloric acid concentrations the intermediate which forms the cis-dichloride is diverted to form the substitution product.

The ion-pair intermediate (p. 144) has been postulated to be the precursor of this adduct. In the scheme, acetic acid is shown as the solvating entity which helps to remove chloride ion and break the Cl-Cl bond. The energy of solvation of chloride ions in acetic acid cannot be large, for there are few salts which are completely ionised in a medium of such low

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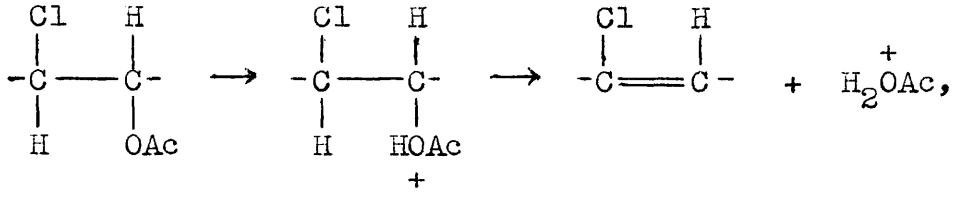
*In acetic acid, salts do not exist preponderantly as ions or even as ion-pairs. (Ref. 88, p. 128)

solvating power, and it is not impossible that an ion could be found which would coordinate more strongly with the incipient halide ion than acetic acid does (e.g. Ag^+). Such an ion would be H_2OAc^+, since hydrogen chloride is a weak electrolyte in acetic acid[88] and there would be competition between the formation of hydrogen chloride

$$H^+ + Cl^- \rightleftharpoons HCl \text{ (unionised)}$$

by perchloric acid, which is extensively ionised in acetic acid[88] and the formation of some sort of solvation force (electrostatic?) between the dipolar acetic acid molecule and the chloride ion. As the concentration of perchloric acid was increased, the probability of the chloride ion being "helped off" by H_2OAc^+ rather than by HOAc would mean that collapse of the ion-pair intermediate would become less likely, with a resulting increase in the formation of the carbonium ionic intermediate.

The decomposition of trans-9-acetoxy-10-chloro-9,10-dihydrophenanthrene by perchloric acid, believed to involve the following sequence:[92]



might well be complete during the time required to work up the reaction mixture when chlorination is carried out in perchloric acid - acetic acid mixture; however, there is no obvious reason why the trans dichloride should be decomposed under these conditions. It seems unlikely that this adduct is decomposed by perchloric acid under the experimental conditions; it has been shown[92] that perchloric acid only slowly decomposes the trans-dichloride, and also the amount of this compound which is found from the acid-catalysed chlorination of phenanthrene is almost independent of the concentration of perchloric acid present.

The diminution in the amount of cis-dichloride has been explained in terms of a solvent effect; the absence of a significant amount of the trans adducts may also be explained in this way. In acetic acid solution, when perchloric acid has been added, there can be little chloride ion present as such in the reaction mixture;

much of the stoichiometric quantity of hydrogen chloride is present as the unionised molecule (*cf.* aqueous solutions of hydrogen chloride and acetic acid). Also, the strongly acidic solution would leave little acetate ion present. The carbonium ion intermediate, when formed, would have only two alternatives: either a proton could be lost, or else the ion could be attacked by the solvent. The latter reaction would give the *trans*-acetoxychloride, which is known to be readily decomposed by perchloric acid - acetic acid mixtures to give 9-chlorophenanthrene, which is the ultimate result of either mode of reaction. The low proportion of *trans*-dichloride in such reaction mixtures is similarly due to the absence of much chloride ion, since the bulk of this ion would be converted to unionised HCl.

This explanation cannot cover the whole of the effect of perchloric acid, since it relies upon the equilibrium

$$H^+ + Cl^- \rightleftharpoons HCl.$$

In very low (0.05M) concentrations of perchloric acid the removal of some of the *cis*-dichloride and much of the *trans*-isomer is still evident; a plot of the

percentage of substitution product against the concentration of perchloric acid present in the reaction mixture shows that at negligible acidities 9-chlorophenanthrene is formed in ca. 70% yield. This is a sharp contrast to the 38-40% yields of substitution product which result in the absence of added perchloric acid, and implies that the effect of perchloric acid is, to some extent, catalytic.

At the lowest concentration of perchloric acid which was used in the present work, (0.05M) the increase in the extent of substitution seems to be due only to the diversion or decomposition of the trans adducts; the amount of cis-dichloride (34-35%) is similar to that found in the absence of added acid (37-39%). It is evident that there is little hindrance to the collapse of the ion-pair intermediate to form this adduct; at low concentrations of perchloric acid, solvation by H_2OAc^+ and not by HOAc does not occur significantly since it is a bulk solvent effect. However, the carbonium ionic intermediate is in some way instantaneously prevented from carrying out any other reaction besides elimination, even at the lowest acidity. If we consider that the extent of formation of the trans

dichloride which is measured (p. 140) is subject to considerable error since it represents a small difference between two values* , the overall slight decrease in the amount of this isomer with increasing acidity can be rationalised (p. 148). It does not seem possible to ascribe the sudden increase in the extent of substitution in the presence of perchloric acid to a general solvent effect.

Although an increase in the ionising power of the solvent would permit the sequence

Zwitterion ⟶ Ion-pair ⟶ Carbonium Ion

to pass completely to the right before the attack of nucleophiles (i.e. to increase the products derived from the carbonium ion intermediate) it seems remarkable that such a small amount of perchloric acid would have such a great effect. For example, the chlorination of phenanthrene in 0.05M-perchloric acid in acetic acid gives 70% 9-chlorophenanthrene, and a total of about 75% of products derived from elimination or from trans addition (i.e. from the carbonium ionic intermediate); in the presence of 0.76M-lithium perchlorate, the figures are 51% and ca. 70%.[92]

*Derived from (Cl^- liberated on hot hydrolysis) - (Cl^- liberated on cold hydrolysis)

Evidently from these results perchloric acid manages to influence the carbonium ion intermediate in such a way as to make elimination of a proton the preferred mode of reaction. It might be possible to postulate that perchloric acid has a greater solvating effect than the salts which were used in the present work, but it is hard to explain the greater extent of the elimination reaction, which dominates the mode of reaction only in the case of chlorination in the presence of this acid.

This effect does not seem consistent with a change in the effective electrophile, for there is no reason to suppose that a more reactive electrophile (e.g. $Cl^+ClO_4^-$) would have any influence upon the reactions of the chlorocarbonium ion intermediate.

The elimination of a proton from the carbonium ionic intermediate to the virtual exclusion of other modes of reaction can only take place (i) if a non-nucleophilic base is present or (ii) some orientation of molecules around the ionic centre prevents attack by nucleophiles.

The nucleophiles present in perchloric acid - acetic acid mixtures are Cl^-, HOAc, ClO_4^-, and traces of OAc^-. Of these, perchlorate ion and acetate ion may be

discounted, since the former is virtually non-reactive and the latter is present in very small quantity. The two nucleophiles which are left, chloride ion and the solvent, are both perfectly capable of combining with the carbonium ionic intermediate, as the products of reaction in the absence of added electrolytes show. There is therefore no basic but non-nucleophilic (towards carbon) reagent in these solutions.

There only remains the postulate that the ionic centre of the carbonium ion is shielded in its solvation. Considering the requirements for solvation of a positively charged ion (dispersal of the charge over a larger area, whether through dipolar solvent molecules or through ionic aggregates) it seems reasonable to expect that a negatively charged ion would be electrostatically preferable to a dipolar and poorly solvating solvent. It is not unreasonable to suppose that, in the formation of the ion-pair intermediate where the positive charge appearing at the carbon atom is partly "solvated" by electrostatic interaction from the negative fragment of the complex, solvation on the other side of the C-C bond is more effective when perchlorate ion, or a

negatively charged aggregate of the formula $(HClO_4)_n.ClO_4^-$ acts as "solvent" than when acetic acid molecules do. This is not a general solvent effect, but the aggregation of suitable ions around a centre when charge is forming. In such a system, the possibility of forming the trans dichloride would be diminished from the smaller quantity of free chloride ion present in the system; the formation of the trans-acetoxychloride would be unlikely because of the shielding of the acetic acid molecules from the carbonium ion centre by the perchlorate ion aggregates, and the only course of reaction left would be the loss of a proton to form 9-chlorophenanthrene.

The higher proportion of substitution product formed when chlorination of phenanthrene is carried out in acetic acid solutions of lithium perchlorate may also be due to such a localised "solvent" effect of the perchlorate ion; however, the present results do not preclude a general solvent effect.

Chlorination of phenanthrene in solvents other than acetic acid

Although the major part of this work was concerned with the chlorination of phenanthrene in acetic acid, studies were made of the reaction in chloroform and in nitromethane. In these cases the possibility of solvent intervention, which gave rise to acetoxychlorides in the previous work, was eliminated.

Products of the chlorination of phenanthrene

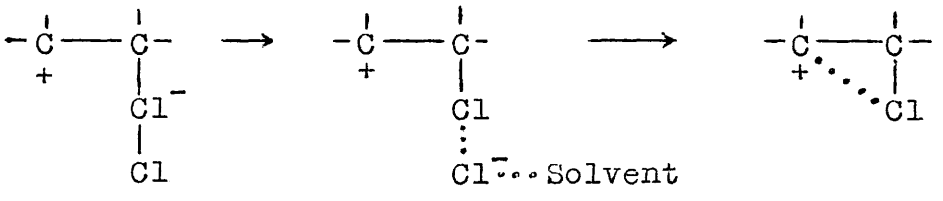
Increasing the dielectric constant of the solvent apparently increases the extent of substitution and decreases the cis/trans ratio in the formation of the dichlorodihydrophenanthrenes.

Solvent:	$CHCl_3$	CH_3CO_2H	CH_3NO_2
Substitution (%):	41.5	38-40	64.8
cis-Dichloride (%):	41.0	36	22.6
trans-Dichloride (%):	17.5	8-10	11.2
cis/trans ratio	2.5	ca. 4*	2.0

*Allowing for the acetoxychlorides, the ratio of cis products to trans products becomes 2.1

The cis products of reaction are the result of the zwitterion or the ion-pair intermediate (p. 144);

the change in the cis/trans ratio and the increase in the extent of substitution is consistent with the postulated mechanism. In the sequence:



a more effective solvent will decrease the possibility of collapse of the ion-pair intermediate and hence allow more of the carbonium ionic intermediate to be formed (cf. p. 151). In all this discussion, a solvent has been judged as "solvating" by its ability to aid in the formation of electric charge and to stabilise such charge. Therefore a "solvating" solvent is one which will not only assist in the removal of chloride ion from the ion-pair intermediate, but will also materially stabilise the chloride ion and the carbonium ion so formed. The most solvating solvent will therefore alter not only the ease with which the ion-pair can collapse to form the cis-dichloride, but also the ease with which solvated chloride ion can attack the solvated carbonium ion to form a trans adduct. Both of these factors tend to increase

the extent of substitution, and to diminish the formation of adducts.

It may be argued that it is energetically unlikely that a solvent would assist the removal of chloride ion from one side of the molecule solely to permit its attachment on the other. However, the zwitterion intermediate cannot collapse to form the cis-dichloride; it cannot provide chloride ion with which to attack the positively-charged carbon atom unless it either forms a three-membered chloronium ion or a structure such as the ion-pair intermediate which has been postulated.

This ion-pair, however, provides a source of chloride ion, which is being formed under the opposing influences of the charged carbon atom, attack of which will give the cis-dichloride, and the solvent which will cause the formation of the chlorocarbonium ion. A slightly solvating solvent will assist the breakage of the Cl-Cl bond, but may not contribute enough energy to allow the chloride ion to leave the environment of the carbonium ion; collapse will take place forming only the cis adduct. A strongly solvating solvent will assist in forming the chloride ion, breaking the Cl-Cl bond and stabilising the chloride ion. Once the halide

ion has been removed and is completely solvated, the carbonium ion shows the normal behaviour and, due to the neighbouring-group effect of the β-chlorine atom, shows a preference to trans attack where nucleophiles attack on the other side of the C-C linkage.

Catalysis of the chlorination of phenanthrene in chloroform

Some attempts were made to study the effect of hydrogen chloride and of iodine upon the rate of chlorination of phenanthrene in chloroform. The hydrogen chloride produced in the reaction seemed to catalyse the reaction, and the kinetics were therefore difficult to reproduce. Iodine, even in very low concentration, had a powerful effect upon the reaction rate; hydrogen chloride had a similar but less powerful effect. (See p. 159)

Catalysis by iodine of the addition of chlorine to ethyl cinnamate in carbon tetrachloride has been examined kinetically.[96] The reaction has been shown to involve one mole of iodine monochloride and one of chlorine in the rate determining stage; catalysis may be due either to the reaction

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96. H.D.C. Waters, A.R. Caverhill, and P.W. Robertson, J.Chem.Soc., 1947, 1168.

$$Cl_2 + ICl \rightleftharpoons Cl^+ ICl_3^-$$

or to a termolecular reaction involving ICl attacking one end of the ethylenic bond as Cl-Cl attacks the other.

Catalysis of the chlorination of phenanthrene

Added compound	k_2 ($\underline{M}^{-1}.min^{-1}$)
None	0.7
2.1×10^{-6} $\underline{M}$-I_2	6.3
9.8×10^{-6} $\underline{M}$-I_2	10.8
2.9×10^{-5} $\underline{M}$-I_2	26
4.7×10^{-3} $\underline{M}$-HCl	1.1
5.0×10^{-2} $\underline{M}$-HCl	2.6

Of the two mechanisms, the former seems preferable, since a termolecular transition state would be comparatively rare when none of the molecules involved is the solvent. The present work, however, sheds no light on this question beyond demonstrating the potent catalytic effect of iodine. The effect of hydrogen chloride may simply be due to a change of solvent properties; it is hard to see it playing any part in modifying either the substrate or the reagent.

General conclusions

The reaction of chlorine with formally unsaturated systems can give rise either to addition products or to substitution products; in some cases, both types of product are able to be isolated. In the case where the aromatic system is the source of unsaturation, substitution by chlorine usually takes place unless addition can occur without great loss of resonance energy (as in phenanthrene and anthracene); in contrast, the simple olefins usually give addition products unless there is some modifying feature in the organic molecule, when rearrangement may take place.

Even deactivated olefins apparently undergo addition rather than substitution, since no evidence of a substitution product has been found in the chlorination of crotonic acid. In keeping with the reactions of maleic and fumaric acid derivatives, however, crotonic acid has been shown to form a β-lactone structure during chlorination. Unlike these dibasic acids, crotonic acid did not form a β-lactone which could be isolated; only a polymer was obtained when direct isolation was attempted, and although the evidence for a β-lactone intermediate

is strong, it is circumstantial. N.m.r. spectroscopy has helped in the analysis of the reaction products of chlorination of crotonic acid; in this way it was shown that α-chlorovinylacetic acid forms no part of the reaction mixture, and that γ-chlorocrotonic acid is also absent. Substitution therefore cannot be detected in the reaction product analysis; it seems that the chlorination of crotonic acid yields only αβ-dichlorobutyric acid, m.p. 63° (the product of trans addition) and α-chloro-β-butyrolactone.

Crotonaldehyde, for which there is evidence of a nucleophilic mechanism of addition in acid solution, has been studied but its reaction products could not be completely characterised due to the instability of the ethylenic bond to reagents which would oxidise the carbonyl group. The major product of chlorination in the presence of water and an excess of the halogen was butyl chloral hydrate; in the absence of water the two isomeric αβ-dichlorobutyraldehydes appear to be formed. A mechanism for the apparent cis and trans addition of chlorine to crotonaldehyde has been proposed.

In contrast with these two olefins, phenanthrene

has been well studied, and the mechanism by which chlorine reacts with it in acetic acid has been elucidated. The present study, which has covered the effects of some electrolytes upon the rates and products of chlorination of phenanthrene in aceticaacid and in chloroform and which has used n.m.r. spectroscopy to aid in the characterisation of the reaction products, has made some addition to the knowledge, especially to the identification of the products of solvent intervention. Koenigsberger's acetoxychloride has been found to be the trans-isomer, in agreement with her assignment, from the effect of electrolytes upon the extent of its formation.

In addition, a new product, cis-9-acetoxy-10-chloro-9,10-dihydrophenanthrene, has been identified. Since it is too unstable to be isolated by column chromatography evidence of its identity and extent of formation was found from n.m.r. spectroscopy. The presence of this adduct and the effect of electrolytes upon both the rate of chlorination and the reaction products has enabled a more detailed definition of the configuration of the reaction intermediates formed after the rate determining step of the chlorination.

Infra-red spectra of some phenanthrene derivatives

(range: 1800-600 $cm.^{-1}$)

cis-Dichloride	*trans*-Dichloride	*trans*-Acetoxychloride
1733s	1728s	1739s
	1520m	
1450Nujol	1450Nujol	1449Nujol
1370Nujol	1368Nujol	1368Nujol
	1345w	1350w
1310s		1308w
1230s	1241s	1235s
1219m	1222s	1220s
	1211m	
	1204m	
1188w		1185w
1163w	1167w	1159w
1150w	1120w	1129w
	1090m	
1050w	1050w	
	1031m	
1010m	1012m	1018s
		972m
954m		954m
944w	942m	
920w	935w	937m
	912m	
813w		855w
	785m	787w
760m	770m	763s
	746w	
734s	734s	734s
	712w	
702m	700m	
696m		

Infra-red spectra of crotonic acid and some derivatives

(range: 1800-600 $cm.^{-1}$)

Crotonic acid	α-Chloro-crotonic acid	α-Chloroiso-crotonic acid	αβ-Dichloro-butyric acid m.p. 63°	αβ-Dichloro-butyric acid m.p. 78°
1695s	1669s	1724s	1724s	1724s
1633m	1626m	1626m		
1450Nujol	1448Nujol	1450Nujol	1450Nujol	1450Nujol
			1408m	1408m
1372Nujol	1370Nujol	1370Nujol	1370Nujol	1370Nujol
1307s	1316w	1333w		
1282m	1290s		1295s	1274s
		1258w	1242w	1258w
1220m				1219w
1163w	1163w	1163w	1198s	1198s
	1117w	1117w	1130w	1109w
1099w			1087w	1087m
	1026w	1031w	1058w	1015w
			1020m	
		990m		990m
967m	952s	968s	943m	943m
930m	901s	917s	917s	916s
893w			897m	893m
840w	843m	847m		855w
			810s	810s
	744s	769s	754w	769w
719m		719m		716s
690m			699s	
	610m			641m
				599m

Infra-red spectra of crotonic acid and some derivatives

α-Chloro-β-hydroxy-butyric acid, m.p. 59°	α-Chloro-β-hydroxy butyric acid, m.p. 86°	Bailey's "Y"	Methyl Y-chloro-crotonate	Synthetic methyl α-chlorovinyl-acetate
1709s		1724m	1730s	1767s
	1689s	1653m	1664m	1668w
	1450Nujol	1439m	1437s	1449s
1408m	1408m			
	1368Nujol	1379m	1319s	1332s
				1304m
1281s	1281s	1290s	1274s	
	1266m			
1235m			1235w	1228s
			1205s	1202s
1190s		1177s	1171m	1175s
1111s	1130w	1143w	1152s	
		1105m		
1087s	1093m	1064m	1078w	1081w
1047w	1069s		1035m	
		1005m	1010m	1012s
	962s	966m	980m	990s
943s	943m	917w	926m	943s
	901w			901w
		897w		
859s	875s	864w	855w	860w
	824s	837m	820m	806m
796s		797w		
		746w	746m	752m
706s	719m			
	699m	690s		
645m	673m		667w	670w
			658w	

Infra-red spectra of crotonic acid and some derivatives

α-Chlorovinyl-acetic acid	Fraction 8 (see p. 74)	Butyl chloral hydrate	Lactone polymer
1724s	1739s	1727m	1744s
	1656s		
1637s	1641s	1626m	
1439s	1427s	1450Nujol	
1408m		1420w	1405m
	1379m	1381Nujol	1384m
	1326m		1300m
1282m	1285m	1299s	
		1277s	
1226m		1247m	1250s
1191m	1198m	1196w	
1143m	1172s	1129m	1168s
	1121w	1114m	1104w
1074w	1087m	1087s	
		1047s	1056s
1012w	1028m	1020s	
980m	990m	957s	988m
935m	924w	935s	
907m			915w
	880w		875w
804m		822s	806w
746w	794w		760s
	770w		
		686s	
	667w	664s	666m
	641m	622s	
		588s	

Chlorination of phenanthrene in chloroform solution

$[\text{Phenanthrene}]_o = 0.0465\underline{M}$; $[\text{Chlorine}]_o = 0.0164\underline{M}$.

2-ml. samples were pipetted into 0.01039N-sodium arsenite (10 ml.) and the mixture was back-titrated with 0.00768N-iodine solution.

Time (mins.)	$V_{arsenite}$	% reaction	log term	k_2 ($M^{-1}.min^{-1}$)
3	5.40 ml.	4.9	0.01419	0.37
8	7.20	26.2	0.09351	0.77
14.25	8.00	34.8	0.1287	0.77
19.5	8.70	43.4	0.1744	0.68
23.5	9.00	47.0	0.1967	0.77
24.25	9.30	50.4	0.2194	0.69
28	9.40	55.2	0.2546	0.70
32	9.99	59.1	0.2865	0.68
39.5	10.51	64.6	0.3391	0.65

Mean k_2: 0.73 ± 0.04 $M^{-1}.min.^{-1}$

This reaction was studied by the sampling technique. For reactions which were faster than this, individual points were taken; the next example demonstrates this technique.

Chlorination of phenanthrene in LiCl - HOAc

[LiCl] = 0.80M

In this experiment, due to the speed of the reaction, individual points were taken. The course of the reaction was measured by quenching the reaction mixture with an excess of aqueous potassium iodide, and estimating the iodine liberated with standard sodium thiosulphate.

$[\text{Phenanthrene}]_o$	$[Cl_2]_o$	Time	$[Cl_2]_t$	$k_2(M^{-1}.min.^{-1})$
0.00870M	0.00360M	28 sec.	0.00157M	239
0.00870M	0.00359M	19 sec.	0.00192M	254
0.00870M	0.00359M	35 sec.	0.00136M	227
0.00870M	0.00355M	50 sec.	0.00078M	266
0.00870M	0.00346M	60 sec.	0.00066M	252

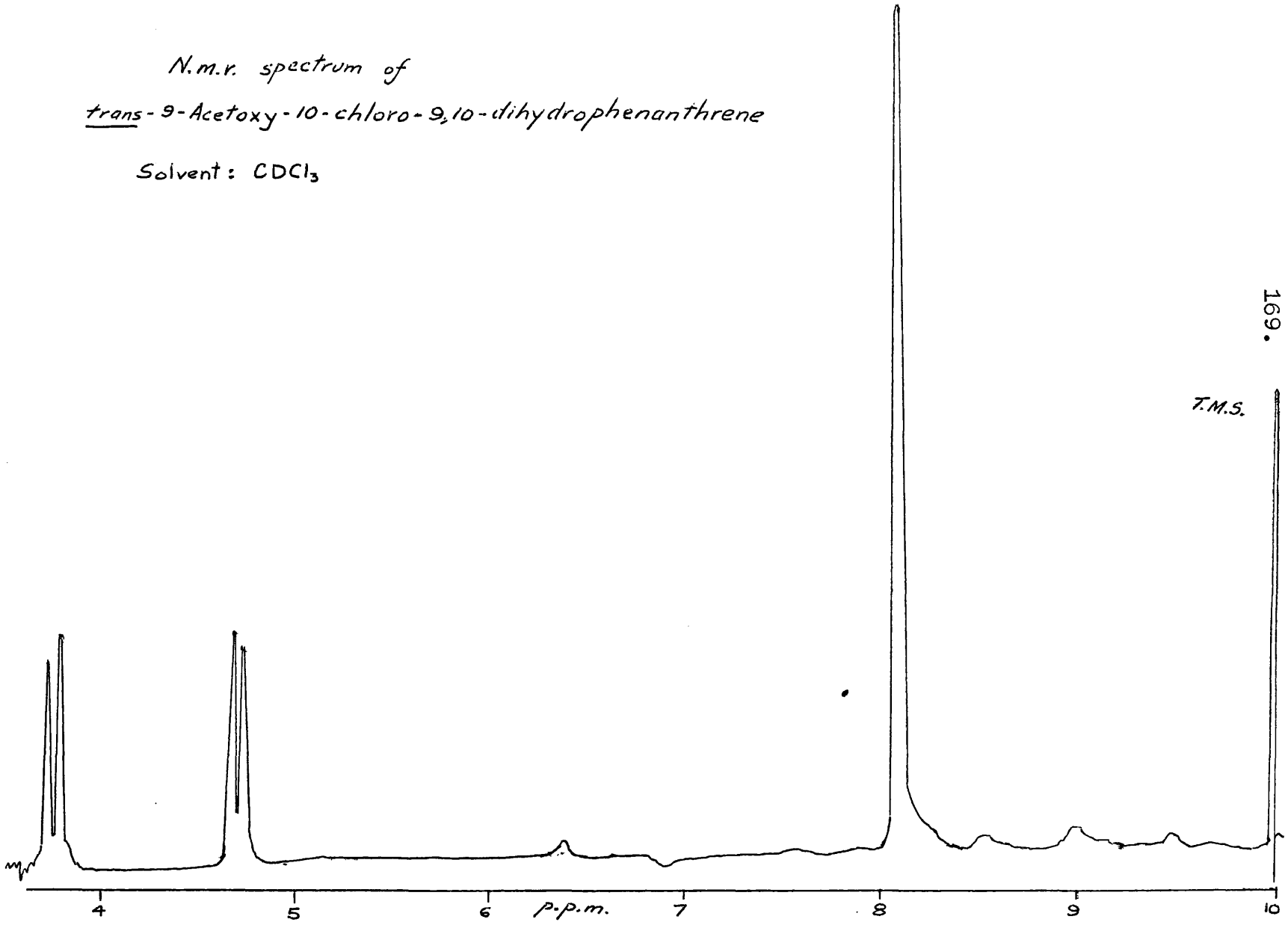
Mean k_2: 248 ± 12 $M^{-1}.min.^{-1}$

The variations in the individual values of k_2 are probably due to the small time intervals and the finite time necessary to start and stop the reaction.

N.m.r. spectrum of

trans-9-Acetoxy-10-chloro-9,10-dihydrophenanthrene

Solvent: $CDCl_3$

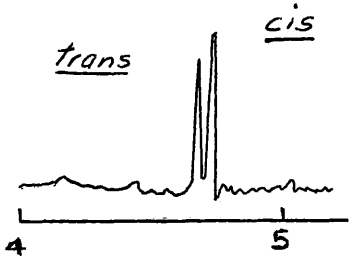


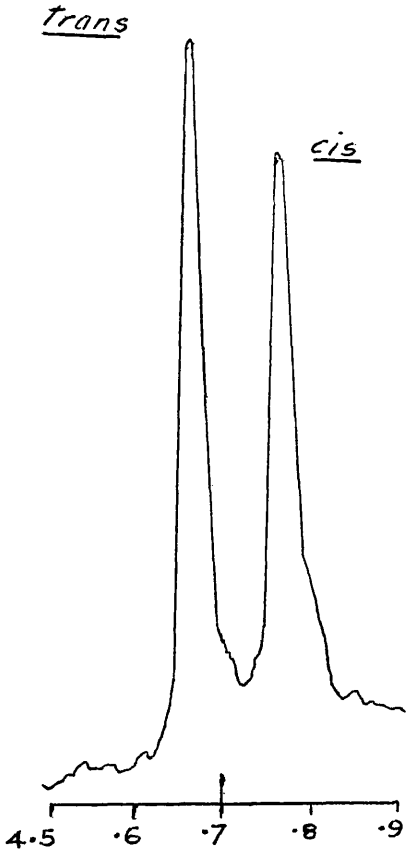
N.m.r. spectrum of

cis and trans-

9,10-Dichloro-9,10-dihydrophenanthrenes

Solvent: CCl_4

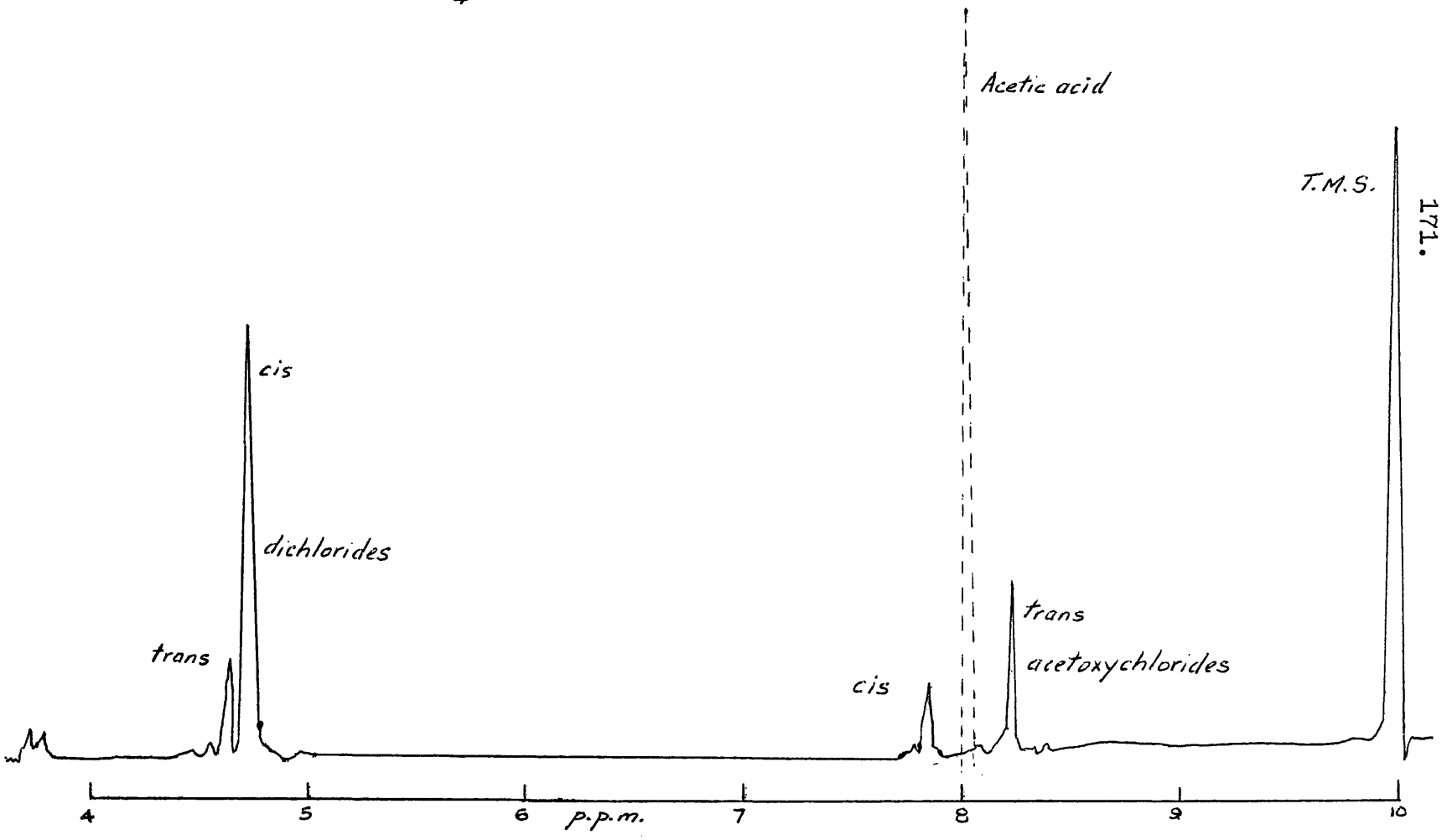




N.B. In $CDCl_3$ no separation could be achieved. In CCl_4, the extent of separation altered with the relative concentrations of each dichloride but only over a small range.

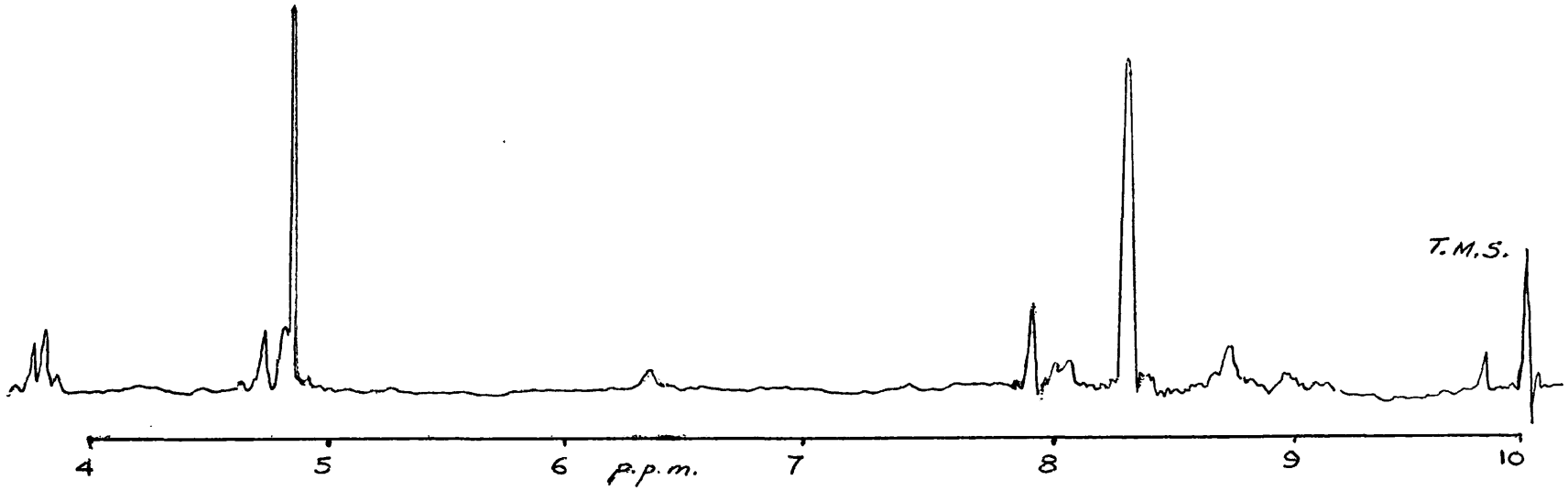
N.m.r. spectrum of the products of chlorination of phenanthrene

Solvent: CCl_4



N.m.r. spectrum of the products of chlorination of phenanthrene in 1M - sodium acetate in acetic acid.

Solvent: CCl_4



N.m.r. spectrum of the products of chlorination of phenanthrene in 1M-lithium chloride in acetic acid.

Solvent: CCl_4