STRUCTURE AND REACTIVITY IN THE NAPHTHALENE SERIES:

Monobromo – Peri-Alkylnaphthalene Isomer Distributions.

A thesis presented for the

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by

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Abstract:

1,8-Dimethylnaphthalene, perinaphthane and pleiadane were synthesized to form, with acenaphthene, a group of structurally analogous hydrocarbons. Acenaphthene was brominated under a variety of conditions and the distributions of the product isomers were measured by vapor phase chromatography. A selection of the brominating conditions was then tried on the group of hydrocarbons in an endeavour to relate the isomer distributions to the structural differences between the hydrocarbons. Finally, pairs of the hydrocarbons were brominated to determine their order of reactivity.

The inferences that may be drawn from the results are discussed together with their reproducibility and reliability.

Contents

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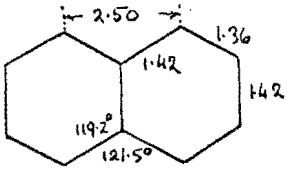
Interpretation of Present Work:

Preface

Introduction: The carboxylic acids of a series of methylnaphthalenes had been studied in this department.[1] This series included 1,8-dimethylnaphthalene and acenaphthene (I) and led to these two compounds being further studied here[2,3,4]. X-Ray crystallography has been used to show that acenaphthene and 3-bromo-1,8-dimethylnaphthalene contain distorted naphthalene nuclei. The established structures are drawn below:



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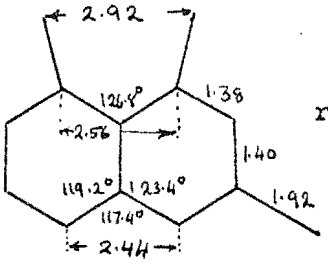

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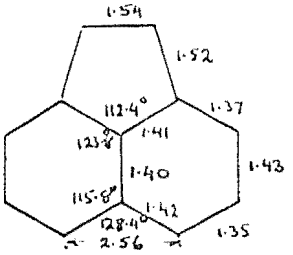

(I)

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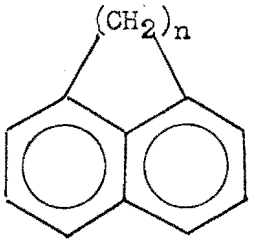
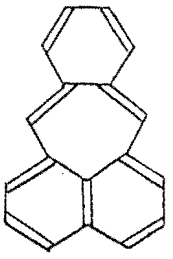
It can be seen that the distortions are of the same order, although in different directions.



Acenaphthene can be considered as a member of a series of tri-cyclic compounds, generalised in the figure. Two other members of this series are known, perinaphthane (n = 3) and pleiadane (n = 4) but compounds corresponding to n = 1, 5 & 6 have yet to be prepared. 1,8-Dehydronaphthalene (n = 0) has been postulated as a reaction intermediate[7].

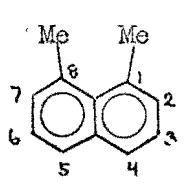
Perinaphthane is now more correctly known as '2,3-dihydrophenalene'[8] (which has supplanted the terms 'perinaphthindane' and '2,3-dihydro-1H benzonaphthene) but the writer agrees with Fieser and Hershberg (1938)[9] that 'perinaphthane', an abbreviation of 'peri-trimethylenenaphthalene' is more consistent with the structure than a name that suggests a benzene derivative. The term 'pleiadane' is used in place of the more correct, but bulkier, '7,8,9,10-tetrahydrocyclohepta(de)naphthalene'. The shorter term was invented by Boekelheide (1951) and it must not be confused with 'pleiadene' (II)[10,11].

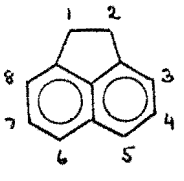
(II)

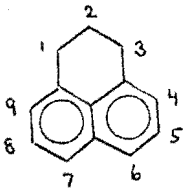


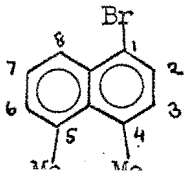
1,8-Dimethylnaphthalene, acenaphthene, perinaphthane and pleiadane form a series of closely related, substituted naphthalenes so it was not expected that they would have markedly different chemical properties, but it was reasoned that the isomer ratios obtained when they were reacted, should reflect the varying structural differences at the peri positions.

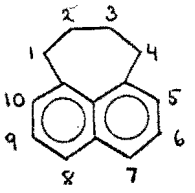
The conventional numbering of these structures, shown below, complicates generalised statements about the group.











For this reason, the positions on the naphthalene nuclei are considered relative to the peri positions and termed ortho, meta and para (o, m, & p) for this work.

Effects involved: Three directive effects need to be considered for substitution reactions of alkylnaphthalenes, these are steric interference, inductive and hyperconjugation effects. It is generally recognized that alkyl groups tend to release electrons to adjacent groups. The inductive (+I) effect can be illustrated by the decreasing acid strengths in a series of acids of the type RCO_2H, where 'R' represents an alkyl group:[12]

R	H	Me	Et	iso-Pr	t-Bu
10^5K_a	17.7	1.75	1.33	1.38	0.89

This tabulation shows, from left to right, an increasing inductive effect.

When the alkyl groups are attached to unsaturated systems the reverse order of electron release is sometimes observed, for example the rate of solvolysis of p-alkylbenzhydryl halides (p-R.Ph.CHPh.Cl):[12]

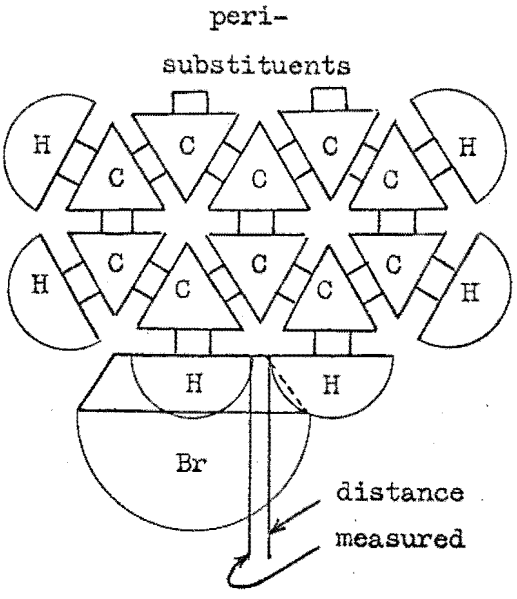
R	H	Me	Et	iso-Pr	t-Bu
Rate	2.8	83.5	62.6	47.0	35.9

It was suggested that the electron pair of a carbon-hydrogen bond could behave like a lone electron-pair and conjugate with the unsaturated system. If this is the case, the same steric requirements should be involved and it follows that a carbon-hydrogen bond in the plane of the unsaturated system should give a negligible effect.

"Courtauld" scale molecular models of the four hydrocarbons and their ortho- and para-bromo isomers were constructed to facilitate comprehension of the possible extent of hyperconjugation and steric repulsion in the systems. In these models hydrogen was represented as a hemisphere and bromine as a modified hemisphere. The aromatic ring carbons were triangular prisms and the aliphatic ring carbons were tetrahedra. The manufacturers scale the hydrogen atoms to a radius of 1.0A. which they consider is a more practical value for their models than Pauling's value of 1.2A. An estimation of the interactions was obtained by measuring the minimum distances between the surfaces of neighbouring hemispheres. The distances of interest were:

1. the p-H/p-H distance in the hydrocarbons
2. the p-H/p-Br distance in the p-bromohydrocarbons
3. the o-H/nearest neighbour distance in the hydrocarbons
4. the o-Br/nearest neighbour distance in the o-bromohydrocarbons.

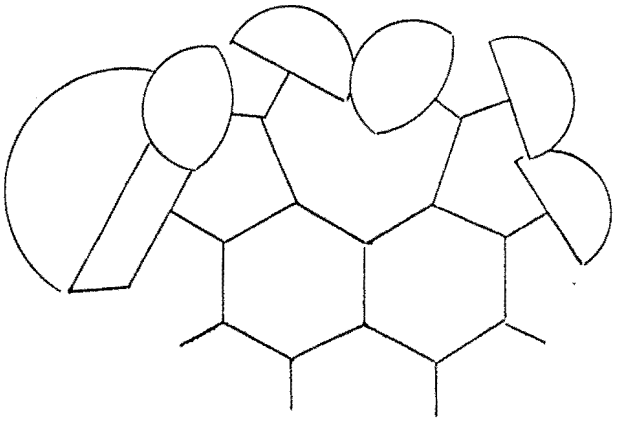
The following set of drawings illustrate the results obtained:

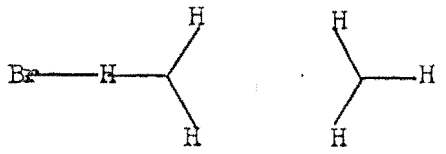


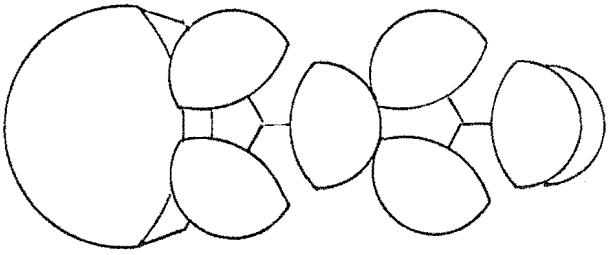
	Distances	
	p-H/p-H	p-H/p-Br
1,8-Dimethylnphth.	0.20"	0"
Acenaphthene	0.52"	0.16"
Perinaphthane	0.34"	0"
Pleiadane	0.30"	0"

Scale: 1cm = 1" of model
= 1.25A.

o-Bromo-1,8-Dimethylnaphthalene





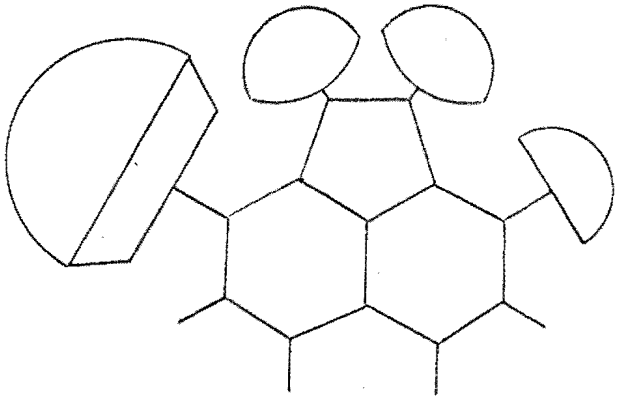


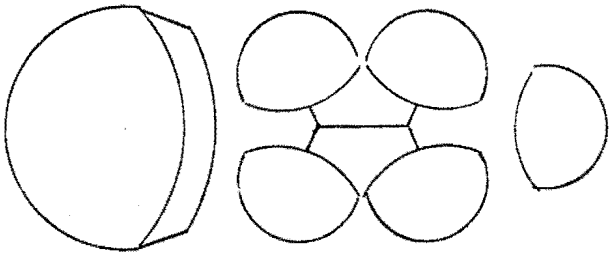
Two stable orientations of the methyl groups are possible in the hydrocarbon, but one (the line sketch) is more strained in the o-bromo compound than the other (top and bottom sketches). Even in the latter model there is contact between the o-hydrogen and a hydrogen atom of the methyl group.

o-H/nearest neighbour distance in the hydrocarbon = 0.3"

o-Br/nearest neighbour distance in the bromohydrocarbon = 0.08"

o-Bromoacenaphthene



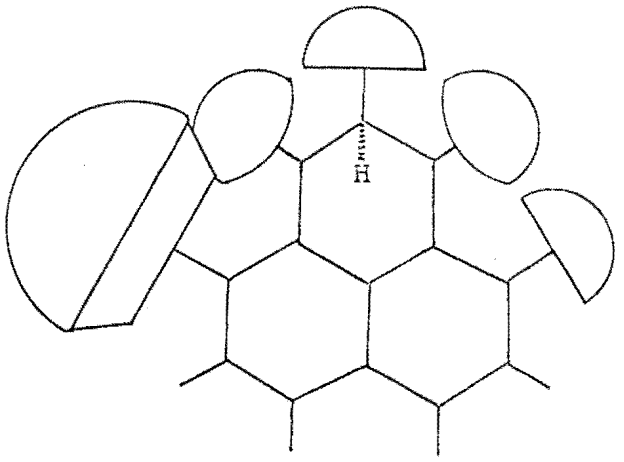


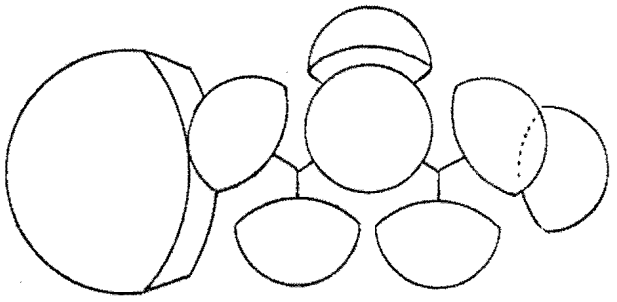
o-H/nearest neighbour distance in the hydrocarbon = 1.0"

o-Br/nearest neighbour distance in the bromohydrocarbon = 0.34"

(The nearest neighbour is taken to be in the peri-group and never as the m-hydrogen atom.)

o-Bromoperinaphthane

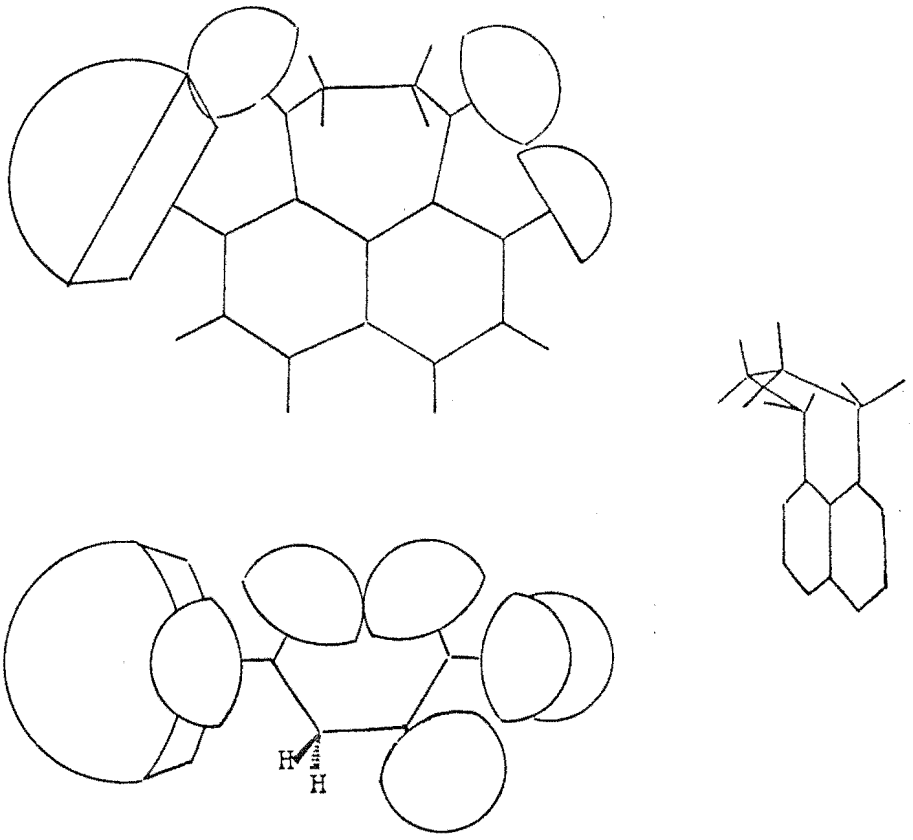




o-H/nearest neighbour distance in the hydrocarbon = 0.34"

o-Br/nearest neighbour distance in the bromohydrocarbon = 0"

o-Bromopleiadane



The line sketch shows the shape of the seven-membered ring.

o-H/nearest neighbour distance in the hydrocarbon = 0.11"

o-Br/nearest neighbour distance in the bromohydrocarbon = 0"

All the drawings are approximately to scale, but they were drawn primarily to illustrate the quantities measured and not to be measured themselves.

The most strained hydrocarbon model is the acenaphthene one, the model of 1,8-dimethylnaphthalene is not nearly so strained and the models of the other two hydrocarbons are not significantly strained at all. The rigid seven-membered ring in the pleiadane model suggests that ring substituted pleiadanes might exist as optical isomers, whereas the six-membered peri ring in the perinaphthane model is comparitively mobile.

Both acenaphthene and 1,8-dimethylnaphthalene have four carbon-hydrogen bonds that could be involved in hyperconjugation but not as effectively as the two carbon-hydrogen bonds in perinaphthane that lie in planes perpendicular to the plane of the naphthalene rings. The equivalent two bonds in pleiadane are probably less effective because they have been rotated out of these perpendicular planes.

Hyperconjugation would tend to favour the para positions[15a] and induction, the ortho positions[15b]. It could be expected that 1,8-dimethylnaphthalene would be the least activated by the inductive effect and that the other three would be closely grouped.

Room at the ortho positions decreases in the order: acenaphthene, 1,8-dimethylnaphthalene, perinaphthane, pleiadane. But room at the para positions decreases in the order: acenaphthene, perinaphthane, pleiadane, 1,8-dimethylnaphthalene.

Predictions are complicated, but if the electronic effects can be ignored as giving only minor differences, the ortho/para ratios (and therefor the percentage of the ortho compound) for mono-substitution should decrease in the order: acenaphthene, 1,8-dimethylnaphthalene, perinaphthane, pleiadane

This is deduced from the ratios of the nearest-neighbour distances at the two positions, the cubes of these ratios are probably more relevant, but they would give the same order.

Scope: The available quantities of perinaphthane and pleiadane, in particular, meant that the chosen reactions would have to be done on a semi-micro scale. The differences in the isomer distributions were expected to be small, so it was essential that the reactions could be standardised, and to avoid the confusion of di-substitution, it was also essential that the hydrocarbon should be in excess of the reagent. Further complications could be avoided if the chosen reactions were irreversible.

Nitration, bromination and chlorination appeared to be suitable reactions so it was originally intended to try each, but the nitro-acenaphthenes could not be resolved on the available vapor phase chromatograph which was the only suitable analytical tool. The chloro- and bromo-isomers could be resolved, but it was more difficult to handle chlorine solutions on a semi-micro scale than it was to handle bromine solutions. Bromination were tried initially and when it was found that the use of various solvents gave different, but reproducible, isomer distributions, it was decided to limit the investigations to brominations.

The following considerations predict that the amount of m-bromo-hydrocarbon will be small and probably negligible. With the parent hydrocarbon, naphthalene, the "meta" and "ortho" positions are equivalent and bromination gives very little 2-bromonaphthalene[14]. In the peri-alkyl

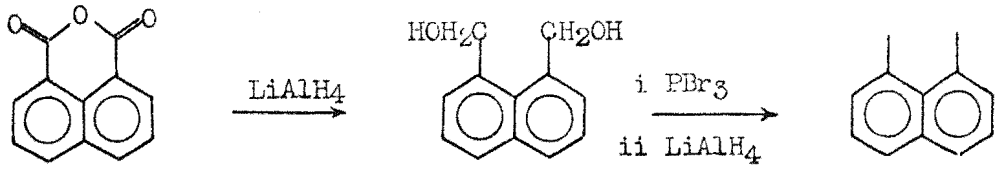
naphthalenes, the alkyl groups activate the ortho and para positions, but not the meta positions, towards electrophilic attack. It follows that bromination of these hydrocarbons will give small amounts of the o-bromo-compound, but much less of the m-bromo.

Experimental

Outline of the Preparation of the Hydrocarbons:

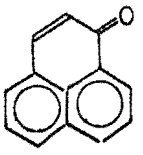
Only three of the four alkyl naphthalenes studied had to be prepared since acenaphthene is available commercially.

The synthesis used for 1,8-dimethylnaphthalene was a standard departmental method. Naphthalic anhydride was reduced with lithium aluminium hydride to 1,8-di(hydroxymethyl)naphthalene which yields the di-bromomethyl compound when treated with phosphorus tribromide. Further use of lithium aluminium hydride then reduced this di-bromo compound to the hydrocarbon.



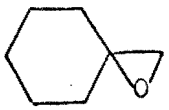
This scheme, with the variations upon which it is based, appears in the literature[15,16,17,18].

The synthesis of perinaphthane had previously been attempted in the department by the reduction of perinaphthanenone, a method reported[9] to give a high yield, but only carbonaceous products had been obtained. This reduction attempt used a hydrogenater made in the department. A commercial model was ordered, but in the interim period, between ordering it and it arriving, another plan for the preparation was investigated.

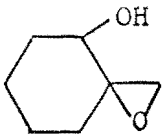


perinaphthenone

Simple cyclic ketones can be enlarged with diazomethane, although another reaction, the formation of the epoxide, may sometimes dominate. Thus, whereas cyclohexanone yields 65% cycloheptanone and 15% epoxide (III), 2-hydroxy-cyclohexanone yields 95% epoxide (IV)[19,20].

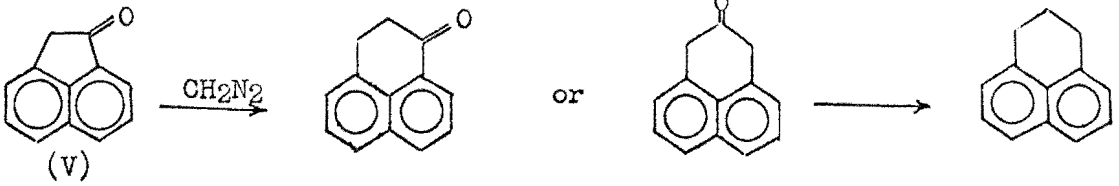


(III)



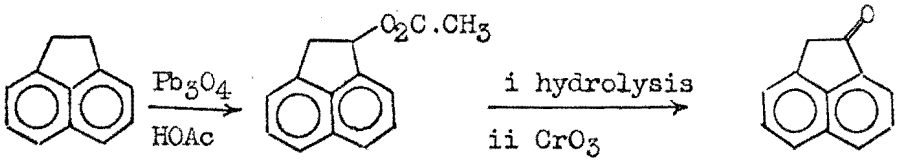
(IV)

It was wondered if acenaphthenone (V) could be converted to peri-naphthanone(s) which could then be reduced to the hydrocarbon:

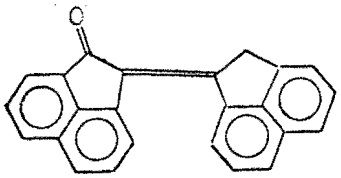


(V)

Acenaphthenone was prepared from acenaphthene by acetoxylation with the equivalent of lead tetra-acetate, hydrolysis of the ester obtained and then oxidation of the resulting alcohol to the ketone [21,22,23].



Diazomethane is usually produced by the action of alkali on one of a variety of compounds containing the N-methyl,N-nitroso group. N-Methyl, N-nitroso,p-toluenesulphonamide (MNTS) was available in this department, so it was tried first. Gutsche[20] states that in situ generation of diazomethane is preferable to ex situ generation, for cyclic ketone ring enlargements. However, the conditions required to generate diazomethane from MNTS (heating in a solution of alcoholic potassium hydroxide) cause acenaphthenone to condense to biacenone (VI)[24].



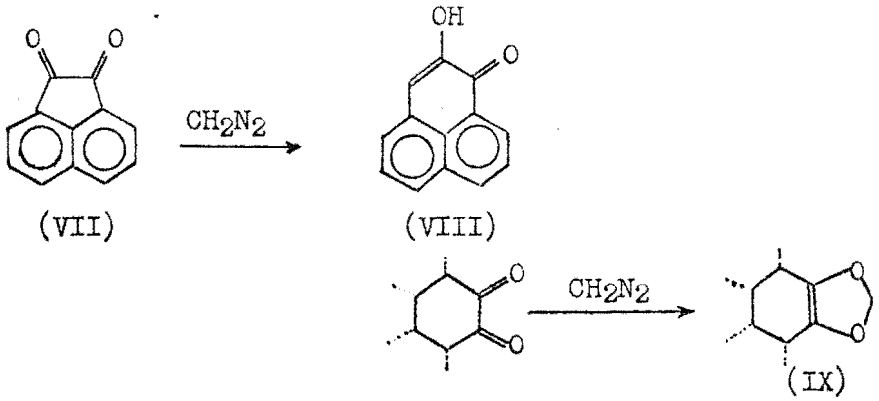
(VI)

Ex situ generation of the diazomethane from MNTS gave a yellow ether solution which showed little reactivity when added to a solution of acenaphthenone in methanol and ether. Methanol generally catalyses the reactions of diazomethane[20] the rate of which can be estimated from the amount of nitrogen evolved. The use of boron trifluoride is mentioned in the literature[25,26] for the improved homologization of cycloaliphatic ketones, so its addition, in the form of boron trifluoride etherate, was tried. Processing such mixtures only led to the conclusion that boron trifluoride, like alcoholic alkali solutions[24], hydrochloric acid in boiling alcohol[27], and even ortho-anthranilic acid[28], facilitates the formation of biacenone from acenaphthenone.

Because the diazomethane solutions obtained from MNTS gave only mild effervescence with substances like benzoic acid which should react vigorously, another source of the reagent was tried. N-Methyl,N-nitroso-urethan in methanolic solution, needs only traces of sodium carbonate for it to liberate diazomethane[20], and under such mildly alkaline conditions the formation of biacenone from acenaphthenone was found to be negligible. When methanolic solutions of the two reagents were mixed a distinct effervescence was observed, but the material recovered from the reaction was almost entirely acenaphthenone. Yet when the residue obtained by recrystallising a higher boiling fraction was analysed by v.p.c., the traces showed a component peak possessing the same retention time as an authentic sample of perinaphthanone on two stationary phases, one non-polar and the

other of medium polarity.

Hence, acenaphthenone, like the structurally analogous tetral-1-one[29,30] gives only trace reaction products with diazomethane. This contrasts with the reaction between acenaphthenequinone (VII) and diazomethane which gives a perinaphthane derivative (VIII)[31]. Usually[20], 1,2-quinones add diazomethane to give a cyclic di-ether (IX).



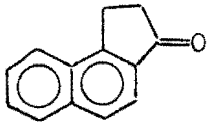
(VII) (VIII) (IX)

Because of the trouble that had been experienced with Fieser & Hershberg's method[9] of preparing perinaphthane, the methods in the literature were reconsidered before their method was re-attempted. Perinaphthane has been made by the reduction of perinaphthanequinone, perinaphthenone and perinaphthanone.

Fleischer & Retze (1922)[32] reacted naphthalene with malonyl bromide in the presence of aluminium chloride and reduced the quinone obtained with iodine and red phosphorus. They then dehydrogenated the product, presumeably tetrahydroperinaphthane, over copper at 500°. The product, if perinaphthane as claimed, must have been impure, since the picrate melted at 134-5°, the accepted value is 151° [9].

Most perinaphthanone preparations are based on the cyclisation of

3(1-naphthyl)propanoic acid or its acid chloride (these compounds can be obtained from naphthalene in three or four steps[33]). Mayer (1922)[34] treated the acid chloride with aluminium chloride and claimed to have obtained perinaphthanone (m.p. 86°), but Cook & Hewett (1934)[35] showed that repeated recrystallisation of such material gave perinaphthenone (m.p. 153-154°); the same product that they obtained by cyclising the propanoic acid with tin tetrachloride. Yet Darzens & Levy (1935)[36] also used aluminium chloride on the acid chloride and demonstrated that their product is perinaphthanone by giving the correct melting point of the oxime. Fieser & Gates (1940)[33] suggested that the confusion may be due to different investigators cyclising different acid chlorides, they themselves used hydrofluoric acid to cyclise the propanoic acid in high yield to perinaphthanone and obtained as a by-product 4,5-benzhydrindan-1-one (X).

(X) 

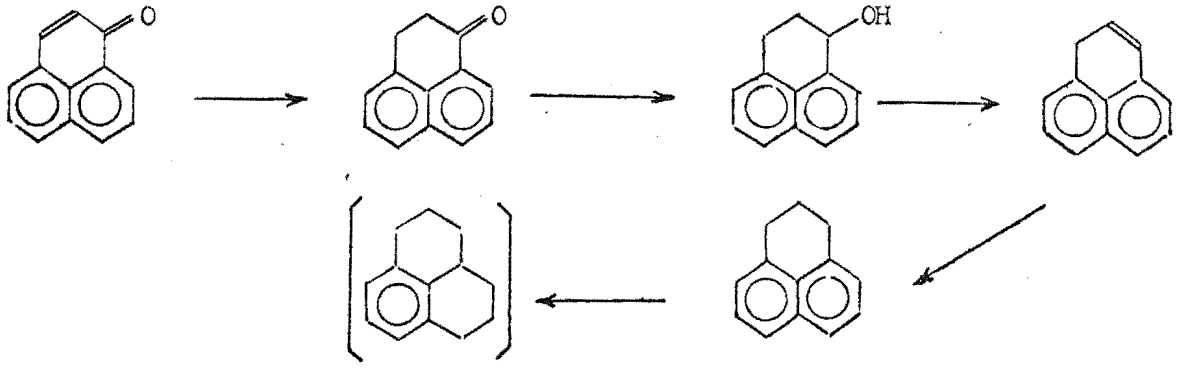
Fieser & Gates reduced perinaphthanone by the Clemmensen method, but did not quote a yield. Topsom (1962)[37] found that this reduction gives a low yield (12%). Heidelberger & Straube (1951)[38] reported that the catalytic hydrogenation of perinaphthanone gave a higher yield of perinaphthane than did the catalytic hydrogenation of perinaphthenone.

Three cases are recorded for the reduction of perinaphthenone. Zil'berman & Barkov (1938)[39] used zinc and hydrochloric acid and then distilled the resulting compound with zinc dust. The melting point of the picrate (132.5°) shows that the material obtained was, at best, impure. Fieser & Hershberg(1938)[9] and Treibs & Heyner (1961)[40] hydrogenated

perinaphthenone over a copper chromite catalyst.

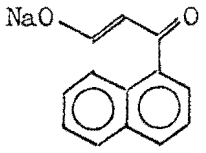
Because perinaphthenone is more readily available than perinaphthanone and because the latter's reduction is not necessarily straightforward, the copper chromite reduction of perinaphthenone was still found to be the equal of any method in the literature for preparing perinaphthane. So, since by this time a modern 'rocking-bomb' autoclave had arrived in the department, it was decided to re-investigate the method.

Fieser & Hershberg[9] dissolved perinaphthenone in dioxan, added a small amount of copper chromite catalyst '37KAF' (the significance of this symbolism is not known) and heated it at 250-260° for ten hours. The initial hydrogen pressure was 1800 psi. The cooled solution separated into two layers and dioxan was added to make the mixture homogeneous before the catalyst was filtered off and the solvent removed. The course of the hydrogenation was assumed to follow the scheme:



The perinaphthenone preparation that they used was that of Kunz & Kochendoefer (1935)[41]. A mixture of 2-naphthol, glycerol, sodium nitrobenzenesulphonate and sulphuric acid is heated for an hour at 135-140°. The cooled mixture is poured into water and perinaphthenone is extracted from the resulting black tar. The yield is low.

A better method is that of Lüttringhaus & Kacer (1926)[42] in which the sodium enolate (XI) formed by reacting together 1-acetylnaphthalene, ethyl formate and sodium, is condensed, by sulphuric acid, to perinaphthenone in good yield. Later workers have preferred this method[43,40] and it was the one used for this work.



(XI)

Several attempts to duplicate the work of Fieser and Hershberg, following their instructions as closely as possible, resulted in mainly carbonaceous material from which could be extracted varying quantities of benzene-soluble substances. The extracted material was largely a mixture of perinaphthane and perinaphthanone. A run, tried with no catalyst gave a similar intractable tar, but the amount of extractable solid was much less. The other extreme was then tried. A comparatively large amount of catalyst was used and the result was a clear liquid, the major component of which was shown to be tetrahydroperinaphthalene. Because of this the nature of the catalyst was studied more closely.

It appears[44] that the catalyst is, essentially, black cupric oxide stabilised by the presence of chromium oxide against reduction to inert, red cuprous oxide. The stabilisation is further assisted by the presence of alkaline earth oxides such as barium oxide. The solvent most recommended for use with the catalyst is dioxan and the best form of the catalyst, for use in a rocking-bomb, is obtained by the thermal decomposition of copper barium ammonium chromate. The activity of the black powder so obtained is

entirely unaffected by exposure to air and moisture. In general, double-bonds and aryl rings are not affected by the catalyst, but poly-nuclear ring systems can be partially reduced. Thus, the catalyst will reduce naphthalene to tetralin if the temperature is above 200°. It is recommended, for the reduction of ketones, that 2-4% of the catalyst should be used, but Grundmann[44] points out that, whereas 2.5g. of catalyst may be necessary for 50g. of ketone, 10-12g. might be quite sufficient for 500g. Now Fieser & Hershberg used only 0.25% of catalyst and their results infer that a high temperature is required to dehydrate perinaphthol to perinaphthene. Under such conditions, over-hydrogenation beyond perinaphthane tends to occur, so a minimum amount of catalyst was used. It follows that the amount of catalyst is critical and altering the reaction parameters (e.g. the quantities of the reagents and possibly the bomb dimensions) will change the optimum amount.

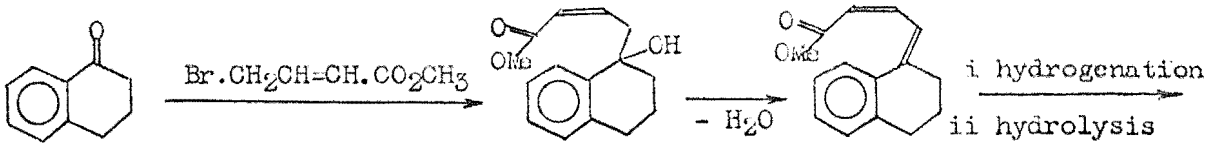
After allowances had been made for the numerous mechanical shortcomings of the autoclave, which complicated run to run comparisons, there still seemed to be another reaction variable besides the amount of catalyst. One particularly satisfactory perinaphthenone preparation yielded such a clean product of excellent melting point it was not distilled before a sample of it was hydrogenated. The conditions used for this hydrogenation had yielded satisfactory results before, but this time only a tar was obtained. However, the hydrogenation of a distilled sample of this batch gave excellent results. It appears that the undistilled perinaphthenone contained a catalyst poison and possibly the distilled samples also contained varying amounts of it.

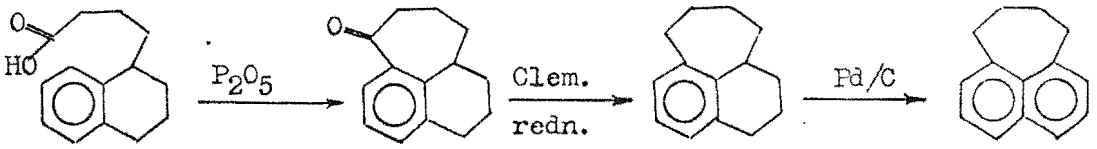
Because the optimum amount of catalyst seems to depend upon the batch

of perinaphthenone, it is suggested, if a quantity of perinaphthane is to be prepared by this method, that a large quantity of perinaphthenone should be accumulated and well mixed, before samples of it are used to find the optimum amount of catalyst. From the thirty-four hydrogenations attempted only 60g. of perinaphthane resulted, mainly because the purity of the ketone, and consequently the optimum quantity of catalyst, fluctuated. It actually may be simpler to use a large excess of catalyst to ensure a clean, if over-hydrogenated product and then dehydrogenate it over a palladium or platinum catalyst (tetrahydroperinaphthalene over palladium-carbon can yield 80% perinaphthane[45]). It was interesting to observe that a higher yield of tetrahydroperinaphthane was obtained, using just copper chromite, than was obtained by Treibs & Heyner[40], who used copper chromite first and then Raney nickel.

Gilmore & Horton (1951)[46] were the first to prepare pleiadane although derivatives of it have been known since 1927 [47]. To establish its structure they prepared it two ways, firstly they started from tetralone and cyclised on to it a seven-membered ring and secondly they started from benzosuberone and cyclised on to it the other six-membered ring. The products of these two paths were shown to be identical. The method based on tetralone gave the higher yield so it was the one followed. A Reformatsky reaction between tetralone and γbromo-methylcrotonate gave, upon distillation of the initial product, a di-ene ester. Hydrogenation over platinum, followed by hydrolysis of the ester group, yielded a butyric acid that was cyclised to tetrahydro pleiadanone with polyphosphoric acid. A Clemmensen reduction of the ketone and dehydrogenation of the product over palladium, yielded pleiadane. The

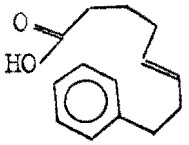
overall yield, based on tetralone and the optimum yields for each step, was 55%. The scheme is outlined below:





(XII)

The intermediate ketone (XII) has also been prepared by the cyclisation of trans-8-phenyloct-5-enoic acid (XIII) with polyphosphoric acid[48], but although this reaction is interesting and of reasonable yield, the above method is still the best seen in the literature.



(XIII)

Experimental Details of the Hydrocarbon Preparations:

1,8-Dimethylnaphthalene:- Lithium aluminium hydride (50g.) was part suspended, part dissolved in anhydrous ether (1l.) by stirring the refluxing mixture for two hours in a two litre flange vessel. The mixture was allowed to cool and anhydrous benzene (200ml.) was added, followed by a slurry of naphthalic anhydride (100g.) in anhydrous benzene (250ml.) added over two hours. No external heat was applied and the mixture was stirred continuously. Three hours of refluxing the mixture completed the reaction and then most of the ether was distilled off. The excess lithium aluminium hydride was destroyed by the cautious addition of ethyl acetate before concentrated , aqueous potassium hydroxide solution (50ml.) was added to precipitate aluminium hydroxide. Usually, the precipitate is sufficiently coagulated for decanting to be the most efficient method of extracting the organic product, but the writer found it necessary to use the more arduous filtration. The inorganic material was extracted by refluxing it with benzene (500ml.) and ethanol (50ml.) and then filtering; this cycle being repeated three times. The organic solutions were combined and concentrated to 250ml. More ethanol (250ml.) was added and the solution was again concentrated to about 250ml. The di-alcohol was precipitated by the addition of 10% sulphuric acid, filtered off, washed thoroughly with water and dried. The yield was 76g.(82%, m.p. 154°) and recrystallisation from ethanol left 67.2g.(m.p. 156-7°, lit. value 158°[15]). Yields of up to 87% have been obtained in the department.

The di-alcohol was dissolved in a mixture of anhydrous benzene and ether (1l.: 200ml.). Then, whilst this solution was being stirred, a solution of

phosphorus tribromide (67.2g.) in anhydrous ether (200ml.) was added over two hours. This addition was followed by an hour of refluxing the mixture before it was poured on to crushed ice (2Kg.). The organic layer that separated was washed with an excess of sodium bicarbonate solution, then with water, dried over anhydrous magnesium sulphate, concentrated to about 100ml. and finally diluted with more ether (100ml.) to prevent precipitation of the product.

This solution of di-bromomethylnaphthalene was added, over two hours, to a solution of lithium aluminium hydride (20g.) in ether (1200ml.) which had been previously prepared by stirring the components under reflux for two hours. The mixture was given a further hour of refluxing after the addition was complete. The mixture was worked up in a similar fashion to that used for the di-alcohol. The organic solution obtained was evaporated to dryness and the residue was distilled under reduced pressure. The crude material (m.p. 49.5°, b.p. 182-4° at 70mm) was recrystallised from ethanol to yield 49.5g. (88%, m.p. 61-62°). Analysis by v.p.c. showed no significant amount of impurity. Yields of 87-90% (m.p. 61-62°, 62.5° after one recrystallisation) have been obtained in this department.

Perinaphthane(unsuccesful attempt):- The acenaphthenone needed for this attempt was obtained from acenaphthene by the following route[21]. Acenaphthene (154g.) was partially dissolved, partially suspended in hot (60°) glacial acetic acid (1100ml.) by constant stirring. The acetic acid had previously been distilled from potassium permanganate to remove oxidizable impurities. Red lead was added in approximately 50g. portions, over one hour, until 820g. had been used.

Stirring was continued during this addition and the temperature was kept in the 60-70° range by external cooling. The colour of the resulting syrup was brown and not the red mentioned in the literature. Fieser & Cason[21,22] estimated that their red lead was 85-90% pure, if the sample used is less than 83.6% pure, 820g. will not be an excess and the final solution will not be red. The syrup was poured into water (2l.) and extracted with ether (3 x 200ml.). The ether solution was washed with water (100ml.), brine (300ml.) and then dried over anhydrous sodium sulphate. Filtration, extraction of the drying agent with more ether (3 x 50ml.) and evaporation of the combined ether solutions, yielded the crude acetate as an oil. Distillation under reduced pressure gave 164g. of product (b.p. 144-150° at approximately 2mm.). The reported yield is 80-82%.

The acetate(164g.) was dissolved in methanol (275ml.) and refluxed with a solution of sodium hydroxide (40g. in 400ml. water) for two hours. This mixture was cooled to room temperature and the solid that precipitated was filtered off and dried to yield 130g. of crude acenaphthenol. This acenaphthenol was dissolved in benzene (2l.) and refluxed with decolorising carbon (8g.). The carbon was removed by filtration and the solution was concentrated to one litre. Crystallisation, filtration and washing the collected solid with cold benzene yielded 110g.(85%, m.p. 144-5°) whereas the literature yield of acenaphthenol is 85-88 % (m.p. 146°).

Acenaphthenol (100g.) was kept suspended in glacial acetic acid (300ml.) by constant stirring whilst a solution obtained by dissolving chromic anhydride (43g.) in the minimum amount of water and diluting with acetic acid (240ml.), was added over approximately an hour.

External cooling kept the reactants in the temperature range 28-37°. After a further hour under the same conditions, the reaction mixture was poured into ice-water (6l.). The precipitate was collected, washed with water and dried. It is claimed[21] that the best method of purifying the crude acenaphthenone is steam distillation, the processes of recrystallisation and vacuum distillation being found to be unsatisfactory. The steam distillation requires the collection of 35 litres of condensate, which is cooled to room temperature before the solid is filtered off. The writer found it more convenient to collect and treat the condensate in portions. The yellowish solid collected (61.5g. or 62%) had a low melting point (113°) so it was recrystallised several times (twice from benzene/petroleum ether mixtures and once from ethanol) to give 38g. (m.p. 119-120.5°). Fieser & Cason obtained 64.5g.(directly from the steam distillation, m.p. 118.1-120.5°).

Lettre & Stratmann[49] reported a higher yield (75%) for the oxidation, but they used small quantities, solutions ten times as dilute, and potassium dichromate.

Diazomethane reaction: Acenaphthenone (16.8g.) was dissolved in methanol (800ml.) and a little sodium carbonate was added (0.2g.). N-Methyl,N-nitroso-urethan (13.2g.) in methanol (50ml.) was added slowly to the cooled solution (10°), with stirring, over one hour. The mixture was allowed to stand overnight. The solution was then evaporated and the solution distilled under reduced pressure (11.9g/157-160°, 2g/170-200° at 1mm). The large fraction was shown to be acenaphthenone and more of it was recrystallised from the small sample. The residue from these recrystallisations was analysed by v.p.c., as has been mentioned on page 14.

Perinaphthane(successful attempt):

Copper chromite catalyst:- When the commercially available material did not give satisfactory results for the perinaphthenone hydrogenations, a fresh sample was prepared. The method used was essentially that given in the literature [50]. A solution of ammonium dichromate (25.2g. dissolved in 120ml. distilled water) was converted to ammonium chromate by the addition of ammonia (30ml. of 28%). ← colour change orange → yellow. This solution was poured, in a fine stream, into a solution of barium nitrate (5.2g dissolved in 160ml. hot water) in which copper nitrate (43.6g.) had been dissolved. The solution was stirred during the addition and for a few minutes afterwards. The red-brown precipitate of copper barium ammonium chromate was filtered off and dried at 100°. The pulverised dry solid was placed in a large porcelain crucible and covered with a glass. An exothermic reaction was then initiated by the application of heat at the side of the crucible. Gases were vigorously evolved and the reaction was completed by further heating. The activity of the resulting powder was increased by washing it with dilute acetic acid (3 x 240ml., 10%) before washing it with distilled water (4 x 240ml.) and drying it at 110°. The yield (26g.) was comparable with the literature's.

Perinaphthenone:- The writer recommends that the ethyl formate used for this preparation should first be refluxed over sodium carbonate and fractionally distilled (b.p. 53-53.5°) to remove the hydrolysis products that will react with sodium. 1-Acetylnaphthalene (170g., 1 mole) was dissolved with ethyl formate (120g., an excess) in anhydrous ether (200ml) and the solution was slowly added to sodium wire (30g., an excess) under

ether (1200ml.). Stirring was continued throughout the addition and the one hour of refluxing that followed it. The solid that had been precipitating during the reaction was filtered from the cooled ether solution and dried. The ether-free salt weighed 233g. which exceeds the literature yield (2 x 114g.)[43] and the theoretical yield (220g.) and hence contained other sodium compounds.

Because of the quantities of reagents needed, the next step was done in sections. A portion (100g.) of the finely ground sodium salt was suspended in carbon tetrachloride (2400ml.) contained in a five-litre beacker. A few floating black specks were removed and shown to be sodium. Diluted sulphuric acid (70ml. water in 600ml. 98% sulphuric acid) was added over 30 minutes with very vigorous stirring. The stirring was continued for another 30 minutes before the mixture was poured into water (12l.) contained in a series of five-litre beakers and well mixed with the water by further vigorous stirring. The aqueous layers were decanted off and the organic layers were washed with more water and then with sodium carbonate solution, before they were combined and dried over calcium chloride. The remaining quantity of sodium salt was similarly treated and the product solutions were combined. Evaporation of most of the carbon tetrachloride by distillation and recrystallisation of the precipitated perinaphthenone from ethanol yielded 87.3g. of the yellow crystals (m.p. 155-6°). The combined ethanolic and carbon tetrachloride residues were concentrated and distilled under reduced pressure to yield a further 28g. (m.p. 154-5°, b.p. 180-185° at $\frac{1}{2}$mm). It was noticed that when the vacuum pump could not reach 0.5mm, and therefore the boiling point was much higher than 185°, the perinaphthenone tended to sublime and to contaminate the vacuum line. The combined yield was 115.3g

(64%). The literature claims an 80% yield[43] (m.p. 149°) but assumes that the acetylnaphthalene contains 40% of the 2-isomer. It was shown (v.p.c) that the acetylnaphthalene used for the above preparation contained 20% of 2-isomer, so the yield was effectively 80%.

perinaphthane:- Fieser & Hershberg[9] obtained satisfactory results by dissolving perinaphthenone (20g.) in peroxide free dioxan (25ml.) and adding copper chromite catalyst '37KAF' (50mg.). This mixture was placed in a glass liner, the lot placed in the bomb, and the hydrogenation was conducted at an initial hydrogen pressure of 1800psi and at 250-260° for ten hours.

The autoclave available was of the 'rocking-bomb' type with a variable angle of inclination of the bomb and a range of rocking speeds. The glass liner was an elongated flask fitted with a porous stopper. When loaded, the free volume of the bomb was approximately 700ml. The amount of solvent used is determined by this free volume since too small a quantity will mean complete vaporisation of the solvent at the temperature of hydrogenation. To prevent needless splashing of the contents of the glass liner, half of the dioxan used was poured outside the glass liner, but, like several other factors concerning this hydrogenation, it was not practical to test the value of this practice.

From the first few attempts some perinaphthane (m.p. 63°, m.p. of picrate 149-149.5°) and perinaphthanone were isolated from the product tar. The perinaphthanone (m.p. 81-81.5°, cf. 82-3°)[33] was shown (v.p.c.) to be contaminated with perinaphthane, but its identity was confirmed by the preparation of its oxime (m.p. 123-124°, cf. 127-8°). These early attempts showed that

too much material was escaping from the glass liner during the reaction so the quantities were reduced to half of the literature ones, except for the volume of dioxan used. The dioxan used for all the runs was purified by refluxing it with sodium until the sodium remained bright.

The following illustrates a satisfactory run. Perinaphthenone (10g.) was dissolved in dioxan (15ml.) contained in the glass liner, along with the catalyst (90mg.). More dioxan (15ml.) was placed in the bomb. The initial pressure was 1700psi and it took approximately an hour for the bomb to reach 250-255°. During this time, and the following seven hours, the contents of the bomb were agitated by moderate rocking. After this time the rocking was stopped and the bomb was allowed to cool. Pentane (50ml.) was added to the liner's contents (a liquid with a greenish fluorescence) and the mixture was poured into water (50ml.) contained in a separating funnel. The organic layer was separated, washed with more water and then dried over anhydrous magnesium sulphate. The pentane solution was evaporated and the residue was distilled under reduced pressure to give perinaphthane (7.5g. or 80%, m.p. 56°, b.p. 120° at 0.5mm). The runs of this type gave variable yields (6.5g. - 8.5g.).

In one run, the above conditions were used except, 0.2g. of catalyst per 10g. of ketone was reacted for ten hours. The product solution lacked the fluorescence mentioned above and yielded tetrahydroperinaphthane (6.2g., or 65%, b.p. 107-108° at 0.5mm) plus some higher boiling material (mainly perinaphthane). The main product gave a satisfactory analysis (C 91.10% H 9.00%, for $C_{13}H_{16}$ C 90.70% H 9.32%). A higher yield could probably be obtained if sought for (Treibs & Heyner obtained a 43.5%

yield from their two-stage hydrogenation of perinaphthenone).

The amassed stock of perinaphthane was fractioned through a spinning band column (length 18")under reduced pressure to give material of reasonable purity (m.p. 63°, the major impurity had been the tetrahydro derivative). Repeated recrystallisations from methanol gave purer material (m.p. 65°) as did the use of a 'preparative' gas chromotograph, but it was less wasteful to recrystallise its picrate and then recover it (m.p. 64.5°) from the purified complex (m.p. 151°). The trace impurity, tetrahydro-perinaphthane, is not known, or expected, to form a picrate. The literature[9] states that pure perinaphthane melts at 65.1-61.4° and its picrate at 150-151°.

Pleiadane:

Tetralone:- The commercial product was initially used for the Reformatsky reaction, but when stocks dwindled more was prepared by the method of Thompson [51]. In this very economic preparation tetralin is oxidised by air and the resulting peroxide is decomposed to the ketone by treating it with sodium hydroxide. It has since been discovered[52] that tetralol contaminates the tetralone produced this way . This probably explains the initial reluctance to react, but subsequent ebullition, observed in the later runs of the Reformatsky reaction.

γ-Bromo methylcrotonate: The preparation of Bailey & Bello[53] was used. It was necessary to prepare some of the N-bromo-succinimide and for this the method described by Vogel[54]was used. The carbon tetrachloride used had been purified by shaking it, in turn,

with: a solution of potassium hydroxide, water and ethanol (twice), water, concentrated sulphuric acid until the washings were no longer green, bicarbonate solution and finally water. The purified solvent was dried over anhydrous magnesium sulphate and distilled from phosphorus pentoxide. Methyl crotonate (150g., 1.5 moles) was added to a mixture of N-bromo-succinimide (163g., 0.915 moles) in refluxing carbon tetrachloride (1050ml.). Freshly recrystallised benzoyl peroxide (0.75g.) was used as a catalyst. When the precipitation of succinimide seemed complete (after 2 hours), the mixture was allowed to cool, the solid was filtered off and the liquid was washed with dilute sodium hydroxide and water. The carbon tetrachloride solution was then dried over anhydrous magnesium sulphate and evaporated down. The residue was distilled under reduced pressure to give γ-bromo-methylcrotonate (110g. or 67% based on N-bromosuccinimide, b.p. 90-92° at 17mm). Other runs gave 73-84% (lit. yield 83%, b.p. 84-86° at 12mm).

Reformatsky reaction:- The zinc used was AnalaR grade that had been washed successively with dilute hydrochloric acid, distilled water and methanol, and then dried in a hot air oven. It was used the same day it was prepared. γ-Bromo-methylcrotonate (66.5g.), zinc (50g.) and a crystal of iodine were added to a solution of tetralone (75g.) in a mixture of benzene and ether (250ml. of each anhydrous solvent). The stirred solution was brought to reflux and over three hours, more ester (30g.) and more zinc (75g.) were added. The mixture was left to reflux for another twelve hours before being left at room temperature for twenty hours. Stirring was continued throughout the thirty-five hour period. The precipitated zinc complex was then dissolved by the addition of a little acetic acid and methanol[55] before the mixture was poured into a dilute

solution of acetic acid. The separated organic layer was washed with water and ammonium hydroxide before being dried over anhydrous magnesium sulphate, and concentrated. Dehydration of the hydroxy-ester was effected by distilling the concentrate under reduced pressure and collecting the fraction (56.5g., 48% cf. 52%[46]) boiling over the range 140-158° at 0.5mm, a range which is inconsistent with that given by Gilmore & Horton (177-183° at 0.15mm). The oily product was characterised by hydrolysing some of it to the acid. The ester (2g.) was refluxed for one hour with potassium hydroxide in aqueous ethanol (2g. in 20ml. of each solvent). Acidifying the resulting solution, extracting with benzene, evaporating and recrystallising the material obtained from carbon tetrachloride gave white crystals, m.p. 197° (Gilmore & Horton quoted 194-5°).

Hydrogenation:- The literature gave the following details. The hydrogenation confirmed the presence of two double bonds, was run over platinum, took 45 minutes and, after saponification of the ester group, gave a 98% yield. Further experimental detail is not given. In a typical run, the writer dissolved the ester (124g.) in acetic acid (100ml.) and added it slowly to a magnetically stirred suspension of platinum black (obtained <u>in situ</u> from 1.9g. PtO_2) in more acetic acid (250ml.). The reaction system had been previously flushed with nitrogen and then hydrogen to avoid contamination of the system with atmospheric oxygen. The hydrogen was fed into the reaction flask at slightly above atmospheric pressure and over two days approximately 28 litres of hydrogen was used. The hydrogenation of a similar quantity of the unsaturated ester took five days when the solvent was ethanol. A gas wash-bottle inserted betweeen the hydrogen source and the reaction allowed hydrogen uptake to be followed and when the

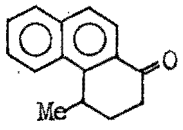
reaction was virtually complete, the mixture was filtered quickly through a sintered-glass funnel. The catalyst collected was washed with acetic acid and water and then left moist. The acetic acid solution was diluted with water and extracted several times with benzene. The combined benzene extracts were washed with water and sodium bicarbonate solution, dried over anhydrous magnesium sulphate and evaporated down. Concentrated potassium hydroxide solution (120g. in 240ml. of a 1:1 mixture of aqueous ethanol) was added to the concentrate and hydrolysis was effected by refluxing this mixture for five hours. The cooled solution was poured into water and extracted with benzene. This benzene extract was evaporated to 7.6g. of an oil that was discarded. The aqueous alkaline solution was neutralized, and extracted with benzene. Concentrating the dried benzene solution and distilling the residue under reduced pressure gave the butyric acid (93g., 78.5% b.p. 190-195° at 2-3mm, cf. 212° at 12mm[56]) as an oil. Crystals were obtained from pentane (m.p. 37-37.5° cf. 36-38.5[46]) and a sample was analysed (C 76.77%, H 8.52%, O(by difference) 14.71% : values for $C_{14}H_{18}O_2$, C 77.05%, H 8.26%, O 14.67%).

Polyphosphoric acid cyclisation:- The literature[57] records that polyphosphoric acid containing 83% of phosphorus pentoxide is the best for cyclisation reactions. It was found that phosphoric acid does not dissolve phosphorus pentoxide very readily so the mixtures were heated for two hours and the material that had not dissolved was ignored. If the temperature was allowed to rise much above 130° the solutions went dark.

The butyric acid (10g.) was added to a solution of phosphorus pentoxide (250g.) in orthophosphoric acid (238g. of 88-93%) to give a light brown

solution which was heated on a boiling waterbath for two hours. Frequent swirlings of the reaction flask gave adequate mixing of the reactants. The cooled solution was poured into an ice and water mixture (1l.) which was stirred to dissipate the syrupy polyphosphoric acid. This mixture was extracted with benzene (4 x 50ml.). The benzene solution was washed with dilute alkali and then with water, combined with the benzene solutions from seven similar runs, dried over anhydrous magnesium sulphate and evaporated down. Distillation of the concentrate under reduced pressure gave tetrahydropleiadanone (50.6g., 69%, b.p. 144-148° at 1-2mm) in a comparitively low yield (lit. 85-95%, b.p. 128-33 at 0.3mm) but some unreacted butyric acid (20.7g.) was recovered from the alkaline washings. Redistillation of this acid followed by its cyclisation yielded more ketone (13.4g.) and increased the yield to 87%. The ketone was recrystallised from hexane and characterised by its melting point (61.5-62° cf. 61.5-63°[46], 60-3°[48]) and by its 2,4-dinitrophenylhydrazone (m.p. 163-4° cf. 162-165°[46],187-88°[48]).

Clemmensen reduction: The method used was a modification of that used for the reduction of (XIV) (94% yield)[58].



(XIV)

Tetrahydropleiadanone (57g.) was dissolved in toluene (125ml.) and acetic acid (750ml.), and added to a mixture of hydrochloric acid (300ml. of 33%) and amalgamated zinc (50g.)(which had just been prepared by mixing zinc (50g.) and mercuric chloride (5g.) with dilute hydrochloric acid, stirring for a few minutes and finally, decanting off the liquid.). The ketone mixture

was refluxed for 24 hours, poured into water (3l.) and the product was extracted with ether (5 x 50ml.). The ether solution was washed with sodium carbonate solution and water, dried over anhydrous magnesium sulphate and evaporated down. The concentrate was distilled under reduced pressure to yield tetrahydropleiadane (46g., 87%, b.p. 118-120° at 1-2mm cf. lit. 93%, b.p. 156-8° at 23mm[46]). A repeat preparation gave a yield of 89%.

Preparation of palladium catalyst:- Purified carbon was warmed with dilute nitric acid until fumes of nitric oxide were observed. The mixture was then filtered and the carbon was washed thoroughly with water and ethanol before being dried in a hot air oven (110°). This activated carbon (1.5g.) was added, with formalin (3ml.), to a hot solution of palladium chloride dihydrate (1g.) in dilute hydrochloric acid (0.6ml. 33% acid in 6ml. water). This mixture was cooled and 50% potassium hydroxide solution (6ml.) was added slowly and the reaction was completed by warming it for ten minutes on a water-bath. The catalyst was filtered off and washed first with dilute acetic acid and then more extensively with water and finally with ethanol, before being dried.[59] This catalyst should contain approximately 30% of palladium.

Pleiadane:- The method of dehydrogenation used was based on a method that has been used for a variety of substituted tetralins [59]. Tetrahydropleiadane (13g.) was heated under nitrogen with 30% palladium carbon (0.3g.) in a modified Claisen flask. The side-arm of the flask was fitted with a cold-finger condenser. Gas emission, as indicated by a gas-wash bottle connected to the flask, began at 260°and had virtually

AFTER 4-5 hrs

finished at 300°, these temperatures being those of the silicone oil bath surrounding the flask. The cooled product was dissolved in pentane, filtered free of catalyst and evaporated down. The products of two runs were combined and fractionally distilled using a spinning band column (18") and reduced pressure to yield pleiadane (21g. 82.5%, b.p. 142-152 at 2mm, m.p. 54.5-55.5 cf. 79.5% yield [46]). Another run gave a yield of 88.5%. Two recrystallisations from ethanol gave material of higher melting point (57-58°, cf 55.5-7° [46], 57-58° [48]). A sample was analysed (C 92.07%, H 7.93% , calculated for $C_{14}H_{14}$, C 92.30%, H 7.69%).

General Notes on the Brominations

The semi-micro apparatus shown in fig.1 was used for all the brominations except for cases that will be mentioned.

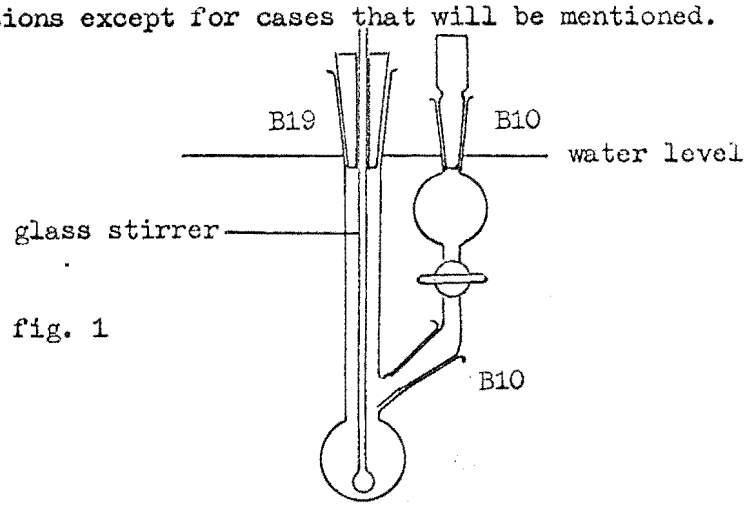


fig. 1

In general, the hydrocarbon (0.005moles) was carefully washed into the flask with the chosen solvent (10ml.) and then the apparatus was placed in a thermostat bath kept at 20° ± 0.2°. The bath contained a dilute solution of black ink to ensure that the quantity of light reaching the immersed reaction vessel was negligible. The brominating solution (0.0025moles of brominating entity in approximately 5ml.) was added to the dropping funnel from a 20ml., 'A' grade burette and made up to 5ml. with the appropiate solvent. The apparatus, loaded with the reactants was allowed ten minutes in the bath, to approach thermal equilibrium, before the brominating solution was added to the stirred hydrocarbon solution over the course of thirty minutes. After a further thirty minutes of being stirred the flask contents were washed into a separating funnel and shaken with benzene (20ml.) and sodium sulphite solution (10ml. of 10%). The benzene layer was separated, washed with water, dried over anhydrous sodium carbonate and evaporated by means of a rotary evaporator. The concentrate was taken up in a little ether and

set aside to await analysis. It was found that even pure samples of bromoacenaphthene darkened under these conditions but that the addition of a small quantity of acetaldehyde, which is very easily oxidised, stabilised the reaction mixtures against darkening, for several weeks.

Each set of conditions chosen was repeated three times and then the products were analysed to give a total of nine v.p.c. traces. The repetitions used the same standard solution of brominating agent and were performed the same day.

Purities of Solvents Etc.

The hydrocarbons were tested by v.p.c. and perinaphthane, the most impure (m.p. 63°), was estimated to be 98% pure. Perinaphthane of higher purity (m.p. 64.5°) was used for the comparitive runs.

Bromine: 'AnalaR' material was dried and distilled at room temperature by passing a stream of nitrogen through bromine and then sulphuric acid, over phosphorus pentoxide and through a bed of calcium chloride, and finally through a flask cooled by an acetone-dry ice mixture. The calcium chloride was intended to serve as a spray trap. The bromine was stored in a glass-stoppered bottle kept in a desiccator, over silica-gel.

Iodine Monobromide: This was from a freshly opened vial supplied by the British Drug Houses.

N-Bromosuccinimide: This was twice recrystallised, and carefully dried, commercial material.

Acetic Acid: This was refluxed for ten hours over an excess of chromium trioxide and then fractionated in the presence of excess acetic anhydride (AnalaR grade) up a four foot column packed with glass helices. The first fraction was rejected and the material used froze at the accepted temperature (16.5-16.6°).

Carbon Tetrachloride: The purification was the same as that given on page 31. The fraction distilling at 76.5° was used.

Dimethyl Formamide: This was supplied by 'Eastman Organic Chemicals'. It was redistilled before it was used (b.p. 149.5-150° cf. $153°^{60}$).

Dioxan: This was 'Fluka' grade that had been shaken with ferrous sulphate solution, dried over potassium hydroxide pellets, refluxed with sodium until the sodium remained bright, and then distilled (b.p. 101°).

Pyridine: 'AnalaR' material was refluxed over sodium hydroxide pellets for an hour and then distilled (b.p. 114-115°). It was stored over sodium hydroxide pellets.

Nitromethane: This was dried over calcium chloride and fractionated up a one foot column packed with glass helices (b.p. 100.6-100.8 cf. 100.5° & 101.5°[60]).

Perchloric Acid: This was taken from a fresh bottle of 'Riedel de Haën AG' material (70%).

Tabulated Results

1. Solvent: carbon tetrachloride

Additive: 3 drops of saturated iodine/CCl_4 solution per run.

Brominating solution: Bromine (4.17g.) in CCl_4 solution (50ml.)

4.80ml. used per run.

Run No.	Wt. of Acenaphthene	100o/(o+p) 1st	2cnd	3rd trace
1	0.770g.	7.8	7.9	7.6
2	0.770g.	7.9	8.1	7.8
3	0.770g.	7.9	7.8	8.1

Average = 7.88

2. Solvent: carbon tetrachloride

Additive: none

Brominating solution: Bromine (4.36g.) in CCl_4 solution (50ml.)

4.59ml. used per run.

Run No.	Wt. of Acenaphthene	100o/(o+p) 1st	2cnd	3rd trace
1	0.770g.	7.9	8.1	8.3
2	0.770g.	7.8	8.2	8.1
3	0.770g.	8.1	8.2	8.3

Average = 8.11

3. Solvent: carbon tetrachloride

Additive: none

Brominating solution: A saturated solution of iodine monobromide in carbon tetrachloride, estimated by titration against sodium thiosulphate to contain 0.0465 moles of IBr per 5ml, the volume used per run. The reaction: $ArH + 2IBr = ArBr + HBr + I_2$, illustrates how only half the bromine in iodine bromide can be utilised for bromination.

Run No.	Wt. of Acenaphthene	100o/(o+p) 1st	2cnd	3rd trace
1	0.770g.	10.6	10.8	10.7
2	0.770g.	10.8	10.8	10.5
3	0.770g.	10.3	10.5	10.7

Average = 10.63

4. Solvent: glacial acetic acid

Additive: none

Brominating solution: Bromine (4.86g.) in acetic acid solution (50ml.) 4.12ml. used per run.

Run No.	Wt.of Acenaphthene	100o/(o+p) 1st	2cnd	3rd trace
1	0.770g.	3.4	3.3	3.4
2	0.770g.	3.5	3.4	3.4
3	0.770g.	3.4	3.5	3.5

Average = 3.42

5. Solvent: glacial acetic acid

Additive: 3 drops of saturated iodine/HOAc solution per run.

Brominating solution: As for case 4. above.

Run No.	Wt. of Acenaphthene	100o/(o+p) 1st	2cnd	3rd trace
1	0.770g.	3.3	3.5	3.5
2	0.770g.	3.3	3.5	3.3
3	0.770g.	3.3	3.5	3.5

Average = 3.40

6. Solvent: glacial acetic acid

Additive: 0.304g. of water per 50ml. of brominating solution.

Brominating solution: Bromine (4.40g) in acetic acid solution (50ml.)

4.54ml. used per run.

Run No.	Wt. of Acenaphthene	100o/(o+p) 1st	2cnd	3rd trace
1	0.770g.	3.7	3.7	3.8
2	0.770g.	3.7	3.6	3.6
3	0.770g.	3.7	3.8	3.8

Average = 3.71

Note: Case 6. was actually investigated after bromine in acetic acid had been tried on the group of four hydrocarbons (see page 53) and had given a slightly different value from case 4.'s. At this stage a second sample of bromine was being used and it now seems more likely that this caused the difference and not the use of wet acetic acid.

7. Solvent: nitromethane

additive; 3 drops of saturated iodine/CH_3NO_2 solution per run.

brominating solution: Bromine (4.17g.) in nitromethane solution(50ml.)

4.80ml. used per run.

Run No.	Wt. of Acenaphthene	100o/(o+p) 1st	2cnd	3rd trace
1	0.770g.	5.8	6.1	5.8
2	0.770g.	5.8	6.1	6.3
3	0.771g.	6.0	5.7	5.8

Average = 5.93

8. Solvent: pyridine

additive: none

brominating solution: Bromine (4.56g.) was added to pyridine cooled by a dry ice-acetone bath. The solution was allowed to reach room temperature and was then topped up to 50ml.

Run No.	Wt. of Acenaphthene	100o/(o+p) 1st	2cnd	3rd trace
1	0.770g	4.9	4.7	4.9
2	0.770g.	4.8	4.9	5.1
3	0.770g.	4.9	4.8	4.8

Average = 4.87

9. Solvent: dimethylformamide

Brominating solution: Bromine (4.65g.) in dimethylformamide soln. (50ml.)

4.30ml. used per run. (except for run 3)

Run No.	Wt. of Acenaphthene	100o/(o+p) 1st	2cnd	3rd trace
1	0.771g	6.5	6.5	6.1
2	0.771g	6.3	6.3	6.4
3	0.770g	6.4	6.3	6.6

Average = 6.33

Note: An accident occurred with the original third run and the replacement third run was obtained two months after the others with a different solution of bromine.

10. Solvent: dimethylformamide

Brominating solution: N-Bromosuccinimide (0.0025 moles) dissolved in dimethylformamide (5ml.)

Run No.	Wt. of Acnph.	Wt. of N-BrS.	100o/(o+p) 1st	2cnd	3rd trace
1	0.770g.	0.445g.	4.8	5.0	5.3
2	0.770g.	0.445g.	5.3	5.2	4.8
3	0.770g.	0.445g.	5.0	5.1	4.9

Average = 5.04

Note: Dimethylformamide solutions of N-bromosuccinimide slowly go yellow.

11. Solvent: carbon tetrachloride

brominating solution: Silver acetate (4g.) was suspended in carbon tetrachloride (160ml.) at 0° and bromine (1ml.) in more solvent (20ml.) was added over 30 minutes. The mixture was shaken for 90 minutes before the precipitate of silver bromide was allowed to settle and samples of the pale yellow solution were drawn off and titrated against 0.1N sodium thiosulphate. It was calculated that 25ml. samples contained 0.0025 moles of bromine acetate.

method: Acenaphthene (0.005 moles) was dissolved in carbon tetrachloride (25ml.) contained in a 100ml. flask immersed in the waterbath (20°). Bromine acetate solution (25ml.) was added over 30 minutes to the stirred solution, the addition period being followed by a further 30 minutes stirring. The reaction was worked up in the same fashion as for the previous cases. The first set were done in subdued daylight and the second set were done at night under dark-room conditions.

Run No.	Wt. of Acenaphthene	100o/(o+p) 1st	2cnd	3rd	
1	0.770g.	11.5	11.4	11.6	
2	0.770g.	8.5	8.8	8.5	
3	0.770g.	8.9	8.5	9.1	
1'	0.770g.	9.7	9.6	10.0	
2'	0.770g.	9.6	9.7	(8.7)	9.5
3'	0.770g.	7.7	7.6	7.9	

Note: For the second set, 25ml. samples of the bromine acetate solution were estimated to contain 0.0023 moles of brominating entity.

12. A parallel of case 11. was attempted with silver trimethyl acetate substituted for silver acetate, but the resulting carbon tetrachloride solution gave very low titres with sodium thiosulphate. An attempt was also made to prepare a solution of bromine acetate in acetic acid, reacting bromine (4g.) with silver acetate (5g.) in 50ml of solution, but the solution was too unstable to be of use.

13. Solvent: pyridine

Brominating solution: Bromine dipyridine nitrate (3.730g.) in pyridine solution (25ml.). 5ml. used per run.

Bromine dipyridine nitrate was prepared by adding a bromine solution (4g. in 10ml. CCl_4) at 0°, to a mixture of silver nitrate in pyridine (5g. in 5ml. pyridine) also at 0°. The mixture was shaken until the colour remained constant before more carbon tetrachloride (5ml.) was added and the mixture was filtered from the precipitated silver bromide. The slow addition of cold petroleum ether (100ml.) gave two layers. When crystallisation did not occur, even on cooling the mix in a dry ice/acetone bath, a small quantity of each layer was shaken with ether, and the crystals obtained were used to seed the bulk quantity. The filtered solid was light yellow, melting at 76-77° (lit.[115] white crystals, m.p. 78-78.5°). The solid slowly decomposes if left to stand.

Run No.	Wt. of Acenaphthene	100o/(o+p) 1st	2cnd	3rd trace
1	0.770g.	5.9	5.9	5.8
2	0.770g.	5.8	5.9	5.8
3	0.770g.	6.2	6.1	5.7
		Average =	5.90	

14. Solvent: Acetic acid & pyridine

Reagent: This was presumed to be bromine dipyridine acetate.

Bromine (4.49g.) was dissolved in glacial acetic acid (45ml.) and shaken with silver acetate (5g.) dissolved in pyridine (5ml.). The precipitated silver bromide was filtered off and samples (5ml.) of the light orange solution were used for brominations. It was later calculated that the quantity of pyridine added was insufficient to give a bromine dipyridine complex if a silver dipyridine complex precipitated. For the second set of runs, a solution prepared as follows was used. Silver nitrate (5.39g.) was placed in a volumetric flask (50ml.) with pyridine (10ml.) and acetic acid (20ml.). This solution was chilled before bromine (4.28g.) was added. The volumetric flask was topped up with acetic acid. The mixture was then shaken well and the precipitate of silver bromide was allowed to settle. Samples (5ml.) of the light orange solution were used for brominations. When a portion of this solution was shaken with water and carbon tetrachloride, a colorless organic layer and a light orange, aqueous layer were obtained. The addition of dilute nitric acid decolorised the aqueous layer and subsequent addition of sodium bromide liberated bromine. Whereas when a solution of bromine in pyridine was shaken with water and carbon tetrachloride, a tinted organic layer was obtained which turned red upon the addition of dilute nitric acid.

Run No.	Wt. of Acenaphthene	100o/(o+p) 1st	2cnd	3rd trace
1	0.770g.	3.5	3.5	3.7
2	0.770g.	3.6	3.7	3.7
3	0.770g.	3.7	3.3	3.7

1'	0.770g.	3.4	3.2	3.4
2'	0.770g.	3.6	3.7	3.5
3'	0.770g.	3.4	3.6	3.4

Average (18 traces) = 3.56

15. Solvent: 75% acetic acid (v/v).

Brominating solution: Hypobromous acid

Method: Bromine (8g.) was shaken with distilled water (400ml.) and then with a suspension of silver sulphate (9g.) in water (100ml.) until the solution was virtually colorless. The resulting hypobromous acid was distilled under reduced pressure (40-50° at approximately 10cm) in apparatus protected against light and with the receiver immersed in ice. The distillate was pale yellow. Before it was used, the solution was shaken with carbon tetrachloride, allowed to settle and samples of the aqueous layer were titrated against standard sodium thiosulphate. This method gave an approximately 0.1M solution of hypobromous acid.

Acenaphthene (0.005 moles) was partially dissolved in a mixture of acetic acid (75ml.) and dilute perchloric acid (2ml. 70% perchloric acid, 23ml. water). The solution was approximately 0.23M with respect to perchloric acid. Over a period of 30 minutes a solution of hypobromous acid (25ml of 0.084M) in a mixture of acetic acid (75ml.) and perchloric acid (2ml.) was added under dark-room conditions, with stirring. The reaction flask, but not the dropping funnel, was immersed in a water-bath held at 20°(for this case, and for the two cases following, the room temperature was very close to 20°). The reaction was stirred for another 30 minutes and left to stand overnight. At the end of the reaction virtually all the

acenaphthene had dissolved. It was found that simple dilution of the reaction mixture with water, extraction with benzene, washing of the benzene extract with aqueous sodium sulphite and drying it over sodium carbonate, sometimes gave dark residues when the benzene solution was evaporated. This was avoided if acetaldehyde was added prior to the evaporation.

Run No.	Wt. of Acenaphthene	100o/(o+p) 1st	2cnd	3rd trace
1	0.770g.	21.3	22.2	21.3
2	0.770g.	22.9	22.2	23.4
3	0.770g.	25.0	24.8	25.6

16. This was as for case 15. but the solutions were approximately 0.02M with respect to sodium acetate and contained no perchloric acid.

Run No.	Wt. of Acenaphthene	100o/(o+p) 1st	2cnd	3rd trace
1	0.770g.	22.4	21.8	21.9
2	0.770g.	21.9	21.7	22.1
3	0.770g.	23.7	22.9	24.0

Dibromination was detected in both cases 14. & 15. which means that the 100o/(o+p) values obtained are, at best, approximate.

17. Solvent: 75% dioxan (v/v)

Method: Apart from the change of solvent, case 17. was the same as case 14. The hypobromous acid used was 0.10M. An error of judgement gave the first run twice as much perchloric acid as was used for the other two.

Run No.	Wt. of Acenaphthene	100o/(o+p) 1st	2cnd	3rd trace
1	0.770g.	32.3	31.9	32.7
2	0.770g.	32.6	32.3	32.8
3	0.770g.	32.2	32.1	32.5
		Average =	32.4	

With this variation, the acenaphthene dissolved completely and no dibromination was observed.

Comparative Brominations of the Four Hydrocarbons:

Cases 2, 4, 10 & 17 were selected as being interesting to try on the four hydrocarbons. As a check on reproducibility of the results, and as a check on a second sample of bromine that had to be used, acenaphthene was re-brominated.

The conditions used for these reactions were the same as those used before, including the amount of hydrocarbon (0.005moles). The reaction solutions from perinaphthane and pleiadan seemed more prone to darkening than did the solutions derived from acenaphthene and 1,8-dimethylnaphthalene.

Bromination with molecular bromine in carbon tetrachloride:

Wt. of hydrocarbon		100o/(o+p)			
0.770g.	Acenaphthene	8.0	8.2	7.9	
0.770g.	"	8.2	8.0	7.8	Average = 8.01
0.780g.	1,8-dimethylnphth.	4.8	4.8	4.7	
0.780g.	"	4.7	4.7	4.4	
0.780g.	"	4.6	4.4	4.5	Average = 4.62
0.840g.	Perinaphthane	6.2	6.1	6.1	
0.840g.	"	6.6	6.3	6.6	
0.840g.	"	6.6	6.7	6.8	Average = 6.44
0.910g.	Pleiadane	5.4	5.4	5.2	
0.910g.	"	5.3	5.5	5.4	
0.910g.	"	5.3	5.3	5.2	Average = 5.34

Bromination with molecular bromine in glacial acetic acid:

Wt. of hydrocarbon		100o/(o+p)			
0.770g.	Acenaphthene	3.5	3.7	3.5	
0.770g.	"	3.6	3.5	3.6	Average = 3.58
0.780g.	1,8-dimethylnphth.	4.6	4.3	4.5	
0.780g.	"	4.5	4.4	4.3	
0.780g.	"	4.4	4.7	4.3	Average = 4.44
0.840g.	Perinaphthane	3.9	4.0	4.2	
0.840g.	"	4.1	3.7	3.9	
0.840g.	"	4.1	4.2	3.8	Average = 4.01
0.910g.	Pleiadane	5.2	5.5	5.1	
0.910g.	"	5.5	5.3	5.2	
0.910g.	"	5.3	5.3	5.6	Average = 5.33

Bromination with N-Bromosuccinimide in dimethylformamide:

Wts. of hydrocarbon,		N-BrS.		100o/(o+p)	
0.770g.	Acenaphthene	0.445g.	5.4	5.3	
0.770g.	"	0.445g.	5.3	5.3	
0.770g.	"	0.445g.	5.9	5.6	Av. = 5.46
0.780g.	1,8-DiMeNphth.	0.445g.	6.0	6.7	6.3
0.780g.	"	0.445g.	5.7	6.0	6.4
0.780g.	"	0.445g.	6.4	6.6	6.5 Av. = 6.30
0.840g.	Perinaphthane	0.445g.	3.9	3.8	3.5
0.840g.	"	0.445g.	3.4	(4.3)	3.5
0.840g.	"	0.445g.	3.0	3.6	3.6 Av. = 3.61
0.910g.	Pleiadane	0.445g.	5.3	5.5	5.3
0.910g.	"	0.445g.	5.3	5.7	5.5
0.910g.	"	0.445g.	5.6	5.6	5.4 Av. = 5.45

Bromination with hypobromous acid in the presence of perchloric acid in 75% dioxan.

	Wt. of hydrocarbon		100o/(o+p)	
a	0.770g. Acenaphthene	30.6	31.3	31.0
b	0.770g. "	32.1	32.2	31.8
c	0.780g. 1,8DiMeNphth.	29.8	29.5	29.3
d	0.780g. "	30.8	30.6	30.3
e	0.840g. Perinaphthane	36.2	36.3	36.8
f	0.840g. "	40.4	40.1	40.7
g	0.910g. Pleiadane	36.8	35.9	36.7
h	0.910g. "	40.2	39.7	39.9

Notes: The eight reactions were run the same night using the same solution of hypobromous acid. They were done in pairs in the order: f & h, b & d, e & g, a & c. This order was used to minimise false deductions in the event of the hypobromous acid solution decomposing. In these traces, the component peaks had characteristic shapes as well as characteristic retention times so, for example, there was no possible confusion between the pairs e & f and g & h. No peaks corresponding to disubstitution were observed.

Competitive Studies

It was observed from studying the retention times of the bromo-hydrocarbons that if pairs of suitably selected hydrocarbons were brominated, it was possible to analyse the mixtures. The retention times indicated that mixtures of perinaphthane and each of the other three hydrocarbons in turn

would give the least overlap of peaks. This idea was tested by analysing pairs of the product mixtures obtained for the hypobromous acid brominations above.

Two cases were selected for competitive studies, hypobromous acid in 75% dioxan and bromine acetic acid. The hydrocarbons were weighed out accurately (0.0025 moles of each) into small flasks. After these small flasks had had their contents washed into the reaction flasks, they were dried in an oven and then (after being allowed to reach equilibrium with the room) reweighed to check the amounts of the hydrocarbons that were actually used.

HOBr in 75% dioxan:

The six reactions were done the same night, using the same solution of hypobromous acid, in pairs, in the order: a & c, e & b, d & f.

Wts. of	Hydrocarbons	100o/(o+p)			Peak-area ratios		
a 0.390g.	1,8-diMeNph.	34.2	34.5		0.444	0.439	
0.420g.	Perinaph.	30.5	30.8				
b 0.390g.	1,8-diMeNph.	35.6	35.6	35.8	0.444	0.444	0.423
0.419g.	Perinaph.	29.2	28.8	28.3			
c 0.386g.	Acenaph.	23.8	24.1	23.7	3.12	3.10	3.12
0.418g.	Perinaph.	44.4	44.4	44.7			
d 0.384g.	Acenaph.	24.4	24.9	24.0	2.89	2.95	2.82
0.420g.	Perinaph.	44.5	44.9	44.4			
e 0.455g.	Pleiadane	41.8	42.1	41.5	0.695	0.696	0.699
0.420g.	Perinaph	33.5	33.6	33.5			
f 0.445g.	Pleiadane	42.0	43.3	42.1	0.687	0.714	0.690
0.420g.	Perinaph.	34.9	34.5	34.0			

The area ratios tabulated were obtained by dividing the sum of the areas of the bromoperinaphthane peaks in a trace into the corresponding quantity for the other bromo-hydrocarbons. The results are arranged so that, for example, the peaks that gave the 100o/(o+p) values of 34.2 & 30.5 (set a) gave the area ratio of 0.444.

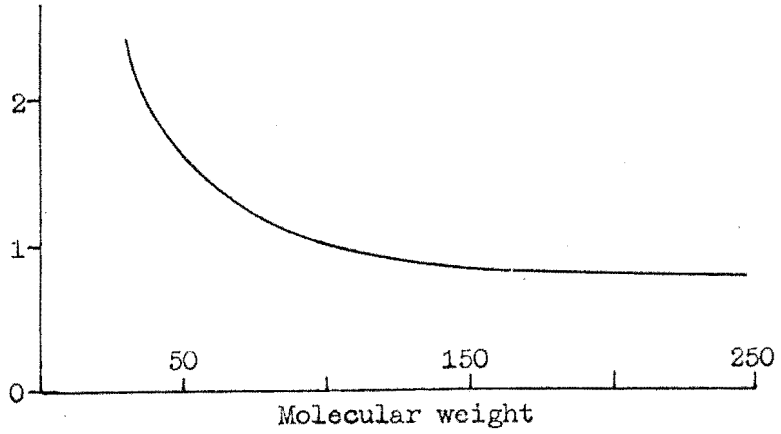
Molecular bromine in acetic acid:

Wts of	Hydrocarbons	100o/(o+p)			Peak-area ratios
a 0.390g.	1,8-diMeNph.	-	-	-	0.275 0.284 0.282
b 0.420g.	Perinaph.	3.4	3.6	3.3	
c 0.390g.	1,8-diMeNph.	-	-	-	0.284 0.278 0.273
d 0.420g.	Perinaph.	3.8	3.7	3.4	
e 0.385g.	Acenaph.	3.7	3.7	3.3	9.12 9.13 9.46
f 0.420g.	Perinaph.	-	-	-	
g 0.385g.	Acenaph.	3.3	3.5	3.4	8.68 9.50 9.28
h 0.420g.	Perinaph.	-	-	-	
i 0.455g.	Pleiadane	-	-	-	0.581 0.577 0.595
j 0.420g	Perinaph.	-	-	3.5	
k 0.455g.	Pleiadane	-	-	5.4	0.567 0.608 0.586
l 0.420g.	Perinaph.	3.5	3.6	3.8	

Trailing effects prevented all the 100o/(o+p) values being determined. Thus, with sets ef & gh the base-line did not straighten out between the very large p-bromoacenaphthene peak and the very small o-bromoperinaphthane peak, even without the increased sensitivity normally used for the measurement of the ortho peaks. Because of this the peak-area ratios are taken as the ratios of the para peak areas and the small ortho peak areas are neglected.

Determination of Isomer Distributions

The Pye Argon Chromatograph:- When using this, a small liquid sample of about one micro-litre is placed at the top of a suitably packed glass column (length 4ft., bore 4mm) and conveyed down the column by a stream of argon. Resolution of the components occurs because of their differing volatilities and polarities. The degree of resolution and the retention times can be altered by increasing the gas pressure, increasing the temperature of the column or by changing the column packing. When the resolved components leave the column they enter a detector chamber containing a source of ionizing radiation (strontium 90). In such a chamber argon atoms can be ionized or excited to a higher energy state. The excited atoms are unusually long-lived and have an excitation potential which is higher than the ionization potentials of most organic molecules. Therefore when organic molecules enter the chamber they are ionized by collisions with excited argon atoms, and since a potential is applied across the chamber, an increase in the number of ions will mean an increase in the ionization current. Such changes are amplified and fed out to the recorder. Because of the design of the machine, the detector response varies linearly with the amount of organic material in the chamber and the areas of the peaks drawn by the recorder are directly proportional to the amounts of the components in the mixture. But this does not mean that the response is identical for different substances and it is usual practice to calibrate the machine using known mixtures of the pure components. The manufacturers supply the following plot of relative mass sensitivity against molecular weight, and this plot indicates that above a molecular weight of



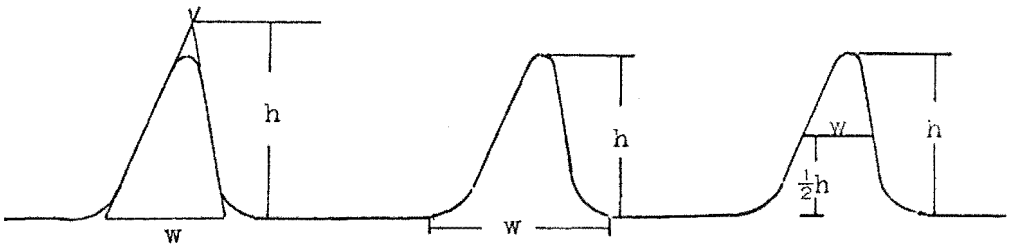
Vertical axis: Mass sensitivity relative to 1-pentanol

Fig. 2.

150, the response is directly proportional to the mass of a component and is independent of the molecular species[61]. (See also ref.[62].)

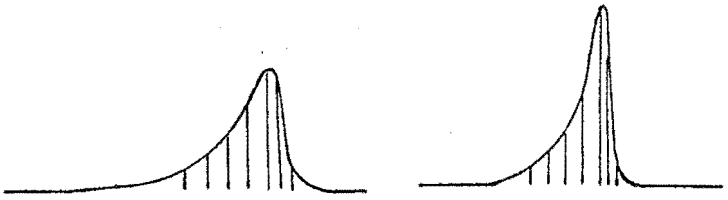
Peak-Area Measurements:- The recorder used was fitted with an integrator but its use was best limited to well-resolved peaks with well-defined base-lines. The peaks studied were not entirely resolved and the first peak of a pair was generally measured at ten times the detector sensitivity as used for the second. The amount of geometrical construction required to get useful results from the integrated trace meant it was simpler to derive the area ratios directly from the unintegrated peaks. Three simple ways of estimating peak areas are: counting squares when the traces are drawn on closely ruled graph paper, cutting out peaks and weighing them (testing the density of the paper at intervals), approximating the peaks to triangles. Because of the number of peaks involved triangulation was the only practical method.

Three variations of this method are illustrated below:



Area = $\frac{1}{2}wh$ Area = $\frac{1}{2}wh$ Area = wh

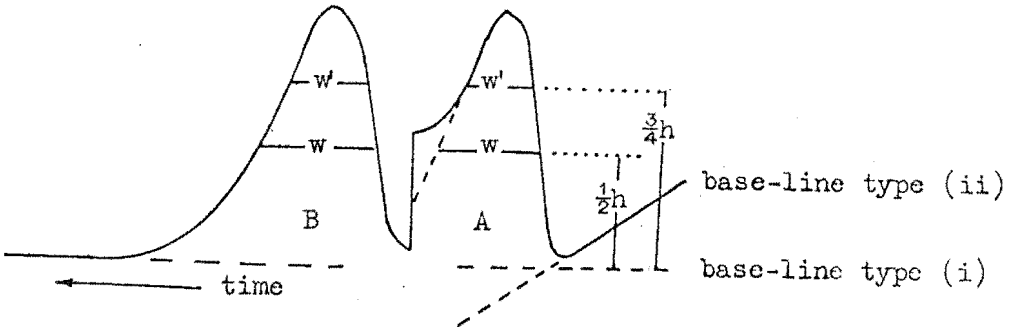
Each requires the contruction of a baseline. The first requires additional construction which is likely to introduce error. The second cannot be used if the peak trails, a difficulty that is overcome by the third variation since the width at half the height is a sharply defined quantity. This method of area estimation disregards the peak shape so comparisons of peak areas so obtained are accurate only if the peaks are of similar shape. This can be illustrated by considering two peaks A and B.



If peak A is divided into n (where n is very large) sections perpendicular to its baseline, the area of the peak is very close to $\sum_{i=0}^{i=n} w_i.h_i$ (where h_i = height, and w_i = width of the ith. section). If peak B can be divided into n sections (with k_i = height, and v_i = width of the ith. section) such that $v_i = aw_i$ and $k_i = bh_i$, it follows that the areas of peaks A and B differ by a factor of a.b . It also follows that the product of the peak height and the width at half this height for peak A will differ from the equivalent quantity for peak B by the same factor a.b, and that this applies regardless

of the common peak shape. The peak shape is largely determined by the stationary phase. The non-polar APL gives more symmetrical peaks than the more polar PEGA, probably because of an adsoption effect.

Further details of the area measurements are best explained with the aid of a diagram.



In this example, drawn with exaggerated defects, peak A is represented as being obtained at ten times the detector sensitivity as used for peak B. The base-line for peak B is obtained by a simple back extrapolation, but that for peak A is less well-defined. The extra sensitivity magnifies base-line irregularities, such as a permanent downward drift and the trailing of preceding peaks. The question arises as to whether type (i), which assumes that the base-line levels out, or type (ii), which assumes a continued drift, should be used. Type (ii) is more likely but possibly the behaviour is intermediate between the two forms. If the resolution is poor, it may be necessary to use the width at two-thirds or at three-quarters of the peak height.

Choice of Stationary Phase:- The boiling points of the naphthalene derivatives involved are high and it was found necessary to have the chromatograph working in the region 180° to 225° (its maximum). The variety of stationary phases for this range is limited. The two most useful were Apiezon L (APL) and polyethylene-glycol-

adipate (PEGA). APL is non-polar and can be used up to 250° whilst PEGA is more polar and can be used up to 190°. On 10% columns at the maximum temperatures, with an argon pressure of 15psi, the retention times were approximately, 15-23 minutes for the bromoacenaphthenes, 23-30 minutes for the bromoperinaphthanes and 30-40 minutes for the bromopleiadanes. The retention times obtained on the PEGA columns were larger than those obtained on APL columns. The resolution of the bromodimethylnaphthalene isomers was very poor at the maximum temperatures. At lower temperatures the resolution on PEGA was promising but a small impurity peak obscured the beginning of the small ortho peak. This impurity peak gave no trouble on APL at lower temperatures but here the resolution of the isomers was still unworkable. A variety of stationary phases were tried e.g. PEG 20M, PDEAS, APJ, SE-30, but the best was found to be a mixture of 7½% PEGA - 2½% APL which gave sufficient resolution at 175° and with an argon pressure of 10psi .

The majority of the bromoacenaphthene cases were analysed on a 10% PEGA and these results refute claims made[63] that peaks with a scale deflection of more than 70% could not be used for quantitative area ratio studies since peaks covering 90% of the scale gave no irregularities. However, when 10% APL columns were used, marked discrepancies were noted. The following figures were obtained by using a 10% APL column and a bromoacenaphthene sample kept as a standard.

peak heights		100o/(o+p)	
o	p		
8.50"	5.90"	9.1	Full scale deflection was
5.44"	5.48"	7.2	eleven inches.
4.62"	5.14"	7.7	
2.88"	3.50"	6.6	

It was noted that with APL columns, but not with PEGA columns, there was a tendency for peaks to split. This phenomenon is generally attributed to over-load of the detector and therefore should be independent of the column. But non-polar columns can presumeably adsorb less material than polar columns, and if the amount of component exceeds, at any stage, the limit, peak irregularities are to be expected. To test this idea, a glass column of approximately twice the normal bore was packed with 10% APL. The same sample size was used, so this column was expected to give more consistent results:

peak heights		100o/(o+p)
o	p	
7.14"	8.36"	6.7
6.32"	7.66"	6.5
5.16"	6.26"	6.7
3.54"	4.36"	6.6
1.97"	2.50"	6.6

Average = 6.62

After this investigation, every new column used was tested with the standard to determine the reliable range.

Reproducibility of Results

The results show that sufficient reproducibility is obtained if the the reaction conditions are standardised. The following show the effects for varying the conditions for one case, molecular bromine in acetic acid.

Run No.	Temperature	100o/(o+p)		
1	18°	3.5	3.4	
2	18°	3.5	3.3	
3	20°	3.6	3.4	
4	22°	3.6	3.7	
5	22°	3.3	3.6	Average = 3.49

Each run used 0.005 moles of acenaphthene and 0.0025 moles of bromine (same sample of bromine as used for case 4.).

Varying the initial concentrations of the reagents gave more serious divergencies:

Wt. of Acenaphthene	Volume of Bromine solution	100o/(o+p)	
0.770g.	2.13ml.	2.9	3.1
0.770g.	2.13ml.	2.9	2.9
0.770g.	1.07ml.	2.7	2.5
0.770g.	1.07ml.	2.5	2.7

(0.770g of acenaphthene = 0.005 moles, the bromine solution contained 0.0025 moles per 4.27ml.)

Varying the initial concentration of acenaphthene was also tried.

Wt. of Acenaphthene	Volume of Bromine solution		100o/(o+p)
0.770g.	1.98ml.	3.0	3.2
0.770g.	1.98ml.	3.3	3.3
0.385g.	1.98ml.	3.1	3.1
0.385g.	1.98ml.	3.3	3.4

(Here the quantity of bromine solution contained 0.0025 moles of bromine.)
In the above tables, the volumes given for the bromine solutions were made up to 5ml. by the addition of acetic acid before the brominations took place.

Justification of Peak Identification:

When each of the hydrocarbons was brominated under conditions expected to produce some mono-nuclear bromination, the v.p.c. trace of the reaction mixture contained three peaks. The first peak was readily assigned to the hydrocarbon. This left a small peak followed very closely by a much larger peak. In each case, the compound corresponding to the big peak was isolated and shown by analysis to be a mono-bromohydrocarbon. Since the bromoacenaphthene and the bromodimethylnaphthalene could be identified as the para isomers by their melting points, it was plausible to assume that the remaining two bromohydrocarbons were also para isomers.

A small quantity of authentic o-bromoacenaphthene had been prepared and this settled the identity of the small peak in the brominated-acenaphthene traces. It is known that bromination of substituted benzenes with hypobromous acid (in the presence of strong acids) increases the percentage of the ortho

compound[93b]. This method of bromination greatly increased both the yield of o-bromoacenaphthene and the size of all the small peaks in the traces of the brominated hydrocarbons, which supports the view that the small peaks correspond to the o-bromohydrocarbons. Isomers should give approximately the same response to a Pye argon detector unit and exactly the same response to a gas-density unit, and therefore (if the two peaks are identified as the ortho and para isomers) the two detectors should give about the same value for 100o/(o+p). This is shown to be the case in the calibration section that follows.

Because small samples of m-bromoacenaphthene and m-bromodimethylnaphthalene were available [1,2], it was possible to show that m- & p-bromoacenaphthenes have almost identical retention times and that m-bromodimethylnaphthalene has a slightly shorter retention time than the para isomer. Although the amount of meta product from these brominations was almost certainly minute, it was better that it should add to the area of the large para peak than to the small ortho peak.

It was important to ensure that di-bromination did not occur since this would almost certainly affect the mono-bromo isomer ratios. Di-bromination was only detected when acenaphthene was brominated with hypobromous acid in 75% acetic acid, and then the di-bromoacenaphthene peaks were first detected because they upset the baseline in consecutive runs. The identity of the di-bromoacenaphthene peaks was established by reacting acenaphthene with excess bromine.

Under the reaction conditions (20°, darkness, often hydroxylic solvents used) side-chain bromination was not expected, especially since acenaphthene

has been nuclear-brominated by one worker[116] under conditions more suitable for side-chain bromination (i.e. use of N-bromosuccinimide in refluxing carbon tetrachloride) although other workers get the expected product[106]. Small amounts of side-chain bromination should not make much difference to the ratio of nuclear products, but with the hydrocarbon mixtures one might be preferentially removed or deactivated by such a process. The side-chain brominated products, except for bromomethyl,methylnaphthalene, would be expected to eliminate hydrogen bromide on a hot chromatographic column.

Side-chain brominations of the four hydrocarbons were attempted, using refluxing carbon tetrachloride, N-bromosuccinimide, benzoyl peroxide and U.V. radiation. Acenaphthylene was detected and identified (on a 10% APL column at 175°, no resolution occured at 225°) in the products from the acenaphthene reaction, but not in selected samples from the previous acenaphthene brominations. The results for the other cases were less definite. The pleiadane case produced a large new peak close to the plicadane peak. The perinaphthane case gave a small, badly trailing peak which diminished when the rapidly darkening product mixture was left to stand. The dimethylnaphthalene case produced a small new peak which was shown to be different from the small peak which hindered the measurement of the bromo peaks.

Calibration:

Samples of the para-bromo hydrocarbons were prepared by reacting each hydrocarbon (0.04 moles) dissolved in acetic acid (200ml.), with bromine (0.04 moles) diluted with acetic acid (50ml.). The bromine solution was added over six hours, with stirring, at room temperature. The flask was

wrapped in silver foil to hinder photo-bromination. The solution was left to stand overnight and then it was poured into water (500ml.) and extracted with benzene (3 x 25ml.). The benzene solution was dried over anhydrous sodium carbonate and evaporated down to give a good yield(v.p.c.) of the bromohydrocarbon.

The crude bromohydrocarbons were distilled under reduced pressure to give oily products that were crystallised and recrystallised from pentane-ethanol mixtures:

compound	melting point
p-bromoacenaphthene	53-53.5°
p-bromodimethylnaphthalene	31-31.5°
p-bromoperinaphthane	24-24.5°
p-bromopleiadane	26.5-27°

A small quantity of o-bromoacenaphthene was prepared from o-aminoacenaphthene by a diazotisation method. The o-aminoacenaphthene had been obtained, in an undergraduate laboratory, by nitrating a large quantity of acenaphthene, recrystallising out the small amount of ortho isomer formed and reducing it [64,65]. The sample of o-bromoacenaphthene obtained had a low melting point (65° cf. 78°[64]) yet v.p.c. indicated it was nearly pure and its analysis was satisfactory.

Analyses	% Br Obtained	% Br Calculated
o-bromoacenaphthene	33.97	34.33
p-bromoacenaphthene	34.52	34.33
p-bromodimethylnaphthalene	33.76	34.04
p-bromoperinaphthane	32.62	32.40
p-bromopleiadane	30.65	30.66

Calibration of 'Pye A':

For acenaphthene, o & p-bromoacenaphthenes:

1st mix: 0.0697g. acenaphthene, 0.0959g. o-bromoacenaphthene,
0.1543g. p-bromoacenaphthene. o:p = 0.713, HC:p = 0.518

Trace values:					Relative Responses	
o':p'	0.769	0.763	0.792	Av = 0.775	o':p'/o:p	= 1.09
HC':p'	0.793	0.734	0.775	Av = 0.767	HC':p'/HC:p	= 1.48

2cnd mix: 0.0520g. acenaphthene, 0.0610g. o-bromoacenaphthene,
0.0397g. p-bromoacenaphthene. o:p = 1.535, HC:p = 1.310

Trace values:					Relative Responses	
o':p'	1.705	1.650	1.680	Av = 1.679	o':p'/o:p	= 1.09
HC':p'	2.16	1.84	1.995	Av = 2.00	HC':p'/HC:p	= 1.53

For the p-bromohydrocarbons:

1st Mix:		Relative areas				Relative
Wt. of	bromohydrocarbon	1st	2cnd	3rd	Av.	Responses
0.1141g.	bromodiMeNph.	1.05	1.09	1.10	1.08	0.982
0.1037g.	bromoperinaph.	1.00	1.00	1.00	1.00	1.00
0.1336g.	bromopleiadane	1.23	1.22	1.26	1.24	0.96
2cnd Mix:						
0.0742g.	bromodiMeNph.	0.505	0.525	0.508	0.513	0.987
0.1428g.	bromoperinaph.	1.00	1.00	1.00	1.00	1.00
0.1336g.	bromopleiadane	1.15	1.145	1.141	1.145	0.955

3rd Mix:		Relative areas				Relative
Wt. of	bromohydrocarbon	1st	2cnd	3rd	Av.	Responses
0.1226g.	bromoacenaph.	1.13	1.065	1.15	1.13	1.045
0.1134g.	bromoperinaph.	1.00	1.00	1.00	1.00	1.00
4th Mix:						
0.0826g.	bromoacenaph.	0.731	0.756	0.762	0.750	1.07
0.1181g.	bromoperinaph.	1.00	1.00	1.00	1.00	1.00

The relative areas are the peak areas with the corresponding bromoperinaphthane peak areas taken as unity. The relative response is given by the expression:

$$\text{relative area} \times \left(\frac{\text{wt. of bromohydrocarbon}}{\text{wt. of bromoperinaph.}}\right)^{-1}$$

The retention times involved made bromoperinaphthane the most convenient standard.

A gas chromatograph fitted with a gas-density detector had been made in the department and the traces from this detector were superior to those from the 'Pye Argon' detector in that they did not require calibration. But the rest of the machine was inferior to the Pye Argon chromatograph. It gave much longer retention times, poorer resolution and unpredictable base-lines. Although it could not be used to determine the small ratios involved in this work, it was used to analyse selected samples, rich in ortho-bromo compounds, that had also been analysed on the Pye Argon chromatograph. The results are given overleaf:

(100$\underline{o}$/($\underline{o}$+$\underline{p}$) values are being considered)

for bromoacenaphthenes:

Av. of 'Pye Argon' traces = 31.0 Av. of 'Gas-density' traces = 29.2

$\therefore$ Relative Response = 1.06

for bromoperinaphthanes:

Av. of 'Pye Argon' traces = 36.31 Av. of 'Gas-density' traces = 34.5

$\therefore$ Relative Response = 1.01

for bromopleiadanes:

Av. of 'Pye Argon' traces = 41.6 Av. of 'Gas-density' traces = 41.3

$\therefore$ Relative Response = 1.01

The 'gas-density' chromatograph did not give sufficient resolution of the bromodimethylnaphthalenes for a similar comparison to be made.

After allowances have been made for experimental errors, it can be seen that the responses for the bromohydrocarbons are virtually identical.

It has therefore been confirmed that the 'Pye Argon' response, for the bromohydrocarbons, is directly proportional to the mass of the components and therefore the relative areas obtained for the competitive reactions must be corrected to give the relative molar amounts:

Results for hypobromous acid in 75% dioxan (p. 56):

Bromohydrocarbons	Averaged relative areas	Rel. molar amounts
bromodimethylnaphthalenes	0.439	0.462
bromoacenaphthenes	3.00	3.18
bromoperinaphthanes	1.00	1.00
bromopleiadanes	0.696	0.659

Results for molecular bromine in acetic acid (p. 57):

Bromohydrocarbons	Averaged relative areas	Rel. molar amounts
p-bromodimethylnaphthalene	0.279	0.293
p-bromoacenaphthene	9.19	9.74
p-bromoperinaphthane	1.00	1.00
p-bromopleiadane	0.586	0.555

Yield Studies:

When the 100o/(o+p) values were being measured for the various acenaphthene brominations, p/HC values were also taken (p/HC = area of p-bromoacenaphthene peak/area of hydrocarbon peak.

The brominations can be represented by the equation:

HC	+	Br_2	. =	BrC	+	HBr	
(2-a)		(1-a)		(a)		(a)	relative molar concns.

The yield would be given by 100a. The area ratio (p/HC) must be corrected to a mass ratio (x 1.50/1.00, see p. 69.) which can be corrected to a mole ratio (x 154/233). As it happens, these correction factors cancel, within the accuracy of the measurements so: $a = 2(p/HC).(1 + p/HC)^{-1}$

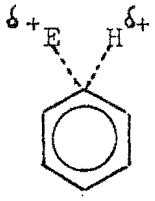
Case No.	Reaction type	p/HC	100a
1	CCl_4/Br_2	0.593	74.3
4	$HOAc/Br_2$	0.626	77.1
5	$HOAc/Br_2/I_2$	0.706	82.8
7	$Nitromethane/Br_2$	0.326	49.2
8	$Pyridine/Br_2$	0.087	16
9	$Dimethylformamide/Br_2$	0.107	19.3
10	Dimethylformamide/N-BrSucc.	0.107	19.3
13	$Pyridine/ BrPy_2NO_3$	0.187	31.5
14 i	$HOAc/ BrPy_2OAc$	0.346	51.4
ii	"	0.346	51.4
17	75% $Dioxan/HOBr/HClO_4$	0.733	84.5

The yields are of limited accuracy (probably ± 10%) because the narrow acenaphthene peaks could be measured only to ± 5%.

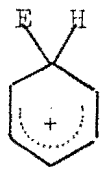
Discussion:

The reaction of an aromatic hydrocarbon in solution with a reagent such as bromine is surprisingly complex. The following pages present an outline of the complexities.

Types of Mechanism: Two mechanisms can be postulated for electrophilic substitution[66a]. One involves a transition state (XV) where the π-electrons of the aromatic ring are polarised by the change but take no part in the formation of the new bond. The other is the two stage mechanism which involves an intermediate (possibly like (XVI), in which two of the π electrons of the aromatic system are now used in bonding and the configuration at the centre of substitution is approximately tetrahedral). This intermediate, which need not be capable of isolation, can lose E^+ to give back the starting material, or lose a proton to give product.



(XV)

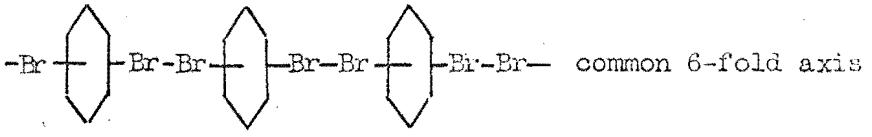


(XVI)

If tritium were substituted for hydrogen, an isotope effect would be expected with the first mechanism, but not necessarily with the second. Isotope effects are not generally observed with nitrations and brominations, although small effects have been detected with sulphonations. This suggests the second mechanism is more likely[66b].

π- & σ- Complexes: Two extremes have been considered for the intermediate (XVI) and these are patterned on the π- and σ-complexes.

In π-complexes the electrophile is loosely bound to the whole aromatic system without being associated with any particular carbon atom. Strictly this explanation only applies when the aromatic system is as symmetrical as benzene, and in less symmetrical types the electrophile is pictured as being as close as possible to the highest π-electron density. These complexes are known to occur between aromatics and: halogens, inter-halogens, hydrogen halides, silver ions, picric acid and related compounds[66c] The π-complexes that could be reaction intermediates are generally too unstable to be isolated, but their existance can be inferred from changes in absorption spectra and other physical properties. Their structures are of interest. Infra-red studies on benzene solutions of the halogens favour an axial model with the halogen atoms on the six-fold axis. X-Ray studies on the solid benzene-bromine complex divulged a similar structure, drawn below:[67]



However, the structure in the solid state need not persist at all in the liquid state and Mulliken[68] has suggested that in solution the bromine molecule is slightly inclined to the six-fold axis.

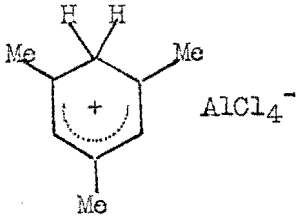
The existence of π-complexes may be incidental to the reaction path. Kinetic measurements would not indicate their degree of involvement unless their formation were rate-determining.

Complexes between hydrogen halides and aromatics are similar to the halogen/aromatic complexes unless aluminium halides are added[66d]. At low temperatures toluene does not react with aluminium chloride unless hydrogen

chloride (or another hydrogen halide) is added and then two series of complexes can be obtained: $(ArH)_nHCl.AlCl_3$ & $(ArH)_nHCl.Al_2Cl_6$. These compounds can be formed reversibly and analogous complexes can be isolated e.g.: $(\underline{m}\text{-xylene})_3HBr.Al_2Br_6$ (m.p. 52-54°)

The hydrogen halide/aromatic complexes are colourless non-conductors of electricity and if deuterium chloride is added to them no exchange of the ring hydrogens with deuterium is observed. Conversely, the complexes involving aluminium chloride are highly coloured, conducting and ring hydrogen exchange is observed if deuterium chloride is added.

This suggests the existence of a second complex type, the σ-complex, in which the π-electrons of the aromatic ring are more deeply interfered with than in the π-complexes. It has been suggested that σ- and π-complexes are extremes of a continuum. The structure suggested for the σ-complexes is of the same pattern as the one postulated for the reaction intermediate (XIV) e.g.:



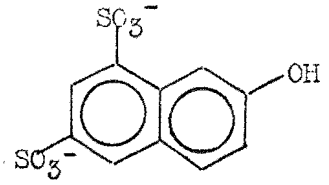
The Intermediate in Aromatic Halogenations: Having established that two types of complexes can exist it remains to show what part they play in the reaction mechanism. The usual approach has been to compare the rates of reaction for a group of substituted benzenes with the stabilities of π- and σ-complexes between the same group of benzene derivatives and reagents as close in nature as possible to the reagent used in the rate studies. The halogenation rates

of alkyl benzenes correlate very well[66e] with the relative equilibrium constants for complexing of the same alkyl benzenes with hydrogen fluoride/boron trifluoride, but less well with the stabilities of the hydrogen chloride complexes. This suggests a σ-complex is involved in halogenation but such correlations can be misleading. Iodine chloride/methyl benzene complexes, known to be π-complexes, have stabilities that correlate equally well with the rates of halogenation and with the stabilities of the hydrogen fluoride/boron trifluoride complexes. It is more profitable to consider the spread of the stabilities since the stabilities of the σ-complexes vary much more than those of the π-complexes with changes of the substituents e.g.:

	Relative Stabilities				
Complex	toluene	o-xylene	m-xylene	mesitylene	(benzene)
ArH.IBr (π)	1.2	1.8	1.8	3.3	1
ArH.HF.BF_3 (σ)	1	2×10^2	2×10^3	3×10^5	-

In going across this series the nuclear electron density is increased and therefore it is to be expected that the stabilities of both π- and σ-complexes will increase. It is not surprising then that mesitylene is more reactive towards electrophilic attack than the xylenes. However, m-xylene is invariably substituted faster than o-xylene, which suggests σ-complexes are more fundamental to substitution than are π-complexes. Furthermore, the stabilities of π-complexes increase in the order $Cl_2 < Br_2 < I_2$, the reverse of the order of reactivity. This is all evidence that σ-complexes dominate electrophilic halogenations, but π-complexes cannot be completely dismissed. When G-salt (XVII) is brominated by either molecular bromine or "Br+" the rate is, anomalously, much the same and is not affected by varying the bromide ion concentration (which generally affects brominations

with molecular bromine) or by varying the pH (which generally affects brominations with "Br^+"). When molecular bromine is used the uptake is rapid but the bromine can be recovered by iodometric titration, although the titre volumes slowly decrease if the solution is left to stand. Careful N.M.R. studies have shown that a structure analogous to a σ-complex is involved. G-salt reacts with iodine in a similar fashion except that all the iodine can be recovered, even after the solution has stood for a week. N.M.R. work infers that a π-complex is obtained; the spectrum being quite different from the bromine case. On these results it was postulated that the bulky iodine can only reach the π-complex stage but bromine can go further to the σ-complex and then reaction slowly occurs to give the substitution product. The formation of a π-complex followed by σ-complex formation and reaction could be the general pattern.



(XVII)

Selectivity in Aromatic Halogenation: Associated with the problem of the structure of the intermediate is the question of selectivity. The ratio of overall reactivity of toluene to benzene is about 600 in bromination, about 25 in nitration and less than 5 in alkylation, and furthermore, the amount of meta product increases in this order. This indicates that bromination is the most discriminating of these three reactions, both to aromatic substrate and to positions on the aromatic nucleus.[66f].

On the simplest basis it might be expected that the faster the reaction the less selective it would be. But several examples are known of slow reactions that are less selective than other similar, more rapid reactions. Thus the rate of chlorination of toluene in acetic acid is increased by the addition of water, but the positional selectivity is not appreciably altered, and the reaction is faster but more selective in acetonitrile than in acetic acid[69]. This lack of correlation between absolute rate and selectivity is attributed to the major importance of prior equilibria and solvation effects.

It might also be expected that substrate and positional selectivities would be more closely related than they are. The relative rates for the nitration of toluene vary with comparatively little variation in the isomer distribution of the products:[66g]

Reagent	relative rate	o%	m%	p%
HNO_3 in HOAc	28.8	56.9	2.8	40.3
HNO_3 in TMS	17	61.9	3.5	34.7
$NO_2^+BF_4^-$ in TMS	1.67	65.4	2.8	31.8
$NO_2^+ClO_4^-$ in TMS	1.60	66.2	3.4	30.4
$NO_2^+PF_6^-$ in TMS	1.40	67.6	1.4	31.0
$NO_2^+AsF_6^-$ in TMS	1.52	65.5	2.6	31.9
$NO_2^+AsF_6^-$ in nitromethane	0.97	66.6	2.1	31.3

TMS = tetramethylene sulphone

(all rates obtained from competitive nitrations of benzene/toluene mixtures)

If $NO_2^+AsF_6^-$ (in TMS) is the least selective reagent it should have the isomer distribution closest to 40%o 40%m 20%p. Four of the reagents involve nitronium ions and low selectivities are expected with positive ions.

The behaviour has been explained[70] in terms of the rate-determining step being the formation of a π- and not a σ-complex. The nitration rates do parallel the stabilities of π-complexes in their common lack of spread and discrimination. It was subsequently deduced that these nitrations do not involve free nitronium ions, but probably nitronium salts since it has been shown that $NO_2^+BF_4^-$ exists in tetramethylene sulphone as practically undissociated ion pairs (its conductivity is now attributed to ion triplets rather than to free ions[71]). The need for the nitronium ion to dis-engage itself from the ion pair, and from solvent molecules, makes it understandable why this step should be rate determining. Thus the anions have little effect upon the isomer distributions but influence the relative rates considerably.

The ferric chloride catalysed bromination of a series of methyl benzenes in nitromethane is also interesting since the relative rates have very little spread (average value, depending on the conditions of mixing the reagents, 2-4 with the value for mesitylene being exceptional, 10-15)[72] and this suggests a π-complex is involved in the rate determining step. The relative rate for toluene is 3.6 (isomer distribution 68.7%o 1.8%m 29.5%p) which contrasts with the relative rates for bromination with molecular bromine in acetic acid (600, isomer distribution 32.9%o 0.3%m 66.8%p)[73] and with "Br^+" (36, isomer distribution 70.3%o 2.3%m 27.4%p).[74]

In general, electrophilic substitutions involve σ-complex transition states, but in some cases it is possible that separate transition states may be involved, one corresponding to a rate determining π-complex formation, the other to a product-determining σ-complex formation[66h].

Solvent Effects: Not much work has been done on the effect of solvent on reaction rates and isomer distributions, but toluene has been chlorinated in a variety of different solvents:[75]

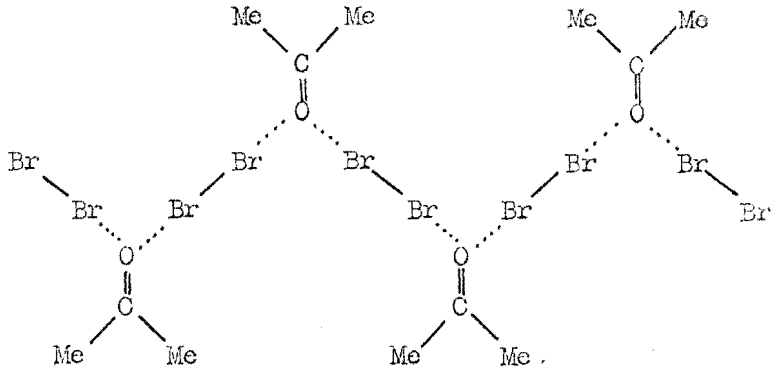
Solvent	Isomer %'s o	p	k_T/k_B	k_B(rescaled)
Acetic acid	60	40	340	1.0
HOAc, 15.3M H_2O	61	39	-	-
HOAc, 20.8M H_2O	63.3	36.7	322	3×10^3
CF_3CO_2H	67	33	464	4.6×10^3
H_2O, 5M HCl	69	31	-	-
t-Butanol	59	41	-	-
Nitromethane	34	66	2020	4.0
2-Nitropropane	47	53	-	-
Acetonitrile	38	62	1650	0.6
Ethylene dichloride	41	59	-	-

k_T/k_B = relative rate of toluene with respect to benzene.

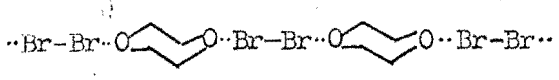
It has been suggested[75] that the reagent is probably a complex between molecular chlorine and the solvent.

It has been claimed for sometime (since 1909)[76] that brown solutions of iodine contain 1:1, iodine:solvent complexes and that violet iodine solutions do not. The suggestion that the colour difference is due to different 'cage' effects does not explain why the addition of a small quantity of ethanol (in which iodine gives a brown solution) to a violet solution of iodine gives a brown solution[77]. More recently (1952)[77] the complexes of iodine with aromatic compounds, ethers, alcohols, water and ketones have been studied by absorption spectroscopy. Although the deductions made

about the structures of these complexes have not been confirmed by the X-ray studies of Hassel[67], this does not alter the fact that the complexes were shown to exist and that because the spectral changes for bromine solutions were similar, that analogous bromine complexes also exist. If bromine complexes with acetic acid, and there is evidence that it does[78], this would explain why the mesitylene/bromine complex is four times as stable in carbon tetrachloride as it is in acetic acid[66c] and why the benzene/bromine complex can be detected in carbon tetrachloride, but not in acetic acid.[79] It would seem that the acetic acid/bromine complex is more stable than some aromatic hydrocarbon/bromine complexes. On a firmer basis is the complex (at low temperatures) between acetone and bromine which consists of chains of the type drawn below:



A well-established bromine/solvent complex is dioxan dibromide (a fairly stable orange solid, m.p. 60°[80]) which has been used for the bromination of a variety of compounds, including naphthalene. Its structure has been determined and it is drawn below:



Stable complexes between thio-ethers and bromine are also known, as well as the moderately stable complexes between compounds like pyridine, and halogens or interhalogens (in all of which, a linear arrangement of N-X-X has been observed[67]).

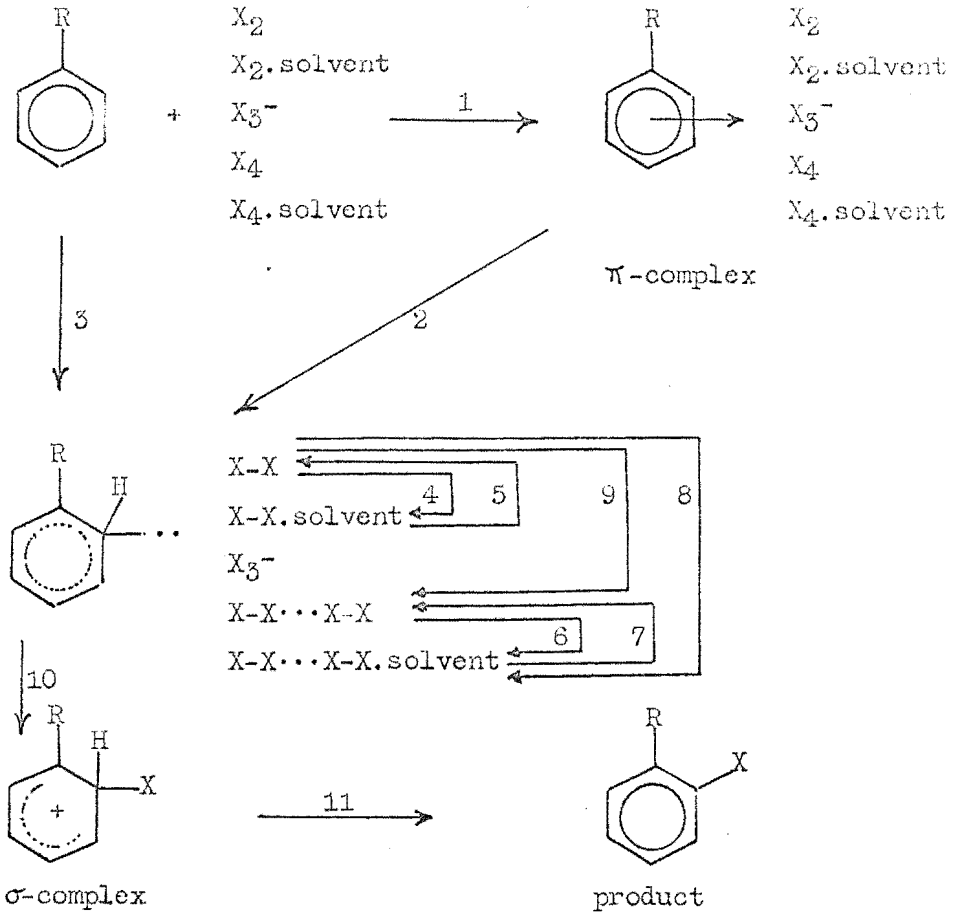
Mechanism(s) of Aromatic Halogenation: The following is an attempt to correlate the available data into a mechanism for halogenation.

On the simplest basis, a molecule of halogen would react with a molecule of hydrocarbon and the kinetics would be of second order. Second order kinetics are observed for chlorinations with molecular chlorine in acetic acid, nitrobenzene and chloroform, but brominations with molecular bromine seldom give such simple kinetics. This simple model would predict an isomer distribution that was independent of the solvent but it is found that isomer distributions, for both brominations and chlorinations, vary with the solvent.

It is reasonable to assume that chlorination and bromination will have similar mechanisms. The diagram on p. 84 covers several possibilities that may occur solely or simultaneously. The main difficulty is to devise a path with which isomer distributions will vary with solvent and still be consistent with third order (and higher) rate equations observed with brominations.

Alkyl substituents can affect substitution by activating the ring by induction or by hyperconjugation, or by taking up space. In the table on p. 81 only toluene is considered so the inductive and spacial effects

Possible Reaction Paths for Aromatic Halogenation:



Steps:

1. formation of various π-complex combinations

2. transformation of π-complex to an "incipient σ-complex"

3. direct formation of an "incipient σ-complex"

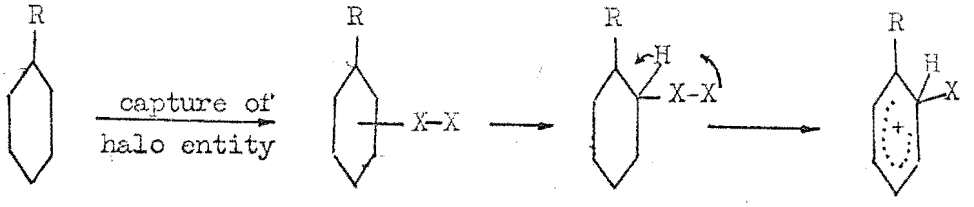
4.-9. various acquisitions and losses, to and from, the "incipient σ-complex"

10. formation of the σ-complex

11. proton loss and product formation

are constant. It has also been deduced, from chlorinations of toluene and t-butylbenzene in aqueous acetic acid solutions, that hyperconjugation does not have its origin in solvation phenomena.[81] This suggests that the isomer distribution variations are determined mainly by the reagent's size and polarity (or possibly its polarisability). The substitution involves the rupturing of the halogen-halogen bond and this can probably be assisted by the solvent, but it is not sufficient to regard the solvent just as an aid to this fission, for unless a halogen/solvent combination exists before the orientation is determined, there can be no variation in the isomer distribution.

The diagram considers the possibility of a π-complex being involved. This is not a necessary step and most of the combinations can be predicted to have little stability, especially when chlorine is considered since its π-complexes are known to have less stability than the bromine equivalents. It does, however, provide a neat path for the formation of the σ-complex. The halogen unit in the π-complex can be imagined as migrating to the substitution centre and rotating about it to eventually give (after the rupture of the X-X bond) the σ-complex.



π-complex σ-complex

A more likely approach considers direct attack by the reagent to give an "incipient σ-complex" which can be thought of as a completely de-centralised π-complex. To explain isomer effects in terms of this "incipient σ-complex" it may be necessary to assume it has a fairly long life. With

chlorination, attack by a Cl_2.solvent entity is consistent with the observed second order kinetics, but attack by a Br_2.solvent entity (which could give variable isomer distributions, depending on the solvent) would generally necessitate the removal of the solvent molecule before another bromine could assist the Br-Br rupture and give the observed kinetic order. Attack by Br_4 would give an invariant isomer distribution and attack by a Br_4.solvent entity seems unlikely.

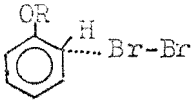
The structures of the postulated entities are not palpable. There appears to be no evidence that I_4 exists in solution and Br_4 would be more unlikely. There is evidence that Br_3^- is a brominating agent[82] and tetra methylamine nonabromide (Me_4NBr_9) has been isolated (m.p. 56.7°) and found to be a better brominating agent than the tribromide (Me_4NBr_3)[83]. Pyridine bromine hydrobromide is another mild brominating agent which presumeably contains the equivalent of Br_3^-.[84] The tribromide ion is linear and nuclear quadrupole moment studies indicate that it has the charge more concentrated over the end atoms than the central one[67]. Its equilibrium constant for its formation from bromine and bromide is 23.6 moles/litre at 25°. The equivalent chlorine entity is probably much more unstable since the equilibrium constant for the formation of Br_2Cl^-, from bromine and chloride, is only 1.47 moles/litre at 25°.[85]

It is difficult to see how a negative ion can be an electrophile, but in non-aqueous solutions it is most likely present in some largely undissociated form, such as HBr_3. It is relevant that whilst neither iodine nor dioxan have a dipole moment, the complex-containing entity does. This suggests that the iodine end of the complex is more negative than in un-

complexed iodine. On the assumption that bromine behaves similarly it is strange that dioxan dibromide is a better brominating agent than bromine viz: $Br\text{-}Br \leftarrow OC_4H_8O$ against Br-Br

Although such a charge distribution is not consistent with the structure in solid dioxan dibromide (see p. 82).

When aryl ethers are brominated with dioxan dibromide in benzene the rate is proportional to $[\text{dioxan dibromide}]^2[\text{R-OPh}]$ whilst bromination of anisole with bromine in carbon tetrachloride gives a rate proportional to $[Br]^2[\text{R-OPh}]$ [86, 79]. Carbon tetrachloride is unlikely to complex with bromine so the reagent at the Br-Br bond breaking step is probably Br_4 but if, with dioxan dibromide, the inital step is the formation of (XVIII) the dioxan unit has to be removed before another $Br_2OC_4H_8O$ (or a Br_2 molecule) can be substituted to give a Br_4 chain.



Br-Br.OC_4H_8O (XVIII)

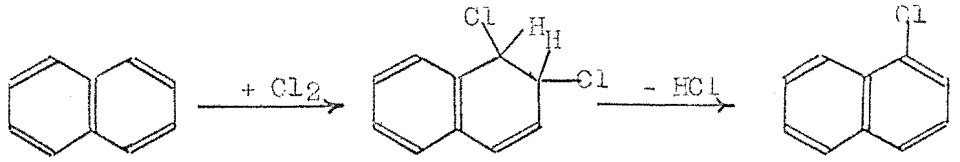
Naphthalene is brominated much faster in acetic acid than in carbon tetrachloride.[88] Since the kinetics for both are of high order, the writer suggests an $ArH.Br_4.HOAc$ linkage may be involved in the acetic acid bromination, which might give more rapid Br-Br bond fission than $ArH.Br_4$ (unsolvated in carbon tetrachloride).

Although it now seems unlikely that the variations in the isomer distributions are caused by changes in the dielectric constant of the solvent[75] it is possible that polar media increase the rate, which is consistent with an ionic mechanism. The third order kinetics observed when brominating toluene with molecular bromine in acetic acid, changes to second order in 50% aqueous acetic acid. This can be interpreted as a

preference for the reaction to go by an $ArH.Br_2OH_2$ path (accelerated by the increased polarity of the medium) rather than by an $ArH.Br_4$solvent one. This general solvent effect is probably the reason why the absolute rates of chlorination of benzene and toluene in aqueous acetic acid and trifluoroacetic acid are much higher than the rates of chlorination in glacial acetic acid (see p. 81). Further, the bromination of mesitylene in carbon tetrachloride is catalysed by moisture and hydrogen bromide, but not by hydrogen bromide alone.[89] Since the tribromide ion (from $Br_2 + Br^- = Br_3^-$) is not such an active brominating species as molecular bromine, this suggests catalysis by an increase in the polarity of the solvent.

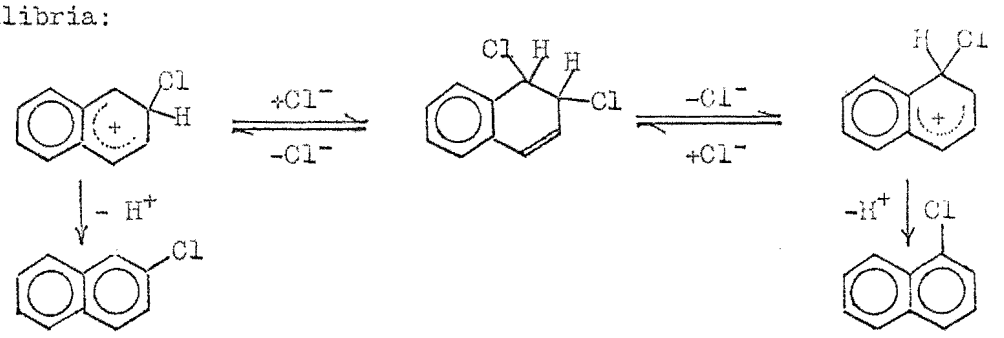
As the rates and composition of a solution change a significant variation in the isomer distribution is expected. This is not really the case for the chlorination of toluene in various aqueous solutions of acetic acid[81]. The writer suggests that this is probably because the predominating attacking entity is the same, molecular chlorine, even though the bond rupture may be assisted by the solvent. The lower percentage of o-chlorotoluene obtained in nitromethane (see p. 81) could be consistent with initial attack by the larger $Cl_2CH_3NO_2$ entity. The nitromethane unit should help the Cl-Cl bond rupture and accelerate the rate. The bromine/acetic acid complex would probably be more stable and a low ortho bromo percentage might be expected. The increased rate of bromination of toluene in nitromethane (x 1000 that in acetic acid[90]) suggests that a complex of the type $ArH.Br_2.CH_3NO_2$ is involved, but since the rate is proportional to $[ArH][Br_2]^{1.5}$ types $ArH.Br_4.CH_3NO_2$ and $ArH.Br_4$ might also be involved.

The Addition-Elimination Sequence: The above section considers the case when the reaction is a straightforward substitution, in some cases it is possible that halogenation proceeds by an addition followed by an elimination. When dry chlorine is mixed with naphthalene at ordinary temperatures an addition compound is formed[91] which is thought to be 1,2-dichloro,1,2-dihydronaphthalene (XIX), and when this is heated, 1-chloronaphthalene is obtained:



(XIX)

It is possible that some 2-chloronaphthalene is also formed. The product(s) may be formed via a σ-complex, but the distribution will depend upon the equilibria:



Considering the small amounts of ortho bromo isomers measured for this thesis it is feasible that addition reactions could give misleading results. Fortunately the addition is not so pronounced with bromine. With naphthalene in carbon tetrachloride it was found that addition was catalysed by light and peroxides, but in the absence of these substitution dominated (up to 85%). Further, substitution was favoured by more polar solvents and by higher concentrations of bromine. In 50% aqueous acetic acid it has been established that bromination of naphthalene gives 1% of the 2-isomer and

the only other product is the major one[92](1-bromonaphthalene).

Summary: It is suggested that the transition state in aromatic brominations usually involves a Br_4 entity which may be complexed with solvent species. This would explain the observed second order kinetic dependence on molecular bromine and also the variation of the isomer distributions with solvent. In solvents of high dielectric constant the observed lower order dependence on bromine can be correlated with a transition state involving a solvated Br_2 entity.

Chlorination appears to involve only Cl_2, although this may be complexed with the solvents. This would reconcile the observed first order kinetic dependence on molecular chlorine with the variations in the isomer distributions.

Whereas addition followed by elimination is a possible alternative to direct substitution, this is more likely for chlorination than for bromination, and is unlikely to be a complicating factor in the present work.

Interpretation of Present Work:

Bromination of Acenaphthene (5 solvents/Br_2): Two of the solvents, acetic acid and carbon tetrachloride were chosen because they are commonly used for brominations. Nitromethane was chosen because it has been shown[75] that its use gave low yields of o-chlorotoluene and it was thought that it would probably also give low percentages of o-bromo compounds. Dimethylformamide was chosen so that the effect of bromine could be compared with the effect of N-bromosuccinimide in this solvent. Pyridine was chosen partly because it has the reputation of being a catalyst for brominations[95a] and partly because bromine dipyridine compounds were to be tried as brominating agents, and bromine in excess pyridine is probably " bromine dipyridine bromide ".

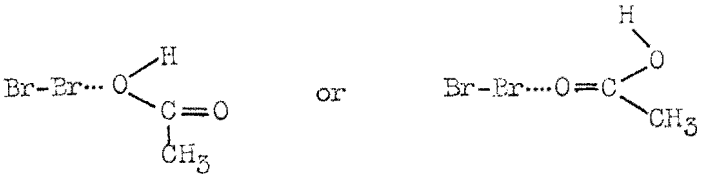
The results of the brominations in these solvents is summarised in the following table:

Solvent	%o-bromoacenaphthene	yield of bromo products
CCl_4	8.11	74.3 (high)
acetic acid	3.42	77.1 (high)
nitromethane	5.93	49.2 (medium)
dimethylformamide	6.33	19.3 (low)
pyridine	4.87	16.0 (low)

The yield figures are based on the amount of brominated product obtained after one hour of reaction (pp. 37 & 73) and therefore give a measure of the rate of reaction. Since they were not obtained under especially standardised conditions it may be better to group them into high, medium or low yields.

On pp. 64-65 the effect of varying the initial concentrations of bromine and acenaphthene are shown. There is a small trend towards lower o-bromoacenaphthene percentages as the concentrations of the reagents are decreased. To minimise the effect of these variations when different solvents were being considered, care was taken to ensure that the initial concentrations were as comparable as was feasible. For this reason it is considered that the variations in the isomer percentages tabulated on p. 91 are, although small, real.

If the isomer distribution variations result from changes in the size of the attacking entity, the species in the carbon tetrachloride solution was, no doubt, the simplest and the smallest, probably Br_2 or Br_4. Br_4 is probably linear and therefore of similar bulk along its axis to Br_2. The bulkiest reagent appears to have been the one in acetic acid viz:



The reagent in nitromethane could have been expected to be more compact, as the ortho % indicates, but the complex with dimethylformamide might have been expected to be bulkier, and therefore to have given the smallest percentage of o-bromoacenaphthene. A small percentage, as was found, would also have been expected with the pyridine solution. The reagent, most likely pyridine perbromide (which has been used for brominations [84]) would have significant bulk.

With this group of brominations the lower yields can be attributed to competition between acenaphthene and the solvent for the bromine; one to react with it, the other to complex with it.

Catalysis by Iodine: As could be predicted from previous considerations, the addition of iodine complicates the issue. Since iodine monobromide is largely undissociated in chloroform and carbon tetrachloride solutions[94], iodine added to bromine solutions is largely present as iodine bromide . Iodine chloride is normally an iodinating agent (chlorination can occur in such sterically hindered molecules as pentamethyl benzene)[95] so iodine bromide would also be expected to be an iodinating agent. It can be (antipyrine is largely iodinated by it)[96] but usually its brominating properties dominate. It has been suggested that iodo compounds are formed reversibly and the more stable bromo compounds dominate the products.[97] A more likely suggestion considers attack by a bromine entity and Br-Br bond fission being assisted by iodine or iodine bromide.

It is curious that the bromination of naphthalene in acetic acid is strongly catalysed by iodine but that the reaction is reported as being checked by the addition of iodine bromide[98]. The addition of hydrogen bromide and alkali metal bromides also check the reaction but hydrochloric acid and sodium acetate have no effect. It could be relevant that naphthalene and mesitylene are less readily brominated with iodine bromide itself than they are with molecular bromine[99].

If, as has been suggested, bromination in carbon tetrachloride involves an entity containing Br_4, the addition of iodine could involve $Br_2.I_2$ and with iodine bromide all the combinations: Br_2Br_2, Br_2I_2, BrI.Br_2 & BrI.BrI could be involved. If the aromatic hydrocarbon is particularly activated the differences between entities of the type Br_2X_2 might be negligible. Acenaphthene is highly activated[100] and no significant difference in the

isomer distributions was noticed in this work when a trace of iodine was added either to the carbon tetrachloride solution (p. 41) or to the acetic acid solution (p. 43). The percentage of o-bromoacenaphthene (10.65%) obtained with iodine bromide in carbon tetrachloride indicates the influence of a different entity from the one involved in bromination with molecular bromine in the same solvent (8.11% o). An iodine bromide molecule would be larger than a bromine molecule so the increased ortho percentage cannot be explained in terms of reagent size unless the attacking entity in the first case is IBr and in the second, Br_4.

Bromination with Bromine Acetate: When silver acetate is shaken with a solution of carbon tetrachloride and bromine the resulting solution can react with a double bond to give a 1,2-bromoacetate [101]. This suggests bromine acetate can exist in carbon tetrachloride solution. Since a standard method of bromo-decarboxylation consists of heating the silver salt of the acid with bromine (Hunsdiecker Reaction), bromine acetate would not be expected to be stable enough to be isolated. Probably the inductive effect of the three methyl groups accounts for the lower stability of bromine pivalate, which the writer could not obtain, even in solution (p. 47).

Two groups of workers [102,103] have used bromine trifluoroacetate to brominate toluene. In excess toluene a high yield of bromotoluene (90%) was obtained but none of the ortho or meta isomers could be detected from infra-red studies[103]. The yield in carbon tetrachloride[102] was lower (73%) but again only the para isomer appeared to be produced. This is inconsistent with the claim[102] that bromine trifluoroacetate is a source of

positive bromine since this is known to give 70.3% o-bromotoluene[74] and even molecular bromine in aqueous acetic acid gives 32.9% o-bromotoluene.[73] For this reason, a neutral entity is probably involved at the orientation determining stage.

Bromine acetate has been found to be less reactive than bromine trifluoroacetate and bromine trichloroacetate was not so convenient to use because the silver salt is light sensitive and silver chloride tends to formed[102].

The results for the bromination of acenaphthene with bromine acetate (p. 46) could reflect the instability of the reagent. The lower o-bromoacenaphthene percentage obtained with molecular bromine in the same solvent suggests that bromine acetate, although bulkier than bromine (Br_2 or Br_4) is less selective because it is a more powerful electrophile. There is the possibility that the following cycle might be involved:

$$Br\ (trace) + ArH = HBr + ArBr$$

$$BrO_2CCH_3 + HBr = HO_2CCH_3 + Br_2$$

This suggests that bromine acetate might be just a source of bromine (Br_2) but this does not agree with the above results nor with the recent (1962) claim that bromine acetate is at least 20,000 times more reactive than bromine in the bromination of biphenyl[104].

Bromination with N-Bromosuccinimide: Because brominations with N-bromosuccinimide in non-polar solvents, usually carbon tetrachloride, give mainly side-chain bromination products, it is considered that a free radical mechanism is involved in these solvents.

It is now thought that succinimidyl radicals are not involved in the reaction but that the process is as follows:[105]

$$Br\cdot + RH = HBr + R\cdot$$

$$Br\text{-Succ.} + HBr = H\text{-Succ.} + Br_2$$

$$Br_2 + R\cdot = RBr + Br\cdot$$

There is, however, strong evidence that this is not the only way in which N-bromosuccinimide can brominate. It has been shown that an ionic mechanism involving a non-atomic bromine entity better fits the nuclear substitutions of N-bromosuccinimide. With N-bromosuccinimide in carbon tetrachloride or benzene fluorene gives a high yield (84%) of 9-bromofluorene. When boron trifluoride is included in the benzene mixture, a good yield of 2-bromofluorene is obtained and this is also obtained in propylene carbonate without the addition of boron trifluoride etherate. That fluorene is not just being brominated by bromine (from Br-Succ. + HBr = H-Succ. + Br_2, Br_2 + ArH = ArBr + HBr) is shown by the rate of this reaction being faster (x 25) than the fluorene/bromine reaction run under the same conditions. Propylene carbonate was chosen as a solvent for this reaction because a more polar solvent than carbon tetrachloride was required. Water or alcohols could not be used since it is claimed that these would give hypobromous acid and alkyl hypobromites. Dimethylformamide was also used as a solvent and when acenaphthene was brominated in it the results were almost identical as when propylene carbonate was used[106].

In 1946 Schmid suggested a cationoid complex of the type $R_2\overset{+}{N}H.Br$ was involved when N-bromosuccinimide was used to substitute benzene and toluene in the presence of concentrated sulphuric acid.[107] Lambert et al (1965) also

used sulphuric acid and N-bromosuccinimide on toluene and obtained an isomer distribution very similar to the one obtained with "positive bromine". But they claimed that "it is patently fallacious to draw strong mechanistic conclusions from this correlation"[108] and they pointed out that N-chloromorpholine[109] apparently chlorinates via a protonated species. Winstein et al (1950)[110] mention, without further detail, that they have used N-bromosuccinimide for several years as a source of positive bromine in hydroxylic solvents (e.g. acetic acid), and this conflicts with the above claims that a cationoid complex is involved.

In this work, the percentage of ortho compound obtained when acenaphthene was brominated with N-bromosuccinimide in dimethylformamide is less than when bromine was used (5.04-5.46% against 6.33%), but the yields of total bromoacenaphthene were actually the same. Comparisons of these low percentages of ortho compound with the much higher percentages obtained with positive bromine entities (pp. 49-51) and with the above results of Lambert et al on toluene indicates that positive bromine is certainly not involved under the conditions used, either as the simple cation or as the cationoid complex. The low ortho percentage indicates a large, selective entity is involved and this is most likely to be molecular N-bromosuccinimide. However, the results from the present work must be treated with caution, since N-bromosuccinimide solutions in dimethylformamide deteriorate on standing and the effect of such deterioration is unknown. Dimethylformamide was used as the solvent because propylene carbonate was not available.

Bromination with Dipyridine Entities: Bromine nitrate has been prepared but its stability is very low.[111] Bromine dipyridine nitrate is much more stable and belongs to a series[112] of bromine dipyridine salts which include the acetate, the perchlorate, the fluoride, $Br(Py)_2SbF_6$ & $Br(Py)_2SO_3F$. Since the simple salts could not be used it was thought that brominating with the dipyridine equivalents might be interesting.

Bromine dipyridine nitrate was isolated and then reacted with acenaphthene in pyridine, but bromine dipyridine acetate was not isolated before it was reacted in acetic acid solution (see pp. 47-49). The bulk of the dipyridine bromo entity would prevent it form reacting directly with the acenaphthene nucleus and the low ortho percentages obtained are not consistent with attack by a free bromine cation . Because the ortho percentage obtained with the acetate compound in acetic acid is very similar to the result for bromine in acetic acid (3.56% cf. 3.42%, pp. 42, 49) it is possible that the following scheme applies:

$$BrPy_2OAc + Br^- = Br_2.2Py + OAc^-$$

$$Br_2 2Py + HOAc = Br_2.HOAc + 2Py$$

$$Br_2.HOAc + ArH = \text{products (including HBr)}$$

An equivalentpath leading to $Br_2.nPy$ (n = 1 or 2) in the pyridine solution is unlikely for the nitrate and would not explain the higher ortho percentage (5.9% against 4.87%) or the higher yield (31.5% against 16%) above those obtained when bromine in pyridine itself was used.

Bromination with "Positive Bromine" : It is now generally accepted that bromination by hypobromous acid in the presence of strong acid, in water, aqueous acetic acid or aqueous dioxan involves a positive entity[113,93b]. This entity is either the bromine cation (Br^+) or a solvated variant (probably $Br\overset{+}{O}H_2$) which would be more stable.

Recently (1964) Olah et al have shown that bromination of toluene in nitromethane with bromine in the presence of ferric chloride gives virtually the same isomer distribution as that obtained when either hypobromous acid or N-bromosuccinimide are used in the presence of a strong acid. These results are tabulated below:

Reagent	%o	%m	%p	
Br_2, $FeCl_3$ in nitromethane	71.1	1.6	27.3	obtained under different mixing conditions
	68.7	1.8	29.5	
HOBr, $HClO_4$ in 50% dioxan	70.3	2.3	27.4	
N-Bromosuccinimide in H_2SO_4	67	2	31	

They have also shown that the ferric chloride catalysed brominations of a series of methyl benzenes have rates that correlate better with the stability of π-complexes than with σ-complexes. Similar evidence has been used to deduce that π-complexes are involved in nitrations and then the partial rate factors of less than one (which infer deactivation with respect to a position on benzene) observed in all cases of meta nitration, were explained as a mis-application of the theory. It was suggested that partial rate factors are only meaningful when individual positions compete directly for the electrophile and that they lose their meaning when molecules

compete first and the individual positions later. Reversing this train of thought, partial rate factors of less than one at meta positions of activated molecules may indicate that the reaction goes by a π-complex. When biphenyl is brominated by hypobromous acid in 50% dioxan in the presence of perchloric acid, the partial rate factor for the meta position is 0.28.[114]

If a π-complex is involved with these high activity brominations it may not be the simpliest $ArHBr^+$ type since Olah et al noticed the o/p ratio increased when the reactants were diluted, suggesting some degree of solvation occurs.

De la Mare et al noticed a marked dependence, when biphenyl was brominated by hypobromous acid in acetic acid, of the isomer distribution upon the acidity of the medium and this is illustrated in the table below:[104]

Molarity of perchloric acid	0.0	0.008	0.11	0.16	0.20
% of p-bromobiphenyl	75	68	47	46	46
Molarity of sodium acetate	0.005	0.01			
% of p-bromobiphenyl	79	79			

(In 50% aqueous dioxan/$HClO_4$ the isomer distribution was 41.7%p 1.5%m 56.8% o.)

In this work, when acenaphthene was brominated by hypobromous acid in 75% acetic acid, no such dependence was observed which suggests that acenaphthene may have more of an affinity for the reagent than has biphenyl, and is therefore less dependent upon the acidity of the solution. The higher percentage of o-bromoacenaphthene formed in 75% dioxan, compared with that obtained in 75% acetic acid (32.4% compared with approximately 23%)

may be due to a solvation effect similar to that observed by Olah (vide supra).

The exceptionally high percentages of o-bromoacenaphthene obtained with hypobromous acid is additional evidence that a different mechanism may be operating with this reagent. Conventional attack by a solvated Br^+ entity, to give a σ-complex, would require it to have very high activity to overcome its size and to give the observed high ortho percentage. The initial formation of π-complex followed by the loss of the bulky solvent molecule and then subsequent formation of the isomer-distribution determining stage, might be more plausible.

Comparison of the four Hydrocarbons: The results for when molecular bromine and N-bromosuccinimide were used are tabulated below:

Hydrocarbon Solvent	o % 's Acenph.	DiMeNph.	Perinph.	Pleiadane
CCl_4 (Br_2)	8.01	4.62	6.44	5.34
HOAc (Br_2)	3.58	4.44	4.01	5.33
DiMe-formamide (N-BrS.)	5.46	6.30	3.61	5.45

Bromine in carbon tetrachloride is the simpliest reagent and therefore the corresponding results are probably the most easily interpreted. The order observed : % o acenaphthene > perinaphthane > pleiadane > 1,8-dimethyl naphthalene, has 1,8-dimethyl naphthalene displaced from the order predicted from consideration of possible steric effects (p. 9). Within each solvent system the attacking entity should be the same, independent of the particular substrate being studied. It is disturbing to find that the order of ortho percentages changes drastically with change in solvent. Whereas in carbon tetrachloride acenaphthene gives the highest ortho percentage, in acetic acid it gives the lowest and in dimethylformamide it is intermediate. Clearly there is no simple explanation, based solely on steric effects, which can explain these results.

The results for bromination with hypobromous acid (p. 56) are similarly obscure, although they suggest that the attacking entity is less selective towards the positions in perinaphthane and pleiadane than it is towards the positions in acenaphthene and 1,8-dimethylnaphthalene.

Competitive Studies: More definite information is given by the competitive studies. These do not give a full picture of the range of reactivities since, for example, near the end of the reaction involving acenaphthene and perinaphthane, the reagent is more likely to react with the then more available perinaphthane than the more reactive, but largely reacted acenaphthene. Since the same order of reactivity is given by the most selective and by the least selective of the reagents investigated during this series of brominations, the order is definite and in decreasing order of reactivity is: acenaphthene, perinaphthane, pleiadane, 1,8-dimethylnaphthalene. It is interesting to note that Berliner (1965)[100] mentioned that the partial rate factor for the *para* bromination (in aqueous acetic acid) of 1,8-dimethylnaphthalene is 257 times smaller than that for acenaphthene. The increased reactivity is ascribed to internal strain in the acenaphthene molecule and a comparison is made with analogous anomalous strain and reactivity in fluorene.

An interesting effect was noted with the brominations with hypobromous acid. The more reactive member of the pair of hydrocarbons gave a depressed value of $100o/(o+p)$, and the less reactive, an exhalted value (compared to the results obtained when the individual hydrocarbons were brominated separately). This effect was most marked with the acenaphthene: perinaphthane pair where the reactivities were most different. The writer suggests that the hypobromous acid contained some free bromine. Since the main reagent (a positive entity) is relatively unselective it would attack either hydrocarbon with little discrimination, but when it was used up the more discriminating bromine would attack mainly the more reactive hydrocarbon to give a low $100o/(o+p)$ value for this hydrocarbon which lower the overall size of this value.

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