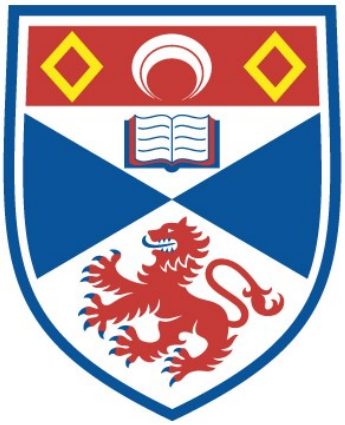
STUDIES IN THE PERINAPHTHENE SERIES

Ronald George Sutherland

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



1962

STUDIES

IN THE

PERUNA-FINLANDIA SERIES

being a Thesis presented by

RONALD GEORGE SUTHERLAND

to the University of St. Andrews in

application for the degree of Ph.D.

CERTIFICATE

I certify that Ronald George Sutherland has spent nine terms at research work under my direction, that he has fulfilled the conditions of Ordinance No.16 (St. Andrews) and is qualified to submit the accompanying Thesis in application for the degree of Ph.D.

Director of Research.

September 1962.

DECLARATION

I hereby declare that the following Thesis is a record of the results of experiments carried out by me, and further that the Thesis is my own composition and has not previously been presented for a higher degree.

The research was carried out in the Department of Chemistry, St. Salvator's College in the University of St. Andrews under the direction of Dr. D. H. Reid.

September, 1962.

UNIVERSITY CAREER

I first matriculated in the Royal College of Science and Technology, Glasgow in October, 1956, and subsequently graduated A.R.C.S.T. with First Class Honours in Chemistry in December, 1959.

I was admitted as a Research Student in the Department of Chemistry, United College, St. Andrews in October, 1959.

I was awarded a Research Studentship by the Department of Scientific and Industrial Research covering the whole period of my research programme.

ACKNOWLEDGEMENTS

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I am grateful to the Department of Scientific and Industrial Research for financial help during the period of my research programme.

I should like to thank the members of the Technical Staff of the Chemistry Department in St. Andrews who gave of their services, especially Mr. Z. M. Zochowski who recorded the infra-red spectra and Messrs. R. Morris and A. Watson for carrying out the photography required for the presentation of this Thesis. I am indebted to Miss G. Forrest who undertook the typewriting of the manuscript.

My thanks are also extended to Professor John Read, F.R.S., for his permission to carry out these researches in the Chemistry Department, University of St. Andrews.

EXPLANATORY NOTES

This thesis comprises three parts, A, B and C. Each part is divided into a number of principle sections which are prefixed by Roman numerals. Most sections are divided into subsections prefixed by Roman numerals.

Part A commences with a brief survey of aromaticity and aromatic reactivity in non-benzenoid aromatic compounds. This is followed by a detailed review of the chemistry of perinaphthane and its derivatives.

Part B is a discussion of the results achieved in the course of investigations on the perinaphthane nucleus.

Part C is the complement to Part B, being a description of experimental details.

Where reference is made to the chemical literature, this is indicated by a number in superscript. At the end of each part is a section headed 'literature cited' and this contains all the literature references made in that part.

CONTENTS

PART A.

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Abbreviations used.

Angew. Chem.	Angewandte Chemie
Ann.	Liebig's Annalen der Chemie
Austral. J. Chem.	Australian Journal of Chemistry
Ber.	Chemische Berichte
Bull. Acad. Sci.	Bulletin de l'Académie des Sciences de l'U.R.S.S.
Bull. soc.	Bulletin de la societe chimique de France
Can. Res.	Journal of Cancer Research
Compt. rend.	Comptes rendus hebdomadaires des Seances de l'Académie des Sciences
Compt. rend. Acad. Sci.	Comptes rendus de l'Académie des Sciences de l'U.R.S.S.
Chem. and Ind.	Chemistry and Industry
Chem. Zentr.	Chemisches Zentralblatt
D.R.P.	Deutsche Reichspatente
Gazz. Chim. Ital.	Gazzetta chimica Italiana
Ginsburg	Non-benzenoid Aromatic Compounds, Interscience, New York, 1959.
J.A.C.S.	Journal of the Americal Chemical Society
J. Biol. Chem.	Journal of Biological Chemistry

J.C.S.	Journal of the Chemical Society
J. Chem. Phys.	Journal of Chemical Physics
J. Gen. Chem.	Journal of General Chemistry (U.S.S.R.) New York
J. Org. Chem.	Journal of Organic Chemistry
Mon.	Monatshefte fur Chemie
Naturwiss.	Naturwissenschaften
Org. Synth.	Organic Syntheses
Rev. Sci.	La Revue scientifique
Stelzner	Stelzner, " Literatur-Register der Organischen Chemie"
Streitwieser	Molecular Orbital Theory for Organic Chemists, 1st Edition, Wiley, New York, 1961
Tetrahedron	Tetrahedron. International Journal of Organic Chemistry
Trans. Farad. Soc.	Transactions of the Faraday Society
U.S.P.	United States Patent
Z. Physik.	Zeitschrift fur Physik

PART A

A.1. Aromaticity and Aromatic Reactivity in Non-Benzenoid Aromatic Compounds.

A.1.1 Non-Benzenoid Aromatics.

In 1865, Kekule[1] recognised the structure of benzene and proposed that the presence of this structural feature be diagnostic of aromatic character. Unfortunately it was also suggested[2] at this time that aromaticity be used to classify substances of similar chemical behaviour rather than those containing common structural features. This latter classification forces us to draw an arbritary limit below which a compound may be considered to be aromatic and above, non-aromatic. According to which property we are considering, e.g., heat of formation, ease of substitution, or resistance to oxidation and addition reactions, a compound may be either aromatic or non-aromatic, depending on which criterion we happen to be applying at the time. Some of these anomalies can be removed if it is made clear whether the aromatic character of a molecule is inherent in its ground state or if it only becomes apparent during chemical reaction, i.e., its aromatic character is reflected in a lowering of the free energy difference between the ground and transition state of the molecule. In this way it is useful if we qualitatively differentiate between aromaticity and aromatic reactivity.

Earlier definitions of aromatic character[3,4] are inadequate to deal with all aspects of non-benzenoid aromatic chemistry. That due to Dewar[4] includes all the necessary conditions for a compound to possess a high delocalisation energy, but it has become apparent in recent years that it is possible for a compound to have a relatively large delocalisation energy and still be unstable. This instability has been correlated with partially filled shells of electrons, particularly in non-bonding orbitals. Vol'pin[5] has modified Dewar's definition to read, 'unsaturated cyclic compounds in which all the ring atoms take part in the formation of a single conjugated system and the π electrons of this system form a closed electron shell'. By the phrase, 'closed electron shell', is meant an electronic system in which the addition or removal of electrons tends to increase the energy of the system and thus diminish the stability of the system. The π-electrons of such a system occur in bonding orbitals, each of which contain two electrons. Thus all aromatic compounds should contain a closed electron shell and their well-known properties, both chemical and physical, depend upon the possession of this electronic system. This definition is the most acceptable to date, although a very apt definition of aromaticity has been given by Elvidge

and Jackman[6] based on nuclear magnetic resonance studies. They state that the essential feature of an aromatic system is a ring of atoms so linked that the π electrons are delocalised right round the ring and so define an aromatic compound as one which will sustain an induced ring current. The advantage of this definition is that it provides a quantitative measure of aromaticity. Their view has recently been endorsed by Sondheimer.[7]

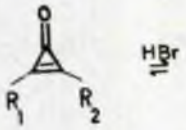
The foundation of modern theory was laid in the 1930's when Huckel[8] applied molecular orbital theory (M.O.) to aromatic systems. All the π-electrons of a conjugated system are considered to be common to all the carbon atoms of the system; this theory leads to the rule that monocyclic, conjugated polyolefins which contain $(4n + 2)$ π-electrons will possess aromatic stability. This M.O. approach explains the, 'aromatic sextet'[9] as a particular case of the general rule where $n = 1$. The aromatic character of Thiele's cyclopentadienyl anion found theoretical justification and the existance of the cycloheptatrienyl cation was predicted along with indications of the possible existance of other aromatic systems. It also suggested that monocyclic polyolefins

(I) $R_1=R_2=R_3=H$.

(II) $R_1=R_2=R_3=Ph$.

(III) $R_1=R_2=Ph$.
$R_3=H$.

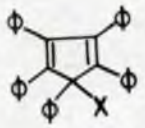
(IV) $R_1=R_2=C_3H_7$.
$R_3=H$.



(V) $R_1=R_2=Ph$.

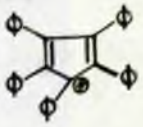
(VI)

(VII) $R_1=R_2=C_3H_7$.



(VIII) X=OH.

(X) X=H.



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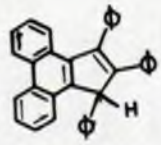

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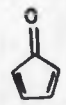

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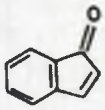

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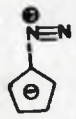

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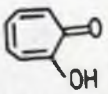

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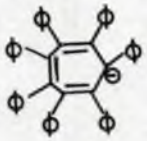


(XX)

(XXI)

(XXVI)

(XXX)

(XXXII)

containing 4n π -electrons would not be aromatic although they contained alternate single and double bonds. Systems of this type have been termed, 'pseudoaromatic' by Craig.[10]

The cyclopropenyl cation.

The system obeying Hückel's rule where n = 0 is a monocyclic system containing two π -electrons; leaving aside the double bond itself the only possibility is the cyclopropenyl cation (I). The parent system has not been isolated although cyclopropene is reported to undergo hydride exchange with the triphenyl methyl cation.[11] The triphenyl cyclopropenylium cation (II) was first synthesised by Breslow,[12] and can also be prepared by the general method of Reid and his co-workers.[13] At first it was suggested that the stability of the system might be the result of a stabilising effect due to the phenyl groups. It has since been shown from theoretical considerations that the phenyl groups stabilise the covalent cyclopropene ring to a larger extent than the cation. Breslow has extended his synthesis to the preparation of the diphenyl cyclopropenylium[14] (III) and the dipropylcyclopropenylium (IV)[15] cations.

An interesting derivative of this system is diphenylcyclopropenone (V). This was first synthesised by Breslow,[16] and later by Vol'pin[17] who prepared it by the addition of dichlorocarbene to diphenylacetylene. It is the three-membered

ring analogue of tropone. It has the remarkably high dipole moment of 5.08D and reacts with gaseous hydrogen halides to form hydroxycyclopropenylium salts,[17] e.g., (VI). The stabilities of both ketone and hydroxy salt are remarkable. At temperatures above 150° the ketone (V) decomposes to give diphenyl acetylene and carbon monoxide.[18] Di-n-propyl cyclopropenone (VII) has been prepared by Breslow and Peterson.[18] It is more basic than (V) being completely extracted from carbon tetrachloride solution by 12N hydrochloric acid and it is more stable to alkali. The diphenylcyclopropenone is cleaved, almost instantaneously, by ethanolic alkali to stilbene carboxylic acid, (VII) being recovered unchanged from a similar reaction after one hour.

The stability of these cations contrasts with the instability of the corresponding radicals. The odd electron will be in an anti-bonding orbital and, as it is also in an uncompleted shell, theory predicts that it will be unstable. The dimer, bis-triphenylcyclopropenyl, has been prepared[19] and shows no tendency to dissociate even under forcing conditions. These qualitative observations have received quantitative support from polarographic evidence.[20]

The anion would have both degenerate anti-bonding

orbitals singly occupied and so would be a diradical with an incompletely filled shell. Therefore theory predicts it to be comparatively unstable.

Cyclopentadienyl

M.O. calculations show that the five-membered ring C_5H_5 contains three bonding and two anti-bonding orbitals. Thus the cation, $C_5H_5^+$ has two vacancies in its bonding orbitals; the radical, C_5H_5, one. In the anion, $C_5H_5^-$, all bonding orbitals are full and we have a closed shell of 6 electrons. The latter thus conforms to Hückel's rule where n = 1. Delocalisation energies calculated by the M.O. method indicate values of 2.47β for the anion, 1.85β for the radical and only 1.24β for the cation[20] (the value of β is taken to be about 17 k.cal.)

The parent cation has not been isolated. In 1925, Ziegler[22] reported that the solution of pentaphenylcyclopentadienol (VIII) in sulphuric acid gave rise to a purple species which he considered to be the cation (IX). Later authors[23] agreed with his conclusions on the evidence of spectroscopic investigation. As (IX) is a derivative of the cyclopentadienyl anion which is predicted to have a triplet ground state the problem was re-examined by Breslow,[24] in particular, he examined the material obtained by pouring the acid solution

into water and which Ziegler had assumed to be the, 'dimeric ether', of (VIII). He obtained a mixture of products and showed that the spectrum assigned to (IX) was, in fact, the composite spectra of the species (X) and (XI) which he obtained from the mixture in 25% and 48% yield, respectively. Thus none of the above cation remains in solution for more than a few seconds.

This reluctance to give up electrons is also obvious in highly substituted derivatives and, in this connection, it is pertinent to consider derivatives of cyclopentadienone especially since the carbon atom of a carbonyl group can be considered to have carbonium ion character. All attempts to prepare (XII) have been unsuccessful only the dimer being obtained.[25,26] This is in accord with M.O. theory.[27] It appears that at least three substituents are necessary to stabilise cyclopentadienones as monomers although indenone (XIII) has recently been prepared.[28] This compound polymerises extremely readily.

The stability of the anion (XIV) is reflected in the acidity of the hydrocarbon. The latter reacts at room temperature with potassium to form the anion.[29] This property is also

shown by derivatives. A consequence of this tendency is the ready formation of fulvenes when cyclopentadienes are allowed to react with aldehydes and ketones under alkaline conditions. The high dipole moments of fulvenes is another indication of the strong attraction that the five membered ring has for electrons. The aromatic cyclopentadienyl system is stabilised when the ring is attached to a positively charged heteroatom. An example of this is the diazocyclopentadienylide[50] (XV) prepared in 1953. When the cyclopentadienyl anion is treated with ferrous iron it yields the completely covalent ferrocene[51] (XVI).

It is regarded by some authors as being more aromatic than benzene in that it combines a greater tendency to undergo aromatic substitution with a greater resistance to addition reactions. Its structure has been discussed in M.O. terms by Craig[52]

Cycloheptatrienyl

The fundamental unit of aromatic seven-membered ring compounds is the tropylium cation (XVII) whose stability had been predicted by Huckel. The delocalisation energies of the cation, radical and anion have been calculated to be 2.99β, 2.45β and 2.10β, respectively. In 1945, Dewar[53] explained the properties of a new class of compounds, the tropolones, e.g., (XVII), on the basis of a stable seven-membered aromatic

system. The preparation of the tropylium was first described, 1954, by Doering and Knox[34] who prepared dibromocycloheptadiene and eliminated the elements of hydrogen bromide thermally to produce tropylium bromide. This reaction had apparently been carried out by Merling[35] who, however, did not recognise the salt-like nature of his product. This method has been extended to the preparation of derivatives substituted in the seven-membered ring.[36,37] Tropylium isocyanate has been obtained by heating norcaradiene carboxazide in benzene; it is converted to tropylium bromide on treatment with hydrogen bromide.[38] Many other methods of preparation of tropylium salts have been described in the literature and have recently been reviewed.[8,39,40] Of special interest however are the methods involving hydride fission from the methylene group in cycloheptatriene (XIX). Reaction with triphenyl methyl salts gives the tropylium salts and triphenylmethane.[41] A general route to salts with a wide variety of anions is due to Reid[18] who showed that cycloheptatriene reacts with high potential quinones in the presence of acids to yield tropylium salts. The equivalence of all the carbon atoms in tropylium has been demonstrated by Vol'pin and his associates.[42] The hydrocarbon (XIX), labelled with [^{14}C] in the methylene group, was converted into [^{14}C]

tropylium bromide which was allowed to react with phenyl magnesium bromide. Oxidation of the product gave benzoic acid which was shown to possess one-seventh of the activity of the initial cation. The infrared and Raman spectra of the cation also indicate a planar seven-membered ring.

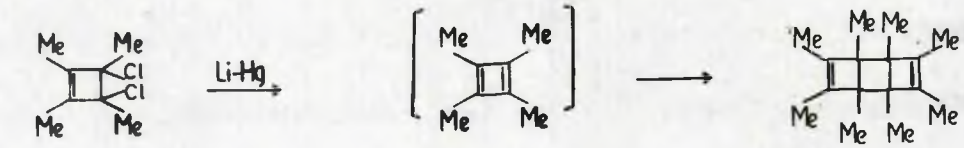
The odd electron in the tropylium radical would have to be placed in an antibonding orbital and therefore it would be easily removed by oxidising agents. The eighth electron required to form the cycloheptatrienide anion would have to be placed in a different anti-bonding orbital. Since this leaves an incompleted shell theory predicts that the anion would have a triplet ground state. The heptaphenyl cycloheptatrienyl anion (XX) has recently been prepared by Breslow and Chang.[43] The potassium salt of (XX) did not give an e.s.r. signal nor was any paramagnetism detected. It cannot therefore be a diradical and has not the predicted triplet ground state Addition of a solution of (XX) to one of heptaphenylcycloheptatrienyl bromide gave a russet solution which gave a strong e.s.r. signal and paramagnetism was detected. Spins appear to have been unpaired in this reaction and the heptaphenylcycloheptatrienyl radical formed.

A.1,11 Pseudoaromatics[10]

Intensive theoretical and experimental efforts have been directed to the problems set by the pseudoaromatic systems, cyclobutadiene, cyclooctatetraene, pentalene and heptalene. Valence bond and M.O. treatments have been at variance in their predictions concerning these systems. Much of the experimental evidence is negative, but this, in itself, lends cogent support to the M.O. viewpoint.

Cyclobutadiene (XXI)

The chemistry of unsaturated, four-membered carbocyclic systems has recently been reviewed in detail.[44] Critical analyses of the experimental data from an M.O. point of view have also become available.[5,45] The lack of success that has attended synthetic approaches to cyclobutadiene indicate that it would be unstable, nevertheless it has recently been shown to be capable of transient existence. In 1956, it was suggested that (XXI) might form stable complexes with transition metals.[46] M.O. theory suggested that the two electrons in non-bonding orbitals might form co-valent bonds with a metal atom. It was suggested that such a complex might well be an intermediate in the Reppe synthesis of cyclooctatetraene by the polymerisation of acetylene in the presence of nickel cyanide. Several such complexes have since been prepared. Criegee and Luis[47] prepared the



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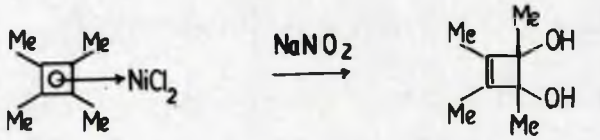
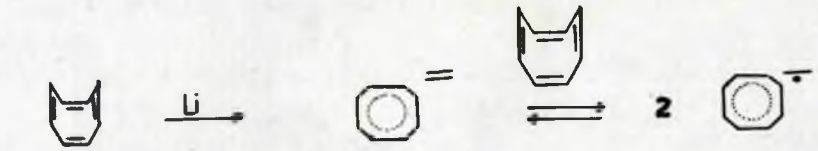
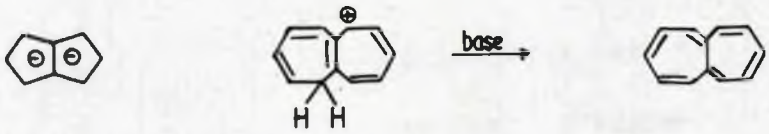


(XXIV) (XXV)



(XXVII) (XXVIII) (XXIX)



(XXXI) (XXXIII) (XXXII)

(XXXV) (XXXVI) (XXXVII)

tricyclic hydrocarbon (XXII) from 3,4-dichloro-1,2,3,4-tetramethylcyclobutene (XXIII) and lithium amalgam. Reaction of (XXIII) with nickel carbonyl yields a stable red-violet compound, $C_8H_{12}NiCl_2$, which is of the type (XXIV).[48] Its n.m.r. spectrum shows twelve equivalent protons and reaction with sodium nitrate yields tetramethyl-cis-cyclobutenediol (XXV). The complex (XXIV) is so stable that it decomposes only above 250°. Nenitzescu and coworkers[49] found that treatment of 1,2,3,4-tetrabromocyclobutane with lithium amalgam gave a mercury derivative which, on reaction with silver nitrate, gave a crystalline complex $C_4H_4.AgNO_3$. This was decomposed by steam giving a dimer related to (XXII) which reverts back to the complex on further treatment with silver nitrate.

Cyclooctatetraene (XXVI).

The hydrocarbon (XXVI) has eight π electrons and M.O. theory predicts that such a molecule, if planar, would be unstable. The chemistry of cyclooctatetraene shows it to be a cyclic polyene, and physical measurements indicate that it consists of alternate double and single bonds. X-ray and electron diffraction data indicate that it has the spatial symmetry corresponding to the 'tub' structure (XXVII).

Cyclooctatetraene forms a dilithio salt, $C_8H_8Li_2$ whose magnetic susceptibility indicates that it has the structure $(Li^+)_2\ (C_8H_8)^{2-}$. This dianion would be an example of Huckels Rule where n = 2. The above process is related to the polarographic reduction of (XXVII)[80,81] which can be regarded as a measure of the electron affinity of the hydrocarbon. Two electrons are involved, and as the half wave potential is independant of pH, i.e., no hydrogen takes part in the reduction step, the reaction can be formulated as :

$$C_8H_8 + 2e = C_8H_8^{11}$$

E.s.r. and n.m.r. studies[82,83] show that the addition of alkali metals in ether to (XXVII) produces the dianion (XXVIII) in equilibrium with a small quantity of the radical anion (XXIX). The evidence shows that the latter species are both planar, so it can be concluded that (XXVII) is non-planar due to π electron instability. The addition of two electrons into non-bonding orbitals results in a planar system with aromatic stability.

Pentalene (XXX).

This system has attracted considerable interest and has been the subject of a recent comprehensive review.[84] It contains eight π electrons and may be regarded as a bridged

derivative of (XXVII). Its eight electrons would occupy four bonding orbitals and recent calculations[55] show that the nearest unoccupied energy level is one of zero energy. The difference between the highest occupied and the lowest unoccupied energy level is therefore comparatively low. It follows from this that (XXX) should be readily converted into an excited triplet state and as this is a diradical the pentalene system should be highly reactive. Another reason for expecting high reactivity is the fact that it could accept a pair of electrons into an unoccupied bonding orbital and thence react with electrophilic reagents. The recent synthesis[56] of dilithium pentalenide (XXXI) confirms this conclusion. Dihydropentalene in tetrahydrofuran reacted with two moles of n-butyllithium in n-heptane. The product was a white crystalline substance whose solutions in tetrahydrofuran are stable at room temperature. The structure of the dianion in solution was confirmed by the n.m.r. spectrum. It is interesting to note that this bears the same relation to the cyclopentadienide anion as naphthalene does to benzene.

Heptalene (XXXII).

Theoretical and experimental approaches to this structure have recently been reviewed by Bergmann.[54] Using a similar

argument to that outlined for pentalene it can be shown that ten of the twelve π electrons are in bonding orbitals, the remaining two being in a non-bonding level of zero energy.[88] Heptalene has recently been synthesised by Dauben and Bertelli.[87] The key step in the synthesis being a hydride ion abstraction from a mixture of 1,5- and 1,10- dihydroheptalenes to give 1-heptalenium fluoroborate (XXXIII) which on treatment with base at low temperature gave (XXXII) as a red oil. The reactions and n.m.r. spectrum of (XXXII) indicate that it is a weakly interacting, cyclic polyene with no aromatic stability.

A.1,111. Bi- and Polycyclic Aromatic Systems.

(i) The startling success of simple M.O. theory as applied to monocyclic systems has prompted attempts to apply the $4n + 2$ rule to bi- and polycyclic systems. The modification used with regard to simple bicyclic systems is the application of the $4n + 2$ rule to the periphery of the molecule making the assumption that the bridging bond does not affect the aromatic character of the peripheral ring. In systems like azulene it can be shown that the central bond helps to maintain the planarity of the ring.

Azulene[88]

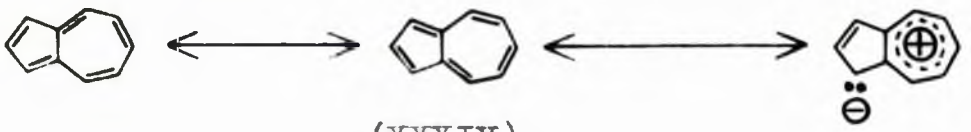
Azulene (XXXIV) can be regarded as a derivative of the unknown polyolefine, cyclodecapentaene. This obeys the

Huckel rule where n = 2 but has not been synthesised. One of the reasons advanced for this is that there would be a steric repulsion between hydrogen atoms lying within the carbon periphery if the molecule, $C_{10}H_{10}$, was planar. This is one of the conclusions reached from scale drawings made by Mislow.[59] In azulene, the central bond is essentially single in character; the order of all the other bonds being intermediate between double and single bonds. Other indications of aromatic character are a relatively high delocalisation energy, and the formation of quantities of azulenes in the dehydrogenation of macrocyclic hydrocarbons.

The π electron cloud of azulene is not symmetrical, there is a slight charge separation which is reflected in the dipole moment of 1.0$_D$.[60] Quantum mechanical calculations[61] confirms this dipole character which has a marked effect on both its chemical and physical properties. It was concluded that electrophilic substitution would occur at position 1 and nucleophilic substitution at position 4. These predictions have been experimentally confirmed.

One of the most interesting features of azulene chemistry is the fact that there must be a considerable decrease in the activation energy of the transition state in

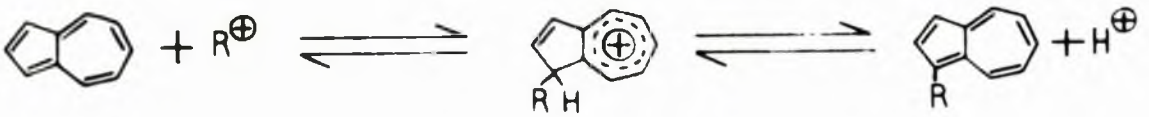
The ground state of azulene:



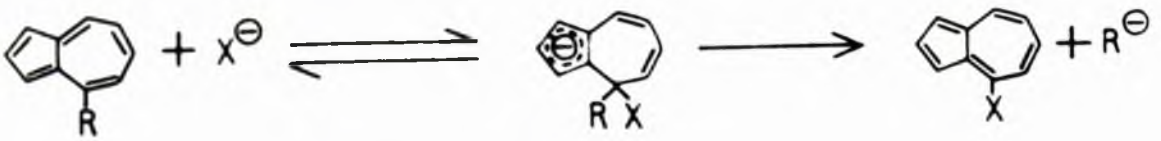
(XXXIV)

Substitution of the azulene nucleus:

1. Electrophilic substitution:



2. Nucleophilic substitution:



R=H or substituent

both electrophilic and nucleophilic substitution. This has been discussed in a qualitative manner by Reid.[62] The activation energy required in a reaction appears to be considerably reduced when a conjugated system of six π electrons is formed in the transition state. In azulene, electrophilic substitution may be thought to proceed through the formation of the electronic analogue of the tropylium cation and nucleophilic substitution through an analogously formed cyclopentadienyl anion as shown opposite. Thus aromatic stability is invested in the delocalisation of 10 π electrons over a cyclic structure which is formally bicyclic but essentially monocyclic with regard to the mobile electron system.

(ii) The 4n + 2 rule cannot be applied directly to polycyclic systems having atoms common to three or more rings without exceptions being met. If we consider only the periphery of the molecule a number of compounds can be made to comply with Huckel's rule, e.g., pyrene has fourteen π electrons in its periphery. This approach has been put on a sound theoretical footing by Platt.[63] Another useful approach has been developed by Dewar.[64] An aromatic molecule is considered as a derivative of one or more cyclic polyenes and the cross links are regarded as small perturbations. Thus pyrene can be considered as a combination of a fourteen and a two π electron system. These

approaches are helpful particularly in the prediction of new aromatic systems[5,64,65] but often the cross links are not small perturbations and, in the last analysis, it is necessary to make an individual M.O. calculation for each individual system.

The anion, radical and cation of the perinaphthyl system.

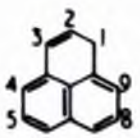
A detailed discussion of the preparation, stability and properties of the perinaphthenide anion (XXXV), perinaphthyl radical (XXXVI) and the perinaphthenylium cation (XXXVII) will be developed in Part B of this thesis.

A.1,IV. Macrocyclic Aromatic Systems.

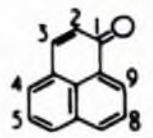
Of the possible cyclopolyolefins, those which contain 10, 14, 18, 22, 26 and 30 π electrons distributed over the same number of annular carbon atoms might be expected to possess some degree of aromatic stability, as these numbers conform to Huckel's rule. In order that the double and single bonds should interact, the molecules should be planar or nearly so. Scale drawings by Mislow[66] suggest that with polyolefins smaller than $C_{18}H_{18}$ there will be a considerable degree of interaction among hydrogen atoms lying inside the periphery of the carbon ring.

Sondheimer and his associates have made important contributions to this field.[7] They have reported the syntheses

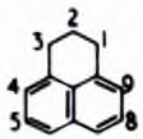
of [18]-, [24]-, and [30]- annulene. The latter two hydrocarbons, one of which obeys Huckel's rule, are somewhat unstable. However [18]- annulene is capable of supporting an induced ring current and the X-ray evidence strongly suggests that there is no bond alternation in this molecule. Thus it would seem to be aromatic, especially in the light of Jackman's definition.[6]



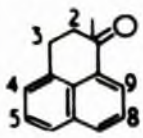
(XL)



(XXXVIII)

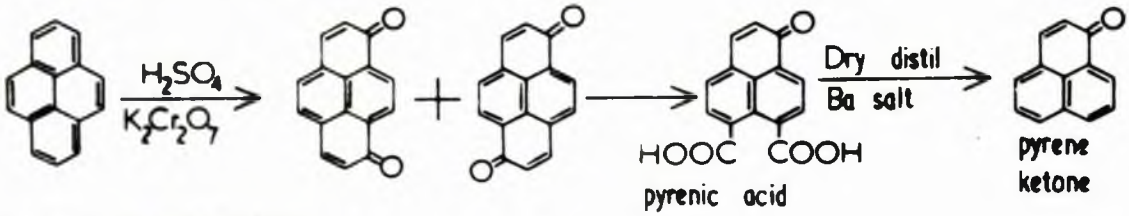


(XLI)

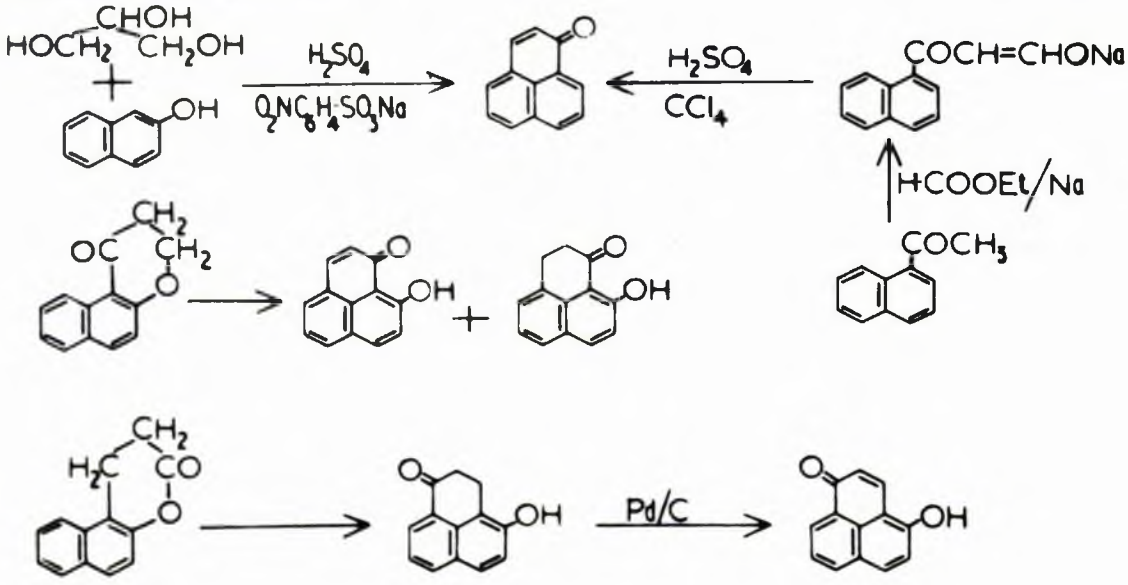


(XXXIX)

The degradation of pyrene :–



Syntheses of perinaphthenone



A.11. The Perinaphthene Ring System.

A.11,1. Nomenclature

Before 1938 the nomenclature of the perinaphthene ring system was somewhat confused. The parent hydrocarbon (XL) has been variously referred to as perinaphthindene,[66,67] phenalene[68] (from phenonaphthene), and benznaphthene[69] (from peribenzonaphthene). None of these names are strictly accurate in their implications. The situation with regard to the unsaturated ketone (XXXVIII) was further complicated due to the fact that it was first isolated as a degradation product of pyrene,[70] and in the literature it is variously referred to as 'pyrene ketone',[70] phenalone-9,[68,71] 1,8-naphthindenone,[72] 9-ketoperinaphthindene,[73] and perinaphthindone.[74,75]

Fieser and Hershberg[76] suggested a rationalisation of the nomenclature. The compounds (XXXVIII), (XXXIX) and (XLI) were named perinaphthenone, perinaphthanone and perinaphthane respectively. In accord with this the parent hydrocarbon (XL) was called perinaphthene. The numbering is based on the ring index system and is illustrated in the formulae (XXXVIII) to (XLI).

The nomenclature of Fieser and Hershberg has been adopted in this thesis.

All,11. Perinaphthen-1-one: Isolation and Preparations.

In 1887, Bamberger and Philip[70] obtained a ketone, $C_{15}H_8O$, on degradative oxidation of pyrene with chromic acid. They noted that the ketone was basic, dissolving reversibly in concentrated hydrochloric acid. Vollman[72] later showed that oxidative degradation of pyrene gives a mixture of quinones which, on further oxidation, yields a perinaphthenone dicarboxylic acid. The latter was decarboxylated to perinaphthen-1-one (XXXVIII).

The first synthesis of this unsaturated ketone was described in a German patent[77] in 1915. The compound was obtained by the action of glycerol on α- or β-naphthol in the presence of 82% sulphuric acid, the latter acting as dehydrating, condensing and oxidising agent. Mayer and Sieglitz[68] cyclised β-(1-naphthyl)-propionyl chloride in ligroin, and obtained a small quantity of a yellow ketone which they assumed to be perinaphthan-1-one (XXXIX). Cook and Hewett[71] repeated this work using both aluminium chloride and stannic chloride as the cyclisation agent, but could only isolate the unsaturated ketone (XXXVIII) together with a colourless dihydro ketone which was later shown to be the isomeric 1-oxobenzo[e]indane (XLII). Although these authors

assumed the identity of their product with that of Bamberger, the first direct comparison was made by Vollman and his co-workers.[72] They showed that the material prepared according to the German patent was identical with 'pyrene ketone'.

Perinaphthenone (XXXVIII) has also been prepared by the condensation of acetyl naphthalene with ethyl formate in the presence of sodium, followed by the cyclisation of the resulting hydroxymethylene compound by 82% sulphuric acid.[78] A modification of this process using 87% sulphuric acid as the cyclising agent gave perinaphthenone in 80% yield.[79] Anhydrous hydrogen fluoride has been used as condensing agent in the preparation of (XXXVIII) from acrolein and α- or β-naphthol.[80]

The cyclodehydration of the β-(1-naphthyl)-acrylic acids (XLIII and XLIV) was studied by Lock and Gergly.[81] Neither (XLIII) nor (XLIV) could be cyclised with anhydrous hydrogen fluoride although the closely related 1-naphthyl methylene malonic acid underwent ring-closure quite readily. They suggested that this was due to the acrylic acids existing in the trans configuration, since cyclisation of the above acids occurred after irradiation with ultraviolet light.

An improved preparation of perinaphthenone has been described in the patent literature[82] and has been utilised

for the preparation of the ketone in quantity from β-naphthol[74,78,88]. This process has been adapted to the synthesis of 6-hydroxyperinaphthenone and some of its derivatives[84]

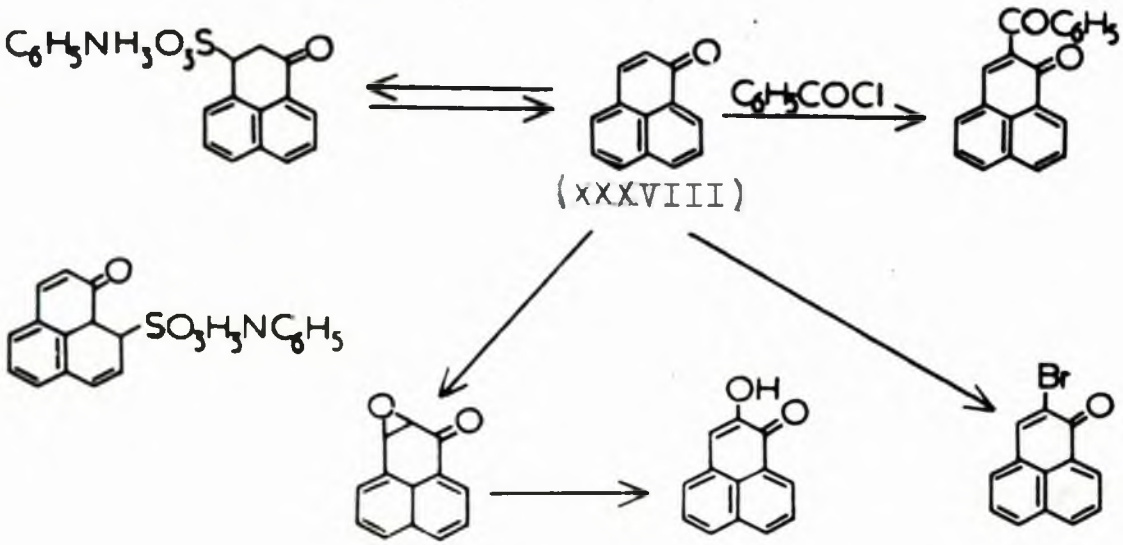
3-Methylperinaphthen-1-one can be prepared from 1,8-diacetylnaphthalene by a piperidine catalysed intramolecular condensation.[85]

A route to certain hydroxyperinaphthenones has recently been described by Loudan and Razdan.[86] Benz[f]chroman-4-one was converted by fusion with aluminium chloride to a mixture of 9-hydroxyperinaphthen-1-one and 9-hydroxyperinaphthan-1-one. In the same way 4-hydroxyperinaphthen-1-one is obtained after dehydrogenation of the primary adduct from the fusion of benz[f]chroman-2-one with aluminium chloride.

The best, and most general method for the preparation of perinaphthenones consists in the dehydrogenation of the appropriate perinaphthanone by triphenyl methyl perchlorate in glacial acetic acid[87] (CIX).

A.11,111. Perinaphthen-1-one: Properties.

Perinaphthenone (XXXVIII), yellow needles, m.p. 156°, is soluble in most organic solvents and dissolves reversibly in concentrated hydrochloric acid to give a golden solution with a green fluorescence. A detailed study of its chemical


$C_6H_5NH_3O_3S$
C_6H_5COCl
COC_6H_5
(XXXVIII)
$SO_3H_3NC_6H_5$
OH
Br

reactions was undertaken by Fieser and Newton.[88]

It gives a red vat with alkali and hydrosulphite and with sodium bisulphite forms a colourless addition product, isolated as the aniline salt. Treatment of the latter substance with boiling, dilute hydrochloric acid reverses the reaction with precipitation of the ketone.

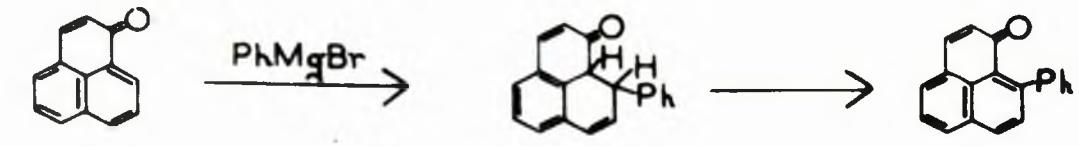
Attempts to utilise the unsaturated ketone as a component in the Michael reaction, the Diels-Alder reaction, or in the Friedal-Crafts reaction with benzene in the presence of aluminium chloride were unsuccessful. However, perinaphthenone does react with benzoyl chloride at 140° using a mixture of aluminium and zinc chloride to form the 2-benzoyl compound. When the double bond 2,3- to the carbonyl function is activated diene addition may occur. Perinaphthen-1-one-2-carboxylic acid reacts with 2,3-dimethylbutadiene to yield the fully aromatic adduct, 9,10-dimethylbenzanthrone-7. If the conditions of the latter reaction are modified the di- and tetra-hydro derivatives may be isolated.[88]

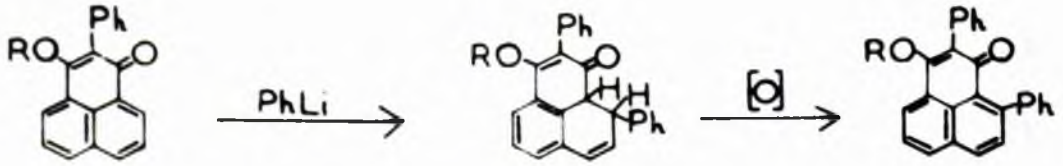
Silberman and Barkov[74] unsuccessfully attempted to prepare the oxime which was, however, prepared by Fieser and Newton[88] by refluxing hydroxylamine hydrochloride with (XXXVIII) in alcohol. The hydrazone was prepared by boiling

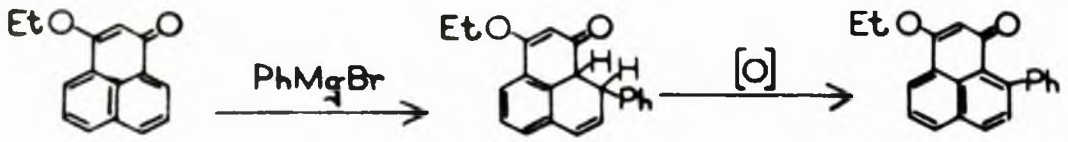
the ketone under reflux with hydrazine hydrate in glycol.[74] Perinaphthen-1-one is slowly attacked by hydrogen peroxide in the presence of sodium carbonate to form the 2,3-epoxide. The isomerisation of this substance is effected by pouring its solution in concentrated sulphuric acid onto ice. The product is 2-hydroxyperinaphthen-1-one, a red, alkali-soluble substance, m.p. 185°, which can also be prepared by the hydrolysis of the violet-black azomethine compound formed by the reaction of perinaphthan-1-one with p-nitrosodimethylaniline in ethanolic potassium hydroxide.[119]

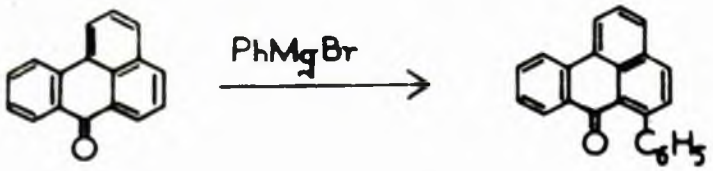
Several investigations[88-92] have been made on the halogenation of perinaphthenone. The reaction is complicated and proceeds through several stages.[94] The product is usually formulated as the 2-halo compound. Attempts to convert 2-bromo-perinaphthenone to the 2-hydroxy compound have been unsuccessful even using silver acetate under forcing conditions.[88] When the bromo-ketone is reacted with an excess of morpholine or piperidine the 3-substituted compound is obtained at room temperature and, at elevated temperatures, the 2-isomer predominates.[88]

Peropyrene and perinaphthane are obtained when perinaphthenone is heated with zinc dust in a melt of zinc and









Abnormal carbonyl reactions in the perinaphthenone series

sodium chlorides.[96]

The properties of the carbonyl group in the perinaphthenone series are abnormal. This is reflected in their reactions with organometallic compounds. The products are usually explained as resulting from 1,4-addition or on the ready prototropic rearrangement of the product. Some examples of these reactions are now given.

(i) Methyl magnesium iodide reacts readily with perinaphthen-1-one. The product has been shown to be 4(9)-methylperinaphthene. This could result from initial 1,4-addition of the Grignard reagent or by the prototropic rearrangement of the dehydration product.[97]

(ii) 9-Phenyl perinaphthenone has been isolated from the interaction of phenylmagnesium bromide and perinaphthenone.[98] Other Grignard reagents which have been shown to react 1,4 with (XXXVIII) are o-toluoyl magnesium bromide, α-2-methyl naphthyl magnesium bromide and mesityl magnesium bromide.[99] The products have been shown to be 9-aryl derivatives.

Benzanthrone, which can be considered to be a derivative of perinaphthenone, reacts with phenyl magnesium bromide to form 4-phenylbenzanthrone.[100]

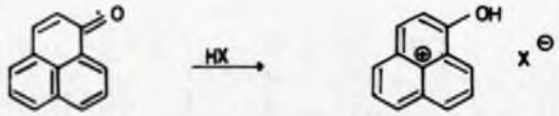
(iii) Phenyl magnesium bromide adds 1,4 to 3-ethoxy-perinaphthenone to yield an intermediate which, on oxidation, gives 3-ethoxy-9-phenylperinaphthenone.[101]

(iv) Phenyllithium reacts with 2-phenyl-3-hydroxyperinaphthenone and its methyl ether to give, after oxidation, 2,9-diphenyl-3-hydroxyperinaphthenone and 2,9-diphenyl-3-methoxyperinaphthenone, respectively.[102]

Lithium aluminium hydride reduction of perinaphthenone is also anomalous.[103] The reaction was carried out in the hope of preparing perinaphthenol. The reaction proceeded with the evolution of hydrogen and the products were perinaphthanone (65%), perinaphthene (14%), and unidentified phenolic material (12%). A mechanism for this reaction was proposed by the authors but does not appear to satisfactorily account for the formation of the hydrocarbon.

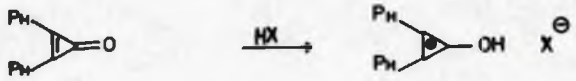
As mentioned earlier the reversible solubility of perinaphthenone in concentrated acid is very useful experimentally and this property also has considerable theoretical significance. This behaviour can be rationalised on one of two explanations:

(i) The carbonyl group is abnormally polarised in the ground state with an unusually high electron density on the oxygen atom.



(XXXVIII) (XLVII)

(XLV) (XLVIII)



(XLVI) (XLIX)

(ii) The carbon-oxygen band has a high polarisability.

Perinapthenone (XXXVIII) shows an obvious analogy with both tropone (XLV) and diphenylcyclopropenone (XLVI). They all form a stable series of salts, e.g., (XLVII), (XLVIII), and (XLIX). The dipole moments of the ketones (Table I) have been measured and shown to be unusually high.

TABLE I

Compound	Dipole Moment	Reference
Perinaphthenone	3.99 D	105
Tropone	4.71 D	104
Diphenylcyclopropenone	5.08 D	17

The dissociation constant (pK_a) for the conjugate acids of perinaphthenone (XLVII) and several of its derivatives, as well as these for the conjugate acids of benzanthrone and benzalacetophenone, have been determined spectrophotometrically by Beckman and Silberman[106] who estimated the degree of partition of the appropriate ketone between sulphuric acid and chloroform. It was concluded that the results were indicative of the ready formation of the hydroxyperinaphthenylium cation (XLVII) compared with the corresponding cations derived from benzanthrone and benzalacetophenone.

These authors also carried out a polarographic investigation on perinaphthenone and a number of its simple

derivatives. Reduction proceeds reversibly and with great ease compared with that of benzanthrone and benzalacetophenone. The process is a one electron addition to the molecule giving the 1-hydroxyperinaphthyl radical (L). Perinaphthenone-3-carboxylic acid displays a greater ease of radical formation than the parent ketone. It is suggested that this is due to the carboxyl group promoting electron uptake at the oxygen site; the effect disappears on the formation of the carboxylate ion. On the other hand 9-hydroxyperinaphthenone shows a considerable resistance to electron uptake. This may be due to strong hydrogen bonding in this molecule. From these results Beckman concluded that perinaphthenone had a tendency to assume an alternating structure of double and single bonds around the periphery of the molecule due to a gain in resonance energy. Their results are tabulated in Table II.

Several publications[107-110] have been concerned with the infrared and ultraviolet spectra of a number of perinaphthanones and perinaphthenones. The normal, undisturbed carbonyl frequencies in aliphatic ketones lies in the range 1705-1725 cm.$^{-1}$ Conjugation with aryl groups usually brings the wave number into the range 1700-1680 cm.$^{-1}$ The carbonyl band is generally found to be 10-20 cm.$^{-1}$ towards higher wave

TABLE II

Half Wave Potentials and Acidity Constants of Perinaphthenones[100]

Compound	$-E_{\frac{1}{2}}$ V(S.C.E)	pK_a (conjugate acid)	pK_a (free radical enol)
Perinaphthenone	0.34	-3.9	9.3
Perinaphthenone-3-carboxylic acid	0.24	-3.4	-
Perinaphthenone-3-carboxylate	0.34	-	9.0
9-hydroxyperinaphthen-1-one	0.62	-4.8	8.0
Perinaphthen-1-one-9-oxide	0.49	-	13.0
Benzanthrone	0.47	-5.8	10.8
Benzalacetophenone	0.52	-7.6	10.4

number in dilute carbon tetrachloride solution than in the condensed phase. Solution data, therefore, gives a more reliable picture of the isolated molecule.

Perinaphthan-1-one (XXXIX) shows a carbonyl stretching frequency of 1677 cm.$^{-1}$ (nujol) and 1690 cm.$^{-1}$ (CCl_4) whereas perinaphthen-1-one (XXXVIII), ν_{CO} 1646 cm.$^{-1}$, shows extensive interaction between the carbonyl group and the tricyclic ring system. As the carbonyl stretching frequency gives evidence of the polarity (single bond character) of the carbonyl group it can be concluded that the molecule is relatively highly

polarised in the ground state. The ultraviolet and visible spectra are not of the same fundamental significance although it can be shown that there is decreased resonance stabilisation in the dihydro derivative as is evident from the decreased intensity and hypsochromic shift (380-400Å) in the absorption band in the 3000-4000Å region.[110]

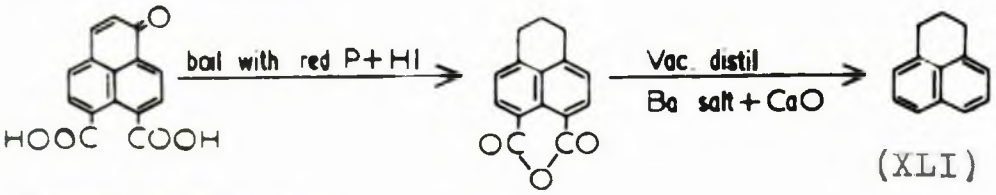
Introduction of a bromine atom at position 2 tends to increase the double bond character of the carbonyl group (1650 cm.$^{-1}$) while the introduction of an α-morpholino (1640 cm.$^{-1}$) or an α-hydroxy group (1630 cm.$^{-1}$) increases the single bond character of the group due to interaction with substituent groups. The literature data together with that compiled by Reid and his associates[111] have been tabulated in Table III.

It can be concluded, from the evidence presented, that the carbonyl group in perinaphthenone has a considerable amount of single bond character in the ground state, e.g., (LI). This is reflected in the high dipole moment, low carbonyl stretching frequency, reversible polarographic reduction, and a ready tendency for the carbonyl oxygen to accept a proton whose charge can be delocalised over the thirteen carbon atom framework.

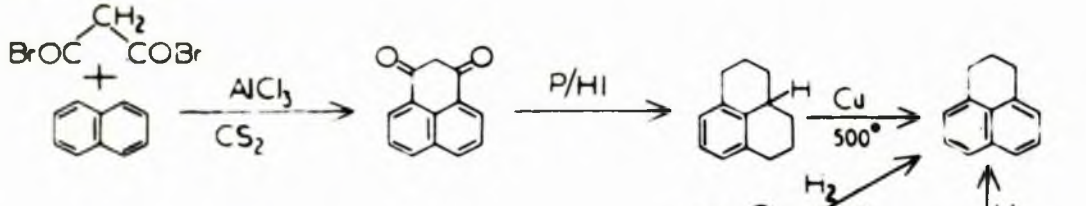
TABLE III

Compound	Wave No.($cm.^{-1}$) Nujol	CS_2	CCl_4	Δ	Reference
Perinaphthenone	1637		1646		110, 111
2-hydroxyperinaphthenone			1630	-16	110, 111
3-hydroxyperinaphthenone	1626			-11	110
9-hydroxyperinaphthenone	1637			0	142
2-hydroxy-3,6,9-trimethyl-perinaphthenone	1608			-29	111
4-methoxyperinaphthenone	1632	1642	1649	+3	108, 111
4,5-dimethoxyperi-naphthenone			1648	+2	111
4,8-dimethoxyperi-naphthenone			1644	-2	111
2-bromoperinaphthenone	1640		1650	+4	110, 111
2-bromo-4-methoxyperi-naphthenone	1628	1646		-9	108
3-methylperinaphthenone			1650	+4	111
4,5-dimethylperinaphthen-one			1649	+3	111
3,6,9-trimethylperi-naphthenone	1639			+2	111
2-piperidinoperinaphthenone	1632		1622	-24	110
2-morpholinoperinaphthenone	1637		1640	-6	110
3-piperidinoperinaphthenone	1633			-4	110
3-morpholinoperinaphthenone	1633		1640	-6	110

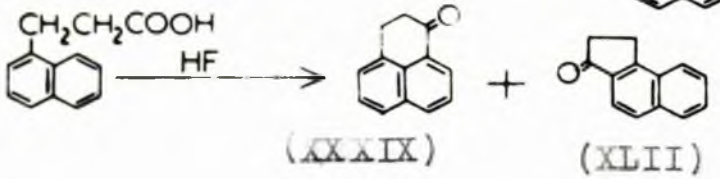
Isolation of perinaphthane

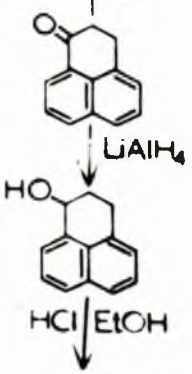


Syntheses of perinaphthane

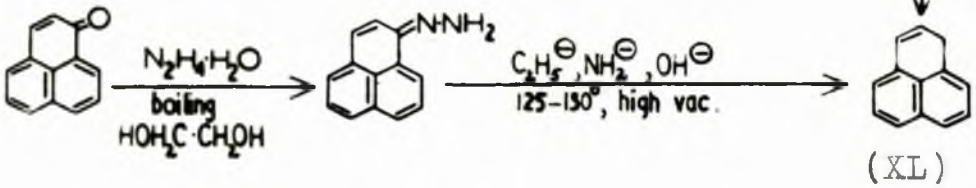


Synthesis of perinaphthanone





Syntheses of perinaphthene



(XL)

Table III (Contd.)

6,7-aceperinaphthenone	1639	1649	+5	111, 112
2,3-cyclopentenoperi-naphthenone	1634		-3	111
7,8-cyclopentenoperi-naphthenone	1639		+2	111
5-oxo-5H-benzo[cd]pyrene	1639		+2	111
Benzanthrone	1649	1654	+12	108

Δ is the difference (in $cm.^{-1}$) between the carbonyl stretching frequency of perinaphthenone and that of the derivative.

A.11,1V. Perinaphthane: Isolation and Properties.

When pyrenic acid (perinaphthenone-6,7-dicarboxylic acid) was reduced with red phosphorus and hydrogen iodide the product, after decarboxylation, was shown to be perinaphthane (XLI).[113] The first synthesis of this hydrocarbon was accomplished by Fleischer and Retze[114] from naphthalene and malonyl bromide. The initial product was perinaphthan-1,3-dione which was then over-reduced by red phosphorus and hydrogen iodide at 160-180°, followed by dehydrogenation over copper. Reduction of perinaphthenone with zinc and hydrochloric acid gives a low yield of perinaphthane.[71] Pressure hydrogenolysis of (XXXVIII),

in the presence of copper chromite catalyst, gives a mixture of perinaphthane and perinaphthanol; the conditions can be modified to give the former in 70% yield.[76]

The method now used for the production of (XLI) in quantity is the catalytic hydrogenation of perinaphthanone.[118] The hydrocarbon has also been prepared by the hydrogenation of perinaphthene (XL).[79] Several alkylated perinaphthanes have been prepared by the Clemmensen-Martin reduction of the corresponding perinaphthanones.[116-118] Boekelheide and Larrabee[124] have also described the preparation of several monomethyl-perinaphthane derivatives.

A.11,V Perinaphthan-1-one: Preparation and Properties.

There was considerable confusion in the earlier literature concerning the preparation and purity of the ketone obtained by the cyclisation of the acid chloride of β-(1-naphthyl)-propionic acid. Fieser and Gates[126] showed that the difficulties were due to the interfering dehydrogenation reaction caused by the cyclisation reagent used and that this could be avoided by use of anhydrous hydrogen fluoride. Perinaphthan-1-one (XXXIX) was obtained in 81% yield together with a small quantity of (XLII), the product of β-cyclisation. This is the most satisfactory way of preparing the saturated ketone in quantity.

Perinaphthanone is reduced to perinaphthane by the Clemmensen reduction. Reduction of the ketone using 'old' Raney nickel forms perinaphthanol in good yield, but unless the catalyst is satisfactorily deactivated much phenolic material results. The alcohol is best prepared by lithium aluminium hydride reduction of (XXXIX).[108]

A.11,V1. Perinaphthene: Preparation and Properties

The parent hydrocarbon (XL) was first prepared in 1944 by Lock and Gergely.[79] They heated the hydrazone of perinaphthenone, in high vacuum at 120-130°, in the presence of ethoxide hydroxide or amide ions when perinaphthene was obtained in low yield as colourless plates. Their product was characterised by reduction to perinaphthane (XLI) and atmospheric oxidation to perinaphthenone. Fieser and Newton[88] attempted to dehydrate perinaphthanol by means of sodium bisulphite, the Tschugaeff reaction or by way of the chloride to perinaphthene but were unsuccessful. However they successfully dehydrated 1-methyl-perinaphthan-1-ol to a methylperinaphthene using ethanolic hydrogen chloride. When this reaction was carried out on perinaphthanol by Bockelheide and Larrabee[108] they obtained perinaphthene in 65-85% yield. They subsequently made use of this reaction in their studies of

isomerism in the perinaphthene series.[124]

Perinaphthene is acidic, forming a lithium salt on treatment with phenyl lithium in ether. Exchange reactions show that it is more acidic than triphenylmethane and less so than cyclopentadiene. The lithio salt, which is bright red, can be alkylated with methyliodide to yield a methylperinaphthene whose structure will be discussed later (A.11,V11). With potassium methoxide, the hydrocarbon yields a potassium salt. These reactions show that the molecule contains an acidic hydrogen atom and that the perinaphthenide anion (XXXV) must represent a stable π-electron system of 14 π-electrons delocalised over a tricyclic framework of thirteen carbon nuclei

Perinaphthene will react with several reagents, including high potential quinones, to form the perinaphthyl radical (XXXVI).[126,127] These reactions corresponding to the loss of a hydrogen atom with the formation of a π-electron system containing thirteen π-electrons delocalised over the tricyclic system.

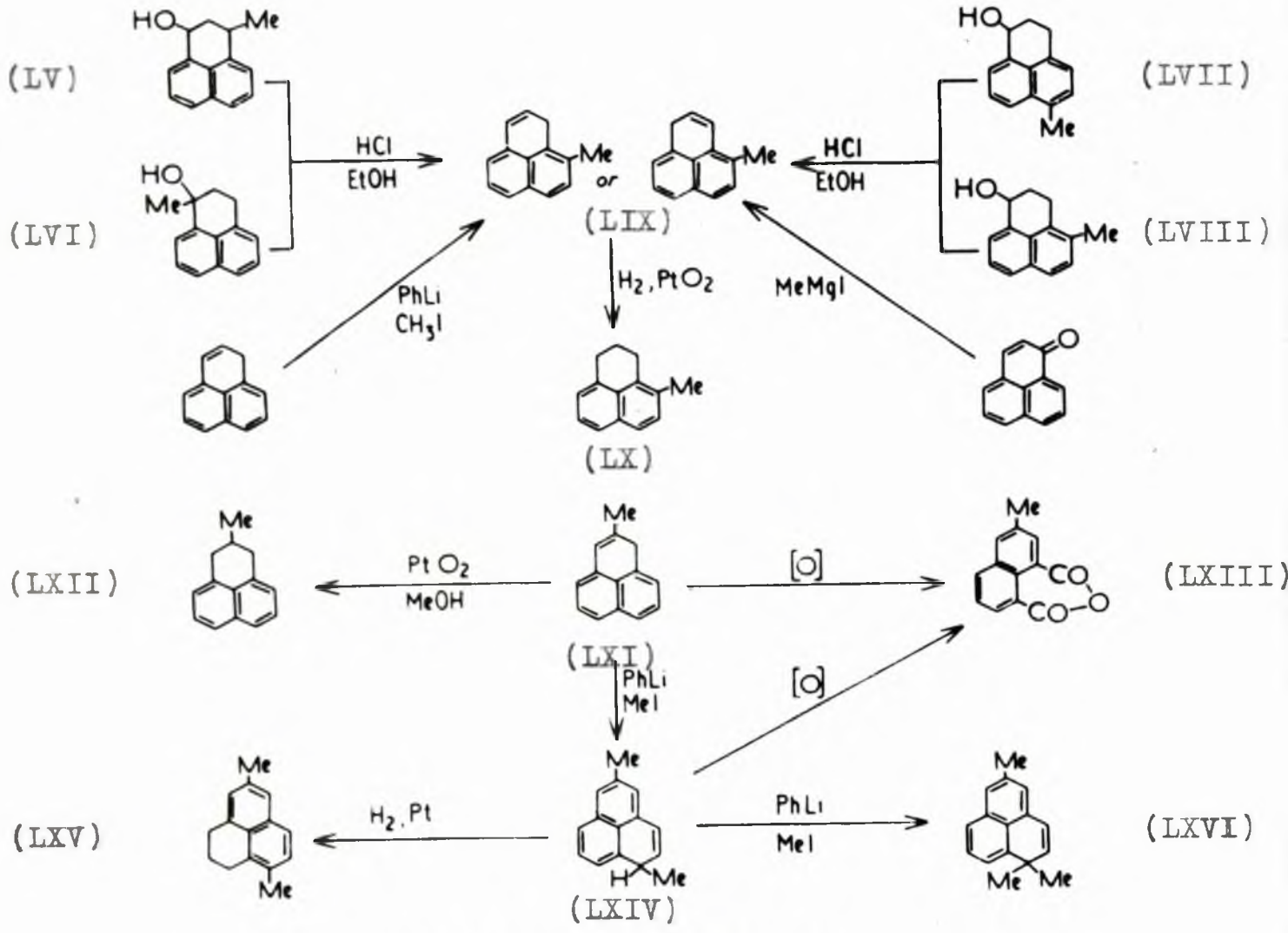
The hydrocarbon (XL) reacts with triphenylmethyl perchlorate, and with high potential quinones in the presence of perchloric acid to form the perinaphthenylium cation.[87,127]

This reaction, which corresponds to hydride exchange, leaves the tricyclic system with twelve π-electrons delocalised over thirteen carbon atoms. It can therefore be concluded that considerable delocalisation energy must be invested in all three states, namely, the anion, cation and radical.

A.11.V11. Isomerisation in the Perinaphthene Series.

In 1938, Klyne and Robinson[128] suggested that, in view of the high symmetry of the perinaphthene nucleus, a monoalkylperinaphthene should exist in six equivalent forms corresponding to the six positions possible for the 'extra' hydrogen atom, i.e., 1-, 3-, 4-, 6-, 7-, and 9-. Their attempts to prepare 9-methyl- and 3,9-dimethylperinaphthene in order to demonstrate prototropy in this system were unsuccessful.

Evidence that perinaphthene derivatives might be readily isomerised was first obtained by Fieser and Gates[128] who found that the reaction product from perinaphthanone and o-chlorophenylmagnesium bromide after dehydration, hydrogenation and treatment with cyanide gave two products (LII) and (LIII). It was suggested that these might have arisen by bond migration but as the intermediate perinaphthene derivative was not isolated and as the results can also be explained on the basis of a 1,4 or a 1,6 Grignard addition isomerisation was not definitely established.



Isomerisation of the methylperinaphthenes.

A similar rearrangement was observed by Badger, Carruthers and Cook.[129] The reaction between 4-methoxyperinaphthanone and o-chlorophenyl magnesium bromide yielding a carbinol which, on treatment with iodine in boiling petrol or cold, dilute methanolic hydrochloric acid, underwent dehydration, rearrangement and demethylation to yield the ketone (LIV) as the sole product. This result supports the conception of Klyne and Robinson of the tautomeric character of the perinaphthene ring system.

The first detailed study of the isomerism in the alkylperinaphthenes was carried out by Bockelheide and his associates[108,130] in 1950. The alcohols (LV)-(LVIII) were dehydrated with the intention of preparing a series of monomethylperinaphthenes with the methyl groups in positions 1-,3-, 7-, and 9-, respectively. All these dehydrations lead to the same hydrocarbon which was assigned the structure 4(9)-methylperinaphthene since 4-methylperinaphthane was obtained on catalytic hydrogenation.[108] The possibility that isomerisation was effected by the catalyst was not considered by the above authors.

The reaction of methyl magnesium iodide with perinaphthenone has been reported to yield a methylperinaphthene;[97] the same hydrocarbon was also prepared by Fieser[98] from perinaphthanone and methyl magnesium iodide. The product was

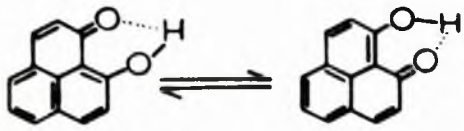
considered to be 1-methyl perinaphthene. Bockelheide repeated the reaction described by Craig and showed that the product was actually 4(9)-methylperinaphthene (LIX). The reaction between perinaphthene, phenyllithium and methyl iodide also gave the hydrocarbon (LIX) in 85% yield. Since the initial product of this reaction must have been 1-methylperinaphthene; isomerisation must have occurred even although no temperature higher than refluxing ether was attained and no acid was present.

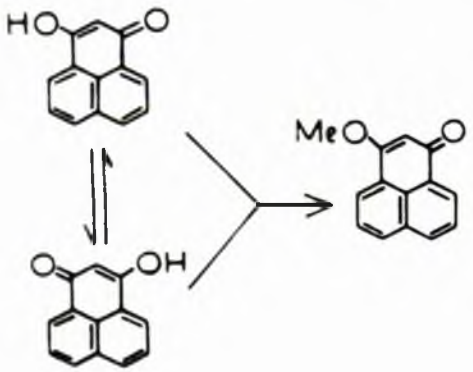
Since all syntheses designed to put a methyl group into positions 1-, 3-, 6-, 7-, and 9- of the perinaphthene ring invariably gave (LIX) it was of interest to see whether a similar behaviour would be found in the alternative series of methyl perinaphthenes where the positions possible for the methyl groups are 2-, 5-, and 8-. Dehydration of 2-methyl perinaphthane-1-ol gave a hydrocarbon which was shown to be 2-methylperinaphthene (LXI) since catalytic dehydrogenation yielded 2-methylperinaphthane (LXII). Oxidation of (LXI) did not give the expected naphthalic anhydride but, instead, 3-methylnaphthalic anhydride (LXIII) was obtained.[130] This result emphasises the tautomeric nature of the ring system; oxidation and reduction attacking different tautomers, preferentially.

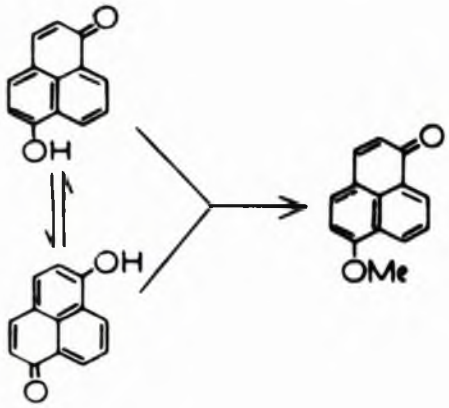
Boekelheide and Goldman studied the alkylation of 2-methylperinaphthene with phenyllithium and methyl iodide.[180] When the hydrocarbon (LXII) was thus treated a dimethyl perinaphthene was obtained in good yield. Synthetic and degradative studies showed that the second methyl group entered in position 6 with respect to the methyl group in position 2 and these workers therefore formulated their product as 1,5-dimethylperinaphthene (LXIV). Once again oxidation and reduction attack different tautomers, oxidation yielding 3-methyl naphthalic anhydride and reduction 4,8-dimethyl-perinaphthene (LXV).

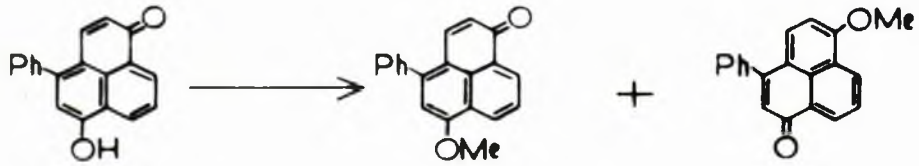
A trimethyl derivative is obtained, in good yield, when (LXIV) is treated with phenyllithium and methyl iodide. It has been formulated as 1,1,5-trimethylperinaphthene since it resisted further alkylation which the authors considered to be due to the formation of a gem-dimethyl group; this conclusion was drawn without any degradative or synthetic evidence. 3,6,9-trimethyl perinaphthene has been prepared in this laboratory and it has been shown that the presence of three methyl groups suppresses the ionisation of the hydrocarbon to such an extent that the anion cannot be prepared.[181] It would seem, therefore, that the failure to methylate (LXVI) is

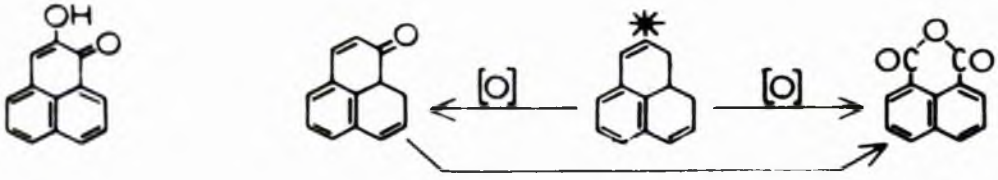
(LXVII) (LXVIII)











not necessarily due to the presence of a gem dimethyl group and so the structure of this compound remains uncertain. The presence or absence of such a grouping in this molecule could be determined if the ability of the hydrocarbon to form a stable cation was examined.

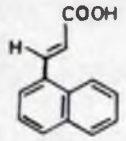
The tautomeric behaviour of certain hydroxyperinaphthenones was first considered by Cooke and Segal in 1955.[138] These compounds can be divided into three classes depending on the position of the hydroxyl group.

(i) 2-, 5-, 6-Hydroxyperinaphthenones which cannot show tautomerism. Of these, only 2-hydroxyperinaphthenone is known at present and it forms one acetate and one benzoate.[88,116]

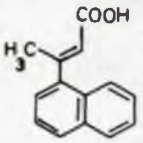
(ii) 4-, 7-Hydroxyperinaphthenones. The former compound has been prepared in an unambiguous manner.[84,138] Methylation of (LXVII) with dimethylsulphate and potassium carbonate in acetone leads to a mixture of products which have been separated and shown to be 4- and 7-methoxyperinaphthenone by degradative experiments. 4-Methoxyperinaphthenone has also been synthesised by alternative routes.[129,137] Evidently the compound formulated as (LXVII) can also react as 7-hydroxy perinaphthenone (LXVIII).

(iii) Because of their symmetry 3-, 6-, and 9-hydroxyperinaphthenone can only give rise to one monomethyl ether. 9-Hydroxyperinaphthenone resists methylation due to strong hydrogen bonding.[86,98,182] Both 3-, and 6-methoxyperinaphthenone have been characterised.[183,184,188] In derivatives of these compounds, where the symmetry has been destroyed, tautomerism is again possible. Thus 4-phenyl-6-hydroxyperinaphthenone gives rise to two monomethyl ethers.[182]

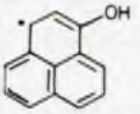
An elegant demonstration of the equivalence of the 2-, 5-, and 8-positions in perinaphthene has been made by Nakasaki in 1957.[186] He synthesised perinaphthene -2-^{14}C, of specific activity 1.42 μc/μm., which was then oxidised by potassium permanganate in acetone to yield naphthalic anhydride of specific activity 0.96 μc/μm. To eliminate the possibility that the loss in radioactivity was due to the formation of the symmetrical perinaphthenide anion, Nakasaki oxidised a sample of the radioactive hydrocarbon to perinaphthenone which was then further oxidised to naphthalic anhydride with an activity of 0.92 μc/μm. This loss of one-third of the radioactivity on oxidation proves the ready tautomerism of the molecule making the 2-, 5-, and 8-positions equivalent.



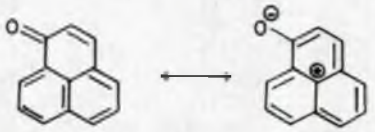
(XLIII)



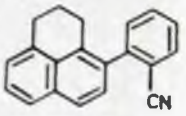
(XLIV)



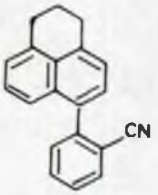
(L)



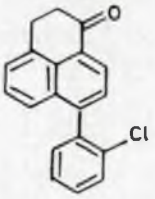
(XXXVIII) (LI)



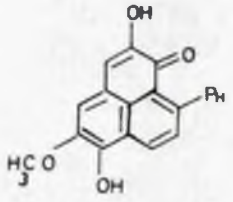
(LII)



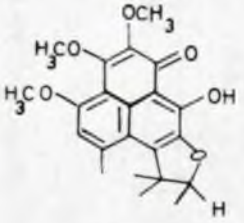
(LIII)



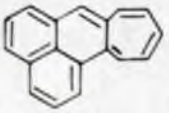
(LIV)



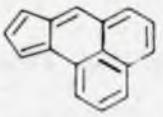
(LXIX)



(LXX)



(LXXI)



(LXXII)

A.11.V111. The Occurrence of Perinaphthene System in Nature.

Until recently the perinaphthene system was of no great interest in the chemistry of natural products except as a dehydrogenation fragment from natural products. The $C_{17}H_{20}$ fragment from the dehydrogenation of agathic acid was shown to be 1,1,4,7-tetramethylperinaphthane by Buchi and Pappas[138] who also synthesised the hydrocarbon. This hydrocarbon has since been obtained from the dehydrogenation of two other terpenic acids, namely, ostavic[139] and eperyic acid.[140]

The first actual occurrence of the ring system in nature was reported by Cooke and Segal[141] in 1955. The bulbous root of haemodorum corymbosum Vahl yielded a red crystalline glycoside, haemocorin, which hydrolysed readily to cellobiose and a purple-red aglycone eventually formulated as 2,6-dihydroxy-5-methoxy-9-phenylperinaphthen-1-one (LXIX) on the basis of its chemical properties, degradative studies and spectroscopic evidence.[141,132,84]

The structure of the fungal pigment, atrovenitin. has recently been established.[142] It has been characterised by Barton, Raistrick and their co-workers as the substituted 9-hydroxyperinaphthenone (LXX) or tautomer. The fungal pigments, herqueninone and norherqueninone have been isolated

from a closely related species and desoxynorherquinone, obtained by zinc acetic acid reduction of norherqueninone was shown to be identical with atrovenetin (LXX).

A.111. Stable π-Electron Systems and New Aromatic Structures.[68,143]

Aromatic character is associated with stable π-electron systems that either exist in the ground state or are capable of development in the transition state. The behaviour of azulene in its reactions indicate that importance must be attached to the stability of the π-electron sextets associated with the five or the seven-membered rings during reaction. The concept of azulene as derived by fusion of a cyclopentadienide anion with a cycloheptatrienide cation has been useful in the search for other aromatic systems. In particular, the perinaphthene nucleus appeared to be a satisfactory replacement for either of the rings in azulene. The outstanding feature of perinaphthene chemistry is the ability of the three six-membered rings to function as a structural unit over which fourteen, thirteen or twelve π-electrons can be localised during reaction (A.11,V1)..

As a result of the recognition of the stable structures (XXXV) and (XXXVII) several new types of potential aromatic systems may be arrived at theoretically. The most important of these are:

(i) Cyclohepta[a]perinaphthene (LXXI) which may be derived by the fusion of a seven-membered ring to the perinaphthene nucleus. In the completely polarised form of this hydrocarbon, fourteen π-electrons are delocalised over the perinaphthene moiety while a sextet of electrons is associated with the seven-membered ring.

(ii) Cyclopenta[a]perinaphthene (LXXII) which results from the fusion of the perinaphthene nucleus to a five-membered ring. The polarisation of this molecule will be in the opposite direction to that in (LXXI). A sextet of electrons is associated with the five-membered ring while twelve π-electrons are delocalised over the perinaphthene ring which assumes the form of the perinaphthenylium cation

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PART B

B1. Synthetic Studies in Perinaphthene Chemistry

B1,1. Introduction

The best and most general method for the preparation of perinaphthan-1-ones involves the cyclisation, best by hydrogen fluoride, of substituted β-(1-naphthyl)-propionic acids. These, in turn, are prepared by the malonic ester synthesis from substituted 1-chloromethylnaphthalenes. In the present work new substituted perinaphthan-1-ones have been prepared by a modification of this route which extends the scope of the reaction. A large number of substituted 1-halomethyl-naphthalenes can be obtained, in high overall yield, by successive formylation (Vilsmeier), reduction with lithium aluminium hydride, and treatment of the alcohols with phosphorus trihalides.

Substituted perinaphthan-1-ols are thence prepared by reduction of the corresponding saturated ketones with lithium aluminium hydride. In many cases the substituted perinaphthene can be obtained by dehydration of the alcohol with ethanolic hydrogen chloride.

B1,11 The Synthesis of 4(9)-Methylperinaphthene

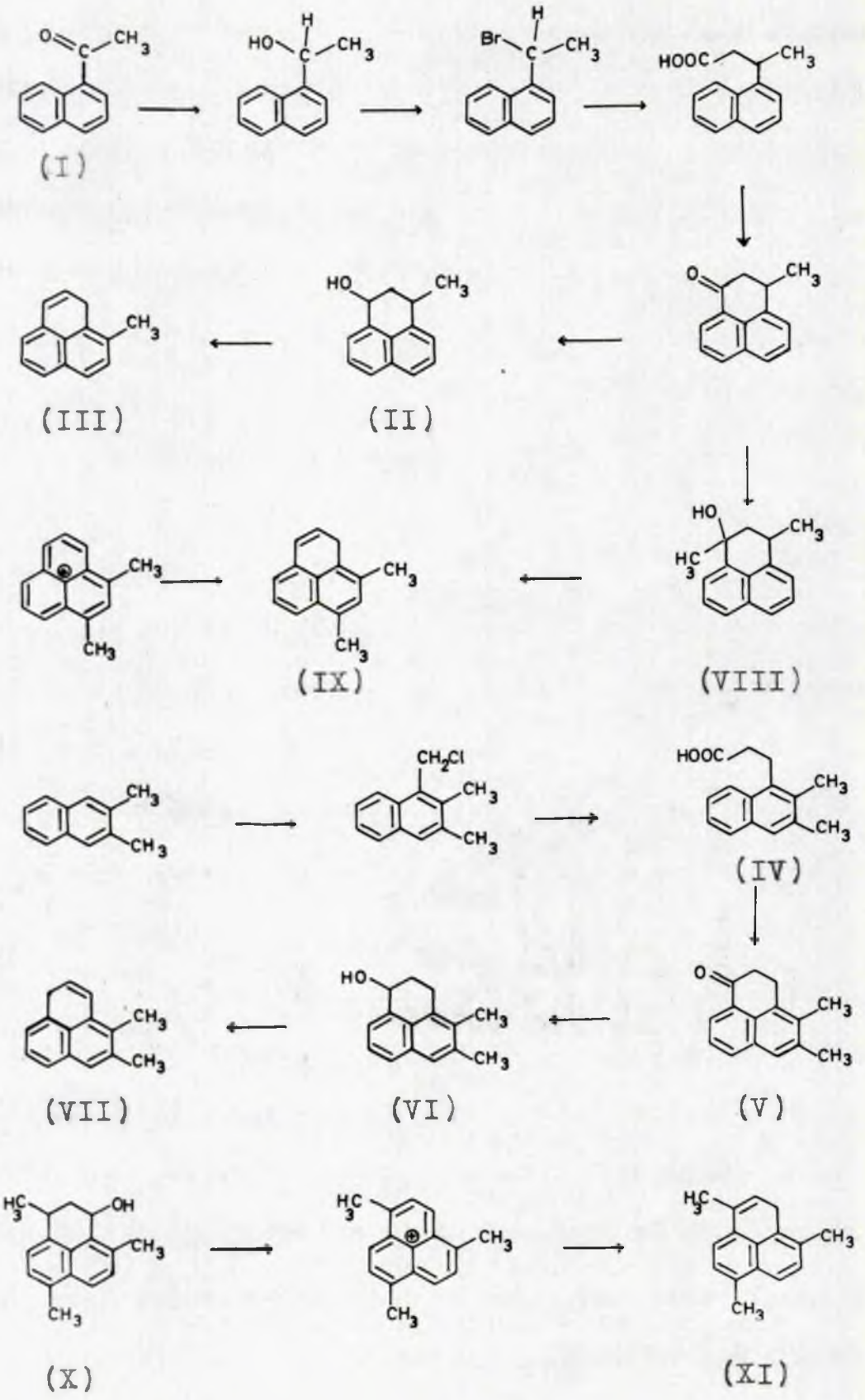
The structure of this hydrocarbon was established in 1950 by Boekelheide and Larrabee.[1] From their work the most attractive route appeared to be that involving the dehydration of 3-methylperinaphthan-1-ol (II) which had been obtained

in an overall yield of 25% in a six-stage synthesis from α-acetylnaphthalene (I). It was considered that some modifications of the synthetic route would increase the overall yield. In our work α-acetylnaphthalene was prepared by the addition of α-naphthyl magnesium bromide to acetic anhydride at -80° according to the general procedure of Newman and Smith.[2] The ketone was reduced quantitatively with lithium aluminium hydride to methyl-1-naphthyl carbinol which was also prepared by the method of Pickard and Kenyon.[3] Phosphorus tribromide was used to convert this alcohol to the corresponding bromomethylnaphthalene which was then transformed to 3-methylperinaphthan-1-ol (II) by the general procedure outlined in the previous section. The overall yield was 44%.

Dehydration of (II) gave 4(9)-methylperinaphthene (III) in 80% yield. This hydrocarbon has also been prepared by the dehydration of 1,4- and 6-methylperinaphthan-1-ols[1] (A.11,V11) and by the dehydration of the alcohols obtained by the alkylation of perinaphthan-1-one[4] and perinaphthen-1-one[5] by methyl magnesium iodide. It has also been obtained by alkylation of the perinaphthenide anion with methyl iodide.

B1,111 <u>The Synthesis of 4,5-Dimethylperinaphthene</u>.

4,5-Dimethylperinaphthan-1-one (V) was prepared essentially as described by Buu-Hoi and Cagnaint[6]


(I)
(II)
(III)
(IV)
(V)
(VI)
(VII)
(VIII)
(IX)
(X)
(XI)

except that the cyclisation of (IV) was effected by hydrogen fluoride. Reduction of (V) by lithium aluminium hydride gave 4,5-dimethylperinaphthan-1-ol (VI) in 90% yield. Dehydration of (VI) yielded a low melting hydrocarbon characterised by its trinitrobenzene derivative. The hydrocarbon was initially obtained as a colourless oil which slowly crystallised but it decomposed rapidly in moist air.

The dehydration product has been formulated as 4,5-dimethylperinaphthene (VII) although the 8,9-isomer must be formed initially. It is possible that the hydrocarbon is actually the 2,3-isomer since studies on the isomerisation of monomethylperinaphthenes[1] have shown that experiments designed to put a methyl group in the 2,5 or 8 position result in a 2-methyl derivative but the above experiments also showed that attempts to put a methyl group in positions 1,3,4,6 always lead to a 4 methyl derivative. It is impossible to differentiate between these three structures chemically but it would be possible to distinguish between the 2,3 and the other isomers by nuclear magnetic resonance. It is possible that the compound exists as an isomeric mixture. The fact that the hydrocarbon is obtained as an oil which gradually crystallises suggests that there may be a slow conversion from the first formed 8,9 to another isomer.

B1,IV 4,6-Dimethylperinaphthene.

1,3-Dimethylperinaphthan-1-ol (VIII) is obtained by the alkylation of 3-methylperinaphthan-1-ol with methyl magnesium iodide. This alcohol gives a hydrocarbon which crystallises from petrol as colourless platelets. It forms an orange-red trinitrobenzene derivative which is characteristic of perinaphthene hydrocarbons. It has an unusually high melting point for a simple perinaphthene and the hydrocarbon was at first thought to be a dimer. The same compound is obtained by lithium aluminium hydride reduction of 1,3-dimethylperinaphthenylium perchlorate. The analyses of the salts formed from 1,3-dimethylperinaphthanol, its dehydration product, and the hydride reduction product from 1,3-dimethylperinaphthenylium perchlorate show that the same compound is formed in all cases. The analytical and molecular weight data also support its formulation as the monomer. No reasons can be advanced for its high melting point, 151-153°, or its low solubility in petrol, ethanol and acetonitrile compared with the other simple alkyl perinaphthenes so far prepared.

The hydrocarbon has been formulated as the 4,6-isomer (IX) rather than 1,3 from analogous reasoning to that advanced in B1,III for 4,5-dimethylperinaphthene.

B1,V 3,6,9-Trimethylperinaphthene.

3,6,9-Trimethylperinaphthan-1-ol (X) was prepared from 1,6-dimethylnaphthalene in a seven-stage synthesis as described by Bonthrone[7] and thence converted into 1,4,7-trimethylperinaphthenylium perchlorate (CIV,II). Reduction of this salt gave a hydrocarbon, m.p. 59-60°, shown to be 3,6,9-trimethylperinaphthene (XI). It is the only perinaphthene hydrocarbon in which the position of the double bond in the 'peri ring' can definitely be located. It's NMR spectrum shows the presence of a methylene group and a methyl group in the ring and so the latter must be in the 3 position.

Hydride reduction of the salt is the best method of preparation of this hydrocarbon. Dehydration of (X) invariably yields an oil which may be an isomeric mixture or a mixture of the hydrocarbon and its dimer. The low yield of salt (37%)[7,46] obtained from this oil compared with that by dehydration-dehydrogenation of (X), i.e., 64% tends to support the latter viewpoint.

B1,VI. 1,2-Dihydro-5H-cyclopenta[gh]perinaphthene.

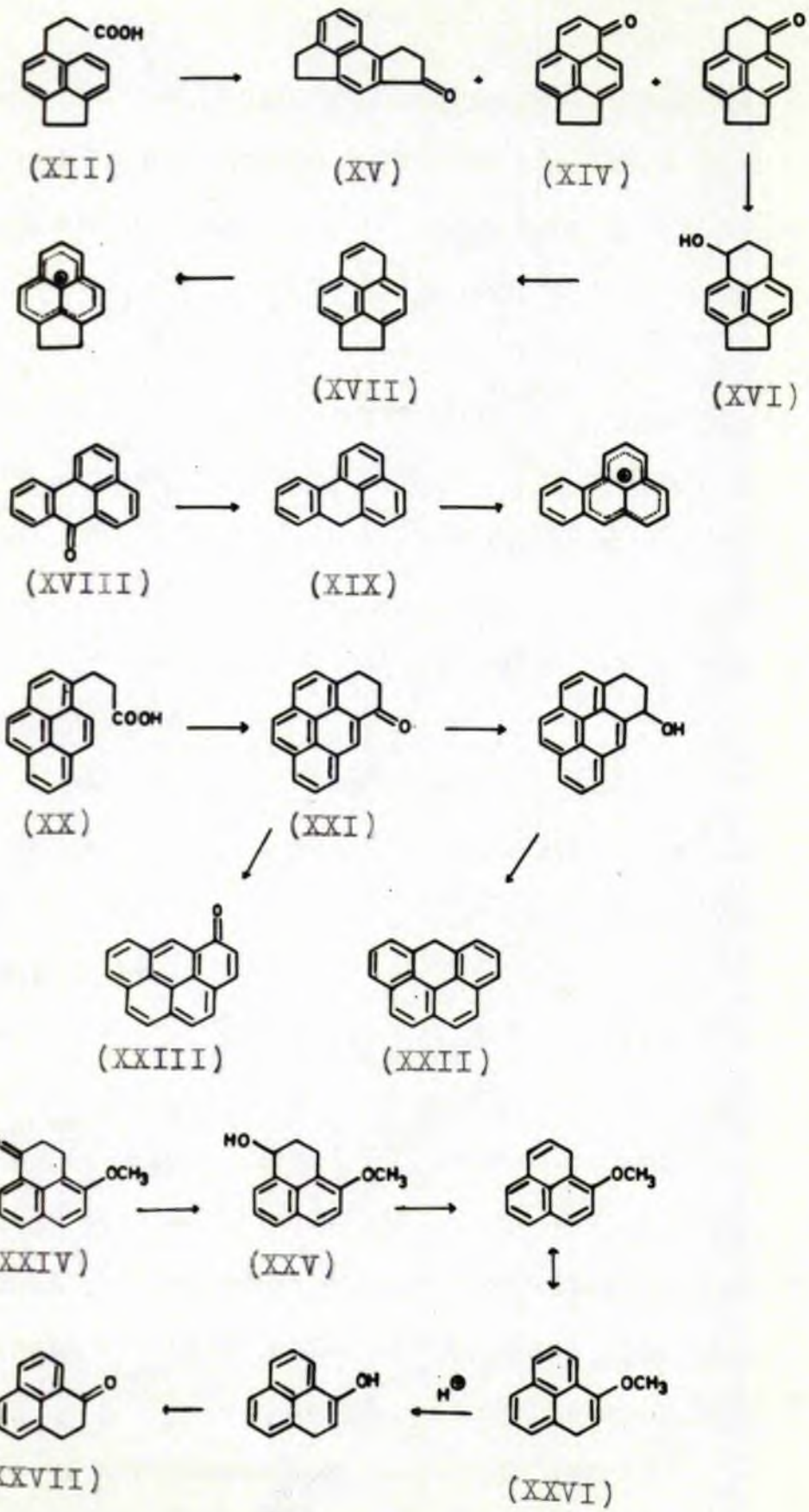
The synthesis of 1,2,5,6-tetrahydro-7-oxo-7H-cyclopenta[gh]perinaphthene (XIII) has been described by several authors.[8,9,10]

The route used in the present work was a modification of that due to Fieser and Jones.[8] These authors report the preparation of 5-formylacenaphthene in 85% yield. The best yield we obtain in this formylation reaction was 30% (C,V,1).

The cyclisation of β-(5-acenaphthenyl)-propionic acid has been effected in several different ways. Buu-Hoi and Cagnaint[9] cyclised the acid chloride of (XII) with aluminium chloride. Hannaberg and his co-worker[10] examined two methods. Using a mixture of phosphorus pentachloride and stannic chloride they obtained a mixture of (XIII) and 4,5,8,9-tetrahydro-6-oxo-6H-cyclopenta[e]acenaphthylene (XV). When polyphosphoric acid was employed a mixture of 1,2-dihydro-5-oxo-5H-cyclopenta[gh] perinaphthene (XIV) and (XV) was obtained. Fieser and Jones[8] used hydrogen fluoride and obtained a green tar from which (XIII) was isolated in 40% yield.

In our present work the acid (XII) was cyclised with hydrogen fluoride and a pale yellow solid was obtained. This proved to be a mixture of three ketones which were separated by chromatography on alumina when (XIII), (XIV) and (XV) were obtained in 60%, 1% and 3.4% yield, respectively.

The saturated ketone on reduction with lithium aluminium hydride gave a mixture of 1,2,5,6-tetrahydro-7-hydroxy-7H-cyclopenta[gh]perinaphthene (XVI) and 1,2-dihydro-


COOH
O
O
(XII)
(XV)
(XIV)
(XIII)
HO
(XVII)
(XVI)
(XVIII)
(XIX)
COOH
O
OH
(XX)
(XXI)
O
(XXIII)
(XXII)
O
OCH3
HO
OCH3
OCH3
(XXIV)
(XXV)
O
OH
H⊕
OCH3
(XXVII)
(XXVI)

-5H-cyclopenta[gh]perinaphthene (XVII). The hydrocarbon (XVII) must have been formed by dehydration of the carbinol (XVI) in the working up procedure. The mixture was readily separated by fractional crystallisation.

The hydrocarbon (XVII) appears to be quite stable. Unlike perinaphthene it does not form an anion with potassium methoxide nor a radical with N-bromosuccinimide. Its solution become green on prolonged standing. It undergoes hydride exchange with trityl perchlorate and with T.B.Q. in the presence of perchloric acid but the product is unstable.

Bl,VII. Benzanthrone (benzo[b]perinaphthene).

Benzanthrone (XVIII) shares many of the properties of perinaphthenone. It is weakly basic, being soluble in concentrated sulphuric acid. Its carbonyl group shows infrared absorption at 1649 cm.$^{-1}$ [11] Grignard reagents add 1,4 to benzanthrone.[12] Red phosphorus and hydrogen iodide reduce (XVIII) to 1,10-trimethylenephenanthrene.[13] This reaction parallels the reduction of perinaphthenone to perinaphthane (1,8-trimethylene naphthalene) by the same reagents. Benzanthrone is formed in 50% yield when (XVIII) is reduced by aluminium isopropoxide,[14] a process which shows analogy with the lithium aluminium hydride reduction of perinaphthenone.[15]

The reduction of benzanthrone by lithium aluminium hydride and aluminium chloride forms (XIX) in greater than

80% yield.[16] The hydrocarbon oxidises slowly in air to benzanthrone, a reaction which can be compared with the aerial oxidation of perinaphthene. Benzanthrene forms an unstable salt by hydride exchange with trityl perchlorate.

B1,VIII 6H-Benzo[cd]pyrene

This hydrocarbon has been prepared and some of its properties investigated. It could be considered as a perinaphthene derivative, i.e., naphtho[4,4a,5-bcd]perinaphthene but in view of the molecular complexity it is best to regard it as a new condensed system.

The ketone, 5-oxo-5H-3,4-dihydrobenzo[cd]pyrene (XXI) was prepared by the cyclisation of 3-pyrenylpropionic acid (XX) which was synthesised by the method of Bachmann.[17] Dehydration of the carbinol obtained by lithium aluminium hydride reduction of (XXI) gave 6H-benzo[cd]pyrene (XXII). The hydrocarbon forms a stable cation by hydride exchange. In ability to form an anion and a radical are currently being investigated.

The analogue of perinaphthenone in this series, 5-oxo-5H-benzo[cd]pyrene (XXIII), dissolves in concentrated hydrochloric acid to form a green cation. Its carbonyl function absorbs at 1639 $cm.^{-1}$

B1,IX The Synthesis and Dehydration of 4-methoxyperinaphthanol.

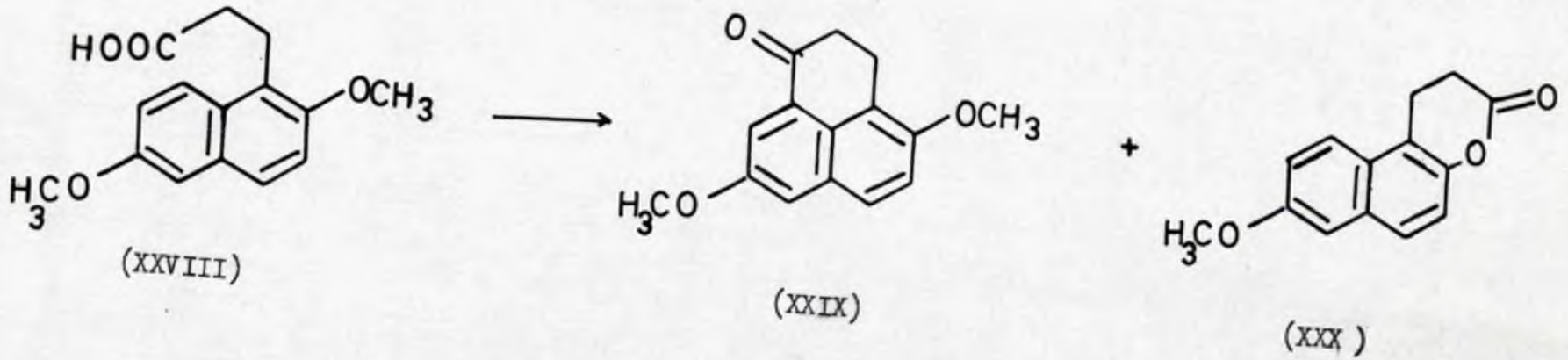
The preparation of 4-methoxyperinaphthan-1-one was

reported by Barger and Starling[18] but it was later shown that their product was a mixture of perinaphthenone and 4-methoxyperinaphthenone.[19] Badger, Carruthers and Cook[19] showed that the interfering dehydrogenation and demethylation reactions could be avoided by using hydrogen fluoride for the cyclisation.

The saturated ketone (XXIV) was prepared essentially as described by these authors[19] except that the halomethylnaphthalene was synthesised by an alternative route since we obtained variable results in the chloromethylation reaction. 4-Methoxyperinaphthan-1-ol (XXV) was obtained by the lithium aluminium hydride reduction of (XXIV).

Badger and co-workers[19] were unsuccessful in their attempt to synthesise 10-methoxy-3,4-benzpyrene from 4-methoxyperinaphthan-1-one and considered that their failure was due to tautomerism of the type postulated by Klyne and Robinson.[20]

An experiment which would have lent strong support to their conclusions on the rearrangement and demethylation reaction was not considered. This was the dehydration of (XXV) This reaction has now been carried out and perinaphthan-1-one (XXVII) was the sole product. The initial dehydration product would be 9-methoxyperinaphthene which is tautomeric with 3-methoxyperinaphthene (XXVI). This latter compound is an



(XXVIII) (XXIX) (XXX)

αβ-unsaturated ether which would undergo ready acid hydrolysis to 3-hydroxyperinaphthene, tautomeric with perinaphthan-1-one (XXVII). This result confirms experimentally the idea that alkoxy-substituted perinaphthenes would be unstable due to the mobility of the double bond system in perinaphthene.

B1,X. 4,8-Dimethoxyperinaphthan-1-ol.

This compound was prepared from 2,6-dihydroxynaphthalene by an eight-stage synthesis.

β-(2,6-Dimethoxy-1-naphthyl)-propionic acid (XXVIII) was cyclised by hydrogen fluoride. Although the β-position of the naphthalene nucleus was substituted a mixture was obtained. The infrared spectrum showed two carbonyl peaks, one at 1681 cm.$^{-1}$ expected of a perinaphthan-1-one, and another at 1730 cm.$^{-1}$ which would accord with either a ketone in a five-membered ring or a δ-lactone. The by-product was shown to be a δ-lactone by its solubility in warm, aqueous alkali. The band at 1730 cm.$^{-1}$ was absent after treatment of the product with the latter reagent The lactone must have been formed by elimination of the elements of methanol from (XXVIII) while dissolved in the hydrogen fluoride. The proportion of δ-lactone formed was small, and not enough was isolated for characterisation. Its structure is assumed to be (XXX).

B1,XI. 4,5-Dimethoxyperinaphthan-1-ol.

2,3-Dimethoxynaphthalene was prepared by the method of

Freidlander and Silberstern.[21] Attempts to formylate this compound produced an oil which, from the yield of the 2,4-dinitrophenylhydrazone, corresponded to a 60% yield of aldehyde. Buu-Hoi and co-workers[22] have reported the formylation of this compound in 23% yield. The oil reacted with malonic acid in the presence of piperidine to give the corresponding acrylic acid but the reaction was not further investigated.

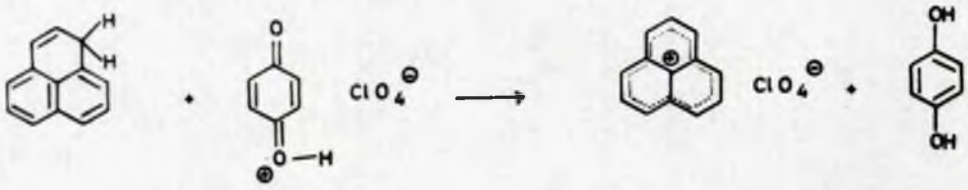
Chloromethylation takes place at room temperature, and the crude reaction product alkylated with diethyl malonate. Hydrolysis gave the substituted malonic acid in 37% overall yield. This acid was decarboxylated to β-(2,3-Dimethoxy-1-naphthyl)-propionic acid which was cyclised by hydrogen fluoride to 4,5-dimethoxyperinaphthan-1-one. 4,5-Dimethoxyperinaphthan-1-ol was obtained by reduction of this ketone.

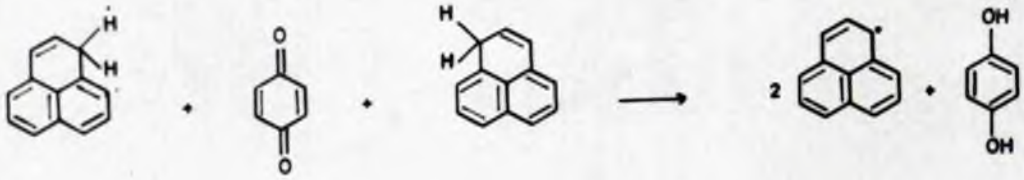
B11. The Hydride Transfer Reaction and the Preparation of Stable Organic Cations.

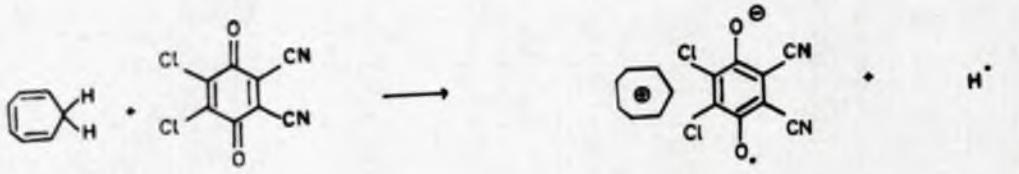
B11,1. Triphenylmethyl Perchlorate and Hydride Transfer.

In view of certain comments made by Dauben and his coworkers[23] on the preparation of trityl perchlorate for use in hydride exchange reactions it is pertinent to discuss some of our observations on this subject. We have prepared this salt on many occasions by a method which is essentially that of Hofmann and Kirmreuther.[24] Triphenyl carbinol is dissolved in a mixture of glacial acetic acid and acetic anhydride (1:1) and the mixture allowed to cool ca.50°. A solution of perchloric acid (72%) in the same volume of acetic acid is added dropwise with cooling to keep the temperature below 50°. The reaction mixture is allowed to cool to room temperature and the product filtered off with slow suction to ensure that the crystals do not become completely free of solvent. The product is then washed with anhydrous ether and finally petrol to remove all traces of acetic acid, anhydride and covalent material. The reddish yellow platelets are then dried in an evacuated dessicator over P_2O_5/KOH for an hour. This product can be stored for long periods in an evacuated dessicator and it can conveniently be weighed in a weighing bottle. We have had no difficulty with this preparation nor with its use in hydride

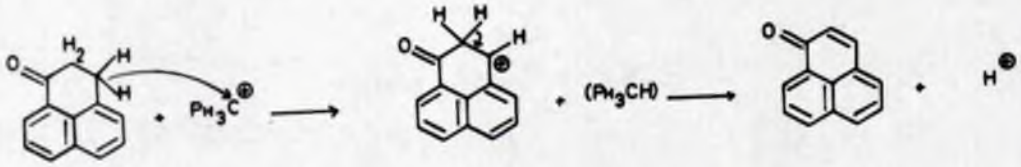
(XXXI)







(XXXIII)



exchange reactions. Trityl perchlorate is sensitive to impurities in triphenyl carbinol and we have found it advisable to prepare this alcohol as described in Organic Syntheses[28] The crude product is steam distilled for some 24 hr. before being dried and recrystallised from carbon tetrachloride. One of the main disadvantages of triphenylmethyl perchlorate is its insolubility in most organic solvents, In some cases this can be obviated by preparing the carbonium ion in situ by the addition of perchloric acid to a solution of the substrate and triphenyl carbinol in glacial acetic acid. An example of this procedure is the preparation of 5-oxo-5H-benzo[cd]pyrene (C.XI, IV).

Preformed carbonium ions have been shown to abstract hydride ion according to the reaction scheme:

$$R'H + R^{\oplus} \rightleftharpoons R'^{\oplus} + RH$$

This reaction leads to the formation of new carbonium ions and the triphenylmethyl cation has been shown to react with cycloheptatriene to form tropylium perchlorate,[26] $(C_7H_8)Mo(CO)_3$ to yield $(C_7H_7)^{\oplus}Mo(CO)_3$,[27] and with triphenylcyclopropene to give the triphenylcyclopropenylium cation.[28]

The known stability of the perinaphthenylium cation[29] (XXXI) prompted the application of this method to the synthesis of perinaphthenylium salts by allowing triphenylmethylperchlorate

to interact with perinaphthenes in glacial acetic acid. In this way perinaphthenylium perchlorate and the 1,4,7-trimethyl derivative were prepared.[30] Dauben and his associates[28] have since reported the preparation of (XXXI) by this method but no experimental details nor any description of their product was given.

Three other preparations of this cation have been described. The iodide has been prepared by the interaction of a solution of the perinaphthyl radical with a solution of iodine in benzene[31] (C,XIV,IV); perinaphthenylium perchlorate has been obtained by treating the radical with an electron acceptor, silver perchlorate, in anhydrous ether.[31] The cation (XXXI) has also been synthesised by Pettit[32] by an adaptation of the method of Dewar and Pettit[33] used for the synthesis of tropylium perchlorate. This latter method[32] cannot readily be modified for the preparation of substituted perinaphthenylium salts.

The method of Bonthrone and Reid[30] has been applied to the preparation of certain substituted perinaphthenylium salts (Table 1. Unstable salts are marked with an asterisk . The extent of hydride transfer in these cases has been estimated by the yield of triphenylmethane obtained).

TABLE I

Substrate	Yield (salt)	Yield (Triphenyl methane)
Perinaphthene	61%	
1,2-dimethylperinaphthene	73.5%	
3,6,9-trimethylperinaphthene	37%	
6H-benzo[cd]pyrene	83%	73%
Benzanthrene	57%	
4(9)-methylperinaphthene	■	86%
1,2-dihydro-5H-cyclopenta [gh]perinaphthene	■	73,90%

Alkoxy-substituted perinaphthenes are unstable due to the mobility of the double-bond system in perinaphthene (cf. B1,1X and A11,V11 for a more detailed discussion of this topic) and it would seem that alkoxy-substituted salts could not be prepared by the general method in its original form since the necessary alkoxyperinaphthenes cannot be obtained.

It has been found, however, that by making use of the equilibrium:

$$CH_3COOH + Ph_3C^{\oplus}\ ClO_4^{\ominus} \rightleftharpoons Ph_3C.OCO.CH_3 + H^{\oplus} + ClO_4^{\ominus}$$

we can use trityl perchlorate in acetic acid as a dehydrating as well as a dehydrogenating reagent. This duality of reaction has been used for the preparation of certain alkyl - and alkoxy- perinaphthenylium salts (Table II). Two types of

secondary reaction are open, in principle, to the transient perinaphthene formed in the primary (dehydrating)step. These are (i) solvolysis by the water produced in the dehydration, (ii) loss of hydride ion to the triphenylmethyl cation. In the case of perinaphthanol the first reaction predominates and (XXXI) cannot be prepared by this method. When the trioyclic ring system is substituted with electron releasing groups such as alkyl or alkoxyl then (ii) is facilitated and the corresponding salts can be obtained in good yield.

TABLE II

Substrate	Yield(Salt)	Yield (Triphenyl-methane)
3,6,9-trimethylperinaphthan-1-ol	64%	
4-methoxyperinaphthan-1-ol	82%	
4,8-dimethoxyperinaphthan-1-ol	75%	
3-methylperinaphthan-1-ol	"	81.5%

B11,11 High Potential Quinones and Hydride Transfer in the presence of Perchloric Acid.

The use of quinones for the dehydrogenation of hydroaromatic compounds was first reported by Clar and John in 1930.[34] Evidence has been presented[35] that the dehydrogenation

proceeds by a two-step ionic process. The rate-determining step is abstraction of hydrogen as hydride ion and is followed by the rapid transfer of a proton from the resulting conjugate acid of the substrate to the quinol anion.

$$RH_2 + Q \xrightarrow[\text{slow}]{} RH^{\oplus} + QH^{2} \qquad \ldots\ldots\ldots (1)$$

$$RH^{\oplus} + QH^{\ominus} \xrightarrow[\text{fast}]{} R + QH_2 \qquad \ldots\ldots\ldots (2)$$

The dehydrogenation is catalysed by acid and this catalysis by a proton donor is ascribed to the formation of the conjugate acid of the quinone, i.e., the quinol cation QH^{+} which has an even higher affinity for anionic hydrogen then the quinone

$$Q + HX \xrightarrow[\text{fast}]{} QH.X^{\oplus\ominus} \qquad \ldots\ldots\ldots (3)$$

$$RH_2 + QH^{+} \xrightarrow[\text{slow}]{} RH^{\oplus} + QH_2 \qquad \ldots\ldots\ldots (4)$$

$$RH^{\oplus} + X^{\ominus} \xrightarrow[\text{fast}]{} R + HX \qquad \ldots\ldots\ldots (5)$$

It seemed, therefore, that the use of suitable substrates might lead to the isolation of stable cations, $RH^{\oplus}$, in quinone dehydrogenations in the presence of strong acids. Isolated instances have appeared in the literature[36] of the formation of heterocyclic quarternary ammonium salts by the action of quinones on heterocyclic hydroaromatic compounds, overall loss of hydride ion having occurred in these cases. In a preliminary communication[37] embodying some of the

work in this thesis we have described the use of quinones in a new general method for the preparation of stable hydrocarbon cations.

The hydrocarbons cycloheptatriene, triphenylcyclo propene, and perinaphthene all react with high potential quinones in the presence of perchloric acid to form the carbonium ion, isolated as its salt. Migration of hydrogen with its bonding electrons to the quinone occurs. The resulting quinol monoanion then abstracts a proton from the solvent.

In view of the ease of formation of the perinaphthenylium cation[29,30] it was of interest to examine the reaction of high potential quinones with perinaphthene in detail. The reaction proceeds almost instantaneously at room temperature and is virtually quantitative with most quinones.

Examination of Table III shows that tetrachloro-1,2-benzoquinone (TBQ) is the most useful hydrogen acceptor from a preparative point of view. It is very soluble in both acetic acid and acetonitrile, the preferred solvents for the reaction, and its quinol is very soluble in ether. This latter property makes isolation of the product much easier. The use of 2,3-dicyano-5,6-dichloro-1,4-benzoquinone (D.D.Q., E°_{2s} = 1.0 v) was not practicable in the dehydrogenation of perinaphthene due to the insolubility of the corresponding quinol. The yield of perinaphthenylium perchlorate falls as the oxidation-reduction

TABLE III

Substrate	Quinone	E°_{ss}	Yield (salt)	Yield (Quinol)
Perinaphthene	2,3-dicyano-1,4 benzoquinone	1.0	87.5%	
Perinaphthene	T.B.Q.	0.87	79.9%	
Perinaphthene	1,4-bensoquinone	0.711	80.5%	91%
Perinaphthene	Chloranil	0.703	75%	90%
Perinaphthene	Chloranil[1]	0.703	44%	84%
Perinaphthene	1,2-naphtho-quinone	0.579	43%	
Perinaphthene	9,10-phenan-threquinone	0.471	54%	
4(9)-methylperinaphthene	Chloranil	0.703	■	65%
1,2-dimethylperinaphthene	TBQ	0.87	73.5%	
1,3-dimethylperinaphthene	TBQ[1]	0.87	88.5%	
3,6,9-trimethylperi-naphthene	TBQ	0.87	92.6%	
1,2-dihydro-5H-cyclo-penta[gh]perinaphthene	TBQ	0.87	■	81.0%

[1] In these experiments acetonitrile was used as solvent, glacial acetic acid was used in all other experiments in the table.

■ Unstable product.

potential (E°_{s}) decreases. In cases where the order is reversed it is generally due to the high solubility of the quinone in acetic acid, e.g., 1,4-benzoquinone.

These quinone dehydrogenations take place in the presence of a strong acid and it was of interest to see if this general method was applicable to the synthesis of alkoxy-substituted salts. Dehydration of substituted perinaphthanols by free perchloric acid takes place in situ. Dehydration-dehydrogenation leads to somewhat higher yields than the corresponding process with trityl perchlorate in glacial acetic acid. The results of these experiments are tabulated below.

TABLE IV

Substrate	Quinone	Yield (salt)	Yield (Quinol)
1,3-dimethylperinaphthan-1-ol	TBQ	89%	-
3,6,9-trimethylperinaphthan-1-ol	TBQ	89%	-
4-Methoxyperinaphthan-1-ol	TBQ	86%	-
4,8-dimethoxyperinaphthan-1-ol	TBQ	79%	-
4,5-dimethoxyperinaphthan-1-ol	TBQ	*	87%

* denotes unstable product.

B111. High Potential Quinones and Hydrogen Atom Transfer

The rate-determining step in quinone dehydrogenations is thought to be

$$RH_2 + Q \xrightarrow[\text{slow}]{} RH^{\oplus} + QH^{\ominus} \quad \ldots\ldots\ldots\ldots (1)$$

This step may, however, represent a summary of two successive steps

$$RH_2 + Q \longrightarrow RH^{\cdot} + QH^{\cdot} \quad \ldots\ldots\ldots\ldots (2)$$

$$RH^{\cdot} + QH^{\cdot} \longrightarrow RH^{\oplus} + QH^{\ominus} \quad \ldots\ldots\ldots\ldots (3)$$

In the case where RH is a stable, long-lived radical it is possible that step (2) would be followed by

$$RH_2 + QH^{\cdot} \longrightarrow RH^{\cdot} + QH_2 \quad \ldots\ldots\ldots\ldots (4)$$

Alternatively, steps (2) and (4) might merge into a single process

$$2RH_2 + Q \longrightarrow 2RH^{\cdot} + QH_2 \quad \ldots\ldots\ldots\ldots (5)$$

Hence by the use of suitable substrates it might be possible to isolate stable radicals, $RH^{\cdot}$, in quinone dehydrogenations.

Perinaphthene reacts with many quinones at room temperature in both polar and non-polar solvents to give the perinaphthyl radical.[88] The stoichiometry of this reaction corresponds to that required by step (5), the yield of quinol dropping from 70% to 34% when the quantity of chloranil

used was increased from 1 mmole/2 mmole of hydrocarbon to 1 mmole/1mmole of hydrocarbon (Table V). This preparation of the perinaphthyl radical demonstrates that quinones can dehydrogenate both by hydrogen atom, and overall hydride ion transfer. The results of the reactions between quinones and perinaphthene, in the absence of acids, are tabulated below.

TABLE V.

Quinone	Molar Ratio (P:Q)	Solvent	Yield (quinol)
Chloranil	2:1	Methylene Chloride	70%
Chloranil	1:1	Methylene Chloride	34%
Chloranil	2:1	Acetonitrile	56%
Chloranil	2:1	Nitromethane	60%
Chloranil	2:1	Glacial Acetic Acid	-
1,4-benzoquinone[1]	1:1	Methylene Chloride	74.5%
T.M.Q.	2:1	Methylene Chloride	73%
1,2-naphthoquinone	2:1	Methylene Chloride	67%
9,10-phenanthraquinone[2]	2:1	Methylene Chloride	-
2,3-dicyanoquinone[2]	2:1	Methylene Chloride	-

When benzoquinone was used the reaction was complicated by the formation of quinhydrone. As this is a 1:1 molecular complex it was decided to use a 100% excess of benzoquinone, i.e. enough benzoquinone present to complex with all the quinol formed if the reaction goes 100% to completion. The quinol was thus isolated as the quinhydrone in 74.5% yield. This result lends support to the formulation of the overall reaction as in step (5)

The quinol obtained in these reactions was somewhat intractable and the radical was identified by its spectrum (Plate 1).

Barnard and Jackmann[39] have recently supported the evidence for the two-stage ionic process of quinone dehydrogenation by molecular orbital calculations. The main chemical evidence for an ionic mechanism comes from the occurrence of a number of neighbouring group effects[40] similar to those which accompany unimolecular solvolysis. Nevertheless the evidence presented by Braude, Linstead, Jackman and their coworkers[38,39,40] does not wholly exclude a free readical mechanism for quinone dehydrogenation and, at this point, it is relevant to summarise some of our observations on this subject.

In our studies, the presence or absence of strong acids in quinone dehydrogenation was found to profoundly affect the

course of the reaction. Generally speaking, the presence of strong acids simplifies the reaction. Thus with the hydrocarbons, cycloheptatriene, triphenylcyclopropene, and perinaphthene the corresponding carbonium ion is isolated as its salt in good yield. The overall reaction corresponds to hydride transfer from the hydrocarbon to the quinone with the acid providing the proton to convert the quinol monoanion to quinol. Some exceptions to this are now known. When ditropyl reacts with quinones in the presence of perchloric acid tropylium perchlorate is formed in yields up to 84% indicating the loss of two electrons from the substrate.[41] It would be of some importance to be able to decide on the origin of these electrons, whether they originate from the π-electron cloud of the molecule, or from the σ-bond connecting the two seven-membered rings. The somewhat lower yields obtained with T.B.Q., a 1,2-benzoquinone, indicates that there may be some steric requirements in this particular reaction, suggesting that the initial attack occurs at the σ bond.

In reactions with quinones alone some considerable difficulties attend the elucidation of the structure of the product obtained. The simplest case is that of perinaphthene which loses a hydrogen atom to form a long-lived free

radical. Both cycloheptatriene and triphenylcyclopropene yield complexes.[87] Subsequent studies have been confined, at present, to that from cycloheptatriene.

This complex was provisionally formulated as tropylium 2,3-dichloro-5,6-dicyano-1,4-isoquinolate. On treatment with strong acids it affords tropylium salts in good yield.[87] Investigation of the fine structure of this complex showed that a much more subtle reaction had occurred. The first conclusive piece of evidence came from a comparison of the complex with that obtained by the interaction of ferrocene with D.D.Q. The only reaction possible in this latter case is the donation of an electron from ferrocene to the quinone and therefore the product is the ferrocenium - D.D.Q. radical-anion. Spectral studies showed that the three complexes, from ferrocene, cycloheptatriene, and triphenylcyclopropene all had one component in common and this can only be the D.D.Q. radical-anion. Further refinements in the case of the cycloheptatriene complex show that the seven-membered ring is present in the complex as tropylium. This also agrees with the stoichiometry of the reactions of the complex and thus we have formulated the latter as tropylium D.D.Q. radical-anion (XXXIII). The course

of the reaction corresponds to electron transfer to the quinone and expulsion of a hydrogen atom. The fate of the hydrogen atom is open to speculation. When phenylmercaptocycloheptatriene is reacted with D.D.Q. the same complex results as from cycloheptatriene itself and diphenyldisulphide can be isolated from the mother liquors.[42] This reaction thus appears to proceed in a similar manner to the dehydrogenation of cycloheptatriene, i.e. by electron transfer to the quinone and expulsion of the phenylmercapto radical which then dimerises to diphenyl disulphide.

Our experimental findings together with the recently reported observations of Calvin and his co-workers[43] on the formation of the crystal violet cation from NN-dimethylaniline by chloranil suggests that more fundamental studies are required to uncover all the mechanisms of quinone dehydrogenation.

BIV. Dehydrogenation by Triphenylmethyl Perchlorate.

Preformed carbonium ions have been used to remove hydride ion (B11,1). This type of reaction has been utilised in the preparation of stable organic cations. Kinetic studies have shown that the rate-determining step in many organic oxidation-reduction reactions appears to be hydride transfer (B11,11). The possibility that preformed carbonium ions might

be able to dehydrogenate suitable substrates to relatively stable intermediate cations capable of losing a proton with the formation of a neutral product containing two fewer hydrogen atoms was not considered until recently.

It has now been shown[80,44] that trityl perchlorate may be used successfully to dehydrogenate hydroaromatic and hetero-hydro aromatic compounds.

Application of the reagent to cyclic ketones has shown that this method is the most satisfactory way of converting perinaphthan-1-ones to perinaphthen-1-ones. Perinaphthan-1-ones are considered to lose a hydride ion from C_9 where a positive charge can be stabilised by the adjacent aromatic nucleus. The aromatic character of perinaphthen-1-ones provides the driving force for the subsequent loss of a proton from the intermediate cation. Several perinaphthen-1-ones have been prepared by this method (Table VI).

TABLE VI

Product	Yield %	Yield % (Triphenylmethane)
Perinaphthen-1-one	80	
3-Methylperinaphthen-1-one	68	80
4,5-Dimethylperinaphthen-1-one	87	
3,6,9-Trimethylperinaphthen-1-one	81	
4-Methoxyperinaphthen-1-one	90	85
4,5-Dimethoxyperinaphthen-1-one	76	
4,8-Dimethoxyperinaphthen-1-one	88	91
5-oxo-5H-benz[cd]pyrene	76	
1,2-Dihydro-5-oxo-5H-cyclopenta[gh]perinaphthene[1]	46	88.5

[1] The yield of this ketone is much lower than any of the others so far prepared. This was due to the concurrent formation of a deep red crystalline compound which was isolated from the neutral fraction (CXI,III) in 32.5% yield. Spectra, analytical and molecular weight data indicate a molecular formula of $C_{30}H_{22}O$ which corresponds to a bimolecular product. Although insoluble in concentrated hydrochloric acid it dissolves in perchloric acid giving a wine-red solution, and its infrared spectrum (nujol) in the region 5μ-14μ is very similar to that of 1,2-dihydro-5-oxo-5H-cyclopenta[gh]perinaphthene.

Attempts to prepare the bimolecular product by the acid catalysed self-condensation of the saturated ketone, 1,2,5,6-tetrahydro-7-oxo-7H-cyclopenta[gh]perinaphthene were unsuccessful, starting material being recovered from the reaction mixture.

All the ketones in Table VI dissolve in organic solvents to give solutions which possess an orange yellow fluorescence. They dissolve reversibly in strong acids giving red or green solutions as a result of protonation of the carbonyl group to form 1-hydroxyperinaphthenylium salts. Some of these salts can be isolated. The visible spectra of the salts have been examined (Plate II). The infrared carbonyl stretching frequencies, occurring in the range 1649-1629 cm.$^{-1}$, reflects the polarisation of the carbonyl group (AII,III; Table III).

B.V. Stable Cations derived from Perinaphthene and its Derivatives.

BV,1 The Perinaphthenylium Cation.

The perinaphthenide anion is converted into the perinaphthyl radical by a one electron transfer to oxygen.[38,48] The subsequent ready conversion of the latter to the cation indicates that these entities all possess a similar order of stability.

Perinaphthyl reacts with halogens to form products whose stabilities follow the order iodide > bromide > chloride.[48] Studies in this series have been confined to the iodide which is prepared by the action of molecular iodine on a solution of the radical (CXIV,1V) and it exists as a black solid with no definite melting point. The properties of the iodide are in accord with the view that the bond between iodine and the perinaphthene moiety is ionic in the solid state. It breaks down in pyridine to reform the perinaphthyl radical.

The properties of the salt (XXXI) prepared from perinaphthyl and by hydride abstraction from perinaphthene are in agreement with those reported by Pettit.[38,48] The salt decomposes in moist air to a black tar, is insoluble in non-polar solvents, but dissolves in nitromethane and acetonitrile. It is solvolysed by hydroxylic solvents. Hydrolysis of the perchlorate yields a mixture of perinaphthene and perinaphthenone (BVI,1).

Attempts to utilise the cation (XXXI) in reactions with Grignard reagents have been unsuccessful. Highly coloured blue-green solutions were obtained and no useful product could be isolated. It is possible that these reactions were frustrated by radical formation due to electron transfer from magnesium in the reaction mixture. We have observed radical formation

from perinaphthenylium salts on reaction with zinc in acetic acid.

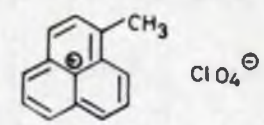
M.O. calculations have been carried out on the perinaphthenylium cation.[46] These indicate that the positive charge is distributed equally among the 1,3,4,6,7 and 9 position, none of the cationic charge being placed on the 13 position. The delocalisation energy of the cation has been calculated to be 5.828β,[22,48] 5.827β.[46] This suggests that the cation is more stable than the experimental evidence warrants.

IV,11. Alkyl-substituted Perinaphthenylium Cations.

The preparation of the parent carbonium ion having been successfully completed, it was decided to investigate the stabilising effect of alkyl groups on the cation.

Attempts to isolate a monomethyl salt have been unsuccessful, green polymeric material being obtained in all experiments which were designed to yield 1-methylperinaphthenylium perchlorate (XXXIV). It has been confirmed that hydride abstraction takes place since high yields of both triphenyl methane and quinol are obtained. It seems that the cation is formed transiently, but that it immediately ejects a proton to form 1-methylene perinaphthene which then polymerises.

Both the 1,2- and 1,3-dimethylperinaphthenylium salts have been prepared and characterised. These are unstable to



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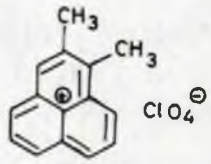

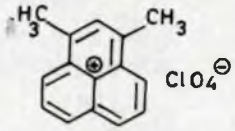

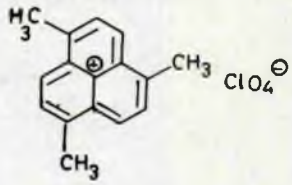

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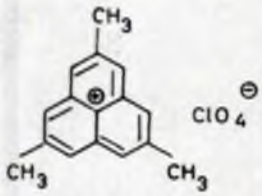

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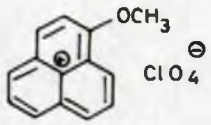

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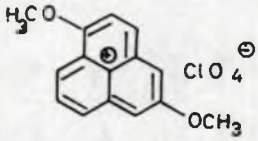

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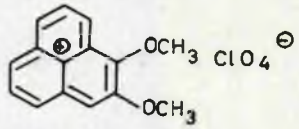

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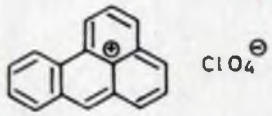

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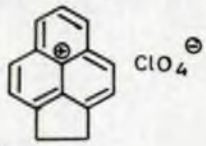

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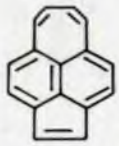

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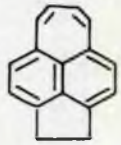


(XLII)

(XLIV)

(XLV)

warm solvents and cannot be recrystallised. They dissolve in acetonitrile to give reddish orange solutions which become green on warming and eventually deposit green, tarry material. The addition of perchloric acid stabilises the solutions for a short time but it is impossible to obtain accurate visible spectral data. It is considered that these compounds polymerise by a mechanism similar to that postulated in the case of methyl perinaphthenylium perchlorate.

In contrast to the above observations is the stability of 1,4,7-trimethylperinaphthenylium perchlorate (XXXV). This skew-symmetrical cation appears to be almost as stable as the tropylium ion. It would be of interest to compare the stability of this compound with that of the as yet unknown 2,5,8-trimethylperinaphthenylium perchlorate (XXXVI). The electron releasing effect of the three methyl groups causes an increased stabilisation of the positive charge in the cation and outweighs any tendancy to form a neutral product by ejection of a proton. 1,4,7-Trimethylperinaphthenylium perchlorate which recrystallises from acetonitrile as bronze needles, is hydrolysed by alkali to a mixture of 3,6,9-trimethylperinaphthenone and trimethylperinaphthene. Hydride reduction of this salt (XXXV) constitutes the best preparation of 3,6,9-trimethylperinaphthene.

BV,111 Alkoxy-substituted Perinaphthenylium Cations.

Dehydration-dehydrogenation of 4-methoxyperinaphthan-1-ol gave 1-methoxyperinaphthenylium perchlorate (XXXVII) in good yield as orange-red needles which could be recrystallised from both acetonitrile and glacial acetic acid. This compound possesses the same order of stability as 1,4,7-trimethylperinaphthenylium perchlorate (XXXV). The structure of the cation in (XXXVII) is very similar to that of 1-hydroxyperinaphthenylium (protonated form of perinaphthenone) and this is reflected in the similarity of their visible spectra. (Plate III).

1,5-Dimethoxyperinaphthenylium perchlorate (XXXVIII) was prepared by the dehydration-dehydrogenation of 4,8-dimethoxyperinaphthan-1-ol. It was expected that the presence of a second methoxy group would further stabilise the cation, and while this appears to be so it also increases the solubility of the salt making isolation of the latter difficult. The salt can be recrystallised from acetic acid as bronze-red needles but can only be obtained from acetonitrile by precipitation with ether

Because of our interest in the solvolysis of these salts (B,VI) we attempted to synthesise 1,2-dimethoxyperinaphthenylium perchlorate (XXXIX) by the dehydration-dehydrogenation of 4,5-dimethoxyperinaphthan-1-ol. This reaction proved to be more complicated than expected. Yields of quinol indicated that

hydride abstraction had occurred, but on only one occasion was a solid product obtained. All other attempts produced a dark red oil insoluble in non-polar solvents but soluble in both acetonitrile and acetic acid. Hydrolysis of the solid product gave 4,5-dimethoxyperinaphthan-1-one in high yield but analytical data for the 'red salt' did not agree with its formulation as 1-hydroxy-4,5-dimethoxyperinaphthenylium perchlorate and was poor for those of the required salt (XXXIX). Cases have been reported in the literature[49] where allylic alcohols are dehydrogenated by quinones to aldehydes or ketones. If such a process were to occur in this case then 4,5-dimethoxyperinaphthen-1-one would result and this would then be protonated by the excess of perchloric acid in the reaction mixture. More work is required to clarify the position.

BV,IV. <u>The Effect of Annellation on the Perinaphthenylium Cation</u>

Several aromatic hydrocarbons whose conjugate acids can be considered to contain the perinaphthenylium unit are highly reactive in electrophilic substitution. Examples are pyrene and perylene which are believed to protonate at the 3 and the 4 positions, respectively. We have, therefore, prepared condensed aromatic hydrocarbons which contain the perinaphthene ring system and examined the effect of annellation on the stability of the perinaphthenylium cation.

Benzanthrene (BI,IV) loses a hydride ion readily to form the benzanthrenylium cation (XL), isolated as the perchlorate. The salt is very unstable and rapidly decomposes to a black tar in air. It is hydrolysed to a mixture of benzanthrene and benzanthrone, presumably through a pseudo base of the type postulated for the parent salt (B,VI).

Thus ortho fusion of a benzene ring causes a considerable decrease in the stability of the cation. The effect of the benzene ring may be to interfere with the delocalisation of the π-electrons over the perinaphthene moiety due to the tendency of a benzene ring to retain a complete sextet of electrons. An alternative explanation may be that the number of positions over which the cationic charge is delocalised may be reduced in this molecule due to the annellation on the a face of the parent cation.

Our attempts to isolate 1,2-dihydrocyclopenta[gh]perinaphthenylium perchlorate (XLI) indicate that the cation is very unstable. This may be due to loss of a proton from one of the methylene groups to form a neutral product which then polymerises as is the case with the methylperinaphthenylium salt (XXXII). The hydrocarbon (XVII) loses a hydride ion to triphenyl methyl perchlorate and triphenyl methane is formed in high yield, but it has not been possible to isolate the salt

or its hydrolysis products. A yellow solid precipitated in the reaction mixture but this rapidly decomposed even in dry ether under nitrogen. Attempts to isolate the salt in quinone dehydrogenations have been unsuccessful although high yields of quinol have been obtained.

The dimethylene bridge evidently destabilises the cation to a high degree. This may be due to distortion of the cation by the five-membered ring, the dimethylene bridge reducing the ability of the system to support a delocalised π-electron system. Alternatively, the delocalisation of 12π-electrons over fifteen carbon atoms may not constitute a stable π-electron system. Thus acepleidiene (XLII) which also has a dimethylene bridge is non-aromatic whereas acepleiadylene (XLIII) is aromatic.[80] The former has 14 π-electrons delocalised over sixteen carbon atoms while the latter has 16π electrons delocalised over the same carbon framework. It would be of interest to examine the stability of the cation (XLIV) derived from cyclopenta[gh]peri-naphthene. If it is stable it would suggest that the instability of the cation (XLI) is due to an unstable delocalised π-electron system rather than to distortion of the cation by the dimethylene bridge.

In connection with the instability of (XLI) it should be noted that 1,2-dihydro-5-oxo-5H-cyclopenta[gh] perinaphthene (XIV) is probably the most unstable perinaphthenone derivative we have prepared.

BV,V <u>The Benzo[cd]pyrenium Cation.</u>

In consequence of our interest in annellation, the hydrocarbon 6H-benzo[cd]pyrene (XXII) was synthesised and found to undergo ready hydride exchange to form the benzo[cd] pyrenium cation [XLV]. This entity can be regarded as a naphtho-perinaphthenylium cation, but in view of the high degree of annellation such a derivation is purely formal. One of the major factors influencing the stability of carbonium ions is that the more the positive charge can be spread among nearby atoms the greater the stability of the ion. In this case the charge can be spread over nineteen carbon atoms. This cation (XLV) shows several interesting structural features. There are two identical canonical structures whose periphery conforms to the annulene, hexadecaoctaene, with an internal three carbon unit which is formally an allylic cation. Although the peripheral conjugation corresponds to a 4n hydrocarbon the number of π-electrons totals eighteen which would comply with Huckels rule where n=4. It would be of interest to see how

'aromatic' this compound is in terms of the definition due to Elvidge and Jackman,[81] i.e., how large a ring current it can sustain. Hydrolysis of this salt was complicated by the possibility of isomerism. Two ketones were obtained but only one, 6-oxo-6H-benzo[cd]pyrene, was identified, while a mixture of hydrocarbons was obtained in which the 6H isomer appears to predominate.

BV1. Hydrolysis of Perinaphthenylium Salts.

BV1,1 Perinaphthenylium and its derivatives (except alkoxy)

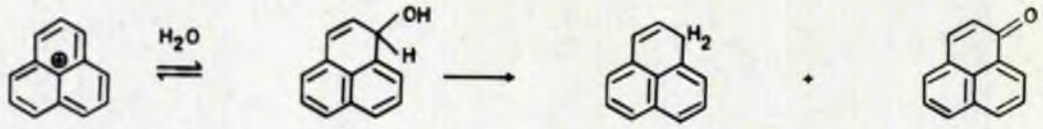
The perinaphthenylium cation and its derivatives are solvolysed by hydroxylic solvents. In aqueous solution the cation is in equilibrium with its pseudo base, perinaphthenol (XLVI), but this equilibrium is displaced to the right due to the instability of this compound which irreversibly disproportionates to an equimolecular mixture of perinaphthene and perinaphthenone. The driving force of this reaction is presumably the aromaticity of perinaphthenone. It is not possible, therefore, to measure the stability of the perinaphthenylium cation in solution as only a small equilibrium concentration of the carbinol is necessary to cause the eventual transformation of all the cation present. Boekelheide

and Larrabee[18] attempted to prepare (XLVI) by lithium aluminium hydride reduction of perinaphthenone when they obtained a mixture of perinaphthan-1-one, perinaphthene and phenolic material; a result which supports the conclusion that this carbinol is unstable.

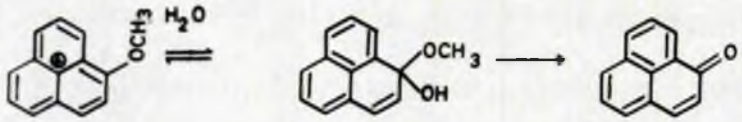
Hydrolysis of the parent cation, its alkyl derivatives and its ring homologues have all resulted in a mixture of hydrocarbon and unsaturated ketone. In the hydrolysis of the benzo[cd]pyrenium cation, two ketones were isolated as well as an isomeric mixture of hydrocarbons. 6-Oxo-6H-benzo[cd]pyrene was the major ketonic product while the 6H-hydrocarbon appeared to be the predominant isomer (C.VII,IV). It is possible that identification of the products will become more difficult when substitution makes the nucleus unsymmetrical since this may lead to nucleophilic attack by water at two chemically distinguishable positions.

B.VI,11. <u>The Hydrolysis of Alkoxy-substituted Cations</u>

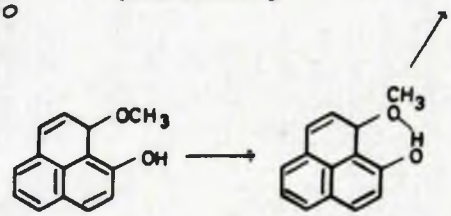
It was thought that alkoxy salts would be hydrolysed by a mechanism similar to that outlined above. The products obtained would depend upon the position of nucleophilic attack with reference to the substituents present in the cation. In the case of the 1-methoxyperinaphthenylium cation these positions are 3,4,6,7, and 9. Attack at all positions would



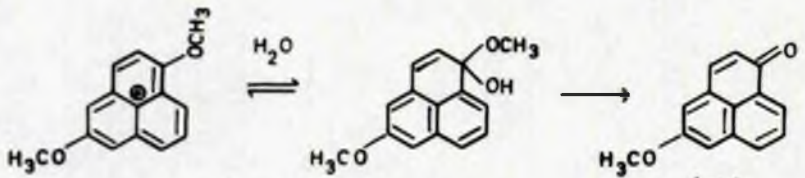
(XLVI)



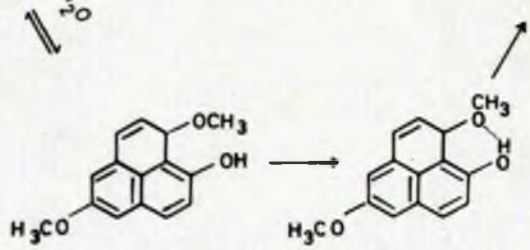
(XLVIII)



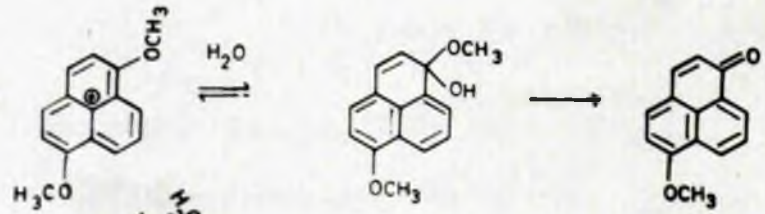
(XLVII) (XLIX)



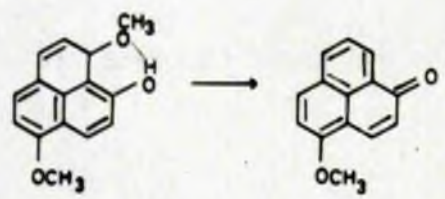
(L)



(LI)



(LII)



(LIII)

lead to a mixture of five isomeric methoxyperinaphthenols. Disproportionation of these should then lead to a mixture of five methoxyperinaphthen-1-ones and perinaphthan-1-one, the latter originating from solvolysis and rearrangement of the first formed methoxyperinaphthenes (cf. B1,1X).

When this hydrolysis was carried out perinaphthen-1-one was obtained as sole product. This behaviour can be rationalised by postulating the formation of either 9-methoxyperinaphthen-1-ol (XLVII) or 1-methoxyperinaphthen-1-ol (XLVIII). In the former case attack by water takes place at the peri postion with respect to the methoxy group, and in the latter at the carbon atom carrying the methoxyl group. Disproportionation of (XLVII) would yield a mixture of 9-methoxyperinaphthen-1-one and perinaphthan-1-one. This does not occur but an attractive possibility is that the initially formed alcohol (XLVII) eliminates the elements of methanol from a cyclic intermediate (XLIX) involving hydrogen bonding between the ether and alcohol oxygen atoms. The carbinol (XLVIII) is a hemi-ketal and this would lose methanol readily to form perinaphthen-1-one, but it is difficult to believe that nucleophilic attack would occur on the carbon atom which already carries an electron-releasing substituent.

The driving force of this reaction is probably the aromaticity of pernaphthen-1-one. In contrast to the path described in B.VI,1, all the cation can be solvolysed to perinaphthenone. The oxidation level of the product is the same as that of the cation which is the methyl ether of the 1-hydroxyperinaphthenylium cation.

The hydrolysis of 1,5-dimethoxyperinaphthenylium proceeded smoothly to give a monomethoxyperinaphthenone which we have formulated as the 5-methoxy derivative (L) on the basis of the above mechanisms and the fact that none of its properties correspond with those quoted in the literature for known monomethoxyperinaphthenones.[19,47,82,85]

Neither of these results distinguishes between the postulated mechanisms, both of which would product the observed results. The hydrolysis of the 1,6-dimethoxyperinaphthenylium cation (LI) would differentiate between the two mechanisms. Solvolysis through a hemi-ketal intermediate would lead to 6-methoxyperinaphthen-1-one (LII), while the alternative mechanism predicts that 4-methoxyperinaphthen-1-one (LIII) would be formed.

The results of the hydrolyses experiments are tabulated below.

Table VII.

Cation	Products Isolated				
	Ketone	% Yield	Hydrocarbon	% Yield	Total Yield
Perinaphthenylium	Perinaphthenone	34	Perinaphthene	23	57
Benzathrenylium	Benzanthrone	39	Benzanthrene	37	76
Benzo[cd]pyrenium	6-Oxo-6H-benzo[cd]-pyrene	24	Isomeric mixture	25	49
1-Methoxyperi-naphthenylium	Perinaphthenone	93	-		93
1,5-Dimethoxy-perinaphthenylium	5-Methoxyperi-naphthenone	58.5	-		58.5

B.V11 The Perinaphthyl Radical.

A consideration of the symmetry of the perinaphthene skeleton lead to the suggestion[8,18,84] that perinaphthyl might be a stable, long-lived radical. Four oxygenated derivatives have been reported. One of these, 1-hydroxy-3-phenylperinaphthyl, was postulated as an intermediate in the reduction of 3-phenylperinaphthen-1-one.[88] The remaining three, 1-methoxy-, 1-acetoxy-, and 1-benzoyloxy- perinaphthyl were observed as blue solutions.[84] Several attempts[8,18] to prepare the parent radical were unsuccessful. The E.S.R. spectrum of perinaphthyl has been obtained from a solution of perinaphthene in carbon tetrachloride which had been stored for several months.[86] According to HMO theory the spin density is equally distributed among the 1,3,4,6,7, and 9 positions and so a pattern of seven equally spaced lines was predicted for this radical. Seven such lines were observed, but each is further split into a quartet which corresponds to a substantial spin density at the 2,5 and 8 positions. Negative spin density is predicted at these positions by VB and advanced MO theories.[87] The detection of the radical in pyrolysed hydrocarbons has also been claimed.[88]

We have observed the formation of the perinaphthyl radical in seven distinct reactions.

(i) The best preparation of the radical consists in mixing a solution of perinaphthene with a solution of high potential quinone when perinaphthyl is formed by hydrogen atom abstraction from the hydrocarbon.

(ii) Perinaphthyl is formed by a one electron transfer from the perinaphthenide anion to molecular oxygen which is converted to the peroxide anion.

(iii) The addition of a catalytic quantity of concentrated hydrochloric acid to a solution of di-1,1'-perinaphthan-1-ol in propionic acid at room temperature results in the immediate formation of the radical.

(iv) Treatment of 1,2-dibromoperinaphthane with organic bases results in the loss of hydrogen bromide, bromine and the formation of perinaphthyl.

(v) Perinaphthyl is formed when perinaphthene is treated with N-bromosuccinimide.

(vi) Perinaphthyl results when perinaphthenylium iodide is dissolved in pyridine.

(vii) Perinaphthyl is formed as a by-product when perinaphthene was allowed to react with osmium tetroxide and pyridine in benzene.

Perinaphthyl is blue in solution and green in the solid state although it has not been isolated pure. It does not react with nitric oxide but reacts with oxygen to form a green peroxide. This breaks down *in vacuo* a mixture of peropyrene and perinaphthenone being obtained.

1,4,7-trimethylperinaphthyl has been prepared by the action of N-bromosuccinimide on 3,6,9-trimethylperinaphthene. When 1,4,7-trimethylperinaphthenylium perchlorate is warmed in dimethyl sulphoxide a blue colouration is observed and this may be due to formation of the radical. This radical could not be prepared by the action of oxygen on a solution of the hydrocarbon in ethanolic ether containing potassium methoxide.

B.VIII Naphtho[1,8a,8-ab]carbazolium Salts.

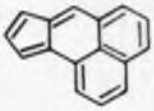
Cyclopenta[a]perinaphthene (LIV) has not yet been synthesised, and all approaches have been frustrated by the facile isomerisation of the perinaphthene nucleus, by the ready formation of the perinaphthyl radical, or, in some cases, failure to obtain the desired product at a critical stage of a projected synthesis.[59,60] However indeno[2,1-a]perinaphthene a ring homologue of (LIV) has been prepared and its properties studied.[59,63]

The most characteristic property of indeno[2,1-a]-perinaphthene(LV) is its high basicity, a measure of which was

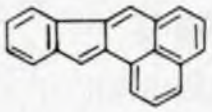
obtained by the method of Plattner.[61] It dissolves in strong acids to form a green cation (LVa), and its basicity is of the same order as that of azulene.[62] The hydrocarbon has one chemically recognisable position, $C_{(12)}$, in the five-membered ring and the conjugate acid is considered to possess the structure resulting from accession of a proton to this position. Addition of a proton at this point is accompanied by the formation, in the perinaphthene nucleus, of the π-electron system present in the perinaphthenylium cation. Electrophilic substitution occurs under mild conditions and, for similar reasons, the position involved is considered to be $C_{(12)}$.[29] The hydrocarbon functions as the diene in Diels-Alder reactions, and addition has been shown to involve the 1 and 12 positions.[29,63]

The phenylhydrazones of perinaphthanone and its derivatives are converted into indoles in low yield by boiling for a short time in glacial acetic acid. The indoles can be prepared directly as is the practise in the Fischer-indole synthesis but aromatisation to the indolo[2,3-a]perinaphthene bases cannot be effected by standard dehydrogenation methods.

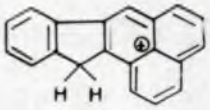
Naphthocarbazolium salts can be obtained directly by boiling a solution of the phenylhydrazone in glacial acetic acid containing perchloric acid, the salt crystallising from the boiling reaction mixture. The initially formed indole undergoes acid



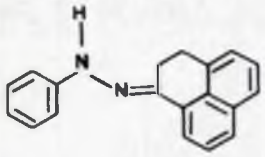
(LIV)

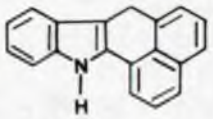


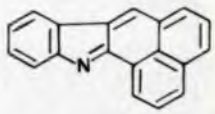
(LV)



(LVa)





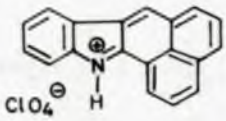


(LVI)

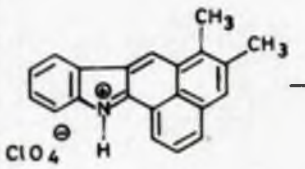
UNSTABLE

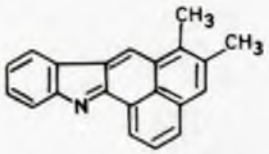
$HClO_4$, CH_3COOH

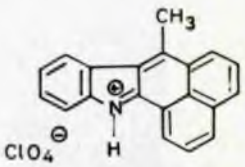
$-H^{\oplus}$



(LVII)

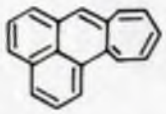




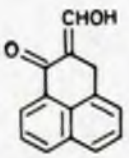


(LIX)

(LVIII)

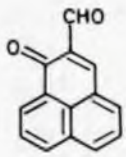


(LX)

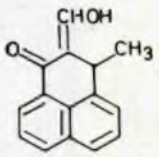


(LXI)

SeO_2



(LXII)



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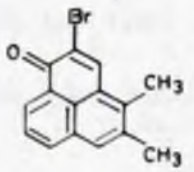
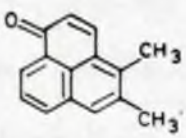


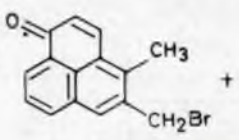
(LXV)

Br_2



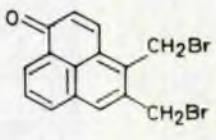
(LXIV)

NBS



(LXVI)

+



(LXVII)

catalysed dehydrogenation without the participation of oxygen.

In view of the readiness with which the π-electron system of the perinaphthenylium cation developes in indeno[2,1-a] perinaphthene we have attempted to synthesis indolo[2,3-a]perinaphthene (LVI) (naphtho[1,8a,8-ab]carbazole) to investigate the effect of the replacement of $C_{(12)}$ in (LV) by nitrogen. This aza-analogue is an indolenine derivative and will, therefore, be basic. The stability of the conjugate acid will be increased due to the possibility of additionally delocalising the cationic charge over the perinaphthene moiety.

Deprotonation of the naphtho[1,8a,8-ab] carbazolium cation (LVII) gives the parent base as a crimson solution in ether. The solutions of the base deposit polymeric material on concentration. The parent base (LVI) is only stable in the form of its salts.

The free base (LVIII) has been obtained from 5,6-dimethylnaphtho[1,8a,8-ab] carbazolium perchlorate (LIX) by treatment of the salt by aqueous ammonia. The crimson, ethereal solution, purified by chromatography, gave the base as dark red needles on concentration. Attempted recrystallisation leads to the precipitation of insoluble polymeric material.

The ultraviolet absorption spectrum of naphtho[1,8a,8-ab] carbazolium perchlorate does not differ markedly from that of

indeno[2,1-a]perinaphthene but the conjugate acid of the latter shows an entirely different type of absorption (Plate IV). Protonation of (LVI), involving the unshared nitrogen 2p electrons, gives the salt in which the π-electron system of the base is still intact. In the formation of the conjugate acid of indeno[2,1-a] perinaphthene, however, a pair of electrons must be withdrawn from the π-electron system of the hydrocarbon, a process resulting in the formation of an entity possessing an entirely different mobile electron system.

B,1X Preliminary Approaches to the Cyclohepta[a]perinaphthene Structure.

The synthesis of cyclohepta[a]perinaphthene (LX) would be of considerable theoretical significance (A,111) and, accordingly, some reactions have been investigated with a view to the preparation of thie compound. A considerable amount of work has been directed towards the synthesis of unsaturated seven-membered rings. The major problem in the synthesis of the hydrocarbon (LX) ie the construction of key intermediates. The approach adopted involves the construction of the seven-membered ring at a late stage, and thus the crux of the problem involves the synthesis of a bis-diformyl perinaphthenone.

B,1X,1. Approaches to 2,3-diformylperinaphthenone.

Perinaphthanone reacts with ethyl formate in the presence of potassium methoxide to form 2-hydroxymethylene

perinaphthanone (LXI) which on oxidation by selenium dioxide gave 2-formylperinaphthenone (LXII) in good yield. 2-Hydroxymethylene-3-methyl-1-oxo-perinaphthane (LXIII) was prepared by an analegous condensation from 3-methylperinaphthanone and ethyl formate. Oxidation of this compound (LXIII) by selenium dioxide gave polymeric material from which no useful product could be isolated.

Direct dehydrogenation of the ketone (LXIII) by either chloranil or triphenylmethyl perchlorate was unsuccessful, intractable tars being obtained by both methods.

The hydroxymethylene ketone (LXIII) did, however, react with N-bromosuccinimide. Succinimide was recovered quantitatively but the product was unstable, and attempts were therefore made to dehydrobrominate the product after removal of succinimide from the reaction mixture. A product was obtained but was very difficult to obtain pure. Purification was by sublimation which had to be conducted about 100° and it took about four days to obtain $>$ 500 mgm. quantities. The product appeared to be the required 2-formyl-3-methylperinaphthenone but the low yield $<$20% precluded its adaptation to any large scale practise. The methyl group in this compound did react with N-bromosuccinimide in the presence of benzoyl peroxide but no useful product was isolated. The route was therefore abandoned.

B.X,11 Approaches to 4,5-diformylperinaphthenone.

One of the complicating factors in the projected synthesis of the 2,3-diformyl compound was that the two groups which had eventually to be converted to formyl were, initially, at different oxidation levels. It was therefore decided to synthesise 4,5-dimethylperinaphthenone (LXIV) and assess its potentialities as an intermediate.

Etards reaction was carried out on the ketone (LXIV) and an orange complex was obtained on addition of chromyl chloride but hydrolysis of this regenerated starting material.

The ketone (LXIV) was brominated by elemental bromine in refluxing carbon tetrachloride in a stream of nitrogen but nuclear bromination alone occurred. The product has been formulated as the 2-bromo compound (LXV) on the basis of the conclusions of previous authors.[64]

N-bromosuccinimide brominates in the side chain of aromatic compounds in the presence of benzoyl peroxide and, in particular, Wenner[65] has reported the preparation of 2,3-bis bromomethylnaphthalene by this method. His procedure was applied to 4,5-dimethylperinaphthenone. The product is unstable but addition of pyridine followed by perchloric acid resulted in the isolation of two products, a mono- and a di- pyridinium perchlorate. These correspond to a mixture of 4(5)-bromomethyl-

-4(5)-methylperinaphthenone (LXVI) and 4,5-bisbromomethylperi-naphthenone (LXVII). This reaction is being further investigated to see if conditions can be modified to produce the latter exclusively. There are several routes available whereby the bisbrommethyl compound might be converted to the required dialdehyde.

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PART C

NOTES

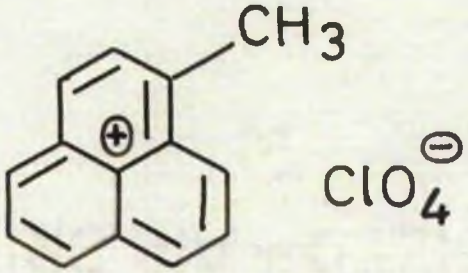
Infrared spectral measurements were carried out with a Grubb-Parsons G.S.2A Double Beam Instrument.

The ultra-violet and visible absorption spectra were measured with a 'Unicam' S.P.500 instrument.

Melting points were determined on a Kofler -type heating stage. Micro-analyses were carried out by Drs. Weiler and Strauss, Oxford.

The terms light petrol and petrol refer to the solvents, petroleum ether (b.p. 40-60°) and petroleum ether (b.p. 60-80°), respectively.

C.1 The Attempted Synthesis of 1-Methylperinaphthenylium Perchlorate



C.1,1 1-Acetylnaphthalene.

A solution of α-naphthyl magnesium bromide, from magnesium (24.2 g.) and 1-bromonaphthalene (139 ml.) in ether benzene (1:1; 1,200 ml.) was added over three hours to a well stirred solution of acetic anhydride (400 ml.) in anhydrous ether (800 ml.) cooled in a three-necked flask (stirrer, condenser and dropping funnel) to -80° by a solid carbon dioxide -ethanol bath. The mixture was stirred for a further two hours after the addition was complete and then allowed to warm up spontaneously to -45° after which ammonium chloride (100 g.) in water (1 l.) was slowly stirred in. The separated organic layer was washed three times with water, dried (Na_2SO_4). Solvent was removed on a boiling water bath, then at reduced pressure (10 mm.) until the temperature rose to 130° when the residue was transferred to a 250 ml. flask and

distillation continued under reduced pressure. The first fraction boiling up to 150°/10 mm. contained naphthalene and was discarded. The product was collected at 154-156°/10 mm. as a pale yellow, viscous oil.

Yield (two runs) 200 g. (60%).

C.1,11. Methyl-1-naphthyl carbinol - 1st preparation.

A solution of 1-acetylnaphthalene (170 g., distilled immediately before use) in ether (400 ml.) was added over forty minutes to a well-stirred solution of lithium aluminium hydride (12.8 g., 30% excess) in ether (800 ml.). After the addition was complete, the solution was refluxed for one hour before being cooled to 10° when it was poured into ice-cold water (1,500 ml.). Hydrochloric acid (5N) was added in excess, the ether phase was separated and washed successively with aqueous sodium hydroxide (20%, 3 x 100 ml.), water (3 x 100 ml.), and dried (K_2CO_3). The aqueous phase was then extracted with a fresh portion of ether (500 ml.) and the latter, after being washed with water, was added to the first extract. After removal of solvent, the residue was distilled under reduced pressure when the alcohol was obtained as a pale yellow oil at 135-140°/0.1 mm which crystallised rapidly. On recrystallisation, it was obtained as colourless needles from petrol-ether (20:1).

Yield 163 g. (95%) m.p. 64.5-65°

(Lit.[1], m.p. 66°)

C.1,111 Methyl-1-naphthyl carbinol - 2nd preparation.

The alcohol was also prepared as described by Pickard and Kenyon[1] from the reaction of acetaldehyde with α-naphthyl magnesium bromide.

Yield 53 g. (61%) m.p. 64.5-66°

C.1.1V β-[Naphthyl]-butyric acid.

Phosphorus tribromide (35 ml.) was added to a solution of methyl-1-naphthyl carbinol (172 g.) in ether (1000 ml.) at 5°. The solution was allowed to warm up to room temperature over one hour and then poured into water (1000 ml.). The ethereal layer was washed free of acid by water (3 x 500 ml.). The aqueous phase was extracted by a fresh portion of ether (500 ml.) and the extract, washed with water, was added to the ethereal solution. The latter was then dried (Na_2SO_4), solvent was removed, and the residual brown oil (which would not crystallise) was dried by azeotropic distillation with a portion of anhydrous benzene (50 ml.), then dissolved in anhydrous benzene (1000ml.)

The benzene solution, cooled to 10°, was added to an ice-cold solution of sodio-malonic ester prepared from sodium (46 g.) and freshly distilled diethyl malonate (380 ml.) in anhydrous ethanol (2000 ml.). Sodium bromide began to deposit

almost at once and the reaction mixture was kept at 0° for 48 hours after which time it was refluxed for two hours. Almost all the solvent was then distilled off (with constant stirring) and the cold semi-solid residue was dissolved in an ether water mixture (1:1, 3000 ml.), the resulting mixture was thoroughly shaken in a separating funnel at intervals over half-an-hour. The ether phase was separated and the ethereal washings of the aqueous phase added to it. The combined ether extracts were washed with water (3 times), dried (Na_2SO_4), and solvent was evaporated. The residual oil was distilled at the water-pump to remove unchanged malonic ester and other low boiling material. The residue was transferred to a 500 ml. flask, and distilled at the oil-pump when the ester was obtained as a pale brown oil, b.p. 182-186°/0.5 mm.

The ester was hydrolysed by refluxing with a mixture of methanol (50 ml.), potassium hydroxide (168 g.) and water (1 l.) for three hours with stirring in a 2 l. flask. The reddish brown oil which separated upon acidification of the cold solution was extracted into ether (3 x 500 ml.). The ethereal extract was washed with water (3 x 300 ml.), and dried (Na_2SO_4) before removal of solvent. The residual oil was heated to 180° in an oil bath when the malonic acid decarboxylated. After the evolution of carbon dioxide had

largely ceased (15 min.) the flask was maintained at this temperature for a further 15 min., then allowed to cool slowly. β-[1-Naphthyl]-butyric acid crystallised and was dissolved in acetone. The solution was filtered and the bulk of the solvent removed by evaporation. The acid was then recrystallised from acetone-petrol when it was obtained as white platelets.

Yield 177 g. (83%) m.p. 109-110°

(Lit.[2], m.p. 109-110°)

C.1,V. 3-Methylperinaphthan-1-one.

β-[1-Naphthyl]-butyric acid was cyclised by anhydrous hydrogen fluoride as described by Bockelheide and Larrabee.[2] 3-Methylperinaphthan-1-one was obtained from benzene-light petrol as massive white prisms.

Yield 37.89 g. (85%) m.p. 62.5-64°

(Lit.[2], m.p. 62-64°)

C.1,VI 3-Methylperinaphthan-1-ol.

This compound was prepared by the lithium aluminium hydride reduction of 3-methylperinaphthan-1-one as previously described. The product crystallised from ethanol as dense

white needles.

Yield 19.0 g. (96%) m.p. 150-151°

(Lit.[2], m.p. 150-151°)

C.1,VII 4(9)-Methylperinaphthene.

3-Methylperinaphthan-1-ol was dehydrated by ethanolic hydrogen chloride solution and the product worked up in the usual manner. The hydrocarbon crystallised from a small volume of light petrol as white plates.

Yield 870 mgm. (90%) m.p. 62-63°

(Lit.[2], m.p. 62.5-63.5°)

C.1,VIII The reaction of Triphenylmethyl perchlorate with 3-Methylperinaphthan-1-ol.

Triphenylmethyl perchlorate (345 mgm.) dissolved in glacial acetic acid (45 ml.) was added to a solution of 3-methylperinaphthan-1-ol (197 mgm.) in glacial acetic acid (10 ml.). The solution turned dark greenish-brown, and the green solid which separated out was filtered off, washed with ether and dried. The filtrate was diluted with water (200 ml.), extracted with ether, and the ethereal extract was washed well with water before drying (Na_2SO_4). Solvent was removed, and the residual solid dissolved in light petrol (50 ml.). This solution was filtered through a short column of alumina and solvent evaporated from the eluates. The residual triphenyl-

methane crystallised from a small volume of light petrol.

Yield of green solid 140 mgm.

Yield of triphenylmethane 197 mgm (81.5%) m.p. 92-93°

C.1,1X <u>The reaction of Triphenylmethyl perchlorate with 4(9)-Methylperinaphthene</u>.

Triphenylmethyl perchlorate (345 mgm.) in glacial acetic acid (80 ml.) was added to a solution of 4(9)-methylperinaphthene in glacial acetic acid (10 ml.). The solution became dark and a green solid separated out. This was filtered off and triphenylmethane recovered from the mother liquors in the usual manner.

Yield of green solid 174 mgm.

Yield of triphenyl methane 208 mgm. (86%) m.p. 92-93°

C.1,X. <u>The reaction of Chloranil with 4(9)-Methylperinaphthene in the presence of perchloric acid</u>.

A solution of 4(9)-methylperinaphthene (179 mgm.) in glacial acetic acid (10 ml.) was added to chloranil (246 mgm.) and perchloric acid (72%; 1 ml.) dissolved in glacial acetic acid (90 ml.) at room temperature. The solution became dark yellow then deep green and precipitated a green solid. Precipitation was completed by the addition of dry ether (50 ml.). The precipitate was filtered off and washed with dry ether. The dark green filtrate on being diluted with water gave a

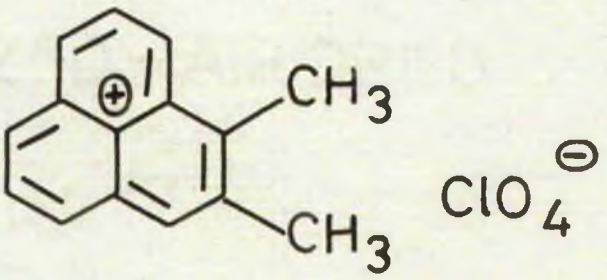
reddish-orange organic layer. This was washed free from acetic acid with water before being extracted with alkali (20% aqueous; 3 x 50 ml.). The white precipitate obtained on acidification of the alkaline extract was extracted into ether, the ether layer was dried (K_2CO_3), and solvent was removed. The white residue, recrystallised from glacial acetic acid, gave 2,3,5,6-tetrachloroquinol as white needles.

Yield of green solid 94 mgm.

Yield of quinol 162 mgm (65%) m.p. 230°

(Lit.[20], m.p. 232°)

C.11. The Synthesis of 1,2-Dimethylperinaphthenylium Perchlorate.



C.11,1 1-Chloromethyl-2,3-dimethylnaphthalene.

This compound was prepared from 2,3-dimethylnaphthalene as described by Hewett.[8]

C.11,11 β-[2,3-Dimethylnaphthyl]-propionic acid.

A solution of 1-chloromethyl-2,3-dimethylnaphthalene (10.2 g.) in benzene (30 ml.), cooled to 5°, was added to an ice-cold solution of sodio-malonic ester made from sodium (2.3 g.) and freshly distilled diethylmalonate (27 ml.) in anhydrous ethanol (250 ml.). A precipitate formed slowly and the temperature of the reaction mixture was maintained at 0° for 48 hours. It was then refluxed for three hours, the bulk of the solvent was distilled off, and the semi-solid white residue was dissolved in a mixture of ether-water (1:1, 1,500 ml.). The aqueous layer was separated, washed with ether, and the ethereal washings were added to the ether layer which was then washed with water (5 x 100 ml.) and dried (Na_2SO_4) before the removal of solvent. The residual oil was then refluxed with water (400 ml.) and potassium hydroxide (11.2 g.) for four hours with constant stirring; some carbon dioxide was evolved during this period. The cold alkaline solution was extracted by ether, filtered, warmed to 80° and acidified (conc. HCl). The voluminous white precipitate was extracted into ether after cooling. The ethereal layer was washed with water, dried (Na_2SO_4), and solvent was evaporated off. The white residue crystallised from light petrol:ether (1:1) as white needles.

Yield 13.3 g. (98%) m.p. 198-200°

β-[2,3-Dimethylnaphthyl]-malonic acid (128 g.), in a 2 l. flask, was heated to 190° in an oil bath. The evolution of carbon dioxide continued for thirty minutes after which the product was allowed to cool slowly. The crystalline cake was dissolved in acetone-ether (4:1) and the solution filtered. Solvent was removed from the filtered solution under reduced pressure. The white residue crystallised from benzene as white needles.

Yield 101 g. (94.5%) m.p. 129-130°

(Lit.[4], m.p. 132°)

C.11,111 4,5-Dimethylperinaphthan-1-one.

β-[2,3-Dimethylnaphthyl]-propionic acid (73 g.) was added to hydrogen fluoride (600 ml.) in a polythene beaker. The mixture became deep red, and was allowed to stand for five hours at 0° before being hydrolysed on crushed ice (1000 g.). A yellow oil was obtained which rapidly crystallised. The mixture was exhaustively extracted with ether (8 x 300 ml.), and the ethereal extract was then washed with water (5 x 200 ml.), aqueous potassium hydroxide (15%, 4 x 250 ml.), water (4 x 250 ml.), and dried before removal of solvent.

The yellow crystalline residue crystallised from ether as lustrous orange-yellow plates.

Yield 62.8 g. (93.5%) m.p. 113-114°

(Lit.[4], m.p. 114°)

C.11,IV **4,5-Dimethylperinaphthan-1-ol.**

4,5-Dimethylperinaphthan-1-one (5.85 g.) in benzene (80 ml.) was added dropwise to a vigorously stirred solution of lithium aluminium hydride (450 mgm.) in ether (200 ml.). The mixture was refluxed for an hour, allowed to cool, and water (18 ml.) was added cautiously to the stirred suspension. The resulting mixture was poured into ice-cold water (800 ml.) acidified by hydrochloric acid. The aqueous phase was washed with benzene and the washings were added to the organic layer. The combined extracts were washed with water, and dried (K_2CO_3). Solvent was removed and the pale yellow crystalline residue was recrystallised from acetone after charcoal screening. The product was obtained as very pale yellow needles.

Yield 5.24 g. (90%) m.p. 133.5-135.5°

$C_{18}H_{16}O$ requires C,84.89% H,7.60%

Found 84.69% 7.82%

C.11,V **4,5-Dimethylperinaphthene**

Ethanol (5 ml.), saturated with anhydrous hydrogen chloride, was added to 4,5-dimethylperinaphthan-1-ol (329 mgm.) dissolved in ethanol (5 ml.). The pale yellow solution was refluxed for 15 min., cooled, and poured into water (150 ml.). The turbid, yellow emulsion was extracted with ether (3 x 80 ml.). The ethereal extract was washed successively with water (2 x 100 ml.),

saturated sodium bicarbonate solution (2 x 100 ml.), distilled water (100 ml.), and dried (K_2CO_3). Solvent was distilled off, and the residual oil, in light petrol (50 ml.), was chromatographed on alumina (12 x 2.7 cm.) using light petrol to develop the column. Solvent was removed from the eluates (800 ml.) and the colourless residual oil, on being kept overnight in an evacuated desiccator, crystallised as colourless platelets. This compound is low melting, and decomposes rapidly in moist air to a green oil.

Yield 218 mgm. (73%) m.p. about 65°

To a solution of the hydrocarbon (39 mgm.) in ethanol (4 ml.) was added a solution of trinitrobenzene (42 mgm.) in ethanol (4 ml.). There was a deep red colouration followed by the crystallisation of orange red needles. These were recrystallised from ethanol.

Yield 73 mgm (90%) m.p. 122-124°

$C_{21}H_{17}N_3O_8$ requires N,10.31%

found 10.21%

C.11,V1 <u>4,5-Dimethyl-1-hydroxyperinaphthenylium perchlorate.</u>

4,5-Dimethylperinaphthan-1-one (210 mgm.), triphenylmethyl perchlorate (344 mgm.), and glacial acetic acid (80 ml.) were refluxed for five minutes during which time the solution became orange-red in colour. Upon cooling, a flocculent orange precipitate separated out from the reaction mixture. The

The precipitate was filtered off, washed with dry ether, and crystallised from acetic acid as orange needles.

Yield 284 mgm. (91.5%) m.p. slow dec. 220-240°

$C_{18}H_{13}ClO_8$ requires C, 58.37%, H, 4.24%

Found 58.45% 4.27%

C.11,V11 1,2-Dimethylperinaphthenylium perchlorate

To a solution of 4,5-dimethylperinaphthene (474 mgm.) in glacial acetic acid (3 ml.) was added a solution of o-chloranil (608 mgm.) in glacial acetic acid (5 ml.) containing perchloric acid (0.6 ml.). The deep red colour of the solution was immediately replaced by a dark greenish brown and orange-red needles precipitated. These were filtered off, washed with dry ether, and dried in a vacuum desiccator over P_2O_5/KOH for one hour. The compound is stable in the solid state but rapidly decomposes to dark green polymeric material on attempted recrystallisation from acetonitrile, acetic acid or methanol containing perchloric acid

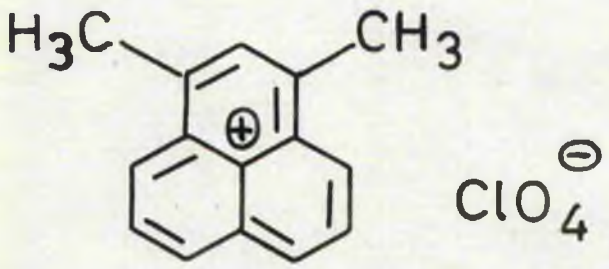
Yield 528 mgm. (73.5%) m.p. slow decomposition on heating

$C_{18}H_{13}ClO_4$ requires ClO_4 33.98%

found 34.21%

34.38%

C.111 1,3-Dimethylperinaphthenylium perchlorate



C.111,1 1,3-Dimethylperinaphthan-1-ol

3-Methylperinaphthan-1-one (9.81 g.) in anhydrous ether (80 ml.) was added slowly to a stirred solution of methyl magnesium iodide from CH_3I (6.2 ml.) and magnesium (2.4 g.) in ether (300 ml.). A pale yellow precipitate formed as the ketone was added. After the additon was complete, the solution was refluxed gently for one hour. The cooled mixture was poured into ice-cold water acidified by hydrochloric acid. The aqueous phase was separated and washed with a fresh portion of ether which was then added to the organic phase. The ethereal extract was washed with water, saturated sodium bicarbonate solution, water, and dried (K_2CO_3). The solvent was distilled off and the pale yellow residue crystallised twice from petrol. It was thus obtained as dense white needles with a satin sheen.

Yield 7.59 g. (71.6%) m.p. 100.5-101.5°

$C_{18}H_{16}O$ requires C,84.89% H,7.60%

Found 84.64% 7.58%

The combined residues from the crystallisations were dissolved in ethanol (50 ml.) and a saturated solution of anhydrous hydrogen chloride in ethanol (50 ml.) was added. The solution was refluxed for 15 minutes, cooled, and poured into water. The aqueous mixture was extracted with ether (5 x 100 ml.) and the ethereal extract was washed with water (5 x 100 ml.), saturated sodium bicarbonate solution (2 x 100 ml.), water (100 ml.) and dried (K_2CO_3). The solvent was then evaporated, and the residual oil, dissolved in light petrol-benzene (1:1; 40 ml.), was chromatographed on alumina (24 x 2.7 cm.) using light petrol for development. Solvent was removed from the eluates (1 l.) and the residue, in light petrol (50 ml.), rechromatographed on alumina (24 x 2.7 cm.). The colourless light petrol eluates (1 l.) were concentrated to ca. 20 ml. when colourless platelets crystallised out. The hydrocarbon was recrystallised from light petrol.

Yield 1.47 g. (15%). m.p. 151-153°

$C_{18}H_{14}$ requires C,92.74% H,7.26% M.W. 194

found 91.09% 7.46% 186

90.93% 7.52%

C.111,11 4,6-Dimethylperinaphthene- 1st preparation.

1,3-Dimethylperinaphthan-1-ol (2.12 g.) was dissolved in ethanol and a saturated solution of anhydrous hydrogen chloride in ethanol (20 ml.) added. The solution was refluxed for 15 minutes and then allowed to cool to room temperature. The cooled solution was poured into water (300 ml.) and the mixture extracted with ether (4 x 100 ml.). The ethereal extract was washed well with water, and dried (Na_2SO_4) before evaporation of solvent. The residue was dissolved in light petrol (50 ml.) and chromatographed on alumina (18 x 2.7 cm.). The column was developed by light petrol and the solvent was then removed from the eluates (1,500 ml.) leaving a white crystalline residue. The hydrocarbon crystallised from light petrol as colourless platelets.

Yield 1.53 g. (78.9%) m.p. 151-153°

$C_{15}H_{14}$ requires C,92.74% H,7.26% M.W. 194

found 92.59% 7.35% 164

The hydrocarbon is unstable in air and slowly decomposes to a yellow oil. It forms a trinitrobenzene derivative as orange-red needles which decompose on heating. No melting point was observed, the compound going black on the heating stage.

C.111,111 1,3-Dimethylperinaphthenylium perchlorate - 1st preparation.

A solution of T.B.Q. (492 mgm.) and perchloric acid (72%, 0.5 ml.) in acetonitrile (5 ml.) was added to 1,3-dimethylperinaphthan-1-ol (423 mgm.) dissolved in acetonitrile (10 ml.).

The solution became dark red in colour, and ether (50 ml.) was immediately added. Orange-yellow needles precipitated out. The product was filtered off and washed with dry ether. The salt is stable in air but solutions rapidly become green on standing. Attempted recrystallisations from acetonitrile, acetic acid, and methanol containing perchloric acid produced green polymeric material.

Yield 489 mgm (83.5%) m.p. dec. on heating

$C_{18}H_{18}ClO_4$	requires	ClO_4	33.98%
	found		34.12%
			34.42%

Cl11,14 <u>1,3-Dimethylperinaphthenylium perchlorate - 2nd preparation.</u>

A solution of T.B.Q. (246 mgm.) in acetonitrile (15 ml.) containing perchloric acid (72% 0.2 ml.) was added to a solution of 4,6-dimethylperinaphthene (194 mgm.) in acetonitrile (10 ml.). The solution became dark red, and anhydrous ether (50 ml.) was added after 45 second. A precipitate of orange-yellow needles came out of solution, and this was filtered off, washed with dry ether, then dried in a desiccator over P_2O_5/KOH.

Yield 259 mgm. (88.3%)

$C_{18}H_{18}ClO_4$	requires	ClO_4	33.98%
	found		34.36%
			34.28%

C.111,V <u>4,6-Dimethylperinaphthene - 2nd preparation</u>.

1,3-Dimethylperinaphthenylium perchlorate (1.27 g.) was added portionwise to a stirred solution of lithium aluminium hydride (465 mgm.)in anhydrous ether over 15 minutes. The gray solution was gently refluxed for 30 minutes and then cooled to 10°. Water was then added dropwise and the mixture was poured into aqueous hydrochloric acid. The aqueous layer was separated washed with ether, and the washings added to the ether layer which was then washed well with water before drying (Na_2SO_4). Solvent was removed, and the residue chromatographed on alumina (20 x 2.7 cm.), using light petrol to develop the column. The eluates (1,500 ml.) were evaporated to dryness. A white crystalline residue remained.

Yield 764 mgm (91%) m.p. softens 105° melts 135-145°

The product was dissolved in light petrol (50 ml.) and rechromatographed (twice) on alumina (20 x 2.17 cm.). The white residue obtained on evaporation of the eluates was recrystallised successively from petrol and ethanol.

Yield 500 mgm (59.3%) m.p. 151-153°

Mixed m.p. with the dehydration product of 1,3-dimethyl perinaphthan-1-ol 146-150°

$C_{15}H_{14}$ requires C,92.74%, H,7.26% M.W. 194

found 92.15%, 7.02 171

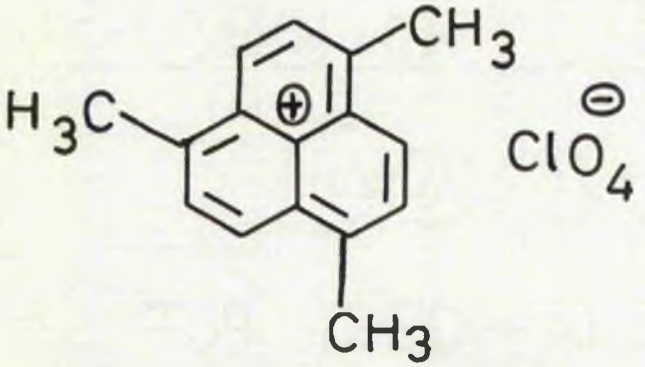
C.111,VI 1,3-Dimethylperinaphthenylium perchlorate - 3rd preparation.

The hydrocarbon (194 mgm), prepared as described in experiment C.111,V, was dissolved in acetonitrile (10 ml.). T.B.Q. (246 mgm.) and perchloric acid (0.2 ml.) in acetonitrile (3 ml.) was added to this solution which became deep red in colour. Anhydrous ether was added after 45 seconds, and orange-yellow needles came out of solution. The precipitate was filtered off, washed with dry ether and dried in a desiccator over P_2O_5/KOH

Yield 258.5 mgm. (81.5%)

$C_{13}H_{13}ClO_4$	requires	ClO_4	33.98%
	found		34.07%
			33.78%

C.IV The Preparation and Reactions of 1,4,7-Trimethylperinaphthenylium perchlorate.



C.IV,1 3,6,9-Trimethylperinaphthan-1-ol.

This compound was synthesised from 1,6-dimethylnaphthalene as described by Bonthrone.

C.IV,11 1,4,7-Trimethylperinaphthenylium perchlorate.

3,6,9-Trimethylperinaphthan-1-ol (6.78 g.), triphenylmethyl perchlorate (10.29 g.) and glacial acetic acid (1,200 ml.), in a 2 l. flask, were warmed until dissolution took place, and the solution was then gently refluxed for five minutes. The solution was then rapidly cooled, and the product crystallised as bronze needles. The salt was filtered off, washed with dry ether and, on recrystallisation from acetonitrile, formed bronze needles.

Yield 5.89 g. (64%) m.p. dec. 240° (lit.,[18] m.p. dec. 240°)

C.IV,111 3,6,9-Trimethylperinaphthene.

1,4,7-Trimethylperinaphthenylium perchlorate (9.21 g.) was added portionwise to a stirred solution of lithium aluminium hydride (750 mgm.) in anhydrous ether (600 ml.) over half-an-hour. Stirring was continued for a further 45 minutes while the solution was boiled gently. The reaction mixture was cooled in an ice bath, and water (18 ml.) added cautiously to destroy the excess hydride. The resulting mixture was filtered, ether (500 ml.) was added, and the ethereal layer was separated. The ethereal solution was washed with water (twice), dried (K_2CO_3), and solvent was evaporated. The residual oil was dissolved in light petrol (50 ml.) and chromatographed on a column of alumina (15 x 2.7 cm.) using light petrol as eluant. Solvent was removed from the eluates, and the white crystalline residue dissolved in methanol-acetone (10:1). The hydrocarbon, 3,6,9-trimethylperinaphthene, crystallised as colourless needles.

Yield 5.5 g. (90%). m.p. 59-60°.

$C_{15}H_{16}$ requires C, 92.3; H, 7.7

found. C, 92.10; H, 7.87.

C.IV,1V 1,4,7-Trimethylperinaphthenylium iodide.

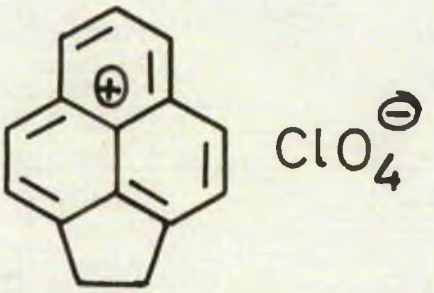
A boiling solution of sodium iodide (300 mgm.) in acetonitrile (10 ml.) was added to 1,4,7-trimethylperinaphthenylium perchlorate (306.5 mgm.) in boiling acetonitrile (50 ml.). 1,4,7-

Trimethylperinaphthenylium iodide immediately precipitated from the solution as grey-black needles. The solution was cooled somewhat and filtered while still hot. The salt was obtained as grey-black needles.

Yield 206 mgm. (60%) m.p. slow dec. without melting
melts with dec. on a block preheated to 185°

$C_{14}H_{13}I$	requires	C, 57.48%	H, 4.5%	I, 37.97%
	found	58.28%	4.3%	37.00%

C.V. 1,2-Dihydrocyclopenta[gh]perinaphthenylium perchlorate



C.V,1 5-Formylacenaphthene.

This was prepared by the formylation of acenaphthene as described by Fieser and Jones[6]

Yield 30 g. (30%) m.p. 106-107° (lit.[6] m.p.107-108°)

C.V,11 5-Hydroxymethylacenaphthene.

5-Formylacenaphthene (37.9 g.) in anhydrous benzene (200 ml.) was added slowly to a vigorously stirred solution of lithium aluminium hydride (2.47 g.) in dry ether (800 ml.). A grey complex separated out, and when the addition was completed the reaction mixture was refluxed gently for 30 minutes before being cooled in an ice-bath. The excess of hydride was destroyed by the dropwise addition of a solution of ethyl formate in ether. The contents of the flask were then poured onto crushed ice (160 g.) acidified with hydrochloric acid.

Some of the product separated at the interface as white needles which were filtered off, washed well with water and recrystallised from acetone.

The organic phase was separated, washed with water (2 x 100 ml.), saturated sodium bicarbonate solution (2 x 200 ml.) and water (100 ml.) and combined with the benzene extracts (2 x 75 ml.) used to wash the aqueous acid phase. The combined extracts were dried (K_2CO_3) before removal of solvent under reduced pressure. The white residue crystallised from benzene as white needles.

Yield 33.89 g. (90%) m.p. 153-154° (Lit.[a] m.p. 153.8-154.8)

C.V,111 5-Bromomethylacenaphthene

Phosphorus tribromide (4 ml.) was added to 5-hydroxymethylacenaphthene (21.05 g.) suspended in dry benzene (300 ml.) The solution was allowed to stand for 30 minutes after which it was hydrolysed by the addition of water (200 ml.).

The aqueous acid phase was washed with benzene (2 x 100 ml.), and then discarded. The combined benzene extracts were washed with water (2 x 100 ml.), saturated sodium bicarbonate solution (2 x 150 ml.), water (100 ml.), and dried (Na_2SO_4). Solvent was evaporated under reduced pressure from the filtered solution. The product crystallised from acetone-petrol (1:1) as colourless prisms. This compound is unstable, turning green on standing, and evolving hydrogen bromide. It could not be analysed.

Yield 20 g. (72%) m.p. 108-109°

C.V,IV β-[5-Acenaphthenyl]-malonic acid:

5-Bromomethylacenaphthene (21.3 g.), dissolved in dry benzene (50 ml.), was added to a cooled solution of sodio-malonic ester from sodium (7 g.) and freshly distilled diethyl malonate (40 ml.) in absolute ethanol (400 ml.). Sodium bromide began to precipitate at once. The reaction mixture was maintained at 0° for 72 hr. then refluxed for 4 hr. The bulk of the solvent was distilled off and a solution of potassium hydroxide (80 g.) in water (400 ml.) was added to the ester. The solution was boiled for 4 hr.

The contents of the flask were allowed to cool and then extracted by ether (2 x 100 ml.). The ethereal extract was discarded. The alkaline layer was filtered, warmed to 80°, and acidified (conc. HCl). The voluminous white precipitate was filtered off after cooling, washed with water, and dried in a vacuum desiccator over P_2O_5/KOH.

Yield 22.45 g. (97.5%) m.p. 181-183.5°

C.V,V β-[5-Acenaphthenyl]-propionic acid:

β-[5-Acenaphthenyl]-malonic acid (42 g.) was heated to 180-190° in an oil bath. At an internal temperature of 170° the acid softened, and evolved carbon dioxide. The reaction was complete after 30 min., and the flask was slowly rotated while cooling to form a loose cake. The acid crystallised as colourless needles from benzene.

Yield 31.9 g. (90%) m.p. 188-19°

Lit.[6] m.p. 191-192°

C.V,VI Cyclisation of β-[5-Acenaphthenyl]-propionic acid by anhydrous hydrogen fluoride.

The substituted propionic acid (26.65 g.) was added to hydrogen fluoride (250 ml.) in a polythene beaker. The red solution was allowed to stand for 25 min., then hydrolysed by pouring onto crushed ice (400 g.), and after 3 hr. the aqueous acid mixture was extracted by ether (3 x 250 ml.). The ethereal extract was washed free of mineral acid by water (5 x 200 ml.), washed with aqueous potassium hydroxide (10%, 2 x 100 ml.) to remove unchange organic acid, then with water (2 x 100 ml.), and dried (K_2CO_3) before removal of solvent under reduced pressure. The residual oil crystallised as a pale yellow solid which melted over the range 78-87°. Neither fractional crystallisation nor sublimation in a closed system improved thie melting point range.

The pale yellow solid, in dry benzene (85 ml.), was chromatographed on alumina (27 x 2.7 cm.).

On development with light petrol-benzene (1:1) a pale yellow band passed down the column. Removal of solvent from the eluates, followed by crystallisation from light petrol: benzene (1:1) gave 1,2,5,6-tetrahydro-7-oxo-7H-cyclopenta[gh] perinaphthene as pale yellow prisms. Further recrystallisation

did not raise the melting point.

Yield 14.5 g. (60%) m.p. 97-98°

(Lit.[6] m.p. 98-99°)

Continued development of the column with benzene removed a very pale orange band from the column. Evaporation of the eluates gave 4,5,8,9-tetrahydro-6-oxo-6H-cyclopenta[e] acenaphthylene as colourless leaflets.

Yield 830 mgm. (3.4%) m.p. 189-190°

(Lit.[7], m.p. 187-188°)

On continued elution with ether, a deep yellow band rapidly passed down the column. Removal of solvent from the golden eluates followed by crystallisation from light petrol benzene (1:4) yielded 1,2-dihydro-5-oxo-5H-cyclopenta[gh] perinaphthene as golden yellow needles.

Yield 280 mgm. (1.1%) m.p. blackening 150° melts 160-165°

(Lit.[7], blackening 158° melts 174°)

Infrared carbonyl absorption was as follows:

1,2,5,6-tetrahydro-7-oxo-7H-cyclopenta[gh]perinaphthene

1672 cm.$^{-1}$ (nujol) lit.[7] 1675 cm.$^{-1}$ (KBr disc).

4,5,8,9-tetrahydro-6-oxo-6H-cyclopenta[e]acenaphthylene.

1690 cm.$^{-1}$ (nujol) Lit.[7], 1689 cm.$^{-1}$ (KBr disc).

1,2-dihydro-5-oxo-5H-cyclopenta[gh]perinaphthene.

1639 cm.$^{-1}$, 1623 cm.$^{-1}$ (nujol) Lit.[7] 1634 cm.$^{-1}$, 1618 cm.$^{-1}$ (KBr disc).

C.V,Vii. Lithium aluminium hydride reduction of 1,2,5,6-Tetrahydro-7-oxo-7H-cyclopenta[gh]perinaphthenes

The saturated ketone (13.23 g.) in dry benzene (50 ml.) was added to a vigorously stirred solution of lithium aluminium hydride (960 mgm.) in anhydrous ether (300 ml.) at such a rate that the reaction mixture boiled gently. When the addition was complete the reaction mixture was refluxed for a further 45 minutes. The excess of hydride was destroyed by the cautious addition of water to the cooled reaction mixture which was then poured into ice-water (800 ml.) acidified with hydrochloric acid.

The separated aqueous acid phase was washed with a fresh portion of ether which was then added to the organic phase. The combined extracts were washed with water (2 x 100 ml.), saturated sodium bicarbonate solution(150 ml.), water (200 ml.), and dried (Na_2SO_4) before the removal of solvent. The white residue was crystallised from petrol-ethanol.

Yield 11.2 g. m.p. 150-159°

Slow crystallisation from light petrol-ethanol gave two crops of crystals. The first was 1,2,5,6-tetrahydro-7-hydroxy-7H-cyclopenta[gh]perinaphthene which was recrystallised from benzene-chloroform as fluffy white needles. The second, much more soluble component, was 1,2-dihydro-5H-cyclopenta[gh] perinaphthene which recrystallised as dense white needles from

petrol or methanol. 1,2,5,6-Tetrahydro-7-hydroxy-7H-cyclopenta [gh]perinaphthenone.

Yield 7.1 g.(54%) m.p. 150-152°

$C_{18}H_{14}O$ requires C,85.7% H,6.7%

found 85.54% 6.67%

1,2-Dihydro-5H-cyclopenta[gh]perinaphthenone.

Yield 3.83 g. (31.5%); m.p. 92-93°.

$C_{18}H_{12}$ requires C,93.71% H,6.30%

found 93.67% 6.52%

C.V,VIII <u>1,2-Dihydro-5H-cyclopenta[gh]perinaphthenone</u>.

1,2,5,6-Tetrahydro-7-hydroxy-7H-cyclopenta[gh]perinaphthenone (2g.) and anhydrous ethanol (20 ml.), saturated with anhydrous hydrogen chloride, were refluxed for 20 min. during which time the solution became deep blue. The cooled reaction mixture was poured into water, and the mixture was extracted with with petrol (3 x 150 ml.). The petrol extract was washed free from acid, dried (K_2CO_3), and solvent was removed. The residual oil was chromatographed on alumina (25 x 2.7 cm.) using light petrol to develop the column. The eluates, evaporated to low volume, gave the hydrocarbon as white needles.

Yield 1.58 g. (87%) m.p. 92-93°.

The hydrocarbon does not react with N-bromosuccinimide or ethanolic potassium methoxide.

C.V,1X <u>1,2-Dihydrocyclopenta[gh]perinaphthenylium perchlorate</u>

A mixture of 1,2-dihydro-3H-cyclopenta[gh]perinaphthene (1.17 g.) triphenylmethyl perchlorate (2.44 g.) and acetonitrile (20 ml.) was refluxed for 10 min. The colour of the solution deepened from orange to pale green. Ether (10 ml.) added to the cooled solution gave a pale yellow precipitate which appeared only to be stable when covered by a layer of anhydrous solvent. The pale greenish solution was diluted with water (150 ml.) and ether (150 ml.). After being shaken the ether layer was separated, washed with water, dried (K_2CO_3), and solvent was removed. The residue, in light petrol-benzene (5:1), was chromatographed on alumina (12 x 2.7 cm.).

The column was first developed with light petrol (800 ml.) Evaporation of solvent from the eluates left a white residue which was obtained as needles after recrystallisation from ethanol.

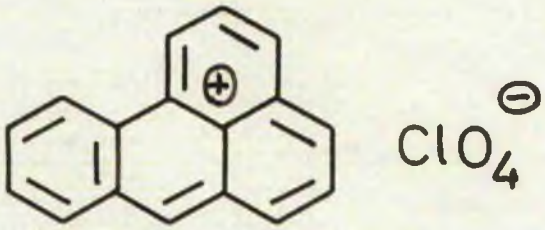
Yield 1.27 g. (73%) m.p. and mixed m.p. with triphenylmethane 91-92°.

Further development of the column with benzene brought off a brown band as orange red eluates. Removal of solvent gave a viscous, dark-brown oil from which no useful product could be isolated.

In another such experiment with the hydrocarbon (815 mgm.) and triphenylmethyl perchlorate (1,470 mgm.) the yield of

crude triphenylmethane was 1,060 mgm. (90%) and 985 mgm (90%) after recrystallisation.

C.V1 Benzanthrenylium perchlorate.



C.V1,1. Benzanthrene.

This was prepared by the reduction of benzanthrone with aluminium chloride and lithium aluminium hydride as described by Brown and White.[8]

Yield 18.1 g. (83.5%) m.p. 83-83.5° (lit.[8], m.p. 83.5-84°).

C.V1,11. Benzanthrenylium perchlorate

Triphenylmethyl perchlorate (756 mgm.) dissolved in glacial acetic acid (85 ml.) was added to a solution of benzanthrene (506 mgm.) in glacial acetic acid (5 ml.). The solution turned purple, and the salt began to crystallise out as purple needles. The flask was rapidly chilled by cold water, and the product was filtered off, and washed successively with glacial acetic acid and anhydrous ether. The salt was transferred rapidly to a vacuum desiccator and dried over P_2O_5/KOH for one hour. The product decomposes to a black tar in air.

Yield 419 mgm. (57%)

$C_{17}H_{11}ClO_4$ requires ClO_4 31.6%

found 31.38%

31.45%

C.VI,111 The Hydrolysis of Benzanthrenylium perchlorate.

Benzanthrenylium perchlorate (1.898 g.) was hydrolysed by warm distilled water (250 ml.). After two hours the hydrolysis products were extracted into benzene (3 x 75 ml.). The combined extracts were washed with water, dried (Na_2SO_4), and solvent was removed under reduced pressure. The residue was dissolved in light petrol-benzene (50 ml.) and chromatographed on alumina (24 x 3.5 cm.).

Benzanthrene was eluted first from the column using light petrol:benzene (1:1) as eluant. Removal of solvent and recrystallisation from ethanol gave the hydrocarbon as pale yellow, lustrous leaflets.

Yield 479 mgm (37% based on salt)

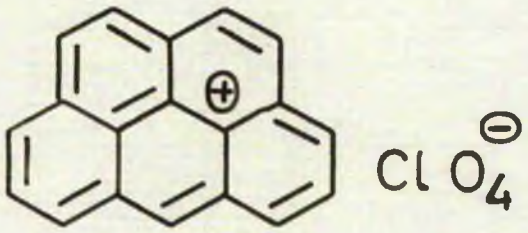
The m.p. and mixed m.p. was 83-84°.

Further development of the column with benzene:ether (1:1) brought a bright orange band down from the top of the column. On evaporation of the solvent the residue crystallised from ethanol as bright yellow needles.

Yield 540 mgm. (34% based on salt).

The m.p. and mixed m.p. with benzanthrone was 171-172°.

C.V11 Benzo[cd]pyrenium perchlorate
(Naphtho-[4.4a.5-bcd]perinaphthenylium perchlorate)



C.V11,1 3.4-Dihydro-5-hydroxy-5H-benzo[cd]pyrene.

Lithium aluminium hydride (100 mgm.) was added portion wise to a solution of 3,4-dihydro-5-oxo-5H-benzo[cd]pyrene (1.1 g.) in ether:benzene (1:1, 50 ml.). When the vigorous reaction had subsided, the mixture was boiled for one minute, and then poured into water. The resulting mixture was acidified by dilute HCl and extracted with ether:benzene (1:2, 750 ml.). The organic phase was washed free from acid, dried, and the solution evaporated to low volume. The alcohol crystallised from benzene (50 ml.) as pink-tinged needles which, after one further crystallisation, were colourless.

Yield 960 mgm (87%) m.p. 165-168°

$C_{19}H_{14}O$ requires C,88.35%, H,5.46%

found 88.63%, 6.22%

C.VII,11 <u>The dehydration of 3,4-Dihydro-5-hydroxy-5H-benzo[cd]pyrene.</u>

Acetic acid (50 ml.), saturated with hydrogen chloride, was added to a boiling solution of 3,4-dihydro-5-hydroxy-5H-benzo[cd]pyrene (4.58 g.) in acetic acid (50 ml.), and the resulting green solution was boiled under reflux for five minutes before being diluted with water. The precipitated solid was extracted into ether (350 ml., 150 ml.), and the ethereal extract was washed successively with water (twice), 5N sodium hydroxide (twice), water (twice), and dried (K_2CO_3) before removal of solvent. The residual oil was dissolved in benzene: light petrol (5:3) and chromatographed on alumina (12 x 3.2 cm.) using benzene:light petrol (1:1) as eluant. The eluates were pale yellow, and an orange, strongly adsorbed band remained at the top of the column. Solvent was removed from the eluates, and the residual oil was rechromatographed on a column of alumina (12 x 3.2 cm.) using benzene:light petrol (1:8) to develop the column. The eluates were evaporated under reduced pressure, and the residue dissolved in benzene (20 ml.). Boiling alcohol (30 ml.) was added, and the hydrocarbon crystallised as pale yellow plates

Yield 2.72 g. (64%) m.p. 127-130°.

After one further crystallisation from acetonitrile the

m.p. was 127.5-129.5. The hydrocarbon, 6H-benzo[cd]pyrene or isomer, dissolves in concentrated H_2SO_4 or 72% $HClO_4$ to give a deep green solution, red to transmitted light.

$C_{19}H_{13}$ requires C,95.0%, H,5.0%

found 94.84% 5.12%

C.V11,111 Benzo[cd]pyrenium perchlorate.

A filtered solution of triphenylmethyl perchlorate (1,370 mgm.) in acetonitrile (15 ml.) was added to a boiling filtered solution of 6H-benzo[cd]pyrene (960 mgm.) in acetonitrile (15 ml.). A solid began to separate at once from the solution as fine black needles. After cooling to room temperature the deep green solution was filtered and the salt washed with a small volume of acetonitrile followed by dry ether (100 ml.), then dried in an evacuated desiccator over P_2O_5/KOH.

Yield 930 mgm (69%)

A further 190 mgm. was obtained from the mother liquors by the addition of ether.

Total Yield 1,120 mgm. (83%) m.pt dec. 185°

The salt is only stable in acetonitrile containing perchloric acid, in its absence the solutions rapidly become yellow.

$C_{19}H_{11}ClO_4$ requires C,67.4%, H,3.27% Cl,10.47%

found 67.49% 3.36% 10.53%

The mother liquors were diluted with a large volume of ether, filtered, and poured into water. The ethereal layer was washed twice with water, dried (K_2CO_3) and the solvent was removed. The residue was dissolved in light petrol and filtered through alumina (10 x 2.7 cm.) which retained a thin orange band at the top of the column. Triphenyl methane was obtained from the eluates concentrated to low volume.
Yield 710 mgm. (73%) m.p. 91-93°.

C.VII,IV Hydrolysis of Benzo[cd]pyrenium perchlorate.

A mixture of the perchlorate (1,560 mgm.), benzene (100 ml.), acetonitrile (25 ml.) and water (25 ml.) was shaken for 40 min. until all the black solid had disappeared. The organic layer, now yellow, was separated, washed with water (twice), dried (K_2CO_3) and the volume of the solution concentrated to ca. 40 ml. On cooling orange brown needles separated out. Solid.

The orange-brown needles (530 mgm., 91%, melting range 220-250°) were dissolved in benzene (100 ml.) and chromatographed on alumina (15 x 2.7 cm.). Initial development with benzene brought a small quantity of a colourless hydrocarbon off the column.

Elution with benzene:chloroform (3:1) gave pale yellow eluates (400 ml.) which, on concentration to ca. 30 ml., deposited 6-oxo-6H-benzo[cd]pyrene. This recrystallised from benzene as yellow needles.

Yield. 275 mgm. (47%) m.p. 251-253°

$C_{19}H_{10}O$ requires C,89.76% H,3.96%

found 90.55% 4.02%

The ketone does not give a vat with alkaline dithionate nor with zinc and aqueous ethanolic sodium hydroxide. It dissolves in conc. H_2SO_4, and in 72% $HClO_4$ to give a red solution with a weak red fluorescence.

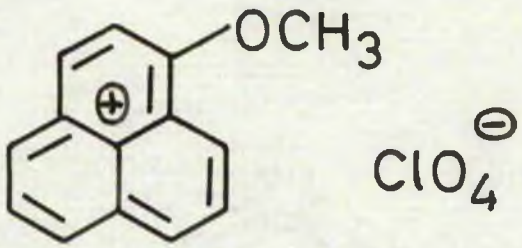
A strongly adsorbed orange-red band moved more slowly down the column and this was eluted with benzene:chloroform (1:1). Evaporation of the orange-red eluates to low volume (ca.0.5 ml.) gave a trace of solid as red needles which could not be obtained pure but appeared to be 5-oxo-5H benzo[cd]pyrene.

The mother liquors from this reaction were absorbed on a column of alumina (15 x 2.7 cm.) and benzene:light petrol (1:8) used to develop the column. The colourless eluates, on evaporation at reduced pressure, gave pale yellow crystals, m.p. 117-124°, which after one crystallisation from acetonitrile was raised to 121-127°. The hydrocarbon gives a deep green colour with conc. H_2SO_4, red to transmitted light. It appeared to be a mixture of isomeric hydrocarbons including 6H-benzo[cd] pyrene.

Yield 270 mgm. (49%)

The yields, based on benzo[cd]pyrenium perchlorate, were hydrocarbon (25%), ketone (24%), totalling 49%.

C.VIII. **1-Methoxyperinaphthenylium perchlorate**



C.VIII,1 **Methyl β-naphthyl ether**

This compound was prepared as described in Org. Syn., Coll. Vol. 1, p.51.

Yield 83% m.p. 72°

C.VIII,11 **1-Formyl-2-methoxynaphthalene**

A mixture of N-methylformanilide (132 g.; 85 ml.), phosphorus oxychloride (159.4 g.; 89 ml.) and β-naphthyl methyl ether (116 g.) was refluxed for 6 hr. on a water bath. The hot mixture was rapidly poured in a thin stream into vigorously stirred cold water (1,500 ml.). The aldehyde was filtered off and washed with a large volume of water. It was then extracted into chloroform (800 ml.), the extract dried (Na_2SO_4) and the solvent was evaporated. The aldehyde crystallised from ethanol as pale yellow needles.

Yield 93 g. (68.4%) m.p. 82° (Lit.[9], m.p. 82°)

C.VIII,III <u>1-Hydroxymethyl-2-methoxynaphthalene</u>.

1-Formyl-2-methoxynaphthalene (24.1 g.) in dry ether (500 ml.) was added to a vigorously stirred solution of lithium aluminium hydride (1.81 g.). The reaction mixture was boiled for 35 min. after the addition was completed. Wet ether was then added to destroy the excess of hydride in the cooled reaction mixture which was then poured onto crushed ice acidified by conc. H_2SO_4.

The organic layer was separated, and washed with water (3 x 100 ml.), saturated sodium bicarbonate solution (150 ml.) and water (100 ml.). The solvent was evaporated to low volume when the product crystallised fromether as white platelets

Yield 18.7 g. (77%) m.p. 100-101°

$C_{12}H_{12}O_2$ requires C,76.58% H,6.43%

found 76.6% 6.45%

C.VIII,IV <u>1-Bromomethyl-2-methoxynaphthalene</u>.

Phosphorus tribromide (3.4 ml.) was added to a solution of 1-hydroxymethyl-2-methoxynaphthalene (18.8 g.) in dry ether (280 ml.). The reaction mixture was hydrolysed after 30 min. by the addition of water (400 ml.). The aqueous phase was separated, and washed with a fresh portion ofether (100 ml.) which was then added to the organic phase. The combined extracts were washed with water (2 x 50 ml.), saturated sodium bicarbonate

solution (100 ml.), water (100 ml.), and dried (Na_2SO_4). When the ether was evaporated to low volume the product crystallised as colourless prisms.

Yield 17.5 g. (70%) m.p. 126-129°

$C_{18}H_{11}OBr$ requires Br, 31.82%

found 31.45%

C.VIII,V. β-[2-Methoxy-1-naphthyl]-malonic acid.

1-Bromomethyl-2-methoxynaphthalene (15.85 g.) in dry benzene (100 ml.) was added to a cooled solution of sodio-malonic ester prepared from sodium (4.39 g.) and freshly distilled diethyl malonate (26 ml.) in ethanol (500 ml.). This mixture immediately deposited sodium bromide and was kept at 0° for 72 hr., then refluxed for a further 4 hr. The bulk of the solvent was distilled off, aqueous sodium hydroxide (40%; 300 ml.) was added, and the solution was boiled for 4 hr. After cooling, the alkaline solution was washed with ether, and the ethereal washings were discarded. The solution was then warmed to 80° and acidified with conc. HCl. The white crystalline product was filtered off, washed with water, and dried in a vacuum desiccator over P_2O_5/KOH

Yield 16.98 g. (98.5%) m.p. 154-156° (Lit.,[10] m.p. 174-175°).

C.VIII,VI β-[2-methoxy-1-naphthyl]-propionic acid.

This compound was prepared by the decarboxylation of β-[2-methoxy-1-naphthyl]-malonic acid as described by Badger,

Carruthers, and Cook.[10]

Yield 22.45 g. (85.5%) m.p. 130-131° (Lit.[10], m.p. 131°)

C.VIII,VII 4-Methoxyperinaphthan-1-one.

This was prepared by the cyclisation of β-[2-methoxy-1-naphthyl]-propionic acid with anhydrous hydrogen fluoride.[10]

Yield 18.6 g. (88.3%) m.p. 64-65° (Lit.[10], m.p. 65°).

C.VIII,VIII 4-Methoxyperinaphthan-1-ol.

A solution of 4-methoxyperinaphthan-1-one (10.74 g.) in ether (200 ml.) was added slowly to a vigorously stirred solution of lithium aluminium hydride (870 mgm.) in ether. The reaction mixture was refluxed for 2 hours, cooled, and the excess of hydride was destroyed by the cautious dropwise addition of water (18 ml.). The mixture was poured onto crushed ice acidified with sulphuric acid. The ether layer was separated, washed with water (2 x 100 ml.), saturated sodium bicarbonate solution (2 x 100 ml.), water (100 ml.), and dried (Na_2SO_4).

Evaporation of the solvent to low volume gave the product as pale yellow needles which were dissolved in benzene and screened by charcoal containing a trace of alumina. The alcohol, recrystallised from benzene-petrol, was obtained as long white needles.

Yield 9.1 g. (85%) m.p. 104.25-105°

$C_{14}H_{14}O_2$ requires C,78.45% H,5.23%

Found 78.73% 6.41%

C.VIII,IX <u>The Dehydration of 4-Methoxyperinaphthan-1-ol.</u>

A solution of 4-methoxyperinaphthan-1-ol (290 mgm.) in ethanol (30 ml.), saturated with hydrogen chloride, was refluxed gently for 15 minutes during which time the colour of the solution changed from pale straw through orange-red to a deep red with a blue-green fluorescence. The cooled solution was diluted with water (200 ml.), and the yellow emulsion was extracted with ether (3 x 100 ml.). The ethereal extract was washed with water (3 x 100 ml.), dried (Na_2SO_4), and solvent evaporated. The residual oil, dissolved in petrol: benzene (1:1; 50 ml.), was chromatographed on alumina (22 x 2.7 cm.).

The column was first developed with light petrol:benzene (1:1) and the eluates (400 ml.) quickly worked up. No material was obtained from this fraction.

Elution with benzene (1,200ml.) brought a pale yellow band slowly down the column. This band was eluted completely with benzene:ether (19:1; 400 ml.). Removal of solvent from the combined yellow eluates gave a pale yellow crystalline residue which was purified by vacuum sublimation followed by one crystallisation from petrol-benzene. The ketone was obtained as very pale yellow, massive prisms.

Yield. 203 mgm. (82.3%) m.p. 83-84°.

A comparison of the infrared spectrum of the above compound with that of an authentic specimen of perinaphthan-1-one showed identity. A mixed melting point determination showed no depression. A comparison of the infrared spectra of the 2,4-dinitrophenylhydrazones prepared from the product with that from perinaphthan-1-one also showed identity.

C.VIII,X <u>1-Methoxyperinaphthenylium perchlorate.</u>

4-Methoxyperinaphthan-1-ol (5.04 g.), triphenylmethyl perchlorate (8.14 g.) and glacial acetic acid (120 ml.) were refluxed together for 10 minutes. A deep red colour developed, and as the reaction mixture cooled orange-red needles crystallised out. The salt was filtered off, washed with glacial acetic acid, and finally anhydrous ether. The product was recrystallised from glacial acetic acid.

Yield 5.62 g. (82%) m.p. 117.5-180.5°

The salt is soluble in acetonitrile, acetic acid and other polar solvents giving wine-red solutions but is insoluble in ether, petrol and non-polar solvents. It is stable to air, and does not decompose on melting or recrystallisation.

$C_{14}H_{11}ClO_5$ requires C,57.06% H,3.76% Cl,12.03%

found 56.35% 3.82% 11.28%

56.65% 3.38% 10.3% R.2.89%

C.VIII,XI <u>Hydrolysis of 1-Methoxyperinaphthenylium perchlorate</u>

The salt (5.62 g.), dissolved in acetone (100 ml.), was

poured into water (900 ml.). The reaction mixture was allowed to stand for 15 minutes during which time the deep red colour faded to pale straw and a yellow precipitate formed.

The mixture was then extracted exhaustively with ether (4 x 100 ml.). The ether extract was washed with water (3 x 150 ml.), dried (Na_2SO_4), and solvent was removed under reduced pressure. The residue was dissolved in ether (50 ml.) and perchloric acid (72%; 5 ml.) was added. The orange-red precipitate which formed was filtered off, and washed with ether. The perchlorate was then hydrolysed by water (200 ml.) and ether (300 ml.). The two phases were shaken together, and the organic phase separated, washed with water (2 x 100 ml.), saturated sodium bicarbonate solution (2 x 100 ml.), water (100 ml.), and dried (Na_2SO_4). Removal of the solvent left a pale yellow solid which melted over the range 150-156°.

The yellow solid (2.73 g.), in light petrol:benzene (1:1; 120 ml.), was chromatographed on a column of alumina (20 x 2.7 cm.). The bright yellow band at the top of the column moved down rapidly when benzene was the eluant. Removal of the solvent from the bright yellow eluates, and crystallisation from light petrol-benzene gave bright yellow needles, m.p. and mixed m.p. with authentic perinaphthen-1-one 154-156°. The infrared spectrum was identical with that of perinaphthen-1-one.

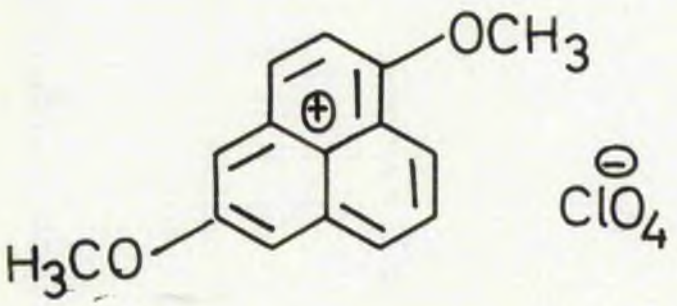
The ethereal washings obtained after the perchlorate precipitation were worked up in the usual manner. A pale red oil was obtained which on being sublimed at 135°/0.5 mm. gave a yellow crystalline solid. This gave yellow needles after two crystallisations from light petrol-benzene. This ketone was shown to be perinaphthen-1-one as described above.

Total Yield: 4.04 g. (93%) m.p. 154-156°

$C_{13}H_8O$ requires C,86.62%, H,4.47%

Found 86.5% 4.37%

C.IX The Synthesis of 1,5-Dimethoxyperinaphthenylium perchlorate.



C.IX,1 2,6-Dimethoxynaphthalene.

This compound was prepared essentially as described by Willstatter and Parnas.[11]

Yield 68 g (65.5%) m.p. 152-153° (Lit.[11], m.p. 151°)

$C_{12}H_{12}O_2$ calculated C,76.58%, H,6.43%

found 76.89%, 6.41%

C.IX,11 2,6-Dimethoxy-1-formylnaphthalene.

This was prepared by the formylation of 2,6-dimethoxynaphthalene with dimethylformamide and phosphorus oxychloride. The preparation has been described by Buu Hoi and Lavit.[12]

Yield 46 g. (58%) m.p. 89.5-90.5 (Lit.[12], m.p. 90°).

$C_{13}H_{12}O_3$ calculated C,72.19%, H,5.60%

found 72.23% 5.77%

C.IX,111 2,6-Dimethoxy-1-methylnaphthalene.

This compound was prepared from 2,6-dimethoxy-1-formylnaphthalene by the Huang-Minlon modification of the Wolff-Kishner reduction.

Yield 119 mgm (70%) m.p. 108-109° (Lit.[12], m.p.109°)

C.IX,1V. 2,6-Dimethoxy-1-hydroxymethylnaphthalene.

2,6-Dimethoxy-1-formylnaphthalene (28.5 g.) in anhydrous ether (200 ml.) was added to a stirred solution of lithium aluminium hydride (1.78 g.) in dry ether (200 ml.). The mixture was refluxed for an hour after the addition was complete. Water (18 ml.) was added dropwise to the stirred, cooled reaction mixture and the contents of flask were poured onto crushed ice (400 g.) acidified by conc. HCl.

The ethereal layer and the ether washings from the aqueous acid phase were combined, washed with water (2 x 150 ml.), satd. sodium bicarbonate solution (2 x 200 ml.), water (100 ml.), and dried (K_2CO_3) before the solvent was distilled off. The white residue crystallised from ethanol as white leaflets.

Yield 24.2 g. (84%) m.p. 124-125°

$C_{13}H_{14}O_3$ requires C,71.55% H,6.47%

found 71.75% 6.41%

C.IX,V 1-Bromomethyl-2,6-dimethoxynaphthalene.

Phosphorus tribromide (3 ml.) was added to a suspension of 2,6-dimethoxy-1-hydroxymethylnaphthalene (11.14 g.) in dry ether (200 ml.) at 0°. The reaction mixture was allowed to stand for 30 minutes before being hydrolysed by the addition of water (300 ml.).

The ethereal layer and the ether washings from the aqueous acid phase were combined, washed with water (2 x 150 ml.), satd. sodium bicarbonate solution (2 x 150 ml.), water (150 ml.), and dried (Na_2SO_4). The product crystallised as white prisms from the ethereal solution concentrated to low volume by distillation under reduced pressure.

Yield 12.48 g. (83%) m.p. 106-107° on a block preheated to 105°

$C_{14}H_{15}O_2Br$ requires Br,28.42%

found 28.00%

C.IX,VI β-[2,6-Dimethoxynaphthyl]-Malonic Acid.

1-Bromomethyl-2,6-dimethoxynaphthalene (12.48 g.) in benzene (30 ml.) of 5° was added to an ice-cold solution at sodio-malonic ester prepared from sodium (3.52 g.) and malonic ester (20 ml.) in abeolute ethanol (400 ml.). Sodium bromide began to separate out and the reaction mixture was maintained at 0° for 72 hours then refluxed for 4 hours. The bulk of the solvent was then distilled off, and a solution of potassium hydroxide

(50 g.) in water (200 ml.) added. The ester was hydrolysed by boiling with this mixture for four hours. The cooled alkaline solution was then washed with ether (2 x 100 ml.), the ethereal extract was discarded, and the alkaline solution was filtered, then warmed to 80°, and acidified by conc. HCl. The white precipitate was collected by filtration, washed with water, and air dried. The acid was obtained as colourless leaflets on crystallisation from aqueous acetone.

Yield 11.1 g. (86%) m.p. 169-171°

$C_{16}H_{16}O_6$ requires C,63.15% H,5.30%

found 63.85% 5.19%

C.IX,VII. β-[2,6-Dimethoxynaphthyl]-propionic acid.

β-[2,6-Dimethoxynaphthyl]-malonic acid (16.97 g.) was heated to 180° in an oil bath. Evolution of carbon dioxide occurred at an internal temperature of 170° and ceased after 15 minutes. The flask was heated for a further 20 minutes before being allowed to cool slowly. The product was purified by distillation in vacuo, and was obtained as colourless leaflets on crystallisation from acetone.

Yield 12 g. (84%) m.p. 152-154°

$C_{16}H_{16}O_4$ requires C,69.23% H,6.19%

found 69.83% 6.53%

C.IX,VIII <u>The Cyclisation of β-[2,6-dimethoxynaphthyl]-propionic Acid by Anhydrous Hydrogen Fluoride.</u>

The acid (4.9 g.) was added to anhydrous hydrogen fluoride (200 ml.) in a polythene beaker. The dark red solution was allowed to stand for 30 min., then hydrolysed by pouring onto crushed ice (500 g.). The deep yellow mixture was extracted by ether (4 x 150 ml.), and the ethereal layer washed with water (4 x 200 ml.), aqueous potassium hydroxide (10%, 150 ml.), water (3 x 100 ml.), and dried (K_2CO_3). Solvent was evaporated under reduced pressure. The pale yellow residue crystallised from light petrol:benzene (1:1) as yellow needles.

Yield 4.7 g. m.p. 90-97°.

The infrared spectrum of the product in nujol showed two peaks in the carbonyl region:

(i) at 1681 cm.$^{-1}$. This is in accord with perinaphthan-1-one

(ii) at 1730 cm.$^{-1}$. This value would accord with either a carbonyl group in a five-membered ring or a δ-lactone.

The product from two such runs (8.77 g.) was placed in a flask and the flask was warmed on a water bath with aqueous potassium hydroxide (10%, 100 ml.). The alkali layer, which became orange-red, was decanted off and the process repeated (3 times) until the extract was colourless. The residual solid was washed with water, extracted into ether, and the extract dried (K_2CO_3) before the solvent was removed.

The pale yellow crystalline residue was chromatographed on alumina (20 x 2.7 cm.) using light petrol:benzene (1:1) to develop the column. The pale yellow eluates (800 ml.) were then evaporated under reduced pressure. The pale yellow residue crystallised from light petrol:benzene (2:1) giving 4,8-dimethoxyperinaphthan-1-one as yellow prisms.

Yield 8.04 g. m.p. 100.3-101.3°

$C_{15}H_{14}O_3$ requires C,74.4%, H,5.83%

found 74.32% 5.78%

C.IX,1X 4,8-Dimethoxyperinaphthan-1-ol.

4,8-Dimethoxyperinaphthan-1-one (6.1 g.), in dry benzene (100 ml.), was slowly added to a vigorously stirred solution of lithium aluminium hydride (472 mgm.) in ether (100 ml.) The reaction mixture was refluxed for two hours, cooled, and water (18 ml.) added dropwise before the contents of the flask were poured onto crushed ice (150 g.) acidified by hydrochloric acid.

The ether layer was separated, washed with water (100 ml.) saturated sodium bicarbonate solution (2 x 150 ml.), water (100 ml.), and dried (Na_2SO_4) before the removal of solvent. The pale yellow residue was screened with charcoal in acetone, and then crystallised from acetone:light petrol (1:4). The product was thus obtained as fluffy white needles.

Yield 5.29 g. (88%) m.p. 140.5-142.5°

$C_{15}H_{16}O_3$ requires C,73.75% H,6.7%

found 73.94% 6.54%

C.1X,X <u>4,8-Dimethoxy-1-hydroxyperinaphthenylium Perchlorate.</u>

4,8-Dimethoxyperinaphthan-1-one (245 mgm.), triphenylmethyl perchlorate (344 mgm.), and glacial acetic acid (50 ml.) were refluxed together for five minutes during which time the solution became wine-red with a blue-green fluorescence. The salt crystallised from the cooled solution as wine-red needles which were filtered off, washed with dry ether and recrystallised from acetic acid:acetonitrile (1:1).

Yield 297 mgm. (87%) m.p. 219-222°

$C_{18}H_{13}ClO_7$ requires C,52.89% H,3.85% Cl,10.41%

found 53.2% 3.53% 10.06%

The acetic-acid mother liquors were worked up in the usual manner. The residue was dissolved in light petrol, and filtered through a column of alumina. Removal of solvent and crystallisation from ethanol gave triphenyl methane as white needles.

Yield 230 mgm. (96%) m.p. 92-93°

C.IX,X1 <u>1,5-Dimethoxyperinaphthenylium Perchlorate.</u>

4,8-Dimethoxyperinaphthan-1-ol (291 mgm.), triphenyl methyl perchlorate (412 mgm.), and glacial acetic acid (30 ml.) were refluxed for one minute. The deep wine-red solution was rapidly chilled by cold water. Dark reddish-bronze needles deposited, and were filtered off, and washed successively with glacial acetic acid and anhydrous ether. The product was

rapidly recrystallised from a small volume of glacial acetic acid.

Yield 294 mgm. (75%) m.p. dec. 187°

$C_{18}H_{18}ClO_3$ requires C,55.5% H,4.04% Cl,10.93%

found 54.6% 4.18% 10.1%

C.IX,XII <u>Hydrolysis of 1,5-Dimethoxyperinaphthenylium Perchlorate.</u>

The salt (937 mgm.) was dissolved in acetone (200 ml.), and the deep wine-red solution immediately poured into water (800 ml.). The solution rapidly became turbid and a yellow precipitate formed. After 10 minutes the pale yellow emulsion was extracted into benzene (3 x 50 ml.), the extract was washed with water, and dried (Na_2SO_4). The benzene solution was deep red with a green fluorescence. Removal of solvent left an orange solid (457 mgm.) which was dissolved in a fresh portion of benzene (100 ml.). The solution was extracted exhaustively with concentrated hydrochloric acid.

The benzene solution, after the acid extraction, was worked up in the usual manner, and a small quantity of tarry residue was obtained. This was discarded.

The acid extract (250 ml.) was poured into water (1000 ml.), and the pale yellow solution extracted with chloroform (4 x 50 ml.). The extracts were washed free from acid, then dried (Na_2SO_4). Removal of solvent left a pale yellow

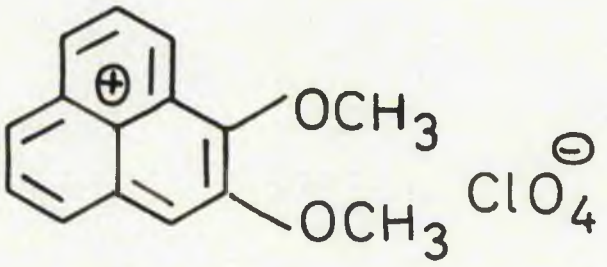
crystalline solid which was sublimed at 160°/0.5 mm. The sublimate crystallised from acetone:light petrol (2:5) as pale yellow platelets. The product has been formulated as 5-methoxyperinaphthen-1-one.

Yield 355 mgm (58.5%) m.p. 138.5-140.5°.

$C_{14}H_{10}O_2$ requires C,80.0% H,4.8%

found 80.05% 4.71%

C.X The Attempted Synthesis of 1,2-Dimethoxyperinaphthenylium Perchlorate.



C.X,1 2,3-Dimethoxynaphthalene.

This was prepared from 2,3-dihydroxynaphthalene as described by Friedlander and Silberstern.[18]

C.X,11 β-[2,3-Dimethoxynaphthyl]-propionic acid.

Anhydrous hydrogen chloride was passed into an ice-cold suspension of para-formaldehyde (3 g.) in glacial acetic acid (150 ml.) until a clear solution was obtained. A suspension of 2,3-dimethoxynaphthalene (15 g.) in glacial acetic acid (100 ml.) was added. The dimethyl ether quickly went into the solution, which developed a pink colour. After four hours, the solution was diluted with water (250 ml.), and the aqueous emulsion was extracted with chloroform (3 x 150 ml.). The extract was washed with water, dried (K_2CO_3), and solvent removed. A very pale pink

viscous oil was obtained which slowly crystallised as rosettes of needles.

This product was dried by azeotropic distillation with anhydrous benzene (50 ml.), and its ice-cold solution in benzene (50 ml.) was added to a cooled solution of sodio-malonic ester prepared from sodium (1.98 g.), and malonic ester (28.5 ml.) in ethanol (500 ml.). Almost immediately a white solid (NaCl) began to separate out of the reaction mixture which was allowed to stand at 0° for 48 hours and then refluxed for four hours. The bulk of the solvent was removed by distillation and a solution of potassium hydroxide (15 g.) in water (500 ml.) added. The ester was hydrolysed by boiling with this solution for four hours. The cooled solution was extracted with ether, and the ethereal extract discarded. The alkaline solution was warmed to 80°, and acidified with hydrochloric acid. A viscous oil separated from the solution, and was extracted into ether. The ether layer was washed with water, dried (K_2CO_3), and solvent was evaporated. The residual pale yellow oil crystallised from acetone as colourless leaflets.

Yield of β-[2,3-dimethoxynaphthyl]-malonic acid 9.71 g. (36.6%), m.p. 142-146° with evolution of CO_2.

The substituted malonic acid (9.71 g.) was heated to 180° in an oil bath. The acid melted and evolved carbon

dioxide. After the evolution of gas had ceased the flask was allowed to cool slowly, and the product crystallised in a solid cake. The product was dissolved in acetone, the solution was filtered, and the solvent evaporated. The acid crystallised from a small volume of acetone as dense white needles.

Yield 8.2 g. (98.5%) m.p. 131-133°.

$C_{18}H_{16}O_4$ requires C,69.23%, H,6.19%

found 69.67% 6.57%

C.X,111 4,5-Dimethoxyperinaphthan-1-one.

β-[2,3-dimethoxynaphthyl]propionic acid (8.3 g.) was added portionwise to anhydrous hydrogen fluoride (200 ml.) in a polythene beaker. As the acid dissolved the solution became deep red, and was allowed to stand for three hours with occasional stirring. The reaction mixture was then poured onto ice (1000 g.), and after one hour the aqueous acid mixture was extracted with ether (4 x 150 ml.). The extract was washed with water (5 x 120 ml.), sodium hydroxide solution (15%, 4 x 100 ml.), distilled water (3 x 100 ml.), and dried (K_2CO_3) before the removal of solvent. The creamy white residue crystallised from petrol-benzene as fluffy white needles.

Yield 6.35 g. (82.5%) m.p. 95-96°

$C_{18}H_{14}O_3$ requires C,74.4%, H,5.83%

found 73.79% 6.04%

C.X,IV 4,5-Dimethoxyperinaphthan-1-ol.

4,5-Dimethoxyperinaphthan-1-one (5.54 g.) in ether (150 ml.) was added slowly to a stirred solution of lithium aluminium hydride (740 mgm.) in ether (200 ml.). The reaction mixture was boiled for two hours, and then cooled to 10° before the cautious addition of water (18 ml.). The resulting mixture was poured into ice-cold dilute HCl (5N, 500 ml.). The ether layer was separated, and the aqueous acid layer washed with a fresh portion of ether. The extracts were combined, washed with water, and dried (K_2CO_3). The product crystallised out when the solution was concentrated to low volume. The alcohol recrystallised as dense white needles from acetone-light petrol.

Yield: 5.2 g. (94%) m.p. 132.5-134°.

$C_{14}H_{16}O_3$ requires C,73.75%, H,6.7%

found 73.52%, 6.58%

C.X,V The Reaction of 4,5-dimethoxyperinaphthan-1-ol with T.B.Q. in the presence of Perchloric Acid.

4,5-Dimethoxyperinaphthan-1-ol (488 mgm.), T.B.Q. (492 mgm.) and glacial acetic acid (10 ml.) were cooled in an ice-bath, and when the mixture was just fluid perchloric acid (72%, 0.6 ml.) was added. The brown-red mixture became deep crimson instantly. The mixture was allowed to warm up slowly

to 15°, then rapidly filtered through a sintered glass disc. When anhydrous ether (80 ml.) was added bright red needles separated. These were filtered off and washed with dry ether. The salt can be recrystallised from acetonitrile containing perchloric acid.

Yield 544 mgm. m.p. softens > 110° melts 124-127°.

$C_{18}H_{18}ClO_8$ requires	C, 55.51%,	H, 4.04%,	Cl, 10.93%
found	56.55%	4.32%	8.95%
$C_{18}H_{14}ClO_7$ requires	52.89%	3.85%	10.41%

This was the only experiment in which a solid perchlorate was obtained. In all other experiments carried out a deep crimson oil was obtained which could not be crystallised. The infrared spectrum (nujol) of this salt shows a broad band 1119-1094 $cm.^{-1}$ which was assigned to the perchlorate anion. No evidence was obtained for the presence of a hydroxyl group in the product.

The mother liquors were worked up in the usual manner for quinol which was recrystallised from acetic acid.

Yield 429 mgm. (87%) m.p. 190° (Lit.[18], m.p. 194°)

C.X,VI. Hydrolysis of Product Obtained in Experiment C.X,V.

The salt (390 mgm.) was dissolved in acetone (35 ml.) and the orange-red solution poured into water (400 ml.). Bright yellow needles immediately precipitated from the solution. These were filtered off, and dried for 36 hours in an evacuated dessicator over P_2O_5/KOH.

Yield 259 mgm. m.p. 135-138°

One crystallisation from light petrol-acetone raised the melting point to 136.5-138.5°. The ketone did not depress the melting point of an authentic sample of 4,5-dimethoxyperinaphthen-1-one on admixture and the infrared spectra of the two substances in nujol were superimposable.

$C_{15}H_{12}O_3$ requires C,74.99%, H,5.04%

found 74.32%, 5.10%

C.XI The Preparation of Perinaphthen-1-ones.

C.XI,1 3-Methylperinaphthen-1-one.

3-Methylperinaphthan-1-one (195 mgm.) triphenylmethyl perchlorate (343 mgm.) and glacial acetic acid (30 ml.) were refluxed for 4 minutes during which time the colour of the solution changed from orange-red to deep green. The cooled solution was poured into water (300 ml.), and the resulting greenish-yellow emulsion was extracted with benzene (3 x 100 ml.). The extract was washed with water, filtered, and extracted with conc. HCl (5 x 100 ml.). The acid extracts were poured into water (3 l.) and the pale yellow solution extracted with chloroform (3 x 200 ml.). The organic phase was washed free from acid with water, and dried (Na_2SO_4) before evaporation of the solvent. The pale yellow crystalline residue was sublimed at 130/0.5 mm. The sublimate crystallised as pale yellow prisms from acetone-light petrol.

Yield 131 mgm. (68%) m.p. 153.5-155° (Lit.[14], m.p. 156°).

$C_{14}H_{10}O$ calculated C,86.50%, H,5.56%

found 86.43% 5.12%

The benzene extract was washed free from acid, dried (Na_2SO_4), and solvent removed. The residue was dissolved in light petrol, and filtered through a column of alumina (16 x 2.7 cm.). Evaporation of the eluates gave triphenylmethane which was crystallised from ethanol.

Yield 200 mgm. (80%) m.p. 92-93°.

C.XI,11 4,5-Dimethylperinaphthen-1-one.

Triphenylmethyl perchlorate (24 g.) and glacial acetic acid (1,200 ml.) were warmed until a homogeneous solution was obtained. A solution of 4,5-dimethylperinaphthen-1-one (14.7 g.) in glacial acetic acid (100 ml.) was added all at once. A flocculent orange precipitate immediately formed, and the reaction mixture was allowed to cool slowly to room temperature. The salt was filtered off, and washed with anhydrous ether to remove all traces of acetic acid.

The orange perchlorate was hydrolysed by suspending it in acetone (150 ml.) and adding a large volume of water (1000 ml.). The suspension was allowed to stand for 15 min. with occasional shaking, and was then extracted with benzene (3 x 400 ml.). The aqueous phase was discarded, and the organic phase was washed with water, then dried (Na_2SO_4). The solution, concentrated to low volume, was chromatographed on a short column of alumina (10 x 2.7 cm.) using benzene:ether (19:1) for development. The eluates (800 ml.) were concentrated to ca. 50 ml. Ether (500 ml.) was added, and the product crystallised as bright yellow needles.

Yield 12.74 g. (87%) m.p. 143.5-144.5°

$C_{18}H_{12}O$ requires C,86.48%, H,5.81%

found 86.24% 5.75%

C.XI,111 1,2-Dihydro-5-oxo-5H-cyclopenta[gh]perinaphthene.

1,2,5,6-Tetrahydro-7-oxo-7H-cyclopenta[gh]perinaphthene (4.3 g.), triphenylmethyl perchlorate (7.1 g.) and glacial acetic acid were refluxed for 10 minutes. The cooled solution was poured into water (900 ml.), and the resulting emulsion was extracted with benzene (6 x 250 ml.). The extract was then washed with water (4 x 150 ml.) before being extracted with conc. HCl (6 x 250 ml.). The red acid extracts were poured into water (4 l.), and the aqueous acid solution was extracted with chloroform (6 x 250 ml.). The organic extract was washed with water (2 x 150 ml.), saturated sodium bicarbonate solution (200 ml.), water (150 ml.), and dried (Na_2SO_4) - Solution 1.

After the acid extraction, the benzene layer was washed with water (2 x 250 ml.), saturated sodium bicarbonate solution (230 ml.), water (150 ml.), and dried (K_2CO_3) - Solution 2.

Solution 1. Solvent was evaporated from the filtered solution, and the pale yellow residue was dissolved in the minimum volume of benzene. This solution was chromatographed on a column of alumina (27 x 2.7 cm.). Development with benzene:ether (1:1) brought a bright yellow band off the column. Removal of solvent from the pale yellow eluates (1.5 l.) left a yellow residue which crystallised as yellow needles from benzene:ether (3:1).

Yield 1.11 g. (46%) m.p. darkens at 150° melts 160-163°
(Lit.,[7] darkening at 158° melts 174°).
The infrared spectrum in nujol shows 1639 cm.$^{-1}$, 1623 cm.$^{-1}$
(Lit.,[7] infrared spectrum (KBr disc.) shows 1634 cm.$^{-1}$, 1618 cm.$^{-1}$).

Solution 2. Benzene was removed from the solution and the residue, dissolved in light petrol, was chromatographed on a column of alumina (28 x 2.7 cm.)

The column was first developed with light petrol. Evaporation of solvent from the colourless eluates followed by crystallisation from ethanol gave triphenyl methane as white needles.

Yield 3.55 g. (88.5%) m.p. 92.5-93.5°

Continued elution with benzene-ether (1:1; 1,200 ml.) brought through a deep red band as wine-red eluates. Removal of solvent gave a viscous red oil which would not crystallise. The oil was rechromatographed twice on alumina (27 x 2.7 cm.) using benzene:ether (1:1) to develop the column. The red oil thus obtained after evaporation of solvent was dissolved in benzene (200 ml.), and screened with charcoal. After filtration, the solution was chilled by immersion in a solid carbon dioxide-acetone bath. As the flask warmed up to room temperature the product crystallised as wine-red platelets. It was recrystallised from benzene:petrol (12:1).

Yield 1.4 g. (32.5% based on starting material)

Found C,91.06%, H,4.91%, M.W. 345.

$C_{30}H_{20}O$ requires 90.88% 5.09% M.W. 396

C.XI,IV. 5-Oxo-5H-benzo[cd]pyrene.

Perchloric acid (72%; 0.25 ml.) was added to a boiling solution of triphenylcarbinol (520 mgm.), and 3,4-dihydro-5-oxo-5H-benzo[cd]pyrene (512 mgm.) in glacial acetic acid (100 ml.). The solution, which had turned deep green, was boiled for 5 minutes. It was then poured into water when an orange solid precipitated. The organic material was taken up in benzene (700 ml.), and the benzene extract was washed once with water before being shaken with conc. HCl (500 ml.). A black solid, which came out of solution, was filtered off, and worked up as described below. The acid layer was washed once with benzene before dilution with water (3 vol.). The precipitated orange ketone was extracted into chloroform, and the extract was combined with that resulting from the decomposition of the black solid by shaking with a mixture of water (500 ml.) and chloroform (750 ml.). The combined extracts were washed free from acid with water (2 x 150 ml.), and dried (K_2CO_3) before concentration of the solution to ca.10 ml. Hot ethanol (20 ml.) was added to the hot saturated chloroform solution, and the solution warmed on a water bath to remove the chloroform.

5-Oxo-5H-benzo[cd]pyrene crystallised from the cooled solution as orange red prisms with a green reflex.

Yield 385 mgm (76%) m.p. 218-221° with sublimation 200°

A further 52 mgm. were obtained from the mother liquors bringing the total yield up to 437 mgm (86%).

Solutions of the ketone in organic solvents display an orange-yellow fluorescence while its solutions in conc. H_2SO_4, conc. HCl, acetic acid, and acetonitrile containing perchloric acid are green with a red fluorescence. It does not give a vat dye with either alkaline dithionate or alcoholic sodium hydroxide and zinc.

$C_{19}H_{10}O$ requires C,89.8% H,3.96%

found 89.67% 3.79%

C.XI,V. 4-Methoxyperinaphthen-1-one.

4-Methoxyperinaphthan-1-one (518 mgm.), triphenylmethyl perchlorate (830 mgm.), and glacial acetic acid (40 ml.) were boiled for 10 minutes. The solution developed a deep red colour and, after cooling, was poured into water (500 ml.). The organic material was extracted into benzene (3 x 100 ml.), and the extract was washed with water before being shaken with conc. HCl (3 x 50 ml.). The combined acid extracts were poured into water (500 ml.), and the red solution was extracted with chloroform (3 x 100 ml.). The combined extract was

washed successively with water (100 ml.), saturated sodium bicarbonate solution (100 ml.), water (100 ml.) and dried (Na_2SO_4) before removal of the solvent. Sublimation of the residue at 140°/ 0.5 mm. followed by crystallisation from light petrol-benzene (1:1) gave 4-methoxyperinaphthen-1-one as orange-yellow needles.

Yield 466 mgm. (90%) m.p. 139-140° (Lit.[10], m.p. 142-143°)

The infrared spectrum shows carbonyl at 1632 cm.$^{-1}$(Nujol), 1649 cm.$^{-1}$(CCl_4)(Lit.[15], 1632 cm.$^{-1}$(solid), 1642 cm.$^{-1}$(CS_2)).

The benzene layer was washed with water (2 x 50 ml.), saturated sodium bicarbonate solution (100 ml.), water (100 ml.), and dried (Na_2SO_4) before removal of solvent. The crystalline residue, in light petrol, was filtered through a short column of alumina. Solvent was removed, and triphenylmethane was obtained from ethanol as colourless needles.

Yield 504 mgm. (85%) m.p. and mixed m.p. 92-93°.

C.XI,VI. <u>4,8-Dimethoxyperinaphthen-1-one.</u>

Triphenylmethyl perchlorate (357 mgm.), 4,8-dimethoxyperinaphthan-1-one (248 mgm.), and glacial acetic acid (40 ml.) were refluxed for five minutes. The perchlorate which separated from the cooled solution as dark red needles was filtered off and washed with dry ether.

The salt (296 mgm.) was hydrolysed with potassium hydroxide solution (2N; 200 ml.). After 15 minutes the organic

material was extracted into benzene (4 x 100 ml.). The extract was washed with water (3 x 100 ml.), dried (Na_2SO_4) and solvent was removed. The residue crystallised from petrol:benzene (1:1) as orange-yellow needles.

Yield 189 mgm. m.p. 137.5-138.5°

The acetic acid mother liquors were poured into water (500 ml.) and the emulsion was extracted with benzene (3 x 100 ml.). The organic layer was washed with water (100 ml.), saturated sodium bicarbonate solution (150 ml.), and water (100 ml.) before being dried (Na_2SO_4). Evaporation of the solvent left a residue which was chromatographed on a column of alumina (10 x 2.7 cm.). Elution with light petrol brought off triphenylmethane which crystallised from ethanol as colourless plates.

Yield 232 mgm. (91%) m.p. and mixed m.p. 92-93°.

Elution with ether and removal of solvent gave a further small quantity of 4,8-dimethoxyperinaphthen-1-one bringing the total yield to 219 mgm. (88%).

$C_{18}H_{12}O_3$ requires C,74.99% H,5.04%

found C,76.5, 76.7% H,5.12%, 5.4%

C.XI,V11 <u>4,5-Dimethoxyperinaphthen-1-one</u>.

4,5-Dimethoxyperinaphthan-1-one (295 mgm.), triphenylmethyl perchlorate (418 mgm.), and glacial acetic acid (30 ml.) were refluxed for 15 minutes. The cooled reaction mixture was

hydrolysed by the addition of water (500 ml.), and the organic material was extracted into benzene (4 x 100 ml.). The benzene layer was washed well with water, dried (K_2CO_3), and the solvent was removed under reduced pressure. The residual oil was dissolved in light petrol-benzene (1:1; 30 ml.), and chromatographed on an alumina column (20 x 2.7 cm.). Initial development with light petrol eluted triphenyl methane from the column. With ether as eluant a pale yellow band moved quickly down the column. Evaporation of solvent from the eluates gave a residue which gave yellow needles after one crystallisation from benzene-light petrol.

Yield 222 mgm. (76%) m.p. 137-137.5°

$C_{18}H_{12}O_3$ requires C,74.99% H,5.04%

found 74.32% 5.10%

C.XII <u>Abstraction of Hydride Ion by Quinones in the presence of Perchloric Acid with the Formation of Organic Cations.</u>

C.XII,1. <u>Perinaphthenylium Perchlorate: 1st Preparation.</u>

Perinaphthene (830 mgm.) in glacial acetic acid (20 ml.) was added to a solution of chloranil (1,2 30 mgm.) and perchloric acid (72%; 1 ml.) in glacial acetic acid (150 ml.) at 50°. Perinaphthenylium perchlorate precipitated immediately as yellow needles. Anhydrous ether (200 ml.) was added to complete precipitation, the salt was filtered off, and washed

with a further portion of dry ether (200 ml.). The product was dried for an hour in an evacuated desiccator over P_2O_5/KOH Yield 995 mgm. (75%).

The mother liquors and the ethereal washes were combined, and diluted with water (1,000 ml.). The ether layer was separated, and washed free from acetic acid with water. The ether layer was then extracted with potassium hydroxide solution (10%, 3 x 100 ml.), and the alkaline extract acidified with dilute hydrochloric acid. The precipitated quinol was extracted into ether. The ethereal solution was dried (Na_2SO_4), and the solvent removed. The residue crystallised from acetic acid as white needles.

Yield 1.09 g. (90%) m.p. 230° (Lit.,[20] m.p. 232°)

This experiment was repeated using acetonitrile (100 ml.) as solvent. Perinaphthenylium perchlorate (587 mgm., 44%) and quinol (1.04 g., 84%) were obtained.

C.XII,11 Hydrolysis of Perinaphthenylium Perchlorate.

The salt (1,987 mgm.), prepared as described in experiment (C.XII,1), was dissolved in acetone (60 ml.), and the solution poured into warm, distilled water (800 ml.). After the hydrolysis was complete the emulsion was extracted with benzene. The benzene layer was washed with water, dried

(Na_2SO_4), and solvent was removed. The residual brown solid was dissolved in light petrol-benzene (1:1; 50 ml.), and chromatographed on alumina (20 x 2.7 cm.). The column was then eluted with light petrol (1.5 l.) followed by ether (2 l.) - Solvent was evaporated from the petrol eluates, and the white crystalline residue (540 mgm.) dissolved in ethanol (10 ml.) Trinitrobenzene (814 mgm.) in ethanol (10 ml.) was added when orange-red needles separated out. These were filtered off and recrystallised from ethanol.

Yield 652 mgm [this accounts for 286 mgm of perinaphthene and thus for 23% of the perinaphthenylium perchlorate].

m.p. 151-153° (Lit.[16], m.p. 151-152°; Lit.[17], m.p. 159°).

Removal of solvent from the ether eluates gave a tarry residue which was dissolved in benzene (50 ml.). The solution was extracted with conc. HCl (8 x 100 ml.), and the combined deep red extracts were poured into water (3 l.). The separated acid phase was extracted with chloroform (3 x 150 ml.), and the chloroform extracts were washed free from acid with water and then dried (Na_2SO_4). Evaporation of solvent left a yellow crystalline residue which was sublimed at 150°/0.5 mm. The sublimate crystallised from acetone-light petrol as pale yellow prisms.

Yield 453 mgm [this accounts for 34% of the perinaphthenylium perchlorate]

m.p. 154-156°; mixed m.p. with an authentic specimen of perinaphthen-1-one 153-155°.

The isolated hydrolysis products account for 57% of the perinaphthenylium perchlorate.

C.XII,111 Perinaphthenylium Perchlorate - 2nd Preparation.

Perinaphthene (830 mgm.) in glacial acetic acid (5 ml.) was added to a solution of 1,4-benzoquinone (540 mgm.) in glacial acetic acid (20 ml.) containing perchloric acid (72%, 1 ml.). The solution at once became greenish-yellow and perinaphthenylium perchlorate crystallised immediately as pale yellow needles. The salt was quickly filtered off, washed with dry ether (200 ml.), and dried in a vacuum desiccator for one hour over P_2O_5/KOH.

Yield 1,080 mgm (80.5%).

The mother liquors and ethereal washes were combined and diluted with water (600 ml.). The ether layer was separated, and to it was added the ethereal washings obtained on washing the aqueous acid layer with ether. The combined extracts were washed free from acid, and then extracted with potassium hydroxide solution (50%, 3 x 50 ml.). The alkaline layer was separated, and acidified with conc. HCl. The precipitated hydroquinone was filtered off, air dried, and recrystallised from benzene.

Yield 493 mgm. (91%) m.p. 172° (Lit., m.p.172°)

C.XII,IV. Perinaphthenylium Perchlorate - 3rd Preparation.

Tetrachloro-1,2-benzoquinone (737.4 mgm.)in glacial acetic acid (15 ml.) containing perchloric acid (72%, 1 ml.) was added to a solution of perinaphthene (498.6 mgm.) in glacial acetic acid (5 ml.). The deep red colour of the quinone was immediately discharged, the solution became greenish-brown and perinaphthenylium perchlorate precipitated. Anhydrous ether (20 ml.) was added to the reaction mixture which was then rapidly filtered. The product was washed with dry ether (100 ml.) and dried in a vacuum desiccator over P_2O_5/KOH for one hour.

Yield 634 mgm (79.9%).

C.XII,V. Perinaphthenylium Perchlorate - 4th Preparation.

Perinaphthene (498.6 mgm.) in glacial acetic acid (5 ml.) was added to a solution of 2,3-dicyano-1,4-benzoquinone (474.4 mgm.) in glacial acetic acid (12 ml.). The orange solution became deep greenish-brown and immediate precipitation of pale yellow needles took place. Dry ether (20 ml.) was added and the salt filtered off immediately, and washed with dry ether. The perchlorate was dried in a vacuum desiccator over P_2O_5/KOH for one hour.

Yield 687.2 mgm. (87.5%).

C.XII,V1 Perinaphthenylium Perchlorate - 5th Preparation.

To perinaphthene (498.6 mgm.) in glacial acetic acid (5 ml.) was added a solution of 1,2-naphthoquinone (474.5 mgm.) and perchloric acid (72%, 1 ml.) in glacial acetic acid (35 ml.) The solution became dark brownish-green, and on the addition of a few drops of dry ether a precipitate of yellow needles slowly came out of solution. Dry ether (60 ml.) was added to complete precipitation. The product was rapidly filtered off, washed with dry ether, and dried for one hour in a vacuum desiccator over P_2O_5/KOH,

Yield 343.4 mgm. (43%).

C.XII,V11 Perinaphthenylium Perchlorate -6th Preparation.

9,10-Phenanthraquinone (624.6 mgm.) and perchloric acid (72%, 1 ml.) were dissolved in glacial acetic acid (50 ml.) and added to a solution of perinaphthene (4986 mgm.) in glacial acetic acid (5 ml.). The orange solution became greenish-brown, and after a few seconds yellow needles precipitated. Anhydrous ether (100 ml.) was added, and the product quickly filtered off, washed with dry ether, and dried in an evacuated desiccator over P_2O_5/KOH for one hour.

Yield 428.2 mgm. (54%).

C.XII,V111 1,4,7-Trimethylperinaphthenylium Perchlorate.

Tetrachloro-1,2-benzoquinone (492 mgm.) and perchloric acid (72%, 1 ml.) in glacial acetic acid (10 ml.) were added to

a solution of 3,6,9-trimethylperinaphthene (416.4 mgm.). The solution darkened, and became slightly warm. It was chilled with cold water while dark brown needles separated. These were filtered off, washed with dry ether and recrystallised from acetonitrile giving the salt as bronze-needles.

Yield 568.3 mgm. (92.6%) m.p. dec. > 240°.

C.XII,1X 1,2-Dihydrocyclopenta[gh]perinaphthenylium Perchlorate.

T.B.Q. (598 mgm.) and perchloric acid (72%, 0.2 ml.) in acetonitrile (8 ml.) were added to a solution of 1,2-dihydro-5H-cyclopenta[gh]perinaphthene (466 mgm.) in acetonitrile (10 ml.). The solution immediately became dark green, and a dark green solid separated out. This was filtered off, and washed with dry ether (50 ml.).

Yield of green solid 287 mgm.

The mother liquors were further diluted with ether (150 ml.) and washed well with water. The solution was then extracted with potassium hydroxide solution (30%, 3 x 80 ml.), and the alkaline extract washed once with ether before acidification with concentrated HCl. The precipitated quinol was extracted into ether (3 x 150 ml.), and the ethereal layer dried (Na_2SO_4) before removal of solvent. The residue was obtained as needles on crystallisation from acetic acid.

Yield 462 mgm. (76.6%) m.p. 192° (Lit.,[18] m.p. 194°)

In another such experiment with the hydrocarbon (1 gm.), T.B.Q. (1.28 g.) and perchloric acid (72%, 0.4 ml.) the yield of quinol was 1.046 g. (81.04%).

C.XIII The Dehydration-dehydrogenation of Some Perinaphthan-1-ols by Quinones in the Presence of Perchloric Acid.

C.XIII,1 1,4,7-Trimethylperinaphthenylium Perchlorate.

Tetrachloro-1,2-benzoquinone (984 mgm.) and perchloric acid (72%; 1 ml.) were dissolved in glacial acetic acid (20 ml.). and added to 3,6,9-trimethylperinaphthan-1-ol (904 mgm.) in glacial acetic acid (20 ml.) at 90°. The salt crystallised immediately from the hot solution as copper coloured needles. The salt was filtered from the cooled solution and washed with dry ether (150 ml.).

Yield 1,093 mgm. (89%) m.p. dec.> 240°.

C.XIII,11 1-Methoxyperinaphthenylium Perchlorate.

A solution of tetrachloro-1,2-benzoquinone (492 mgm.) and perchloric acid (72%; 0.35 ml.) in glacial acetic acid (20 ml.) was added to 4-methoxyperinaphthan-1-ol (428 mgm.) in glacial acetic acid (20 ml.). The solution became dark red, and the salt crystallised as orange-red needles which were filtered off and washed with dry ether.

Yield 516 mgm (88%) m.p. 177.5-180.5°

C.XIII,11 1,5-Dimethoxyperinaphthenylium Perchlorate.

4,8-Dimethoxyperinaphthan-1-ol (244 mgm.) in glacial acetic acid (10 ml.) was added to a solution of T.B.Q. (246 mgm.) and perchloric acid (72%, 0.2 ml.) in glacial acetic acid (10 ml.).

The solution became deep red, and on addition of dry ether (30 ml.) precipitated red needles which were filtered off and washed with dry ether.

Yield 259 mgm. (79%) m.p. dec. > 187°

C.XIV. The Abstraction of a Hydrogen Atom From Perinaphthene by Quinones.

C.XIV,1. The Perinaphthyl Radical - 1st Preparation.

Chloranil (615 mgm., 2.5 mmole) was dissolved in methylene chloride (90 ml.), and the pale yellow solution cooled to room temperature in a flask through which a stream of dry nitrogen was passed. Perinaphthene (630 mgm., 5 mmole) in methylene chloride (10 ml.) was then added to the solution which immediately became deep blue due to radical formation.

The deep blue solution was diluted with ether (200 ml.), and the ethereal solution was then extracted with aqueous potassium hydroxide (15%, 3 x 100 ml.). The alkaline extract was washed once with ether before being acidified with conc. HCl. Tetrachloro-1,4-hydroquinone which separated out was extracted into ether. The ethereal extract was dried (Na_2SO_4), and solvent removed. The white residue crystallised from glacial acetic acid as white needles.

Yield 430 mgm. (70%). m.p. 230° (Lit.[18], 230°).

This experiment was carried out with chloranil in several different solvents. In each case, radical formation was observed.

Solvent	Volume	% Quinol.
Acetonitrile	90 ml.	56
Nitromethane	90 ml.	60
Acetic Acid	90 ml.	not isolated

C.XIV,11 Perinaphthyl - 2nd Preparation.

A solution of perinaphthene (415 mgm., 2.5 mmole) in methylene chloride (10 ml.) was added to chloranil (630 mgm., 2.5 mmole) in methylene chloride (90 ml.) under nitrogen. The blue colour of the perinaphthyl radical was immediately observed. The reaction mixture was diluted with ether, and worked up as described in (C.XIV,1). Recovered quinol was recrystallised from glacial acetic acid.

Yield 210 mgm. (34%).

C.XIV,111 Perinaphthyl - 3rd Preparation

A solution of perinaphthene (166 mgm., 1 mmole) in methylene chloride (5 ml.) was added to chloranil (126 mgm., 0.5 mmole) in methylene chloride (20 ml.). The deep blue colour of the radical was observed. The solution was diluted with ether (100 ml.) and chromatographed without delay on an alumina column (20 x 2.17 cm.). The radical travelled rapidly down the column, and was obtained as a clear blue solution freed from traces of yellow material formed on exposure to light. The bulk of the radical was collected in 200 ml. of eluates.

The visible spectrum of the radical in (Plate 1) shows a broad absorption maximum at 610-615 mu. Its absorption spectrum was identical in the region 750-500 mu with that of the radical prepared from the perinaphthenide anion.[19]

C.XIV,IV Perinaphthenylium Iodide from Perinaphthyl.

A solution of perinaphthyl, prepared in methylene chloride as described in (C.XIV,1) was treated dropwise with a solution of iodine in methylene chloride (2 gm. iodine in 150 ml. methylene chloride) until the blue colour of the radical had almost been discharged. The black solid which came out of solution was removed immediately by filtration and washed with benzene and dry ether. It is insoluble in non-polar solvents but dissolves readily in polar solvents giving blue-green to green solutions which become yellow on standing. The salt can be stored in definitely under nitrogen.

Yield 213 mgm. (14.1% based on perinaphthene)

C.XIV,V. Perinaphthyl - 4th Preparation.

Perinaphthene (650 mgm.; 5 mmole) in methylene chloride (20 ml.) was added to a solution of benzoquinone (540.5 mgm., 5 mmole) in methylene chloride (20 ml.). The addition was followed by the formation of a deep red colour which persisted for 30 seconds, and then became deep green. Quinhydrone began to crystallise out. The deep green lustrous plates were filtered off and recrystallised from ethanol.

Yield 405 mgm. (1.86 mmole which will contain 204 mgm. of hydroquinone, i.e., 74.5%)

m.p. 172° (Lit., m.p. 172°)

C.XIV,V1 Perinaphthyl - 5th Preparation.

A solution of T.B.Q. (246 mgm.; 1 mmole), dissolved in methylene chloride (10 ml.), was added to a solution of perinaphthene (332 mgm.; 2 mmole) in methylene chloride (5 ml.). The solution, which became deep blue, was diluted with ether, and was then extracted with aqueous potassium hydroxide (50%; 3 x 25 ml.). The extract was washed once with ether, acidified by conc. HCl, and the resulting white precipitate was extracted into ether. The ethereal layer was dried (Na_2SO_4) before removal of solvent. Crystallisation of the residue from glacial acetic acid gave tetrachlorocatechol as white needles. Yield 193 mgm (78%) m.p. 190-192° (Lit.[18], m.p.194°

C.XIV,V11 Perinaphthyl - 6th Preparation.

A brownish-red solution of 1,2-naphthequinone (158 mgm.; 1 mmole), in methylene chloride (20 ml.) was added to perinaphthene (332 mgm.; 2 mmole) in methylene chloride (10 ml.). The colour deepened to red, and slowly to deep greenish blue over about two minutes. The solution of the radical was diluted with ether (120 ml.), then extracted by aqueous alkali (15% KOH; 3 x 50 ml.). The alkaline extract was acidified by conc. HCl, the precipitated quinol was extracted into chloroform (3 x 100 ml.). The extract was washed once with water, dried (Na_2SO_4) and solvent removed. The residue was then

crystallised from carbon disulphide.

Yield 107 mgm (67%) m.p. 103-104°

C.XIV,VIII. Perinaphthyl - 7th Preparation.

To perinaphthene (332 mgm; 2 mmole) in methylene chloride (10 ml.) was added a solution of 9,10-phenanthraquinone (208 mgm; 1 mmole) in methylene chloride (80 ml.). The solution became dark greenish-blue at once, and was diluted with ether (150 ml.). The solution was quickly chromatographed on alumina (20 x 2.7 cm.). The radical moved quickly down the column. The eluates were clear blue in colour and the spectrum in the region 750-500 mu was identical with that obtained in (C.XIV,III).

C.XIV,IX. Perinaphthyl - 8th Preparation.

2,3-Dicyano-1,4-benzoquinone (158 mgm.; 1 mmole) in methylene chloride was added to perinaphthene (332 mgm.; 2 mmole) in methylene chloride (10 ml.). The bright blue colour of perinaphthyl formed instantly. Ether (120 ml.) was added, and the solution was chromatographed on alumina (20 x 2.7 cm.) at once. The radical was collected as a clear blue solution in the first 200 ml. of eluate. The visible spectrum in the region 750-500 mu was identical with that obtained in (C.XIV,III).

C.XV Naphtho[1,8a,8-ab]carbazolium Salts.
(Indolo[2,3-a]perinaphthenylium Salts).

C.XV,1 4,5-Dimethylperinaphthan-1-one Phenylhydrazone.

Freshly distilled phenylhydrazine (5.4 g.) was added to a solution of 4,5-dimethylperinaphthan-1-one (10.5 g.) in ethanol (160 ml.) followed by hydrochloric acid (0.5 ml.). The orange-red solution was boiled for six minutes during which time a flocculent orange-yellow solid precipitated. The reaction mixture was rapidly cooled, and the solid filtered off. The latter was washed with ethanol (100 ml.) and recrystallised from methanol as straw coloured needles.

Yield 13.6 g. (91%) m.p. 132-135° dec.

$C_{23}H_{20}N_2$ requires C,83.94%, H,6.71%, N,9.33%.

found 83.89%, 6.74% 9.43%

C.XV,11 3-Methylperinaphthan-1-one Phenylhydrazone.

Phenylhydrazine (2.45 ml.) was added to a solution of 3-methylperinaphthan-1-one (4.9 g.) in ethanol (50 ml.) followed by conc. HCl (0.25 ml.). The solution was refluxed for 10 minutes while the colour of the solution changed from pale straw to deep red. On cooling, a pale yellow solid crystallised out. This was filtered off, washed with ethanol, and on recrystallisation from methanol formed straw coloured needles.

Yield 3.88 g. (54.3%) m.p.112-114° dec.

$C_{20}H_{18}N_2$ requires C,83.89%, H,6.33%, N,9.78%
found 83.47% 7.45% 9.56%

C.XV,111 4,8-Dimethoxyperinaphthan-1-one Phenylhydrazone.

Phenylhydrazine (0.4 ml.) was added to 4,8-dimethoxyperinaphthan-1-one (820 mgm.) dissolved in ethanol (10 ml.) followed by conc. HCl (0.05 ml.). The solution was refluxed for 5 minutes. Orange-yellow needles separated from the cooled solution, and were filtered off. The product was washed with ethanol, and recrystallised from methanol-ethanol (8:1) as pale yellow needles.

Yield 689.5 mgm. (61.3%) m.p. 132-135°

$C_{24}H_{20}N_2O_2$ requires C,75.88% H,6.07%, N,8.45%
found 76.15% 6.59% 7.95%

C.XV,IV 5,6-Dimethylnaphtho[1,8a,8-ab]carbazolium Perchlorate

4,5-Dimethylperinaphthan-1-one phenylhydrazone (7.23 g.), glacial acetic acid (200 ml.) and perchloric acid (72%, 2 ml.) were refluxed for 15 minutes during which time dark brown needles separated from the dark red solution. The product was filtered from the cooled reaction mixture, washed with dry ether, and the dried salt stirred in distilled water (60 ml.) for 5 minutes. The solid was then filtered off, washed with ether and air dried. Recrystallisation from acetonitrile containing

a trace of perchloric acid gave the perchlorate as bronze needles.

Yield 4.43 g. (47.5%) m.p. 340°

$C_{21}H_{16}NClO_4$ requires C,66.06%, H,4.23% N,3.67%

found 65.7% 4.5% 3.59%

C.XV,V. 5,6-Dimethylnaphtho[1,8a,8-ab]carbazole.

A mixture of 5,6-dimethylnaphtho[1,8a,8-ab]carbazolium perchlorate (431 mgm.), methanol (50 ml.), and aqueous ammonia (1:1 of water: 880 ammonia; 100 ml.) was shaken for 10 minutes. Ether (200 ml.) was then added, and the mixture was shaken at frequent intervals over a period of one hour. During this time the ether layer became deep red. This process was repeated with fresh portions of ether till no more colour was imparted to the ethereal layer. The combined extracts were then washed free from ammonia (water), dried (Na_2SO_4), and the volume of solvent reduced to 150 ml. The deep wine red solution was then filtered through alumina (5 x 2.7 cm.). A red band moved through quickly leaving a dark band at the top of the column. The solution was concentrated to ca. 75 ml., and was then filtered through a sintered glass disc before being cooled. The brownish-red needles which separated were filtered off, and further evaporation of the solvent gave a second crop. Complete removal of the solvent left a brown residue which was not completely soluble in organic solvents.

Yield 155, 115 mgm. (85.14%) m.p.170° on block preheated to 170°

$C_{21}H_{15}N$ requires C,89.64% H,5.38%, N,4.98%

found 88.01% 5.84%, 5.53%

The base could be recrystallised from carbontetrachloride, acetonitrile, and ethanol giving a microcrystalline product. Prolonged heating in any solvent leads to polymerisation, and considerable loss.

C.XV,V1 1-Methylnaphtho[1,8a,9-ab]carbazolium Perchlorate.

The dark red solution of 3-methylperinaphthan-1-one phenylhydrazone (1.75 g.), perchloric acid (72%, 1 ml.) and glacial acetic acid (50 ml.) was boiled under reflux for 20 minutes, during which time dark red needles separated out. After cooling, these were filtered off washed free from acetic acid with ether, and the product shaken with distilled water (50 ml.) for five minutes. The filtered and dried product was recrystallised from acetonitrile.

Yield 666 mgm. (31.6%) m.p. 340°

$C_{20}H_{14}NClO_4$ requires C,65.3%, H,3.84%, N,3.81%

found 64.38%, 4.03% 3.67%

C.XVI Some Approaches to the Preparation of 2,3-Diformyl-perinaphthen-1-one and to 4,5-Diformylperinaphthen-1-one.

C.XVI,1 2-Hydroxymethylene-3-methyl-1-oxo-perinaphthane.

Dried ethyl formate (44.4 g.; 48.2 ml.) was added to powdered sodium methoxide (from sodium, 13 g.) suspended in benzene. After 10 minutes, 3-methylperinaphthan-1-one (50 g.) in benzene (450 ml.) was added over 5 minutes. The mixture became yellow-brown with a green tinge, and the bulk of the sodium methoxide went into solution. After 10 minutes a yellow solid began to precipitate from the solution. The mixture was allowed to stand for a further 4 hours at room temperature. The flask was swirled frequently and a voluminous yellow precipitate came out of solution.

The mixture was poured into water (1.2 l.) and the sodium salt extracted by shaking the mixture. The benzene phase was washed with aqueous sodium hydroxide (5%; 250 ml.). The combined alkaline extracts were washed with ether (2 x 100 ml.) before acidification (conc. HCl). The pale yellow oil which separated out quickly crystallised, and was extracted into benzene. The extract was washed free from acid with water, then dried (Na_2SO_4) before removal of solvent under reduced pressure.

Ether (250 ml.) was added to a solution of the hydroxymethylene compound in benzene (120 ml.), and the product crystallised immediately in clusters of bright yellow needles.

Yield 49 g. (85%) m.p. 116.8-119°

$C_{18}H_{12}O_2$ requires C, 80.4% H, 5.4%

found 79.9% 5.1%

C.XVI,11 The attempted oxidation of 2-hydroxymethylene-3-methyl-1-oxoperinaphthane by selenium dioxide

The hydroxymethylene ketone (6.73 g., 0.03 mole) was dissolved in glacial acetic acid (60 ml.) and selenium dioxide (freshly sublimed, 1.83 g., 0.0165 mole) was added to the solution followed by glacial acetic acid (40 ml.). The flask was heated on a boiling water bath for 45 minutes. Selenium began to precipitate out immediately on the walls of the flask. The cooled solution was diluted with chloroform (500 ml.) and water (200 ml.), then shaken up and filtered through a bed of celite to remove colloidal selenium. The filtered solution was washed free from acid with water, then extracted with aqueous alkali until the extracts were colourless. The chloroform solution was then washed with water, dried (K_2CO_3), and solvent removed. A brittle dark brown residue remained. This appeared to be polymeric, and could not be crystallised from any of the usual solvents.

Yield 3.88 g. m.p. no observable melting point.

C.XVI,111 The attempted bromination - dehydrobromination of 2-hydroxymethylene-3-methyl-1-oxo-perinaphthane.

The hydroxymethylene ketone (2.1 g.), freshly prepared

N-bromosuccinimide (1.96 g., 10% excess), and carbon tetrachloride (180 ml.) were refluxed for 2½ hours. During this time the N-bromosuccinimide dissolved completely, and succinimide floated to the surface. The flask was then immersed in an ice-bath for two hours. Succinimide was filtered off, and the solvent was removed under reduced pressure. The product was obtained as a pale yellow oil which decomposes on standing. Triethylamine (freshly distilled, 8 ml.) was added to the residual oil in ethanol (30 ml.), and the dark red solution was refluxed for 2 hours. White needles separated from the solution on cooling, and dissolved on the addition of water (100 ml.). The organic material was extracted into chloroform (500 ml.), the chloroform layer washed free from amine by much water, and the unchanged hydroxymethylene ketone by dilute alkali solution (7% KOH, 150 ml.), and water (100 ml.) before being dried (Na_2SO_4). The solution was reduced to low volume, charcoal screened (3 times), and solvent removed completely. The residue was dissolved in the minimum volume of benzene petrol was added, and the resulting solution cooled in a solid carbon dioxide-acetone bath. A dirty yellow microcrystalline solid was obtained. This was filtered off, and sublimed with difficulty at 100°/0.1 mm. The substance sublimed slowly, and any increase in the block temperature resulted in much decomposition.

Yield 490 mgm. (23.5%) m.p. softens > 130° melts 142-145°.

In an experiment using 10.5 g. of the hydroxymethylene ketone and 8.9 g. of N-bromosuccinimide the following yields of products were obtained:

Succinimide, 4.62 g. (93%).

Sublimate 1.94 g. (19%).

C.XVI,1V. The reaction of bromine with 4,5-dimethylperinaphthen-1-one.

4,5-Dimethylperinaphthen-1-one (1.04 g.) and carbon tetrachloride (60 ml.) were warmed gently until a homogeneous solution was obtained, and a stream of dry nitrogen was then bubbled through the solution. A gas bottle containing dry bromine (0.25 ml.) was then introduced into the gas stream, and the bromine vapour was slowly carried over into the reaction flask. Almost immediately a reddish-orange solid began to precipitate out of the solution. The addition of bromine took almost 3 hours for completion, and the solution was refluxed for a further 15 minutes. The solid was filtered from the cooled solution, and air dried. Evaporation of the solvent from the filtrate left an intractable oil which was discarded.

Yield 1.159 g.

A portion of the product (332 mgm.) was shaken with acetone (10 ml.), and water (100 ml.) was added to the suspension.

Almost immediately a pale yellow solid came out of solution. After standing for 10 minutes the solid was extracted into benzene (2 x 50 ml.), and the benzene layer was washed with water (3 x 50 ml.) before being dried (Na_2SO_4). The solvent was then removed.

The pale yellow residue chromatographed homogeneously on alumina (10 x 2.7 cm.) using benzene to develop the column. The pale yellow eluates were concentrated, and the product crystallised three times from light petrol-benzene giving yellow lustrous needles. The product has been formulated as 2-bromo-4,5-dimethylperinaphthen-1-one.

Yield 200 mgm. m.p. 151.5-154.5° dec.

$C_{15}H_{11}OBr$ requires Br,27.83%

found 26.85%

C.XVI,V <u>The Reaction of Chromyl Chloride with 4,5-Dimethyl perinaphthen-1-one</u>.

4,5-Dimethylperinaphthen-1-one (1.04 g.) was dissolved in carbon tetrachloride (200 ml.), and the solution was cooled to 15°. A freshly prepared solution of chromyl chloride (1.65 ml.) in carbon tetrachloride (10 ml.), added dropwise to the solution, gave an immediate orange precipitate. When the addition was complete the orange solid was filtered off, and air dried.

Yield 2.204 g.

This solid was hydrolysed by stirring a suspension of it in a mixture of sodium dithionate solution and benzene for 45 minutes. The organic layer was separated, washed with water, dried (Na_2SO_4), and solvent removed. The residue was charcoal screened in benzene-chloroform solution and crystallised as needles from benzene-ether.

Yield 612 mgm. M.p. and mixed m.p. with 4,5-dimethylperinaphthen-1-one 140-142°.

C.XVI,VI. <u>The Reaction of N-Bromosuccinimide with 4,5-Dimethylperinaphthen-1-one in the Presence of Benzoyl Peroxide.</u>

4,5-Dimethylperinaphthen-1-one (1.04 g.), N-bromosuccinimide (3.56 g.), a trace of benzoyl peroxide, and carbon tetrachloride (180 ml.) were refluxed for 20 hr., cooled, and the precipitated solid filtered off. Upon the addition of pyridine (5 ml.) to the cooled solution there was an immediate precipitation of an orange-yellow solid. This quarternary salt was filtered off and dissolved in ethanol (25 ml.), and perchloric acid (72%, 1 ml.) added. An orange-red precipitate, filtered from the cooled mixture, recrystallised as yellow platelets from acetonitrile.

Yield 486 mgm (17.3%) m.p. darkens > 265° melts 273-277°

$C_{26}H_{20}O_9N_2Cl_2$ requires C,53.3%, H,3.58%, N,4.99%

found 49.84% 3.79% 5.09%

The mother liquors on standing produced another crop of yellow crystals which crystallised as yellow prisms from acetonitrile on the addition of a few drops of anhydrous ether.

$C_{20}H_{16}O_3NCl$ requires C, 62.25%, H, 4.18%, N, 3.63%

found 61.55% 4.02% 4.09%

Yield 373 mgm. (19.33%) m.p. 229-231°

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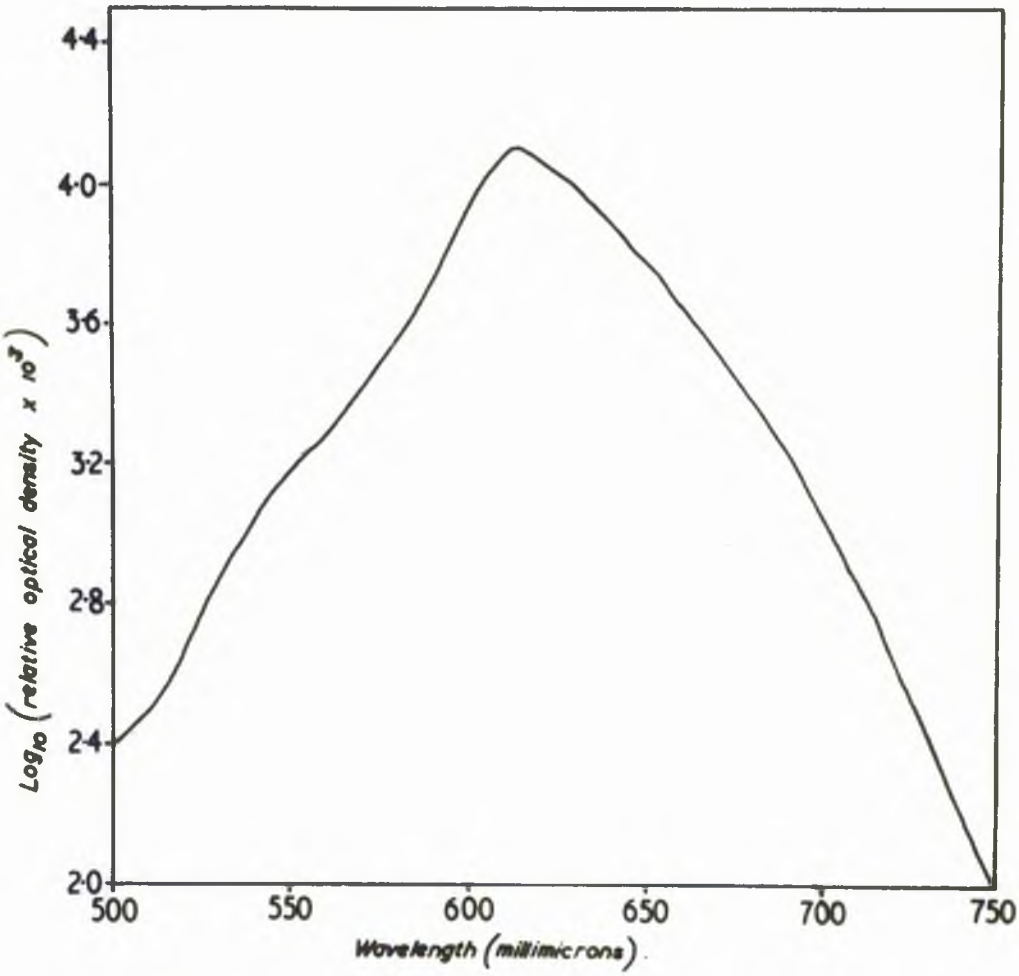

PLATE I Absorption spectrum of perinaphthyl in ether.

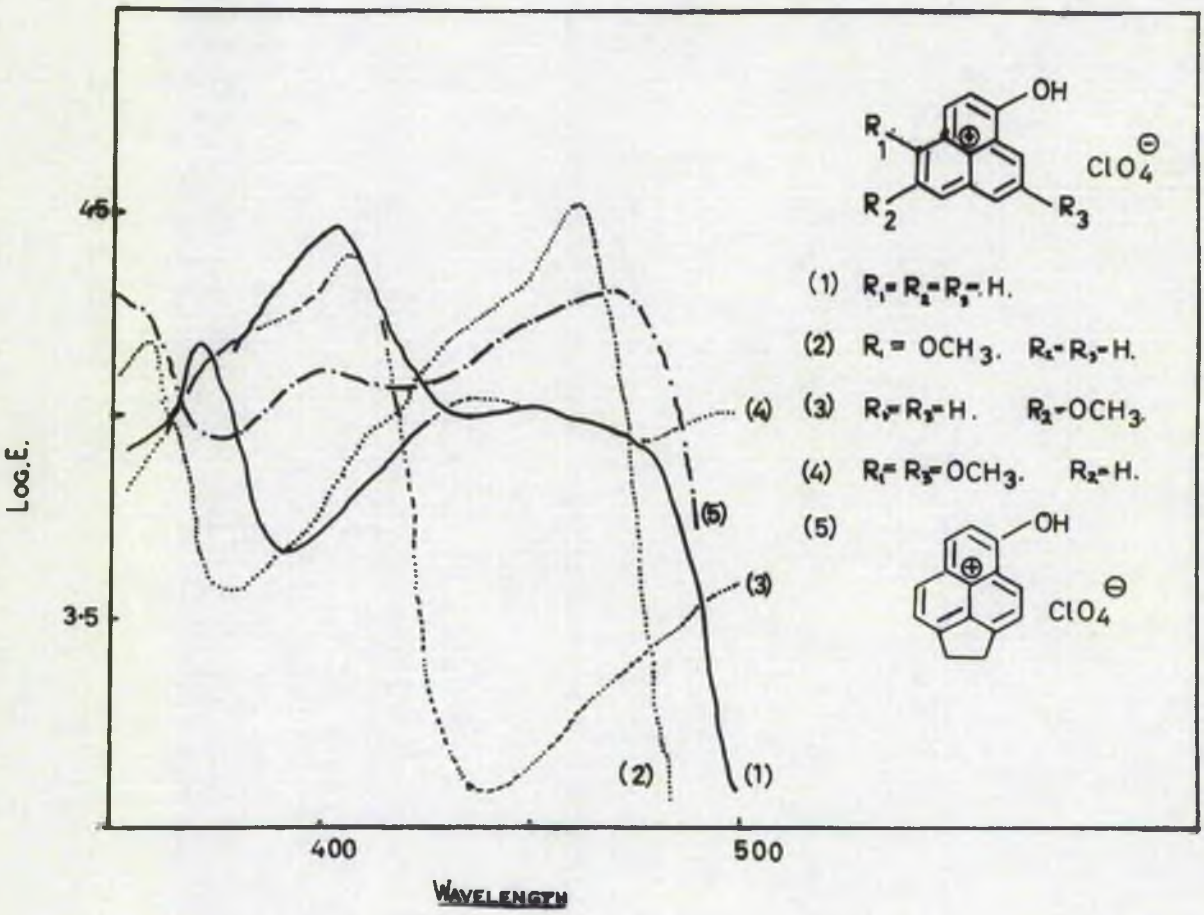

PLATE II VISIBLE ABSORPTION SPECTRA OF

HYDROXYPERINAPHTHENYLIUM PERCHLORATES.

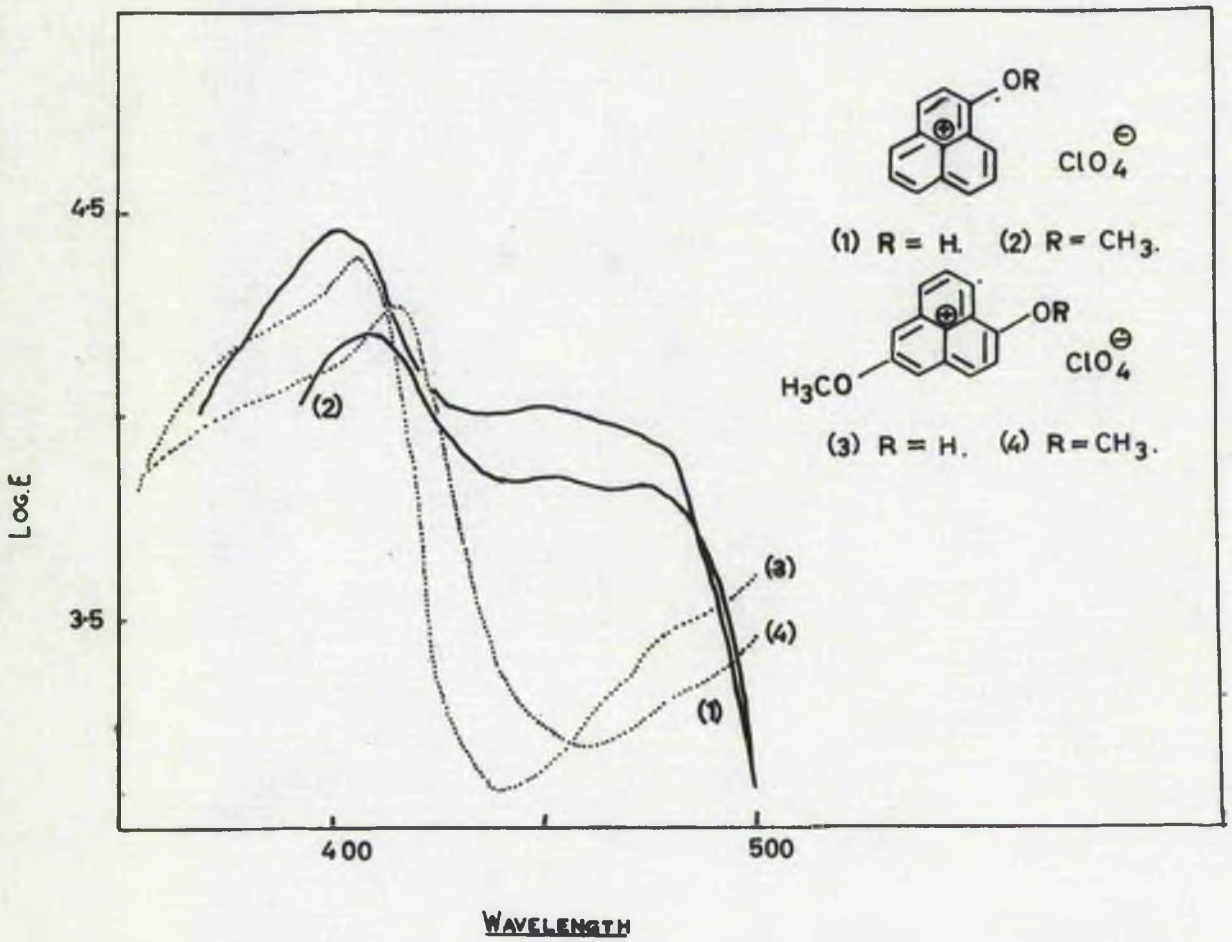

PLATE III. VISIBLE ABSORPTION SPECTRA OF

ALKOXY-PERINAPHTHENYLIUM SALTS AND THEIR HYDROLYSIS PRODUCTS

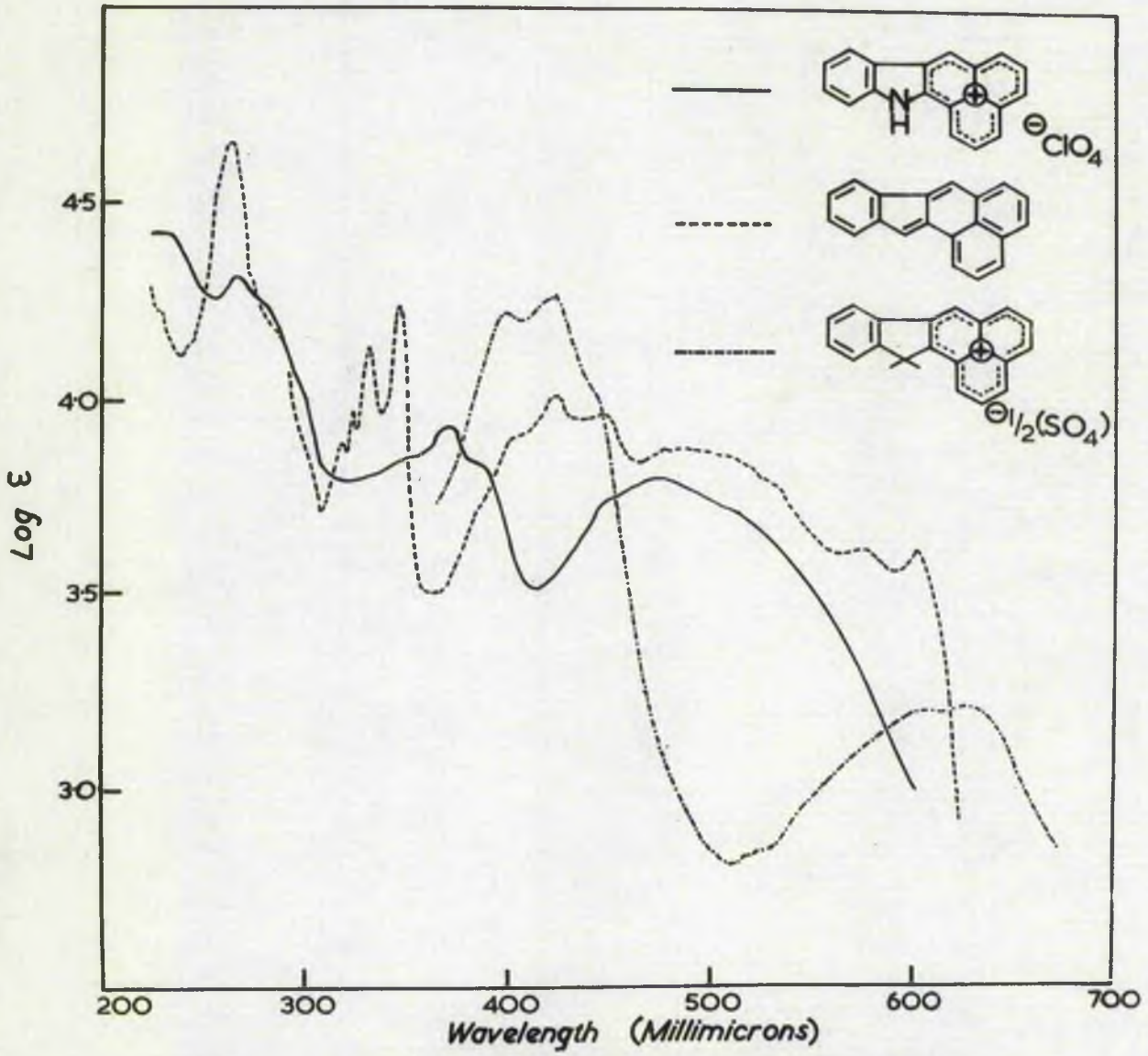

PLATE IV. Visible and ultra-violet absorption spectra of indolo[2,3-a]perinaphthene perchlorate in methanol, and indeno[2,1-a]perinaphthene in cyclohexane and in 77% sulphuric acid.