

" SOME ASPECTS OF THE FORMATION OF ADDITION PRODUCTS
IN THE CHLORINATION OF POLYCYCLIC AROMATIC COMPOUNDS "

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by

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ABSTRACT

This thesis describes some aspects of the formation of addition products in the chlorination of polycyclic aromatic compounds.

The chlorinations of polycyclic hydrocarbons, represented by naphthalene and related compounds, have been investigated mainly from the point of view of adduct formation, and numbers of new addition products derived from those, as well as old ones of still unknown structure, have been clarified with regard to their structures and properties, using infrared, ultraviolet and proton magnetic resonance spectroscopy. As a chlorinating agent, either sulphuryl chloride or molecular chlorine has been used, and the electrophilic nature of the former reagent has also been qualitatively established.

Naphthalene, alkylnaphthalenes and halonaphthalenes, when treated with sulphuryl chloride with or without a solvent, give products similar to those obtained with molecular chlorine. By heating naphthalenes with sulphuryl chloride in excess, more highly chlorinated adducts were obtained together with some poly-

chlorotetralones. Under conditions in which naphthalene reacts slowly with sulphuryl chloride, chloronaphthalenes do not react significantly, whereas alkyl naphthalenes react more rapidly, than naphthalene itself does, and give adducts as well as products of substitution. Addition of chlorine always occurs in the ring, to which the substitution takes place in accordance with the rules governing the electrophilic substitution.

1-Alkyl naphthalenes with straight chain and acenaphthene give side-chain chlorinated tetrachlorides as the main addition products. The formation of these unexpected adducts has been explained on the basis of the hyperconjugative loss of proton during the chlorine addition process.

Chlorination of naphthols in acetic acid gives various ketopolychlorides, the structures of which have been spectroscopically investigated. 2,4-Dichloro-naphth-1-ol and related naphth-1-ols of similar structure have been found to involve the initial electrophilic attack on the 2- rather than on the 4-position, giving unstable 1-keto-1,2-dihydronaphthalenes which then undergo the anionotropic isomerisation to yield stable 1-keto-1,4-dihydronaphthalenes. Esters of naphth-1-ols behave

differently, depending on the solvents used; in acetic acid the products are similar to those obtained from naphth-1-ols, however, in chloroform, 2,3,4-trichloro-1⁰ tetralones are formed, which are not highly stable and gradually lose hydrogen chloride to give 2,4-dichloro-naphth-1-ols.

By similar treatment with chlorine, naphthylamines readily afford polychlorotetralones, for which a sequence involving the hydrolysis of the intermediary ketimine hydrochlorides has been suggested.

Infrared, ultraviolet and proton magnetic resonance spectra of more than forty addition products have been recorded.

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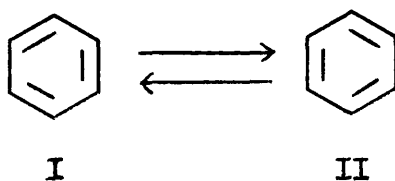
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PART I

INTRODUCTION

1. Aromatic Compounds and their Stability¹

Soon after Kekule had proposed his benzene formula, a certain difficulty arose. According to this formula, two isomeric o-disubstituted derivatives should be formed, but these have never been found. To resolve this difficulty, he further made the suggestion that benzene consists of two structures I and II in dynamic equilibrium.



Yet this theory, while accounting for the observed structural features of benzene, could not account for the differences in properties between benzenoid compounds and the formally similar olefins. Such failure of benzenoid compounds to exhibit typical olefinic properties has been referred to as aromatic character, which is now defined as a property shown by particular cyclic compounds with high thermodynamic stability and in which all of the annular atoms form a single conjugated system. Although various attempts have since been made to explain the stability of benzene, this

aspect of the problem in itself has remained unsolved until modern theories of molecular structure develop enough to settle the subject.

According to the current concept, the stability of benzene may be understood in terms of both the Molecular Orbital (MO) and the Valence Bond (VB) theories. The classical formula of benzene has three double bonds. In accordance with the MO theory these can be arranged as shown below:



If a molecular orbital treatment is applied to this system, two occupied orbitals are obtained. The lower is occupied by two electrons with opposed spins which are not free to travel round the ring. The next higher orbital is filled with two pairs of π -electrons. These pass round the ring pairwise in opposite directions. Therefore, the system is diamagnetic and anisotropic. Benzene built up in this way can be represented by the following structure.



The energy resulting from the delocalisation of the π -electrons is expressed in terms of an energy unit β . This amounts to 18-20 kcal/mol. The bond involving two π -electrons in ethylene yields 2β . Thus one Kekule structure with three double bonds should give 6β . The MO treatment predicts from the interaction of the π -electrons an energy of 8β . The 2β excess aromatic energy therefore must originate from the delocalisation of the double bonds.

In the ground state of benzene the double bonds disappear and are replaced by a new bond type, which has about 50% double bond character. In fact, various physicochemical methods such as X-ray structure, electron diffraction, infrared, Raman and ultraviolet spectroscopy have successfully shown that there are no alternating long single bonds (1.54 Å) and short double bonds (1.33 Å). Instead benzene has hexagonal symmetry, each hexagon side being 1.392- 1.397 Å long. If the aromatic bond were 50% double bond in character one would expect a bond length of 1.435 Å. The compression of 0.045 Å for each bond is taken as a result of the energy obtained by delocalisation.

According to the VB method, there are two

Kekule structures III and IV for benzene:



The interaction between these structures is called the resonance. The result of the resonance interaction is that benzene in its ground state is not represented by any of the Kekule structures but by a resonance hybrid which has a lower energy than a single Kekule structure. The ground state of benzene does not therefore contain double bonds but bonds which are of a form between single and double bond. Besides the two Kekule structures the three Dewar structures V - VII^{*} have to be considered, but they contribute less to the ground state of benzene. The VB theory calculates that the two Kekule structures contribute 78% and the Dewar structures 22% to the ground state.



^{*} Dewar benzene itself has recently been isolated and has a half-life of two days.² Therefore, discrimination in use of term should be made between the Dewar benzene in VB theory and the so-called Dewar benzene (cyclo-(2,2,0)-hexadiene).

The resonance energy is calculated in units of α , the interaction energy of the two p_z -electrons which convert the single bond in ethylene into a double bond. The resonance energy calculated from the two Kekule structures and the three Dewar structures is 1.11α .

The energy resulting from the interaction of the structures of benzene can be derived from two experimental data: heat of combustion and heat of hydrogenation. Benzene possesses the heat of combustion of 1323 kcal/mol., the value being 37 kcal/mol. less than the calculated value (1286 kcal/mol.) for the heat of formation of a single non-interacting Kekule structure. The heat of hydrogenation of the double bond in cyclohexane is 28.59 kcal/mol. and that of benzene is 49.80 kcal/mol. The latter value is again 35.97 kcal/mol. less than three times the former (85.77 kcal/mol.), which assumes three non-interacting double bonds in benzene. The difference of 37 kcal/mol. or 35.79 kcal/mol. therefore must result from the aromatic interaction and is called resonance energy. From the comparison with experimental results α is found to have a value of 33-37 kcal/mol.

The VB theory has been extended further to

polycyclic and heterocyclic compounds, and the following resonance energies were calculated: naphthalene 2.04α , anthracene 2.95α , phenanthrene 3.02α .

Concept of resonance was more related to the classical structure of organic chemistry, and therefore it has been welcomed to many workers in this field of chemistry. However, most of the early estimates of resonance energy made by comparing heats of combustion and hydrogenation of benzene and olefins are in recent times subject to some criticisms, and the observed stabilisation of molecules is interpreted as due to changes in bond energy with hybridisation rather than to resonance. According to these,³ resonance is said to play a minor role even in benzene, of which energy is found to be only about 10 kcal/mol., less than a quarter of the stabilisation energy.

Marked aromatic character is attached to a group of cyclic compounds with a closed shell of $(4N + 2)$ π electrons, where the association of a large stabilisation energy was first pointed out by Hückel through a MO treatment of the systems. It is referred to as the Hückel's rule and has been applied with success to various cyclic systems with two, six,

ten, fourteen, eighteen, etc. π -electrons. However, the delocalisation of π -electrons diminishes with increasing ring size and eventually double-single bond alteration will prevail in larger annulenes. With those compounds, although the cyclic systems are kept in a plane and all double bonds are obviously conjugated, that is, although they are still aromatic according to the definition, they are no longer aromatic in a chemical sense. They behave just like a cyclic polyene, undergoing addition rather than substitution.⁴

2. Reaction of Aromatic Compounds ⁵

Aromatic compounds gain considerable stabilisation energy owing to the interaction of π -electrons. As a consequence of it, addition reactions which result in the loss of this stability are rendered energetically less favourable relative to addition to olefins. Thus the aromatic compounds are comparatively unreactive and tend to undergo substitution rather than addition, because substitution in these systems does not practically result in loss of the stabilisation energy.

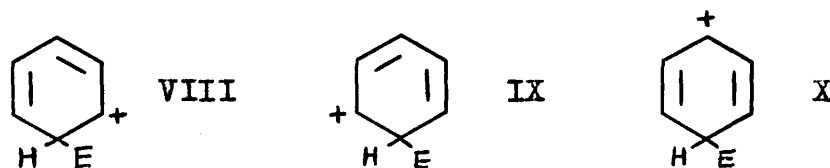
Substitution in aromatic compounds may be divided into three types: electrophilic, nucleophilic and free-radical substitutions. In electrophilic substitution, the two electrons which form the covalent bond between the aromatic compound and the reagent are both supplied by the former. In nucleophilic substitution, two electrons are supplied for the formation of the new bond by the reagent, while in the free-radical substitution the aromatic compounds provide an unpaired electron in its π -orbitals in the intermediate. The last two types of reaction are less important in aromatic systems than the electrophilic substitution and therefore will

not be described here.

There are two ways possible in which an aromatic compound might react with an electrophile.

- i) By a synchronous formation of the C-E bond (E = electrophile) and the cleavage of the C-H bond.
- ii) By addition of the electrophile to the nucleus followed by loss of a proton from the adduct.

Many evidences derived from the studies on the isolation of intermediates and the kinetic measurements of isotopic effects support the view that the reaction proceeds through the latter two-step process,⁶ which is known as S_E2 mechanism. The addition of an electrophile to a benzenoid system causes a temporary destruction of aromatic sextet and the stabilisation energy of the system is lost. However, the loss is in part offset by the resonance energy of the resulting carbonium ion intermediate, which is represented as the hybrid of three canonical structures VIII - X.



The re-establishment of the complete aromatic structure can take place by the removal of a proton from the inter-

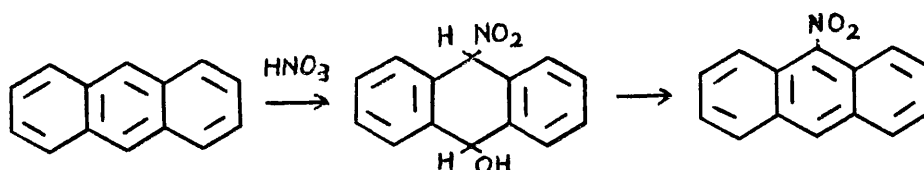
mediate. The driving force of this process originates from the re-acquisition of the stabilisation energy, which was lost in the primary stage of the reaction. Therefore, the more the stabilisation energy is acquired in the second stage, the more the aromatic compound will tend to undergo the substitution. Thus, when attacked by most electrophiles, benzene usually undergoes substitution rather than addition, and this behaviour has historically often been considered to provide a characterisation of aromaticity.

However, aromatic systems in which two or more benzene nuclei are fused together are often quite susceptible to addition reaction. As has been described, the extent as to how far a particular aromatic compound will undergo substitutive or additive reaction depends on the magnitude of stabilisation energy, lost and regained by the substrate during the electrophilic process. The amount of stabilisation energy lost in forming the adduct with an electrophilic reagent decreases with the increase of the number of benzene nucleus contained in the polycyclic system concerned. For naphthalene, such loss of stabilisation energy caused by the formation of addition product is roughly that (61 kcal/mol.) of

naphthalene less than (36 kcal/mol.) of benzene or about 25 kcal/mol. This value is far less than that of benzene, and in itself low enough to produce a certain amount of addition product. Thus, as early as 1833 Laurent observed the formation of a naphthalene tetrachloride by passing chlorine over solid naphthalene at room temperature.⁷ Higher polycyclic aromatics lose less stabilisation energy in the additive process: benzene 34, naphthalene 23, phenanthrene 20, anthracene 12 kcal/mol., so the addition product can be more readily obtained from higher polycyclic aromatics such as phenanthrene and anthracene.

3. Addition Reactions in Aromatic Compounds

Until very recently the mechanism of electrophilic substitution was only imperfectly understood. Electrophilic reagents were known to add to ethylenic double bonds under suitable conditions, and similar addition compounds have sometimes been obtained with certain polycyclic aromatic compounds. For example, with HO-NO_2 in the presence of the appropriate anion, anthracene was found to give isolable adducts which on treatment with mineral acid undergo the elimination of H-OH with the formation of 9-nitroanthracene.⁸



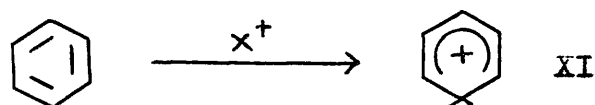
For this reason, it was suggested that electrophilic substitution takes place by addition of the reagent X-Y , and subsequent elimination of H-Y , to give the substitution product Ar-X . Thus bromination was supposed to occur by addition of bromine to an aromatic double bond followed by elimination of hydrogen bromide. Addition products of this kind have actually been isolated from many aromatic hydrocarbons, including benzene, naphthalene, anthracene and phenanthrene. These addition products

are usually relatively unstable, and give rise to substitution products with the elimination of hydrogen halide on heating.

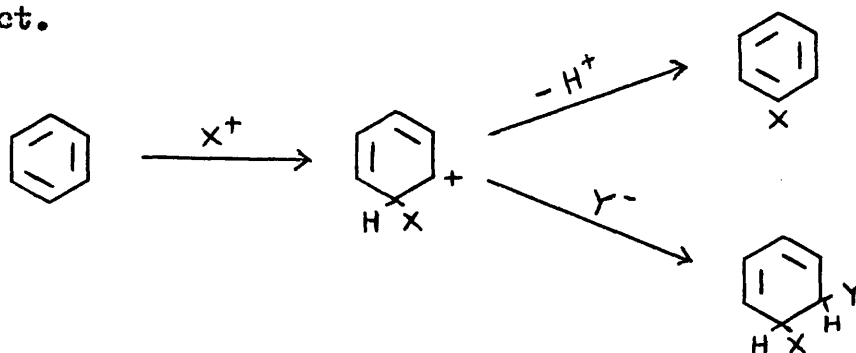
This addition-elimination theory of aromatic substitution received considerable attention from organic chemists for many years, but evidences against it have gradually accumulated. For example, it has been shown that the addition of bromine to the 9,10-bond of phenanthrene is largely photochemical, but that in the presence of certain catalysts, such as aluminium chloride or iodine, hydrogen bromide is evolved and the substitution product is formed. According to the addition-elimination theory, these catalysts would have to act by promoting the elimination of hydrogen bromide from the adduct, but Price was able to show that the addition of iodine to a solution of phenanthrene dibromide produced no change, and did not result in the elimination of hydrogen bromide.⁹ These catalysts must therefore promote the elimination of hydrogen bromide in some other way, and thus the addition-elimination theory has almost been discarded.

According to the modern theory of electrophilic substitution in benzenoid compounds, addition

of the electrophile to the aromatic nucleus to form the carbonium ionic intermediate XI constitutes the initial stage of the reaction. Then this intermediate is considered to lose a proton more rapidly than it reacts with the nucleophiles to give a substitution product:

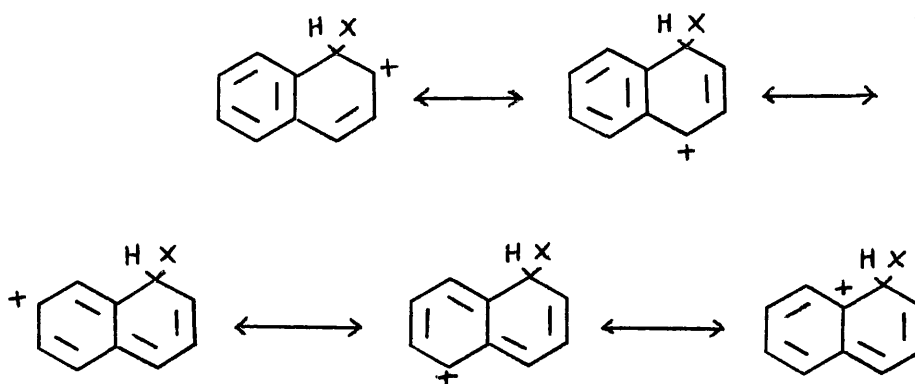


With a slight modification of the structure, however, such ionic intermediate is subject to a considerable stabilisation through the inductive, mesomeric or hyperconjugative delocalisation of positive charge. Under these circumstances, it is reasonably expected that the capture of nucleophiles could well compete with the proton expulsion, leading to the formation of the addition product.



This is especially the case with polycyclic aromatics,

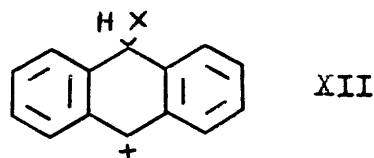
where the positive charge can be readily delocalised by mesomerism and the loss of stabilisation energy involved in the addition process is less significant. For example, the delocalisation of the positive charge in the transition state for 1-substitution in naphthalene is considerably more extensive than that in benzene, resulting in the increased stability of ionic intermediate (consequently the increased opportunity for the capture of nucleophile) and decreased activation energy. A similar situation also applies to 2-substitution in naphthalene.



The stabilisation energy of naphthalene is considerably greater than that of benzene, but it is apparently less than twice as great. Benzene has a stabilisation energy of 36 kcal/mol.; its adduct with one molecular equivalent of chlorine, if it is considered analogous

to butadiene, has a stabilisation energy of 3 kcal/mol.; therefore 33 kcal/mol. is lost by such process. The corresponding process with naphthalene, if it is assumed that a styrene-like system is formed, involves a loss of stabilisation energy of only 23 kcal/mol. Thus naphthalene undergoes addition reactions more readily than does benzene. The situation for the anthracene is much more favoured, giving a considerably delocalised structure to which dibenzenoid XII is the most important contributor. Stabilisation energy lost for this canonical form is only 11.5 kcal/mol. So the reaction of anthracene with electrophiles

usually proceeds through the addition reactions in the 9,10-positions. Hence, higher



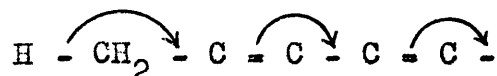
polycyclic aromatics are generally more reactive than their lower homologues, and the formation of addition products becomes thermodynamically more favoured than the substitution reactions.

Recently this aspect of the addition reaction in electrophilic aromatic substitution has been extensively investigated by de la Mare and his co-workers,¹⁰ and the formation of adducts of this kind is established

to be consistent with the view that the ordinary substitution proceeds through an intermediate of the carbonium type, which loses a proton; and that this intermediate gives products of addition by an alternative process in which the nucleophile is captured. This concept has been adopted with success in the interpretation of some unusual substitution processes.¹¹ In the electrophilic substitution of polycyclic benzenoid compounds, the addition-elimination sequence may well be involved more frequently than has generally been supposed.

4. Hyperconjugation and Adduct Formation

The inductive electron release increases with chain-branching, giving the order $\text{CH}_3 < \text{C}_2\text{H}_5 < \text{i-C}_3\text{H}_7 < \text{t-C}_4\text{H}_9$. However, under certain circumstances this order is inverted. The reversal of the inductive electron release was first observed by Baker and Nathan in 1935.¹² As it usually occurs in the adjacent conjugating system, it has been attributed to a form of mesomerism in which the electron pairs of the C-H bond are delocalised and are able to conjugate with an unsaturated system.



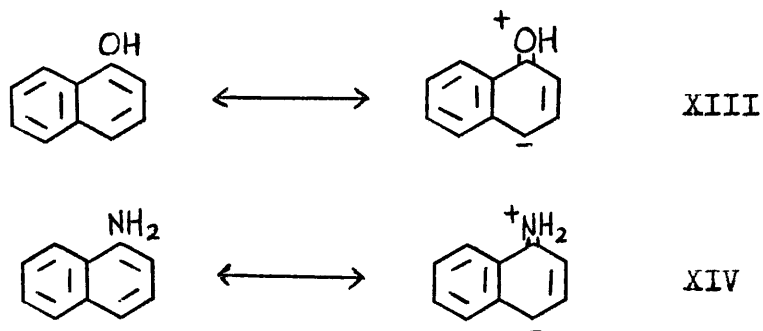
Such conjugation between the electrons of a single bond and those of multiple bonds is called hyperconjugation.

This conjugative mode of electron release by alkyl groups has received considerable support on physicochemical grounds, but present theories are still unable to provide enough evidences to account for all the experimental results concerned. To explain the enhanced electron release by OH and NH_2 substituents, a similar idea was extended by de la Mare to N-H, C-C and O-H hyperconjugation.¹³ There are some criticisms about

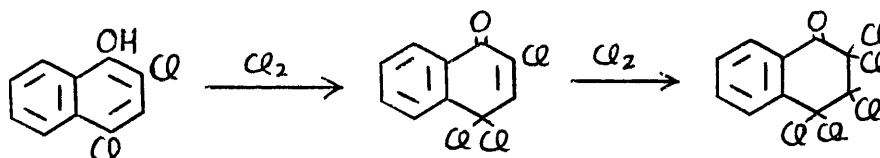
the hyperconjugation. Nevertheless, the concept of hyperconjugative mechanism of electron displacement is so useful for the interpretation of a wide variety of experimental data that it is finding general acceptance in various fields of organic chemistry. Although it may be a minor factor with respect to ground state, it is certainly a dominant factor in stabilising excited and transition states of molecular species.

This mode of electron displacements is necessarily electron-releasing. Thus the reactivity of the aromatic nucleus is always enhanced by hyperconjugation, as has been manifested in numbers of electrophilic substitutions.⁵ Under suitable circumstances, however, this hyperconjugative interaction between the aromatic ring and a substituent goes so far in the transition state that the loss of hyperconjugating proton to the medium and the breakdown of aromatic character in the compound occurs, the inevitable consequence of which would make additive reactions preponderate over substitutive reactions. These are especially the case with amino and hydroxyl derivatives of polycyclic aromatic compounds, which are already subject to the increased reactivity due to the combined effect of the

-I inductive effect of the aromatic system and the resonance stabilisation of the excited structure XIII or XIV.

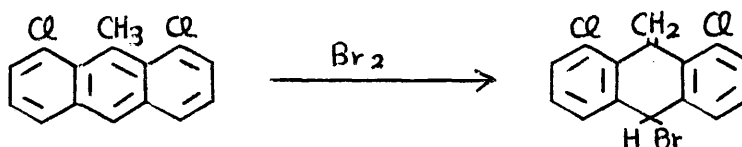


Thus as early as 1888, Zincke and Kegel¹⁴ observed that on treatment with excess halogen, naphthols are halogenated with extraordinary ease to give not the expected polyhalonaphthols but the polychlorotetralones.

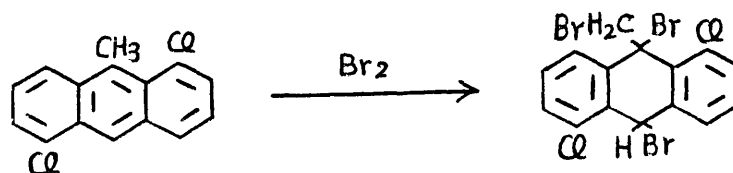


Later, similar phenomena were described by Fries and his co-workers¹⁵⁻¹⁶ for the chlorination of certain naphthylamines. The easy formation of adducts from these compounds can be interpreted consistently in terms of the O-H and N-H hyperconjugation, which would play an important role in the transition state to reduce the charge separation on the oxygen or nitrogen atom. If such an effect is actually operating in the process of adduct formation, with alkyl derivatives of polycyclic

aromatics there is enough reason to expect a similar addition product, in which one of the α -hydrogen atoms of alkyl group is split off or replaced by appropriate nucleophile as a result of the hyperconjugative release of the proton. A brief survey of the literature well backs the view that this kind of proton expulsion may be operative in the side-chain substitution of polycyclic aromatic compounds, as the formation of such products has often been demonstrated in the analogous reactions. Thus 1,8-dichloro-9-methylantracene gives on bromination an addition product, in which a proton has been split off from the alkyl side-chain,



whereas 1,5-dichloro-9-methylantracene has been reported to yield a side-chain substituted addition product.¹⁷



5. Addition Products from Polycyclic Aromatics [ⓧ]

Up to now more than forty addition products from polycyclic aromatic compounds have been recorded in the literature. However, some results are contradictory to each other and need further investigations. In this chapter, a brief survey of those adducts will be made.

Naphthalene

The best known adducts from naphthalene and electrophiles are those obtained by chlorination. A naphthalene dichloride of unknown structure was reported by various workers to have been prepared from the reaction of solid naphthalene with chlorine or hypochlorous acid. ^{7, 18-22} Recent studies, however, cast some doubt upon those results. ²³⁻²⁴ Of the six possible geometrical isomers of naphthalene tetrachloride (1,2,3,4-tetrachloro-1,2,3,4-tetrahydronaphthalene), four have been well characterised. ²⁵⁻²⁷ A fifth isomer remains unconfirmed. ^{20, 28} Chlorination

[ⓧ] Addition products formed by hydrogenation, oxidation, metallation, dienophilic reagents or carbene captures are excluded.

in acetic acid affords besides the above tetrachlorides a trichloroacetoxy compound as a minor product.²⁶ A naphthalene tetrabromide of unknown structure was also prepared.²⁹ The addition of tetrachlorodiborane to naphthalene yields an interesting adduct (1,2,3,4-tetrachloroboryl-1,2,3,4-tetrahydronaphthalene), for which the α -structure is allocated.³⁰ 1-Chloronaphthalene gives depending on the conditions used either 1,1,2,3,4-pentachloro-1,2,3,4-tetrahydronaphthalene or 1,2,3,4,5,8-hexachloro-1,2,3,4-tetrahydronaphthalene,^{18, 21, 31-33} while 2-chloronaphthalene has been claimed to yield a liquid adduct in which chlorine addition had taken place in the unsubstituted ring.³² Under the homolytic conditions in carbon disulphide, 1-chloronaphthalene is also said to give 1,1,2,3,4,4-hexachloro-1,2,3,4-tetrahydronaphthalene.³⁴ Chlorination of 1,5-dichloronaphthalene is known to give a tetrachloride (1,1,2,3,4,5-hexachloro-1,2,3,4-tetrahydronaphthalene), together with a trichloronaphthalene dichloride of unknown structure.^{32, 35-36} Similar tetrachlorides were obtained from 1,8- and 2,7-dichloronaphthalene, too.³⁶⁻³⁷ Exhaustive chlorination of naphthalene under drastic conditions gives a perchloronaphthalene dichloride, to which a

1,4-addition structure (1,1,2,3,4,4,5,6,7,8-decachloro-1,4-dihydronaphthalene) is assigned.³⁸ Treatment of naphthalene with aqueous hypochlorous acid has been reported to form a dichlorodihydrotetralin.³⁹ 1-Methyl and 2-methylnaphthalene give the corresponding methylpentachlorotetralins in which addition-substitution of chlorine had occurred in the substituted ring,⁴⁰⁻⁴¹ whereas two tetrachlorides from naphthalene 1- and 2-sulphonyl chlorides were found to have undergone the chlorine addition in the opposite ring in accordance with the electrophilic mechanism of the addition reaction.⁴² Following the chlorination of 1- and 2-naphthol, numbers of ketochloro derivatives of 1,2-dihydronaphthalene, 1,4-dihydronaphthalene and 1,2,3,4-tetrahydronaphthalene were prepared.^{14, 43-58} Dihydroxynaphthalenes similarly yields ketopolychlorides or polychloroquinones.⁵⁹⁻⁶⁰ In some cases, similar ketopolychlorides were obtained from naphthylamines, probably through the hydrolysis of the initially formed ketoimine hydrochlorides.^{15-16, 61-62} Various chlorine adducts of interesting structures were reported by Claus and Jäck,⁶³ following the partial dehydrochlorination of the addition products from 1-chloro-2-acetylaminonaphthalene. However, proposed structures seem

to need further examinations.

Biphenyl

With chlorine in acetic acid, biphenyl has recently been found to give a tetrachloride with a conjugated double bond.⁶⁴

Acenaphthylene and Acenaphthene

Acenaphthylene may be ~~a~~ styrene analogue of naphthalene, so it readily reacts ^{regarded} with electrophiles to give 1,2-addition products.⁶⁵ In the chlorination of acenaphthene, a trichlorodichloride and a dichlorotetrachloride has been isolated,⁶⁶ whereas a wide variety of inconsistent results has been described concerning the bromine adducts of acenaphthene.⁶⁷ Recent works by Dashevskii and Petrenko seem to provide the most reliable results.⁶⁸

Anthracene

Anthracene readily undergoes substitution and addition with fluorine, the product being perfluoroanthracene, $C_{14}F_{24}$.⁶⁹ Chlorine and bromine give initially anthracene dichlorine and dibromide respectively, which are 9,10-dihydroanthracenes.⁷⁰ These

compounds decompose even at room temperature, and especially on warming, giving hydrogen halide and 9-haloanthracenes, anthracene, and 9,10-dihaloanthracenes. 9,10-Dihaloanthracenes undergo addition with the formation of either 9,9,10,10-tetrahalogeno-9,10-dihydroanthracene or 1,2,3,4,9,10-hexahalogeno-1,2,3,4-tetrahydroanthracene, which may be obtained in stereoisomer forms.⁷¹ Low temperature in chloroform favour the formation of the former, and high temperatures and benzene that of the latter. The presence of substituents in the 1-positions has the effect of making the adduct more stable. Addition products of similar nature are also obtained from the reaction with nitric acid or nitrogen dioxide.⁸ If the substituents at 9- or 10-positions are alkyl or aralkyl groups, the addition reactions have often been accompanied by the simultaneous side-chain substitution or the expulsion of an α -hydrogen from the alkyl groups.^{17, 72}

Phenanthrene

Phenanthrene forms addition products, but less readily than anthracene, at the 9,10-bond. With chlorine and bromine, the initial products are relatively unstable 9,10-dichloro- and dibromo-9,10-dihydrophenan-

threne.^{9, 73} With bromine the reaction is reversible, and equilibrium being established. In nitration, there is also evidence that addition may be the primary reaction, but no definite addition products have been isolated.⁷⁴ Little is known concerning addition in other positions in the phenanthrene nucleus. No adduct with other electrophiles is known either.

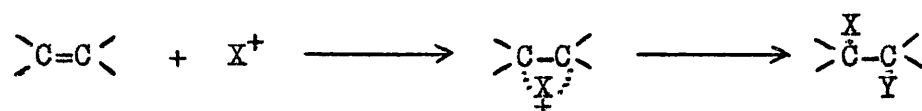
Other Polycyclic Systems

Other polycyclic aromatic hydrocarbons have not been so intensively investigated yet. Naphthacene is known to react with sulphuryl chloride at high temperature to give 9,9,10,10,11-pentachloro-9,10-dihydronaphthacene.⁷⁵ With chlorine in trichlorobenzene, pyrene yields 1,2,3,5,6,7,8,10-octachloro-1,2,6,7-tetrahydropyrene.⁷⁶

6. Stereochemistry of Addition Products

6.1 Stereochemistry of Adducts Formation in Polycyclic Aromatic Systems¹⁰

It is well known that addition to double bonds initiated by electrophiles usually proceeds in the trans sense. This type of additions were theoretically first interpreted by Roberts and Kimball,⁷⁷ who proposed that the interaction between the attacking species and the carbonium ionic centre would prevent free rotation about the original double bond, and would make the entering nucleophile approach from the opposite side of the double bond, resulting in the conversion of configuration at the carbon atom attacked.

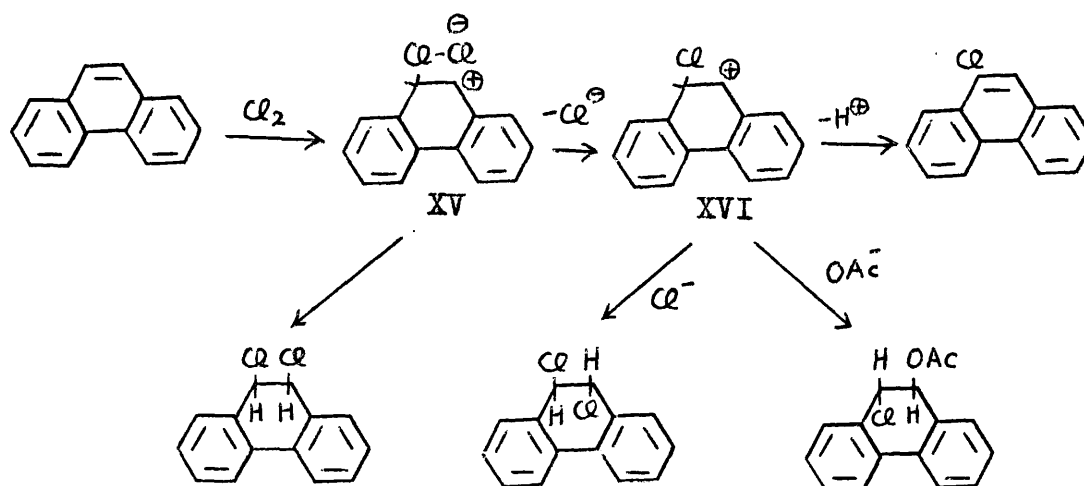


This theory has been elaborated by various workers,⁷⁸ and cis-additions to olefinic bond now and then observed were rather regarded as exceptional.⁷⁹

The new aspect of cis-additions to olefinic bond has in recent times been studied extensively by de la Mare and his co-workers concerning the chlorine addition to polycyclic aromatic systems. The addition of chlorine to phenanthrene in acetic acid gives

more of the cis than the trans-dichloride, accompanied by some amounts of trans-acetoxytrichloride.⁷³ Environmental change has been found to have little effect on the proportion of products. Similar treatment of naphthalene was found to give mainly α -naphthalene tetrachloride, together with δ -tetrachloride and acetoxytrichloride as minor components.^{26, 80} Since added electrolytes make the proportion of the stereoisomeric δ -isomer preponderate over the α -isomer, it is suggested that the latter has not been formed through the capture of a carbonium intermediate ArHCl^+ by chloride ion from the environment, but through the direct two successive cis 1,2-additions. The reactions have been shown to be heterolytic in character. To account for the nature of the products and their stereochemistry, the result was interpreted that the intermediate of the type ArHCl_2^+ , involving halogen with an expanded octet, plays an important role in aromatic substitutive and additive reactions. According to this suggestion, the cis-addition products is formed directly through the ion-pair-like intermediate XV which lies earlier on the reaction path than the carbonium intermediate XVI. Alternative route for this intermediate XV is to lose chloride ion to form the

carbonium ionic intermediate XVI, which then reacts with external nucleophiles to give trans-adducts or splits off the proton to yield substitution products. For example, the chlorination of phenanthrene can be depicted as follows:

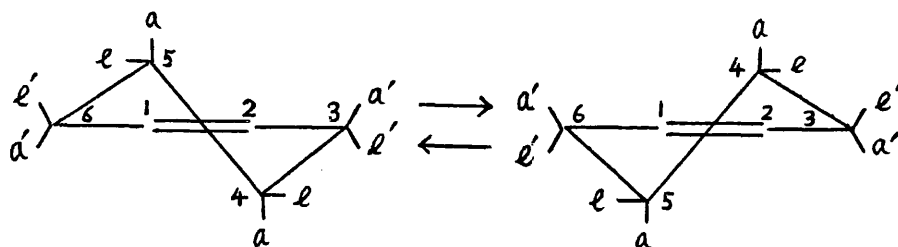


6.2 Conformation of Addition Products

Among the addition products from polycyclic aromatic systems, the best known are those obtained by halogenations. According to the number of halogen molecules involved in the addition reaction, they are divided into two categories: dihalides and tetrahalides. As the first member of polycyclic hydrocarbons having fused rings, naphthalene has two ways possible for the initial halogen addition: 1,2- and

1,4-additions. Although the dichloride of unknown structure χ has been described in the literature and its structural elucidation seems of great interest, none of the recent attempts has so far succeeded. Under a variety of conditions, the products have been found to be a mixture of chloro-substituted naphthalene and tetrachlorides.

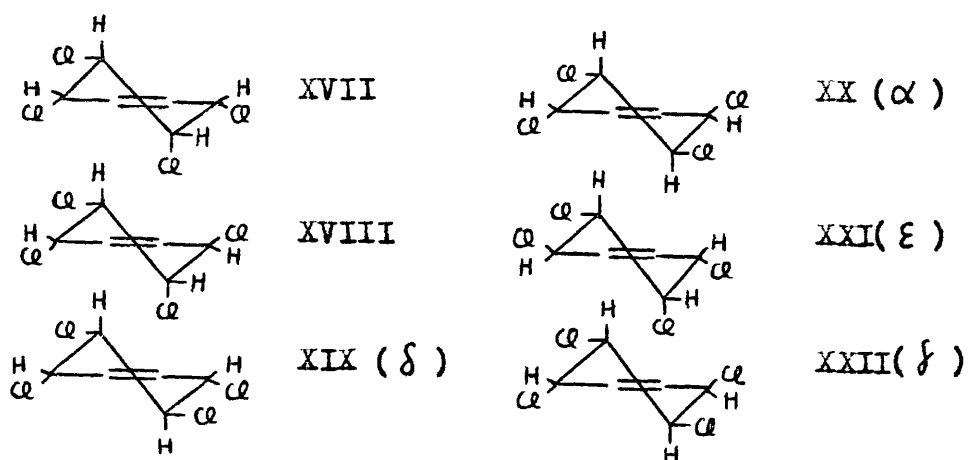
Naphthalene tetrachlorides may be regarded as a benzo-derivative of cyclohexane, whose conformation exactly corresponds to that of cyclohexene. The conformation of cyclohexene is that of a flattened chair or half-chair as shown below, since carbon atoms 1,2,3, 6 are in a plane.



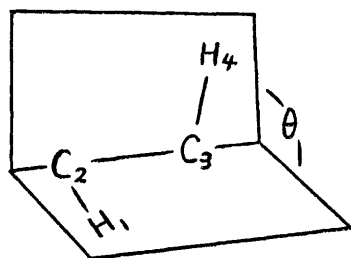
In cyclohexene, two axial a and equatorial e bonds are formed only at C_4 and C_5 . The bonds at C_3 and C_6 are somewhat differently disposed than in cyclohexane, and are called pseudoaxial a' and pseudoequatorial e'.

There are six possible geometrical isomers XVII - XXII for naphthalene tetrachlorides, of which

four have been thoroughly authenticated.²⁶



Configurations and conformations of these addition products can be established by proton magnetic resonance spectroscopy. A hydrogen nucleus in an axial position is usually shielded more than one in an equatorial position by about 0.1 - 0.6 p.p.m. This has been attributed to the shielding from neighbouring anisotropic effects associated C-C bonds.⁸¹ The coupling constant for two vicinal protons in a substituted ethane $H^1-C^2-C^3-H^4$ has been shown to depend on the dihedral angle (θ) formed between the planes that contain $H^1-C^2-C^3$ and $C^2-C^3-H^4$. The relationship has been calculated from valence bond theory for substituted ethanes.⁸²



$$J = 8.5 \cos^2 \theta - 0.28 \text{ c.p.s.}$$

$$0 \leq \theta \leq 90^\circ$$

$$J = 9.5 \cos^2 \theta - 0.28 \text{ c.p.s.}$$

$$90^\circ \leq \theta \leq 180^\circ$$

These equations were successfully applied to estimate coupling constants for certain cyclohexane derivatives of known structure: the coupling constants between two axial hydrogen nuclei on adjacent carbon atoms,

$J_{aa} = 5 - 8 \text{ c.p.s.}$, $\theta = 180^\circ$; two equatorial hydrogen nuclei on a pair of adjacent carbon atoms, $J_{ee} = 3 - 4 \text{ c.p.s.}$, $\theta = 60^\circ$; and an axial and equatorial hydrogen nucleus on adjacent carbon atoms, $J_{aa} = 2-3 \text{ c.p.s.}$, $\theta = 60^\circ$, in fairly good agreement with the theoretically expected values. The relationship appears to hold reasonably well for naphthalene tetrachlorides, where for axial-axial interactions, $J_{aa} = 10-12 \text{ c.p.s.}$; for axial-pseudoaxial, $J_{aa'} = 6-8 \text{ c.p.s.}$ and for all equatorial-equatorial J_{ee} , axial-equatorial J_{ae} , pseudoaxial-equatorial $J_{ea'}$, axial-pseudoequatorial $J_{ae'}$, and equatorial-pseudoequatorial $J_{ee'}$, all couplings are in the range of 2-4 c.p.s.

The couplings are also affected by the substituents on the $-\text{CH}-\text{CH}-$ fragments, and are linearly dependent on the sum of the electronegativities E of the first

atoms of the substituent groups.⁸³

$$J = 18.97 - 0.80 \sum E$$

For the cyclohexene ring which has a rigid structure, the orientation dependence of this electronegativity effect has not been elucidated yet. In the stereochemical studies of addition products, much useful information concerning the configurational and conformational aspects of the adducts can be obtained by using these semi-empirical principles.

Chemical approach to the structural study is the alkaline dehydrochlorination of addition products. From^{an} early date of the organic chemistry, there have been many indications that trans 1,2-elimination is the mode for the base-promoted eliminations, and ever since 1940 when Hückel had realized that the stereochemistry should be dependent on the mechanism, this aspect of elimination reaction has been greatly investigated.

In the cyclohexane field, the dehydrochlorination of benzene hexachloride has been examined from the point of view both of products and of relative reactivity, and it has been concluded that hydrogen is removed preferentially from the allylic position and relative ease of elimination follows the order,



However, this order has been in part questioned by de la Mare and his co-workers,²⁷ who had investigated the rates and products of alkaline dehydrochlorination of naphthalene tetrachlorides. The relative rates as well as the composition of products agree qualitatively well with what would be expected from the configurations of the individual isomers.

Relative rates of dehydrochlorination of
naphthalene tetrachlorides

Isomer	Main conformation disposition of chlor- ines	(1.mole ⁻¹ min. ⁻¹) k ⁻¹
α	a'eea'	3.00
β	e'eee'	0.15
δ	a'eee'	5.9
ε	a'ace'	0.23

The α and δ -tetrachlorides which have hydrogen and chlorine atoms configurationally trans to each other undergo rapid second order dehydrochlorination, whereas the β -tetrachloride which have no hydrogen and chlorine atoms trans to each other on the adjacent carbon atoms, and the ε -tetrachloride for which 2,3-trans elimination of axial hydrogen and chlorine

is structurally unfavoured, both undergo slow dehydrochlorinations. Following the interpretation of products composition, the reactivity sequence trans-1,2 > cis-1,2 > cis-1,4 has been confirmed, but concerning the relative ease of trans-1,4 and cis-1,4-eliminations, no conclusive evidence has been derived yet.

For polycyclic homologues higher than naphthalene, addition reaction tends to occur more readily in such a way as to isolate two fully benzenoid residues, rather than to occur in the outermost ring of a polycyclic system. Thus, both anthracene and phenanthrene usually undergo addition reaction at 9,10-position. For anthracene-9,10-dichloride, cis-1,4-elimination was found to be more rapid than the trans-1,4-elimination.⁸⁵ With phenanthrene-9,10-dichloride, of course, the order trans-1,2 > cis-1,2 elimination holds.

7. Aims and Objects of the Present Investigation

As a part of the studies concerning the electrophilic chlorine addition to benzenoid systems, the chlorination of polycyclic hydrocarbons, represented by naphthalene and related compounds, have been investigated mainly from the point of view of adduct formation.

Although the literature contains numbers of chlorine addition products from a variety of naphthalene compounds, little attempt seems to have been made yet to classify these addition products systematically according to the structures as well as the reaction sequences. In the present work, main effort has been made to elucidate the general character of various addition reactions in naphthalene series, and to systematise these results as well as those of previous workers in accordance with the modern concept of organic chemistry. Emphasis has also been laid on the structural establishment of the addition products, and a number of new adducts as well as old ones of unknown structure have been clarified with regards to their constitutions, by the help of the modern techniques of infrared, ultraviolet, and proton magnetic resonance spectroscopy.

As a chlorinating agent, either sulphuryl^l chloride or molecular chlorine has been chosen, depending on the reactivity of substrates. The electrophilic behaviour of the former reagent has also been established qualitatively in the present work.

PART II

EXPERIMENTAL

8. Chlorine Addition to Naphthalene

Materials

Sulphuryl chloride was shaken repeatedly with mercury, and was redistilled before use. Carbon tetrachloride was dried over calcium chloride. Naphthalene (m.p. 80°) was purified by chromatography on alumina and recrystallised from light petroleum.

Chlorination of Naphthalene

Without Solvent

1. Naphthalene (25.6 g.) and sulphuryl chloride (27.0 g.) were mixed and the mixture was kept in the dark place at room temperature. An intense yellow colour immediately developed and crystals of naphthalene slowly disappeared under gentle evolution of hydrogen chloride and sulphur dioxide. After 4 days the dark red solution was diluted with ligroin and unchanged sulphuryl chloride was removed under reduced pressure. Crystals of naphthalene α -tetrachloride (m.p. $182-184^{\circ}$, 0.92 g.) was filtered off and the mother liquor was chromatographed on silica gel. Elution with light petroleum gave products of substitu-

tion (30.1 g.), accompanied by some unchanged naphthalene. Further elution with benzene gave a mixture of naphthalene α - and δ -tetrachlorides (1.39 g.).

Use of somewhat excess sulphuryl chloride gave similar results, except the complete consumption of naphthalene.

2. Naphthalene (2.57 g.) and sulphuryl chloride (10 g.) were heated together under gentle reflux for 5 hr. The mixture was then left to stand at room temperature overnight. Crystals of the α -tetrachloride (0.49 g.) were filtered off. The filtrate was poured into water; extraction with ether followed by evaporation of the solvent gave an oil from which a further 0.27 g. of the α -tetrachloride separated. Chromatography of the remaining oil gave (1) products of substitution (1.92 g.), which showed by g.l.c. to contain 1-chloronaphthalene (41%), 1,4-dichloronaphthalene (32%), and 1,5-dichloronaphthalene (22%), with only trace of trichloronaphthalenes; (2) the δ -tetrachloride (0.74 g., m.p. 90-95°); (3) a light brown syrup containing keto-compounds (0.22 g.). The last fraction slowly solidified, and gave an impure ketone of the formula $C_{10}H_7Cl_3O$ (Found: C, 47.84; H, 2.08. $C_{10}H_7Cl_3O$ requires

C, 48.12; H, 2.83%). Infrared (ν_{\max} , 700s, 753s, 788ms, 1203ms, 1250ms, 1271s, 1600ms, 1712s cm.^{-1}) as well as ultraviolet spectra (λ_{\max} , 253, 291 and 298-298.5sh $\text{m}\mu$, $\log_{10} \epsilon$ = ca. 4.1, 3.3 and 3.2 respectively). On reduction with sodium bisulphite in boiling acetic acid it gave an impure naphthol (m.p. 78-79°), purified by repeated precipitation from alkaline solution with aqueous hydrochloric acid and shown to be 2,4-dichloronaphth-1-ol (m.p. 104-105°, Found: C, 56.53; H, 3.02. $\text{C}_{10}\text{H}_6\text{Cl}_2\text{O}$ requires C, 56.3; H, 2.8%). The main component of the ketonic products was later identified as 1-keto-2,3,4-trichloro-1,2,3,4-tetrahydronaphthalene by comparison with the authentic specimen obtained from 1-acetoxynaphthalene by independent method (cf. Section 15.3).

In solvent

Naphthalene (12.8 g.) was dissolved in a mixture of sulphuryl chloride (13.5 g.), chloroform (10 ml.) and ligroin (10 ml.) and was left to stand for 9 days at room temperature. Crystals of the α -tetrachloride (0.59 g.) was filtered off. The filtrate was concentrated under reduced pressure, and then chromatographed on silica gel. Elution with light petroleum and

benzene gave products of substitution (14.8 g.) and addition products (0.74 g.) respectively.

In Presence of Inorganic Salt

Naphthalene (7.68 g.) and sulphuryl chloride (30 g.) were gently heated in presence of small amounts of lithium chloride (0.32 g.). Part of the salt remained undissolved, but the reaction proceeded so smoothly that after 2 hr. the mixture, when cooled, partly solidified to crystalline mass. Usual working-up gave a mixture of di- and trichloronaphthalenes (7.09 g.), addition products (2.72 g.) and light brown syrup containing keto compounds (0.57 g.).

In Presence of Organic Peroxide

Naphthalene (2.58 g.) and sulphuryl chloride (10 g.) dissolved in carbon tetrachloride (6 ml.) were heated in presence of benzoyl peroxide (ca. 50 mg.) for 7 hr. under gentle reflux. After having stood overnight, crystals of the α -tetrachloride (0.98 g.) were filtered off, and the filtrate was worked up as usual. Products of substitution (1.77 g.), naphthalene γ -tetrachloride (m.p. 131-133°, 0.17 g.), naphthalene δ -tetrachloride (0.86 g.), and a light brown syrup containing naphthalene pentachloride and keto compounds (0.66 g.)

were separated from each other by chromatography.

In Liquid Sulphur Dioxide

Finely powdered naphthalene (2.56 g.) was dissolved in liquid sulphur dioxide (70 ml.). To the yellow solution, sulphuryl chloride (5.4 g.) was added all at once. No change was observed. The mixture was left to stand at about -20° for 3 days, with intermittent cooling to -75° . Then liquid sulphur dioxide was slowly evaporated over a period of 24 hr. When most of the sulphur dioxide had evaporated, light petroleum (b.p. $80-100^{\circ}$) was added, and then removed under reduced pressure, together with the unreacted sulphuryl chloride. The residue, a yellow oil (3.25 g.) was chromatographed on silica gel, with light petroleum as eluent. The solvent was evaporated from the resulting fractions at room temperature. 1-Chloronaphthalene (2.19 g., 71%) was first eluted, followed by unchanged naphthalene (0.26 g., 10%). Further elution with light petroleum-benzene (1:1) gave a white solid (0.38 g., 7%), which was identified spectroscopically as a mixture of the α - and δ -tetrachlorides. The final benzene elute gave a brown solid (0.07 g.) containing ketones.

In no case was evidence of the presence of naphthalene dichloride obtained.

9. Chlorine Additions to 1-Phenylnaphthalene and 1,1'-Binaphthyl

Materials

1-Phenylnaphthalene and 1,1'-binaphthyl were both commercial products.

1,2,3,4-Tetrachloro-1-phenyl-1,2,3,4-tetrahydro-naphthalene

1-Phenylnaphthalene (7.5 g.) was mixed with sulphuryl chloride (9.0 g.) and the resulting yellow mixture was left to stand overnight. Considerable amounts of white crystals separated were filtered off and recrystallised from hot mixture of benzene-ligroin. White prisms (3.8 g.), m.p. 192-194°. (Found: C, 56.34; H, 3.60; Cl, 40.19. $C_{16}H_{12}Cl_4$ requires C, 55.52; H, 3.49; Cl, 40.98%),

Use of solvent (light petroleum) retarded the reaction, but gave the similar result. Yield, 3.7 g.

Its n.m.r. spectrum consisted of the two superimposed doublets at 4.87 τ (area attributable to two hydrogens), a quartet (apparent triplet) at 4.37 τ (one hydrogen), and a multiplet at 2.34-3.03 τ (nine hydrogens). Both coupling constants for the alicyclic

systems can be assigned as $J = 1.5$ and $J' = 1.5$ c.p.s. The infrared spectrum had prominent peaks at 1485, 1444, 1347, 1316, 1269, 1261, 1228, 1203, 1189, 1176, 1164, 1112, 1100, 987, 892, 839, 830, 795, 767m, 753-750vs (broad), 701s, 693s, 645m cm.^{-1}

1,2,3,4-Tetrachloro-1,2,3,4-tetrahydro-1,1'-binaphthyl

A pasty mixture of 1,1'-binaphthyl (8.5 g.) with sulphuryl chloride (9.2 g.) gradually became fluid under evolution of hydrogen chloride and sulphur dioxide, and after a few hours solidified to crystalline mass, which was dissolved in a boiling mixture of benzene-ligroin and allowed slowly to cool. White crystals separated (2.7 g.), melts at $196-197^{\circ}$ under darkening and evolution of gas. (Found: C, 60.26; H, 3.90; Cl, 35.50. $\text{C}_{20}\text{H}_{14}\text{Cl}_4$ requires C, 60.63; H, 3.56; Cl, 35.80%).

Its n.m.r. spectrum had a quartet at 4.60τ (one hydrogen atom), two doublets at 4.32 and 4.19τ (two hydrogen atoms), and a multiplet at $1.36-3.13 \tau$ (eleven hydrogen atoms). The coupling constants for the aliphatic system are 3.4 and 10.5 c.p.s. respectively. The infrared spectrum of the tetra-

chloride had bands at 1603, 1512, 1485, 1400, 1341, 1271, 1234, 1216, 1202, 1186, 1166, 1095, 1050, 1015, 985, 959, 893, 871, 847, 832, 808, 797vs, 778vs, 773sh, 726vs, 682vs, 637 cm.⁻¹

In the present work, ultraviolet spectra were recorded by using a Unicam SP 500 spectrophotometer, with n-hexane as the solvent. Infrared spectra were recorded by using a Grubb-Parsons double beam infrared spectrophotometer. Proton magnetic resonance spectra were determined by using a Perkin-Elmer 60 Mc instrument, with deuteriochloroform as solvent and tetramethylsilane as reference; the Author is indebted to Dr. M. D. Johnson (University College London) and Mr. E. Tarelli (Queen Elizabeth College). Vapour-phase chromatographic analysis was done on a Griffin and George instrument, with a column of silicone oil on Celite, nitrogen as carrier gas.

10. Chlorine Additions to Halonaphthalenes

Materials

1-Chloronaphthalene (b.p. 256-260°) and 1-bromonaphthalene (b.p. 110-111°/3 mm Hg) were prepared from naphthalene by chlorination and bromination respectively. 2-Chloronaphthalene (m.p. 58-59°) was prepared from naphthyl-2-amine by the Sandmeyer reaction. 1,2-Dichloronaphthalene (m.p. 34-35°) was a commercial product, purified by alumina chromatography. 1,4-Dichloro (m.p. 66-68°) and 1,5-dichloronaphthalene (107-108°) were prepared from 1-chloronaphthalene-4-sulphonyl chloride and 1,5-dinitronaphthalene by fusion with phosphorus pentachloride. 2,7-Dichloronaphthalene (m.p. 114-116°) was similarly prepared from 2,7-disulphonyl chloride. 1-Chloro-2-deuteronaphthalene (b.p. 100-101°/4-5 mm Hg) and 1-chloro-4-deuteronaphthalene (b.p. 92-94°/2-3 mm Hg) were prepared by quenching the Grignard reagent of 1-chloro-2-iodonaphthalene (m.p. 79-81°) or 1-chloro-4-iodonaphthalene (m.p. 32-45°) with deuterium oxide, in 44.5 and 50.2% yields respectively. Chlorination of naphthyl-2-amine sulphate in 80% sulphuric acid at 90-100° gave 5,8-dichloronaphthyl-2-amine, which was transformed into

the corresponding iodo compound and then converted into the Grignard reagent. Quenching of the reagent with deuterium oxide, followed by fractional distillation and recrystallisation from light petroleum gave 1,4-dichloro-6-deuteronaphthalene, m.p. 65-67°. Partial deuteration of 1,5-dichloronaphthalene was carried out by heating the dichloronaphthalene (1.4 g.) with 91% deuteriosulphuric acid (10.8 g.) at 110-115° for 2 hr. Under this condition, nearly half of the peri-hydrogen atom was replaced.

1,1,2,3,4-Pentachloro-1,2,3,4-tetrahydronaphthalene

1-Chloronaphthalene (32 g.) was dissolved in light petroleum (35 ml.) and chlorine was slowly introduced into the mixture under ice-cooling. When about 12 g. of chlorine had been absorbed, the adduct began to separate. Then the chlorination was stopped and the mixture was allowed to stand overnight. Crystals were filtered off, washed several times with light petroleum and crystallised from ligroin. White prisms, m.p. 133-134°. Chlorination by sulphuryl chloride under gentle reflux gave the same adduct in less yields. Its n.m.r. spectrum contained a quartet at 5.23 τ (3-H), two doublets at 4.75 τ (2-H) and 4.51 τ (4-H), and two multi-

plets at 2.24-2.77 (three aromatic protons), and 1.74-2.06 τ (an aromatic proton). The infrared spectrum of the pentachloride had bands at 1484, 1450, 1342, 1301, 1269, 1255, 1219ms, 1197ms, 1187ms, 1116, 1094, 1053m, 1034m, 989, 921, 879ms, 861, 835m, 814s, 775, 750s, 725vs, 674vs, 627s cm.^{-1}

1,1,2,3,4-Pentachloro-4-deutero-1,2,3,4-tetrahydro-naphthalene

1-Chloro-4-deuteronaphthalene (2.4 g.) was placed in a 10 ml. test tube and diluted with about double the amounts of light petroleum. The mixture was cooled with ice-water and a fine stream of chlorine was introduced slowly with occasional shakings. When the whole wall of the vessel had been covered with a thin layer of the white deposit, the passing of chlorine was stopped and the mixture was left overnight. The liquid part was then decanted off and the deposit was dissolved in boiling ligroin (b.p. 80-100°) and very slowly cooled to let the crystals grow large enough for the mechanical separation. The deposit usually contained some amounts of 1,2,3,4,5,8-hexachloro-1,2,3,4-tetrahydronaphthalene (m.p. 173-174°) beside the pentachloride. The former usually crystallised out as clusters of long prisms while the latter separated out

as large cubes, so the mechanical separation could be readily achieved. The recrystallisation from ligroin gave the pentachloride (0.84 g., 18.7%) as large cubes melting at 131-133°. Its m.p. showed no depression on admixture with the ordinary pentachloride. (Found: C, 39.61; H, 2.29; Cl, 58.07. $C_{10}H_7Cl_5$ requires C, 39.45; H, 2.32; Cl, 58.23%). The n.m.r. spectrum had a quarter at 5.22 τ (3-H), a doublet at 4.52 τ (4-H), and two multiplets at 2.28-2.78 τ (three aromatic protons) and 1.80-2.08 τ (an aromatic proton). The coupling constant for the aliphatic system was 3.6 c.p.s. The minor splitting ($J = 1.4$ c.p.s.) observed for the doublet at 5.22 τ is interpreted as due to the spin-spin coupling with the axial deuteron at 2-position. Its infrared spectrum had bands at 1483, 1449, 1217m, 1195, 1099, 1085, 1053, 960, 945, 857m, 846m, 827m, 792m, 772, 742s, 722vs, 662s, 629 s cm^{-1} .

1.1.2.3.4-Pentachloro-2-deutero-1.2.3.4-tetrahydronaphthalene was similarly obtained from 1-chloro-2-deuteronaphthalene (3.0 g.) by the above procedure, as white large cubes (0.92 g.) melting at 131-133°. Yield, 16.4%. (Found: C, 39.64; H, 2.46; Cl, 58.05. $C_{10}H_7Cl_5$ requires C, 39.45; H, 2.32;

Cl, 58.23%). Its n.m.r. spectrum consisted of two doublets at 5.23 τ (3-H) and 4.74 τ (2-H) and two multiplets at 2.25-2.74 (three aromatic protons) and 1.77-2.06 τ (an aromatic proton). Its infrared spectrum showed bands at 1484, 1449, 1335, 1298, 1256, 1212, 1198m, 1186, 1110, 1072m, 1046, 1002, 931ms, 907m, 872, 850, 818m, 792ms, 772m, 746ms, 723vs, 666s, 627s, 607s cm.^{-1}

1,2,3,4-Tetrachloro-1-bromo-1,2,3,4-tetrahydro-naphthalene

1-Bromonaphthalene (21 g.) was dissolved in light petroleum (30 ml.) and chlorinated in a way similar to that used for 1-chloronaphthalene. The tetrachloride was readily obtained as colourless prisms, m.p. 129-130°, which on standing became slightly coloured and evolved hydrogen halide. By the chlorination with sulphuryl chloride, considerable migration of bromine atom occurred. The main addition products were a mixture of 1-chloronaphthalene tetrachloride, 1-bromonaphthalene tetrachloride, and 1,2,3,4-tetrachloro-5-bromo-1,2,3,4-tetrahydronaphthalene of m.p. 156-157° (Found: C, 34.21; H, 2.14, $\text{C}_{10}\text{H}_7\text{Cl}_4\text{Br}$ requires C, 34.42; H, 2.01%).

1,2,3,4,6-Pentachloro-1,2,3,4-tetrahydronaphthalene

2-^{Cl}chloronaphthalene (4.2 g.) was dissolved in ethylene dichloride (20 ml.) and chlorine was slowly introduced until saturation. After having stood overnight, the solvent was removed and the residual oil (6.68 g.) was chromatographed on silica gel. Products of substitution eluted rapidly with light petroleum, and the adduct appeared with a mixture of light petroleum and benzene (1:1). Removal of the solvent from the latter elutes^a gave a syrup, which on standing gave crystals of 2-chloronaphthalene tetrachloride. Recrystallisation from ligroin gave white prisms (0.72 g.) m.p. 139-140°. (Found: C, 39.63; H, 2.20; Cl, 58.11. $C_{10}H_7Cl_5$ requires C, 39.45; H, 2.32; Cl, 58.23%). Its n.m.r. spectrum had two apparent triplets at 5.06 and 4.37 τ (each area attributable to two hydrogen atoms) with low coupling constants (below 2 c.p.s.), and a singlet at 2.55 τ (three aromatic protons). On alkaline dehydrochlorination, the adduct gave a mixture of trichloronaphthalenes which, on chromatography over alumina with light petroleum as eluent, gave impure 1,3,6-trichloronaphthalene (m.p. 65-77°, lit., 80°) as a rapid elute^a and 1,3,7-trichloronaphthalene (m.p.

109-110°) as a slow elute^a.

Chlorination by sulphuryl chloride under gentle reflux for 40 hr. gave the same product as the main adduct.

1,2,3,4,5,8-Hexachloro-1,2,3,4-tetrahydronaphthalene

1-Chloronaphthalene (32 g.) in chloroform (50 ml.) was treated with chlorine until saturation, under vigorous stirring with external cooling. The precipitated crystals were filtered off and crystallised from benzene. White prisms (14.0 g.), m.p. 172-74°. (Found: C, 35.2; H, 1.9; Cl, 62.9. $C_{10}H_6Cl_6$ requires C, 35.4; H, 1.8; Cl, 62.8%). Its n.m.r. spectrum consisted of two apparent triplets (possibly quartets) at 4.87 and 4.29 τ (each area attributable to two hydrogen atoms), and a singlet at 2.50 τ (four aromatic protons). Both coupling constants were unusually small (below 1.5 c.p.s.).

Similar treatment of 1-bromonaphthalene gave an adduct of m.p. 176-177°. This was, however, found not to be a single substance but a mixture of 1,4-dichloronaphthalene tetrachloride and 1-chloro-4-bromonaphthalene tetrachloride by its n.m.r. spectrum as well as by elemental analysis. (Found: C, 30.85; H, 1.61;

Cl, 39.74; Br, 30.15. $C_{10}H_6Cl_5Br$ requires C, 31.29; H, 1.56; Cl, 46.28; Br, 20.85%). 1,2,3,4,5,8-Hexachloro-6-deutero-1,2,3,4-tetrahydronaphthalene was obtained from 1-chloro-2-deuteronaphthalene, together with 1,1,2,3,4-pentachloro-2-deuteronaphthalene. Its n.m.r. spectrum was similar to that of the ordinary adduct, except that the integration area of the aromatic proton had diminished to the half value. Its infrared spectrum had peaks at 1422ms, 1395, 1346m, 1307m, 1255, 1230, 1222, 1207, 1184, 1167ms, 1151m, 1116, 1024, 940, 932m, 907m, 853, 825, 770m, 749m, 719m, 702vs cm^{-1} . On the other hand, 1,2,3,4,5,8-Hexachloro-2-deutero-1,2,3,4-tetrahydronaphthalene similarly obtained from 1,4-dichloro-6-deuteronaphthalene showed a different pattern on the n.m.r. spectrogram; although the peaks at 4.25 τ (two hydrogens attached to 1-C and 4-C) and 2.48 τ (two aromatic protons) remained unaffected, the aliphatic peak centred at 4.86 τ was turned into an irregular triplet, possibly consisted of a singlet and a doublet with very small coupling constant (ca. 0.5 c.p.s.).

1,2,3,4,5,6-Hexachloro-1,2,3,4-tetrahydronaphthalene

1,2-Dichloronaphthalene (10.0 g.) was added to a cold chlorine (6.3 g.) solution in chloroform (150 ml.). After having stood for 2 days, the solvent was removed under reduced pressure and a yellow syrup (ca. 13.2 g.) was chromatographed on silica gel, with light petroleum as eluent. Products of substitution eluted rapidly, then a pale yellow syrup mainly composed of the lower-melting tetrachloride, and finally a brown sticky syrup containing the higher-melting isomer. From the middle fractions, large prisms of m.p. 72-74° (4.57 g.) was obtained. (Found: C, 35.56; H, 1.67, Cl, 62.61%. $C_{10}H_6Cl_6$ requires C, 35.44; H, 1.79; Cl, 62.77%). Its p.m.r. spectrum had two quartets at 5.46 and 4.88 τ (2- and 3-hydrogens), two doublets at 4.30 and 4.03 τ (1- and 4-hydrogens), and two aromatic doublets at 2.20 and 2.01 τ (two hydrogen)s. Coupling constants were assigned as $J_{1,2} = 8.8$ c.p.s., $J_{2,3} = 2.8$ c.p.s., $J_{3,4} = 2.7$ c.p.s., and $J_{7,8} = 8.8$ c.p.s. Its infrared spectrum showed bands at 664w, 698vs, 758, 770ms, 800ms, 814ms, 835ms, 853w, 930s, 1026, 1118, 1143m, 1161s, 1186, 1206, 1229w, 1240ms, 1255w, 1284w, 1304m, 1342, 1402ms, 1558w, and 1580 cm^{-1} . From the final

fractions, on prolonged standing, a small amount (0.5 g.) of the higher-melting tetrachloride was separated as plates, m.p. 103-104°. (Found: C, 35.67; H, 1.31; Cl, 63.00. $C_{10}H_6Cl_6$ requires C, 35.44; H, 1.79; Cl, 62.77%). Its p.m.r. spectrum showed two quartets at 5.57 and 4.82 τ (2- and 3-hydrogens), two doublets at 4.56 and 4.30 τ (1- and 4-hydrogens), and two aromatic doublets at 2.56 and 2.24 τ (two hydrogens). Coupling constants were assigned as $J_{1,2} = 3.3$ c.p.s., $J_{2,3} = 10.3$ c.p.s., $J_{3,4} = 4.4$ c.p.s., and $J_{7,8} = 8.6$ c.p.s. Its infrared spectrum had bands at 653ms, 672, 709ms, 720vs, 760ms, 821s, 839ms, 854s, 951ms, 976ms, 1050w, 1105, 1139, 1171vs, 1190, 1198m, 1230, 1245, 1265m, 1299, 1337w, 1397m, 1563w, and 1578 cm^{-1} .

1,2,3,4,8-Pentachloro-1,2-dihydronaphthalene

1,5-Dichloronaphthalene (8.5 g.) was added all at once to chlorine (6.2 g.) in chloroform (150 ml.). The reaction mixture was allowed to stand in the dark for three days; the pale yellow solution was then transferred to a Claisen flask and the solvent was removed under reduced pressure. The residual yellow syrup (14.0 g.) was chromatographed on silica gel, light petroleum being used as eluent. The trichloro-

naphthalene dichloride was eluted comparatively readily; on evaporation of the appropriate fraction, a pale yellow oil was obtained, which was then redissolved in a minimum of hot light petroleum and was left in a cool place. The pure trichloronaphthalene dichloride (7.8 g.) separated out as colourless prisms, m.p. 94-96° (lit.,³⁶ 94°).

(Found: C, 39.86; H, 1.62; Cl, 58.61. Calc. for $C_{10}H_5Cl_5$: C, 39.72; H, 1.66; Cl, 58.61%).

On dehydrochlorination with dilute methanolic alkali, the trichloronaphthalene dichloride gave 1,2,3,5-tetrachloronaphthalene, m.p. 141-142° (lit., 141°). The p.m.r. spectrum of the dichloride showed two doublets ($J = 2.5$ c.p.s.) at 4.32 and 5.02 τ assignable to methine hydrogen atoms, together with a multiplet at 2.2-2.9 τ , attributable to the aromatic hydrogen atoms. Its infrared spectrum had bands at 684vs, 731, 744vs, 778vs, 804s, 874s, 1032m, 1080, 1114m, 1156m, 1185, 1195, 1209m, 1232m, 1255, 1269, 1350, 1558, 1590, and 1608 cm^{-1} . Its ^{ultraviolet} ~~infrared~~ spectrum had a band at 238 $m\mu$ ($\log \epsilon_{max} = 3.76$) with inflection on the long wavelength side at 290-291, 304-305, and 315-316 $m\mu$ ($\log \epsilon = 3.73, 3.52$ and 3.32 respectively).

1.1.2.3.4.5-Hexachloro-1.2.3.4-tetrahydronaphthalene

Further elution of the reaction mixture from the above chlorination with light petroleum gave this tetrachloride, which on crystallisation from hot ligroin gave colourless prisms, m.p. 84-86° (lit., 84°). Its p.m.r. spectrum consisted of two doublets at 4.55 and 5.67 τ (each of area attributable to one hydrogen): a quartet at 5.20 τ (one hydrogen), and two multiplets at 2.0-2.2 τ (one hydrogen) and 2.4-2.8 τ (two hydrogens). The coupling constants for the aliphatic system can be assigned as $J = 4.8$ and 10.8 c.p.s. The infrared spectrum of the tetrachloride had peaks at 677vs, 716s, 747vs, 754, 794vs, 817, 833m, 865s, 915, 951, 1020, 1053, 1086, 1106, 1149s, 1182s, 1215m, 1230m, 1247, 1330, 1433, 1570, 1587 cm.^{-1}

Partially deuterated trichloronaphthalene dichloride and 1,5-dichloronaphthalene tetrachloride were similarly prepared from the partially deuterated 1,5-dichloronaphthalene. However, the separation of the dichloride from the tetra^hchloride was carried out as follows: the mixture of crystalline adducts (0.67 g.) was dissolved in light petroleum, and the solution was allowed to evaporate slowly. The re^hsulting crystals

were large enough to be separated by hand-picking; the ^(t)tetrachloride was obtained as transparent prisms, m.p. 82-84° (0.18 g.) and the dichloride as opaque irregular cubes, m.p. 95-96° (0.21 g.).

The p.m.r. spectrum of the partially deuterated tetrachloride showed that the doublet at high field (5.6 γ) and the quartet at 5.20 γ , though somewhat altered in shape, were unchanged in area, whereas the doublet at 4.55 was very much reduced in intensity, and was now an apparent triplet. In the partially deuterated dichloride, the strong signal at 5.03 γ remained strong, whereas that at 4.34 γ was remarkably reduced in intensity. This peak must therefore be correlated with the doublet at 4.55 γ in the tetrachloride.

11. Chlorine Additions to Naphthols

11. 1 Naphth-1-ols

Materials

Naphth-1-ol was a commercial product, which on treatment with two equivalents of chlorine gave 2,4,-dichloronaphth-1-ol (m.p. 107-108°). 2,3,4-Trichloronaphth-1-ol (m.p. 158-160°) was obtained by sodium bisulphite reduction of 1-keto-2,2,3,4,4-pentachloro-1,2,3,4-tetrahydronaphthalene. 4-Methylnaphth-1-ol (m.p. 81-84°) was prepared by the Steiger's method.⁸⁶ 2,3-Dichloro-4-methylnaphth-1-ol (m.p. 130-132°) was obtained by the lithium aluminium hydride reduction of 1-keto-4-methyl-2,2,3,4-tetrachloro-1,2,3,4-tetrahydronaphthalene. 2-Methyl-3,4-dichloronaphth-1-ol (m.p. 132-133°) was similarly obtained by the reduction of 1-keto-2,3,4,4-tetrachloro-2-methyl-1,2,3,4-tetrahydronaphthalene. In the preparation of the latter two naphthols, the conventional reducing method using sodium bisulphite in acetic acid gave only coloured syrupy substance, while stannous chloride often led to the partial elimination of a chlorine atom.

1-Keto-2,2,4-trichloro-1,2-dihydronaphthalene

Chlorination of 2,4-dichloronaphth-1-ol (4.3 g.) in chloroform (50 ml.) with chlorine (1.4 g.) in chloroform (50 ml.), followed by rapid removal of the solvent under reduced pressure gave a syrup, which was dissolved in the minimum amount of warm ligroin and allowed to stand at room temperature. Nearly colourless prisms separated; they were dissolved in ligroin and chromatographed on silica gel. Removal of the solvent yielded the ketodihydronaphthalene (3.2 g.), m.p. 74-75°. (Found: C, 48.36; H, 1.95; Cl, 42.88. $C_{10}H_5Cl_3O$ requires C, 48.52; H, 2.03; Cl, 42.97%).

Reduction of this with sodium bisulphite in acetic acid gave 2,4-dichloronaphth-1-ol, m.p. 106-107°. On boiling with aqueous ethanol, it gave 2-chloro-1,4-naphthoquinone as yellow needles, m.p. 116-117°. With aniline it gave the anil of 2-anilino-1,4-naphthoquinone as dark red crystals, m.p. 180-182°. These chemical properties accord with those of the following isomer 1-keto-2,4,4-trichloro-1,4-dihydronaphthalene, into which it is converted on standing or on solution in acetic acid containing hydrogen chloride.

1-Keto-2,4,4-trichloro-1,4-dihydronaphthalene

This was prepared by suspending 2,4-dichloronaphth-1-ol (4.03 g.) in acetic acid (20 ml.), and agitating this vigorously with a solution of chlorine (1.4 g.) in acetic acid (30 ml.). The mixture was then allowed to stand overnight, and the solvent was removed under reduced pressure in a rotary evaporator. The resulting brown solid was dissolved in a warm mixture of benzene and ligroin (1:3), and was chromatographed on a short column of silica gel, ligroin being used as the eluent. The resulting solution was evaporated under reduced pressure, and the product (3.7 g.) as large prisms, m.p. 118-120°. The ketone slowly became coloured when kept in diffused light.

1-Keto-2,2,3,4-tetrachloro-1,2-dihydronaphthalene

2,3,4-Trichloronaphth-1-ol (2.5 g.) was dissolved in chloroform (30 ml.), and the solution was saturated with chlorine. The solvent was then removed under reduced pressure; the resulting yellow solid was recrystallised from hot ligroin to give the ketone as yellow needles (2.3 g.) melting at 102-104°. The mother liquors contained some of the isomeric 1-keto-2,3,4,4-tetrachloro-1,4-dihydronaphthalene.

This 1-keto-1,2-dihydronaphthalene is stable on storage, but on prolonged heating under reflux with sulphuryl chloride is partly isomerised to the 1,4-compound.

1-Keto-2,3,4,4-tetrachloro-1,4-dihydronaphthalene

The original procedure for the preparation of this compound from 2,3,4-trichloronaphth-1-ol is tedious and difficult; the following method is preferable. A solution of 1-keto-2,2,3,4,4-pentachloro-1,2,3,4-tetrahydronaphthalene (1.3 g.) in benzene (50 ml.) was gently heated, and to it was added a solution of potassium methoxide (0.1 N) in benzene (B.D.H. reagent; 40 ml.) dropwise with vigorous agitation. The precipitated potassium chloride was filtered off, and the solution was concentrated, and cooled. The ketone separated as long prisms (0.9 g.), m.p. 114-115°. The crystals are amethyst on exposure to light, but fade to a pale yellow colour on storage in the dark. The mother liquors from the precipitate contained a little of the isomeric 1-keto-1,2-dihydronaphthalene.

1-Keto-2-methyl-2,3,4-trichloro-1,2-dihydronaphthalene

2-Methyl-3,4-dichloronaphth-1-ol (1.0 g.) was

dissolved in chloroform (20 ml.) and the solution was cooled and saturated with chlorine. The solvent was then removed, leaving a yellow syrup from which a solid slowly separated. Repeated crystallisation from light petroleum gave the ketone (0.2 g.), m.p. 66-69°. (Found: C, 50.68; H, 2.73; Cl, 40.66. $C_{11}H_7Cl_3O$ requires C, 50.51; H, 2.69; Cl, 40.67%). The yield of crystalline material was poor, but its infrared examination of the syrupy residue showed that the isomeric derivative was no more than a minor component of the reaction mixture.

1-Keto-4-methyl-2,3,4-trichloro-1,4-dihydronaphthalene

A solution of the naphthol (1.0 g.) in chloroform was saturated with chlorine, and the solvent was removed under reduced pressure. From the resulting syrup, long needles, m.p. 86-89°, of 1-keto-4-methyl-2,3,4-trichloro-1,4-dihydronaphthalene separated. (Found: C, 50.61; H, 2.55; Cl, 40.73%. $C_{11}H_7Cl_3O$ requires C, 50.51; H, 2.69; Cl, 40.67%). It was obtained more conveniently by the dehydrochlorination of 1-keto-4-methyl-2,2,3,4-tetrachloro-1,2,3,4-tetrahydronaphthalene with potassium methoxide in benzene, essentially as described above. Its n.m.r. spectrum had signals at

$\gamma = 7.69$ (CH_3 group), and at 1.42-2.46 (four aromatic protons).

1-Keto-2,2,3,4,4-pentachloro-1,2,3,4-tetrahydro-naphthalene

Saturation of a suspension of naphth-1-ol (3.0 g.) in acetic acid (20 ml.) with chlorine gave white crystals of the above ketone which on recrystallisation from hot ligroin had m.p. 158-159°. Its n.m.r. spectrum showed a single proton ($\gamma = 4.76$), and four aromatic protons, (multiplet, $\gamma = 1.60-2.65$).

1-Keto-2,2,3,3,4,4-hexachloro-1,2,3,4-tetrahydro-naphthalene

A solution of 1-keto-2,2,3,4-tetrachloro-1,2-dihydronaphthalene (1.0 g.) in chloroform (30 ml.) was saturated with chlorine and kept in a bright place for two weeks. After the solvent had been removed, the product was dissolved in the minimum quantity of light petroleum and was allowed to stand. The ketohexachloride crystallised as plates (0.2 g.), m.p. 128-130°.

1-Keto-4-methyl-2,2,3,4-tetrachloro-1,2,3,4-tetrahydronaphthalene

4-Methylnaphth-1-ol (4.8 g.) was dissolved in acetic acid (20 ml.), and the cooled solution was

saturated with chlorine. Crystals of the ketone readily precipitated; its solution in light petroleum was passed through a column of silica gel, and evaporation of the ^adistillate gave colourless crystals, m.p. 120-122° (7.2 g.). (Found: C, 44.5; H, 2.6; Cl, 47.5. $C_{11}H_8Cl_4O$ requires C, 44.3; H, 2.7; Cl, 47.6%). Reduction of this with lithium aluminium hydride in ether gave 2,3-dichloro-4-methylnaphth-1-ol as fine needles after recrystallisation from ligroin, m.p. 130-132° (sintering at 123-125°). (Found: C, 58.03; H, 3.53; Cl, 31.50. $C_{11}H_8Cl_2O$ requires C, 58.17; H, 3.55; Cl, 31.22%).

11.2 Naphth-2-ols

Materials

Naphth-2-ol was a commercial product, from which 1-bromonaphth-2-ol (m.p. 82-84°) was readily obtained by bromination. 1-Iodonaphth-2-ol (m.p. 93-94°) was similarly prepared, using hydrogen peroxide as oxidising agent. 2,2'-dihydroxy-1,1'-dinaphthylmethane (m.p. 200°) was prepared by the condensation of naphth-2-ol with formaldehyde in the presence of potassium acetate.

1-Methylnaphth-2-ol (m.p. 110°) was prepared by the reductive cleavage of the above dinaphthol according to the Fries' method,⁴⁷ but the separation of 1-methylnaphth-2-ol from the dinaphthol was carried out by steam distillation. The former readily distilled over, while the latter remained in the flask. 1,3-Dichloronaphth-2-ol (m.p. $78-79^{\circ}$) was obtained by the sodium bisulphite reduction of 2-keto-1,1,3-trichloro-1,2-dihydronaphthalene in hot acetic acid. 1,4-Dichloronaphth-2-ol (m.p. $120-121^{\circ}$) was prepared by the acid-catalysed rearrangement of 1,1-dichloro-2-keto-1,2-dihydronaphthalene, following the Burton's procedure.⁵⁵ 1,3,4-Trichloronaphth-2-ol (m.p. $160-161^{\circ}$) was readily obtained by the lithium aluminum hydride reduction of 2-keto-1,1,3,3,4-pentachloro-1,2,3,4-tetrahydronaphthalene in anhydrous ether. 6-t-Butylnaphth-2-ol (m.p. $118-119^{\circ}$) and 1,6-di-t-butyl-naphth-2-ol (m.p. $138-139^{\circ}$) were prepared by the t-butylation of naphth-2-ol with t-butyl chloride in ligroin.

2-Keto-1,1-dichloro-1,2-dihydronaphthalene

As the original procedure had been found unsatisfactory, the following method was taken: A suspension of naphth-2-ol (4.8 g.) in acetic acid (20 ml.)

was chlorinated under vigorous agitation with chlorine (4.7 g.) in acetic acid (70 ml.). Immediately after, the solution was transferred to a rotary evaporator and the solvent was removed under reduced pressure. The dark brown residue was dissolved in a mixture of benzene-ligroin (2:1) and the solvent was again removed in vacuo. This process was repeated until nearly all acetic acid had been replaced. During this procedure, crystallisation of the adduct often occurred, but it was usually aroused by scratching the cooled syrup. The dark yellow solid was squeezed between clay-plate to remove the accompanying syrup. Yellow powder free from syrup was then placed on a short silica gel column and eluted with warm (35-40°) ligroin. The pale yellow elute^(a) was concentrated slowly under a slightly reduced pressure, avoiding the intrusion of moisture. The ketone crystallised out as nearly colourless plates, m.p. 52-54°. Average yield, 65%. On storage it turned to dark brown resinous substance. The infrared spectrum of the dichloro-ketone had bands at 652s, 695s, 726w, 757s, 794m, 807s, 843m, 882, 916w, 932s, 872w, 982w, 990w, 1108w, 1129m, 1159w, 1199s, 1215w, 1236, 1245w, 1279, 1302, 1395m, 1453, 1567, 1621m, 1676s cm.⁻¹ Its ultraviolet

spectrum had maxima at 241 and 325 $m\mu$ ($\log_{10} \epsilon = 4.40$ and 3.86 respectively).

2-Keto-1,1,3-trichloro-1,2-dihydronaphthalene

2-Keto-1,1,3,4-tetrachloro-1,2-dihydronaphthalene was dissolved in a small amount of acetic acid and heated for 5 min. The dark yellow solution was poured into water and the precipitated oil which had soon solidified was crystallised from ligroin to give yellow needles, m.p. 93-95°. Its infrared spectrum had absorptions at 670s, 691m, 730, 761s, 818s, 835s, 874, 926s, 956, 970s, 1117w, 1157m, 1200w, 1215m, 1233s, 1254w, 1276w, 1308, 1345m, 1564m, 1594w, 1608m, 1692s cm.^{-1} . Its ultraviolet spectrum had peaks at 247.8 and 340 $m\mu$ ($\log_{10} \epsilon = 4.37$ and 3.86 respectively).

2-Keto-1,1,3,4-tetrachloro-1,2-dihydronaphthalene

1,3,4-Trichloronaphth-2-ol was dissolved in chloroform and the solution was saturated with chlorine. Evaporation of the solvent gave a yellow solid, which after recrystallisation from light petroleum melted at 87-89°, far below the reported value¹⁴ (m.p. 96-97°). Melting point could not be raised by repeated crystallisation from ligroin. Its infrared spectrum had bands at 678s, 726s, 767s, 811m, 832w, 881w, 898w, 945m,

960w, 998m, 1057w, 1129w, 1168w, 1215s, 1256m, 1289w, 1309w, 1477, 1546m, 1585, 1704s cm.^{-1} The ultraviolet spectrum of the dichloroketone had maxima at 249 and 337 $\text{m}\mu$ ($\log_{10} \epsilon = 4.36$ and 3.84 respectively).

2-Keto-1,1,4-trichloro-1,2-dihydronaphthalene

1,4-Dichloronaphth-2-ol was dissolved in chloroform and treated with the calculated amounts of chlorine. Removal of the solvent and the subsequent recrystallisation of a yellow residue gave the ketone as pale yellow needles, m.p. 85-87°. Treatment of the naphthol with excess chlorine either in chloroform or in carbon disulphide gave not the expected 2-keto-1,1,3,4,4-pentachloro-1,2,3,4-tetrahydronaphthalene, but its dehydrochlorination product 2-keto-1,1,3,4-tetrachloro-1,2-dihydronaphthalene.

2-Keto-1,1-dichloro-6-t-butyl-1,2-dihydronaphthalene

6-t-butyl-naphth-2-ol (4.0 g.) was dissolved in chloroform (20 ml.) and, with cooling and vigorous stirring it was treated with a solution of chlorine (1.4 g.) in chloroform (50 ml.). As soon as the addition had ended, the solvent was evaporated under reduced pressure and the remaining brown syrup was taken up in a minimum

quantity of light petroleum and allowed to stand in a cool place. The ketone separated as fine prisms which on recrystallisation from light petroleum melted at 95-96°. (Found: C, 62.61; H, 5.33; Cl, 26.24. $C_{14}H_{14}Cl_2O$ requires C, 62.47; H, 5.24; Cl, 26.34%). Its infrared spectrum had absorptions at 643s, 677, 712, 759w, 814m, 850m, 883w, 894s, 918w, 945s, 1026w, 1099w, 1122m, 1145, 1200s, 1207s, 1222s, 1232s, 1283, 1360, 1558, 1595, 1616, 1691s $cm.^{-1}$

2-Keto-1,3-dichloro-1,6-di-t-butyl-1,2-dihydro-naphthalene

1,6-Di-t-butyl-naphth-2-ol (2.5 g.) was dissolved in acetic acid (30 ml.) and treated with excess chlorine. Pouring into water gave a yellow solid, which after purification on silica gel gave yellow needles (3.1 g.), m.p. 116-117°. Initially formed 2-keto-1,3,4-trichloro-1,6-di-t-butyl-1,2,3,4-tetrahydronaphthalene readily undergoes dehydrochlorination to give this unsaturated ketone. (Found: C, 66.29; H, 6.79; Cl, 21.74. $C_{18}H_{22}Cl_2O$ requires C, 66.46; H, 6.82; Cl, 21.80%). Its infrared spectrum had bands at 670s, 687s, 709m, 745w, 761, 816s, 840m, 890w, 907w, 856m, 945w, 981, 1028w, 1034, 1105, 1167, 1200w, 1230s, 1255m, 1309w, 1346w, 1365, 1389w, 1404w, 1499, 1570, 1589w, 1599, 1693s $cm.^{-1}$

2-Keto-1,1,3,4-tetrachloro-1,2,3,4-tetrahydronaphthalene

Naphth-2-ol (5.0 g.) was dissolved in acetic acid (50 ml.) and chlorine was passed until saturation, then the mixture was immediately poured into a large amount of water, and white crystals were collected by filtration. Large prisms from light petroleum, m.p. 100-102°. Yield, 7.1 g. This ketone had infrared absorptions at 686, 722s, 745m, 760s, 781w, 786, 803, 847s, 882, 904, 923m, 1029m, 1115w, 1153s, 1163w, 1188, 1201, 1220m, 1239, 1306w, 1348, 1453, 1485w, and 1751s cm.⁻¹ Its ultraviolet spectrum had no maximum above 225 m μ . On prolonged standing, the ketone slightly decomposed to give a naphthol (probably 1,3,4-trichloronaphth-2-ol).

2-Keto-1,1,3,3,4-pentachloro-1,2,3,4-tetrahydro-naphthalene

2-Keto-1,1,3-trichloro-1,2-dihydronaphthalene was dissolved in acetic acid and chlorine was saturated under cooling. The mixture was allowed to stand for a couple of days; during the period the pentachloro-ketone slowly separated as a heavy powder at the bottom. Filtration and subsequent recrystallisation from hot ligroin gave colourless prisms, m.p. 114-116°. Its infrared spectrum had bands at 671s, 693s, 720s, 749s,

765w, 787, 826s, 861s, 882m, 923w, 930s, 1126m, 1206m, 1231s, 1265w, 1304w, 1337w, 1455, and 1761s cm.^{-1}

2-Keto-1,1,3,3,4,4-hexachloro-1,2,3,4-tetrahydro-naphthalene

2-Keto-1,1,3,4-tetrachloro-1,2-dihydronaphthalene was dissolved in chloroform, saturated with chlorine and the solution was left in a bright place for a fortnight. After removal of the solvent, colourless syrup was dissolved in a minimum amount of warm light petroleum and set aside. The ketone separated out as a cluster of needles melting at 128-129°. The infrared spectrum of the hexachloroketone had bands at 683s, 699s, 750s, 796m, 805m, 853s, 871w, 890m, 928m, 951, 1048w, 1068, 1068, 1120, 1130m, 1197m, 1224s, 1448, 1478w, 1763s cm.^{-1}

2-Keto-1,1,4-trichloro-1-bromo-1,2,3,4-tetrahydro-naphthalene

1-Bromonaphth-2-ol was dissolved in acetic acid and treated with excess chlorine under cooling. The product readily separated as white crystals. Recrystallisation from ligroin gave the expected adduct as colourless plates, m.p. 106-108°. No bromine migration was observed. (Found: C, 36.43; H, 1.70; Cl, 32.43; Br, 24.35. $\text{C}_{10}\text{H}_6\text{Cl}_3\text{BrO}$ requires C, 36.56; H, 1.83; Cl, 32.39; Br,

24.33%). Its infrared spectrum had bands at 686w, 704sh, 720s, 755s, 760sh, 779, 785, 798, 833m, 848, 881, 903, 923m, 1028m, 1044w, 1112w, 1146s, 1174, 1209, 1222w, 1232, 1239w, 1348, 1453, 1486w, and 1742s cm.^{-1} . Its n.m.r. spectrum had two pairs of doublets at 4.44 and 4.85 τ ($J = 5.0$ c.p.s.), and 4.39 and 4.89 τ ($J = 3.8$ c.p.s.), and aromatic multiplets at 1.52-1.68 τ and 1.96-2.48 τ . The relative intensity of two pairs of methine doublets was 1:1, therefore this product is considered to be a mixture of two conformational isomers in the ratio of 1:1.

2-Keto-1,3,4-trichloro-1-methyl-1,2,3,4-tetrahydro-naphthalene

1-Methylnaphth-2-ol was chlorinated as above, and the product was recrystallised from ligroin, m.p. 76-78°. The infrared spectrum of the ketone had bands at 692s, 702s, 751s, 762, 778, 814w, 829w, 840w, 865w, 880w, 1013, 1046, 1067, 1088, 1107, 1171m, 1187, 1215w, 1233w, 1242m, 1294w, 1303w, 1348, 1486w, 1580w, and 1743 cm.^{-1} . Its n.m.r. spectrum showed two methyl singlets at 7.73 and 7.89 τ , two pairs of methine doublets at 4.49 and 4.69 τ ($J = 5.8$ c.p.s.), and at 4.38 and 5.17 τ ($J = 4.5$ c.p.s.), and an aromatic multiplet 1.88-2.28 τ . This product was therefore a mixture of

two conformational isomers in the ratio of 1:1.

On dehydrochlorination with a dilute solution of potassium acetate in acetic acid, it gave 2-keto-1,3-dichloro-1-methyl-1,2-dihydronaphthalene as a syrup, which on further chlorination in acetic acid yielded 2-keto-1,3,3,4-tetrachloro-1-methyl-1,2,3,4-tetrahydronaphthalene as colourless prisms, m.p. 114-115°. The taking-up of chlorine was very slow. Its infrared spectrum had bands at 682, 704s, 745m, 762s, 803s, 836, 868, 890, 1015, 1046, 1073, 1101, 1124, 1161, 1192, 1216, 1240m, 1267, 1493, 1759s cm.⁻¹

2,2'-Diketo-1,1',3,3',4,4'-hexachloro-1,1',2,2',3,3',4,4'-octahydronaphthalene

2,2'-Dihydroxy-1,1'-dinaphthylmethane (2.0 g.) was suspended in acetic acid (20 ml.) and treated with excess chlorine. The ketone readily precipitated as a white powder in nearly quantitative yield (3.3 g.). This was filtered off and recrystallised from boiling mixture of benzene and ligroin. White powder, m.p. 156-157° (turns green). Very poorly soluble in common organic solvents. (Found: C, 49.48; H, 2.87, Cl, 41.59. C₂₁H₁₆Cl₆O requires C, 49.35; H, 2.76; Cl, 41.62%). Its infrared spectrum had bands at 679s, 713s, 730s, 733s,

756w, 766s, 769s, 781w, 812m, 825m, 867w, 869w, 896w,
 905m, 926m, 969m, 969w, 991m, 1008w, 1031w, 1047w,
 1069w, 1075w, 1087w, 1104w, 1122w, 1139w, 1171w, 1176w,
 1186w, 1203w, 1216, 1238w, 1248s, 1258w, 1309m, 1335,
 1420, 1445, 1484 and 1753s cm.^{-1}

2-Keto-1,1,3,4-tetrachloro-6-t-butyl-1,2,3,4-tetra-
hydronaphthalene

6-t-Butylnaphth-2-ol (3.0 g.) was suspended in acetic acid (20 ml.) and chlorine was introduced until saturation. Pouring into water, filtration of the solid, and recrystallisation from light petroleum gave colourless plates (4.2 g.), m.p. 102-103°. (Found: C, 49.47; H, 4.17; Cl, 41.66. $\text{C}_{14}\text{H}_{14}\text{Cl}_4\text{O}$ requires C, 49.44; H, 4.15; Cl, 41.70%). Its infrared spectrum had bands at 672s, 707w, 736s, 760s, 770w, 801m, 833s, 854, 873, 896, 907w, 930m, 1029w, 1038w, 1106, 1134, 1157m, 1189, 1205w, 1230m, 1272, 1294w, 1338w, 1364, 1416w, 1496, and 1750 cm.^{-1} The n.m.r. spectrum showed signals at 8.58 (singlet due to t-butyl group), 4.85 τ (doublet due to 4-H, $J = 5.2$ c.p.s.), 4.45 τ (doublet due to 3-H, $J = 5.2$ c.p.s.) and 1.70-2.28 τ (ABC multiplet due to three aromatic protons, $J_{AB} = 8.4$ c.p.s., $J_{BC} = 1.8$ c.p.s., $J_{AC} = \text{ca. } 0$). (Found:

C, 49.47; H, 4.17; Cl, 41.66. $C_{14}H_{14}Cl_4O$ requires
C, 49.44; H, 4.15; Cl, 41.70%).

2-Keto-1,3,3,4-tetrachloro-1,6-di-t-butyl-1,2,3,4-tetrahydronaphthalene

2-Keto-1,3-dichloro-1,6-di-t-butyl-1,2-dihydronaphthalene (2.0 g.) was dissolved in acetic acid (30 ml.) and chlorine was passed until saturation. Taking-up of chlorine was so slow that the mixture was left to stand for a few days, then poured into water. The separated pale yellow solid was recrystallised from ligroin. Colourless needles (1.6 g.), m.p. 161-162°. (Found: C, 54.55; H, 5.62; Cl, 34.49. $C_{18}H_{22}Cl_4O$ requires C, 54.54; H, 5.60; Cl, 35.79%). Its infrared spectrum showed peaks at 669, 687s, 736m, 765m, 774s, 816, 821, 881, 908w, 932, 942, 971, 1031, 1080w, 1105, 1113sh, 1199w, 1221s, 1270w, 1366, 1404, 1499w, 1604, and 1739s $cm.^{-1}$. Its n.m.r. spectrum showed signals at 8.95 and 8.59 τ (two singlets due to t-butyl groups), 4.23 τ (singlet due to 4-H) and 1.69-2.44 τ (aromatic multiplet).

11.3 Anomalous Chlorine Addition to 1-Iodonaphth-2-ol

The conventional procedure involving the chlorination in acetic acid, followed by pouring into water gave

a dark brown resinous substance; considerable amounts of iodine being eliminated. Repeated extraction of the polymeric substance with warm ligroin and subsequent evaporation of the solvent yielded a small amount of white crystals, which was identified as 2-keto-1,1,3,4-tetrachloro-1,2,3,4-tetrahydronaphthalene (m.p. 100-102°). The use of chloroform as solvent gave a similar syrup containing carbonyl compounds, titration of which with hot ligroin yielded 1,2,3,4,5,7-hexachloro-6-hydroxy-1,2,3,4-tetrahydronaphthalene as pale yellow needles melting at 149-150°. (Found: C, 33.99; H, 1.72; Cl, 59.88; O, 4.72. $C_{10}H_6Cl_6O$ requires C, 33.84; H, 1.70; Cl, 59.94; O, 4.53%). Its infrared spectrum had peaks at 619s, 694w, 709ms, 732ms, 757m, 806m, 829s, 857m, 879m, 901m, 966w, 1010, 1077, 1107, 1192vs, 1232ms, 1253w, 1273w, 1296s, 1314ms, 1334w, 1349w, 1416s, 1589 and 3460s $cm.^{-1}$. Its n.m.r. spectrum consisted of two quartets at 4.84 and 5.57 τ (each of area attributable to one hydrogen); two doublets at 4.38 and 4.60 τ (two hydrogens); a broad peak at 4.6 τ (hydroxylic proton), and an aromatic singlet at 2.43 τ (one hydrogen). The coupling constants for the aliphatic system can be assigned as $J_{1,2} = 3.1$, $J_{2,3} = 10.1$ and $J_{3,4} = 4.4$ c.p.s.

11.4 Esters of Naphthols

Materials

Naphthols were acetylated with a mixture of glacial acetic acid and acetic anhydride using a small amount of pyridine as catalyst. 1-Acetoxy-naphthalene (m.p. 48-49°), 2-acetoxy-naphthalene, (m.p. 71-72°) and 1,5-diacetoxy-naphthalene (m.p. 162-163°).

1-Keto-2,3,4-trichloro-1,2,3,4-tetrahydronaphthalene

1-Acetoxy-naphthalene (7.5 g.) dissolved in chloroform (30 ml.) was chlorinated under ice-cooling and vigorous agitation with chlorine (9.5 g.) in chloroform (150 ml.). The solvent was removed under reduced pressure and the brown syrupy residue dissolved in a small amount of warm ligroin, was allowed to stand overnight. Brown prisms separated, were washed with hot light petroleum to remove the accompanying syrup, redissolved in hot ligroin and rapidly chromatographed on a short silica gel using the same solvent as eluent. The elute was slowly concentrated under reduced pressure and crystals deposited were recrystallised from ligroin to give nearly colourless prisms (1.52 g.), m.p. 120-121°. (Found: C, 48.31; H, 3.03; Cl, 42.40. $C_{10}H_7Cl_3O$ requires C, 48.13; H,

2.83; Cl, 42.63%). Its n.m.r. spectrum showed a quartet at 5.12 τ (3-H), a doublet at 5.01 τ (4-H), a doublet at 4.12 τ (2-H), and an aromatic multiplet at 1.74-2.64 τ . The coupling constants can be assigned as $J_{2,3} = 2.7$ and $J_{3,4} = 7.3$ c.p.s. On exposure to air, it soon became coloured, but its spontaneous transformation into 2,4-dichloronaphth-1-ol was very slow and even after months of standing, the bulk remained as the ketone.

1-Keto-2,3,4-trichloro-5-acetoxy-1,2,3,4-tetrahydro-naphthalene

1,5-Diacetoxynaphthalene (4.88 g.) was suspended in chloroform (20 ml.), and a solution of chlorine (4.26 g.) in chloroform (60 ml.) was slowly added with vigorous agitation. Immediately after the end of addition, the solvent was removed under reduced pressure, and a light brown syrup was dissolved in a mixture of benzene-ligroin, chromatographed on a short silica gel column and concentrated under reduced pressure, by replacing benzene with intermittent addition of ligroin. During the course of this procedure, crystallisation of the new adduct often occurred. Colourless prisms, m.p. 116-119°. Its melting point soon depressed down to around

110-114^o, probably because of partial decomposition. It was not highly stable and on exposure to air and light it readily decomposed to dark grey substance within a couple of days under evolution of hydrogen chloride. However, it could be stored for a comparatively long time with only slight decomposition when kept under the cover of light petroleum in a cool place. (Found: C, 46.8; H, 2.89; Cl, 34.2. $C_{12}H_9Cl_3O_3$ requires C, 46.86; H, 2.62; Cl, 34.58%). Its n.m.r. spectrum had a singlet at 7.54 τ (acetoxy group), an apparent quartet at 5.20 τ (probably 4-hydrogen, J and J' = ca. 1 and 3 c.p.s.), a quartet at 4.85 τ (probably 3-hydrogen, J and J' = ca. 2 and 3 c.p.s.), an apparent quartet at 4.34 τ (probably 2-hydrogen, J and J' = ca. 1 and 2 c.p.s.), and two aromatic multiplets at 2.23-2.70 τ and 1.80-1.89 τ .

The dark grey substance formed by the spontaneous decomposition of the ketone was extracted with boiling mixture of benzene-ligroin and chromatographed on a short alumina column. Black insoluble substance remained on the top of the column and the concentration of the elute gave pale yellow leaflets, m.p. 141-143^o, which was identified as 2,4-dichloro-5-acetoxy-naphth-1-ol

by comparison with the authentic specimen of m.p. 163-164°. The melting point of this naphthol varies depending on the solvent used for the recrystallisation; glacial and aqueous acetic gives pale yellow needles melting 163-164° whereas benzene and ligroin gives colourless leaflets of m.p. 143-144°. (Found: C, 53.21; H, 2.97; Cl, 26.02. $C_{12}H_8Cl_2O_3$ requires C, 53.16; H, 2.97; Cl, 26.16%). Its infrared spectrum had bands at 718m, 749ms, 803m, 833ms, 861m, 883, 917, 943, 966, 1017m, 1046, 1080, 1134, 1163ms, 1186s, 1200s, 1225s, 1247s, 1323, 1257, 1366, 1418, 1503w, 1590s, 1621w, 1745s, 3367s cm^{-1} . Its ultraviolet spectrum showed maxima at 229, 307, 323, and 338 $m\mu$ in 96% ethanol. When dissolved in alkaline ethanol, characteristic bathochromic shift occurred and its fine structures disappeared. It showed maxima at 256 and 355 $m\mu$ ($\log_{10} \epsilon = 4.30$ and 3.02 respectively). Its n.m.r. spectrum had peaks at 7.58 τ (acetoxy group), 3.84 τ (aromatic hydroxyl group), 2.75 τ (3-hydrogen, J and J' = ca. 2 and 8 c.p.s.), 2.50 τ (3-hydrogen atom), 2.41 τ (7-hydrogen atom, J and J' = ca. 8 and 8.5 c.p.s.) and 1.78 τ (6-hydrogen atom, J and J' = ca. 2 and 8 c.p.s.). Both multiplicities and relative intensities

satisfy the requirement of the structure.

1-Keto-2,4,4-trichloro-5-acetoxy-1,4-dihydro-naphthalene

The following procedure has been found more convenient than those described by previous workers;⁴⁹⁻⁵⁰ a suspension of 1,5-diacetoxynaphthalene (4.88 g.) in acetic acid (40 ml.) was magnetically stirred, and accurately weighed chlorine (4.26 g.) in acetic acid (60 ml.) was added slowly. After standing overnight, the light brown solution was concentrated under reduced pressure and the solid separated was dissolved in hot ligroin, purified by chromatography on silica gel and finally crystallised from ligroin. Colourless needles (4.4 g.), m.p. 173-174° (lit.,⁶⁰ 174°).

1-Keto-2,2,4-trichloro-5-acetoxy-1,2-dihydronaphthalene

2,4-Dichloro-5-acetoxynaphth-1-ol (1.3 g.) was dissolved in chloroform (20 ml.) and chlorinated with chlorine (0.4 g.) in chloroform (30 ml.). The solvent was immediately removed and a yellow syrup was dissolved in a minimum amount of hot ligroin. On standing the ketone separated as pale yellow prisms (1.2 g.), m.p. 112-113°. On storage it soon became light brown and gradually transformed itself into the isomeric 1-keto-

2,4,4-trichloro-5-acetoxy-1,4-dihydronaphthalene.
(Found: C, 47.05; H, 2.38; Cl, 34.61. $C_{12}H_7Cl_3O_3$
requires C, 47.16; H, 2.31; Cl, 34.81%).

Table 1

Ultraviolet and infrared spectra
of polychloro-1-tetralones

Compound	Maxima		Minima	
	Wavelength (Å)	log ϵ	Wavelength (Å)	log ϵ
1-Keto-2,2,4-tri- chloro-1,2-dihydro- naphthalene (690s, 716, 768s, 817s, 840s, 936s, 1156, 1196m, 1234m, 1282s, 1334, 1589s, 1628, 1698s cm^{-1}).	2390-	4.52	2670	2.97
	2400 (sh.)		3000	3.12
	2430	4.54	3130	3.07
	2840-	3.12		
	2850 (infl.)			
	2930	3.17		
	3040	3.14		
3390	3.28			
1-Keto-2,4,4-tri- chloro-1,4-dihydro- naphthalene (687s, 693, 708s, 781, 800, 841s, 877m, 890, 899m, 1069, 1097, 1128, 1163, 1243s, 1339m, 1549m, 1627m, 1674s cm^{-1}).	2410-	4.17	2290	4.02
	2420 (sh.)		2530	4.16
	2480	4.22	2760	3.43
	2555	4.17		
	2870	3.47		

* Ultraviolet spectra in hexane as solvent:

sh.= shoulder, infl.= inflection.

1-Keto-2,2,3,4-tetra- chloro-1,2-dihydro- naphthalene	2422	4.59	2450	4.55
	2495	4.64	2710	3.10
(662s, 703s, 720s, 770m, 803s, 822s, 858m, 959m, 1022, 1152s, 1232s, 1240sh, 1254s, 1285m, 1449, 1559, 1586s, 1701s cm^{-1}).	2900-		3160	3.10
	2910	3.26		
	(sh.)			
	2960	3.27		
	3070-			
	3080	3.17		
	(sh.)			
	3530	3.44		
1-Keto-2,3,4,4-tetra- chloro-1,4-dihydro- naphthalene	2470-		2290	3.67
	2480	4.06		
	(sh.)		2590	4.10
(663, 698, 707s, 719s, 806m, 818s, 875m, 885, 931, 1092, 1107, 1145s, 1168m, 1301s, 1570m, 1595m, 1675s cm^{-1}).	2540	4.15	2750	3.50
	2620	4.12		
	2920	3.65		
1-Keto-2-methyl-2,3,4- trichloro-1,2-dihydro- naphthalene	2420	4.62	2450	4.59
	2480	4.63	2690	3.23
(656s, 698, 758s, 766, 791m, 831, 923m, 959m, 1014m, 1034, 1105, 1201, 1242s, 1261s, 1289s, 1562, 1594s, 1604, 1690s cm^{-1}).	2850	3.30	3120	3.10
	3450	3.41		
1-Keto-4-methyl-2,3,4- trichloro-1,4-dihydro- naphthalene	2450-2460	4.10	2290	3.92
	(sh.)		2710	3.79
(658m, 686m, 704s, 725, 763s, 769sh, 801m, 822, 850m, 880, 888sh, 969, 997m, 1020m, 1037, 1064, 1103, 1144s, 1158m, 1163sh, 1267s, 1302s, 1569m, 1596s, 1668s, cm^{-1}).	2520	4.17		
	2570-			
	2590	4.13		
	(sh.)			
	2820	3.86		

1-Keto-2,2,3,4,4-penta- chloro-1,2,3,4-tetra- hydronaphthalene	2540 2870- 2890 (infl.)	4.09 3.16	2350 2750	3.73 2.95
(665s, 675m, 746s, 792s, 798, 838m, 873s, 901s, 976, 1011, 1045m, 1058, 1095m, 1116, 1167, 1200m, 1244s, 1286s, 1447, 1592m, 1712s cm ⁻¹).	2950 3035 (sh.)	3.26 3.17		
1-Keto-2,2,3,3,4,4- hexachloro-1,2,3,4,- tetrahydronaphthalene	2530 2945- 2950 3000- 3020 (sh.)	4.09 3.24 3.19	2380 2770	3.92 3.00
(686s, 708s, 762s, 793s, 815, 839m, 876, 899m, 907, 1038m, 1058, 1115, 1200, 1242s, 1286m, 1499, 1595m, 1720s cm ⁻¹).				
1-Keto-2-methyl-2,3,4,4- tetrachloro-1,2,3,4- tetrahydronaphthalene	2500 2780- 2790 (infl.)	4.10 3.02	2340 2720	3.89 2.90
(667s, 701s, 746s, 751sh, 786, 813s, 890, 930, 967, 1104, 1139, 1163, 1198m, 1239s, 1248, 1285s, 1592, 1709s cm ⁻¹).	2910 3000- 3010	3.23 3.16	2980	3.15
1-Keto-4-methyl-2,3,2,4- tetrahydro-1,2,3,4- tetrahydronaphthalene	2540 2850- 2860 (infl.)	4.08 3.16	2330 2770	3.62 3.03
(653, 661s, 700m, 748m, 763m, 775, 824m, 857s, 917, 1025, 1035, 1055, 1068, 1080, 1094, 1114, 1160, 1205, 1242s, 1282s, 1590s, 1704s cm ⁻¹).	2940 3020- 3030 (sh.)	3.24 3.14		

** Infrared spectra in nujol mulls:

s=strong, m=medium, sh=shoulder, all others weak.

1-Keto-2,3,4-trichloro- 1,2,3,4-tetrahydronaph- thalene	2530 2910	4.07 3.16	2290 2770	3.50 3.05
(644s, 700s, 735, 754s, 789ms, 829m, 853m, 870, 890, 986, 1010m, 1045, 1109m, 1160, 1184, 1202ms, 1250ms, 1271s, 1306, 1337, 1599ms, 1711s cm ⁻¹).	2980- 2990 (sh.)	3.10		
1-Keto-2,2,4-trichloro- 5-acetoxy-1,2-dihydro- naphthalene	2410 2460- 2470 (sh.)	4.48 4.46	2710 3200	3.01 3.27
(655m, 686ms, 715m, 742ms, 779, 810ms, 826m, 875s, 928, 936, 951m, 988, 1006, 1038, 1076m, 1167ms, 1190s, 1211, 1243, 1269ms, 1290, 1339, 1367, 1591m, 1620m, 1710s, 1766s cm ⁻¹).	3030- 3040 (sh.) 3120 3440- 3450	3.26 3.29 3.35		
1-Keto-2,4,4-trichloro- 5-acetoxy-1,4-dihydro- naphthalene	2250 2420- 2430 (sh.)	4.03 4.03	2360 2530	3.98 4.04
(680m, 696, 717s, 749, 809, 831s, 874s, 893s, 965, 1011, 1103, 1132m, 1188sh, 1196s, 1227m, 1253m, 1340m, 1367m, 1595, 1630m, 1677s, 1767s cm ⁻¹).	2490 2560 2900- 2910 (sh.) 3105	4.10 4.09 3.37 3.39	2700- 2710	3.27
1-Keto-2,3,4-trichloro- 5-acetoxy-1,2,3,4-tetra- hydronaphthalene	2540 2980	4.02 3.27	2380 2750	3.73 2.86
(692s, 730, 746, 759, 781, 804m, 846, 866m, 929m, 937sh, 962, 989, 1012m, 1042, 1058, 1075, 1127, 1168, 1182s, 1233, 1245m, 1288s, 1334m, 1584, 1599, 1704s, 1763s cm ⁻¹).	3050- 3060 (infl.)	3.23- 3.24		

Figure 1

Ultraviolet absorption spectra
of polychloro-1-keto-1,2-dihydro-
naphthalenes

- 1-Keto-2,2,4-trichloro-
1,2-dihydronaphthalene
- 1-Keto-2,2,3,4-tetrachloro-
1,2-dihydronaphthalene
- 1-Keto-2-methyl-2,3,4-tri-
chloro-1,2-dihydronaph-
thalene

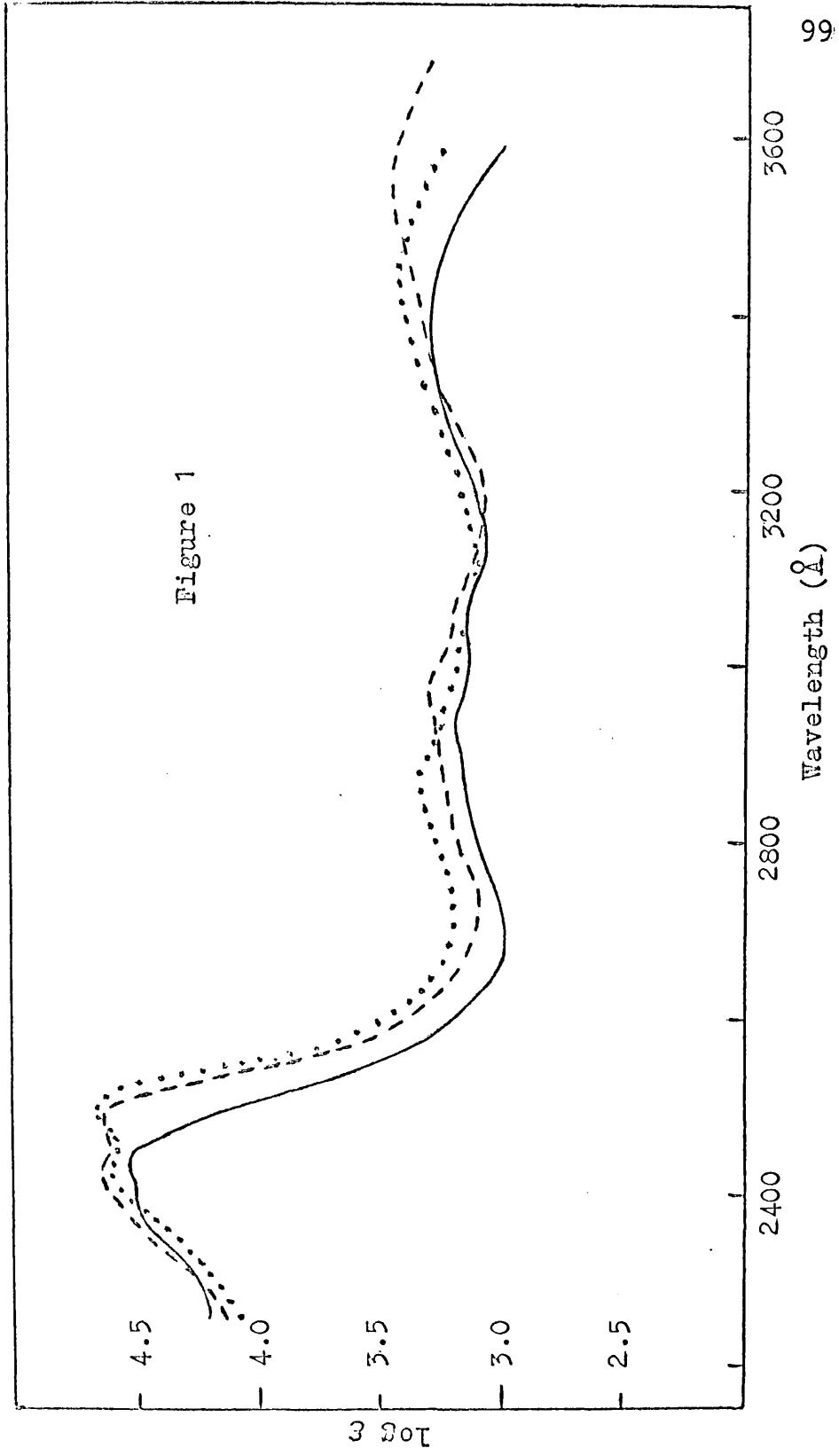


Figure 2

Ultraviolet absorption spectra
of polychloro-1-keto-1,4-dihydro-
naphthalenes

- 1-Keto-2,4,4-trichloro-
1,4-dihydronaphthalene

- 1-Keto-2,3,4,4-tetrachloro-
1,4-dihydronaphthalene

- 1-Keto-4-methyl-2,3,4-tri-
chloro-1,4-dihydronaphthalene

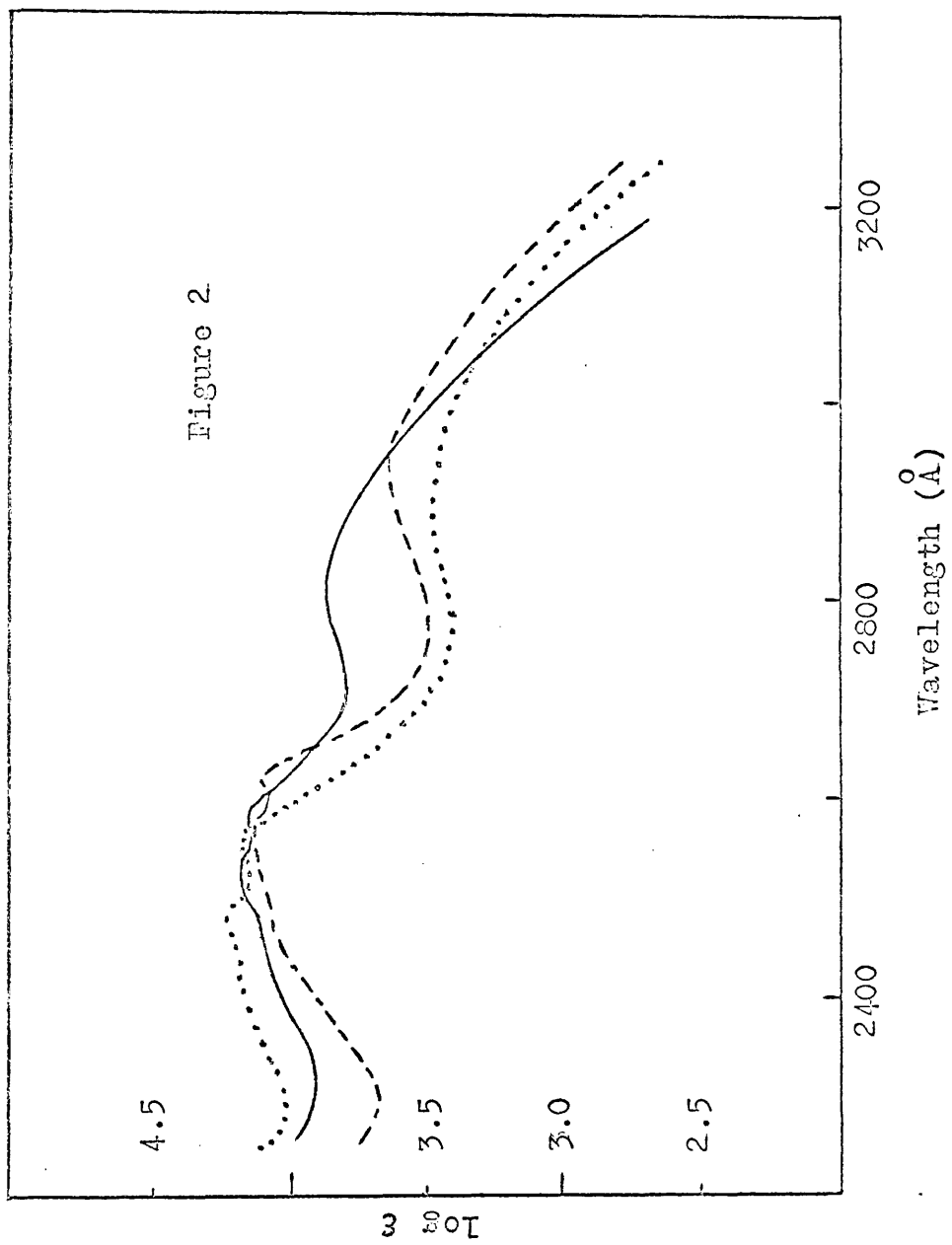
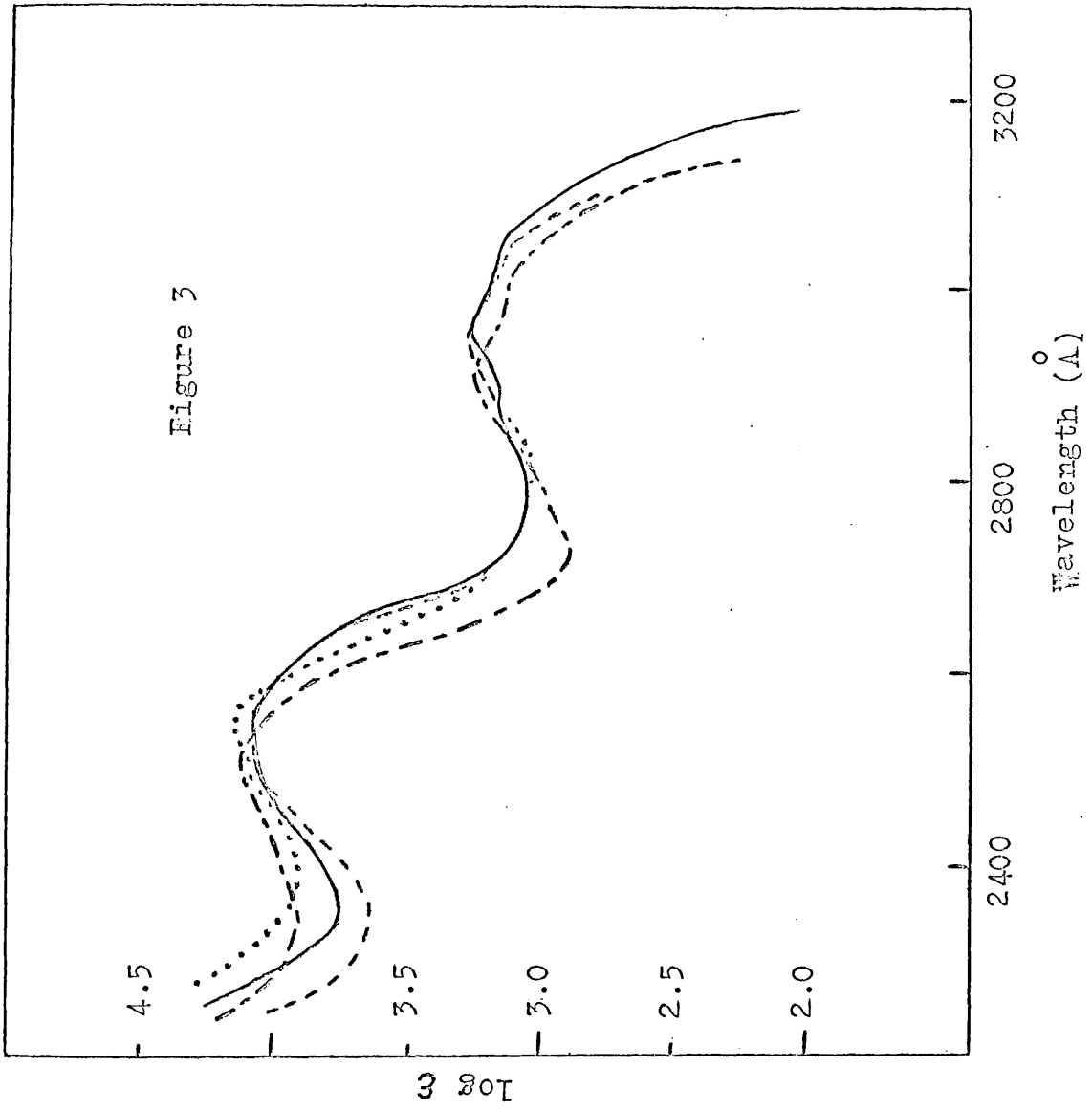


Figure 3

Ultraviolet absorption spectrum
of polychloro-1-tetralones

- 1-Keto-2,2,3,4,4-pentachloro-
1,2,3,4-tetrahydronaphthalene
- - - - - 1-Keto-2-methyl-2,3,4,4-tetra-
chloro-1,2,3,4-tetrahydro-
naphthalene
- 1-Keto-4-methyl-2,2,3,4-tetra-
chloro-1,2,3,4-tetrahydro-
naphthalene
- 1-Keto-2,2,3,3,4,4-hexachloro-
1,2,3,4-tetrahydronaphthalene



12. Chlorine Additions to Naphthylamines

Materials

Naphth-1-ylamine and naphth-2-ylamine were commercial products. 2-Methylnaphth-1-ylamine was prepared by the reduction of 1-nitro-2-methylnaphthalene. 2-Chloro-4-methylnaphth-1-ylamine (m.p. 84-85°) was obtained by the careful chlorination of 1-acetylamino-4-methylnaphthalene and the subsequent hydrolysis of the product. (Found: C, 68.84; H, 5.23; N, 7.20. $C_{11}H_{10}ClN$ requires C, 68.98; H, 5.26; N, 7.31%). Acetylamino compounds were readily prepared by the acetylation of the appropriate amines; 1-acetylamino-naphthalene (m.p. 159-160°), 2-acetylamino-naphthalene (m.p. 133-134°).

1-Keto-2-methyl-2,3,4,4-tetrachloro-1,2,3,4-tetrahydronaphthalene

2-Methylnaphth-1-ylamine was converted into hydrochloride (m.p. ca. 230° decomp.), of which (9.7 g.), after drying, was placed in a small flask, and moistened with glacial acetic acid (30 ml.) containing concentrated hydrochloric acid (2-3 ml.). Chlorine was slowly introduced with hand-shaking and occasional cooling under running water, until the mixture was saturated.

Crystals of the hydrochloride gradually disappeared to give a dark-red solution, which after standing overnight faded to yellow and a mixture of the ketone and ammonium chloride precipitated. Extraction with hot ligroin and recrystallisation from the same solvent gave the ketone (7.1 g.) as large prisms, m.p. 117-118° (lit.,¹⁵ 118°). This ketone (3.0 g.) on reduction with lithium aluminium hydride in anhydrous ether gave 2-methyl-3,4-dichloronaphth-1-ol (1.6 g.) as long needles melting at 132-133° (Found: C, 58.06; H, 3.52; Cl, 31.11. $C_{11}H_8Cl_2O$ requires: C, 58.17; H, 3.55; Cl, 31.22%).

The use of wet amine hydrochloride, or a larger amount of acetic acid had decreased the yield considerably, owing to the formation of a red-brown syrupy substance.

By a similar treatment, 2-chloro-4-methylnaphth-1-ylamine hydrochloride gave 1-keto-4-methyl-2,2,3,4-tetrachloro-1,2,3,4-tetrahydronaphthalene, m.p. 121-122°.

1-Keto-2,2,3,4,4-pentachloro-1,2,3,4-tetrahydronaphthalene

Naphth-1-ylamine hydrochloride (5.6 g.) was moistened with glacial acetic acid (20 ml.) containing concentrated hydrochloric acid (1.5 ml.), and chlorine

was slowly introduced until the white salt was converted into a dark liquid saturated with chlorine. The mixture was allowed to stand overnight, then poured into water. The dark precipitate was dissolved into a mixture of benzene-cyclohexane, and chromatographed on a short silica gel. The removal of the solvent from the elute gave a light brown syrup, from which the ketone (m.p. 157-158°) slowly separated out. The infrared inspection of the mother liquor indicated the presence of two other keto-compounds as minor components.

2-Keto-1,1,3,3,4-pentachloro-1,2,3,4-tetrahydro-naphthalene

Naphth-2-ylamine hydrochloride (3.6 g.) in acetic acid (20 ml.) and hydrochloric acid (1.5 ml.) was similarly treated with chlorine. The reaction proceeded with ease and soon ammonium hydrochloride began to precipitate. No resinous substance, as seen in the chlorination of naphth-1-ylamine, was formed. After having stood for a while, the mixture was poured into water, and the precipitate was chromatographed on silica gel using cyclohexane as eluent. The removal of the solvent gave the ketone (3.1 g.) as white prisms, m.p. 113-114°. Its spectroscopic as well as physical

properties coincided with those of the authentic specimen prepared from naphth-2-ol.

1.1.2.3.4-Pentachloro-2-acetylamino-1.2.3.4-tetrahydronaphthalene

2-Acetylamino-naphthalene was dissolved in chloroform and slowly saturated with chlorine. The adduct readily separated as white prisms, which could be further increased by the addition of light petroleum. The adduct begins to decompose at around 135-145° (lit.,⁶³ 140-145°) to give light brown crystals, which are still stable above 200°; poorly soluble in ordinary solvents and degraded on storage to dark brown substance. Its n.m.r. spectrum taken in acetone showed a complicated pattern in the higher field at 7-9 τ , but a singlet at 5.7 τ in the ordinary methine proton absorption regions. Thus, although the structure of this adduct had been formulated as above by Claus and Jäck, the spectrum cast a doubt over the proposed structure as well as the homogeneity of the addition product.

Similar treatment of 1-acetylamino-naphthalene gave 2,4-dichloro-1-acetylamino-naphthalene, which was considerably stable to the further attack of chlorine. In acetic acid the dichloro compound precipitates, and no elimination of acetyl group was observed.

13. Chlorine Additions to Alkylnaphthalenes

Materials

1-Methylnaphthalene (b.p. 243-245°) and 2-methylnaphthalene (m.p. 32°) were commercial products. 1-Chloromethylnaphthalene (b.p. 129-131°/4.5 mm Hg) was obtained by the chloromethylation of naphthalene.⁸⁸ 1-Ethylnaphthalene (b.p. 94-95°/2-2.5 mm Hg) was prepared according to the Gilman and Hoyle's method.⁸⁹ 1-Isopropylnaphthalene (b.p. 106-108°/3.5-4 mm Hg) was prepared chiefly following Cook's procedure.⁹⁰ 1,2-Dimethylnaphthalene (b.p. 109-110°/4 mm Hg) was prepared by Mayer and Sieglitz's method⁹¹ and 1,8-dimethylnaphthalene (m.p. 62-63°) by the Mitchel, Topsom and Vaughan's method.⁹² Acenaphthene (m.p. 93-94°) was a commercial product, purified through the alumina chromatography. 1-Methyl-4-deuteronaphthalene was prepared by quenching the Grignard reagent of 1-methyl-4-bromonaphthalene with deuterium oxide. 1-Isopropylnaphthalene was directly iodinated with iodine and periodic acid in aqueous acetic acid to give 1-isopropyl-4-iodonaphthalene (b.p. 152-154°/3.5-4 mm Hg), which was then converted into the Grignard reagent and quenched

with deuterium oxide. 1-Isopropyl-4-deuteronaphthalene (b.p. 109-110°/4 mm Hg).

1,2,3,4-Tetrachloro-1-chloromethyl-1,2,3,4-tetrahydronaphthalene

To a solution of 1-methylnaphthalene (5.68 g.) in light petroleum (20 ml.), sulphuryl chloride (16.2 g.) was added and the mixture was allowed to stand for 6 days. Then the excess sulphuryl chloride and the solvent was removed under reduced pressure, and a pale yellow oily residue (8.29 g.) was chromatographed on silica gel. Substitution products eluted with light petroleum, and a light brown syrup containing adducts with benzene. The latter slowly solidified to crystalline mass (1.26 g.), which on silica gel chromatography and recrystallisation from hot ligroin gave colourless prisms, m.p. 136-137°. Its melting point could hardly be raised by recrystallisation, but it was found to be slightly impure by n.m.r. spectroscopy and otherwise to be identical with the compound, m.p. 155°, obtained by molecular chlorination. Its p.m.r. spectrum had a singlet at 5.49 τ (two methylene protons), a quartet at 5.06 τ (one proton), two doublets at 4.54 and 4.50 τ (each area attributable to one proton), and an aromatic

multiplet (four protons). The coupling constants were assigned as $J_{2,3} = 11.4$ and $J_{3,4} = 3.5$ c.p.s. by the partially deuterated adduct 1,2,3,4-tetrachloro-1-chloromethyl-4-deutero-1,2,3,4-tetrahydronaphthalene, m.p. $136-137^{\circ}$, similarly obtained from 1-methyl-4-deuteronaphthalene (Found: C, 41.56; H, 3.03; Cl, 55.59. $C_{11}H_9Cl_5$ requires C, 41.48; H, 2.85; Cl, 55.67%). On dehydrochlorination it gave 1-methoxymethyl-2,3-dichloro-4-deuteronaphthalene, m.p. 75° , as was readily identified by the disappearance of an isolated proton singlet (2.17 τ .) from the n.m.r. spectrum of the ordinary compound. From the final fractions eluted with benzene, a small amount of 1,2,3-trichloro-4-hydroxy-4-methyl-1,2,3,4-tetrahydronaphthalene, m.p. $126-127^{\circ}$, was obtained.

From the reaction of equimolecular amounts of 1-methylnaphthalene (20 g.) and sulphuryl chloride (19 g.) in light petroleum (50 ml.), the adduct (3.1 g.) was obtained, together with a mixture of unchanged hydrocarbon and substitution products (23.1 g.). At elevated temperature ($60-70^{\circ}$), however, the reaction mainly led to the formation of resinous substances.

1,2,3,4,5-Pentachloro-8-methyl-1,2,3,4-tetrahydro-naphthalene

A solution of 1-methyl-4-chloronaphthalene (13.4 g.) in light petroleum (30 ml.) was slowly treated with chlorine under ice-cooling until saturation, and the mixture was allowed to stand for a few days. The separated tetrachloride was recrystallised from ligroin (b.p. 100-120°) to give white prisms, m.p. 177-178°. Its p.m.r. spectrum had a methyl singlet at 7.48 τ , three apparent triplets peaks with low couplings (below 2 c.p.s.) at 4.84 τ (two hydrogens), 7.40 τ (one hydrogen), and 4.20 τ (one hydrogen), two aromatic doublets ($J = 8.6$ c.p.s.) at 2.48 and 2.71 τ (each area attributable to one hydrogen atom).

Chlorination by sulphuryl chloride gave besides the above tetrachloride another tetrachloride of m.p. 151-152°. (Found: C, 41.43; H, 3.04. $C_{11}H_9Cl_5$ requires C, 41.4; H, 2.8%). Its p.m.r. spectrum showed a very complicated pattern in the region for alicyclic hydrogens, and remains unsolved yet.

Attempted synthesis of the corresponding tetrachlorides from 1-methyl-4-bromonaphthalene

1-Methyl-4-bromonaphthalene (22.1 g.) and

sulphuryl chloride (20.2 g.) were mixed and allowed to stand at room temperature for a week. The separated crystals were filtered off and recrystallised from ligroin (b.p. 100-120°). White prisms (4.8 g.) m.p. 165-166°. Although this had a sharp melting point, its n.m.r. spectrum and analysis showed that this adduct was a mixture of several adducts derived from 1-methyl-4-chloronaphthalene and 1-methyl-4-bromonaphthalene. A part of bromine migrated and seems to have been taken into the alicyclic system, as the dehydrochlorination products of this adduct (m.p. 95-99°) was found to contain more bromine than the expected value (Found: C, 43.20; H, 2.27. $C_{11}H_7Cl_2Br$ requires C, 45.52; H, 2.41%). Chromatography of the mother liquor on silica gel gave besides the substitution products another addition product of m.p. 175-177°. This again was not the single substance, as the analysis had indicated the higher chlorine value than the expected tetrachloride. Interestingly enough, the infrared spectrum of the higher melting adduct from 1-methyl-4-bromonaphthalene bears close resemblance to that of the lower-melting tetrachloride from 1-methyl-4-chloronaphthalene, whereas the spectrum of the lower-melting product from 1-methyl-4-bromonaphthalene resembles very much that of the higher-

melting isomer from 1-methyl-4-chloronaphthalene.

Since the change of substituent from chlorine to bromine does not affect the total balance of the dipole in the system so much, each pair of the products are supposed to have the same configuration, and therefore the reversal change of the product ratio indicates the drastic change of the reaction mechanism according to the change from the chloro compound to the bromo compound.

1,2,3,4-Tetrachloro-2-methyl-1,2,3,4-tetrahydro-naphthalene

2-Methylnaphthalene (2.80 g.) and sulphuryl chloride (5.53 g.) were heated in carbon tetrachloride (6 ml.) under gentle reflux for 3 hr. A pale yellow oil obtained by the ordinary procedure was chromatographed on silica gel. Substitution products (2.07 g.) eluted rapidly with light petroleum, and the adducts (1.19 g.) slowly with a mixture of benzene-light petroleum. The substitution products were mainly 1-chloro-2-methylnaphthalene and dichloro-2-methylnaphthalenes. A light brown syrup containing adducts on standing gave the tetrachloride as needles, m.p. 97-99°. The mother liquor seems to contain a substantial amount of another

adduct which, however, could not be isolated in crystalline form.

1,1,2,3,4-Pentachloro-2-methyl-1,2,3,4-tetrahydro-naphthalene

2-Methylnaphthalene (2.86 g.) and sulphuryl chloride (10 g.) were heated under gentle reflux for 4 hr. After having stood overnight, the mixture was poured into water and extracted with ether. Evaporation of the solvent gave an oil (5.1 g.) which on standing gave the pentachloride (0.76 g.) as white prisms. On alkaline dehydrochlorination it gave 1,3,4-trichloro-2-methylnaphthalene, m.p. 182-183°.

1,2,3,4,5-Pentachloro-6-methyl-1,2,3,4-tetrahydro-naphthalene

1-Chloro-2-methylnaphthalene (14.5 g.) and sulphuryl chloride (14.5 g.) were mixed and allowed to stand for a week at room temperature. The mixture was then diluted with ligroin and unreacted sulphuryl chloride was removed with the solvent under reduced pressure. A white precipitate (3.54 g.) was crystallised from hot ligroin to give prisms, m.p. 148-149°, and was identified as 1,1,2,3,4-pentachloro-2-methyl-1,2,3,4-tetrahydronaphthalene. Chromatography of

the mother liquor (17.0 g.) gave a mixture of substitution products (14.7 g.) and a pale yellow syrup containing adducts (1.62 g.). When the latter was kept in a cool place, crystals of another adduct gradually separated. Colourless prisms (0.35 g.) from ligroin, m.p. 137-138°. (Found: C, 41.5; H, 2.8. $C_{11}H_9Cl_5$ requires C, 41.4; H, 2.8%). Its p.m.r. spectrum showed a methyl singlet at 7.61 τ , two methine doublets at 4.56 and 4.88 τ , two methine quartets at 5.08 and 5.83 τ , and an aromatic multiplet, at 2.7-3.1 τ (two hydrogens). Integration was correct for 1,2,3,4,5-pentachloro-6-methyl-1,2,3,4-tetrahydronaphthalene. Alkaline hydrolysis of this adduct gave a mixture of trichloro-2-methylnaphthalenes, whose infrared spectrum showed the absence of 1,3,4-trichloro-2-methylnaphthalene.

1,2,3,4-Tetrachloro-5-chloromethyl-1,2,3,4-tetrahydronaphthalene

1-Chloromethylnaphthalene (13.2 g.) was dissolved in ligroin (ca. 300 ml.) and chlorine was slowly introduced with careful cooling, avoiding the separation of the starting material as white leaflets, in such a way that the system could be maintained in a chlorine saturated condition. After having stood overnight,

the solvent was removed under reduced pressure and nearly colourless syrup (ca. 20 g.) was set aside for weeks. White crystals separated out were collected by removing the syrupy part with hot ligroin. On recrystallisation from hot ligroin, it gave colourless prisms (2.15 g., 9%), m.p. 154-155°, very difficult in solubility in cold ligroin. (Found: C, 41.61; H, 2.95; Cl, 55.71. $C_{11}H_9Cl_5$ requires C, 41.48; H, 2.85; Cl, 55.67%). Its p.m.r. spectrum had two doublets at 4.97 and 5.41 γ (two protons attributable to the chloromethyl group, $J = 12.2$ c.p.s.), three apparent quartets at 4.13, 4.43 and 4.94 γ (attributable to four methine protons) with characteristic low coupling constants (below 2 c.p.s.), and an aromatic singlet at 2.52 γ (three protons). Its infrared spectrum showed bands at 688vs, 708s, 726s, 768ms, 811, 826m, 850ms, 865m, 964, 1029ms, 1151w, 1172, 1180, 1199, 1207, 1235w, 1248, 1259, 1266, 1274w, 1297w cm^{-1}

1,2,3,4-Tetrachloro-1-(1'-chloroethyl)-1,2,3,4-tetrahydronaphthalene

1-Ethyl-naphthalene (7.8 g.) was dissolved in light petroleum (20 ml.) and sulphuryl chloride (13.4 g.) was added all at once. After having stood over a week,

the solvent was removed under reduced pressure and the residual oil was set aside for weeks. Crystals slowly began to separate from the oil. Filtration and subsequent crystallisation from ligroin gave large colourless prisms (1.16 g.), m.p. 146-147°. (Found: C, 43.42; H, 3.46; $C_{12}H_{11}Cl_5$ requires C, 43.35; H, 3.34%). The mother liquor (10.5 g.) was a mixture of unchanged hydrocarbon and nuclear substitution products. The n.m.r. spectrum of the adduct had signals at 8.00 τ (methyl doublets, $J = 7.2$ c.p.s.), 5.14 τ (quartet due to 3-H, $J = 3.2$ and $J' = 11.5$ c.p.s.), 4.87 τ (doublet due to the α -hydrogen of the side-chain, $J = 7.2$ c.p.s.), 4.40 and 4.42 τ (two doublets due to 2-H and 4-H, $J = 11.5$ and $J' = 3.2$ c.p.s. respectively), and 1.88-2.48 τ (aromatic multiplet). Its infrared spectrum had bands at 678s, 704s, 756s, 789m, 820m, 851m, 894m, 943, 967, 1001m, 1025, 1046, 1100m, 1144, 1190, 1217m, 1233, 1259, 1267, 1305, 1326, 1347, 1381, 1447, and 1491 $cm.^{-1}$

1,2,3,4-Tetrachloro-1-isopropyl-1,2,3,4-tetrahydro-naphthalene

1-Isopropyl-naphthalene (8.5 g.) was dissolved in light petroleum (20 ml.) and sulphuryl chloride

(13.5 g.) was added all at once. The mixture gave a bright yellow colour, but any change except colouration could not be observed. The mixture was left for a fortnight, then the excess sulphuryl chloride was removed together with the solvent under reduced pressure. An oily residue (9.86 g.) on chromatography gave a mixture of unchanged hydrocarbon and substitution products (7.05 g.) from light petroleum elutes^a, and the syrup containing adducts (1.55 g.) from light petroleum-benzene elutes. On prolonged standing the latter gave small amounts of crystals (ca. 0.6 g.), which on recrystallisation from ligroin melted at 116-117°. (Found: C, 49.90; H, 4.47; Cl, 45.43. $C_{13}H_{14}Cl_4$ requires C, 50.03; H, 4.52; Cl, 45.45%). Its infrared spectrum had bands at 693vs, 747vs, 784ms, 815, 841m, 862, 877, 898m, 950, 961, 1010m, 1048, 1099, 1138, 1167, 1182m, 1189m, 1221m, 1261, 1269, 1300, 1342, 1394 and 1489 $cm.^{-1}$. This tetrachloride was found to be readily accessible by passing chlorine into a stirred solution of 1-isopropylnaphthalene in light petroleum, in presence of seed crystals of the adduct. The n.m.r. spectrum had two methyl doublets at 9.00 and 8.65 τ ($J = 6.9$ c.p.s.), a methine septet at 7.05 τ ($J = 6.9$ c.p.s.), a methine quartet at 5.27 τ

($J = 3.1$ and $J' = 11.5$ c.p.s.), two methine doublets at 4.58 and 4.907 ($J = 3.1$ and 11.5 c.p.s.), and aromatic multiplet at 2.15-2.75 τ . By employing the latter method, 1,2,3,4-tetrachloro-1-isopropyl-4-deutero-1,2,3,4-tetrahydronaphthalene was prepared from 1-isopropyl-4-deuteronaphthalene, and the coupling constants were assigned as $J_{2,3} = 11.5$ c.p.s. and $J_{3,4} = 3.1$ c.p.s.

1,2,3,4-Tetrachloro-1-chloromethyl-2-methyl-1,2,3,4-tetrahydronaphthalene

1,2-Dimethylnaphthalene (7.8 g.) was mixed with sulphuryl chloride (13.5 g.) in light petroleum (20 ml.). After a week, the solvent was removed under reduced pressure and the residual oil (ca. 12.1 g.) was chromatographed on silica gel using light petroleum as eluent. The mixture of substitution product and unchanged hydrocarbon (6.46 g.) eluted first with light petroleum, then the syrup (4.19 g.) containing adducts slowly appeared with the mixture of light petroleum-benzene. From the earlier elutes^a of the adduct fractions, white prisms melting at 139-141° was obtained and identified as above (Found: C, 43.19; H, 3.28; Cl, 53.28. $C_{12}H_{11}Cl_5$ requires C, 43.35; H, 3.33; Cl, 53.32%). Its infrared spectrum had bands at 624s, 696vs, 711vs, 730vs, 756m,

779, 803, 814, 852, 873, 917m, 985, 1029, 1054, 1067, 1124, 1166m, 1189, 1221m, 1250w, 1292m, 1334, 1446, and 1488w cm.^{-1} Its p.m.r. spectrum had a methyl singlet at 7.92 τ , two doublets due to protons of chloromethyl group at 5.12 and 5.39 τ ($J = 13.2$ c.p.s.), two doublets due to alicyclic protons at 4.32 and 4.60 τ ($J = 5.7$ c.p.s.), and an aromatic singlet at 2.47 τ (four protons).

From the later parts of elutes^a, on standing for weeks, another adduct (0.27 g.) was separated, which after recrystallisation from ligroin gave white cubes melting at 162-164° and identified as 1,2,3,4,x-pentachloro-1,2-dimethyl-1,2,3,4-tetrahydronaphthalene.

(Found: C, 43.43; H, 3.53; Cl, 53.25. $\text{C}_{12}\text{H}_{11}\text{Cl}_5$ requires C, 43.35; H, 3.34; Cl, 53.32%). Its infrared spectrum had absorptions at 632vs, 690vs, 733m, 754vs, 813s (broad), 880ms, 945, 1038m, 1064m, 1075m, 1127, 1164, 1203, 1231, 1308m, 1447 cm.^{-1} Its p.m.r. spectrum showed two methyl singlets at 7.76 and 8.39 τ , a methine singlet at 4.19 τ , and two aromatic multiplets at 2.3-2.9 and 1.8-2.2 τ .

By similar treatment of 1,8-dimethylnaphthalene with sulphuryl chloride, however, no crystalline adduct

could be isolated. The p.m.r. spectrum of adduct fractions showed prominent methyl peaks in the 7-8 τ region, but signals corresponding to methylene protons were weak. Therefore, the main adducts are supposed not to be the side-chain chlorinated, but the ordinary tetrachlorides.

1,2,5,6,7-Pentachloro-5,6-dihydroacenaphthene and
2,3,4,5,6,7-hexachloro-3,4,5,6-tetrahydroacenaphthene

Acenaphthene (7.7 g.) was suspended in light petroleum (20 ml.) and sulphuryl chloride (20.3 g.) was added all at once. Orange colour immediately developed and crystals slowly disappeared under gentle evolution of hydrogen chloride. After a few hours, the addition products began to separate on the bottom of the vessel. The increase of the precipitate seemed almost to have stopped after 2 days. The crystals (3.47 g.) were collected and washed with small amounts of light petroleum. As the chromatographic separation on silica gel had been proved ineffective, two adducts were separated by hand-picking: the product was dissolved in a hot mixture of ligroin-benzene and allowed to cool very carefully, thus making the crystals grow large enough for mechanical separation. First, fine needles separated

as clusters, then slightly yellow coloured prisms began to deposit. The former (recovery, 0.46 g., 13%) melted at 210-212° under darkening and bubbling (all the solid disappeared up to 214° under microscope), while the latter (recovery 1.21 g., 35%) melted at 168-169°. The remaining part (1.79 g.) was mostly a mixture of the two adducts, the major component of which was the higher-melting product as the hand-picking disfavours the recovery of this adduct owing to its minute crystal size. The melting points of both adducts differed considerably from those reported in literature,⁶⁶ (m.p. 150° decomp. and 204-205° decomp., respectively), so they were analysed. The higher-melting product had the formula $C_{12}H_7Cl_5$ (Found: C, 43.82; H, 2.14; Cl, 53.97. $C_{12}H_7Cl_5$ requires C, 43.77; H, 2.13; Cl, 53.95%), the lower-melting one came to the formula of $C_{12}H_8Cl_6$ (Found: C, 39.63; H, 2.17; Cl, 58.17. $C_{12}H_8Cl_6$ requires C, 39.45; H, 2.19; Cl, 58.35%). Therefore, the former is a trichloro-dichloride and the latter a dichloro-tetrachloride.

The syrupy part (10.2 g.) from which the above adducts had been separated was chromatographed on silica gel. The evaporation of the earlier elutes^a gave yellow

needles of impure 6,7-dichloroacenaphthene (ca. 3.2 g.) melting between 115-135°. The later elutes^(a) gave a dark brown syrup of complicated composition, from which some amounts of the dichloride was further obtained.

The chlorination of acenaphthene (7.7 g.) with more sulphuryl chloride (27 g.) in light petroleum (20 ml.) proceeded similarly, giving more precipitate of the addition products (4.99 g.) and a syrupy part (10.93 g.). The composition of the product was nearly the same.

By treatment with alkaline methanol, the dichloride gave orange needles of 2,5,7-trichloroacenaphthylene, m.p. 164-165° (lit., 165°), and the tetrachloride, yellow needles of 2,4,6,7-tetrachloroacenaphthylene, m.p. 191-193° (lit., ⁶⁶ 192-194°, and highly purified specimen, 197-198°).

The infrared spectrum of the dichloride had bands at 635, 678s, 711s, 737ms, 757, 787m, 811ms, 826ms, 897, 937, 951w, 990, 1064w, 1094ms, 1117ms, 1126w, 1182, 1206m, 1214w, 1252m, 1304, 1346ms, 1581w, 1621ms cm.⁻¹ The tetrachloride had infrared absorptions at 678w, 693s, 714w, 732vs, 764ms, 785m, 797m, 829s, 850m, 898ms, 949w, 963w, 975m, 1011m, 1052, 1126, 1152, 1188, 1202, 1215,

1261, 1275ms, 1342, 1429 cm.^{-1} The p.m.r. spectrum of the dichloride had signals at 6.29 τ (two protons of probably ethylene bridge), 4.79, 4.52 and 4.30 τ (ill-split quartets, each area attributable to one hydrogen), and 2.48 τ (singlet due to two aromatic protons). All the coupling constants were small (below 2 c.p.s.). The tetrachloride showed signals at 6.62, 6.45-6.49, 4.98, 4.33, 4.70-4.76, 4.55-4.59, 4.22 τ , and two aromatic doublets at 2.30 and 2.55 τ ($J = 8.4$ c.p.s.). Because of the lack of comprehensive data, aliphatic protons could not be assigned. The coupling constants were also small (below 2 c.p.s.).

PART III

DISCUSSIONS

14. Chlorine Additions to Naphthalene and Related Compounds

14.1 Historical Survey

Electrophilic addition to benzenoid system can occur either through 1,2-addition or through 1,4-addition. Although the 1,2-addition product is thermodynamically more stable than that derived by 1,4-addition owing to the conjugation, it does not always mean that the formation of 1,2-addition product is kinetically favoured. Thus, in the kinetically controlled addition of halogen or hydrogen halides to conjugated systems, de la Mare et al. observed the preponderent formation of the thermodynamically less stable isomer.⁹³ In the chlorine additions to benzenoid compounds, however, this situation is not clear yet.

Naphthalene is the most important member of the polycyclic hydrocarbons with fused ring, and also the first benzenoid compound to be recognised to undergo the simultaneous additive and substitutive chlorinations. As early as 1833, Laurent, who first investigated the chlorination of naphthalene, allowed chlorine gas to react with solid naphthalene and observed the formation of liquid naphthalene dichloride and naphthalene

α -tetrachloride.⁷

Faust and Saame similarly treated molten naphthalene and obtained a mixture of a naphthalene dichloride, the α -tetrachloride, a monochloronaphthalene tetrachloride, and a dichloronaphthalene tetrachloride.¹⁸

Leeds and Everhardt prepared this tetrachloride in a high yield of 45% in sunlight.¹⁹

By passing chlorine into a chloroform solution of naphthalene, Shwarzer obtained the same adduct.¹⁹

Other procedures involving the treatment of naphthalene with a variety of reagents such as hypochlorous acid, a mixture of sulphur dioxide and chlorine, sulphuryl chloride, or potassium perchlorate and hydrochloric acid, are reported to yield the same tetrachloride.^{21-23, 25-26}

By the last-mentioned method, the isolation of an isomeric β -tetrachloride was also reported.^{20, 28}

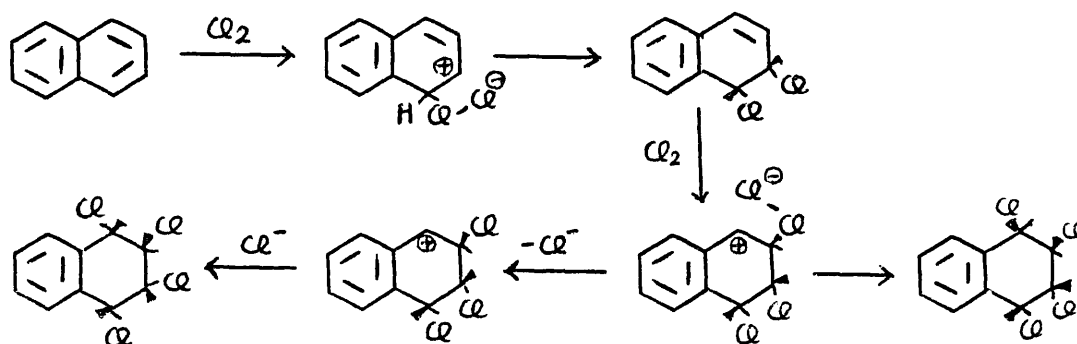
The stereochemistry of the α -tetrachloride was first investigated by Laschen,⁹⁴ using X-ray diffraction method and the conformation of chlorine atoms was allocated as 1a'.2e.3e.4a'. In the same year, Hahn and Schutz isolated two other isomers (γ and δ), and the probable structure of three (α , γ , and δ) of the four known tetrachlorides were deduced from kinetic

analysis.²⁵ In recent times, systematic investigations of these tetrachlorides have been carried out by de la Mare and his pupils, and the conformation of four (α , γ , δ , and ϵ) of the known five, including the fifth new isomer (ξ), has been established by the kinetic study and proton magnetic resonance spectroscopy.²⁶⁻²⁷

<u>Isomers</u>	<u>Conformations</u> (chlorine positions)
α -Tetrachloride	1a'.2e.3e.4a'
γ - "	1e'.2e.3e.4e'
δ - "	1a'.2e.3e.4e'
ξ - "	1a'.2a.3e.4e'

They have observed the remarkable dependence of the structure of conformers on the reaction conditions: in the dark and without catalyst, the product was found mainly to be the α -isomer (over 90%), together with the δ -isomer as a minor component: added electrolytes, however, change the proportion greatly (50:50), and some amounts of 1-acetoxytrichloride were also isolated. Under the homolytic conditions involving irradiation or catalysis of peroxide, the products were the γ - and the ξ -tetrachlorides in the approximate ratio of 2:3, quite different from those obtained under heterolytic conditions. On these findings they

have proposed that in the non-catalytic chlorinations, the intermediate of the type ArHCl_2^+ plays an important role in the addition reactions and the α -tetrachloride is produced by two successive cis-additions to naphthalene. The formation of the δ -isomer and 1-acetoxytrichloride is explained by the attack of chloride or acetoxy anions on the carbonium ionic intermediate ArH^+ .



By passing chlorine into a chloroform solution, Widman obtained a tetrachloride from 1-chloronaphthalene, 2-chloronaphthalene, 1,4-dichloronaphthalene and 1,5-dichloronaphthalene.³⁵ These results were later confirmed by Wynne and his pupil,^{34, 36} who also prepared 1,1,2,3,4,4-hexachloro-1,2,3,4-tetrahydronaphthalene under homolytic conditions. Spontaneous decomposition of unstable naphth-1-yl iododichloride is reported to give a chloronaphthalene tetrachloride.³³ Stereochemistry of all these tetrachlorides has not been clarified yet.

14.2. Naphthalene Dichlorides

From the theoretical point of view, the structure of the naphthalene dichloride would be of great interest. Although a number of workers have claimed to have isolated naphthalene dichlorides by the controlled chlorination of naphthalene, and its chemical as well as physical properties have been recorded in detail,^{7, 18-22} any recent references do not provide confirmation about this point. Under a variety of conditions the original procedures were faithfully reproduced, and the products have been shown to contain mixtures of chloro-substituted naphthalenes and tetrachlorides, but no direct evidence for the presence of any dichloride in this mixture has been obtained.

Some polychloronaphthalenes, however, seem to give isolable dichlorides, probably because the accumulation of chlorine atoms reduces the reactivity of the double bond. Thus 1,5-dichloronaphthalene has been reported to give, on chlorination by molecular chlorine in chloroform, a dichloride of m.p. 94° , together with a tetrachloride, 1,1,2,3,4,5-pentachloro-1,2,3,4-tetrahydronaphthalene.^{32, 35-36} On treatment of a solution of 1-chloronaphthalene in acetic acid with chlorine,

the isolation of a dichloride of mp. 152° has also been claimed.²⁰ The former has formula $C_{10}H_5Cl_5$, and has been variously formulated as 1,2,3,5-x-pentachloro-x,x-dihydronaphthalene,⁹⁵ or as 1,1,2,3,5-pentachloro-1,4-dihydronaphthalene.⁹⁶ The latter also has the same formula $C_{10}H_5Cl_5$ and is formulated as 1,3,5,9-pentachloro-x,x-dihydronaphthalene. Exhaustive chlorination of naphthalene with catalyst has been known to give 1,1,2,3,4,4,5,6,7,8-decachloro-1,4-dihydronaphthalene, together with a variety of degradation products caused by ring-fission.³⁸

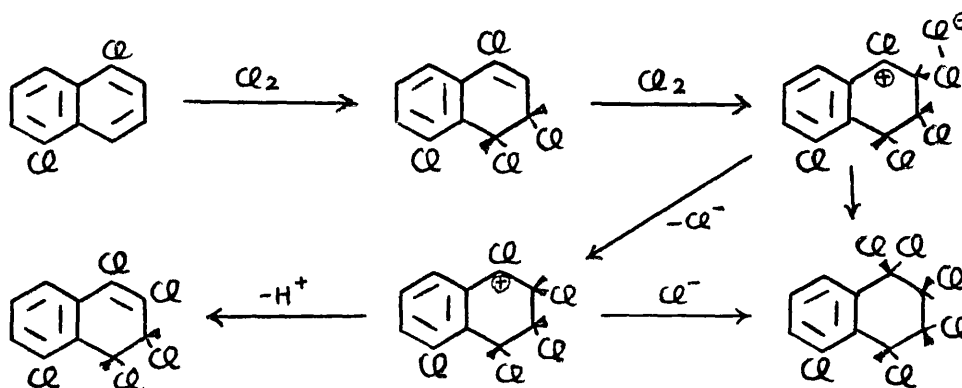
The structure of a trichloronaphthalene dichloride from 1,5-dichloronaphthalene has now been clarified by the use of infrared, ultraviolet and proton magnetic resonance spectroscopy, combined with the chemical techniques such as partial deuteration and dehydrochlorination.

The dichloride has the formula $C_{10}H_5Cl_5$, proving that one substitution and one addition of chlorine has occurred. Since dehydrochlorination gives 1,2,3,5-tetrachloronaphthalene, both substitution and addition must have occurred in the same ring. Its ultraviolet spectrum is so similar in general features to that of

1,2-dihydronaphthalene, which in ethanol has a main band with maxima at 274 and 282 $m\mu$ ($\log_{10} \epsilon =$ both 3.50) and inflections on the long wavelength side at 297 and 313.5 $m\mu$ ($\log_{10} \epsilon =$ 3.24 and 2.45 respectively),⁹⁷ that it must be a 1,2- rather than a 1,4-dihydronaphthalene.

The infrared spectrum also supports this assignment; the absorption at 1608 cm.^{-1} may be correlated with the presence of the double bond in conjugation with the aromatic ring, since the C=C stretching vibration of 1,2-dihydronaphthalene usually appears at about 1600 cm.^{-1} , whereas that of 1,4-dihydronaphthalene is at about 1670 cm.^{-1} .⁹⁸ Finally the n.m.r. spectrum establishes that the two aliphatic hydrogens are on adjacent carbon atoms, so the dichloride isolated can be no doubt formulated as 1,2,3,4,8-pentachloro-1,2-dihydronaphthalene. The low coupling constant, $J_{1,2} = 2.5$ c.p.s., could be attributed to either a cis-(axial, pseudoaxial) or a cis-(equatorial, pseudoaxial), or a trans-(equatorial, pseudoequatorial) pair of hydrogen atoms; but since it is likely that both dichloride and tetrachloride are derived from a common precursor, the compound is considered to have the same cis-configuration about the 3 and 4 carbon atoms as that of the tetrachloride which will be described in the following section.

The formation of the stable dichloride can be explained by the sequence shown below: the first stage in the chlorination of 1,5-dichloronaphthalene is a cis-addition to give an intermediate dichloride, which then undergoes concurrent substitution (to give the dichloride) and addition (to give the tetrachloride) through the common intermediate of a carbonium ionic character.



On the same basis, another known dichloride from 1-chloronaphthalene may be formulated as 1,2,4,5,8-pentachloro-1,2-dihydronaphthalene.

14.3 Chlorinations by Sulphuryl Chloride and Formation of Keto-compounds

In the present work, chlorinations of polycyclic benzenoid hydrocarbons with condensed ring, represented by naphthalene and related compounds, have been investigated mainly from the point of view of adduct formation.

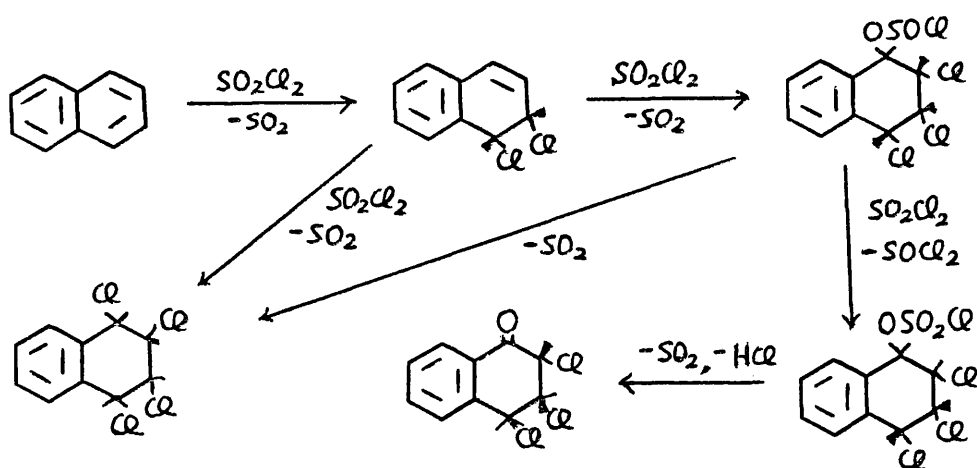
As a chlorinating agent, either sulphuryl chloride or chlorine has been used. Although the addition concurrent with substitution in molecular chlorination has recently been studied in detail,¹⁰ there has been until now little information about the corresponding mode of action by sulphuryl chloride towards aromatic hydrocarbons. In the naphthalene field, Dubois first observed the simultaneous formation of naphthalene α -tetrachloride with 1-chloronaphthalene by the action of sulphuryl chloride on naphthalene;⁹⁹ Pongratz and Eichler confirmed this result with benzene as solvent.¹⁰⁰ 1-Methylnaphthalene and 2-methylnaphthalene, on the other hand, have been recorded as giving only products of substitution.¹⁰¹

Treatment of naphthalene with one molecular proportion of sulphuryl chloride gives a mixture of 1-chloronaphthalene (93%), naphthalene α -tetrachloride (4%), and naphthalene δ -tetrachloride (3%), which are usual products of electrophilic chlorination. The proportion of the adducts is not greatly affected by change of solvent over a range including liquid sulphur dioxide, sulphuryl chloride, chloroform, carbon tetrachloride, and light petroleum. Neither does the change in

temperature alter the general nature of the products, which are not apparently obtained through the dissociation of sulphuryl chloride into sulphur dioxide and molecular chlorine, since the reactivities are not diminished and the products are not affected much by the presence of added sulphur dioxide in the reaction mixture. Therefore, it is likely that molecular sulphuryl chloride can act as a direct source of electrophilic chlorine, through the incipient heterolysis $\text{Cl}^{\delta+}-\text{SO}_2\text{Cl}^{\delta-}$. The predominant formation of the α -tetrachloride, as in the molecular chlorination of naphthalene, suggests the two phases of cis-addition involving a cyclic transition state of the type shown in the Chart on the next page; one stage of trans-addition can give the δ -tetrachloride as a minor product. The γ -tetrachloride, one of the characteristic products in ^{the} homolytic process and obtained by two successive trans-additions, was isolated only when benzoyl peroxide was added as a catalyst for free-radical reactions. However, even under conditions in which sulphuryl chloride and benzoyl peroxide were refluxed with naphthalene in carbon tetrachloride, the heterolytic process appears to be dominant.

In almost all cases, the formation of poly-

chlorides is accompanied by the formation of small amounts of keto-compounds, and these do not seem to be derived by the hydrolysis of gem-dichlorides during working-up, since a number of gem-dichlorides have been isolated and quite stable under the ordinary experimental conditions. Hydrolysis of these gem-dichlorides under forced conditions led to the formation of dehydrochlorination products and resinous substances rather than the formation of keto-compounds. In the chlorination of naphthalene, a main component was isolated from the syrup containing keto-compounds. Its infrared as well as ultraviolet spectrum indicates the presence of the carbonyl group conjugated with a benzene ring, and in fact it was reduced to give 2,4-dichloronaphth-1-ol. On the basis of these findings and the analytical data, this keto-product was formulated as 1-keto-2,3,4-trichloro-1,2,3,4-tetrahydro-naphthalene, and confirmed by the independent synthesis of this from 1-acetoxynaphthalene. The formation of oxidation products of this kind may be explained by a sequence depicted on the next page:



The capture of oxygen rather than chlorine during addition sequence, followed by the ester-exchange is a reasonable process, and the final decomposition of esters has analogies in the decomposition of benzyl esters of strong acids to give benzaldehydes.¹⁰²

14.4 Orientation of Additive Chlorinations

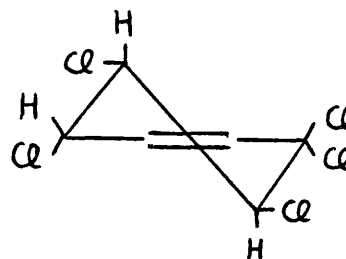
Under conditions in which naphthalene reacts slowly with sulphuryl chloride, 1-chloronaphthalene does not react significantly; but reaction was found to occur at reflux temperature (ca. 70°). It also proceeded more rapidly and smoothly in the presence of lithium chloride. The main adduct isolated was 1,1,2,3,4-pentachloro-1,2,3,4-tetrahydronaphthalene, which could be obtained more easily by the molecular chlorination of 1-chloronaphthalene in light petroleum. 2-Chloro-

naphthalene is less reactive and undergoes the addition reaction in the unsubstituted ring to give 1,2,3,4,6-pentachloro-1,2,3,4-tetrahydronaphthalene, which so far has been described as a viscous oil with turpentine-like odour,³⁵ as white prisms, together with 1,6- and 1,7-dichloronaphthalene, as products of substitution. These results are in accord with the view that these two types of products can arise by way of the same intermediate.

1-Methyl and 2-methylnaphthalene react with one molecular proportion of sulphuryl chloride more rapidly than naphthalene itself, giving 1,2,3,4-tetrachloro-1-chloromethyl-1,2,3,4-tetrahydronaphthalene and 1,2,3,4-tetrachloro-2-methyl-1,2,3,4-tetrahydronaphthalene as the main addition product. Since activating substituents facilitate the reaction markedly and make the chlorine enter into the substituted ring, and deactivating substituents retard the reaction and direct the chlorine into the less substituted ring, additive chlorination of naphthalene by either sulphuryl chloride or molecular chlorine is no doubt an electrophilic process.

14.5 Stereochemistry of Addition Products and Possible Sequence for their Formation

The p.m.r. spectrum of 1,1,2,3,4-pentachloro-1,2,3,4-tetrahydronaphthalene showed two coupling constants, $J = 3.5$ and 11.9 c.p.s., for its aliphatic system. By the selective deuteration of either the 2- or the 4-position of this adduct, they are assigned as $J_{2,3} = 11.9$ and $J_{3,4} = 3.5$ c.p.s. Thus, the configuration and conformation of this adduct can be shown as below; with the 3,4-chlorine atoms cis to each other. The fact that the addition to 1-chloronaphthalene involves at least one stage of cis-addition suggests that the process analogous to that found in the heterolytic chlorination of naphthalene to give the α - and δ -tetrachloride is influential in this additive reaction, too. The second phase of addition could involve either cis or trans addition, or both.



Chlorination of 1,5-dichloronaphthalene gives 1,1,2,3,4,5-hexachloro-1,2,3,4-tetrahydronaphthalene, together with 1,2,3,4,8-pentachloro-1,2-dihydronaphthalene, already described in section 14.2. By p.m.r.

spectroscopy of the partially deuterated derivative, two coupling constants of the tetrachloride are assigned as $J_{2,3} = 10.8$ and $J_{3,4} = 4.8$ c.p.s., indicating that the 1,5-dichloronaphthalene tetrachloride has the same conformation as 1-chloronaphthalene tetrachloride and probably is formed by the similar sequence.

The p.m.r. spectrum of 1,2,3,4,6-pentachloro-1,2,3,4-tetrahydronaphthalene and 1,2,3,4,5,8-hexachloro-1,2,3,4-tetrahydronaphthalene (Widman's adduct) shows quite interesting patterns for their aliphatic protons, giving rise to two sets of apparent 1:2:1 triplets with low coupling constants (below 2 c.p.s.). According to the Karplus rule, such small couplings are consistent only with these conformations; e'eee', e'aea', e'ea'e' and a'eea'. Considering the fact that these adducts have been formed under the ordinary heterolytic conditions, and that their dehydrochlorination products are qualitatively similar to those from naphthalene α -tetrachloride, the last-mentioned conformation seems most probable. One interpretation of these spectra may be that both triplets are actually quartets, and higher one comes from the equatorial 2- and 3-hydrogens, and lower one arises from the pseudoaxial 1- and 4-

hydrogens interacting one another through the long-range coupling. Replacement of 2-hydrogen of 1,4-dichloronaphthalene tetrachloride by deuterium, however, altered the absorption pattern in a puzzling way; the lower signal remained unchanged while the higher one was split into a singlet and a doublet with a very low coupling (ca. 0.5 c.p.s.). The result contradicts with the above interpretation, and further investigations are needed.

On treatment with excess chlorine or sulphuryl chloride, 1-chloro-4-methylnaphthalene undergoes addition reaction in the opposite ring to give 1,2,3,4,5-pentachloro-8-methyl-1,2,3,4-tetrahydronaphthalene of m.p. 177-178°, p.m.r. spectrum of which also showed a simple pattern of three apparent 1:2:1 triplets with low couplings for the alicyclic protons. Therefore, its stereochemistry is considered to be similar to that of the Widman's adduct, probably the α -structure. On the other hand, the lower-melting isomer of m.p. 151-152° showed a very complicated spectrum, interpretation of which remains still unsolved.

Under the same conditions 1-bromo-4-methylnaphthalene afforded two kinds of addition products;

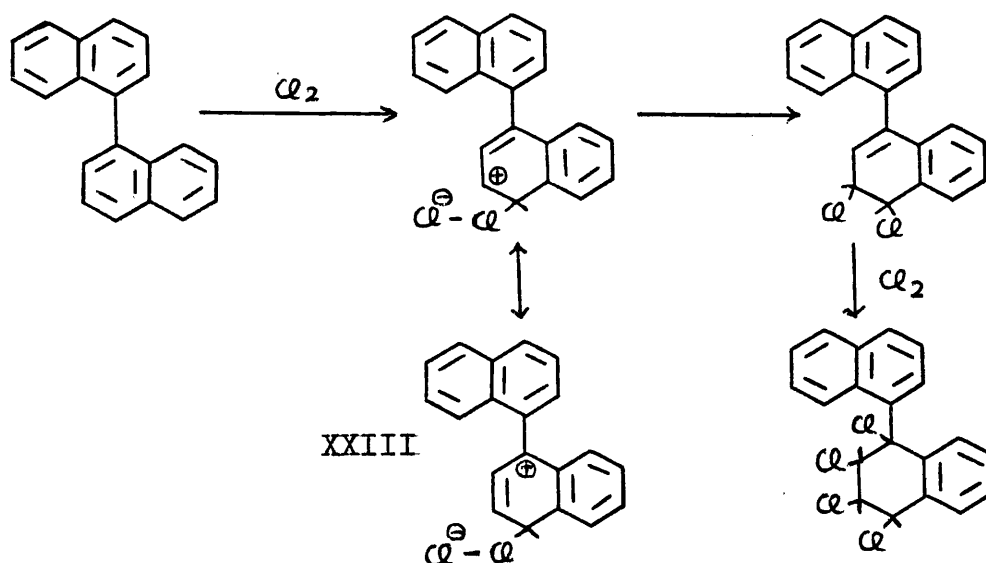
however, neither of them was found by analysis to be a simple compound, but a mixture of products formed by the partial replacement of bromine by chlorine or vice versa. The main product of m.p. 165-166° possessed infrared and p.m.r. spectra very similar to those of the lower-melting isomer of the corresponding chlorine compound, whereas the minor product of m.p. 175-177° showed spectra similar to those of the higher-melting tetrachloride from 1-chloro-4-methylnaphthalene. As the change of nuclear species from chlorine to bromine cannot have much effect on their infrared as well as p.m.r. spectra, the higher-melting tetrachloride from 1-chloro-4-methylnaphthalene and the lower-melting product from 1-bromo-4-methylnaphthalene are considered to have the same conformation; likewise so are the lower-melting tetrachloride and the higher-melting product from 1-bromo-4-methylnaphthalene. Such a drastic change in composition of products, therefore, should mean a change in the character of the reaction, possibly from the heterolytic to the homolytic. The reaction of aromatic bromo compounds with sulphuryl chloride often involves the migration of bromine atoms, and it has been referred to as a homolytic process.¹⁰³ Indeed, despite the fact that in the chlorination of 1-chloro-4-methylnaphthalene, any side-chain chlorinated

products could not be detected within the experimental error, the corresponding reaction of 1-bromo-4-methylnaphthalene afforded substantial amounts of side-chain substituted products. Certain bromine compounds, such as bromine chloride, must have worked as a chain carrier.

Interestingly enough, the chlorination of 1,2-dichloronaphthalene proceeds in a little different way from the ordinary heterolytic process; the major product being 1,2,3,4,5,6-hexachloro-1,2,3,4-tetrahydronaphthalene of the ξ -structure. A minor product was a tetrachloride with the α -structure. The reason why such a tetrachloride with the rare conformation can be readily formed from 1,2-dichloronaphthalene is not clear. The ease with which dichloronaphthalenes undergo the additive chlorination varies to a considerable extent, depending on the relative location of chlorine atoms in the ring; thus 2,6- and 2,7-dichloronaphthalene mainly underwent the substitution reaction, and gave little adduct under ordinary conditions.

The introduction of benzene ring into the naphthalene nucleus, as would be expected, facilitates greatly the formation of addition products. Thus, on treatment with sulphuryl chloride, 1-phenylnaphthalene

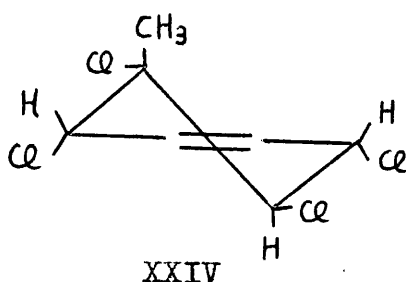
and 1,1'-binaphthyl yielded the tetrachlorides with great ease. Benzenoid nucleus in the 1-position is expected to contribute to the delocalisation of positive charge of the intermediate ArHCl_2^+ , thus stabilising the carbonium ion of the type XXIII to increase the opportunity for the 1,4-addition. However, this was not the case. The p.m.r. spectrum of the tetrachloride from 1,1'-binaphthyl was found to be similar to that of 1-chloronaphthalene tetrachloride, with two coupling constants of $J_{2,3} = 10.5$ and $J_{3,4} = 3.4$ c.p.s. Therefore, its stereochemistry must be similar to that of the latter compound, and the sequence for its formation must be analogous to the common heterolytic addition process involving at least one phase of cis-addition.



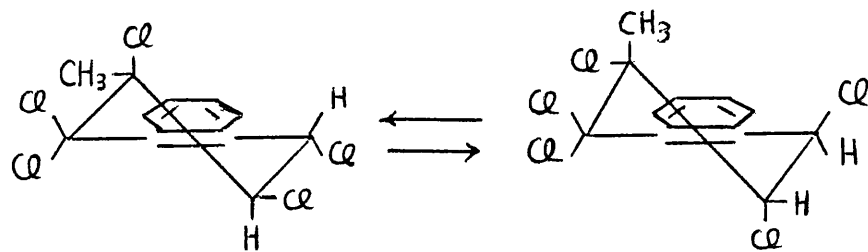
From the structural point of view, there is no reason to devise a different route for the additive reaction of 1-phenylnaphthalene. Thus, the tetrachloride from this hydrocarbon is considered to have the similar conformation. However, its p.m.r. spectrum showed two one-proton singlets and an apparent 1:2:1 triplet with low coupling (below 2 c.p.s.) in the aliphatic proton region. The interpretation that the two singlets are actually a superimposed doublet due to the 2- and 4-hydrogen, and a triplet is a quartet due to the 3-hydrogen may be possible, but its general feature reminds us of those of the Widman's adduct and related compounds. For the time being, no definite conclusion could be deduced from the spectrum only.

The additive chlorination of methylnaphthalenes proceeds in a different way from those of the naphthalene derivatives already mentioned. 1-Methylnaphthalene yields anomalous side-chain chlorinated adduct, and therefore will be described in the later Section (cf. Sec.17). 2-Methylnaphthalene affords either tetrachloride or monochloro-tetrachloride depending on the quantity of chlorinating agent used. With one or two molecular proportion of chlorinating agent, the addition product was 1,2,3,4-

tetrachloro-2-methyl-1,2,3,4-tetrahydronaphthalene, whose stereochemistry was established by p.m.r. spectroscopy as XXIV.¹⁰⁴

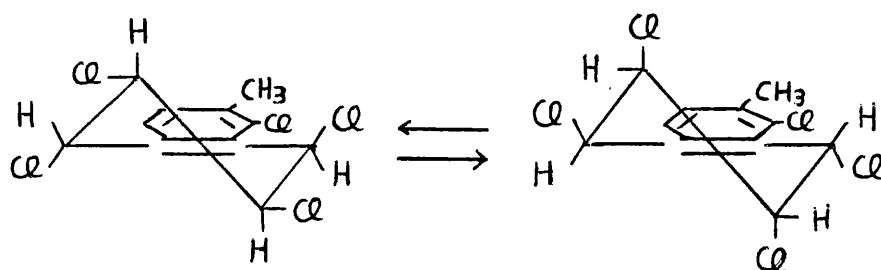


With excess chlorinating agent, two monochloro-tetrachlorides were obtained as the main addition products; one was 1,1,2,3,4-pentachloro-2-methyl-1,2,3,4-tetrahydronaphthalene first described by Scherler and recently established by p.m.r. spectroscopy as XXV.¹⁰⁴ The other one was 1,2,3,4,5-pentachloro-6-methyl-1,2,3,4-tetrahydronaphthalene, which showed a large coupling constant of $J_{2,3} = 8.0$ c.p.s. and two small constants of $J_{1,2} = 2.5$ and $J_{3,4} = 3.5$ c.p.s., indicating its stereochemistry is similar to that of naphthalene α -tetrachloride. However, the value of the coupling constant $J_{2,3}$ is markedly less than the value (11.0) observed in the spectrum of the latter compound, and in the other analogous adducts. The tetrachloride, therefore, probably exists in equilibrium with a substantial proportion of the conformer XXVIa.



XXVa

XXVb

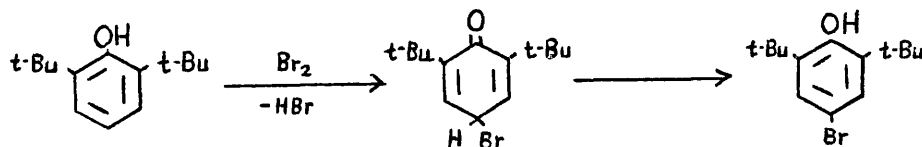


XXVIa

XXVIb

15. Chlorine Additions Involving the O-H Hyperconjugation

The greater reactivity of phenols than their alkyl ethers with electrophilic reagents has long been recognised and a part of this enhanced reactivity has been attributed to the electron release by O-H hyperconjugation. An extreme result of this mode of electron release would involve loss of the hyperconjugating proton to the medium, as has been suggested by Robinson for C-H hyperconjugation.¹⁰⁵ In recent times there has been considerable accumulation of evidences concerning the occurrence of this mode of electron release. Thus, the electrophilic substitution of 2,6-di-t-butylphenol was shown to proceed through the hyperconjugative proton loss; the initial addition of the attacking species to the ring to give the dienone, which then undergoes the anionotropic rearrangement to yield the substitution product.¹⁰⁶

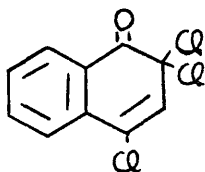


Numerous similar reactions have been described in the hydroxy derivatives of polycyclic aromatics, although

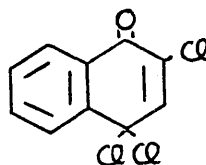
their mechanistic implications seem never to have been mentioned before. Thus,

15.1 Naphth-1-ols

Naphth-1-ol is readily chlorinated first to give a mixture of 2- and 4-chloronaphth-1-ol, which further chlorinated to yield solely 2,4-dichloronaphth-1-ol. On further introduction of chlorine, however, this naphthol undergoes not the substitutive but the additive reaction to give two different adducts, depending on the conditions employed. Derivatives of naphth-1-ol produced in this way could be the products of electrophilic attack either at 2- or at the 4-position; 2,4-dichloronaphth-1-ol could give either the 1-keto-1,2-dihydronaphthalene **XIVII** or the 1-keto-1,4-dihydronaphthalene, **XIVIII**.



XIVII



XIVIII

Despite the fact that both possibilities were recognized by earlier workers in this field, no positive evidence has up till now been presented to enable a decision to be made concerning the structures of the characterized products. Thus the usual procedure involving the

chlorination in acetic acid gives an adduct of m.p. 120-121° from 2,4-dichloronaphth-1-ol, whereas in chloroform as solvent an isomeric substance of m.p. 74-75° is obtained from the same naphthol.

Chemical properties of both adducts are exactly the same; both compounds on reduction give 2,4-dichloronaphth-1-ol; both on boiling with aqueous ethanol give 2-chloro-1,4-naphthoquinone; both on warming with aniline give 2-anilino-1,4-naphthoquinone-4-anil. So, attempted distinction between the two isomeric structures by chemical transformations gives no positive results.

A similar situation occurs with 2,3,4-trichloronaphth-1-ol. It has long been known that this compound with chlorine in chloroform gives a mixture of two different crystalline materials, one (XXIX) being yellow in colour and melting at 104-105°, and one (XXX) being amethyst and phototropic, m.p. 115.5°. These forms could be separated by hand-picking the crystals or by fractional crystallisation. Both compounds on reduction give 2,3,4-trichloronaphth-1-ol, both with aqueous ethanol give 2,3-dichloro-1,4-naphthoquinone; both with aniline give the anil of 2-anilino-3-chloro-

1,4-naphthoquinone. Both with concentrated alkali give 2,2-dichloro-1-hydroxyindene-1-carboxylic acid, presumably by benzylic rearrangement of 3,4-dichloro-1,2-naphthoquinone. So, again, ~~unambiguous~~ ^{definite} distinction could not be made on the basis of chemical transformations.

Distinction, however, can be made easily and unambiguously on the basis of their ultraviolet spectra. The ultraviolet spectra of the isomers are shown by the solid lines (XXVII and XXIX) and dotted lines (XXVIII and XXX) in Figs. 1 and 2. They are highly characteristic and establish that both the higher-melting isomers are 1-keto-2,4,4-trichloro-1,4-dihydronaphthalene and 1-keto-2,3,4,4-tetrachloro-1,4-dihydronaphthalene, whereas both lower-melting isomers are 1-keto-2,2,4-trichloro-1,2-dihydronaphthalene and 1-keto-2,2,3,4-tetrachloro-1,2-dihydronaphthalene respectively. This follows by comparison of the spectra with those of some 4,4-dimethyl-1-keto-1,4-dihydronaphthalenes described by Campbell and Cromwell.¹⁰⁷ These compounds have no strong absorption nearer to the visible region of the spectrum than ^o about 3000 Å. The same is true of the higher-melting adducts from 2,4-dichloro and 2,3,4-tetrachloronaphth-1-ol. The lower-melting isomers of

both, on the other hand, has a strong absorption band with a maximum much farther towards the visible region at ca. 3400 Å. The fully conjugated $-\text{CH}=\overset{\text{O}}{\text{C}}-\text{CH}-\text{Ar}(\text{C}=\overset{\text{O}}{\text{O}})-$ system should have absorption at longer wavelength than the cross-conjugated $-\text{Ar}(\text{C}=\overset{\text{O}}{\text{O}})-\text{CH}=\text{CH}-$ system, in agreement with the assignment. This argument can be supported by the fact that whereas benzylacetone ($\text{Ph}-\text{CH}=\overset{\text{O}}{\text{C}}-\text{CH}_3$) has a strong absorption maximum at 2790 Å, ethylidene acetone ($\text{Ph}-\overset{\text{O}}{\text{C}}(\text{CH}_3)-\text{CH}=\text{CH}_2$) has no strong maximum below 2500 Å.¹⁰⁸

This assignment can also be endorsed by the infrared spectra of these adduct. The frequency of the stretching vibration of a carbonyl bond (ca. 1710 cm.^{-1} in acetone) is reduced by conjugation about 25 cm.^{-1} to 1685 cm.^{-1} in acetophenone and further to 1655 cm.^{-1} in benzophenone.¹⁰⁹ Correspondingly there is a frequency difference of ca. 25 cm.^{-1} between each of the pairs of compounds (XXVII and XXVIII), (XXIX and XXX), in which we compare a 1,2-with 1,4-dihydronaphthalene system. Although all these frequencies are partially also modified by the adjacent hydrogen substituents, the resulting change would be expected similar for all of them, since the change in the C=O stretching frequency is approximately

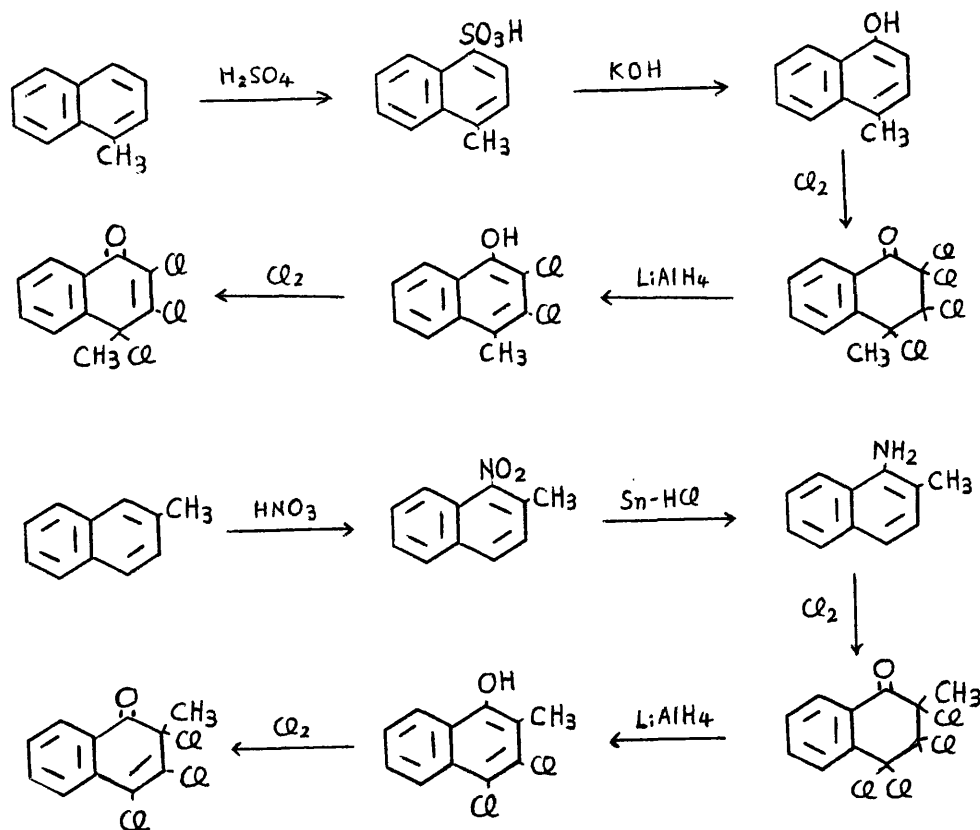
the same, whether one or two chlorine atoms are introduced adjacent to a carbonyl substituent.

1-Keto-1,4-dihydronaphthalene systems are more stable than 1-keto-1,2-dihydronaphthalene's, in agreement with the thermodynamic deductions. Thus, the latter can be isomerised under certain circumstances to the more stable former; on storage, the new ketone XXVII gradually isomerised to XXVIII, and this anionotropic rearrangement was shown to occur more readily when XXVII was dissolved in acetic acid containing hydrogen chloride. The ketone XXIX, although rather stable, can also be isomerised to the 1,4-compound XXX, on prolonged heating under reflux with sulphuryl chloride containing a trace of hydrogen chloride.

It is clear, therefore, that chlorination of 2,4-dichloronaphth-1-ol or of 2,3,4-trichloronaphth-1-ol can involve electrophilic attack on the 2- rather than the 4-position, despite the intrinsically greater reactivity of α - than of β -positions in the naphthalene ring, and despite the fact that the product of attack on the 4-position is thermodynamically more stable than that of attack on the 2-position. Similar phenomena are manifested in the chlorinations of certain polyhydroxy-

naphthalenes; 1,5-dihydroxynaphthalene reacts with electrophiles to give 2,6-disubstituted products.¹¹⁰

It is interesting, therefore, to extend our knowledge of the influence of structures on the ease of attack on these positions. The steric requirements of a methyl group are similar to those of a chlorine substituent, and an alkyl group should, by virtue of its electron releasing power, facilitate electrophilic attack not only on the ortho and para positions with which it is hyperconjugated, but also on the carbon atom to which it is directly attached. Thus, 2,3-dichloro-4-methylnaphth-1-ol and 3,4-dichloro-2-methylnaphth-1-ol are synthesised and chlorinated. The ultraviolet spectra of these products are shown in Table 1 and Figs. 1 and 2. The 2-methyl-3,4-dichloronaphth-1-ol gives a product with a strong absorption maximum at $3450 \overset{\text{O}}{\text{Å}}$, a result of which established that chlorine has attached to the 2-position and given 1-keto-2-methyl-2,3,4-trichloro-1,2-dihydronaphthalene XXXI, whereas the 4-methyl-2,3-dichloronaphth-1-ol gives a product which has no strong absorption at such long wavelength, and therefore 1-keto-4-methyl-2,3,4-trichloro-1,4-dihydronaphthalene XXXII.



It seems therefore the methyl group is more favourable than the chlorine substituent for the promotion of electrophilic attack on the carbon atom to which it is attached, in agreement with what would be expected on simple electronic considerations.

Treatment of naphth-1-ols with excess chlorine yields saturated ketones; 1-keto-2,2,3,4,4-pentachloro-1,2,3,4-tetrahydronaphthalene and its 2-methyl or 4-methyl derivatives can readily be obtained from naphth-1-ol and its 2- and 4-methyl derivatives. These are all very

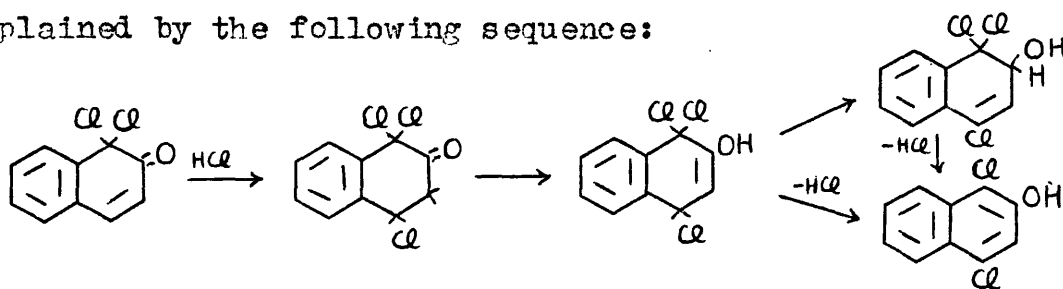
stable and have no tendency to lose hydrogen chloride under ordinary conditions. Fully chlorinated 1-keto-2,2,3,3,4,4-hexachloro-1,2,3,4-tetrahydronaphthalene can be obtained by the homolytic process involving the chlorination of XXIX or XXX under sunlight or at elevated temperatures in sealed tubes. The ultraviolet and infrared spectra of these ketones are summarised in Table 1 and represented in Fig.3.

15.2 Naphth-2-ols

Additive chlorination of naphth-2-ols was first observed in 1888.¹⁴ This reaction was extensively studied by Zincke, and later by Fries in connection with the problem of bond fixation in naphthalene nucleus. The fact that many of these reactions involve electrophilic substitution with prototopic rearrangement has recently been established by Zollinger and his co-workers,¹¹¹ who chlorinated O-deuterated naphth-2-ol in aprotic solvent and observed the initial liberation of deuterium chloride from the reaction system.

In acetic acid naphth-2-ol readily undergoes chlorination at the 1-position first to give 1-chloro-naphth-2-ol. On further passing chlorine into this

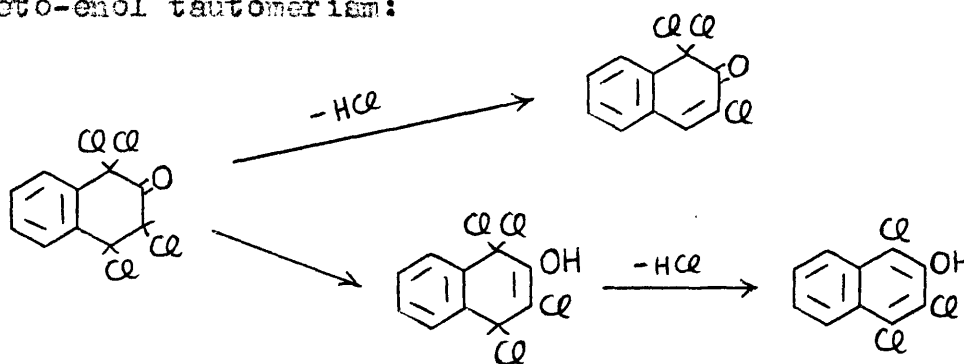
solution, 2-keto-1,1-dichloro-1,2-dihydronaphthalene is formed. This adduct is comparatively stable, but on prolonged storage it gradually transformed into 1,4-dichloronaphth-2-ol and black polymeric substances. The transformation into naphthol can be effected smoothly by the catalysis of hydrogen chloride and has been explained by the following sequence:



The formation of these sorts of dienones has commonly been observed in various halogenations of naphth-2-ols; the chemical properties of these adducts are similar to that of 2-keto-1,1-dichloro-1,2-dihydronaphthalene, except that in presence of acid catalyst bromine atom migrates to the 6-position rather than to the 4, giving 6-bromonaphth-2-ols.

With an excess chlorine, naphth-2-ol readily yields 2-keto-1,1,3,4-tetrachloro-1,2,3,4-tetrahydronaphthalene, which on standing in contact with protic solvent or on warming, release hydrogen chloride to give 2-keto-1,1,3-trichloro-1,2-dihydronaphthalene. On prolonged storage in dry air, however, this ketone

slightly loses hydrogen chloride in a different way to afford a nphthol (1,3,4-trichloronaphth-2-ol), which may perhaps be formed by the sequence involving the keto-enol tautomerism:



Chlorine addition to the double bond seems to occur through the initial attack at the carbon atom adjacent to the carbonyl group. This follows by the comparison of the reactivity of 2-keto-1,1,3-trichloro-1,2-dihydronaphthalene and 2-keto-1,1,4-trichloro-1,2-dihydronaphthalene; chlorine adds to the former only too slowly, but very readily to the latter to yield 2-keto-1,1,3,4,4-pentachloro-1,2,3,4-tetrahydronaphthalene, which instaneously ^{tan} begins to lose hydrogen chloride to give 2-keto-1,1,3,4-tetrachloro-1,2-dihydronaphthalene.

From the mechanistic point of view, the stereochemistry of the addition reaction seems of interest. The p.m.r. spectrum of 2-keto-1,1,3,4-tetrachloro-1,2,3,4-tetrahydronaphthalene showed a coupling constant of

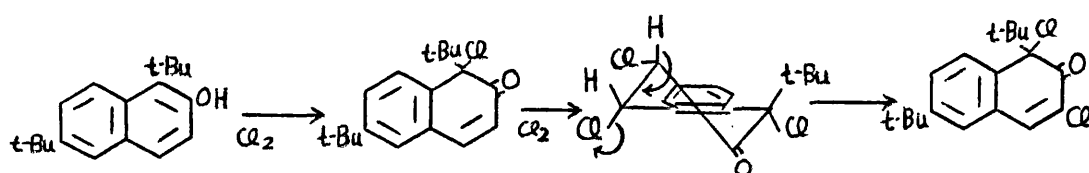
4.8 c.p.s. for the aliphatic protons. This low value could be attributed either to a cis(axial-pseudoequatorial or equatorial-pseudoaxial) or to a trans (equatorial-pseudoequatorial) pair of hydrogens. Similar compounds prepared from 1-methylnaphth-2-ol and 1-bromonaphth-2-ol have been found by n.m.r. spectroscopy to be 1:1 mixtures of two isomers, no doubt formed by the difference of conformation about the 1-carbon atom, chlorine addition having occurred with an equal probability from both sides of the dienone. These mixtures of adducts had a pair of two AX proton system of $J_{3,4}^{\text{Me}} = 5.8$ and 4.5 c.p.s., and $J_{3,4}^{\text{Br}} = 5.0$ and 3.8 c.p.s. Some of these constants are too high to exclude the possibility of the axial-pseudoaxial conformation for the two aliphatic hydrogens. Furthermore, the steric requirement of a chlorine substituent is not so much different from those of a methyl or a bromine atom. So the chair to chair interconversion of the tetralone ring could be effected without difficulty in these systems. Therefore, no definite conclusion about the stereochemistry could be drawn from the p.m.r. spectra only.

The introduction of t-butyl group into the 1-position is expected to prevent the ring from free

interconversion and favour the conformation in such a way in which the bulky t-butyl group is located in pseudoaxial position. Since 1-t-butyl naphth-2-ol is not known yet, 1,6-di-t-butyl naphth-2-ol was chosen as a starting material. However, chlorination of this naphthol in common solvents has been found to give not the expected product, but a substitution-addition product, 2-keto-1,6-di-t-butyl-1,3-dichloro-1,2-dihydronaphthalene, which must have been formed by the dehydrochlorination of the initially formed 2-keto-1,6-di-t-butyl-1,3,4-trichloro-1,2,3,4-tetrahydronaphthalene.

As there is no compulsory reason to expect the instability of this ketone from the mere chemical formula, the extraordinary ease of expulsion of hydrogen chloride must be explained on the basis of its conformation. If t-butyl group is present in a pseudoaxial conformation in this ketone, a chlorine atom at the 3-position must be in an equatorial position; otherwise great steric interaction with t-butyl group arises. When the 3-hydrogen is axially situated, the chlorine atom at the 4-position must be present in a pseudoaxial conformation in accordance with the observed easy splitting-off of hydrogen chloride. Hence, the equatorial-pseudoaxial

pair of chlorine atoms is the most probable location in this unstable ketone, indicating that chlorine atoms had undergone the cis addition to the double bond of 2-keto-1,2-dihydronaphthalene system.



Then, the comparatively marked reluctance of adducts from naphth-2-ol and its methyl as well as bromine derivatives to undergo the β -elimination of hydrogen chloride may be taken to indicate that part of the chlorine atoms are present in alternative form of a cis addition, axial-pseudoequatorial. Of course, the possibility of trans addition cannot be excluded.

2-Keto-1,1,3,4-tetrachloro-1,2-dihydronaphthalene is quite stable towards the further action of chlorine, but under catalysis by sunlight it slowly takes up chlorine to give fully chlorinated 2-keto-1,1,3,3,4,4-hexachloro-1,2,3,4-tetrahydronaphthalene.

15.3 Esters of Naphthols

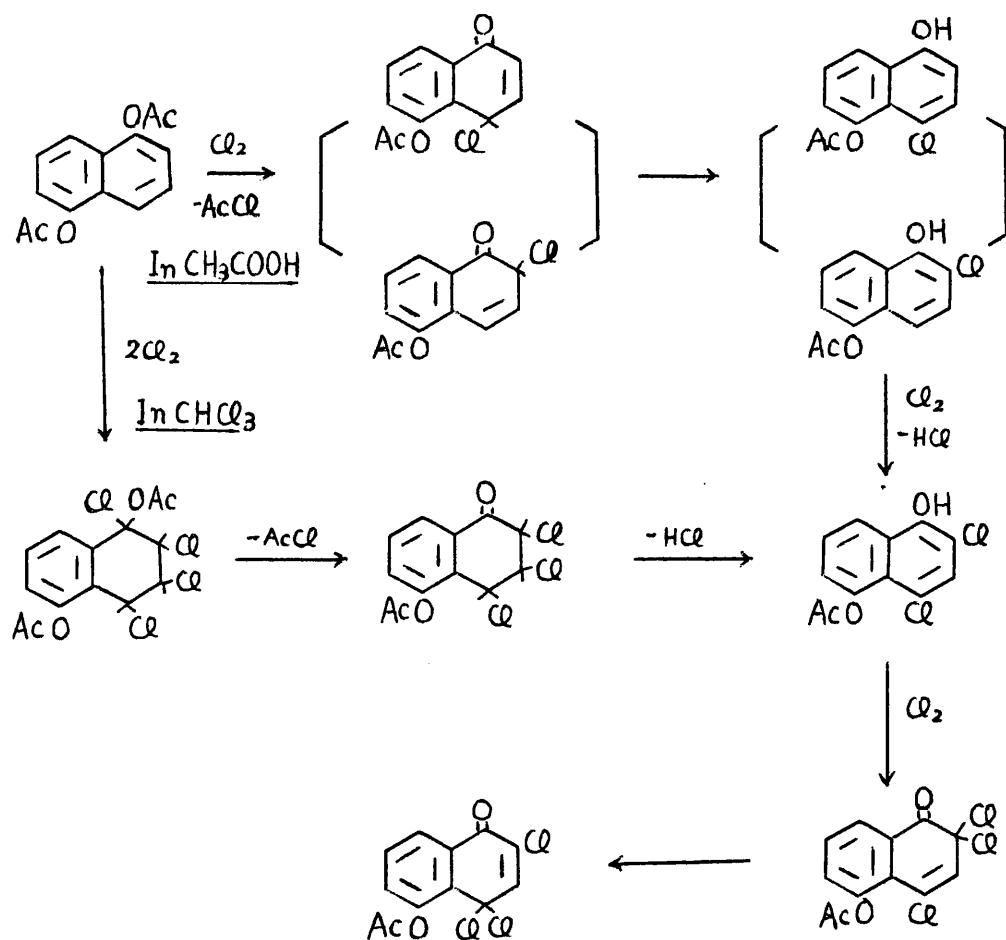
As would be expected, the replacement of the hyperconjugating proton of naphthol by an appropriate substituent results in the remarkable decrease of reactivity. Thus, in contrast to the highly electron-releasing hydroxy group, acetoxy group acts as a weak electron-releasing one in the naphthalene series. 1-Acetoxy-naphthalene behaves differently depending on the solvent used; in protic solvents such as acetic acid, this compound readily undergoes hydrolysis, simultaneously with nuclear chlorination, to give 2,4-dichloronaphth-1-ol, which by further action of chlorine gives a series of products already described in section 15.1. In aprotic solvents such as chloroform, however, the reaction proceeds in a different way to yield a new ketone 1-keto-2,3,4-trichloro-1,2,3,4-tetrahydro-naphthalene.

This new aspect of chlorine addition is more clearly manifested in the chlorination of 1,5-diacetoxy-naphthalene. The chlorination of this compound was first investigated by Wheeler and Mattox,⁴⁹ who treated a suspension of 1,5-diacetoxy-naphthalene in carbon tetrachloride with chlorine in presence of iodine or under

sunlight, and isolated a dichloro product at room temperature and a trichloro compound at 80°. In each case one acetyl group was hydrolysed. These products were erroneously stated to be 4,8-dichloro-5-acetoxynaphth-1-ol and 4,4,8-trichloro-5-acetoxy-1-hydroxy-3,4-dihydronaphthalene respectively, and later corrected by Thomson⁵⁰ as 2,4-dichloro-5-acetoxynaphth-1-ol and 1-keto-2,4,4-trichloro-5-acetoxy-1,4-dihydronaphthalene. We confirmed their results in acetic acid, but in chloroform 1,5-diacetoxynaphthalene was found to undergo additive chlorination in a different way to give an unstable 1-keto-2,3,4-trichloro-1,2,3,4-tetrahydronaphthalene of m.p. 116-119°, which on standing in contact with air spontaneously released hydrogen chloride to give 2,4-dichloro-5-acetoxynaphth-1-ol. This naphthol reacted with chlorine in two different ways depending on the solvent used; in chloroform it gave 1-keto-2,2,4-trichloro-5-acetoxy-1,2-dihydronaphthalene of m.p. 112-113°, which on storage slowly transformed into the isomeric 1-keto-2,4,4-trichloro-5-acetoxy-1,4-dihydronaphthalene of m.p. 173-174°. During the course of the isomerisation, which occurred more readily in acetic acid than in light petroleum, a slight amount of hydrogen chloride was liberated. In

acetic acid the product was the higher-melting 1,4-addition product.

In the chlorination of acetoxy compounds, the elimination of acetyl group is supposed to occur in the early stage of the reaction; otherwise the second chlorine atom would prefer the opposite ring, because of the accumulation of electron-withdrawing groups in one ring. This view may be supported by the observations that on chlorination in carbon tetrachloride or glacial acetic acid, 1,5-diacetoxynaphthalene yields 2,4-dichloro-5-acetoxynaphth-1-ol as a sole product. Similar phenomena have been described in the bromination and nitration of 1,5-diacetoxynaphthalene.¹¹² The removal of the acetyl group would probably be facilitated by the high polarisability of the C-O bond, and especially in acetic acid by the presence of a strong nucleophile. In aprotic solvent such as chloroform, the expulsion of the acetyl group is supposed to occur not directly, but through the intermediacy of the unstable tetrachloride from 1,5-diacetoxynaphthalene. One of the possible sequences for the formation of these keto-polychlorides may be depicted as shown on the next page.



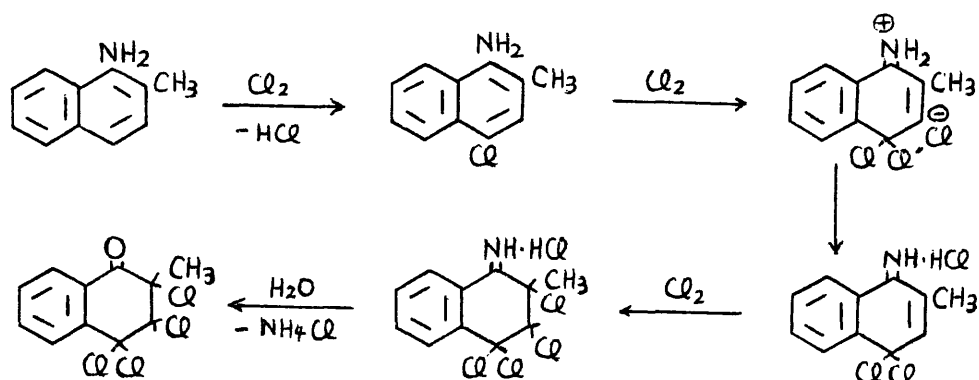
On similar treatment with chlorine in chloroform, 2-acetoxynaphthalene gave a sticky syrup, in which the ketonic products were no more than minor components, and the reaction seems to have proceeded mainly in a substitutive way. Likewise, the ethers of naphthols chiefly gave products of substitution under the ordinary conditions.

16. Chlorine Additions involving N-H Hyperconjugation

One can expect the participation of the electrons of N-H bond in the electron-releasing hyperconjugation, but here proof has been rendered difficult by proton mobility and the presence of unshared electrons. Evidences relating the N-H hyperconjugation was first put forward by de la Mare in 1958;¹³ remarkable decrease in reactivity (ca. 10^3 times) of N-methylacetanilide in chlorination, compared with that of 2-methylacetanilide was satisfactorily explained on the basis of N-H hyperconjugation.¹¹³

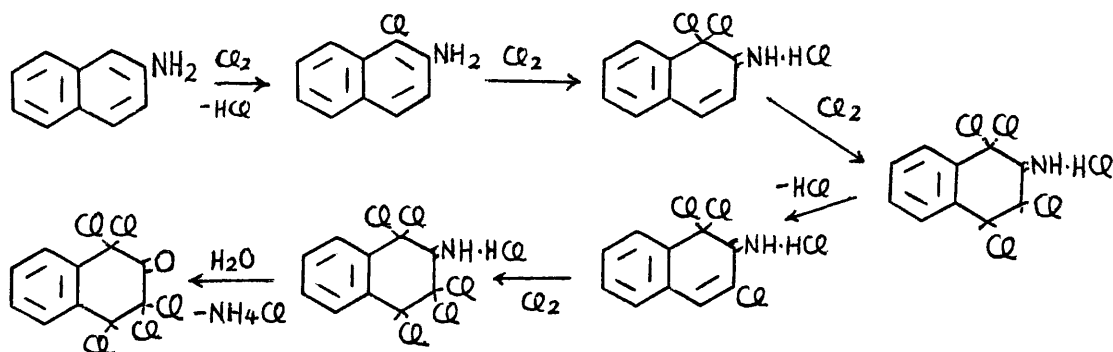
In a field of polycyclic aromatic amines, there are only a few observations concerning the chlorine additive reactions. However, these clearly point out that the hyperconjugative electron release of a similar nature is also operative in adduct formations. In 1921 Fries and Lohmann chlorinated 2-methylnaphth-1-ylamine in acetic acid and obtained 1-keto-2-methyl-2,3,4,4-tetrachloro-1,2,3,4-tetrahydronaphthalene.¹⁵ Although they do not seem to have paid much attention to this phenomenon, it is almost certain that the ketone has been formed by the hydrolysis of the intermediate ketimine hydrochloride. The formation of the ketimine can readily be explained on

the basis of a similar concept applied for the ketone formation from naphthols. Development of the interaction between amino group and nucleus results in the surrender of a hyperconjugating proton to the medium, forming the unstable ketimine hydrochloride, acidolysis of which affords the corresponding ketone and ammonium chloride as shown below:



The N-acetylation results in the decrease of the number of hyperconjugating protons and the increase of steric hindrance to adoption of a planar configuration. These effects would inevitably lead to the loss of the hyperconjugative power of the amino group. Thus, despite the fact that the naphth-1-ylamine hydrochloride readily undergoes the substitutive and additive chlorination in acetic acid to give 1-keto-2,2,3,4,4-pentachloro-1,2,3,4-tetrahydronaphthalene, 1-acetylamino-naphthalene gives only 2,4-dichloro derivative as a final product.

The additive chlorination of naphth-2-ylamine gave an interesting result; the product was not the expected 2-keto-1,1,3,4-tetrachloro-1,2,3,4-tetrahydronaphthalene, but the 2-keto-1,1,3,3,4-pentachloro-1,2,3,4-tetrahydronaphthalene. Since chlorine is known to add to 2-keto-1,1,3-trichloro-1,2-dihydronaphthalene comparatively slowly, the easy formation of the pentachloro-ketone must be explained by the sequence other than that involving the intermediacy of 2-keto-1,1,3-trichloro-1,2-dihydronaphthalene. One possible sequence may be that as shown below:

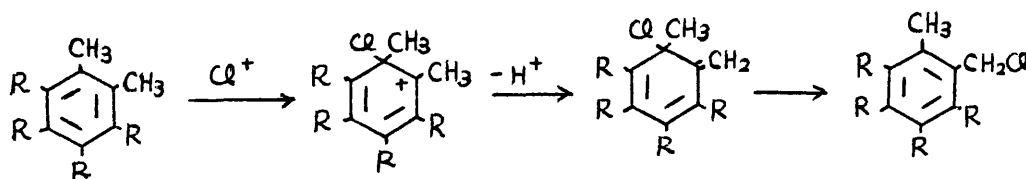


Chlorine reacts with 2-acetylamino-naphthalene to give substitution products in acetic acid, but it adds to that system in chloroform to yield an adduct as a poorly soluble powder, first described by Claus and Jäck⁶³ as 1,1,2,3,4-pentachloro-2-acetylamino-1,2,3,4-tetrahydronaphthalene. However, its p.m.r. spectrum does not pro-

vide information compatible with the proposed structure; probably this may be a mixture of certain adducts. By heating this adduct releases hydrogen chloride to give unidentified polychloronaphthilides.

17. Chlorine Additions involving C-H Hyperconjugation

Since the homolytic process of alkyl chlorinations had been established, it became customary to regard the side-chain chlorination of alkyl aromatics to proceed through the radical mechanism. However, there have gradually been accumulated the evidences that alkyl groups attached to the unsaturated system can be chlorinated under certain circumstances through the non-radical process involving the hyperconjugative participation of the C-H bond of alkyl group. Such an electrophilic nature of some side-chain chlorinations of polyalkylaromatics has recently been elaborated and several mechanisms have been put forward.¹¹⁴ The formation of a benzenonium ion, the hyperconjugative loss of a proton from the side-chain, and the allylic rearrangement of the chlorine atom constitute the essence of these mechanisms.



These processes are dependent upon the ease of loss of the hyperconjugating proton and the amount of resonance

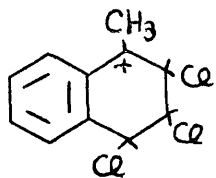
energy obtained by the restoration of the aromatic system. Annelation of benzo rings facilitates the delocalisation of positive charge, and diminishes the relative loss of stabilisation energy caused by the partial destruction of aromatic systems. The necessary consequence of this would increase the stability of the aronium intermediates, make the alkyl aromatics more susceptible to the hyperconjugative loss of one of the protons from the alkyl groups, and provide them the greater opportunity to undergo the additive chlorination involving the side-chain substitution. In fact, as early as 1926 Barnett and Matthews observed the simultaneous formation of side-chain halogenated adducts with substitution products in the halogenation of some 9-alkylanthracenes.¹⁷

17.1 Additive Chlorinations of 1-Alkylnaphthalenes

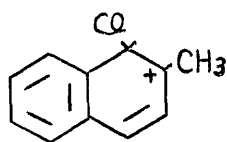
Chlorination of 1-methylnaphthalene with one or two molar proportion of sulphuryl chloride or chlorine in solvents has been found to yield not the ordinary tetrachloride but the side-chain chlorinated one, 1,2,3,4-tetrachloro-1-chloromethyl-1,2,3,4-tetrahydronaphthalene, as the main addition product. The suspicion that this adduct might be formed from 1-chloromethylnaphthalene, which in turn might have been derived homolytically from

1-methylnaphthalene under the catalysis by light or by peroxide, can readily be denied, since 1-chloromethylnaphthalene have been found to be almost unreactive towards such a weak chlorinating agent as sulphuryl chloride under the same conditions. Instead, it undergoes additive chlorination to the unsubstituted ring, giving the 1,2,3,4-tetrachloro-5-chloromethyl-1,2,3,4-tetrahydronaphthalene as the only main addition product. It must be derived, therefore, through some sequence other than that involving the formation of 1-chloromethylnaphthalene by homolytic or heterolytic substitution.

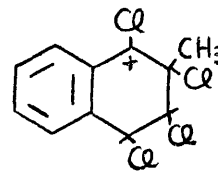
Simultaneous addition and side-chain chlorination does not occur with 2-methylnaphthalenes. This is readily understood by the comparison of three forms, XXXIII, XXXIV, and XXXV, of the corresponding intermediate species. XXXIII can easily be stabilised by the conjugation with the benzene ring; thus there is a great chance for the hyperconjugative loss of a proton from the methyl group, whereas XXXIV has the form stabilised not much more than the ordinary aliphatic carbonium ion. XXXV has no possibility for the C-H hyperconjugative stabilisation.



XXXIII



XXXIV



XXXV

A similar product with a chlorine atom at the α -position of the side-chain, 1,2,3,4-tetrachloro-1-(1'-chloroethyl)-1,2,3,4-tetrahydronaphthalene, is also obtainable from 1-ethylnaphthalene in somewhat less yield.

The significance of the C-H hyperconjugation in these rather anomalous addition reactions can clearly be demonstrated by a series of experiments involving the chlorination of 1-isopropylnaphthalene, acenaphthene, and 1,8-dimethylnaphthalene.

1-Isopropylnaphthalene offers an important clue for the elucidation of the reaction character. If the additive chlorination occurs heterolytically through the hyperconjugative participation of alkyl side-chain, the tendency to form the side-chain chlorinated adducts should decrease in the order of 1-methyl, 1-ethyl, and 1-isopropylnaphthalene. Especially with the last-mentioned compound, besides the decrease of the number of hydrogens which can take part in the hyperconjugation, the sterical interaction between one of the methyl groups of the isopropyl substituent with the peri-hydrogen would prevent

in the activated state the isopropyl group from taking the planar configuration which is necessary for hyperconjugation. Therefore, assuming the heterolytic process, we can reasonably expect the formation of the ordinary tetrachloride as the main addition product from 1-isopropylnaphthalene. On the other hand, if the reaction proceeds through the homolytic process, the chlorination of isopropyl side-chain should be inevitable, because the secondary C-H bond of 1-isopropylnaphthalene is supposed to be about 4 times as reactive as that of 1-methylnaphthalene. (Relative reactivities of the secondary C-H bond of cumene towards chlorine atoms determined in liquid phase at 80° is 4.0, taking toluene as standard).¹¹⁵

Under the same conditions used for 1-methyl and 1-ethylnaphthalene, 1-isopropylnaphthalene gave a tetrachloride of m.p. 116-117°, which was established by p.m.r. spectroscopy as 1,2,3,4-tetrachloro-1-isopropyl-1,2,3,4-tetrahydronaphthalene. The isopropyl side-chain therefore remained unattacked by chlorine atom, in agreement with the ionic proposition.

Acenaphthene provides another support for the hyperconjugative mechanism. Although the distance between

C_1 — C_3 carbon atoms in naphthalene is much longer than 2 Å (ca. 2.5 Å), the actual bond length of two methylene carbons in acenaphthene has been found by X-ray analysis to be 1.54 ± 0.014 Å.¹¹⁶ The strain caused by the arrangement of such structure is said to be relieved by the distortion of carbon bond angles and distributed among all rings concerned. Thus, the highly enhanced reactivity of acenaphthene in comparison to that of 1,8-dimethylnaphthalene,¹¹⁷ the lower chemical shift of aliphatic protons,¹¹⁸ and anomalous numerical values found in the measurement of pK as well as ultra-violet spectra¹¹⁹ are attributed to the presence of internal strain, which would inevitably lead to the decrease of the stabilisation energy due to resonance. That is, acenaphthene would possess the less aromatic character, and consequently be more susceptible to the chlorine addition than the substitution. On the other hand, the ethylene bridge has been shown to exist in the same plane with the naphthalene ring. This spatial arrangement seems ideal for the aliphatic C-H bonds to be overlapped with π -electrons of aromatic nucleus, because even if these C-H bonds are in gauche positions relative to the aromatic plane in the ground state, considering the slight energy required to distort the carbon

bond angles, the co-planar configuration would be readily achieved by the acquisition of the stabilisation energy arisen from the hyperconjugative overlapping of p-orbitals. The presence of hyperconjugation in this system is supported by the observations such as the increased electron-donating power in the order of ethylene bridge, 1-methyl, and 1,8-dimethyl groups;¹¹⁷ or the good coincidence of the observed magnitude and ratio of splittings for methylene protons in the negative acenaphthene ion with those calculated on the assumption of the hyperconjugative participation of π -electrons.¹²⁰ Therefore, if we assume that the side-chain chlorinated adducts are formed by the heterolytic process analogous to that postulated for 1-methylnaphthalene, acenaphthene is expected to undergo more easily the addition reaction accompanied by the simultaneous side-chain substitution, because of the ideal location of alkyl side-chain for the hyperconjugative loss of the proton from the carbonium intermediate.

The chlorination of acenaphthene has so far been exclusively concerned with the substitution products, only with an exception of a recent work by Daschewski and Petrenko,⁶⁶ who have claimed the isolation of two addition products and formulated them as 1,2,5,6,7-pentachloro-5,6-dihydroacenaphthene and 2,3,4,5,6,7-hexachloro-

3,4,5,6-tetrahydroacenaphthene respectively. In presence of iodine, the latter was the major product, while the former was preferentially formed in presence of ferric chloride. As the details of the original paper had not been available, acenaphthene was chlorinated using sulphuryl chloride as a chlorinating agent and light petroleum as a solvent. Acenaphthene reacted readily and briskly at either room temperature or under ice-cooled conditions. Two major products separated by hand-picking were pale yellow fine needles of m.p. 210-214^o and slightly yellow prisms of m.p. 168-169^o. Since these melting points differ greatly from those reported in the literature⁶⁶ (204-205^o, and 150^o respectively), both adducts were analysed; the higher-melting product was a trichlorodichloride (C₁₂H₇Cl₅) and the lower-melting one a dichlorotetrachloride (C₁₂H₆Cl₆). On dehydrochlorination with alkaline methanol, these gave the tri- or tetrachloro-acenaphthylene recorded in the literature.⁶⁶ The chlorination of acenaphthene with molecular chlorine in light petroleum gave similar results.

The extraordinary ease of the formation of the side-chain chlorinated addition products from acenaphthene supports the idea that the hyperconjugative electron

donating effect of the alkyl groups is highly enhanced by the ideal spacial configuration of the methylene C-H bonds for the loss of proton from the carbonium intermediate XXXIII. The increased unsaturated character of acenaphthene owing to the internal strain might be partly responsible for the easy production of the adducts.

The further evidence can be obtained from the chlorination of 1,8-dimethylnaphthalene. The difference between the strain energies of 1-methylnaphthalene and 1,8-dimethylnaphthalene, calculated by the Brown's method¹²¹ assuming the constancy of strain in a series of homophic compounds, is ca. 6 kcal/mol.¹²² The strain of 1-methylnaphthalene, caused by the interaction of the methyl group with the peri-hydrogen atom is estimated to be 1.6 kcal/mol. Thus, as a first approximation, a value of 7.6 kcal/mol. can be assumed as the strain energy of 1,8-dimethylnaphthalene. This value exceeds the strain energy between methyl and t-butyl group of o-t-butyl-toluene (ca. 4-6 kcal/mol.) by at least a few kcal/mol. Therefore, the realisation of an ideal structure of 1,8-dimethylnaphthalene, characterised by normal magnitudes of the valence angles and bond lengths, is no doubt greatly hindered by the mutual repulsion of

the two peri-methyl groups. As a natural consequence of this, two methyl groups would be pulled apart in the plane of the naphthalene ring and be bent out of the plane. Structural analysis by X-ray studies confirms the deformed structure.¹²³ The results obtained from octamethylnaphthalene indicates that the molecule is no longer planar; the methyl groups in the peri-positions are displaced from the average planarity of the molecule by 0.73 Å, which corresponds to a deviation of the C-CH₃ bond from the plane by an angle of 28°. The equilibrium distance between two peri-methyl groups are 2.98 Å.

Thus, as a result of van der Waals' repulsion, the two methyl groups (ca. 2 Å in diameter) of 1,8-dimethylnaphthalene is considered to be distorted substantially from the positions corresponding to an ideal structure for the hyperconjugation. This means that 1,8-dimethylnaphthalene would probably undergo the normal chlorine addition to give chiefly tetrachloride, the methyl groups being unaffected throughout the reaction, because in the carbonium intermediate as XXXIII the aliphatic methyl group can no longer exist in the same plane with the aromatic ring and surrender one of its protons in such a way/^{as}to form the ethylene bond.

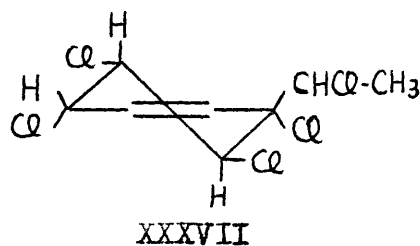
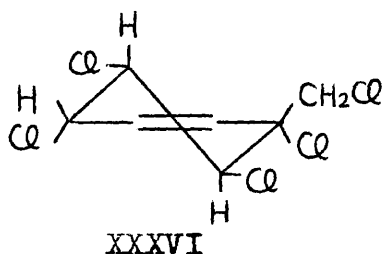
The chlorination of 1,8-dimethylnaphthalene proceeded much slower than those of acenaphthene and 1-methylnaphthalene. Although no crystalline product could be isolated from the syrup containing the addition products, its p.m.r. spectrum indicated strong methyl peaks, but signals in the methylene region were far less prominent. Therefore, 1,8-dimethylnaphthalene seems to have undergone the additive chlorination through the ordinary course, giving the tetrachloride as the main addition product.

The steric interference is not so marked if the neighbouring group is present in the β -position of the ring. Thus, 1,2-dimethylnaphthalene on treatment with sulphuryl chloride in solvent readily affords 1,2,3,4-tetrachloro-1-chloromethyl-2-methyl-1,2,3,4-tetrahydronaphthalene as the main addition product, although the reaction rate is considerably slowed down in comparison to that of 1-methylnaphthalene.

17.2 Stereochemistry and Possible Sequence for the Formation of Side-chain Chlorinated Adducts

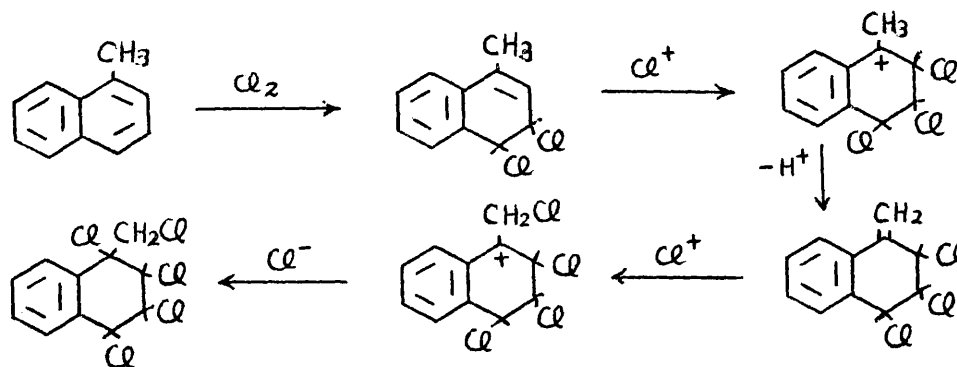
P.m.r. spectroscopy in combination with the partial deuteration technique enabled us to establish the stereochemistry of those adducts from alkylnaphthalenes.

By replacing the 4-hydrogen by deuterium, two coupling constants of 1,2,3,4-tetrachloro-1-chloromethyl-1,2,3,4-tetrahydronaphthalene are readily recognised as $J_{2,3} = 11.4$ c.p.s. and $J_{3,4} = 3.6$ c.p.s. Since $J_{2,3}$ is so large, both H-2 and H-3 must be axial. Consequently, since $J_{3,4}$ is small, the other hydrogen atom must be in the pseudoequatorial conformation. The stereochemistry about the 1-position can not be readily deduced, but by comparing the γ -values for the protons with those for protons in compounds of known structure, some inference can be drawn: the expected γ -value for the axial 3-hydrogen atom if the 1-chlorine were pseudoequatorial is ca. 5.5, whereas if the 1-chlorine were pseudoaxial, it would have $\gamma =$ ca. 5.0. The observed value $\gamma = 5.06$ indicates to a high degree of probability that the 1-chlorine atom is pseudoaxial as shown in XXXVI



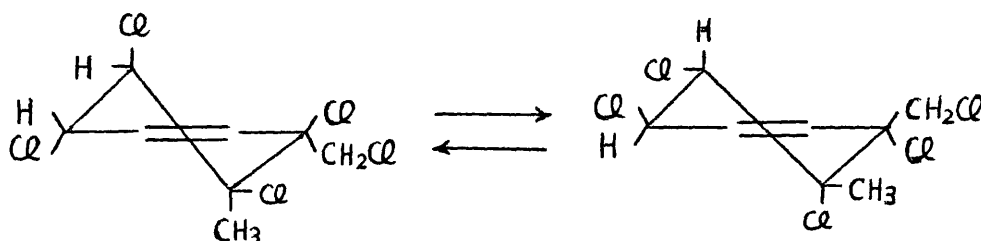
As there cannot be so much difference between methyl and ethyl groups concerning the stereochemical as well as magnetochemical properties, 1,2,3,4-tetrachloro-1-(1'-chloroethyl)-1,2,3,4-tetrahydronaphthalene must have the

structure similar XXXVII. The observed γ -value (5.14) for the axial 3-hydrogen also supports the suggested structure. From these as well as the fore-going discussions described in section 17.1, the formation of the side-chain chlorinated addition products may be explained by the sequence as shown below, involving a 1,2-cis additions followed by an attack of chlorine at the 2-position, a hyperconjugative loss of a proton from the methyl group, and 1,2-chlorine addition to the resulting exomethylene compound.



1,2,3,4-Tetrachloro-1-chloromethyl-2-methyl-1,2,3,4-tetrahydronaphthalene has two aliphatic methine protons with a coupling constant of 5.6 c.p.s. Such an intermediate value has been found for 1,1,2,3,4-pentachloro-2-methyl-1,2,3,4-tetrahydronaphthalene ($J = 5.8$ c.p.s.) and naphthalene ϵ -tetrachloride ($J = 5.8$ c.p.s.). Comparison of γ -values for protons of 1-chloromethyl-2-methylnaphthalene tetrachloride with

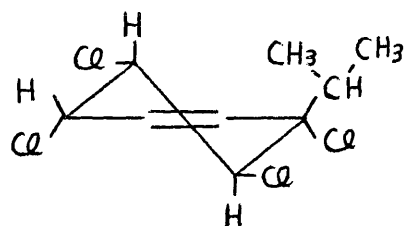
those for 1-chloro-2-methylnaphthalene tetrachloride shows great similarity among them (both 4.60 τ for 3-H; 4.32 and 4.26 τ for 4-H respectively). Thus, both adducts are considered to have similar stereochemistry about the 2-carbon atom and exist in a state of equilibrium mixture of two rapidly interconverting conformations, with the 3- and 4-hydrogen atoms trans to each other. The CH_2Cl group of this adduct gives rise to two doublets of $J = 13.2$ o.p.s., which indicates the inhibition of free rotation about the $\text{C}_{\text{aliph.}}-\text{C}_{\text{CH}_2\text{Cl}}$ bond by the neighbouring 2-methyl group. By the use of the Stuart model, it is understood that such strong interference can occur when both groups are located in positions cis to each other. The most probable structure, therefore, is as shown below:



In this adduct, 3- and 4-chlorine atoms are trans one to another. This is probably due to the fact that the combined inductive effect of two methyl groups in 1,2-dimethylnaphthalene retards the nucleophilic access of chlorine anion so much that the 1,2-additive chlorination

occurs in a trans sense in the first stage of the reaction.

On the basis of the similar discussions, the stereochemistry of 1,2,3,4-tetrachloro-1-isopropyl-1,2,3,4-tetrahydronaphthalene can readily be established by replacing the 4-hydrogen of the tetrachloride with deuterium; two coupling constants are easily assigned as $J_{2,3} = 11.5$ c.p.s. and $J_{3,4} = 3.1$ c.p.s. Therefore, both 2- and 3-hydrogen atoms must be axial, and the 3-hydrogen atom be pseudoaxial. Comparatively high γ -value (5.27) for the 3-hydrogen suggests that the 1-chlorine atom is pseudoequatorially and the isopropyl group pseudoaxially located. The conformation in which the bulky 1-isopropyl group is in a pseudoaxial position would be energetically favoured, too. The most probable structure is, therefore, as shown below.



The formation of this tetrachloride may be explained by the two successive 1,2-additions: the initial chlorine addition to the aromatic system occurs at 3,4-positions in a cis sense, then the third chlorine preferentially attack the 2-position, probably from the

less hindered direction leading to the axial conformation of chlorine atom. The fourth chlorine atom is supposed to add to the system in a trans sense to the third one, since the increased inductive effect and bulkiness of the alkyl group would retard the capture of the chlorine anion, thus favouring the opportunity for the trans addition of chlorine atom.

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