FORMATION OF SUBSTITUTED PHENALENES FROM THE BIRCH REDUCTION OF PYRENE AND PERYLENE

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Requirements of the Degree of
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PREFACE

The original aim of this research was to prepare the di-cation of pyrene.

(1) It is known that compounds with a phenalene structural unit[1] are capable of giving a stable cation in reaction with some hydride acceptors, such as quinones in strong acids[2].

(2) We thought that 1, 6- or 1, 8-dihydropyrene reported by Otto Neunhoeffer et al.[3] (obtained from Birch reduction of pyrene) would be a model compound to start with for the synthesis of pyrene di-cation, as this particular dihydro-compound of pyrene has two phenalene structural units. 1, 6- or 1, 8-Dihydropyrene might then give a di-cation when treated with a hydride abstractor in the presence of a strong acid.

With this purpose in mind, we followed the procedure of Neunhoeffer in order to obtain the required dihydropyrene. We found however, that the reported 1, 6- or 1, 8- dihydro-compound is not a dihydropyrene but a mixture of tetrahydropyrenes. All our attempts to synthesize the required dihydropyrene failed.

We then concentrated our work on the structure elucidation of the tetrahydropyrenes and found they contain phenalene type unsaturation, capable of giving a mono-cation, mono-anion and a neutral radical.

In this thesis, we have reported the identification and separation of the Birch reduction products of pyrene and the synthesis, properties and reactions of the trihydropyrene cation, anion and radical, obtained from tetrahydropyrenes with suitable reagents. We also successfully demonstrated that the same tetrahydropyrenes can also be obtained from the reduction of pyrene with lithium in ethylenediamine (modified Birch reduction). The latter method is also capable of producing a phenalene structural unit in the reduction product of perylene and other higher polycyclic aromatic hydrocarbons.

Since we are concerned mainly with "phenalene structure" and "Birch reduction", our introduction has been divided into two parts. The first part deals with the synthesis, properties and reactions of phenalene and its cation, anion and radical and the second part deals with the probable mechanism and different applications of Birch reduction.

ACKNOWLEDGMENTS

It has been my proud privilege and pleasure to work under Dr. D. H. Paskovich, and I take this opportunity of expressing my deep sense of gratitude to him for kind supervision, able guidance, constructive suggestions and timely encouragement throughout the progress of the present work. I also give my sincere thanks to Professor J. L. Holmes and to Professor R. R. Fraser for their kind suggestions during this work. The active help of DR.H.A.Reddoch(N.R.C.) in the E.S.R.studies is gratefully acknowledged.

I am also very grateful to my mother, whose kindness and affections are a constant source of inspiration throughout my student life. Finally, I would like to thank my wife for her patience and understanding during this work. The assistance of Mrs. Eriksen in the typing of this thesis is gratefully appreciated.

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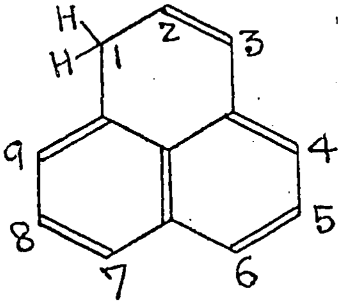

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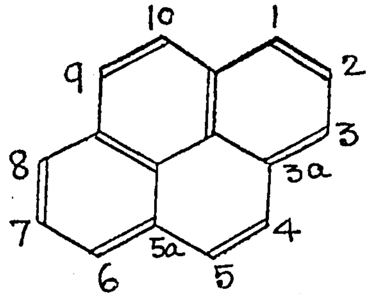

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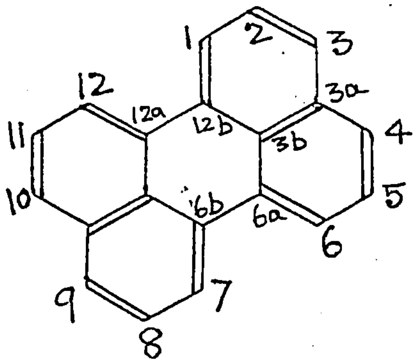

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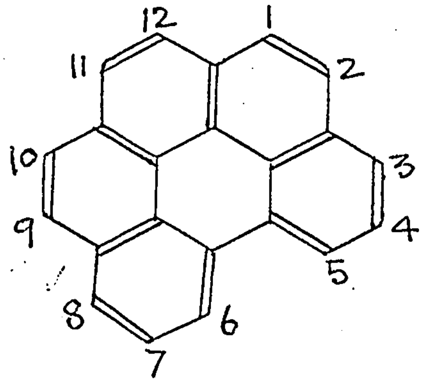

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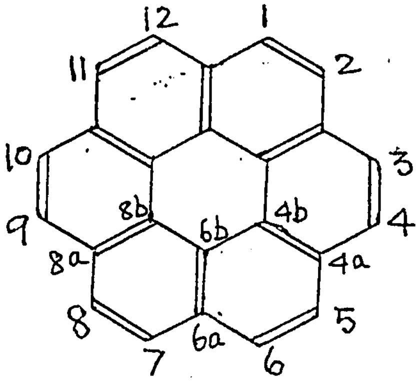


CORONENE

ABSTRACT

The Birch reduction of pyrene and perylene was investigated under a variety of conditions.

1. The reduction of pyrene (1) with four equivalents of sodium in liquid ammonia in the presence of ethanol (ether was used as co-solvent) gave 89% of a mixture of 1, 2, 3, 6-tetrahydropyrene (2) and 1, 2, 3, 5-tetrahydropyrene (3) (in a ratio 2:1), 8% 1, 2, 3, 3a, 4, 5, 5a, 6, 7, 8-decahydropyrene (5) and 3% recovered pyrene.

2. The reduction of pyrene with two equivalents of sodium under the same experimental conditions as [1] gave 45% tetrahydropyrenes (2 and 3), 2% decahydropyrene (5) and the balance was recovered pyrene.

3. The protonation of pyrene anion (prepared from pyrene with two equivalents of sodium in liquid ammonia - ether used as co-solvent) with ethanol or t-BuOH gave 30% tetrahydropyrenes (2 and 3), 10% 4, 5-dihydropyrene (12) and the balance was recovered pyrene.

4. The protonation of pyrene anion (prepared as in [3]) with water gave 55% 1, 2-dihydropyrene (16), 5% 4, 5-dihydropyrene (12) and the balance was recovered pyrene.

5. Methylation of the above pyrene anion gave 4-methylpyrene (76) and 2-methylpyrene (78) in the ratio 3:1 respectively.

6. Reduction of pyrene (1) with lithium in ethylenediamine (modified Birch reduction) gave tetrahydropyrenes (2 and 3) as absolute products.

7. Tetrahydropyrenes (2 and 3) were separated from decahydropyrene (5) and unreacted pyrene (1) and their ratio was determined by VPC and NMR. We were unable to separate the tetrahydropyrene isomers 2 and 3 from each other.

8. The structures of the tetrahydropyrenes (2 and 3) were established from I. R., U. V., mass spec. and NMR, as well as by comparing their physical and chemical properties with those of phenalene (6).

9. Tetrahydropyrenes (2 and 3) on hydrogenation gave 1, 2, 3, 6, 7, 8-hexahydropyrene (17) and 1, 2, 3, 3a, 4, 5-hexahydropyrene (18) in the ratio 3:1 respectively.

10. Tetrahydropyrenes (2 and 3) on oxidation with $Na_2Cr_2O_7$ gave 1, 8-pyrenequinone (48) in 30% yield and the rest was an unidentified chromium complex. Oxidation of (2 and 3) with various oxidizing agents yielded no isolable products.

11. Tetrahydropyrenes (2 and 3) gave 1, 2, 3-trihydropyrenium perchlorate, fluoroborate and tri-iodide with $HClO_4$, HBF_4 and HI respectively in the presence of chloranil in acetic acid.

12. Azobenzene was used as a hydride acceptor in the preparation of 1, 2, 3-trihydropyrenium cation and phenalenium cation.

13. Tetrahydropyrenes (2 and 3) gave 50% 1, 2, 3-trihydropyrenium cation in 98% H_2SO_4 (measured by U. V. and NMR) and in 72% $HClO_4$ (isolated as perchlorate salt). A 50% yield of 1, 2, 3, 3a, 4, 5-hexahydropyrene (18) was also isolated from the reactionof tetrahydropyrenes (2 and 3) with perchloric acid.

14. 1, 2, 3-Trihydropyrenium cation was found to be more stable than tropenium and phenalenium cations with respect to the transfer of hydride ion from the respective hydrocarbon, as determined by equilibrium studies.

15. 1, 2, 3-Trihydropyrenium cation, on reduction with $LiAlH_4$, gave tetrahydropyrenes (2 and 3) in the ratio 2:1 respectively.

16. Hydrolysis of 1, 2, 3-trihydropyrenium cation with water yielded di-tetrahydropyrenyl ether (73).

17. The mixture of tetrahydropyrenes (2 and 3) gave an anion with n-BuLi, which on methylation followed by dehydrogentation, yielded 4-methylpyrene (76) and 2-methylpyrene (78) in the ratio 3:1 respectively.

18. The mixture of tetrahydropyrenes (2 and 3) gave 1, 2, 3-trihydropyrenyl radical (86) with chloranil in carbon tetrachloride, which was isolated as 1, 2, 3-trihydropyrenium perchlorate (54) with $AgClO_4$ and 1, 2, 3-trihydropyrenium triiodide with iodine.

19. 1, 2, 3-Trihydropyrenyl radical (86) was studied by electron spin resonance in different solvents and at various temperatures and its structure has been established.

20. The Birch reduction of perylene (87) gave 1, 2, 3, 10,-11, 12, 12a, 12b-octahydroperylene (91) as the only product.

21. The dehydrogenation of 1, 2, 3, 10, 11, 12, 12a, 12b-octahydroperylene (91) with chloranil in the presence of perchloric acid gave 1, 2, 3, 10, 11, 12-hexahydroperylene (94).

22. The reduction of perylene (87) with lithium in ethylenediamine gave 1, 2, 3, 3a, 4, 5, 6, 6a-octahydroperylene (98) in 90% yield and a hexadecahydroperylene (97) of unknown structure in 10% yield.

23. 1, 2, 3, 3a, 4, 5, 6, 6a-Octahydroperylene (98), on hydrogenation, gave 1, 2, 3, 3a, 3b, 4, 5, 6, 6a, 6b, 7, 8, 9, 12b-tetradecahydroperylene (100).

24. 1, 2, 3, 3a, 4, 5, 6, 6a-Octahydroperylene (98) gave 1, 2, 3, 3a, 4, 5, 6-heptahydroperylenium perchlorate (101) with chloranil and perchloric acid in acetic acid.

25. 1, 2, 3, 3a, 4, 5, 6-Heptahydroperylenium perchlorate (101) gave octahydroperylene (98) on reduction with $LiAlH_4$ and the perchlorate salt (101) on hydrolysis with water gave a di-octahydroperylenyl ether (102).

26. 1, 2, 3, 3a, 4, 5, 6-Heptahydroperylenyl radical was detected by e. s. r. but it is still under study.

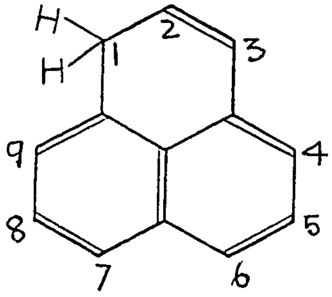
27. 1, 12-Benzoperylene (103) on Birch reduction gave an unidentified reactive hydrocarbon, capable of giving a cation and a substituted phenalenyl radical. The structure of the material is not known.

28. Birch reduction of coronene (105) gave an eicosahydrocoronene (106) of unknown structure in 70% yield and 3, 4, 4a, 4b, 5, 6, 6a, 6b, 7, 8, 8a, 8b, 9, 10-tetradecahydrocoronene (107).

INTRODUCTION

PART I

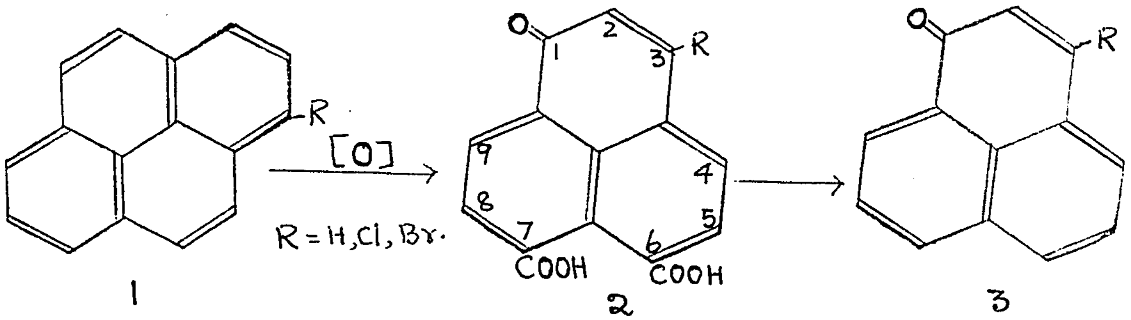
PHENALENE



Synthesis of Phenalene

The chemistry of phenalene and phenalenone has been much studied during the past twenty years. The phenalene hydrocarbons have only recently become accessible and their easy synthesis has been followed by experimental and theoretical studies of the phenalene cation, anion and radical. Moreover, several highly oxygenated derivatives of phenalenene have been isolated as plant and fungal pigments[4-9].

The first recorded phenalene derivative was reported by E. Hintz[10]. Oxidation of pyrene (1) with chromic acid gave phenalenone-6, 7-dicarboxylic acid (2), which was decarboxylated to phenalenone[11] or phenalen—1-one (3).



The best method for the synthesis of the parent phenalene hydrocarbon is that used by Boekelheide and Larrabee[1] and is illustrated in Figure I.

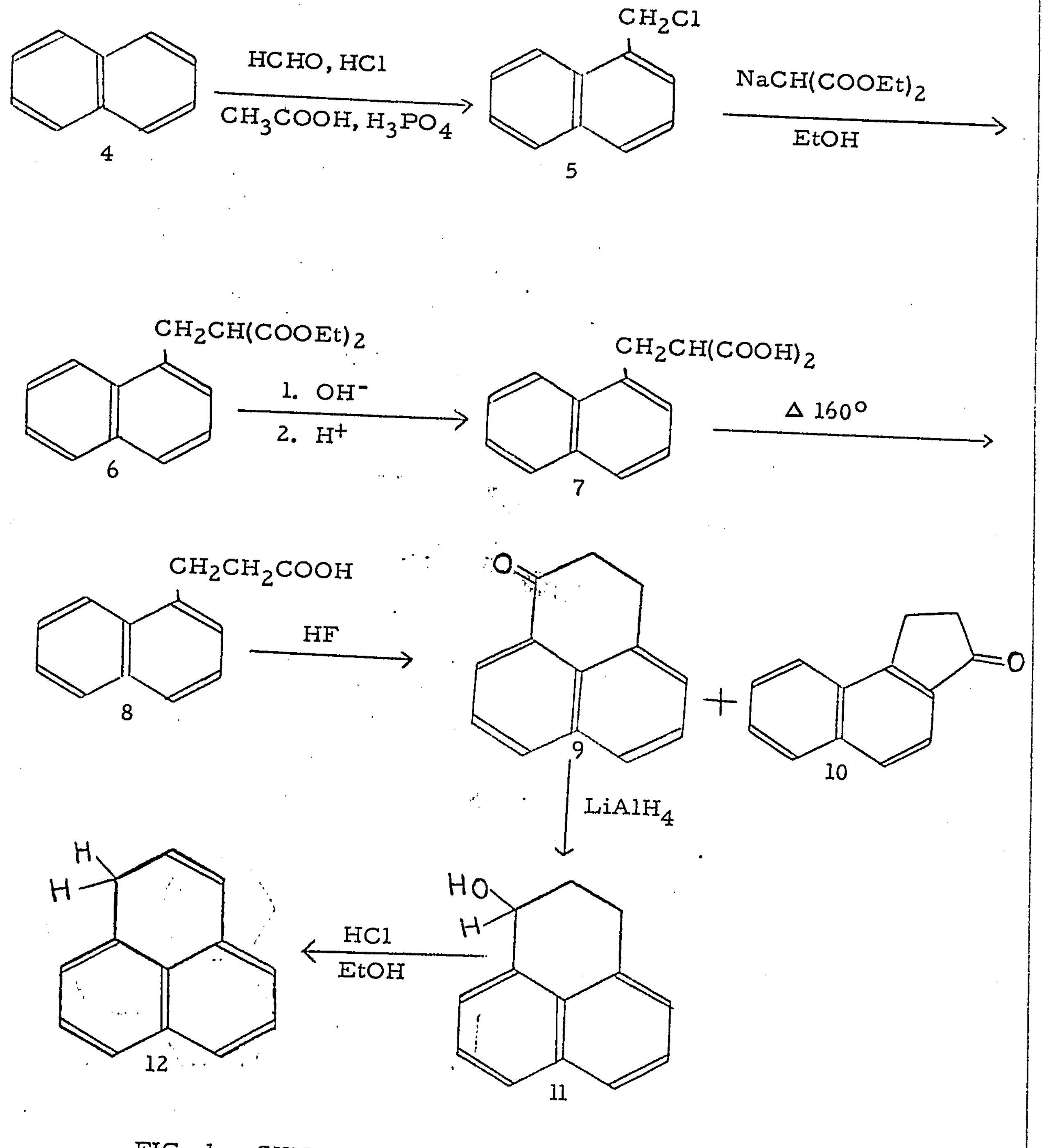


FIG. 1. SYNTHESIS OF PHENALENE

Naphthalene (4) is converted to α-chloromethylnaphthalene (5) by the standard chloromethylation procedure[12]. This chloro-derivative is treated with sodium diethylmalonate and the resulting ester (6) is hydrolyzed to the acid (7) and then decarboxylated to β-1-naphthylpropionic acid (8). The acid (8) is then cyclized by anhydrous hydrofluoric acid[13] to give 2,3-dihydrophenalen-1-one (9) and 4,5-benzhydrindone (10). 2,3-Dihydrophenalen-1-one is then reduced to 2,3-dihydrophenalen-1-ol (11) with lithium aluminum hydride. This is dehydrated by refluxing it with absolute ethanol, saturated with hydrogen chloride to yield phenalene (12).

Properties of phenalene and phenalenone

Phenalene is a remarkable hydrocarbon. It can give rise to a relatively stable anion (13), cation (14) and radical (15) by loss of one of the methylene hydrogens as proton, hydride ion or hydrogen atom respectively as shown in Figure 2.

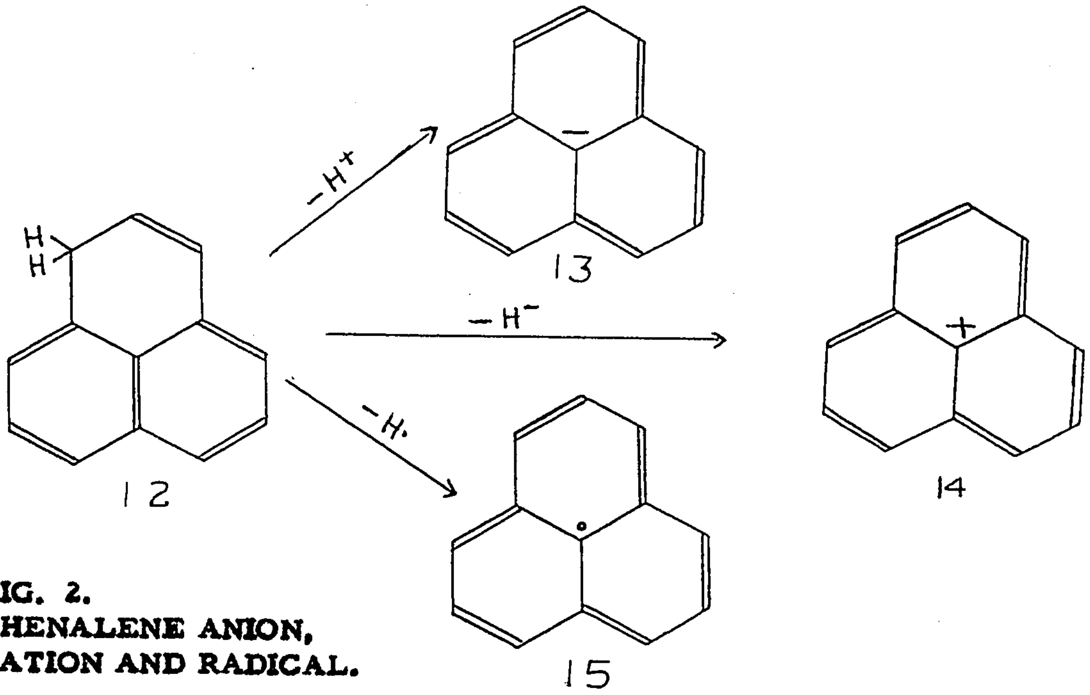
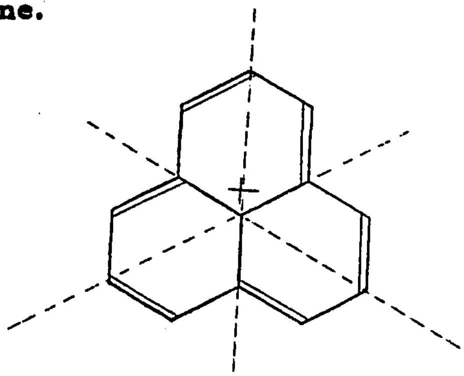


FIG. 2.
PHENALENE ANION, CATION AND RADICAL.

All the three species possess three-fold rotational symmetry about an axis which passes through the internal carbon atom perpendicular to the molecular plane, and also three identical two-fold axes in the molecular plane.



V. Boekelheide[1] first pointed out that this symmetry might make possible considerable resonance stabilisation of these entities. Simple Hückel molecular orbital (HMO) calculations [14-16] indicate that the phenalene cation, anion and radical should all possess the same π-electron delocalisation energy, namely 5.83β ($\beta = 20$ kcals). This follows from the fact that like the allyl and triphenylmethyl systems, the phenalenium system is an odd alternant hydrocarbon and the extra one and two electrons possessed by the radical and anion respectively, occupy a molecular orbital of zero energy (with reference to the energy of an electron in the p_z-orbital of an isolated sp^2-hybridized carbon atom) known as non-bonding molecular orbital. The HMO energy levels of the phenalenyl system are shown in Fig. 3. The phenalenium cation possesses 12-π-electrons which exactly fill pairwise the six bonding molecular orbitals.

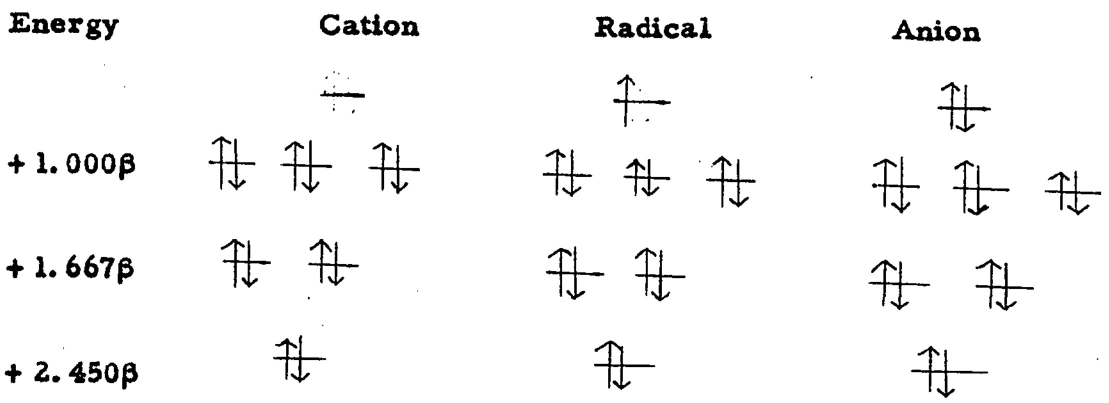
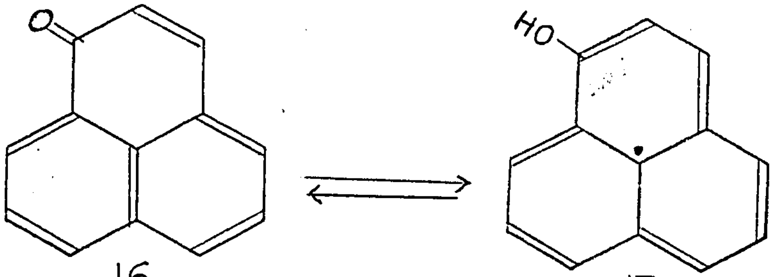


Fig. 3. HMO energy levels for phenalenyl systems.

Furthermore, similar calculations show that the gain in π-electronic energy in creating each of the above entities, following loss of a hydride ion, hydrogen atom or proton from phenalene should be 1.7β or 34 kcals. The value of the π-electron delocalization energy of 1-vinylnaphthalene is given as 4.13β[17]; hence total resonance energy of the phenalenium system is 5.83β. These two facts together then predict that the phenalenium cation, anion and radical might display unusual stability.

Even prior to these reports, there was considerable evidence supporting the molecular orbital predictions. Phenalenone, for example, was found to be soluble in strong acids, presumably due to the formation of the hydroxy derivative of the phenalenium cation, a reaction very similar to that of tropone with acids to form hydroxytropenium salts[18]. Moreover, phenalenone is a highly polarized ketone, resembling in many of its properties tropone and cyclopropenones. The polarization of the carbonyl is attested to by the high dipole moment (3.89 D)[19] and the low infrared carbonyl frequency (1637 cm^{-1})[20] of phenalenone.

A polarographic investigation[21] showed that phenalenone takes one electron to give 1-hydroxyphenalenyl radical (17).

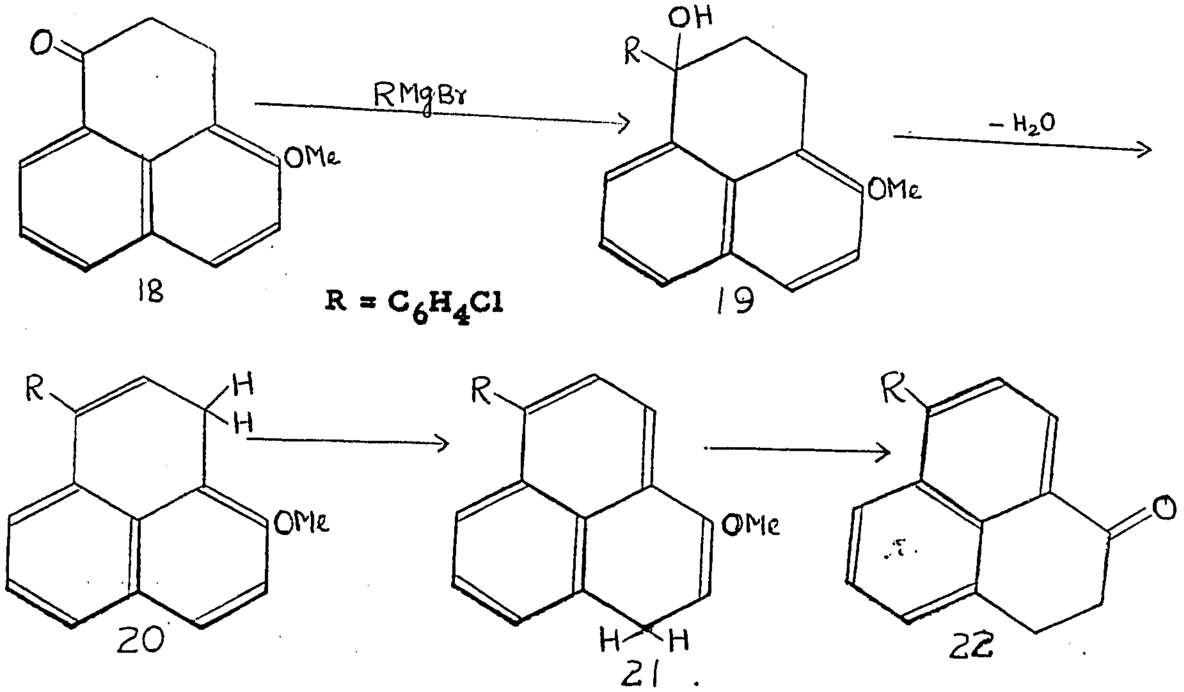


16 17

Irradiation of phenalenone in certain polar solvents, notably isopropylalcohol produces the above radical (17) and was identified by its e.s.r. spectrum[22]. Phenalenone also forms an anion radical[23] with sodium in THF.

Tautomerism of Phenalene

Possibly the most interesting chemistry of phenalene is the tautomerism of the ring system. Klyne and Robinson[24] suggested that phenalene might exhibit six fold tautomerism, each of the three rings assuming the aromatic and the unsaturated character in turn. In case of phenalene the six isomers are identical with one another but for a mono-substituted phenalene, the isomers are not identical. Hence if one oxidizes 1-methyl phenalene, three isomeric naphthalic acids should result. Unfortunately, 1-methyl phenalene is not known, hence this assumption could not be tested. However, Badger et al.[25] showed that dehydration of the carbinol (19) gave (20), which tautomerized to the isomeric phenalene (21); this, on hydrolysis, rearranged to the ketonic product (22).



R = C_6H_4Cl

In a series of experiments, Boekelheide and Larrabee[26] attempted to prepare four different methylphenalenes (23 - 26) by the acid-catalysed dehydration of the alcohols (27 - 31) respectively. But in all cases only one type of methylphenalene (26or31) was obtained. (i. e. 4-methylphenalene or 9-methylphenalene). This is shown in Fig. 4.

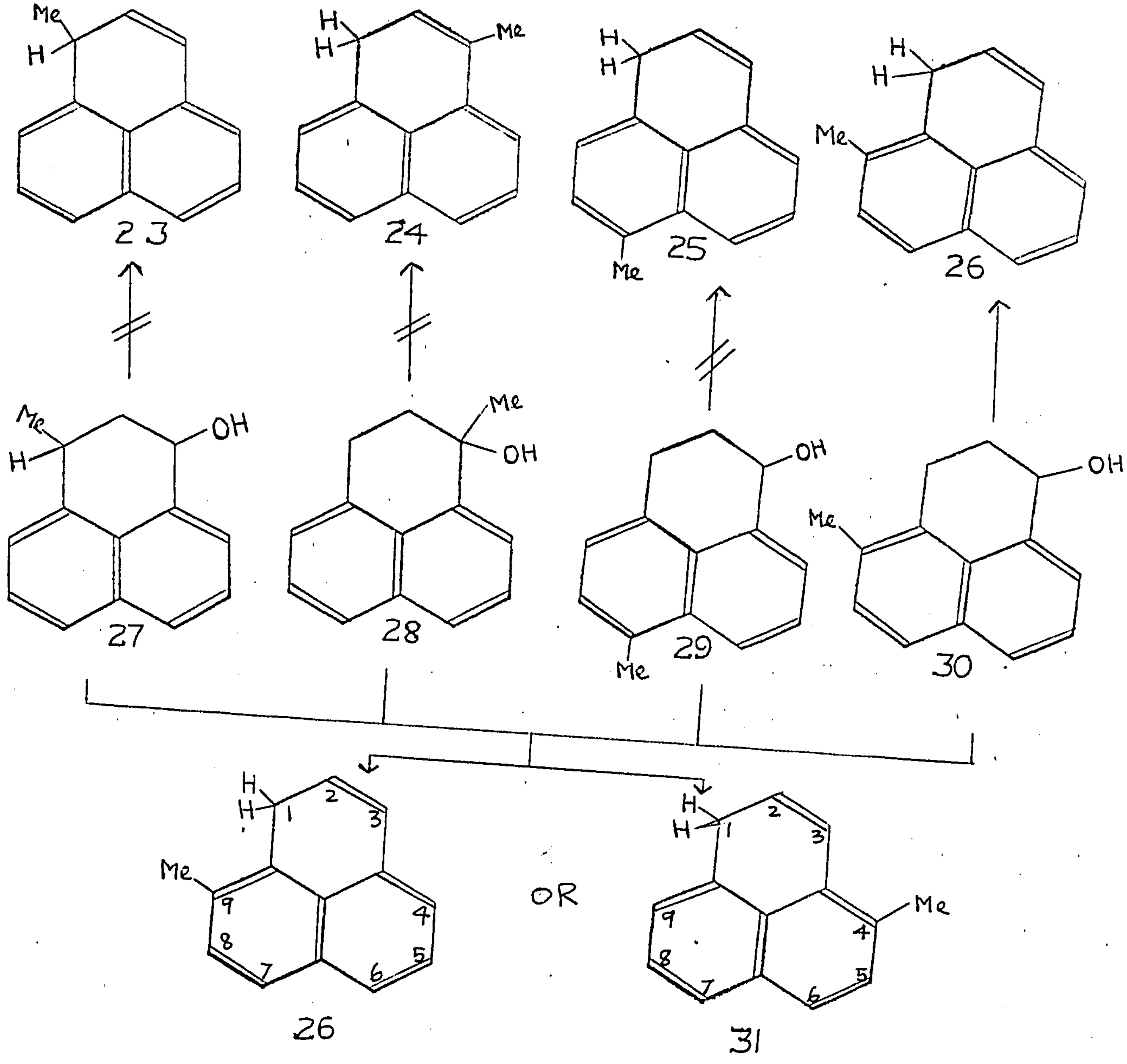
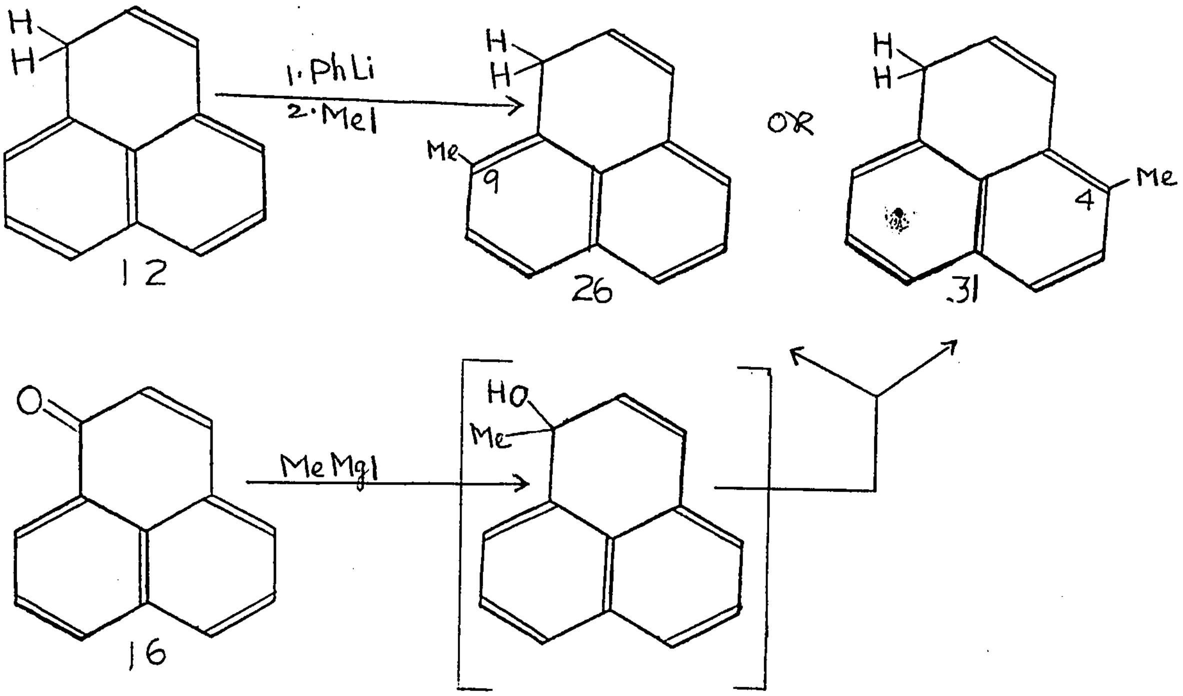


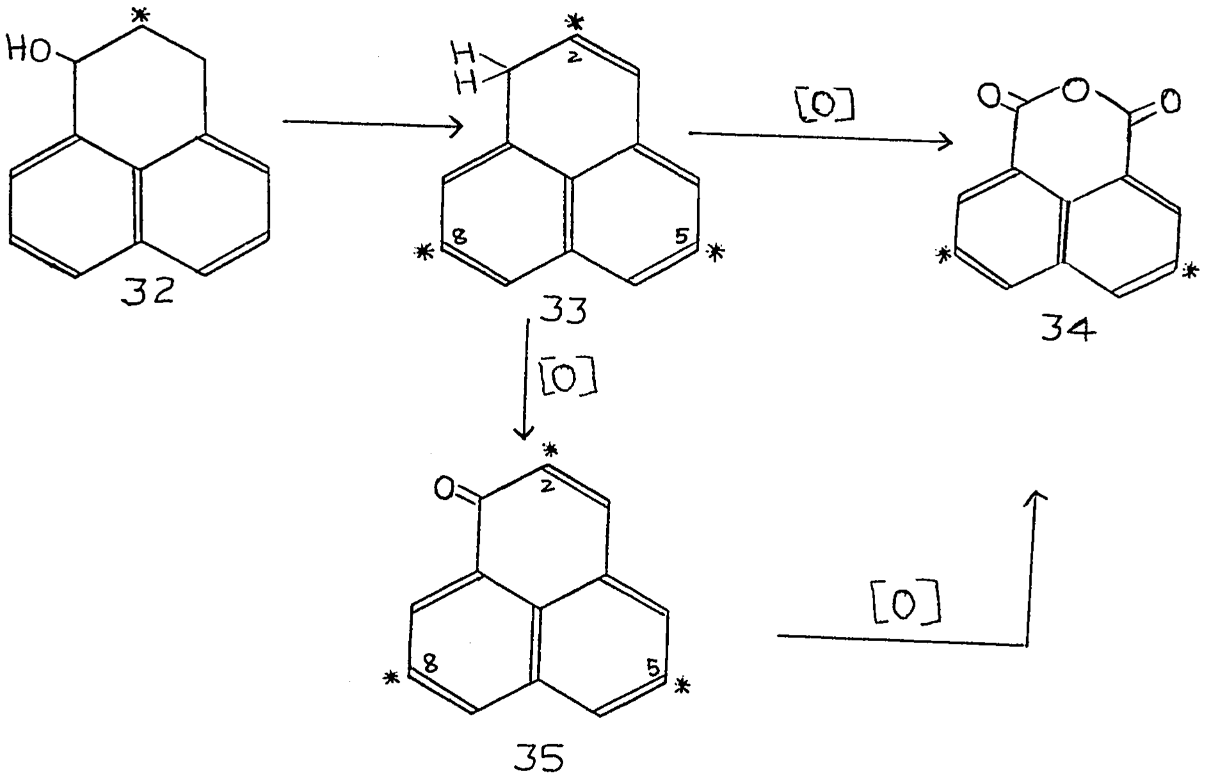
FIGURE 4. SYNTHESIS OF 4- or 9-METHYLPHENALENE

The same methylated hydrocarbon was also obtained by the treatment of phenalene with n-butyl lithium or phenyl lithium followed by methylation with methyl iodide or by the action of methylmagnesium iodide on phenalenone (16).



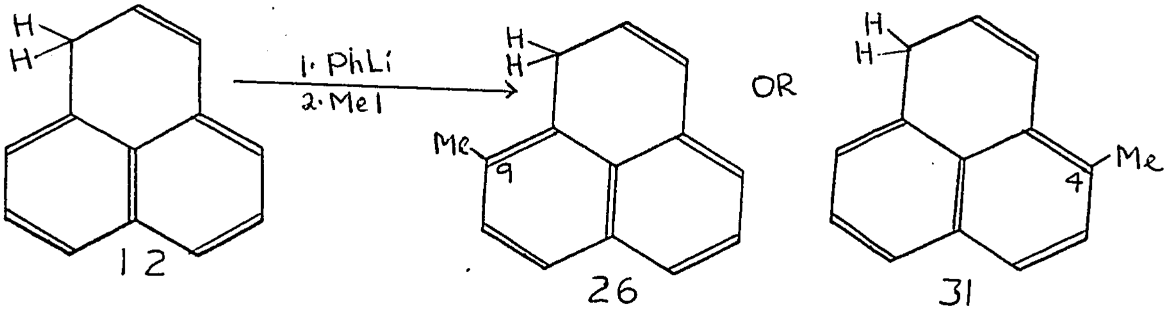
These results show that the phenalene ring system behaves as a unit and hence a substituent in the "peri-ring" will likely end up in another position of the molecule when the reaction involves an ion.

Later, M. Nakazaki [27] studied the preparation and degradation of a C^{14}-labelled phenalene. The alcohol (32) was synthesised from 1-chloromethylnaphthalene and diethyl-(2-C^{14})-malonate and dehydrated to the labelled phenalene (33). On oxidation with permanganate, (33) gave naphthalic anhydride (34) having two-thirds of the specific activity of compounds (32) and (33). In another experiment, (33) was first oxidised to the ketone (35) with sodium dichlormate in acetic acid and the ketone (35) was further oxidised with permanganate to naphthalic anhydride (34). The specific activity of the anhydride in both degradations was the same. Hence it was concluded that the even distribution of C^{14} between positions 2, 5 and 8 had occurred at the dehydration step.



Phenalene anion

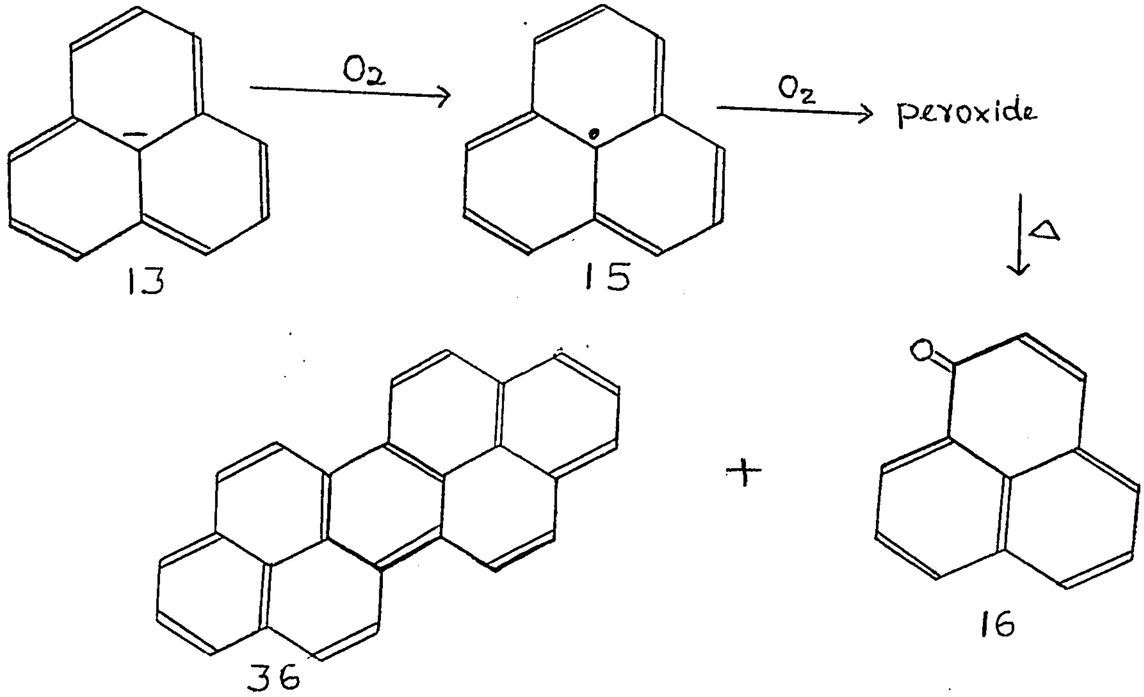
Phenalene in dry ether gives the red anion with n-butyl lithium or with phenyl lithium[1]. This anion reacts with methyl iodide to give 4(9)-methyl phenalene.(26 or 31).



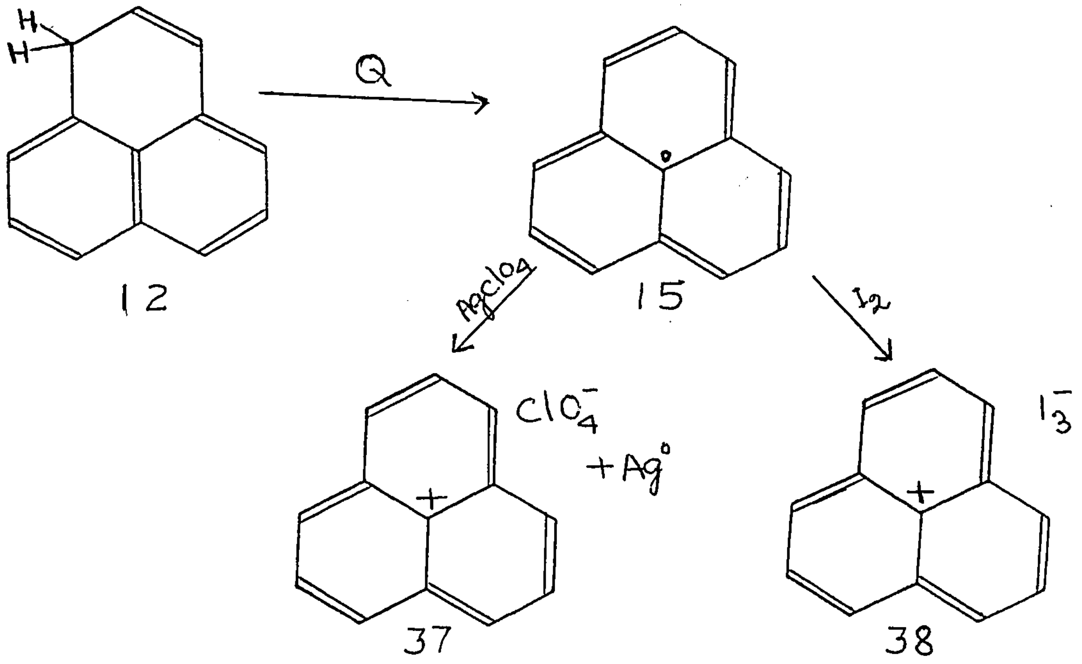
The anion (13) also gives an unidentified yellowish solid[1] with carbon dioxide.

Phenalenyl radical preparation

The stable existence of the phenalenyl radical was demonstrated by Sogo, Nakazaki and Calvin[28]. In their studies a solution of the phenalenyl radical was produced by allowing a solution of phenalene in carbon tetrachloride, sealed in air, to stand for several months. Somewhat later, the radical (15) was prepared by Reid[29] by shaking a solution of the anion in an atmosphere of oxygen. The phenalenyl radical has not been isolated as such in the crystalline state, but exists in solution. This radical in presence of excess of oxygen gives a green peroxide of unknown constitution, which breaks down thermally to a mixture of phenalenone (16) and supposedly peropyrene [29](36).



Later on, Reid[30] also reported that this radical can be produced by the action of quinones on phenalene in non-polar solvents such as carbon tetrachloride, methylene chloride, etc. The radical can be converted to the perchlorate salt with $AgClO_4$, or to tri-iodide salt with iodine.



E. S. R. Studies of Phenalenyl Radical

In the absence of an oxidizing agent the phenalenyl radical is stable in CCl_4 solution for long periods at room temperature[31, 32]. Although the electron density at each position of an odd-alternant hydrocarbon radical is unity[33], the density distribution of the electron in the non-bonding molecular orbital is not uniform. HMO calculation predicts that the unpaired electron density in the phenalenyl radical should be zero on seven carbon atoms and have positive values at the remaining six. This is shown in(Fig. 5).

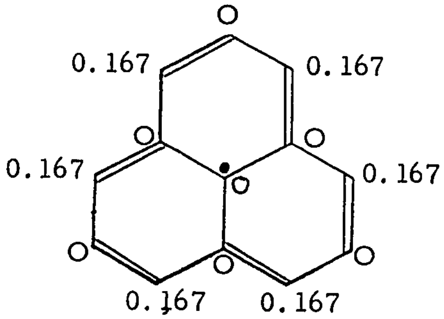


FIGURE 5. UNPAIRED ELECTRON DENSITY IN THE PHENALENYL RADICAL

The above structure should give a seven-line pattern in the electron spin resonance spectrum with a spread of about 28 gauss. Seven such lines are actually observed in the ratio of 1:6:15:20:15:6:1 but each is further split into a quartet (1:3:3:1) corresponding to substantial spin density at the 2, 5 and 8 positions[28].

The construction of the first-order valence bond resonance forms clearly shows the presence of the odd electron on the six symmetrically located positions, 1, 3, 4, 6, 7 and 9, thus providing a primary hyperfine interaction with six equivalent protons and accounting for the seven lines with a splitting of about 6.3 gauss. Second order or excited valence bond resonance forms would be required to permit the odd electron to reside on the remaining three symmetrically located protons, 2, 5 and 8, thus accounting for the quartet with the smaller splitting of about 1.82 gauss. The structures of the e.s.r. spectra of phenalenyl and other odd-alternant hydrocarbon radicals are accounted for by more refined molecular orbital theory which introduces the concept of negative spin density[34]. The spin densities at positions 2, 5 and 8 of the phenalenyl radical are negative and those at positions 1, 3, 4, 6, 7 and 9 positive and greater[35]. This negative spin density is responsible for the fine structure of the e.s.r. spectrum of phenalenyl radical. The large spread, 49 gauss in the case of phenalenyl radical, can be accounted for, since the total width of the e.s.r. spectrum is a measure of the sum of the absolute values of the spin densities.

Phenalenium Cation Synthesis

The phenalenium cation was first prepared as its perchlorate by R. Pettit[36]. Diazoacetic ester was treated with acenaphthylene (39) in decalin to give 3'-carbethoxy-1:2-cyclopropanoacenaphthene (40). Hydrolysis of this ester followed by Curtius' rearrangement of the corresponding acid azide (42) gave the isocyanate (43). Hydrolysis of the isocyanate afforded the hydrochloride salt of 3'-amino-1:2-cyclopropanoacenaphthene (44). This with conc. hydrochloric acid and sodium nitrite furnished 3'-chloro-1:2-cyclopropanoacenaphthene (45) in good yield. The chloro compound (45) showed no ionic properties, it was readily soluble in non-polar solvents and gave no immediate reaction with silver nitrate. It also showed no unsaturated behavior and hence the molecule undoubtedly possessed the covalent structure (45). Treatment of the chloro compound with silver perchlorate in dry nitromethane at 70° for two hours did result in almost quantitative precipitation of silver chloride. Addition of ether to the remaining deep green solution caused precipitation of a yellow microcrystalline solid in good yield, which was shown to be phenalenium perchlorate by its physical, chemical properties as well as from I.R.; U.V. and N.M.R. spectral evidence. The above synthetic route is shown in Fig. 6.

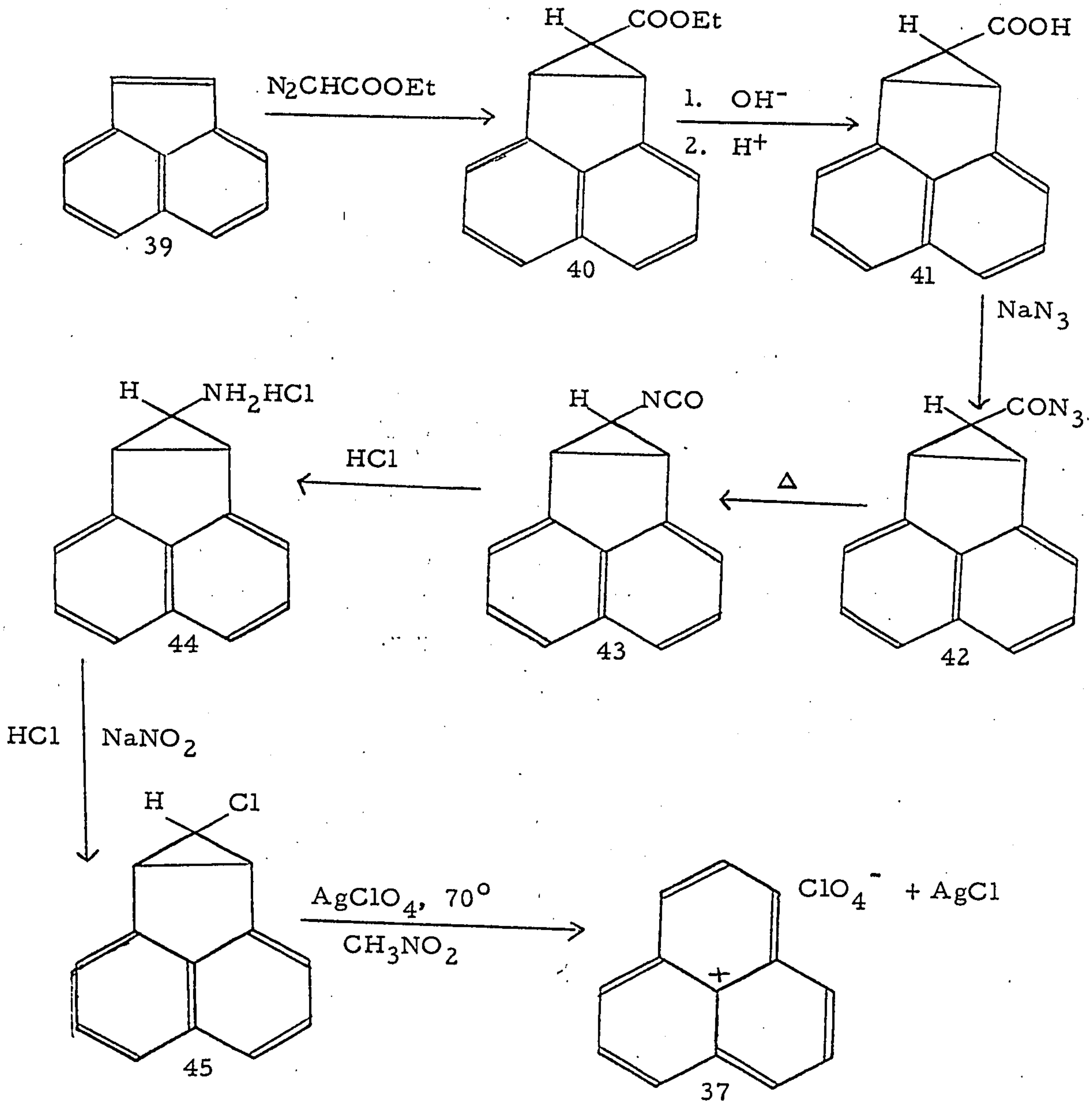
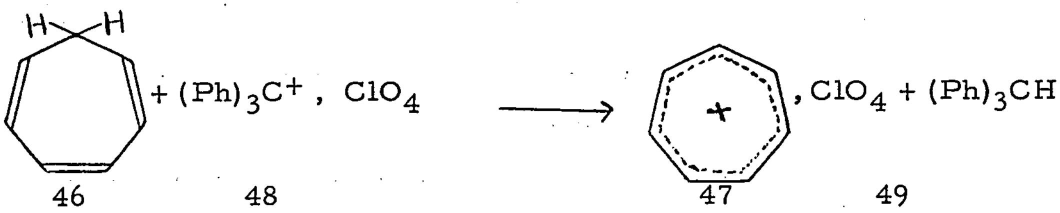
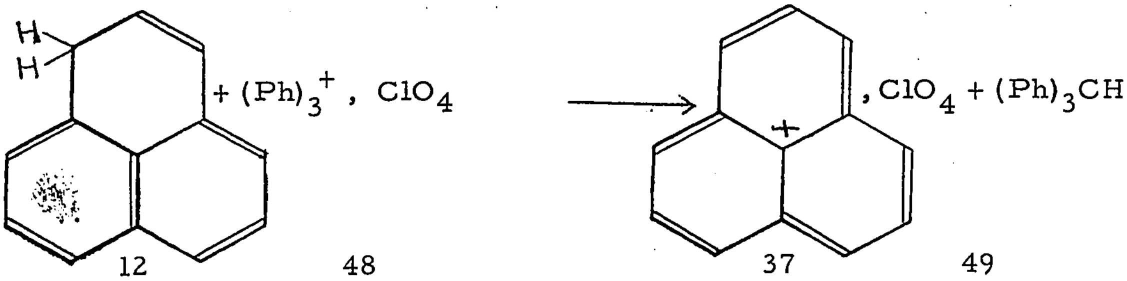


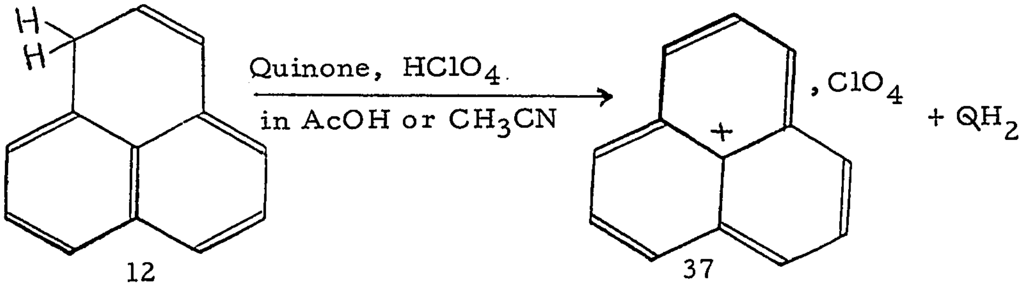
FIGURE 6. SYNTHESIS OF PHENALENIUM PERCHLORATE

The next method[37] for the synthesis of phenalenium perchlorate was identical to that employed by Dauben and Pearson[38] for the preparation of tropenium perchlorate. Their method of synthesis involves the direct transfer of a hydride ion from cycloheptatriene to the trityl carbonium ion in liquid sulfur dioxide or acetronitrile.





Later on, D. H. Reid[2] put forward a more general synthesis of phenalenium salts. This involves a hydride abstraction from phenalene by quinones in the presence of perchloric acid.



Reaction is best carried out in acetic acid or acetonitrile, with stoichiometric amounts of the hydrocarbon and the quinone in the presence of an excess of perchloric acid. The efficiency of a number of quinones as hydride acceptors was tested qualitatively, with phenalene as the substrate. Increased yields and greater purity of product were obtained with quinones having high redox potentials. 2, 3-Dichloro-5, 6-dicyano-1, 4-benzoquinone (E $\approx$ 1.0V) is a very efficient hydride acceptor. It is very soluble in the reaction solvents but has the disadvantage that its sparingly soluble quinol is not readily separated from the phenalenium salt. Tetrachloro-1, 2-benzoquinone is the most useful quinone owing to its high redox potential ($E^{o} \approx 0.87V$), its high solubility in acetic acid and acetonitrile, and the high solubility of its quinol in ether. Chloranil (tetrachloro-1, 4-benzoquinone) is also a good hydride acceptor but it is not very soluble in the solvents.

Action of acids on phenalene

Phenalenium cation can also be produced by dissolving phenalene in mineral acids such as 96-98% sulfuric acid, or 70% perchloric acid. It has been demonstrated by Dauben and Pearson[37] and later by Kursanov and Volpin[39] that the tropenium ion is produced by the action of sulfuric acid upon cycloheptatriene. The yield of tropenium ion from this interaction was reported to be 22.5%, measured from its U.V. spectrum. This conversion suggested that the phenalenium ion might also be preparable by this route. Accordingly and in essentially the same manner, L.R. Honnen[37] treated samples of phenalene with concentrated sulfuric acid and reported the quantitative spectra of the resulting solutions. The solutions gave a spectrum quite similar to that of the phenalenium cation. Quantitative data showed that the intensity of the absorption maxima at 399.5 mμ. was 25,000. This is almost exactly one half of that found for phenalenium cation (e_{max} for phenalenium cation is 49,000 at λ_{max} 399.5 mμ). Almost exactly 50% conversion of phenalene to the phenalenium ion leads the author to attempt explanation of this result in terms of possible mechanistic routes available for this transformation. Three possible mechanistic paths were suggested.

One of these involves the direct hydride abstraction by the sulfur trioxide in the medium as shown below:

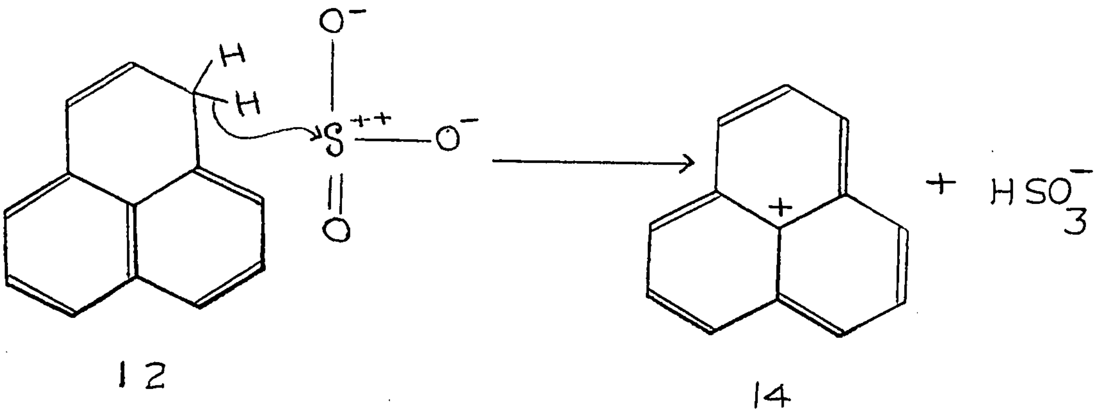


FIG. 7A. ACTION OF SULFURIC ACID ON PHENALENE

This mechanistic path requires that the conversion to the phenalenium ion be 100%, but only 50% spectral yield of the ion can be recorded. Alternatively, an attack by the electrophilic agent sulfur trioxide could occur at such a position as to lead to intermediates like A or B as shown below:

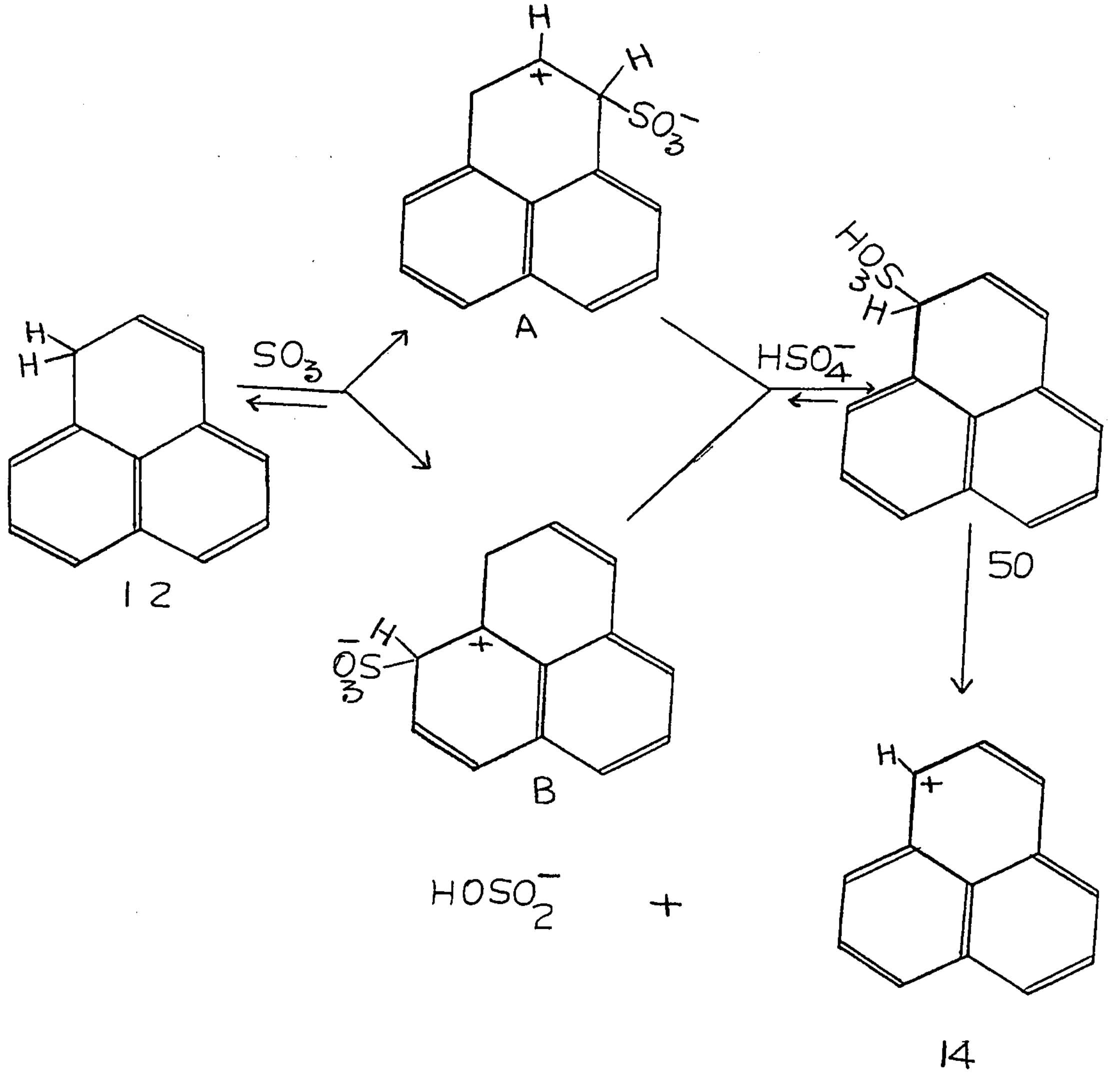


FIG. 7B. ACTION OF SULFURIC ACID ON PHENALENE

Either of these intermediates, A or B, could then lose a proton to an available base such as the bisulfate ion. The resulting product is phenalene-sulfonic acid (50). This acid probably would decompose slowly in the reaction medium giving the bisulfite and phenalenium ion (14). This course of reaction also needs a quantitative yield of the phenalenium ion.

Finally, an electrophilic attack by sulfur trioxide or a proton could be envisioned, yielding an intermediate which could then abstract a hydride ion from available phenalene, as shown below:

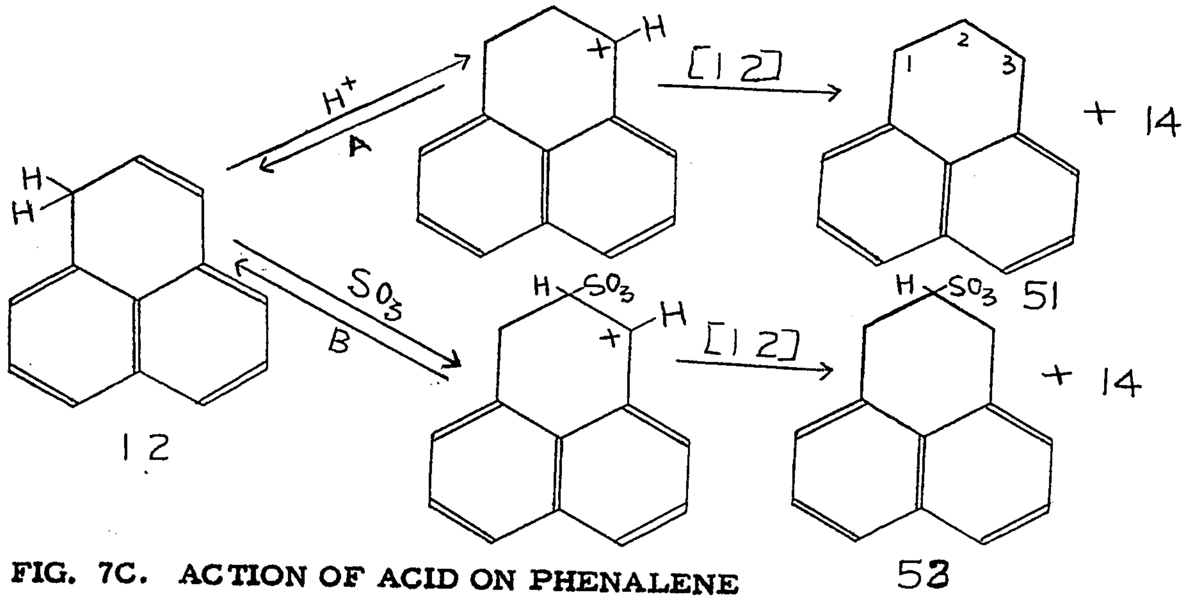


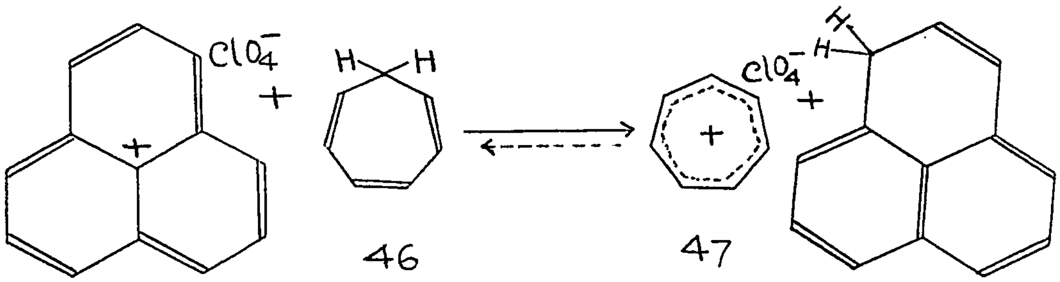
FIG. 7C. ACTION OF ACID ON PHENALENE

The reduction of the carbonium ions yields a sulfonic acid (52)or 2, 3-dihydrophenalene (51), ..., depending upon whether the attacking agent is a proton or sulfur trioxide, and a phenalenium ion (14). This course of the reaction agrees very well with the yield of the phenalenium ion (approximately 50%). The author suggested that either of the two routes are possible, because of the following facts.

Firstly, phenalene dissolved in 71% perchloric acid, giving an oil phase which was insoluble in acid phase. The acid phase showed a U. V. spectrum which was identical to that of the phenalenium ion (14). The oil phase was proposed to contain 2, 3-dihydrophenalene (51), as indicated by its U. V. spectrum which was similar to that of the authentic sample. But the author neither isolated the 2, 3-dihydrophenalene from this reaction mixture, nor identified it by other means than its U. V. spectrum.

Stability of phenalenium perchlorate

Phenalenium perchlorate is less stable than tropenium perchlorate since tropenium perchlorate is precipitated by adding cycloheptatriene into a solution of phenalenium perchlorate in aceto-nitrile as shown below[37]:



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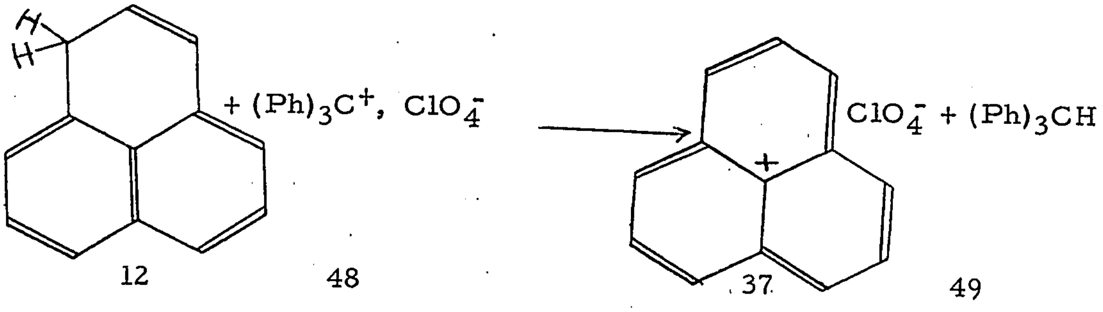
But phenalenium perchlorate is more stable than trityl (triphenyl methyl) perchlorate (48) as the former is precipitated by adding phenalene to trityl perchlorate in acetonitrile or nitromethane solution[37].



12 48 37 49

Hydrolysis of Phenalenium perchlorate

An interesting reaction of phenalenium perchlorate is its hydrolysis with water. It is well known that phenalenium perchlorate is not stable in moisture[40]. Pettit[14] reported that direct hydrolysis of solid phenalenium perchlorate gave 15% phenalene and 39% phenalenone. Pettit has suggested that the isolation of these products demonstrates the instability of phenalenol with respect to disproportionation. Later on, L. R. Honnen[37] showed that the ratio of phenalene and phenalenone formed from the hydrolysis of the salt was approximately 1:1. It was found that the attempted hydrolysis by direct treatment of the solid phenalenium perchlorate in water gave poor yields of phenalene;on the other hand, prior dissolution of the salt in acetonitrile followed by rapid addition of copious quantities of water, markedly improved the relative yield of phenalene. The yields of phenalene and phenalenone were 37% and 47% respectively.

D. H. Reid[41] explained the formation of phenalene and phenalenone from the hydrolysis of phenalenium cation as follows: attack by water at position (1) on the carbon skeleton, followed by the loss of proton, presumably to water, would give rise to phenalenol (54).

This product could then transfer a hydride ion to a second phenalenium ion to give the hydroxyphenalenium ion and phenalene. A second reaction course involving intermediate formation of diphenalenyl ether (56) would be expected to yield the same products. Interaction of phenalenium cation (37) with the oxygen of the presumed phenalenol (54), followed by the loss of a proton to a base such as water would give the ether (56). The detection of this intermediate ether was claimed by L. R. Honen[37], who obtained it by the rapid hydrolysis of phenalenium fluoroborate. The steps involved in the hydrolysis of phenalenium perchlorate are shown in Fig. 8.

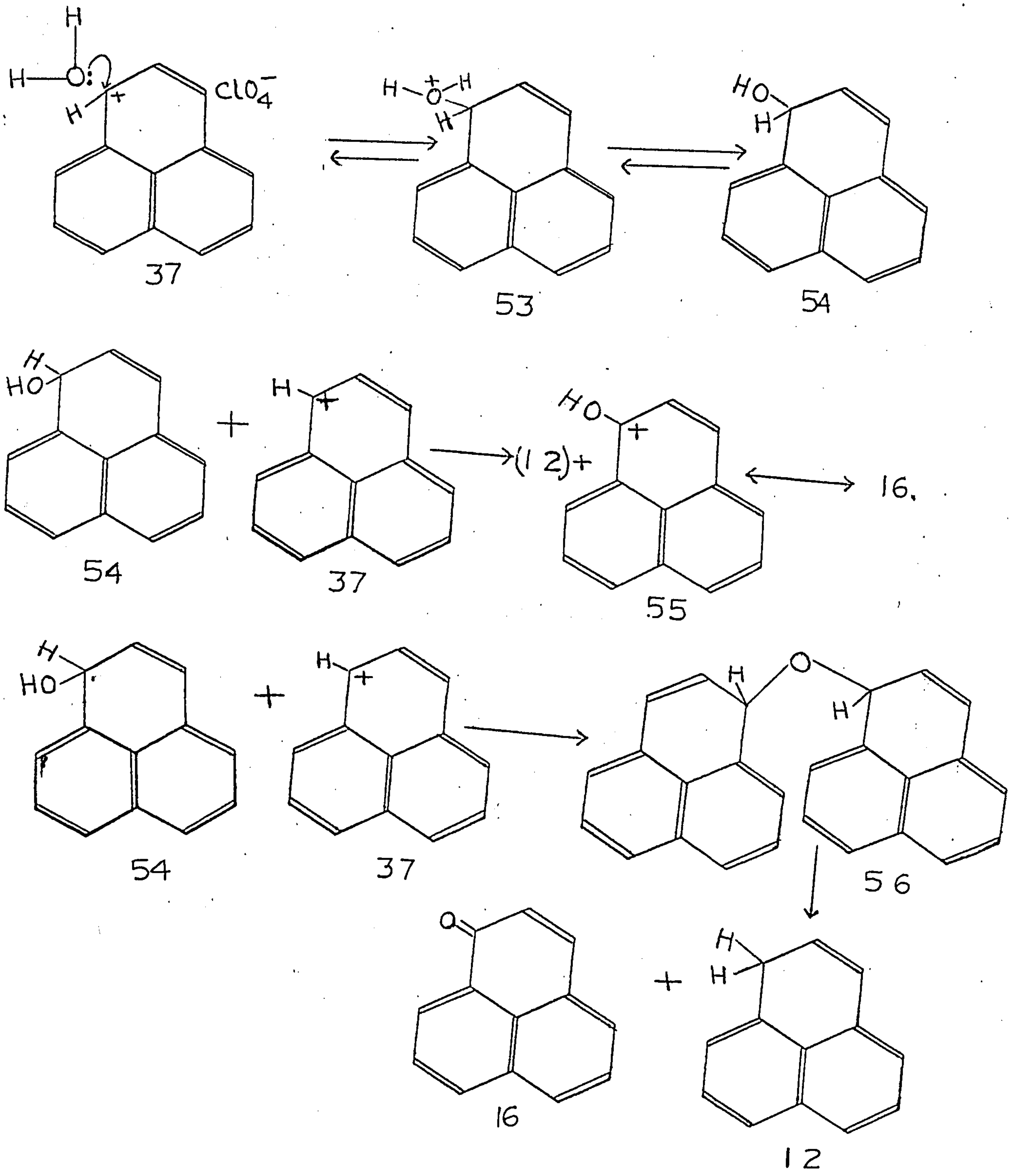
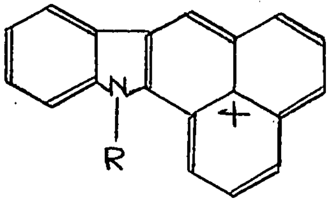


FIG. 8. HYDROLYSIS OF PHENALENIUM CATION

Systems containing phenalene skeleton

Finally, Reid[42] reported the synthesis of other systems having the phenalenium ring system. A few examples are given below:



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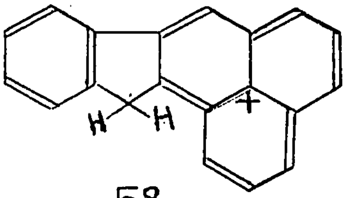

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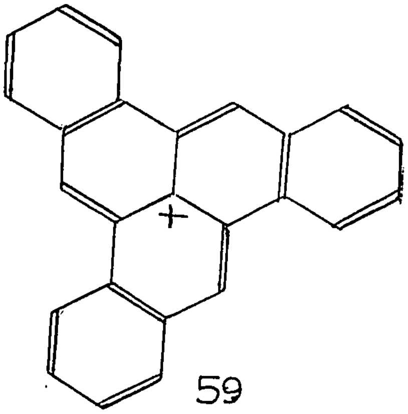

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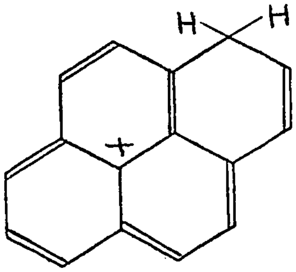
R = H, CH_3 , C_6H_5

Many polycyclic hydrocarbons dissolve in strong acids to give protonated species which may be considered to contain the phenalenium resonance system as a principal contributor to the resonance hybrid. Amongst these are pyrene (60), 3,4-benzo-pyrene (61) and peropyrene (62).



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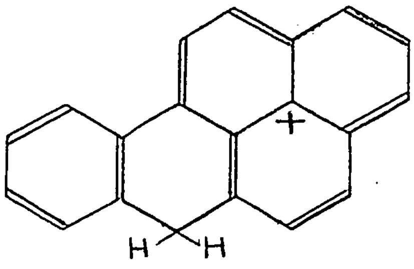

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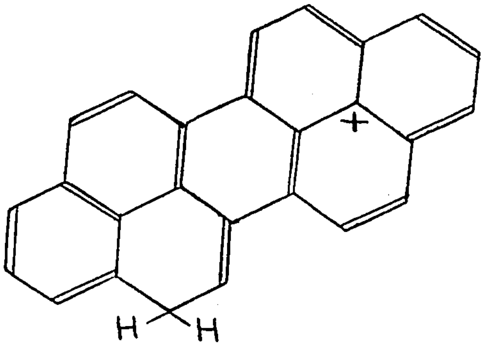

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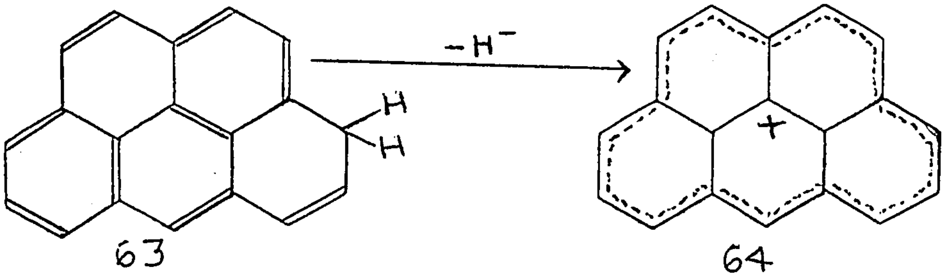
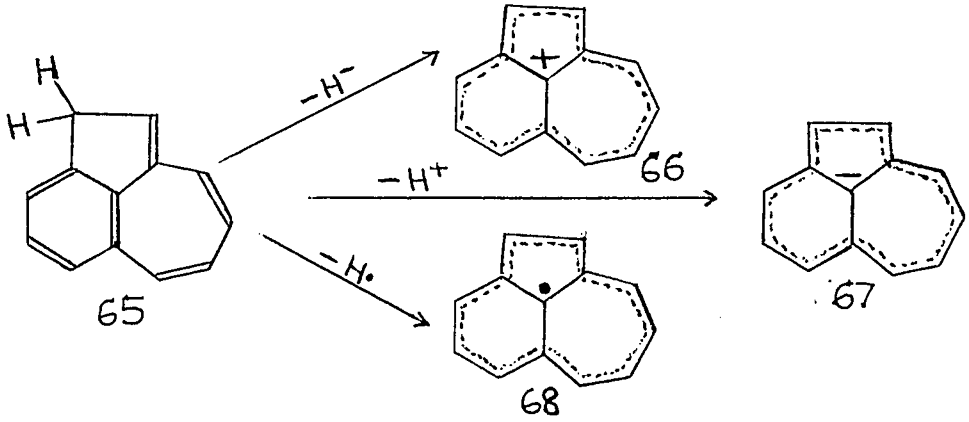
D. H. Reid and Bonthrone[43] reported the synthesis of a stable benzo[cd]pyrenium cation (64). Benzo[cd]pyrene (63) also has the phenalene skeleton.



Boekelheide and Smith[44] have recently described the synthesis of 2H-benz[cd]azulene (65), an odd-nonalternant hydrocarbon and an isomer of phenalene. 2H-Benz[cd]azulene is also capable of giving cation, anion and free radical species like phenalene as shown by HMO calculations. The delocalization energy for phenalenium cation is 5.83β, whereas the value for 2H-benz[cd]azulene cation is found to be 5.57β. This suggests that the properties of 2H-benz[cd]azulene will be similar to those of phenalene.



On oxidation, 2H-benz[cd]azulene also gives a ketone, the properties of which are very close to those of phenalenone (16).

INTRODUCTION

PART II

BIRCH REDUCTION

Mechanism and Applications of Birch Reduction

a) Structure of Alkali Metal-Ammonia Solution:

The reduction of aromatic compounds by solutions of alkali metals in liquid ammonia is generally known as "Birch Reduction". One of the most important properties of a solution of an alkali metal in liquid ammonia is its powerful reducing action. This property[45] is attributed to the solvated electrons. Liquid ammonia is a very good solvent for a large number of organic compounds as well as for alkali metals. Solutions of the alkali metals in liquid ammonia were first investigated by Weyl[46] in 1864. He observed that sodium and potassium were soluble in liquid ammonia, producing highly coloured solutions. Weyl concluded that the metals were joined to the nitrogen of ammonia, forming substituted ammonium groups, with the metal taking the place of one of the hydrogen atoms.

A few years later, Seely[47, 48, 49] reported further information on the solutions of alkali metals in liquid ammonia. He suggested that the metals are in solution in ammonia as such and that they are not united to nitrogen in the form of an ammonium radical. He proposed that liquid ammonia acts as a solvent without definite chemical action on the alkali metals. He observed that dilute solutions of alkali metals in liquid ammonia are blue and after evaporation of ammonia, the alkali metals can be recovered as such in the form of nice crystals. The inevitable conclusion from such facts is that the blue liquid is a simple solution of alkali metals in ammonia, not at all complicated or modified by any definite chemical action.

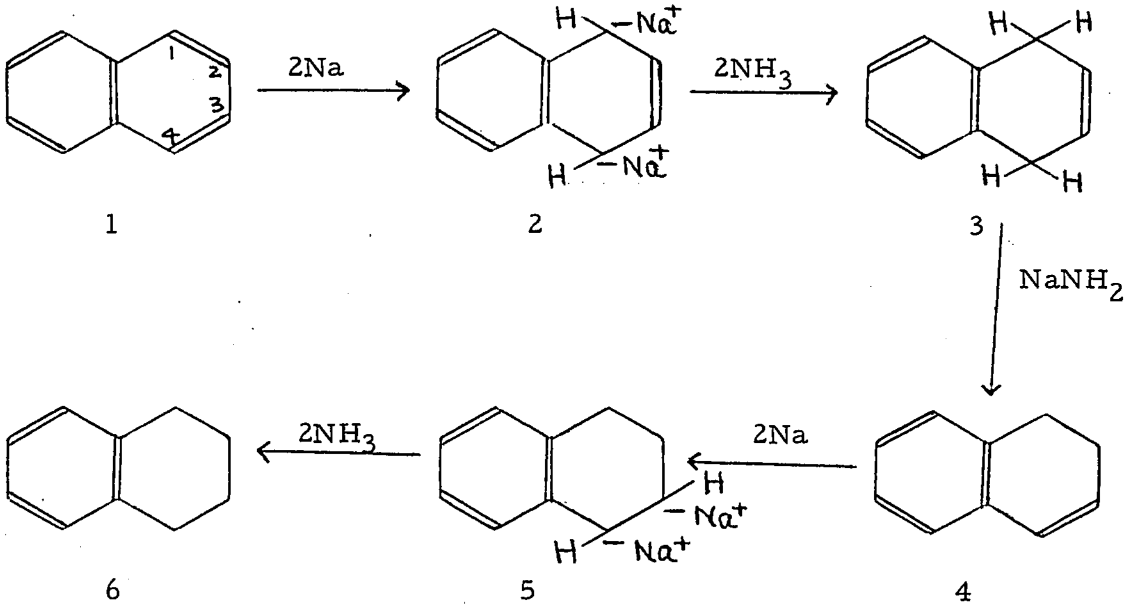
Neither of the investigators presented any evidence of a quantitative nature to support their views. Later on, many workers studied the properties of a solution of alkali metals in liquid ammonia, amongst which the studies of vapour pressure by Kraus[50], molecular weight determination by Joannis[51], determination of density of the solution by Seely[48] and the studies of electrical properties by Cady[52] are worth mentioning. But from these studies no conclusion was reached regarding the exact structure of the solution of the alkali metals in liquid ammonia.

All the facts known so far concerning solutions of metals in liquid ammonia may be summarised as follows: First, as the solution is formed, the metal releases its electron to the solvent and either through polarization of the solvent media[53,54] or by occupying vacancies already present in the media[55], it is solvated. All evidence seems to support the fact that the electron is solvated in a cavity-like form with its electrical properties explained in terms of tunneling[56,57]. As the concentration increases, the electrons in their cavities are brought closer and closer together to finally couple with the solvated metal cations to give the association as suggested by Gold and Jolly[58].

An expanded-metal model suggested by Becker et al.[59] sees the solute as four species in equilibrium; (i) a metal species called a monomer M, which consists of the metal ion surrounded by six oriented ammonia molecules with an electron moving around the metal ion on the protons of the ammonia; (ii) a solvated metal ion M^+; (iii) a solvated electron, which were both formed from dissociation of the monomer M, and finally (iv) a dimer consisting of two monomers bound together by exchange forces. Since we are mainly concerned only with the reducing property of the alkali metal-ammonia solution, an extensive study on its structure is not possible here. Hence the next part of the introduction deals with the reducing-property of this solution.

b) Reduction of Naphthalene:

The benzene nucleus is not attacked by ammonia solutions of metals. Naphthalene, on the other hand, is easily reduced by sodium in liquid ammonia. Lebeau and Picon[60] first studied this reaction at -30° and obtained 1, 2, 3, 4-tetrahydronaphthalene and sodium amide. They concluded that the reduction was preceded by the formation of an organo-sodium compound. Baeyer[61] proposed a 'nascent' hydrogen theory for such reductions. But Wooster and Smith[62] in the course of a detailed study of this reaction, showed that the 'nascent' hydrogen theory of Baeyer was untenable. When naphthalene and sodium were allowed to react in liquid ammonia, titration showed that only four atoms of sodium reacted per molecule of naphthalene, regardless of the presence of excess sodium. Later work of Hückel et al.[63] showed, however, that the reaction of sodium with naphthalene in liquid ammonia follows a stepwise course. At low temperatures (-75° to -60°), a 1, 4-disodium-naphthalene (2) is formed. This disodium salt is stable at these low temperatures, but at higher temperatures, it is ammonolyzed, giving 1, 4-dihydronaphthalene (3). At -33°, this dihydronaphthalene in the presence of sodium amide, rearranges to the 1, 2-dihydronaphthalene(4), which is reduced by sodium in liquid ammonia to tetrahydronaphthalene (6). They proposed the following scheme:



c) Reduction of α- and β-Naphthoxides in the Presence and in the Absence of Proton Source:

In 1944, Birch[64] first made a comparative study of the reduction of aromatic hydrocarbons in sodium-liquid ammonia in the presence and in the absence of a proton source. At that time it was thought that since sodium in liquid ammonia behaves as a solution of metal cations and solvated electrons, it might be expected that it reduces the hydrocarbons by electron addition. The action of sodium in liquid ammonia on a number of naphthalene derivatives was studied by Birch in order to determine whether the presence of the proton source alters the course of the reaction. He indicated that a considerable change was produced by addition of tertiary-amyl alcohol as a proton source in a reaction of α- and β-naphthoxides in sodium-liquid ammonia. He found that sodium alone produced little reduction but in presence of the alcohol good yields of dihydro-derivatives were obtained. Some of his results are given in Table I.

TABLE I

BIRCH REDUCTION OF α- and β-NAPHTHOXIDES

Substance Reduced (2 atoms of sodium)	Products
Sodium α-naphthoxide	5, 8-Dihydro-α-naphthol (trace)
α-Naphthol + tert-$C_5H_{11}OH$ (1 mol)	5, 8-Dihydro-α-naphthol (65%)
Sodium α-naphthoxide + tert. -$C_5H_{11}OH$ (2 mols)	5, 8-Dihydro-α-naphthol (85%)
Sodium β-naphthoxide	5, 8-Dihydro-β-naphthol (trace) and β-tetralone (trace)
β-Naphthol + tert. -$C_5H_{11}OH$ (1 mol)	β-Tetralone (65%)
Sodium β-naphthoxide + tert.-$C_5H_{11}OH$ (2 mols)	β-Tetralone (55%)

A theory for such reductions was put forward by Geib and Harteck[65]. They thought that the reduction was due to atomic hydrogen.

Metallic iron catalyses the combination of hydrogen atoms to hydrogen molecules, and it was found that sodium β-naphthoxide was not reduced in the presence of a little finely divided iron. But this evidence was not very conclusive, since the removal of sodium by reaction with ammonia was also catalysed by iron.

The presence of alcohols in ammonia solutions also exercised a profound influence on the course of reduction of monocyclic benzene derivatives. In the absence of alcohols, benzene and its derivatives are not reduced noticeably but in the presence of alcohols benzene[66] gives 1, 4-dihydrobenzene and anisole[64] gives 2:5-dihydro anisole.

Kziegler[67] also demonstrated the role of an acid in ammonia solution. 1,1-Diphenyl ethylene is reduced by sodium in ammonia solution to tetraphenyl butane (10) and he suggested the following mechanism for the reduction:

$$\underset{7}{(C_6H_5)_2C = CH_2} + 2e \longrightarrow \underset{8}{(C_6H_5)_2\bar{C} - \bar{C}H_2}$$

$$\xrightarrow{(C_6H_5)_2C = CH_2} \underset{9}{(C_6H_5)_2\bar{C}.CH_2.CH_2.\bar{C}(C_6H_5)_2} \xrightarrow[2H^+]{}$$

$$\underset{10}{(C_6H_5)_2CH.CH_2.CH_2.CH(C_6H_5)_2}.$$

But in the presence of an alcohol a different product is formed according to the following mechanism:

$$\underset{7}{(C_6H_5)_2C = CH_2} + 2e \longrightarrow \underset{8}{(C_6H_5)_2\bar{C} - \bar{C}H_2}$$

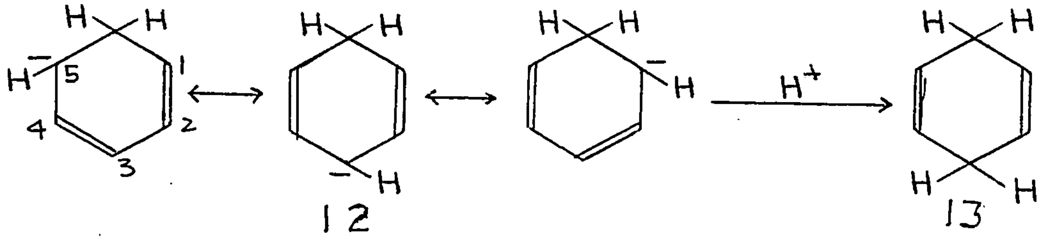
$$\xrightarrow{2H^+} \underset{11}{(C_6H_5)_2CH.CH_3}$$

d) Point of Proton Addition to Anion and Acidity of Proton Source:

The products of the reduction are determined both by the position of the electron addition equilibrium and also by the rate of proton addition. The proton addition can be either reversible or irreversible. The primary products are those of irreversible addition.

From experimental facts it has been shown that proton-addition occurs at the point of highest electron density[68, 69]. With aromatic hydrocarbons the positions occupied by the two incoming hydrogens can be predicted to a remarkable degree by HMO theory[70]. Hückel[70] suggested that the protons occupy positions of highest electron density in the dianion or monoanion as calculated by MO theory. This has been verified for the reduction of unsaturated hydrocarbons at the dropping mercury electrode by Hoijtink and Van Schooten[71, 72]. The protonation of the dianion and monoanion at the point of highest electron density has not only been predicted by HMO theory but is also justifiable on grounds of simple Coulombic attraction. In alternant hydrocarbons all the positions have unit electron density[73] and the positions of highest electron density are identical in the mono- and dianion of the aromatic hydrocarbon.

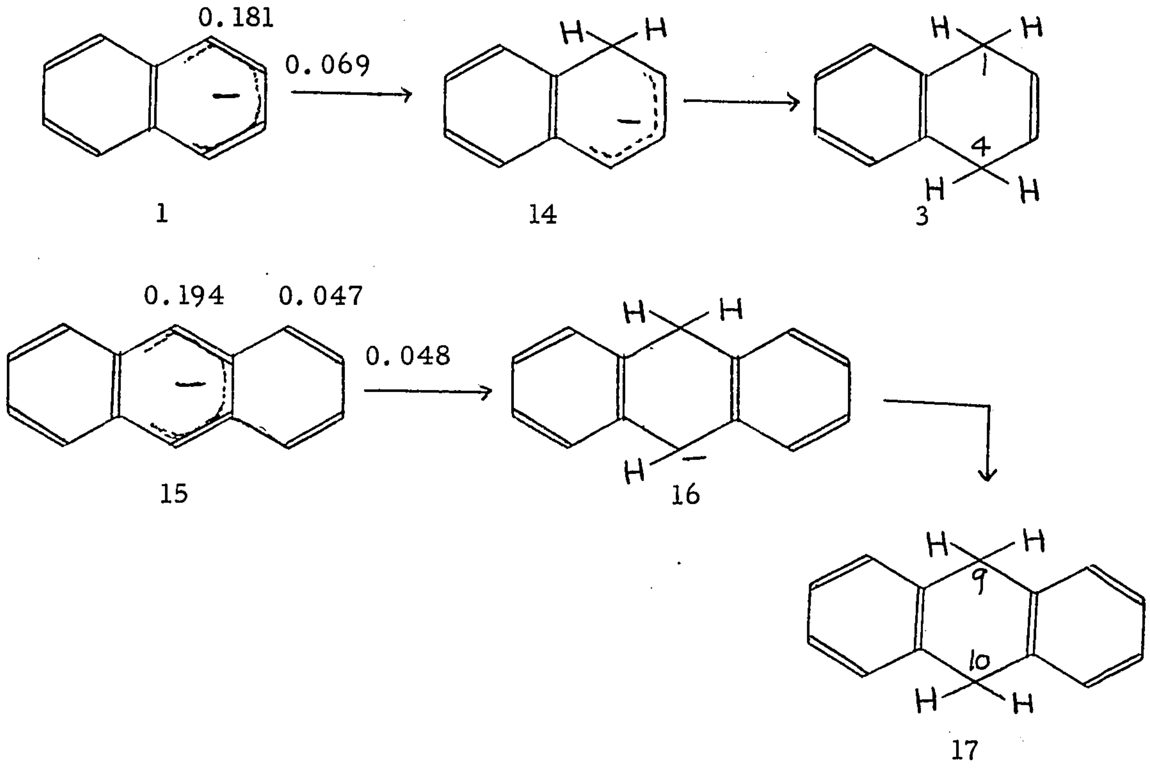
Having considered the course of the first protonation step, one should examine where the second protonation occurs. In a simpler case of the metal-ammonia reduction of benzene[74], the final step involves the protonation of mesomeric anion (12). Since 1, 4-dihydrobenzene (13) is actually the major product[75], it is seen that the central carbon atom 3 is preferentially protonated, though the simple LCAO MO theory predicts[76] equal electron density at 1, 3 and 5 carbon atom of the mesomeric anion (12).



But from qualitative resonance consideration[74] it can be shown that the central carbon atom, i.e. the carbon atom 3, does contain higher electron density. The bonds 1-2 and 4-5 are shorter and involve greater overlap than bonds 2-3 and 3-4; this is because in two of the three resonance structures written for (12), bonds 1-2 and 4-5 are double, while in only one of the three structures are bonds 2-3 and 3-4 double. Furthermore, when unequal overlap is taken into account, the ratio of electron densities on atoms 1 and 3 of (12) is given by:

$$\frac{Q_1}{Q_3} \simeq \frac{q_1 - 1}{q_3 - 1} = \frac{S_{23}^2}{S_{12}^2}$$

where Q_1 and Q_3 are the net charges, q_1 and q_3 are the total electron densities and S_{12} and S_{23} are the overlap integrals for π-bonds 1-2 and 2-3, respectively. Therefore, since $S_{12} > S_{23}$, the electron density at carbon 3 is higher than at carbon 1. It is suggested[74] that this bond order effect is responsible for the central protonation of mesomeric anions. On similar grounds, naphthalene and anthracene[76] on similar reduction give 1,4-dihydronaphthalene (3) and 9,10-dihydroanthracene respectively (17).



[Charge densities as calculated by the Hückel Theory]

Some of the dihydro-compounds predicted by HMO calculations are given in the following table[76].

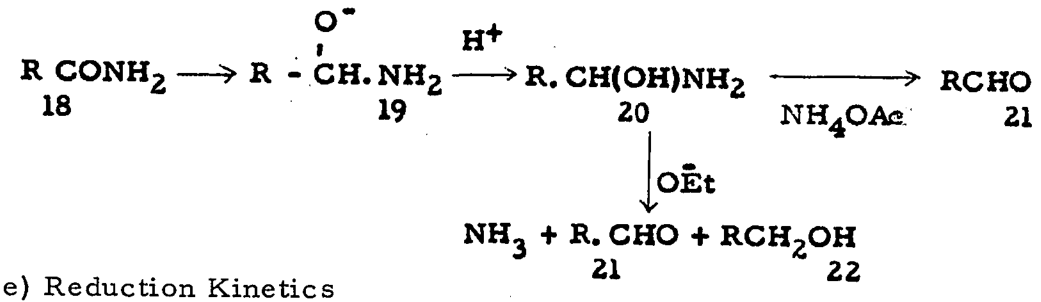
TABLE 2

ALKALI METAL REDUCTIONS OF AROMATIC HYDROCARBONS

Hydrocarbon	Calculated Dihydro-reduction Product
Benzene	1, 4-Dihydrobenzene
Naphthalene	1, 4-Dihydronaphthalene
Anthracene	9, 10-Dihydroanthracene
Phenanthrene	9, 10-Dihydrophenanthrene
Pyrene	1, 6-Dihydropyrene, or 1, 8-Dihydropyrene
Perylene	la, 3-Dihydroperylene

In most of the above cases the predicted dihydro-compounds have been isolated except in the case of pyrene and perylene. Even when the dihydro-compound is not the isolated reduction product, MO theory helps to interpret the course of the reduction.

In the case of aromatic compounds, it was previously thought that protons are added more or less simultaneously to the dianion formed by the addition of two electrons to the aromatic ring. Later works[77, 78] showed that the addition of a proton is a stepwise process and the first proton is added to an anion-radical. The acidity of proton donors plays an important role in Birch reduction. An example is the sodium-ammonia reduction of amides. When ammonium acetate is added to the reduction mixture of amides in place of ethanol, aldehydes are formed rather than alcohol[79]. The formation of alcohol from the reduction of amide is ascribed to the ethoxide catalysed decomposition and further reduction of the intermediate aldehyde-ammonia addition compound. Buffering of the medium by use of the more acidic ammonium acetate as proton source avoids this decomposition and the aldehyde-ammonia is converted into the aldehyde during the working up.



$$\begin{tikzcd} \underset{18}{R\,CONH_2} \arrow[r] & \underset{19}{R-\overset{O^-}{C}H.NH_2} \arrow[r, "H^+"] & \underset{20}{R.CH(OH)NH_2} \arrow[r, "NH_4OAc"'] \arrow[d, "\bar{O}Et"] & \underset{21}{RCHO} \\ & & NH_3 + \underset{21}{R.CHO} + \underset{22}{RCH_2OH} & \end{tikzcd}$$

e) Reduction Kinetics

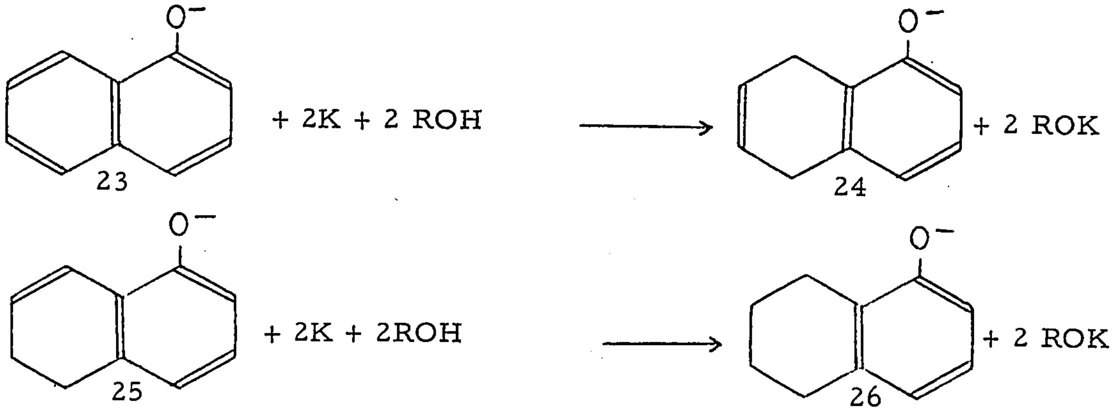
Of the many applications of reductions by metals in ammonia, most of them were concerned with the syntheses rather than the mechanism of the reduction. Most of the investigators employed excess reducing agent and were interested in only qualitative knowledge of the products. Little quantitative data are available on the kinetics of any reduction by an alkali metal in liquid ammonia and few systematic experiments have been carried out to compare the effects of many variables associated with metal-ammonia reductions. Jerome et al.[77] reported for the first time some preliminary experiments which do not show any detailed kinetic measurements but they do show some qualitative effects of certain variables on the reduction reactions-rate. They also showed the effect of these same variables on the competing reaction for alkali metals, the hydrogen liberation. In a solution of electrons (from the metal), proton source and reducible substrate, the substrate competes with the proton source for electrons (equations 1 and 2). Equations 2 and 3 show how the substrate carbanion competes with electrons for the proton source.

$$2e^- + S \longrightarrow S^= \qquad (1)$$

$$2e^- + 2BH \longrightarrow 2B^- + H_2 \qquad (2)$$

$$S^= + 2BH \longrightarrow 2B^- + HSH \qquad (3)$$

The authors determined the total time required to complete the reaction after mixing an ammonia solution of potassium metal with a solution, containing a stoichiometric amount of 1-naphthoxide ion or 5, 6-dihydro-1-naphthoxide ion and a proton source (t-amyl alcohol or ethyl alcohol) with and without certain additives.



$$2K + 2\,ROH \qquad H_2 + 2\,ROK$$

The results obtained are summarized in Table 3. Unless otherwise indicated, all the runs were carried out under nitrogen. The completion of the reaction was determined by the disappearance of the red colour of the anion produced from (23) and (25) with potassium.

TABLE 3

BIRCH REDUCTION OF 1-NAPHTHOXIDE

Run	Initial Molarity of Reactants			Additives	Reaction Time in secs.
	Naphthoxide	Alcohol	Potassium		
1	0.28	-	0.24	-	2600
2	-	0.46	0.24	-	1620
3	0.12	0.46	0.24	-	29
4	0.12	0.37	0.24	-	26
5	0.12	0.34	0.24	-	27
6	0.13	0.46	0.26	Air	22
7	-	0.46	0.26	Air	170
8	0.12	0.37	0.24	0.04 M H_2O	24
9	0.12	0.34	0.24	-	19
10	-	0.34	0.24	-	840
11	-	0.34	0.24	O_2	20
12	0.12	0.34	0.24	O_2	23
13	-	0.34	0.24	Ether	622
14	-	0.34	0.24	Ether + 0.34M EtOK	10600
15	0.12	0.34	0.24	Ether + 0.34M EtOK	17

Lines 2 through 8 represent runs made with t-amyl alcohol and lines 9 - 15 with ethyl alcohol.

The first line in the table shows that the reaction between the substrate and the metal is very slow in the absence of a proton source. The liberation of hydrogen is also very slow from the same quantity of metal and excess of proton source, as shown in line 2. Under the same conditions, when all the three reactants are present, the reduction proceeds much faster (line 3).

Subsequent runs show the effects on reduction and hydrogen liberation of varying the alcohol and its concentration and of the presence of certain additives such as water, oxygen, ether and alkoxide ion. It is apparent that the concentration of excess alcohol does not significantly affect the rate of reduction, as shown by lines 3, 4 and 5. The nature of the alcohol, tertiary (line 3), or primary (line 9) does affect the reduction rate somewhat. The nature of the alcohol has an even greater effect on hydrogen liberation (lines 2 and 10). The effect for both reactions is an acceleration by the primary over the tertiary alcohol. Air has a tremendous effect on the rate of reduction. Both the rate of the reduction and hydrogen liberation increase (lines 6 and 7) when the reaction solution is exposed to air. It was first thought that the moisture in air was responsible for such acceleration in rate for both reduction and hydrogen liberation. However, addition of a small amount of water to the reduction under nitrogen had no appreciable effect (lines 4 and 8). Later on, it was found that oxygen effectively promotes both the hydrogen liberation (lines 10 and 11) and the reduction (lines 9 and 12).

For many reductions it is convenient to add an organic solvent such as ether to the reaction mixture. Ether apparently has no significant effect on the reaction rate, as shown by lines 10, 13 and 9, 15. Alkoxide ion, on the other hand, has a profound effect on the rate of hydrogen liberation (lines 13 and 14). It appears that with sufficient added alkoxide ion the reaction between alcohol and metal can be brought virtually to a halt. However, this same alkoxide ion has no effect on the reduction. Although the evidence is not needed, this divergent action of alkoxide ion on the two reactions is further evidence against the old "nascent hydrogen" theory of reduction. If some prior reaction between proton source and metal produces a "hydrogen" which actually causes reduction, then surely an additive which profoundly affects the rate of formation of hydrogen would also have some effect on the rate of reduction.

The results obtained, using 5, 6-dihydro-1-naphthoxide ion are shown in Table 4.

TABLE 4

BIRCH REDUCTION OF 5, 6-DIHYDRO-1-NAPHTHOXIDE

Initial Molarity of Reactants

	Dihydro-naphthoxide	EtOH	Potassium	Additives	Reaction time in secs.
1.	0.12	0.34	0.24	Ether	3×10^{-3}
2.	0.12	-	0.24	Ether	128
3.	-	0.34	0.24	Ether	622
4.	-	0.34	0.24	Ether + 0.34M EtOK	10,600
5.	0.12	0.34	0.24	Ether + 0.34M EtOK	3×10^{-3}

A stoichiometric amount of 5, 6-dihydronaphthoxide was reduced in less than 3×10^{-3} sec. by the electrons from 0.2M potassium and excess alcohol. For such rapid reduction a proton source is needed (line 2), although the source may liberate hydrogen only slowly (line 3). The presence of alkoxide ion which greatly retards hydrogen liberation (line 4) still has no measured effect on the reduction (line 5).

A possible mechanism for reduction is:

$$\begin{tikzcd}
\underset{27}{:S} \arrow[r, shift left, "e^-"] & \underset{28}{:S\cdot^-} \arrow[l, shift left] \arrow[r, "AH", "\text{fast}"'] & A^- + HS\cdot \arrow[d, "\text{slow}"', "e^-"] \\
& \underset{30}{HSH + A^-} & \underset{29}{HS:^-} \arrow[l, "\text{fast}"', "AH"]
\end{tikzcd}$$

Although this scheme is highly speculative, it is consistent with the findings. Initial acceptance of an electron is rapid and reversible, hence the necessity of a proton source to take the reaction to completion. The uptake of the first proton is irreversible and fast; if it were rate determining or were reversible, then change in the alcohol concentration or addition of excess alkoxide ion should have a significant effect on the reduction rate. The pick up of the second electron is slow and is considered to be the rate determining step, since the presence of a negative charge on the substrate slows the reaction, and the final proton addition is also fast and irreversible.

A. P. Krapcho and Bothner-By[78] tried to determine the order of the reaction of the metal-ammonia-alcohol reduction of benzene and substituted benzene and the effect of proton source on the yield of the reduction products, as well as the nature of metal on routes of reduction. In Table 5, the effectsof variations in the kind and amount of alcohol or acid used as a proton source on the yield of reduced hydrocarbon are shown. All the experiments were done with 2 mols. of lithium, except in experiment (5). The major product in each case is the corresponding dihydro-compound.

TABLE 5

EFFECT OF PROTON SOURCE ON YIELD OF REDUCED HYDROCARBONS

Hydrocarbon	Molar proportion and kind of proton source	Analytical method	Reduction product (dihydro-compound)%
1. Benzene	$2NH_4Cl$	V P C	3
2. Benzene	$2NH_4Cl$	U. V.	2
3. Benzene	$3C_2H_5OH$	V P C	94
4. Benzene	$4C_2H_5OH$	V P C	92
5. Benzene	$1.4C_2H_5OH$	V P C	50
6. Benzene	$5H_2O$	V P C	36
7. Toluene	$2C_2H_5OH$	V P C	88
8. Toluene	Excess H_2O	V P C	28
9. Toluene	$2NH_4Cl$	U. V.	2
10. Toluene	4 i-PrOH	U. V.	96
11. Toluene	4-t-BuOH	U. V.	91

The data show a general trend toward lower yields with more strongly acidic proton source. Ammonium chloride gives very little reduction product when used as a proton source. Water also gives a low yield of dihydro-product. Unlike alcohols, both ammonium chloride and water react rapidly with alkali metals dissolved in liquid ammonia and it seems very probable that this direct reaction competes effectively with the reduction of benzene under the reaction conditions employed.

The main reaction occurring during the reduction of benzene may be represented as follows:

31

13

The concentration of benzene, alkali metal and alcohol may be represented at any time by C, 2C and 2C respectively. One may then assume an equation of the form:

$$-dC/dt = KC^{\alpha}(2C)^{\beta}(2C)^{\gamma} = 2^{\beta+\gamma}KC^{\alpha+\beta+\gamma} \qquad (1)$$

which after integration gives:

$$C^{1-(\alpha+\beta+\gamma)} - C_0^{1-(\alpha+\beta+\gamma)} = (\alpha+\beta+\gamma-1)\,2^{\beta+\gamma}K(t-t_0) \qquad (2)$$

where the subscript zero refers to the concentration at time t_0. It is assumed that a single reaction path predominates and no large concentrations of intermediates or side products occur in this reduction. A plot of $C^{1-(\alpha+\beta+\gamma)}$ against time will give a straight line intercepting the zero-time axis at $C_0^{1-(\alpha+\beta+\gamma)}$. By assuming successively values of

-1, -2, -3 etc. for $1-(\alpha\pm\beta\pm\gamma)$, it can be shown that for the reduction of benzene with lithium and ethanol a good fit for a straight line is obtained in the case of $1-(\alpha+\beta+\gamma) = -2$. The reaction is therefore of third order and the rate law may be expressed as:

$$-d(ArH)/dt = K(ArH)(M)(ROH)$$

where (Aγ H) is the concentration of aromatic hydrocarbon, (M) is the concentration of metal and (ROH) is the concentration of alcohol. The rate law is valid when the concentration of aromatic hydrocarbon is in the range 0.02 - 0.10M. Some kinetic data for the metal-ammonia-alcohol reductions of benzene are given in Table 6.

TABLE 6

THIRD ORDER RATE CONSTANTS FOR METAL-AMMONIA-ALCOHOL REDUCTIONS OF BENZENE

Alkali Metal	Alcohol	Temp. C°	K, l. 2/moles^{2}sec.
Li	t-BuOH	-34	0.10
Li	t-BuOH	-74	0.015
Li	EtOH	-34	1.40
Li	EtOH	-76	0.40
Na	EtOH	-34	0.0064
K	EtOH	-34	0.0015

The relative rates of reduction with lithium, sodium and potassium were found to decrease in that order, reductions with lithium being much faster than with the other two metals. The apparent superiority of lithium over sodium was attributed in large part to its greater reduction potential (-2.99 V) in liquid ammonia, compared to those of sodium (-2.59 V) and potassium (-2.73V). The rate of reduction with ethanol was also found to be greater than that with t-BuOH.

f) Mechanism of Reduction of Benzene and Miscellaneous Applications of the Birch Reduction:

It was suggested by Birch[80] that a reactive intermediate is formed by the transfer of one or two electrons to the aromatic nucleus, giving a radical anion or a dianion, respectively. These intermediates would be very strong bases, and would react very fast with proton donors. Lipkin et al.[81] and Tuttle and Weissman[82] showed that an anion-radical is the most probable intermediate under certain conditions, as shown by E. S. R. studies. A solution of naphthalene in tetrahydrofuran, when allowed to react with sodium, gives a solution which shows electron paramagnetic resonance absorption. A hyperfine splitting of the electron absorption line by the protons of the naphthalene indicates that a single electron is transferred from sodium to naphthalene in such solutions. Addition of naphthalene to the solution broadens the lines, indicating that an exchange process is occurring. The solution of sodium naphthalenide in tetrahydrofuran is green, and it is not possible to alter this colour by the addition of more sodium. The addition of one mole of sodium or lithium per mole of naphthalene in liquid ammonia solutions initially produces a green solution. The further addition of another mole of metal products an orange-red solution, which presumably contains the dianion. T. L. Chu et al.[83] showed that phenanthrene and anthracene anion-radical, formed in tetrahydrofuran in the presence of sodium can be converted into the respective dianion slowly. It seems that at least three factors are important in assessing the probable stability of the anion radical or the dianion in solutions:

1) the resonance possibilities for distributing the charge or charges over the molecule;
2) the specific solvating capacity of the solvent for the anions, and
3) the extent to which the counter ions may be solvated or held in ion-pairs with the negatively charged species.

From the experimental facts, the following mechanism for the reduction of benzene and alkyl benzenes with alkali metal and alcohol in liquid ammonia, seems to be most probable.

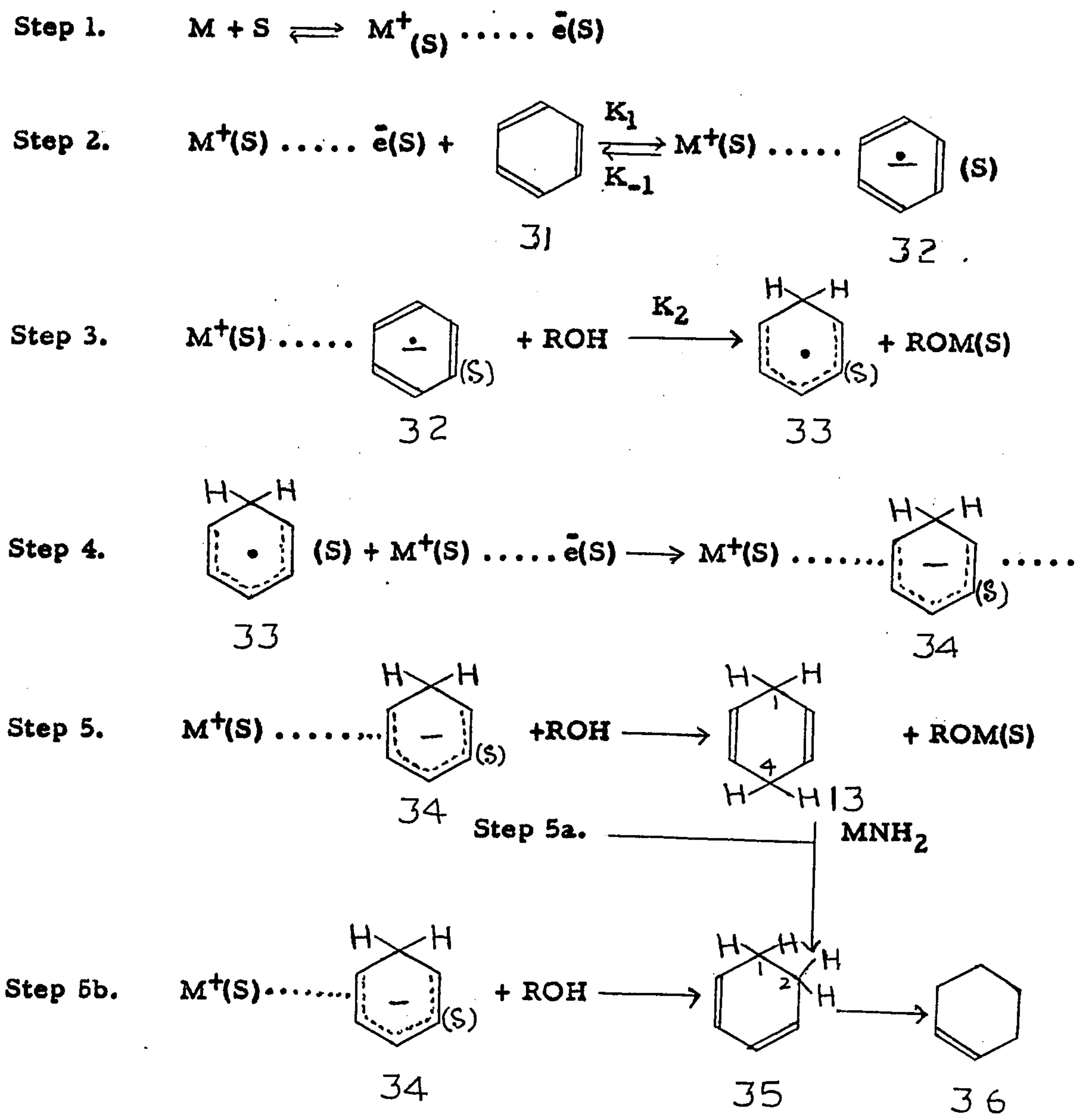
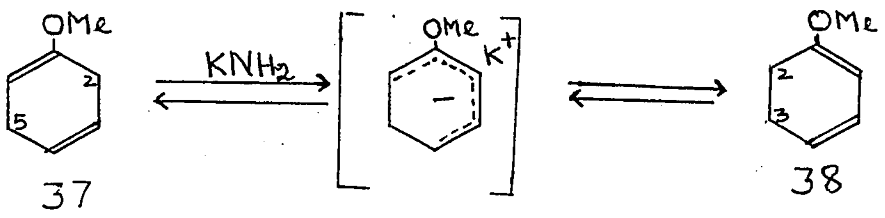


Fig. 9. Probable steps in the reduction of benzene by metal and alcohol in liquid ammonia at -34°C.

In this scheme, solvation by ammonia is represented by the symbol (S). In step 1, the dissolved metal dissociates to form "solvated electrons". In step 2, a reversible equilibrium is set up, in which the electron is transferred to the aromatic ring, and the ion-pair (32) now consists of the solvated metal ion and the solvated anion radical. Step 3 is the rate determining step, in which the anion-radical reacts with a molecule of alcohol to give an alkoxide and a radical intermediate (33). In the following steps this radical acquires an additional electron to give an anion, which then abstracts a proton from either alcohol or solvent to give 1,4-dihydro (13) or the 1,2-dihydro derivative (35).

The formation of 1,4-dihydrobenzene is more probable than the 1,2-dihydro derivative, since the point of highest electron density in the anion (34) is the 4-position with respect to the methylene group. The formation of 1,2-dihydro derivative, more probably takes place by step 5a rather than step 5b. The 1,2-dihydrobenzene is further reduced to cyclohexene (36) very easily, because of the conjugation of the two double bonds in 1,2-dihydro derivative. There are experimental evidences that the 1,4-dihydro derivative is first formed and this in the presence of an alkali metal-amide can be isomerized to 1,2-dihydro derivative. Anisole gives 2,5-dihydroanisole by sodium-liquid ammonia-alcohol reduction and this can be isolated. If a small molecular proportion of potassium amide in ammonia is added to the unconjugated 2,5-dihydroanisole (37), the conjugated 2,3-dihydroanisole (38) results.[80]



Although the mechanism of Fig. 9 accounts satisfactorily for the metal-ammonia-alcohol reductions of simple benzene derivatives, it seems likely that the reduction of polynuclear aromatic hydrocarbons follows a different path. According to some authors[74], polycyclic aromatic hydrocarbon molecules can carry two electrons in liquid ammonia solution. Addition of ammonium salts or alcohols to such a solution gives high yields of dihydro-reduction products, which suggests that the reduction may proceed in this case by the addition of protons to a solvated dianion.

Facile reduction requires the simultaneous presence of alkali metal and proton source in liquid ammonia; reaction here may involve principally the protonation of the mono-anion which is continuously generated[78, 84]. But so far no systematic studies have been done on the mechanism of Birch reduction with polycyclic aromatic hydrocarbons.

The application of Birch reduction is enormous. This particular reduction is not only applicable to aromatic hydrocarbons but can also be employed in heterocyclic compounds such as pyridine, quinoline[85] and thiophene[86]. Another important application of the metal-ammonia reagent is the stereospecific reduction of various $\alpha\beta$-unsaturated ketones[87]. Metal-ammonia-alcohol reductions have also been widely used in the sterols[88] and hormones[89] syntheses and in determining the structure of many natural products, especially of alkaloids[90].

Reduction with Alkali Metals-alkylamines (Modified Birch Reduction)

Mechanism and applications

Solutions of alkali metals particularly of lithium in alkylamines, such as methylamine, ethylamine and propylamine constitute very powerful reducing agents. The amines are generally more powerful solvents for organic compounds than liquid ammonia and have higher boiling points. The use of amines as solvents avoids a serious difficulty often encountered in liquid ammonia reductions, namely the low solubility of the substrate in the solvent system. The higher working temperatures appear to facilitate the initial steps in the reduction and favour the isomerization of the unconjugated dihydro-derivative to a conjugated dihydro-derivative and therefore further reduction of the primary products. For example, metal-ammonia-alcohol reduction of benzene gives the 1,4-dihydro-derivative, whereas lithium-ethylamine reagent gives the conjugated 1,2-dihydro-derivative, which is then rapidly reduced to cyclohexene and cyclohexane.

It is generally believed that the course of the reduction with metal-amine is similar to that with the metal-ammonia reagent, but alkylamine systems offer the practical advantage of greater solvent power and reactivity. Little experimental evidence is available regarding the exact mechanism of the reduction. However, the formation of an organometallic intermediate is strongly suggested by the definite ratio of metal absorbed to aromatic compound, even in the presence of excess metal. This intensely coloured solution, on hydrolysis gives no hydrogen but an extensively reduced hydrocarbon.

a) Reduction of Some Aromatic Hydrocarbons:

Benkeser *et al.*[91] reported the reduction of a few aromatic hydrocarbons by lithium-ethylamine in the absence of a proton source. Benzene was reduced to a mixture of cyclohexene and cyclohexane and naphthalene to a mixture of $\Delta^{9,10}$- and $\Delta^{1,9}$-octalin (50:1). A small amount of decalin was also detected.

TABLE 7

Li-Alkylamine Reduction Products of Some Aromatic Hydrocarbons

Hydrocarbon (mole)	Metal (g. atom)	Solvent	Yield %
Benzene (0.1)	Li (0.7)	$EtNH_2$	Cyclohexene -51 Cyclohexane - 17
Naphthalene (0.1)	Li (1.2)	$EtNH_2$	Octalin - 71 Decalin - 5
Naphthalene (0.1)	Li (1.2)	$MeNH_2$	Octalin - 54 Decalin - 4
Naphthalene (0.1)	Li (0.9)	NH_3	Tetralin - 66
Naphthalene (0.05)	Na (0.45)	$EtNH_2$	Polymeric-materials
Ethyl benzene (0.1)	Li (0.8)	$EtNH_2$	1-Ethylcyclohexene - 25 Ethylcyclohexane - 18

The marked difference between the lithium-amine and sodium-ammonia system is seen clearly by comparing the reduction products obtained from the individual reducing agents. Naphthalene is reduced by the lithium-amine reagent to the isomeric octalin, whereas sodium-ammonia reduces it to tetralin[92]. Similarly biphenyl is reduced by the lithium-amine system to 1-cyclohexylcyclohexene and by sodium-ammonia to 1-phenyl-1-cyclohexene[93].

The above authors later[94] showed that, in the presence of alcohol, the lithium-amine combination can be used quite successfully to form dihydro-aromatics. The yields of the dihydro-compounds are quite comparable to those obtained in Birch reduction.

Reggel et al.[95] replaced the low boiling alkylamines by ethylenediamine (b.p. 117°) and showed that the reduction with this amine is more advantageous. Their results show that the lithium-ethylenediamine system, at 90 - 100°, is a convenient and effective metal-amine combination for carrying out reductions. They were able to reduce phenanthrene to decahydro- and do-decahydrophenanthrenes and anthracene to do-decahydro- and tetradecahydroanthracenes by using lithium-ethylene diamine.

In 1964, Brooks et al.[96] extended the lithium-ethylenediamine combination to other polycyclic hydrocarbons. They carried out the reduction at 90 - 100° and using 100% more lithium than that theoretically required for complete reduction.

TABLE 8

Li-Ethylenediamine Reduction of Some Polycyclic Aromatic Hydrocarbons

Hydrocarbons	Yield %
Diphenyl	Decahydrodiphenyl - 75
Naphthalene	Decalin - 80 Octalin - 20
Phenanthrene	Dodecahydrophenanthrene - 75 Some perhydrophenanthrene.
Chrysene	Dodecahydrochrysene - 50
Pyrene	Very reactive unidentified products
Perylene	Octahydroperylene - 82 Hexadecahydroperylene - 18 Unknown structure.

RESULTS AND DISCUSSION

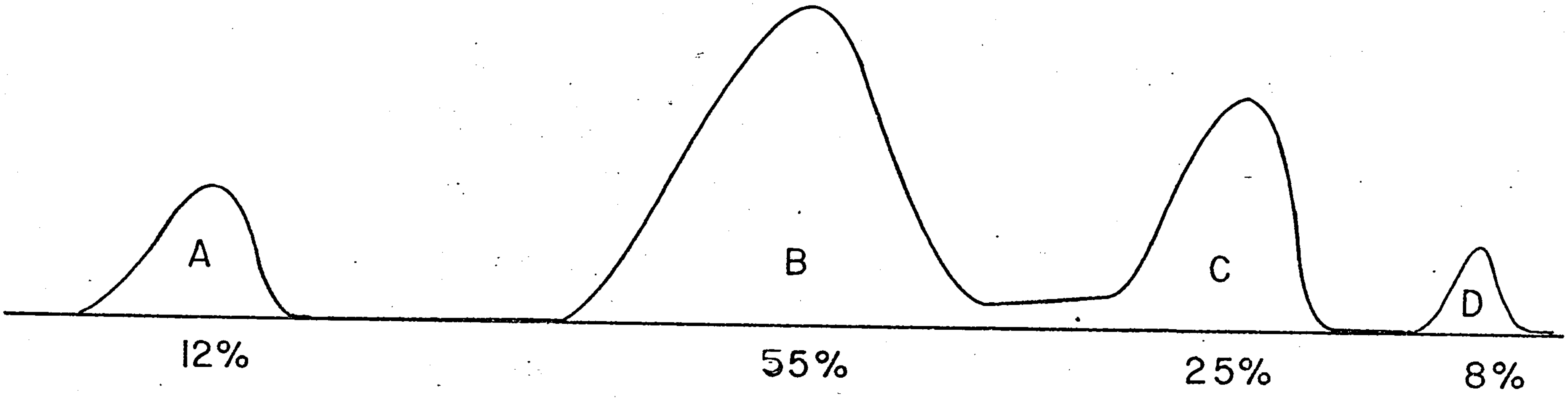
Results of Birch Reduction of Pyrene (Method A)

In 1958, Otto Neunheeffer et al.[3] reported that Birch reduction of pyrene (1) using sodium (4 equivalents)-ethanol-liquid ammonia, yielded 1, 6-dihydro- or 1, 8-dihydropyrene. When we repeated their experiment in supposedly making 1, 6- or 1, 8-dihydropyrene, we observed a reduction product, which had the same reported physical and spectral properties as their product.

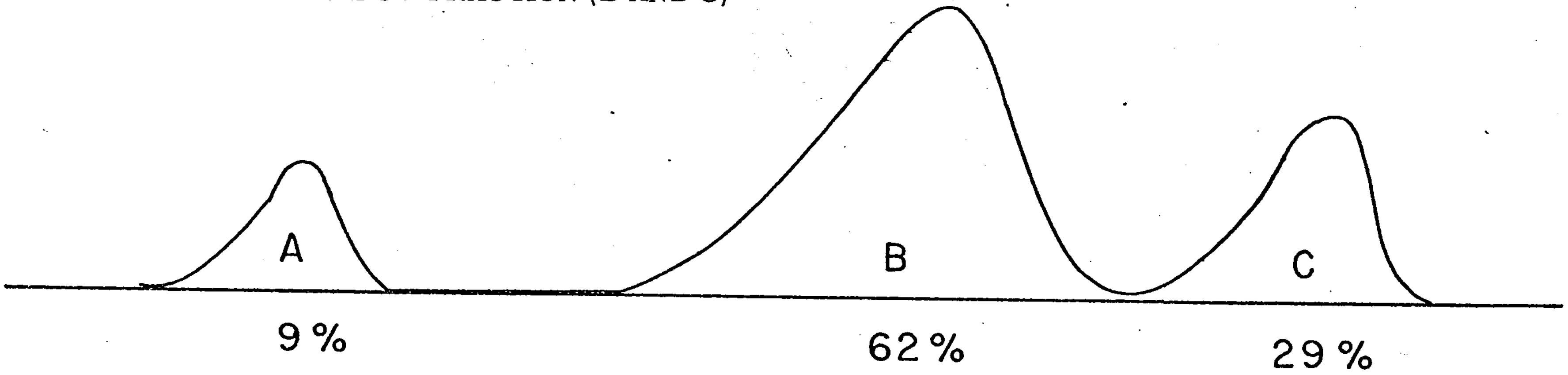
Analysis of the reduction product by VPC indicated that the product was a mixture of four components (Fig. 10). Component 'A" was shown to be pyrene by comparison of the retention time with an original sample of pyrene and by similar thin layer chromatography (TLC) characteristics. The two major components B and C were separated from the other two minor components A and D by column chromatography, but fractions B and C could not be separated from each other. The components B and C, when re-analyzed by VPC, gave three peaks B (62%), C (29%) and A(9%) (Fig. 10), but TLC of column-separated B and C showed no pyrene to be present. Hence by comparing the VPC spectrum of the crude product and that from the fraction (B and C), we concluded that 3% unreacted pyrene was present in the crude reduction product. It was later shown that a high injection block temperature of the chromatograph leads to total decomposition of the fraction (B and C) into pyrene; no other peaks were observed.

FIG. 10

VPC SPECTRUM OF BIRCH REDUCTION PRODUCT (CRUDE) OF PYRENE.

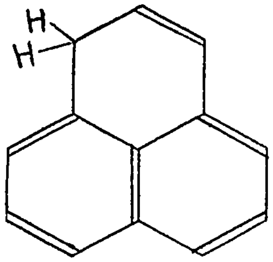


VPC SPECTRUM OF FRACTION (B AND C)



Fraction(B and C)had a mass of 206 (as shown by mass spectrometry), which corresponded to tetrahydropyrene. The crude reduction product showed a minor peak in mass spectrum at 212, besides the major peak at 206, due to tetrahydropyrene. From this evidence, we suspected that the minor component (D) in the reduction product was a decahydropyrene (mass 212). We could not totally separate this decahydropyrene (D) and the unreacted pyrene (A) from the crude reduction product by column chromatography as they were always contaminated with tetrahydropyrenes (B and C). We were able to separate these two components (A and D) by another method, which we will discuss later.

There are numerous possible tetrahydropyrene isomers. Our next aim was to determine the structure of the two tetrahydropyrene isomers (B and C). The two tetrahydropyrene isomers (B and C) are very air-sensitive materials; the pure compounds are white solids which rapidly turn yellow on exposure to air and slowly to a black tar. The isomers (B and C) are capable of giving a stable ionic salt with suitable reagents and also they show an electron spin resonance signal in carbon tetrachloride solution. The e.s.r. spectrum is very similar to that of a neutral radical of phenalene[28](6). Since phenalene(6) is also an air-sensitive hydrocarbon and is capable of giving a cation, anion and neutral radical, we thought that the two tetrahydropyrene isomers (B and C) possessed a phenalene skeleton. The following three isomers of tetrahydropyrene are the only ones having a phenalene skeleton.



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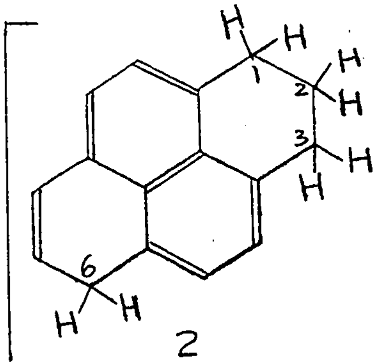

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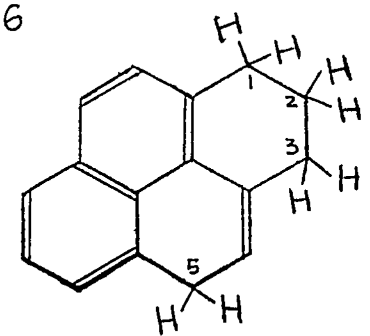

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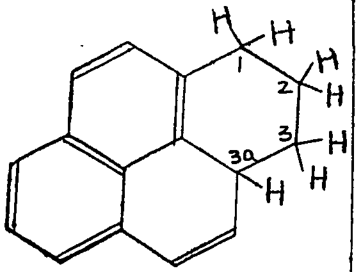

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The I. R. and U. V. spectra of tetrahydropyrenes (B and C) are compared to those of phenalene (Fig. 11 and 12 respectively).

The proton NMR spectrum of tetrahydropyrenes (B and C) in carbon disulfide (Fig. 13) showed three complex multiplets of aliphatic protons centered at 8.15, 7.65 and 7.20 τ (6H), a broad singlet at 6.18 τ (2H), a multiplet at 4.35 τ (1H), two triplets at 3.20 and 3.52 τ (0.70 H) and a multiplet at 3.0 τ (4.3H). Phenalene (6) in carbon disulfide gives a very similar proton NMR spectrum (Fig. 13), a broad singlet at 6.16 τ (2H), a multiplet at 4.18 τ (1H), two triplets at 3.87 and 3.50 τ (1H) and the aromatic protons give a multiplet at 3.0 τ (6H). The isomer (2) has 4 aromatic protons and two vinylic protons, whereas isomer (3) has 5 aromatic and one vinylic protons. Since the integration of the NMR spectrum of the

FIG. 11.

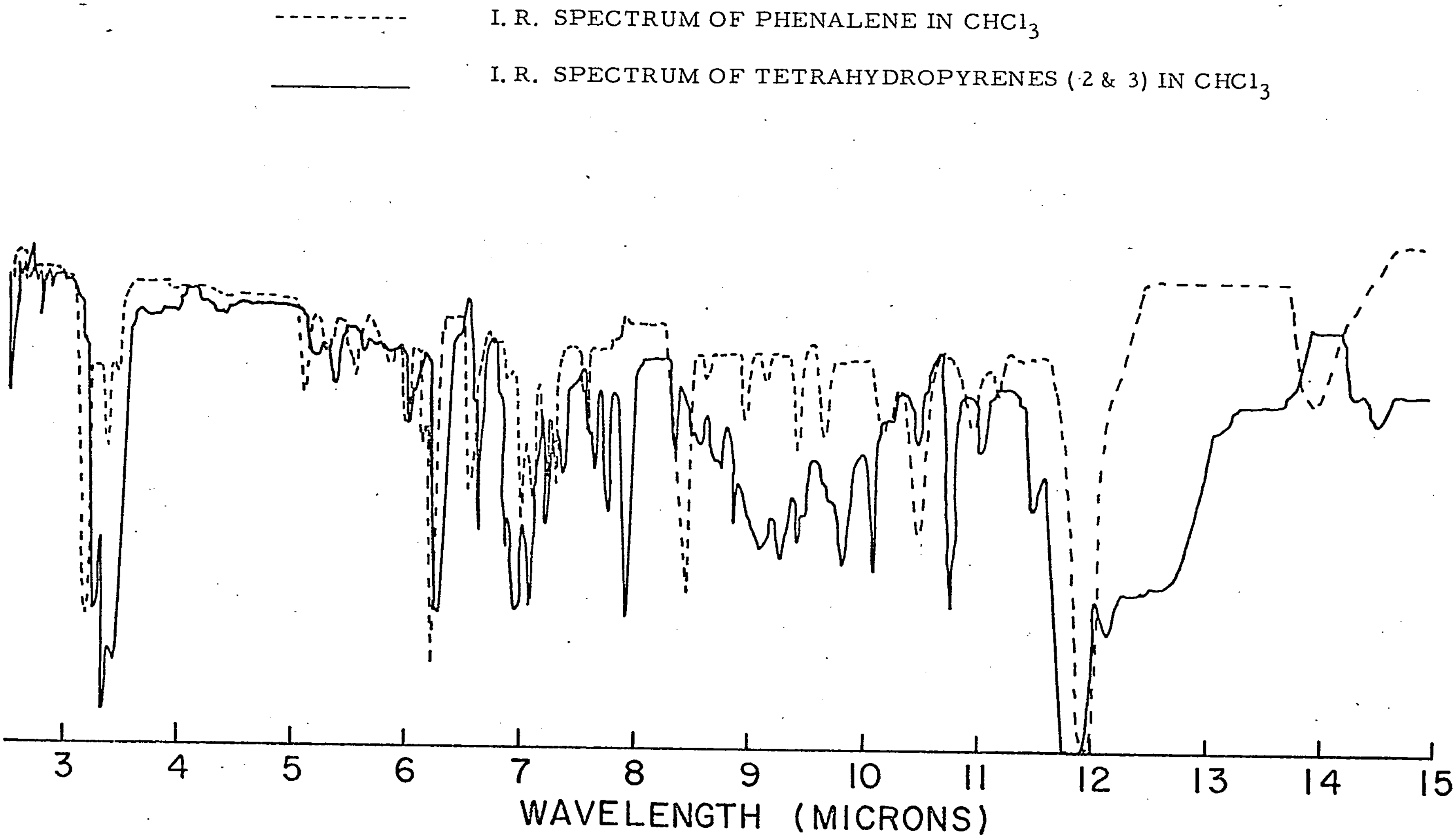
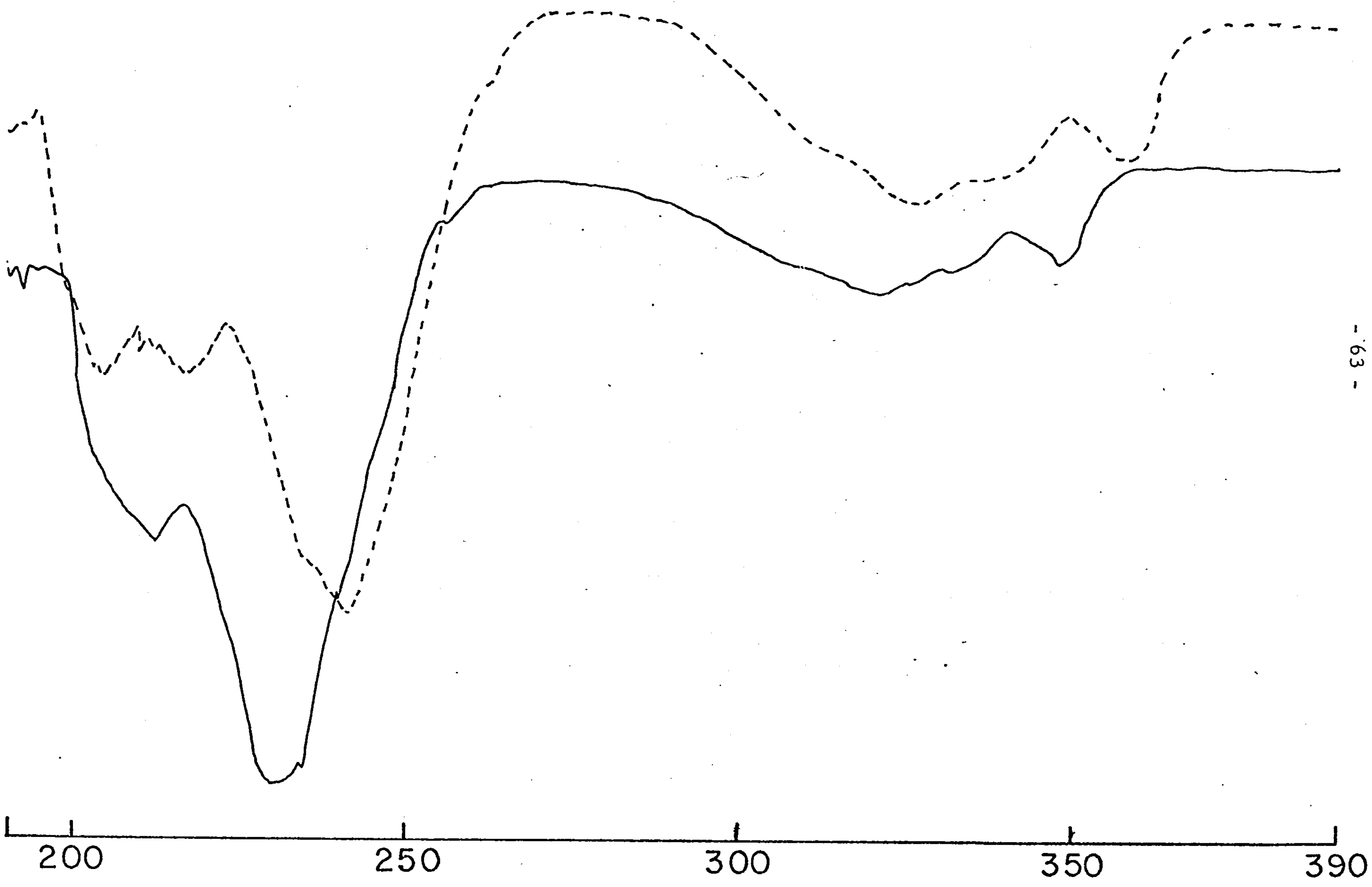

---------- I. R. SPECTRUM OF PHENALENE IN $CHCl_3$
——— I. R. SPECTRUM OF TETRAHYDROPYRENES (2 & 3) IN $CHCl_3$
3
4
5
6
7
8
9
10
11
12
13
14
15
WAVELENGTH (MICRONS)

FIG. 12. ——— U. V. SPECTRUM OF PHENALENE IN CYCLOHEXANE.

------- U. V. SPECTRUM OF TETRAHYDROPYRENES (2 & 3) IN CYCLOHEXANE



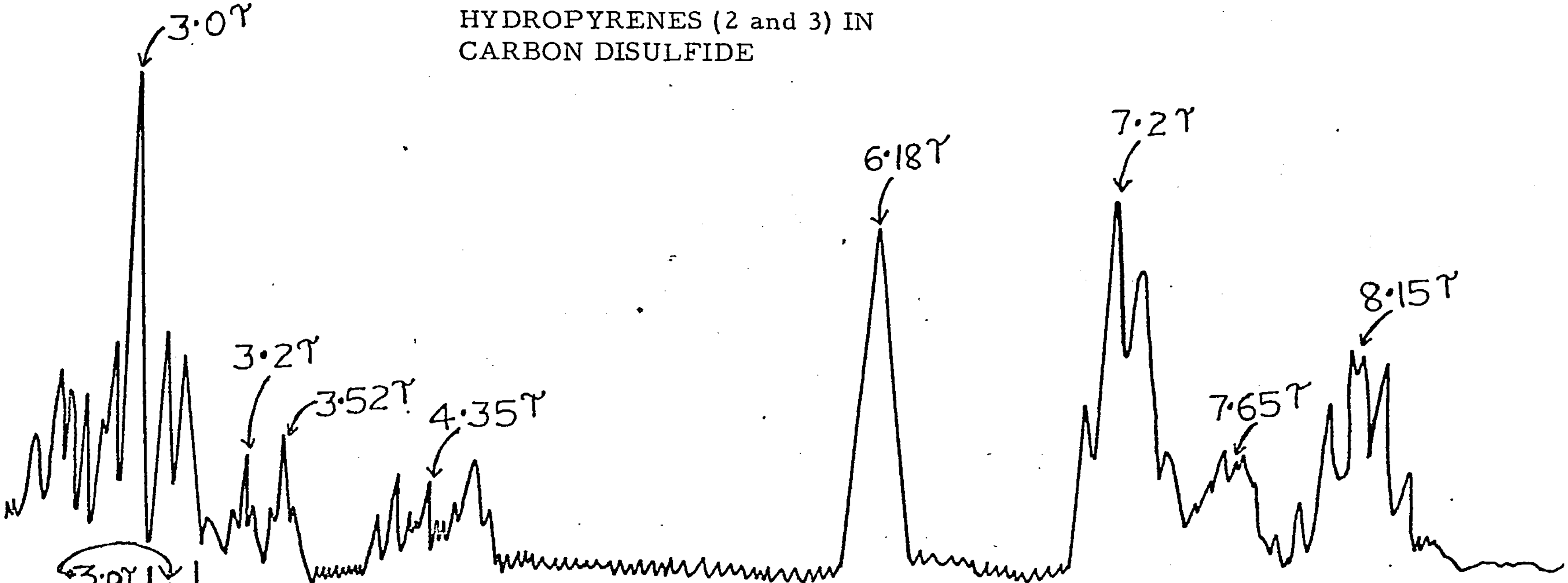


FIG. 13. NMR SPECTRUM OF TETRAHYDROPYRENES (2 and 3) IN CARBON DISULFIDE

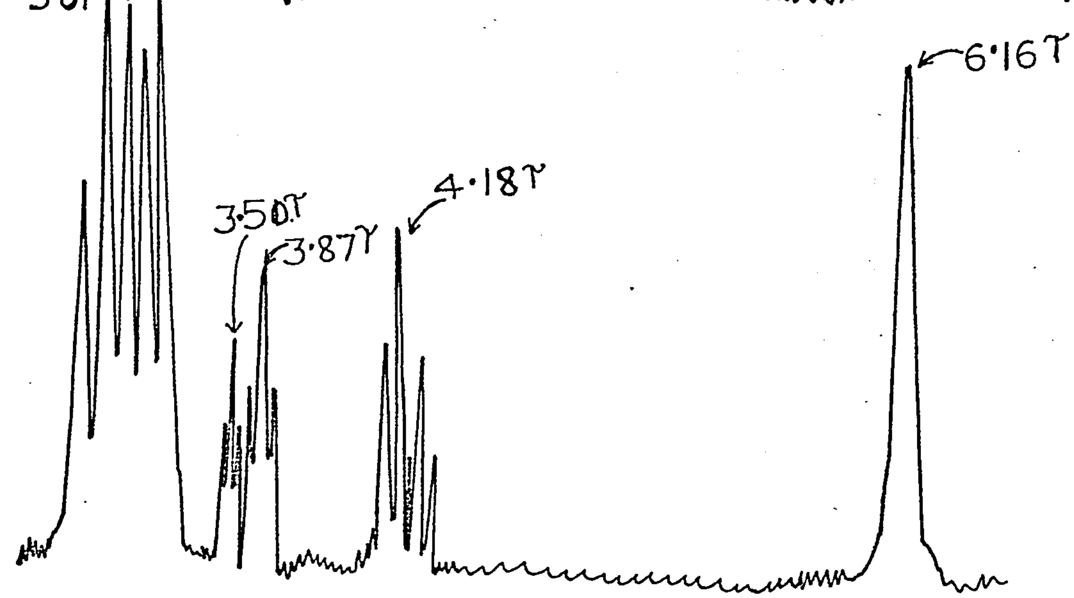


FIG. 13. NMR SPECTRUM OF PHENALENE (6) IN CARBON DISULFIDE.

isomers (B and C) showed 4.3 aromatic and 1.7 vinylic protons, we estimated the mixture of tetrahydropyrenes (B and C) to be composed of approximately 65% 1,2,3,6-tetrahydropyrene (B or 2) and 35% of 1,2,3,5-tetrahydropyrene (C or 3). We believe that 1,2,3,3a-tetrahydropyrene (4) is either absent or present in less than 5% for the following reasons:

a) The 6.18 'CH_2' integration of the proton NMR spectrum gives 2.0 ± 0.1H.

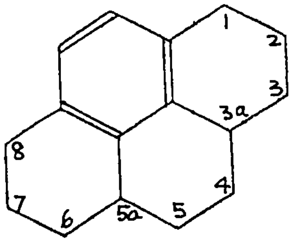
b) There is no absorption for a tertiary aliphatic proton in the proton NMR spectrum. This type of proton has been observed to occur at 6.4τ.

[We observed that 1,2,3,3a,4,5,6,6a-octahydroperylene (98) shows an absorption at 6.4τ for its tertiary aliphatic proton in the proton NMR spectrum.]

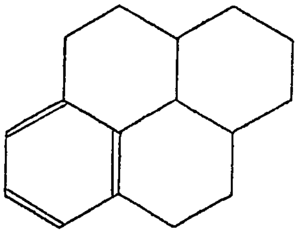
Separation of Decahydropyrene (D or 5) and Unreacted Pyrene (A or I):

Since the two isomeric tetrahydropyrenes (2 and 3) have a phenalene skeleton they should form a perchlorate salt with perchloric acid in the presence of a hydride acceptor such as chloranil[2]. The crude reduction product when treated at room temperature with such reagent in acetic acid did form a perchlorate salt.

The acetic acid mother liquor of the perchlorate salt preparation was diluted with ether and washed with water to free it from acetic acid. Extraction of the ether solution with 10% sodium hydroxide solution separated the hydroquinone from the remaining ether soluble material. The ether layer, after removal of the solvent, gave a mixture of decahydropyrene and unreacted pyrene (1). These two were separated by taking advantage of the fact that pyrene forms a picrate with picric acid in ethanol but not the decahydropyrene. The mother liquor of the pyrene picrate was triturated with petroleum ether (b. p. 30-60°), which dissolved only decahydropyrene. The pyrene picrate was decomposed with aqueous sodium bicarbonate solution and a 3% yield of pyrene (as calculated from the crude reaction product) obtained. The structure of pyrene was confirmed by comparing its mp and I. R. spectrum with that of an authentic pyrene sample. The petroleum ether fraction gave a crude decahydropyrene which was purified by molecular distillation. The pure decahydropyrene showed an apparent peak in mass spectrum at 212 and gave a correct elemental analysis for decahydropyrene. Two isomeric decahydropyrenes (5 and 7) are possible, but VPC and TLC showed evidence for the presence of a single isomer.



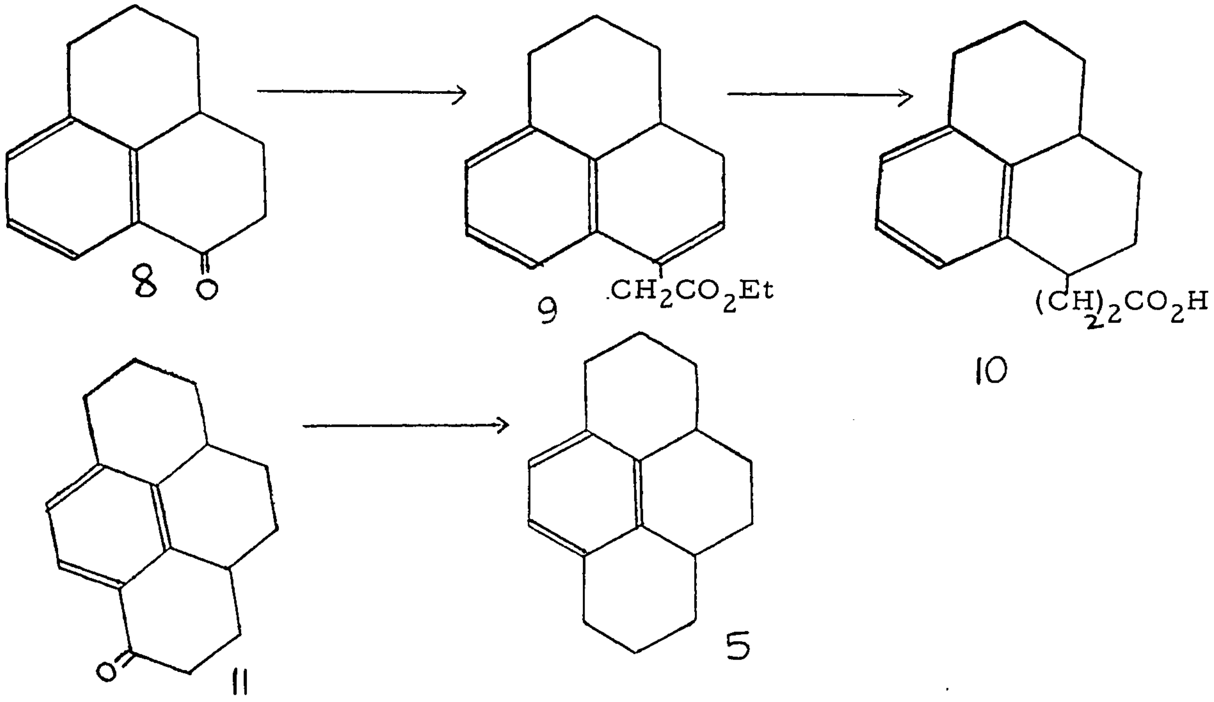
5



7

Both the isomers (5 and 7) are known[97, 98]. Isomer (7) is a needle-shaped white solid, mp 127-129° and the isomer (5) is a white flake-like solid, mp 34° and bp 151-152°/12 mm. The physical constants of our decahydropyrene corresponded well with those of isomer (5). Two isomers (5 and 7) can also be distinguished easily from their NMR spectra. Isomer (5) has only two equivalent aromatic protons and should give rise to a singlet, whereas isomer (7) has three (AB_2 type) aromatic protons and should give rise to a multiplet. Our decahydropyrene showed a singlet in the aromatic region of its proton NMR spectrum at 3.3τ and corresponded to two protons, and the aliphatic part of the spectrum corresponded to 18 protons (Fig. 14). Hence, we concluded portion D to be 1, 2, 3, 3a, 4, 5, 5a, 6, 7, 8-decahydropyrene, as shown in isomer (5).

The synthesis of compound (5) was reported by von Braun et al.[98]. The ketone (8), obtained from α-tetralone was condensed with bromoacetic ester to (9). The isolated double bond was hydrogenated and the $-CH_2CO_2C_2H_5$ group reduced to $-CH_2CH_2OH$. Substitution of the hydroxyl by bromine and reaction with KCN gave the corresponding nitrile which was saponified to the acid (10). Cyclization of the corresponding chloride with $AlCl_3$ yielded keto-decahydropyrene (11). Clemensen reduction of this ketone gave the decahydropyrene (5).



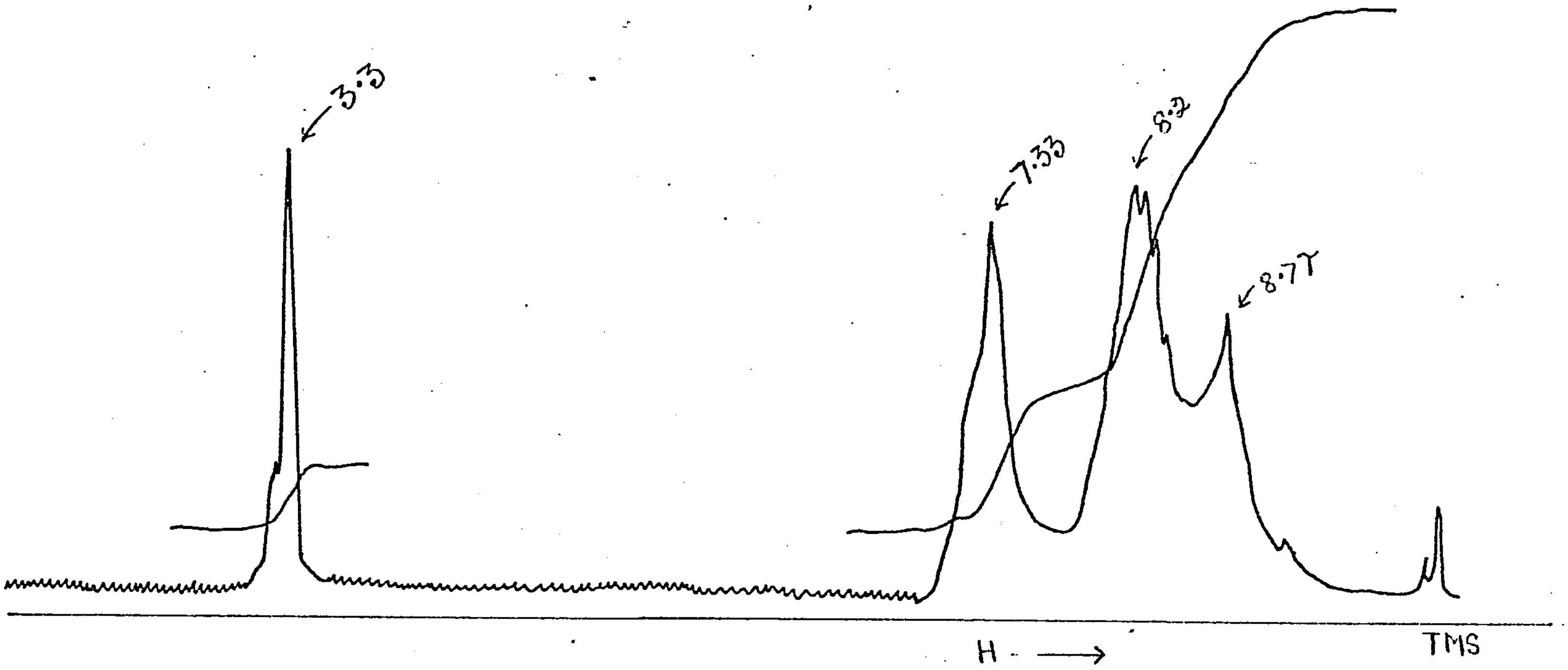
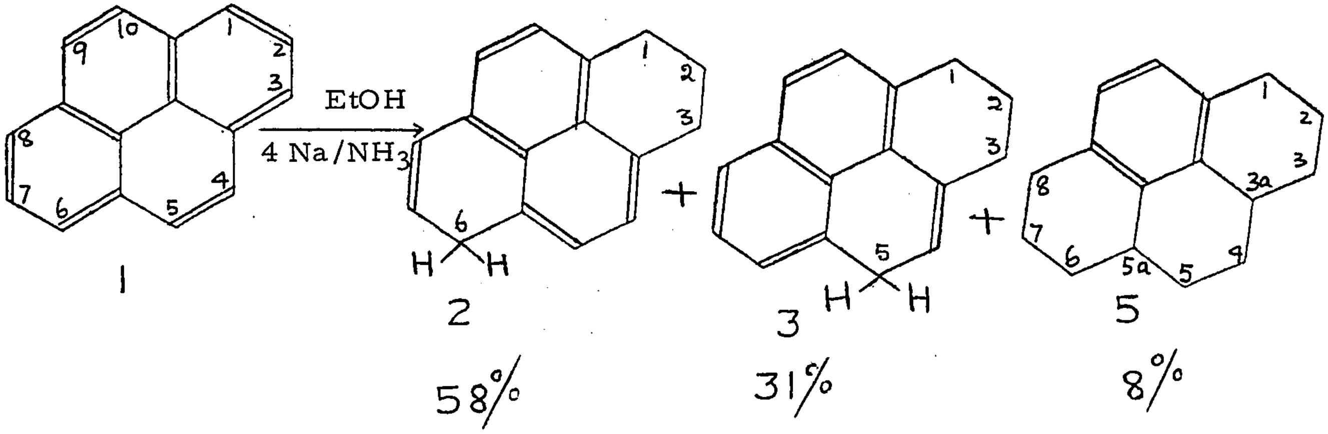


FIG. 14. NMR SPECTRUM OF 1, 2, 3, 3a, 4, 5, 5a, 6, 7, 8-DECAHYDROPYRENE (5) IN DEUTEROCHLOROFORM

After assigning the structure to the tetrahydropyrenes (2) and (3) and decahydropyrene (5), we can now represent the Birch reduction of pyrene according to the following equation:



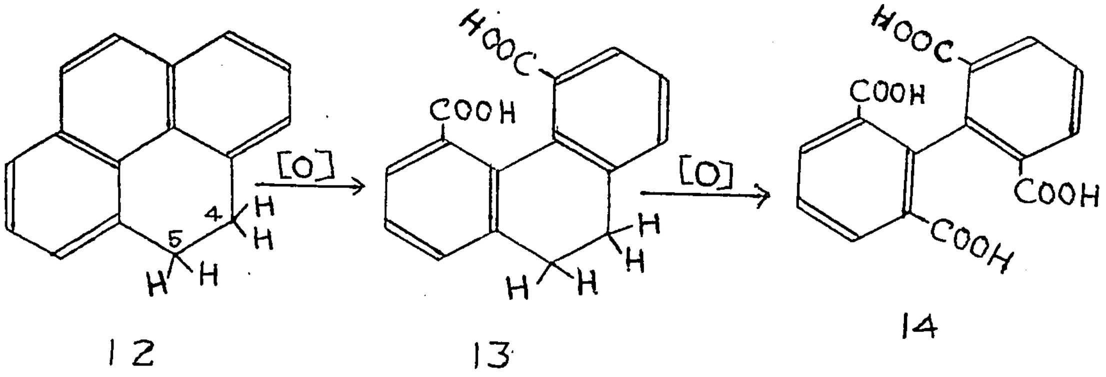
In an attempt to prepare 1, 6- or 1, 8-dihydropyrene, we tried a second reduction experiment with two equivalents of sodium under the same experimental condition as before. In this case we obtained 45% tetrahydropyrenes (2 and 3) in the ratio 2:1 respectively, 2% decahydropyrene (5) and 54% unreacted pyrene (1) as shown by VPC analysis.

<u>Protonation of Pyrene Anion with Ethanol:</u>

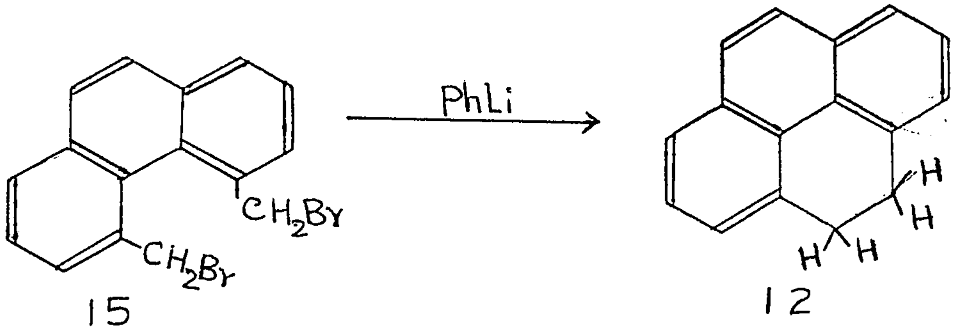
Further attempts were made for the preparation of 1, 6- or 1, 8-dihydropyrene by protonating the pyrene anion with ethanol or water. The pyrene anion was made by stirring (for 4 hr.)

an ethereal solution of pyrene with two equivalents of sodium in liquid ammonia under a nitrogen atmosphere (at - 33°) and in the absence of any proton source. Protonation of the pyrene-anion with ethanol was carried out by adding ethanol to the red anion, after or before the evaporation of ammonia. We found no difference in products, when ethanol was added after the evaporation of ammonia or before the evaporation of ammonia. The ethanol-protonation of pyrene anion showed the following products when analyzed by VPC: unchanged pyrene (1) 55%, tetrahydropyrene isomers (2 and 3) 30% and 4, 5-dihydropyrene (12) 10%; the remaining 5% was an unidentified tarry material. The above products were separated from each other by the following method: The crude product was dissolved in acetic acid (the tarry material did not dissolve). The undissolved tarry material was separated, which turned to brown insoluble solid when treated with petroleum ether. This was not further identified. The acetic acid solution was treated with perchloric acid and chloranil and the two tetrahydropyrene isomers (2 and 3) were separated as their perchlorate salt. This perchlorate salt was identical with an authentic sample, prepared from pure tetrahydropyrenes (2 and 3) and also this perchlorate salt gave the hydrocarbons, tetrahydropyrenes (2 and 3) back on reduction with lithium aluminum hydride. The mother liquor of the perchlorate salt contained unreacted pyrene (1) and 4, 5-dihydropyrene (12). Both pyrene and 4, 5-dihydropyrene form picrate with picric acid in ethanol but pyrene picrate is insoluble in ethanol, whereas the 4, 5-dihydropyrene picrate is soluble. Hence pyrene picrate can be separated by filtration and the mother liquor, containing the 4, 5-dihydropyrene picrate was decomposed by aqueous sodium bicarbonate solution into the free hydrocarbon (12). The compound, thus obtained, was shown to be a dihydropyrene as shown from its mass spectrum (mass 204). That this dihydropyrene was the 4, 5-dihydropyrene has been confirmed by comparing its mp with the reported[99] mp for that compound as well as from its NMR spectrum. The NMR spectrum of the dihydropyrene (12) gave a singlet at 6.75 τ (4H) and a multiplet at 2.5 τ (8H), (Fig. 15).

The constitution of 4, 5-dihydropyrene (12) was established by oxidation of (12) with hydrogen peroxide in acetic acid[100], which yielded a 9, 10-dihydrophenanthrene-4, 5-dicarboxylic acid (13). The acid (13) on potassium permanganate oxidation gave diphenyl-tetracarboxylic acid (14).



4, 5-Dihydropyrene (12) has also been synthesized by Marvel and Wilson[99] from the phenanthrene derivative (15), which was cyclized to 4, 5-dihydropyrene (12) by phenyl lithium.



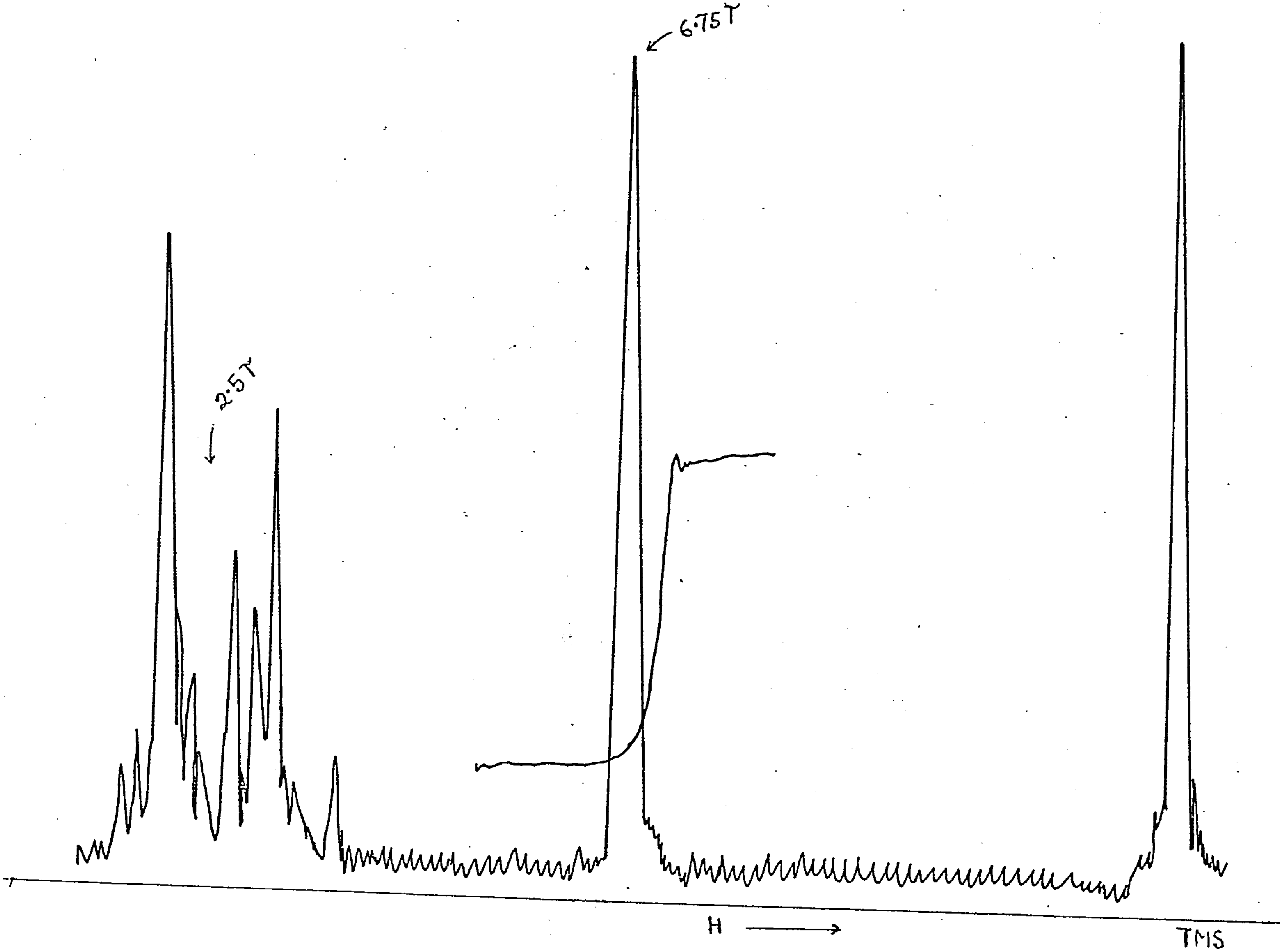
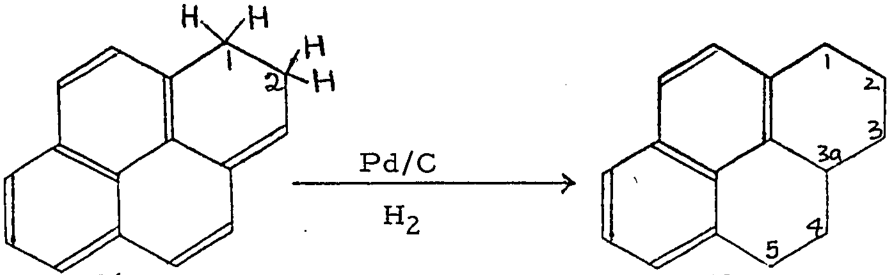


FIG. 15. NMR SPECTRUM OF 4, 5-DIHYDROPYRENE (12) IN CARBON TETRACHLORIDE

The protonation experiment was repeated, using t-BuOH as a proton source, but we observed the same product as in the protonation experiment with ethanol.

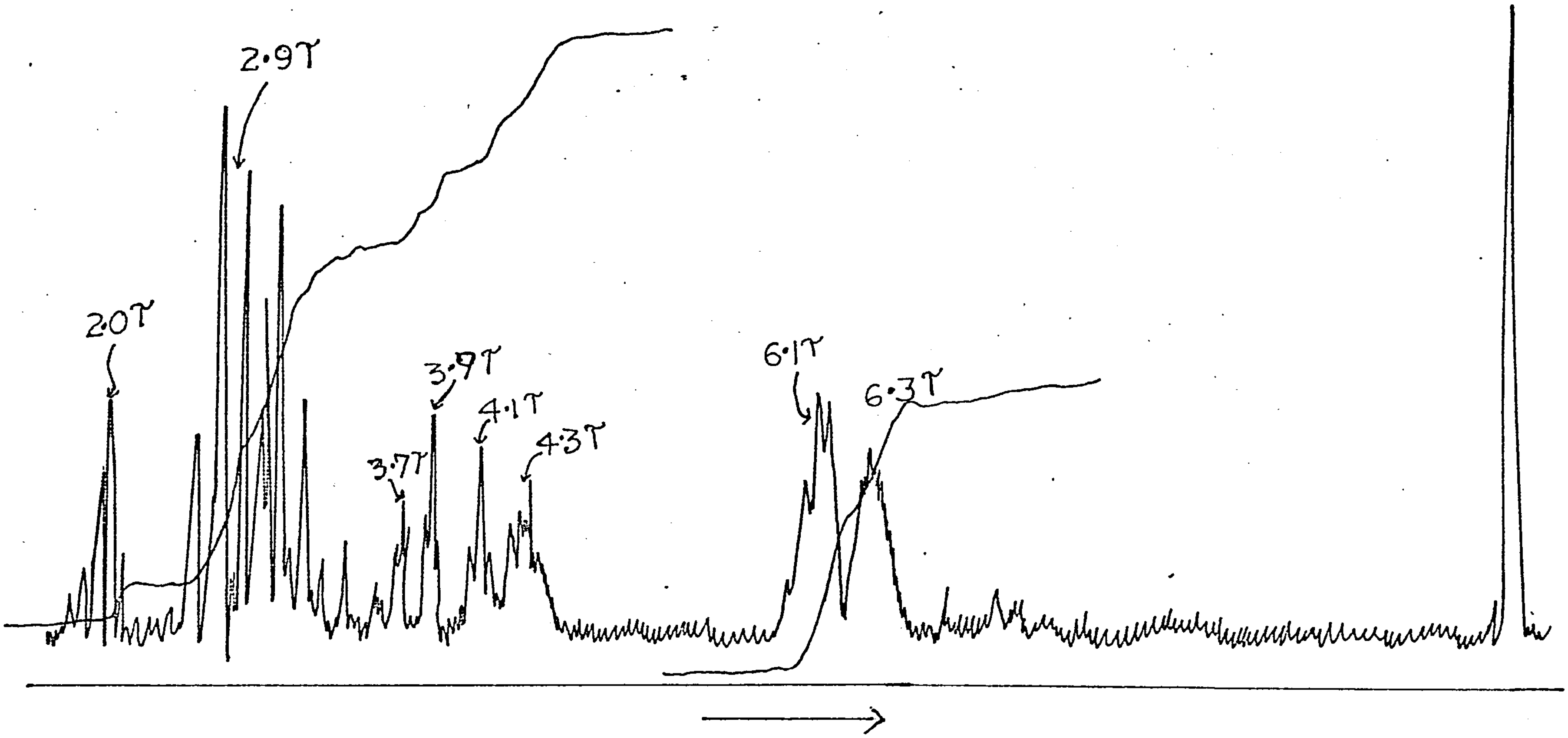
Protonation of Pyrene Anion with Water:

The protonation of pyrene anion with water gave 55% 1,2-dihydropyrene (16), 5% 4,5-dihydropyrene (12) and the balance was unreacted pyrene. 1,2-Dihydropyrene was separated from pyrene and 4,5-dihydropyrene by fractional crystallisation from ethanol. The structure of 1,2-dihydropyrene was established from its mass spectrum (mass 204) and NMR spectrum. The NMR spectrum of 1,2-dihydropyrene (16) showed two multiplets at 6.3 and 6.1τ (4H), two triplets at 3.7 and 3.9 τ (1H), a multiplet at4.3τ,(t) at 4.1 τ (2H) and the aromatic protons were centered at 2.9 τ (m, 5H) (Fig. 16). The confirmation of the structure of 1,2-dihydropyrene also came from the hydrogenation experiment. On hydrogenation with 5% Pd/C under one atmospheric pressure of hydrogen, 1,2-dihydropyrene took two moles of hydrogen, giving 1,2,3,3a,4,5-hexahydropyrene (17), identical with an authentic sample.

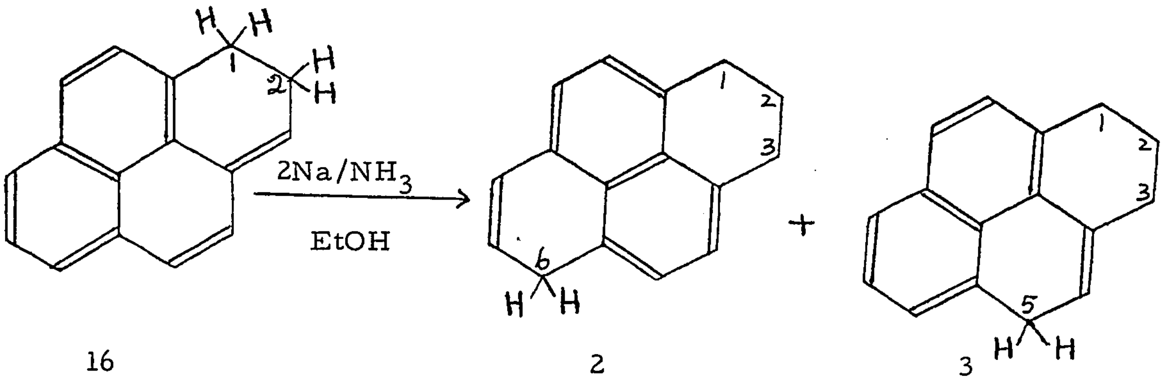


16 18

FIG. 16. NMR SPECTRUM OF 1, 2-DIHYDROPYRENE (16) IN CARBON TETRACHLORIDE. [MINOR PEAK AT 2.0τ IS DUE TO PYRENE]



Birch reduction of 1, 2-dihydropyrene (16) with two equivalents of sodium-ethanol-liquid ammonia, yielded tetrahydropyrene isomers (2 and 3), identical with an authentic sample.



16 2 3

The protonation of pyrene anion (prepared from pyrene with two equivalents of sodium in boiling THF) with water also gave the same 1, 2-dihydropyrene (16) 40%, 4, 5-dihydropyrene 5% (12) and the rest was unchanged pyrene.

Methylation of Pyrene Anion:

We carried out a methylation experiment on the pyrene anion (generated in liquid ammonia with two equivalents of sodium in the absence of ethanol). The red anion of pyrene was methylated with methyl iodide. The product was composed of 60% mono-methylated dihydro-pyrene and 40% unreacted pyrene, separated by column chromatography over alumina. Dehydrogenation of this methylated product with Pd/C, yielded two isomers of monomethyl pyrene, 4, -methyl pyrene and 2-methyl pyrene in the ratio 3:1 respectively. The two monomethylpyrenes were identical to those obtained from the dehydrogenation of methylated tetrahydropyrene, which in turn was obtained by the methylation of tetrahydropyrene-anion with methyl iodide. The NMR spectra and the other evidence regarding the structure of two monomethyl-pyrenes will be discussed later.

Birch Reduction of Pyrene (Method B):

J. D. Brooks et al.[96] reported that the reduction of pyrene in ethylene diamine with 16 equivalents of lithium at 90-100° gave a highly reactive unidentified hydrocarbon. They further reported that the reduced product of pyrene thus obtained was very air sensitive and decomposed to tar on exposure to air. From the reported reactiveness of the reduced hydrocarbon we suspected it to be our tetrahydropyrenes (2 and 3), obtained from the Birch reduction of pyrene. Accordingly, we repeated their experiment with 8 equivalents of lithium under the same experimental condition. The product thus obtained was identical to tetrahydropyrene isomers (2 and 3) in all respects. No decahydro or unreacted pyrene was detected in this reduction.

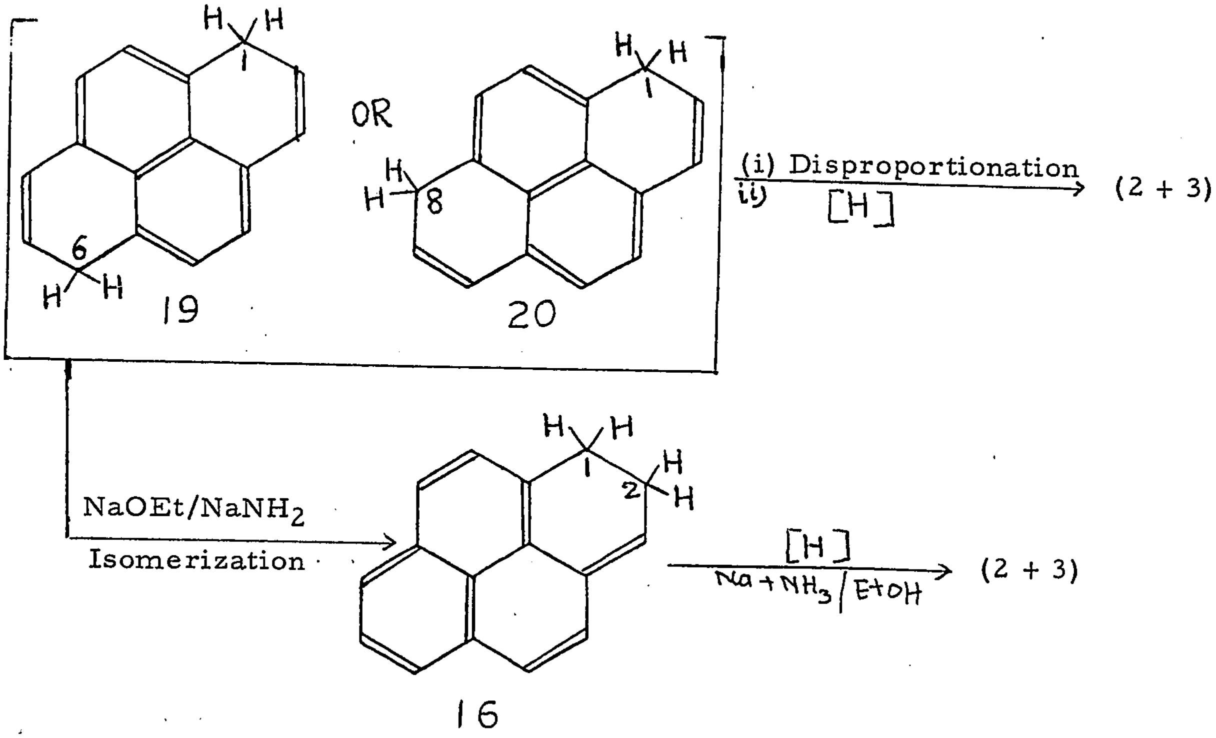
Discussion on the Birch Reduction of Pyrene

The absence of 1, 6- or 1, 8-dihydropyrene under Birch reduction conditions leads us to examine the possible reasons for the non-existence of these compounds under the conditions employed.

(i) 1, 6- or 1, 8-Dihydropyrene may be unstable under the reaction conditions, i. e. it or its anion may disproportionate to tetrahydropyrenes (2 and 3) and pyrene.

(ii) A second possibility is that it is subject to selective reduction, i. e. the oxidation potential of 1, 6- or 1, 8-dihydropyrene (19 or 20) is less than that of pyrene and hence it is preferentially reduced under the reaction conditions employed.

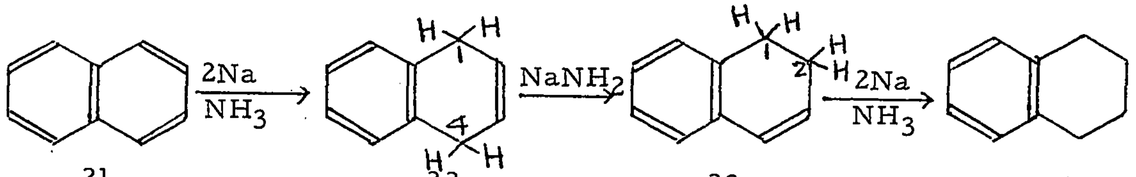
(iii) According to HMO calculations[76] 1, 6- or 1, 8-dihydropyrene should be the first formed product which then may isomerize to a more conjugated 1, 2-dihydropyrene in the presence of a strong base like sodamide or sodium ethoxide and once it is conjugated, further reduction becomes very facile.



G. J. Hoijtink[101] predicted that 1, 2-dihydropyrene (16) on further reduction would give rise to possibly the three tetrahydropyrene isomers (2, 3 and 4).

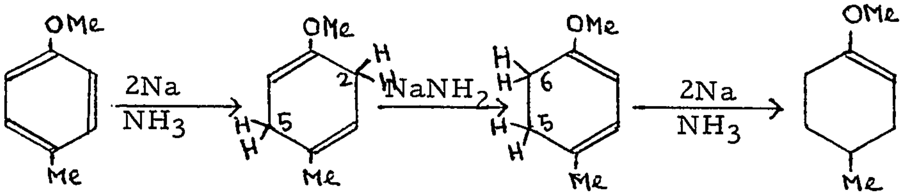
In a separate experiment we reduced 1, 2-dihydropyrene (16) under Birch condition (i. e. sodium + ethanol + liquid NH_3) into tetrahydropyrene isomers (2 and 3) in 95% recovered yield.

There is evidence that the first product in the Birch reduction of an aromatic hydrocarbon is a kinetically controlled less stable unconjugated dihydro-compound. This isomerizes to a thermodynamically more stable conjugated dihydro-compound in the presence of a base and once it is conjugated, further reduction becomes facile. For example, naphthalene[62, 63] first gives an isolable 1, 4-dihydronaphthalene (22), but which in the presence of excess of metal amide rearranges to the conjugated 1, 2-dihydronaphthalene (23). The 1, 2-dihydro compound (23) can be easily reduced to tetralin (24) by sodium in liquid ammonia.



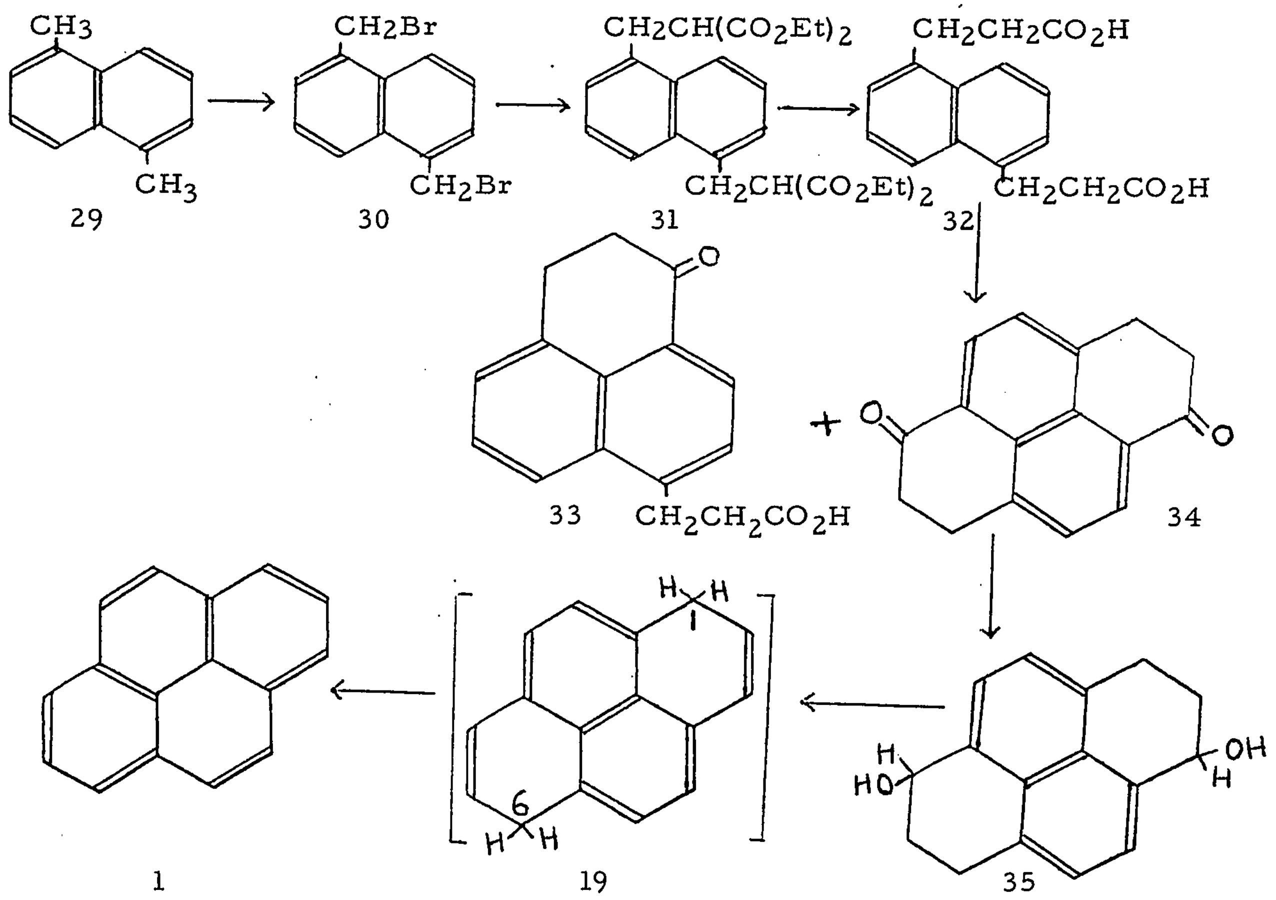
21 22 23 24

Another example is the reduction of p-tolyl-methyl ether[102](25). Unconjugated 2, 5-dihydro-derivative (26) can be converted to conjugated 5, 6-dihydro derivative (27) by the action of sodium amide and then reduced to cyclohexene derivative (28) by the action of sodium in ammonia.



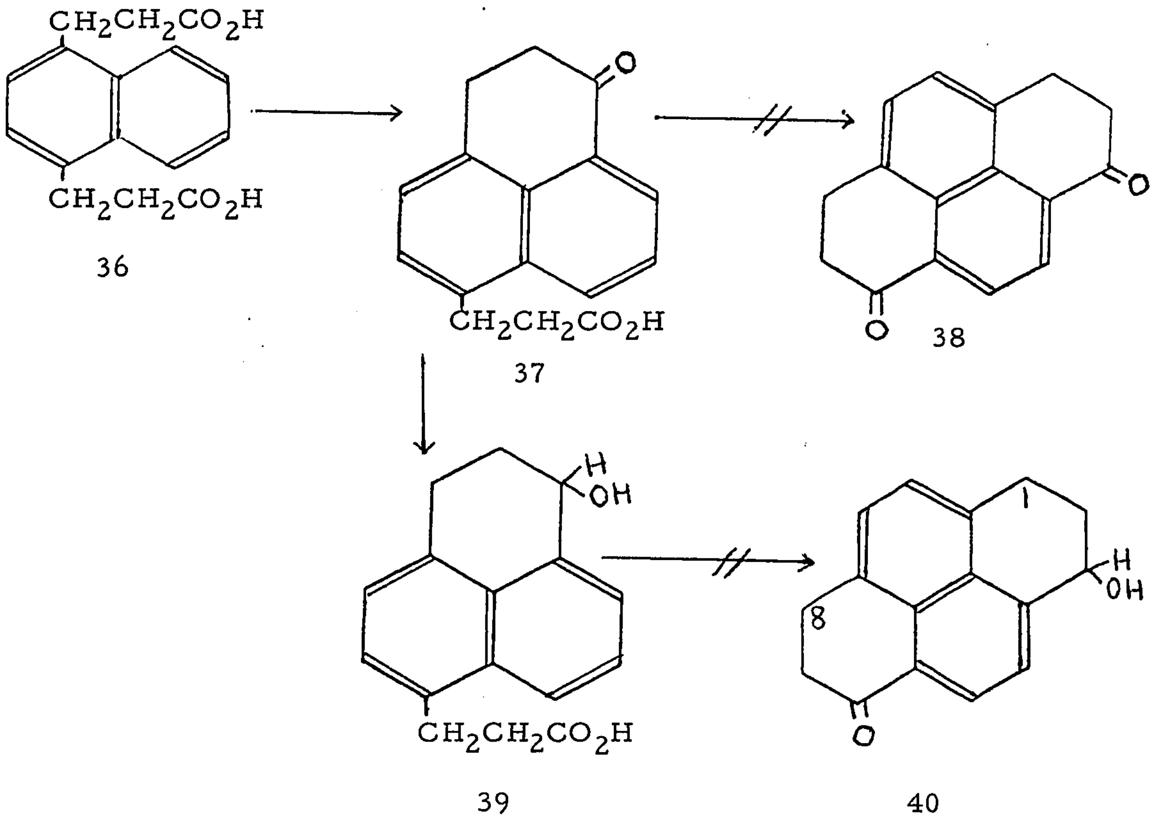
25 26 27 28

The instability of 1, 6- or 1, 8-dihydropyrene was demonstrated by Marvel and Wilson[99]. They tried to synthesize 1, 6- and 1, 8-dihydropyrenes but were unsuccessful. The following series of reactions was selected for the synthesis of 1, 6-dihydropyrene (19).



Conversion of diketone (34) to the dihydroxy compound (35) went smoothly. Dehydration of (35) was expected to yield the desired 1, 6-dihydropyrene (19) but instead only pyrene was isolated in 90% yield.

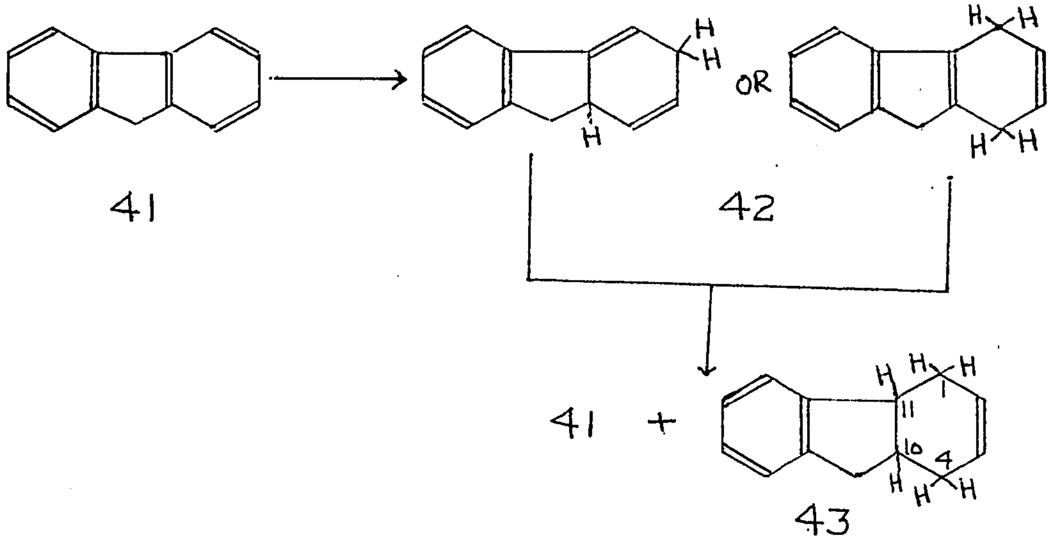
Attempted synthesis of 1, 8-dihydropyrene (20) by Marvel and Wilson:



The keto-acid (37) could not be cyclized to the diketone (38). The keto-acid (37) was reduced to the known alcohol-acid (39), but all attempts to cyclize (39) to the tetracyclic ketone (40) failed.

As already shown, when we used two equivalents of sodium instead of four in the Birch reduction of pyrene, we did not isolate any dihydropyrene but instead we isolated about 45% of tetrahydropyrene isomers (2 and 3). This result can be compared to the reduction of benzene and substituted benzene derivatives[78]. Using one equivalent of alkali metal, approximately

50% of 1, 4-dihydro-derivatives were obtained. There is no available mechanism for such results except experimental facts. But it is known that unstable mono-hydro or dihydro-derivatives can sometimes disproportionate into a stable dihydro- or tetrahydro-derivative respectively, together with the formation of the parent compound. For example, fluorene[103] with two equivalents of sodium in liquid ammonia, in the absence of a proton source, gives a dihydrofluorene of unknown structure (42). During its purification by the distillation, this dihydro-compound disproportionates to 1, 4, 10, 11-tetrahydrofluorene (43) and fluorene (41).



G. J. Hoijtink and Velthorst[104] in a recent paper, proposed, on the basis of experimental and thermodynamic calculations, that the carbanion MH^- (M = aromatic hydrocarbon) derived from the dinegative ion M^{2-} disproportionates to various products:

$$M \xrightarrow[\text{THF}]{\text{2Na}} M^{2-} \qquad (1)$$

$$M^{2-} + H^{+}\ (\text{steryl alcohol}) \rightleftharpoons MH^{-} \qquad (2)$$

$$2MH^{-} \rightleftharpoons MH_2 + M^{2-} \qquad (3)$$

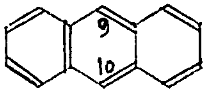
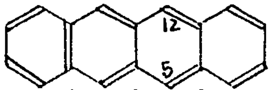
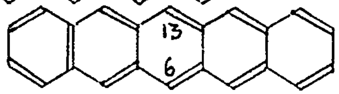
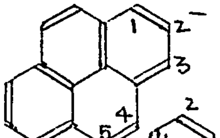
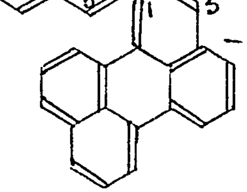
$$2MH^{-} \rightleftharpoons MH_2^{-} + M^{-} \qquad (4)$$

$$2MH^{-} \rightleftharpoons MH_2^{2-} + M \qquad (5)$$

Estimated equilibrium constants for disproportionations for various MH^{-} ions are given in Table 9.

TABLE 9

ESTIMATED EQUILIBRIUM CONSTANTS FOR DISPROPORTIONATIONS

Aromatic Hydrocarbons	Carbon Atom (to which a proton is attached) MH$^-$	MH$_2$	$2MH^- \rightleftarrows MH_2 + M^{2-}$ log K$_1$	$2MH^- \rightleftarrows MH_2^- + M^-$ log K$_2$	$2MH^- \rightleftarrows MH_2^{2-} + M$ log K$_3$
	9	9, 10	- 11	- 27	- 60
	5	5, 12	+ 1	- 5	- 26
	6	6, 13	+ 6	- 7	- 31
	4	4, 5	- 3	0	- 12
	1	1, 2	- 12	4	+ 6
	1	1, 2	+ 1	+ 6	- 2
	3	2, 3	- 3	+ 11	+ 13

From Table 9 it is seen that anthracene-H⁻ is stable towards disproportionation. Tetracene-H⁻ and pentacene-H⁻ disproportionate to give the dinegative ion of the original aromatic molecule, M^{2-} and a dihydroproduct MH_2. Pyrene-H⁻ and perylene-H⁻ disproportionate, giving the original molecule M and the dinegative ion of a dihydro-product, MH_2^{2-}, which in the presence of a proton source would give tetrahydro-product. On the basis of their calculations, Hoijtink and Velthorst proposed that the pyrene-H_2^{2-} ion was that of the 1, 2-dihydropyrene. They had no experimental proof to support their prediction.

Krapcho and Bothner-By[78] suggested that simple monocyclic aromatic hydrocarbons undergo Birch reduction in the presence of a proton source, according to the following scheme:

$$\mathrm{Ar} \xrightleftharpoons[-e]{e} \mathrm{Ar}^{\dot{-}} \xrightarrow{H^+} \mathrm{ArH}\cdot \xrightarrow{e} \mathrm{ArH}^- \xrightarrow{H^+} \mathrm{ArH}_2$$

In the case of polycyclic aromatic hydrocarbons, the Birch reduction may proceed either through radical-anion intermediate as above or possibly via the dianion[76] :

$$\begin{tikzcd}
\mathrm{Ar} \arrow[r, shift left, "e"] & \mathrm{Ar}^{\dot{-}} \arrow[l, shift left, "-e"] \arrow[r, "H^+"] \arrow[d, shift right, "e"'] & \mathrm{ArH}\cdot \arrow[d, shift left, "e"] & \\
& \mathrm{Ar}^{=} \arrow[u, shift right, "-e"'] \arrow[r, "H^+"] & \mathrm{ArH}^- \arrow[u, shift left, "-e"] \arrow[r, "H^+"] & \mathrm{ArH}_2
\end{tikzcd}$$

Streitwieser[76] suggested that in the absence of a proton source (i. e. protonation of the anion at the end of the reaction), the reduction may well be with the dianion, whereas in simultaneous presence of alkali metal and proton source in liquid ammonia, the reaction may proceed via the protonation of radical-anion which is continuously generated in the reaction.

According to the scheme of Hoijtink[104], just presented, the carbanion ArH^- can undergo disproportionation to give rise to ArH_2^{2-}.

$$\begin{tikzcd} 2ArH^- \arrow[r] & ArH_2^{2-} + Ar \arrow[d, "2H^+"] \\ & ArH_4 \end{tikzcd}$$

Although the reaction conditions under which Hoijtink observed the disproportionation of pyrene H^- and those of the Birch reduction are not alike, it is now apparent that the formation of the tetrahydropyrene isomers by such a mechanism must be considered. In our protonation experiment on pyrene anion with ethanol and water, we observed different products. Protonation of pyrene anion with ethanol or t-BuOH gave 30% tetrahydropyrenes (2 and 3), 10% 4, 5-dihydropyrene (12) and the rest was unchanged pyrene (1), whereas protonation with water yielded 55% 1, 2-dihydropyrene (16), 5% 4, 5-dihydropyrene (12) and the balance was unchanged pyrene.

The role of the different proton source cannot be accounted for without extensive studies in this particular field. In order to do that, first of all one should know the type of reacting species involved (Ar^- , $Ar^=$, ArH^-) in the protonation reaction and for this an extensive examination of the physical and chemical properties of the reacting species will be needed. The methylation experiment showed only mono-methylation, which suggested the possibility of the presence of mono-anion. Boekelheide et al.[105] also reported that methylation of pyrene anion (prepared from pyrene with sodium in boiling 1,2-dimethoxyethane) afforded a mono-methylpyrene. Under such extreme conditions, one can expect the formation of pyrene dianion, but no dimethyl derivative of pyrene was reported by those authors. So in the absence of knowledge of the type of reacting species, we cannot predict the role of the protonating agents in the protonation of pyrene anion. But the following are the possibilities:

A) $\mathrm{py}^{=} \xrightarrow{H_2O} \mathrm{pyH_2}$ (≈55% 1,2-dihydropyrene and ≈5% 4,5-dihydropyrene)

B) $\mathrm{py}^{=} \xrightarrow{EtOH} \mathrm{pyH_2}$ (10% 4,5-dihydropyrene)

or

$$\begin{tikzcd} \mathrm{py}^{=} \arrow[d, "EtOH"'] \arrow[dr, "EtOH"] & & & \\ \left[1,2\text{-}\mathrm{pyH_2}\right] \arrow[r, "^{-}OEt"] & \mathrm{pyH^-}\ ;\ 2\mathrm{pyH^-} \arrow[r] & \mathrm{pyH_2^{-2}} \arrow[d, "2H^+"] & +\ \mathrm{py} \\ & & \mathrm{pyH_4} & \end{tikzcd}$$

C)

$$\begin{tikzcd} \mathrm{py}^{\dot{-}} \arrow[r, "NH_3"'] & \mathrm{pyH}\cdot \arrow[r, "py^{-}"] \arrow[d, "e"] & \mathrm{pyH^-} + \mathrm{py} \\ & \mathrm{pyH^-} & \end{tikzcd}$$

$$\mathrm{pyH^-} \xrightarrow{H_2O} 4,5\text{-}\mathrm{pyH_2} + 1,2\text{-}\mathrm{pyH_2}$$

$$\begin{tikzcd} 4\ \mathrm{pyH^-} \arrow[r, "EtOH"] \arrow[dr, "^{-}OEt"'] & \left[1,2\text{-}\mathrm{pyH_2}\right] \arrow[d, "^{-}OEt"] & +\ 4,5\text{-}\mathrm{pyH_2} \\ & \mathrm{pyH_4} + \mathrm{py} & \end{tikzcd}$$

We observed two interesting facts in these protonation experiments:

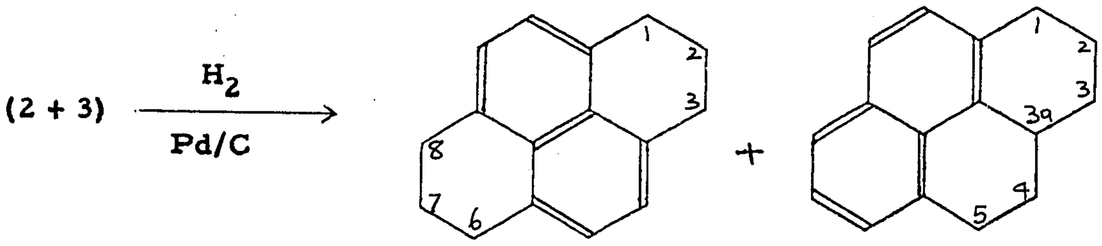
(i) Protonation of red pyrene anion with water destroys the red colour of the anion in 1-2 minutes, whereas the red colour persists after protonation of the same anion with ethanol or t-BuOH;

(ii) 1, 2-Dihydropyrene when treated with dry sodium ethoxide, disproportionates to tetrahydropyrenes (2 and 3) and pyrene.

These two observations suggest that water may protonate the dianion or monoanion directly to the 1, 2-dihydropyrene, which is stable under the experimental conditions. Ethanol may convert py = to pyH$^-$ or the 1, 2-dihydropyrene formed as an intermediate product, is converted to pyH$^-$ in the presence of ethoxide, and pyH$^-$ then slowly disproportionates to tetrahydropyrene and pyrene. The presence of the red anion colour even after the protonation with ethanol and the absence of 1, 2-dihydropyrene in ethanol-protonation experiment support the above possibilities.

Hydrogenation of 1, 2, 3, 6- and 1, 2, 3, 5-Tetrahydropyrenes (2 and 3)

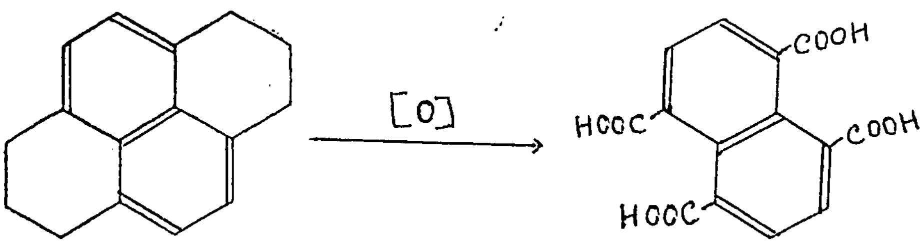
The hydrogenation of tetrahydropyrene isomers (2 and 3) in ethanol or in cyclohexane in the presence of 5% Pd/c under one atmospheric pressure of hydrogen yielded two hexahydropyrene isomers in the ratio 3:1, as shown by VPC analysis. The two hexahydropyrene isomers were separated by fractional crystallization from ethanol or by picrate method; the picrate of minor isomer is insoluble in ethanol and the major isomer does not form picrate in ethanol. By comparing the melting points of the two isomers with the reported melting points[106, 107], the major isomer was found to be 1, 2, 3, 6, 7, 8-hexahydropyrene (17) and the minor isomer 1, 2, 3, 3a, 4, 5-hexahydropyrene (18).



17 18

The structures of the two isomeric hexahydropyrenes (17 and 18) were also confirmed from their respective NMR spectrum. The isomer (17) gave a triplet at 6.9τ (8H), a multiplet at 7.9τ (4H) and a singlet at 2.98τ (4H) (Fig. 17). The isomer (18) showed two multiplets at 8.2 and 7.2τ (11H) and a multiplet at 2.7τ (5H), (Fig. 18).

The structures of the two hexahydropyrenes were also established by Cook[106] and Hewett. The isomer (17) gave naphthalene tetracarboxylic acid (44) on oxidation with permanganate but the isomer (18) was unaffected under the same condition.



17 44

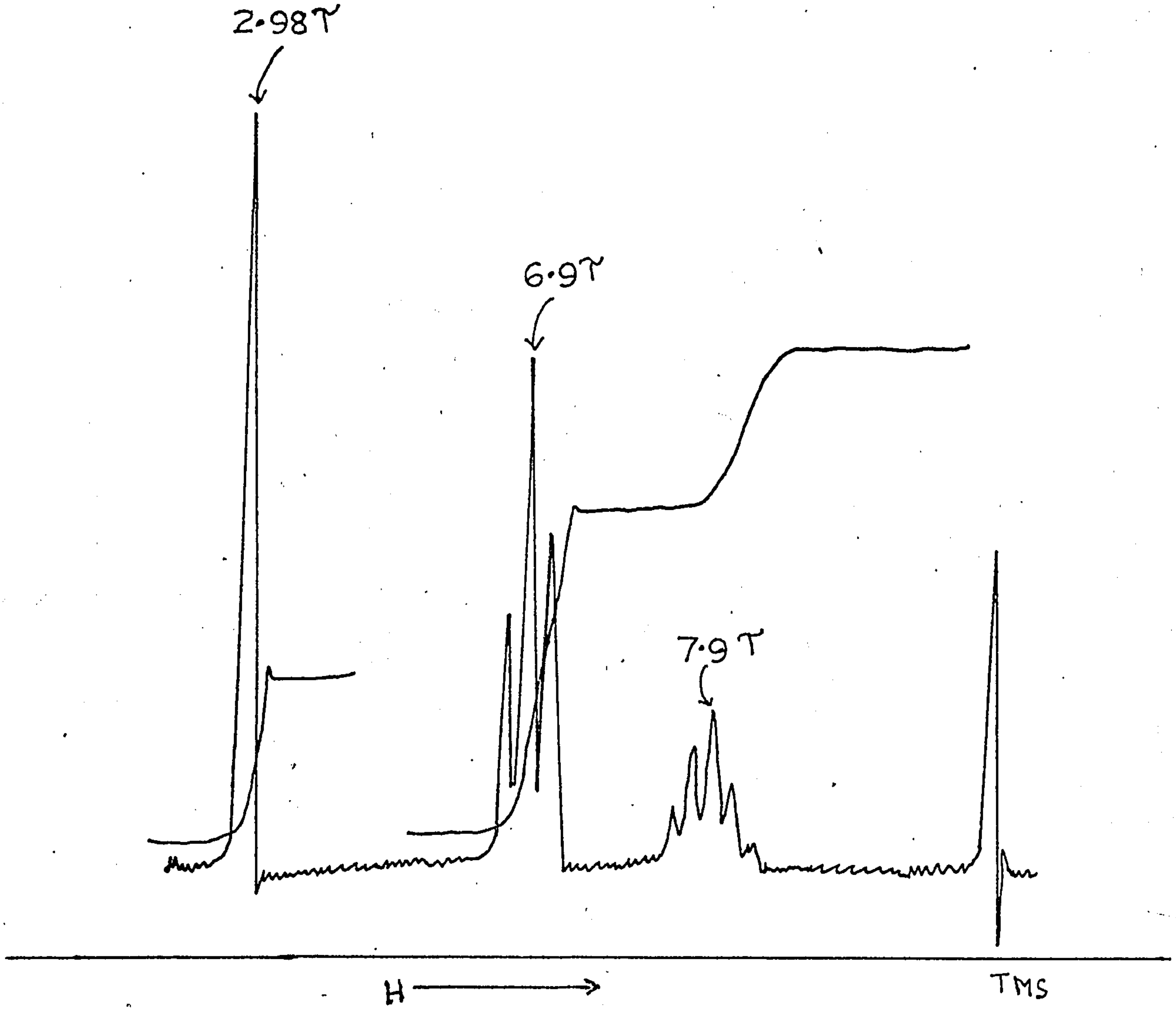
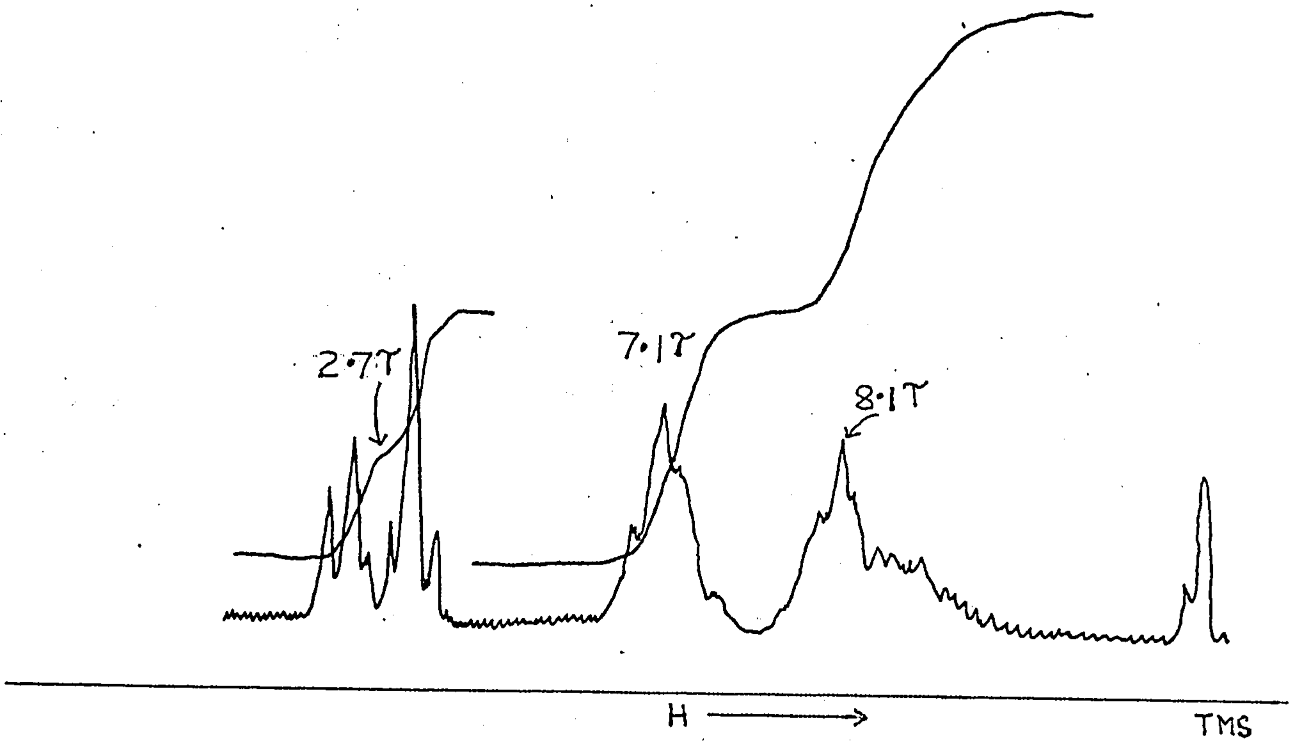


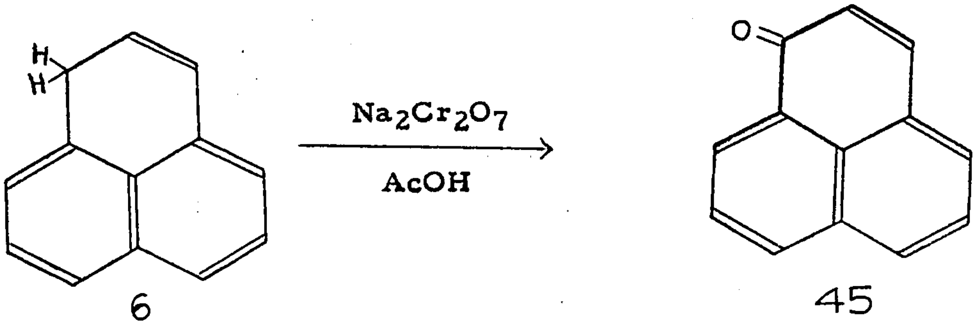
FIG. 17. NMR SPECTRUM OF 1, 2, 3, 6, 7, 8-HEXAHYDROPYRENE (17) IN CARBON TETRACHLORIDE

FIG. 18. NMR SPECTRUM OF 1, 2, 3, 3a, 4, 5-HEXAHYDROPYRENE (18) IN CARBON DISULFIDE

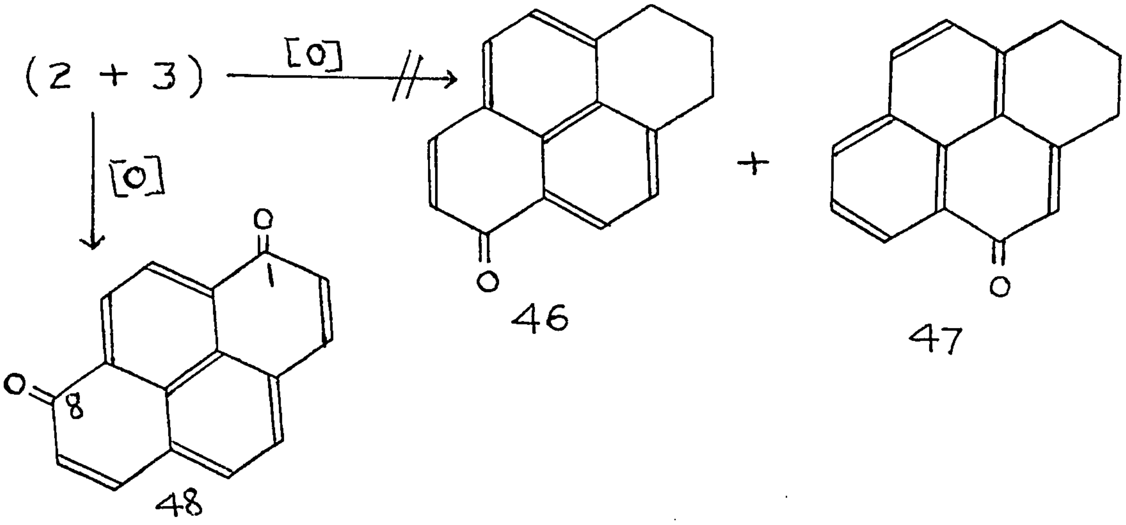


Oxidation of Tetrahydropyrenes (2 and 3)

Boekelheide and Larrabee[1] reported that phenalene (6) on oxidation with sodium dichromate in acetic acid at 100° gave phenalen—1-one (45)



We applied this procedure for the oxidation of tetrahydropyrenes (2 and 3) and expected that we would get two ketones (46) and (47) corresponding to two tetrahydropyrenes (2 and 3), but instead we obtained only 10% of 1,8-pyrene quinone (48) and the rest was an insoluble chromium complex. When the oxidation was attempted with sodium dichromate in acetic acid in the presence of conc. sulfuric acid, we obtained 30% of 1,8-pyrene quinone (48) and the rest was chromium complex. In neither case was the ketone (46) or (47) isolated.



The chromium complex was extremely paramagnetic and only soluble in DMSO. In anhydrous acetic acid or in acetic anhydride, incomplete reduction of chromium (VI) is sometimes observed and brown insoluble complexes of chromium (III), chromium (VI) and chromium acetate are known to be formed in these cases[108].

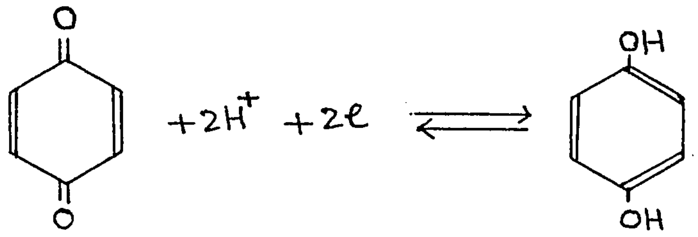
The structure of pyrene quinone (48) was confirmed from its I.R. spectrum and comparing its mp with the reported[109] mp for that particular quinone. Oxidation of pyrene itself gives the 1,8- and 1,6-quinones; the former is the major isomer (≈ 80%), mp 270° and the second is minor isomer (≈ 20%), mp 309°. The 1,6-quinone was synthesized[107] by the oxidation of 1,6-diaminopyrene whose constitution was known. The other quinone was thus obviously the 1,8-isomer.

The attempted oxidation of tetrahydropyrenes (2 and 3) with various oxidizing agents yielded no isolable products. Tarry materials isolated from these oxidations showed two carbonyl peaks at 1637 cm^{-1} and 1665 cm^{-1} in I.R. (hopefully of ketone [46] and [47] respectively). The carbonyl absorption for phenalen-1-one (45) in I.R. appears at 1637 cm^{-1}. The white tetrahydropyrene isomers (2 and 3) turn yellow when exposed to air and finally are oxidized to black tar. These air-oxidized products also showed the same two carbonyl absorptions at 1637 cm^{-1} and 1665 cm^{-1} in I.R. We were unable to isolate these carbonyl containing materials.

1, 2, 3-Trihydropyrenium Salts

The method of synthesis chosen for the preparation of 1, 2, 3-trihydropyrenium salts was identical to that employed by D. H. Reid[2] for the preparation of phenalenium salts. His method of synthesis involves the apparent transfer of a hydride ion from phenalene to quinone in the presence of a suitable acid. Reaction is best carried out in acetic acid or acetonitrile with stoichiometric amounts of the hydrocarbon and the quinone in the presence of an excess of the acid. In the present work chloranil (2, 3, 5, 6-tetrachloro-1, 4-benzoquinone) was used as a hydride acceptor.

The reduction of quinone to quinol may be represented as follows:



The hydride abstracting power of quinones increases with increasing redox-potential. Electron-withdrawing substituents such as chloro-, raise the potential, shifting the above equilibrium to the right, whereas electron-donating groups such as methyl- have the opposite effect. The following quinones were proved to be very useful: tetrachloro-1, 2-benzoquinone, $E^{o} \gtrsim 0.87$ V; 2, 3-dichloro-5, 6-dicyano-1, 4-benzoquinone (DDQ), $E^{o} \gtrsim 1.0$ V, and chloranil, $E^{o} \gtrsim 0.71$V.

E. A. Braude et al.[110, 111, 112] proposed that the dehydrogenation of 1,4-dihydronaphthalene by quinone in polar solvents may be rationalised by a two-step heterolytic mechanism involving a rate-determining transfer of a hydrogen atom with its pair of bonding electrons from the hydrocarbon to the quinone, followed by rapid proton transfer between the resulting conjugate acid of the aromatic hydrocarbon and the quinol anion. The mechanism via radical was discarded because radical producing agents such as light or benzoyl peroxide were without any influence on the reaction rate and no coupling products derived from the hydrocarbon were obtained.

$$\underset{51}{RH_2 + Q} \xrightarrow{\text{Slow}} \underset{52}{RH^+ + QH^-} \xrightarrow{\text{Fast}} \underset{53}{R + QH_2} \qquad (1)$$

Recently Trost[113] proposed that the first step in such dehydrogenation reactions is the hydride transfer from the hydrocarbon to the quinone but the transfer of the second hydrogen from the conjugate acid of the hydrocarbon to the quinol anion goes via a classical carbonium ion intermediate.

Acids generally catalyse these reactions and the catalysis by acids is ascribed to the formation of the conjugate acid of the quinone, i.e. the quinol cation QH^+, which has an even higher affinity for anionoid hydrogen than the quionone.

$$Q + HX \xrightarrow{\text{Fast}} QH^+ X^- \qquad (2)$$

$$RH_2 + QH^+ \xrightarrow{\text{Slow}} RH^+ + QH_2 \qquad (3)$$

$$RH^+ + X^- \xrightarrow{\text{Fast}} R + HX \qquad (4)$$

If the carbonium ion (RH^+) is stable enough, it can be isolated as RH^+X^- (e. g. phenalenium salts[2]).

In a non-polar solvent and in the absence of acids the reaction may proceed via a radical mechanism[30]. Step (1) may then be represented by two successive reactions.

$$RH_2 + Q \longrightarrow RH^{\cdot} + QH^{\cdot} \qquad (1a)$$

$$RH^{\cdot} + QH^{\cdot} \longrightarrow RH^+ + QH^- \qquad (1b)$$

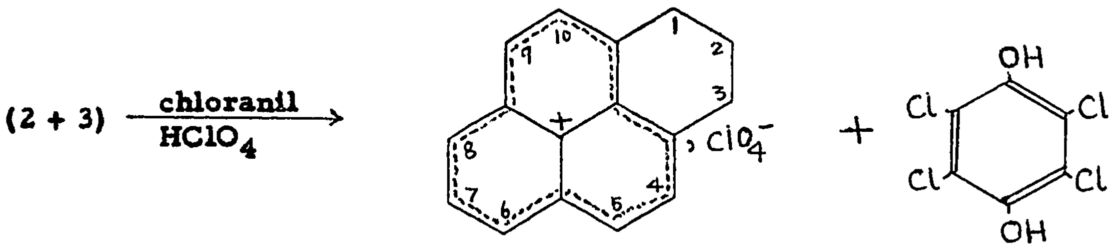
In the case where $RH^{\cdot}$ is a stable, long-lived radical (e. g. phenalenyl radical), it is likely that reaction (1a) would be followed by:

$$RH_2 + QH^{\cdot} \longrightarrow RH^{\cdot} + QH_2 \qquad (1c)$$

Alternatively, steps (1a) and (1c) might merge into a single process:

$$2RH_2 + Q \longrightarrow 2RH^{\cdot} + QH_2 \qquad (1d)$$

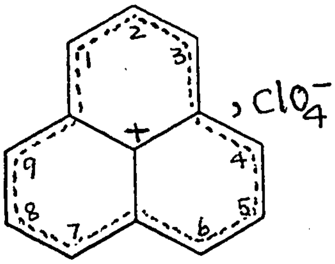
1, 2, 3-Trihydropyrenium perchlorate (54) was prepared in 90% yield by adding a solution of chloranil and perchloric acid in acetic acid to a solution of tetrahydropyrenes (2 and 3) also in acetic acid at room temperature. Recrystallization of the salt (54) either from acetonitrile or nitromethane was unsuccessful. But the salt (54) even without recrystallization gave a satisfactory analysis for C, H and Cl.



54 55

The perchlorate salt (54) is quite stable and can be stored for months under a vacuum. From the mother liquor of the perchlorate salt, 2, 3, 5, 6-tetrachlorohydroquinone (55) was recovered in 95% yield.

The structure of the perchlorate salt (54) was established from its I. R., U. V. and N. M. R. spectra. The salt showed strong absorption band at 1120 cm^{-1} in I. R. (characteristic absorption band for perchlorate ion). Also the U. V. spectrum of the salt in acetonitrile was similar to that of phenalenium perchlorate (56) in the same solvent.



56

The NMR spectrum of the perchlorate salt (54) in 98% sulfuric acid was not very well resolved; it showed two broad absorption bands at 7.64 τ and 6.5 τ (6H), a broad triplet at 1.85 τ (3H) and a broad doublet at 1.06 τ (4H) (Fig. 19a). The spectrum in perchloric acid, however, was better resolved. The aliphatic part of the spectrum showed two broad triplets at 7.64 and 6.5 τ (6H) and the aromatic part showed two multiplets at 1.85 and 1.06 τ (7H), Fig. 19b).

The NMR spectrum of phenalenium perchlorate (56)[37] in deuterosulfuric acid shows a broad triplet at 2.21 τ (3H) and a broad doublet at 1.46 τ (6H). The resonance doublet centered at 1.46 τ may be ascribed to the protons at (1, 3, 4, 6, 7 and 9). These protons are split into a doublet by the protons at (2, 5 and 8). Conversely, the

FIG. 19a. NMR SPECTRUM OF 1, 2, 3-TRIHYDROPYRENIUM PERCHLORATE (54) IN 98% SULFURIC ACID (EXTERNAL TMS)

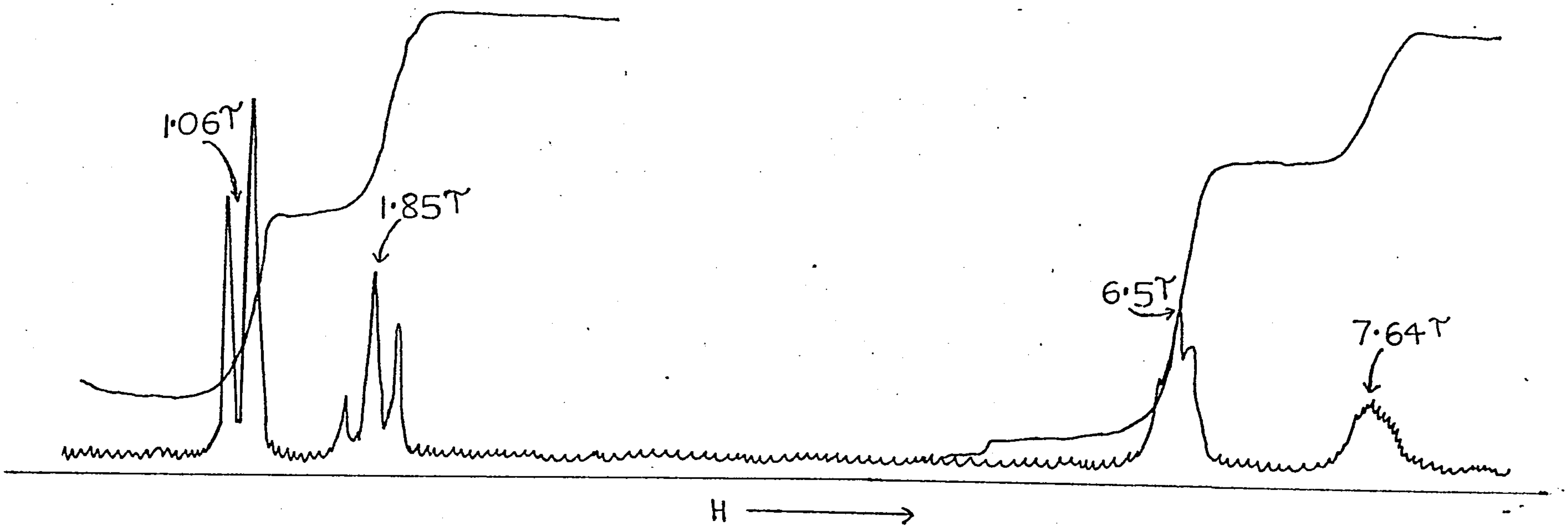
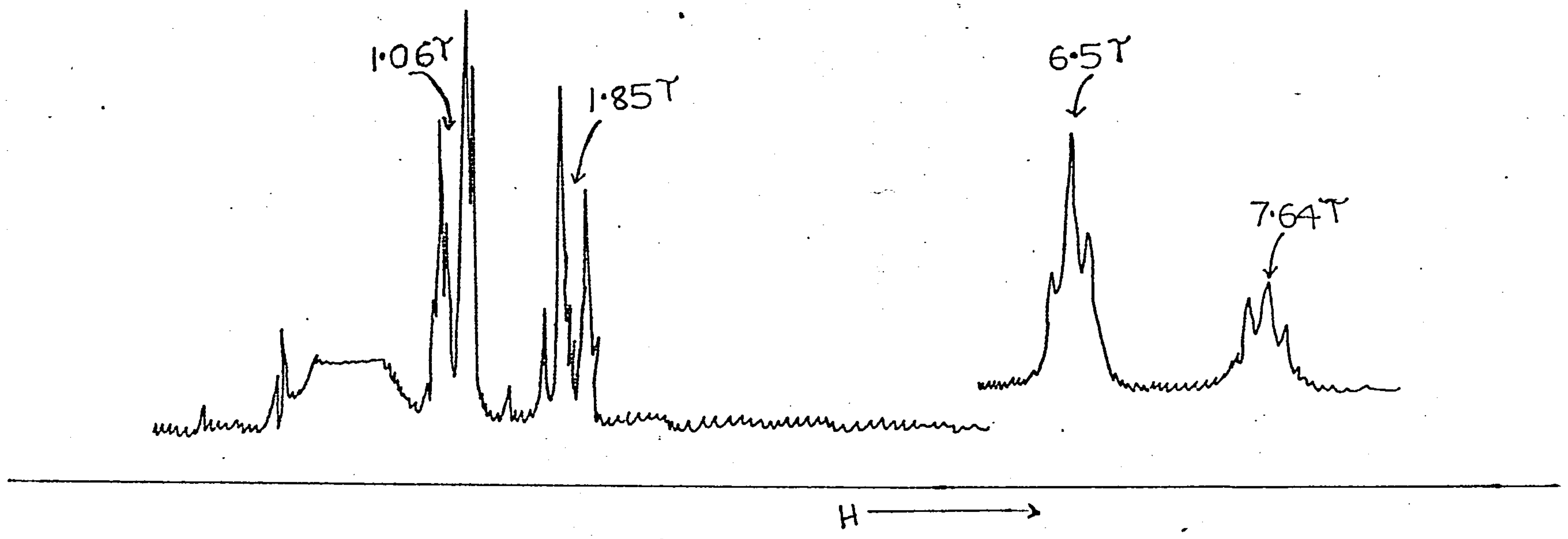


FIG. 19b. NMR SPECTRUM OF 1, 2, 3-TRIHYDROPYRENIUM PERCHLORATE (54) IN 72% PERCHLORIC ACID (EXTERNAL TMS)



protons in the latter positions are split into a triplet by the action of those protons on either side of each of them. The NMR spectrum of 1, 2, 3-trihydropyrenium perchlorate in sulfuric acid is very similar to that of phenalenium perchlorate in the same solvent. But the protons at (4, 7 and 10) positions of the 1, 2, 3-trihydropyrenium perchlorate should give an AB_2 type spectrum and the protons at (5, 6, 8 and 9) should show on A_2B_2 type spectrum. This was actually observed when the spectrum was taken in perchloric acid. The resonance multiplet centered at 1.06 τ may be ascribed to the protons at (5, 6, 8 and 9) and the multiplet centered at 1.85 τ may be ascribed to the protons at (4, 7 and 10).

Tetrahydropyrenes (2 and 3) also gave a tetrafluoroborate salt and a tri-iodide salt when treated with tetrafluorboric acid and hydriodic acid respectively in the presence of chloranil. The tetrafluoroborate salt is a yellow crystalline solid which is, however, less stable than the corresponding perchlorate salt, decomposing to a black tar in a few minutes when exposed to the atmosphere. The tri-iodide salt is a violet-black solid and is much more stable than the corresponding perchlorate salt. The estimation of iodine in the iodide salt as silver iodide and the elemental analysis for C, H and iodine, showed that the iodide salt was a tri-iodide rather than a mono-iodide. The same tri-iodide also resulted when the 1, 2, 3-trihydropyrenyl radical was treated with iodine. No chloride or bromide salt of 1, 2, 3-trihydropyrenium cation was isolated. Tropenium tri-iodide, which is also a violet-black solid, is quite readily formed by the action of iodine on tropenium mono-iodide and also results from the decomposition of mono-iodide[114]. Reid[29] also reported a violet-black solid, presumably a tri-iodide salt of phenalenium cation, obtained from phenalenyl radical with iodine.

1, 2, 3-Trihydropyrenium Perchlorate (54) in the Presence of Azobenzene:

Tetrahydropyrenes (2 and 3) can give rise to 1, 2, 3-trihydropyrenium perchlorate (54) in the presence of azobenzene and perchloric acid. Sir Hinshelwood *et al.*[115, 116] reported that the reduction of azobenzene in the presence of strong acids goes via transfer of two electrons from the reducing agents to a species of the type $Ph\overset{+}{N}H = \overset{+}{N}HPh$. The protonation of azobenzene is a fast process and the transfer of electrons from the reducing agent to the protonated azobenzene is the rate determining step.

$$\begin{tikzcd} ArN = NAr \arrow[r, "Fast", "2H^+"'] & Ar\overset{+}{N}H = \overset{+}{N}HAr \arrow[r, "Slow", "2e"'] & ArNHNHAr \arrow[d, "Fast"', "H^+"] \\ 57 & & Benzidine \\ & & 58 \end{tikzcd}$$

Reeves pictured the reduction of azobenzene with hydroquinone as follows[117, 118]:

$$ArN = NAr \overset{2e + 2H^+}{\rightleftarrows} ArNHNHAr \xrightarrow{H^+} Benzidine$$

The kinetic study of the azobenzene-reduction with hydroquinone in the presence of acid showed that the only protonated species of kinetic significance in the system was the mono-protonated azobenzene. They failed to find any evidence of the presence of a doubly protonated ($ph\ \overset{+}{N}H = \overset{+}{N}HPh$) azobenzene in the range of acid concentration which they studied (0.5 - 3.5 N).

The experimental condition for the preparation of 1, 2, 3-trihydropyrenium perchlorate in the presence of azobenzene was identical to that used when it was prepared in the presence of chloranil. But in the case of azobenzene we isolated a mixture of 1, 2, 3-trihydropyrenium perchlorate and benzidine perchlorate as shown from its physical properties as well as from its NMR spectrum in 98% sulfuric acid. Though azobenzene behaved as a good hydride acceptor, the disadvantage of this procedure was that the benzidine perchlorate and 1, 2, 3-trihydropyrenium perchlorate were difficult to separate from each other. One interesting point in this experiment was the reduction of azobenzene to hydrazobenzene which in the presence of strong acid ($HClO_4$) rearranged to benzidine. The mixture of 1, 2, 3-trihydropyrenium perchlorate and benzidine perchlorate was reduced with lithium aluminum hydride in ether to the tetrahydropyrenes (2 and 3) and benzidine (58). Benzidine was separated by triturating the mixture of tetrahydropyrenes and benzidine with petroleum ether (bp 30-60°) in which only the tetrahydropyrenes dissolved. The mp of benzidine agreed well with the reported[119] mp of p-benzidine. The TLC of the compound showed only one isomer to be present and the NMR spectrum of the crude benzidine in deuterochloroform showed a broad singlet at 6.4 τ (4H) and two multiplets at 3.3 and 2.65 τ (8H) (Fig. 20).

In a similar experiment it was shown that phenalene (6) can also reduce azobenzene into hydrazobenzene which then rearranged to p-benzidine in the presence of perchloric acid.

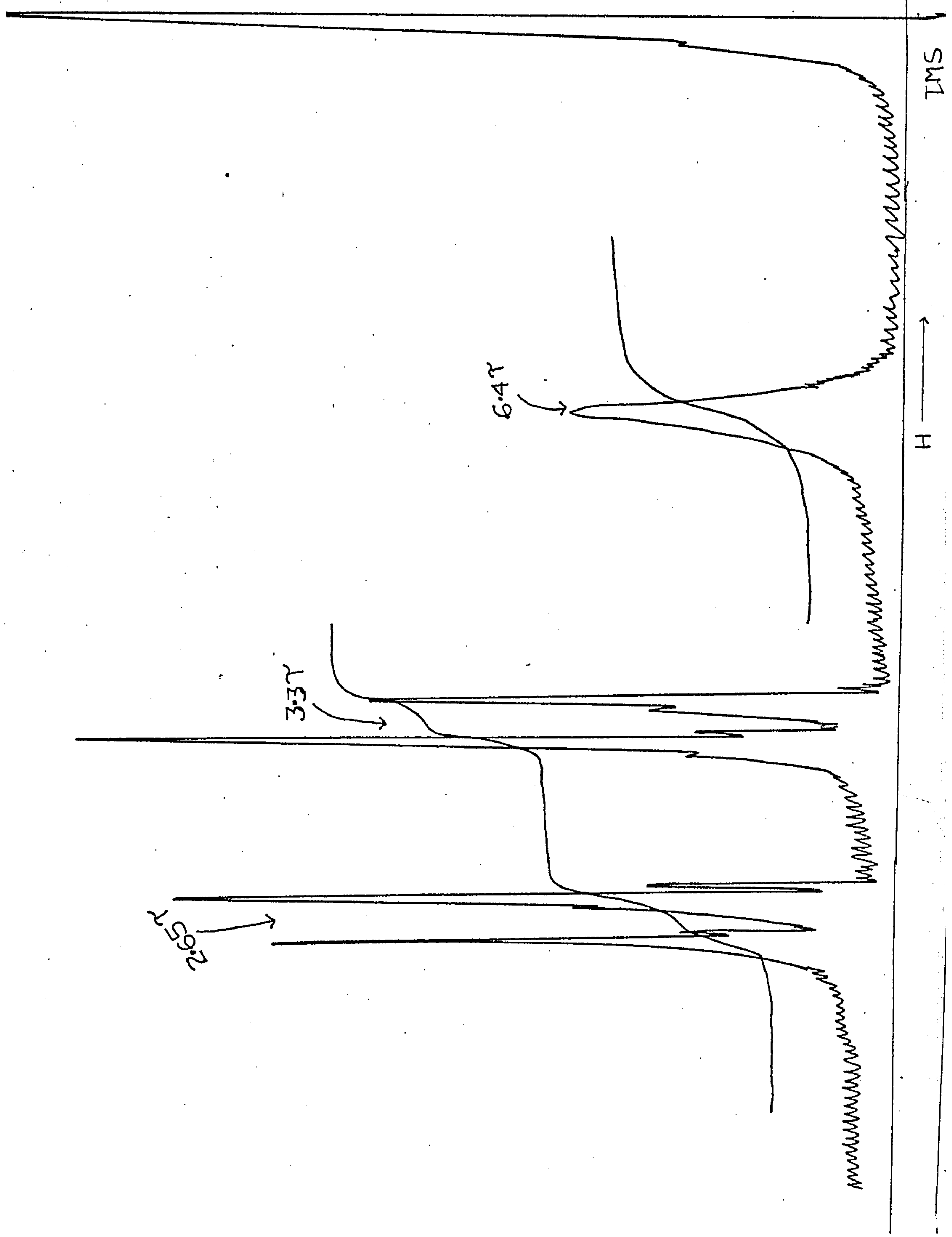
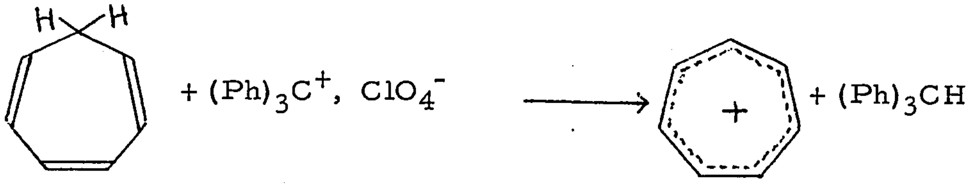


FIG. 20 NMR SPECTRUM OF p-BENZIDINE (58) IN DEUTEROCHLOROFORM

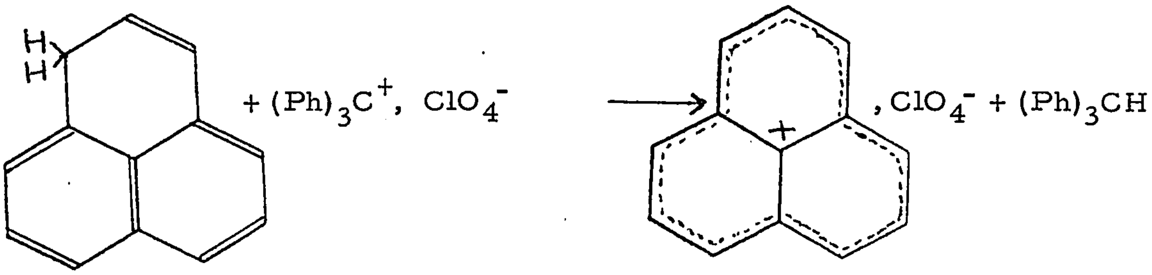
Action of Perchloric Acid on Tetrahydropyrenes (2 and 3):

In the previous methods we have discussed the preparation of 1, 2, 3-trihydropyrenium perchlorate (54) in the presence of hydride acceptors such as quinone and azobenzene. We found, however, that the preparation of 1, 2, 3-trihydropyrenium perchlorate (54) was also possible in the absence of any external hydride acceptor. Tetrahydropyrenes (2 and 3), dissolved in either acetic acid or acetonitrile when treated with 72% perchloric acid gave a yellowish green solution. Addition of dry ether precipitated the 1, 2, 3-trihydropyrenium perchlorate (54) in 45% yield (in the presence of quinone the yield of the same perchlorate salt was 90%). This perchlorate salt was identical to that obtained in the presence of chloranil in all respects (same mp., I.R., U.V. and NMR spectrum). From the mother liquor of the perchlorate salt we isolated only 1, 2, 3, 3a, 4, 5-hexahydropyrene (18) as shown by VPC and TLC analysis.

It is known[120] that in strong acids such as sulfuric or perchloric acid, certain olefinic bonds are protonated to yield a carbonium ion that undergoes a hydride exchange reaction. The oxidation ability of carbonium ion is well known in the literature[121-124]. Carbonium ions can abstract hydride ion from alcohols, esters, hydrocarbons etc. A few examples[37, 38] are given below:

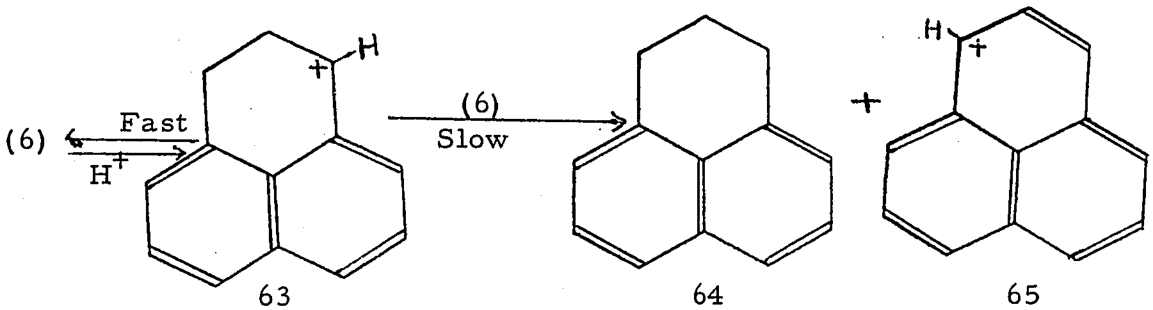


59 60 61 62



6 60 56 62

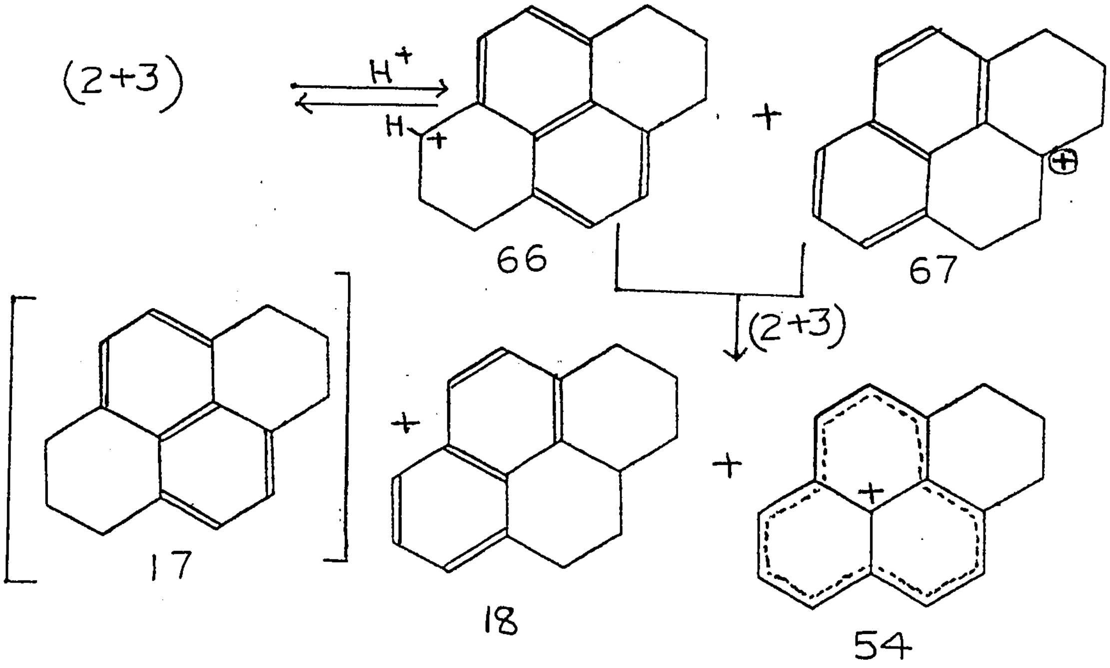
Honěn[37] reported that phenalene in the presence of 71% perchloric acid gave an oil phase, insoluble in acid. The acid phase gave a U. V. spectrum identical to that of phenalenium ion, and the oil phase gave a U. V. spectrum similar to that of 2, 3-dihydrophenalene (64). He suggested the following possible mechanism for the formation of phenalenium ion from phenalene with perchloric acid:



63 64 65

Honěn proposed an electrophilic attack by a proton on the vinylic double bond should give rise to a less stable carbonium ion (63) which oxidizes a molecule of phenalene (6) to the more stable phenalenium cation (65) and itself reduced to 2, 3-dihydrophenalene (64).

So, we can express his reaction scheme for the tetrahydropyrene system as follows:



We might then expect a mixture of two hexahydropyrene isomers (17 and 18) from the perchlorate (54) mother liquor, but we isolated only one isomer (18). We originally suspected that the isomer (17) isomerized to isomer (18) in the presence of perchloric acid. This possibility was tested by subjecting (17) to the condition of reaction, i.e. treated with perchloric acid in the presence of acetic acid but even after 24 hr. reaction time, pure (17) was recovered unchanged. Thus it would appear that a more deep seated rearrangement mechanism is involved in the above reaction.

In an effort to elucidate the mechanism of this hydride exchange reaction we ran the disproportionation in anhydrous acetonitrile using deuteroperchloric acid. The unsymmetrical hexahydropyrene (18), obtained from this reaction, contained 60% d_1 and the 1, 2, 3-trihydropyrenium perchlorate (54) contained 10% deuterium (as determined by reducing the perchlorate salt (54) with lithium aluminum hydride and the analysis of the resulting tetrahydropyrenes (2 and 3)). The NMR spectrum of the deuterium containing (18) indicated that deuterium was distributed in the aromatic and aliphatic part of the molecule (18).

Five experimental facts must then be accounted for in any proposed scheme:

1. Only isomer (18) is isolated from the disproportionation reaction.
2. Isomer (17) is not isomerized to (18) under the reaction conditions employed.
3. The deuterium content of (18) is significantly less than 100%.
4. The deuterium content of (18) is distributed in the aliphatic and aromatic part of the molecule.
5. The pyrenium perchlorate (54) contained a small amount of deuterium (10%).

We feel further work would be necessary to establish a mechanism for the above reaction.

Action of Concentrated Sulfuric Acid on Tetrahydropyrenes (2 and 3)

Tetrahydropyrenes (2 and 3) in 98% sulfuric acid gave a U. V. spectrum similar to that of 1, 2, 3-trihydropyrenium perchlorate (54) in the same solvent. A 48.8% yield of 1, 2, 3-trihydropyrenium cation was recorded in sulfuric acid solution of the hydrocarbons (2 and 3) as determined from the λ_{max} value. The NMR spectrum (Fig. 21) of the tetrahydropyrenes in 98% deuterosulfuric acid was almost identical to that of 1, 2, 3-trihydropyrenium perchlorate in the same solvent, but the integration of the spectrum showed more aliphatic protons (10H, in place of 6H). For pure 1, 2, 3-trihydropyrenium cation the ratio of aromatic to aliphatic protons was 7:6, but for tetrahydropyrenes in sulfuric acid, we obtained a 7:10 ratio. One would expect the action of sulfuric acid on tetrahydropyrenes to be similar to that of perchloric acid on these hydrocarbons, i.e. the attacking entity is a proton. In that case, we should isolate 1, 2, 3, 3a, 4, 5-hexahydropyrene (18) from the mother liquor of 1, 2, 3-trihydropyrenium sulfate, but instead of that we isolated a black tar. We believe the hexahydropyrene (18), formed in this case was further reacted by conc. sulfuric acid. In a separate experiment we found that both the hexahydropyrenes (17) and (18) were unstable in conc. sulfuric acid, slowly turned to a black tarry material; the isomer (18) was more unstable than the isomer (17) in conc. sulfuric acid.

Honěn^{37} proposed a second possibility, i.e. an electrophilic attack by 'SO_3' instead of H^+. But 98% sulfuric acid contains very little free 'SO_3' and hence an attack by 'SO_3' is the least likely possibility.

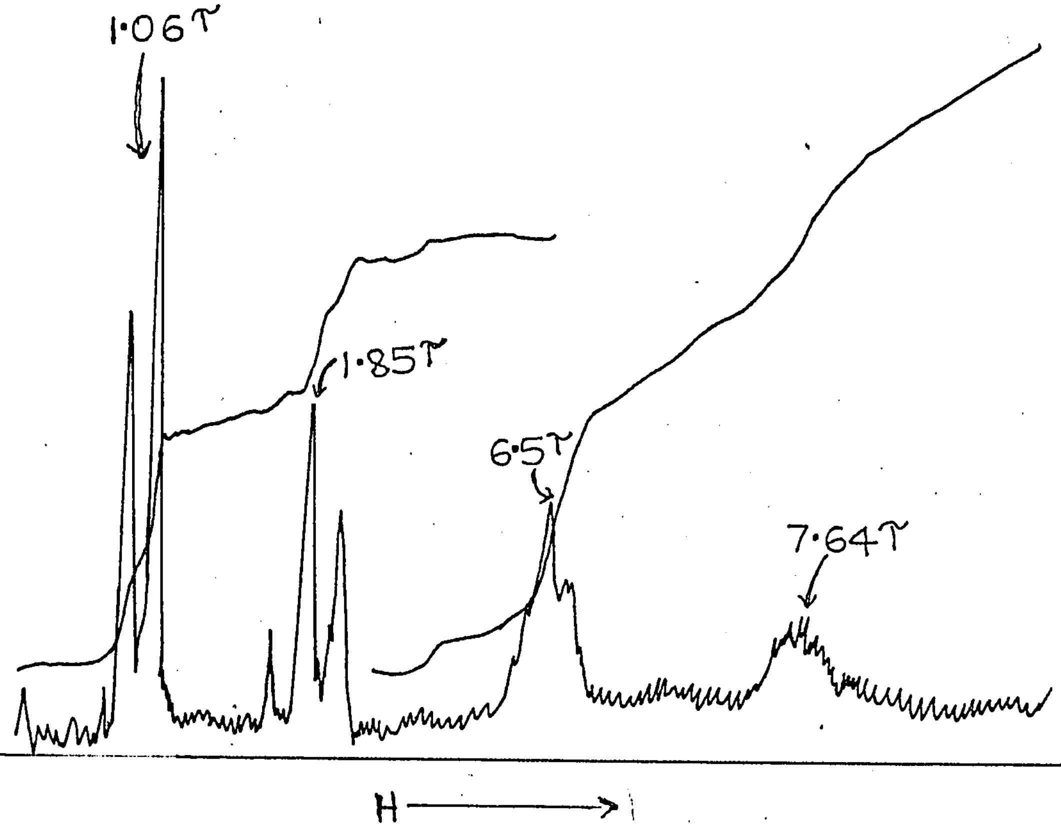


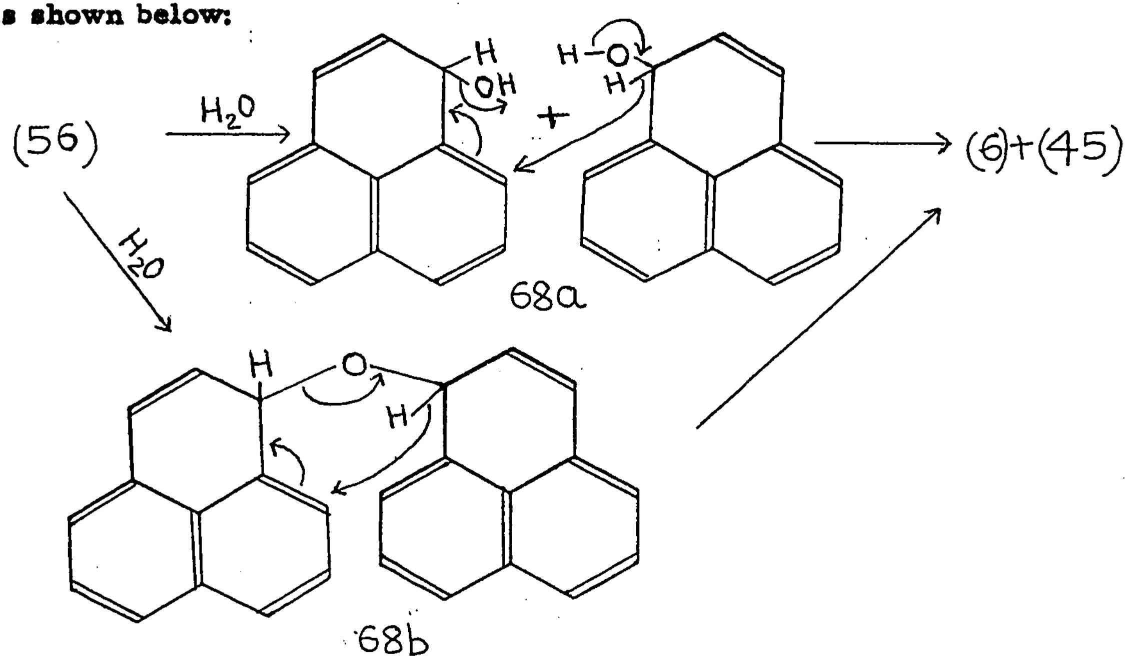
FIG. 21. NMR SPECTRUM OF TETRAHYDROPYRENES (2 and 3) IN D_2SO_4. (EXTERNAL TMS)

It was reported that cycloheptatriene[39] gave 22% yield of tropenium cation in sulfuric acid and from the mother liquor of the cation no identifiable material was isolated except a polymerized tarry material. Honen[37] also reported 51% yield of phenalenium cation in the case of phenalene in 96% sulfuric acid and again no identifiable product was reported from the mother liquor of the cation.

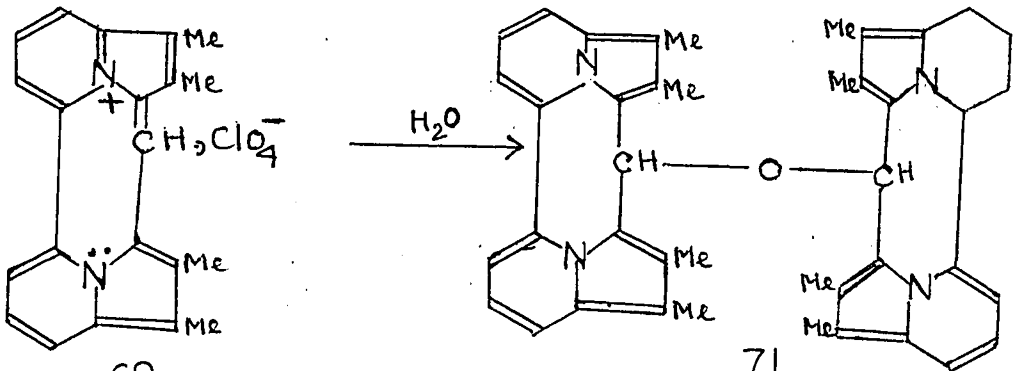
Reduction and Hydrolysis of 1, 2, 3-Trihydropyrenium Perchlorate (54):

The reduction of 1, 2, 3-trihydropyrenium perchlorate with lithium aluminum hydride in dry ether gave the two tetrahydropyrenes (2 and 3) again in the ratio 2:1 respectively, as shown by VPC analysis. The isomers obtained by the reduction of the perchlorate salt were identical in all respects with an authentic sample of tetrahydropyrenes (2 and 3). This reduction was found to be very helpful in obtaining a pure sample of tetrahydropyrenes (2 and 3) free from decahydropyrene (5) and unreacted pyrene. A similar reduction of the perchlorate salt was carried out with lithium aluminum deuteride. A total of 82% d_1 (as determined by NMR) was accounted for in the tetrahydropyrenes, 48% in the vinylic methylene group and the rest was distributed in the aromatic and vinylic part of the molecule. A similar deuteration experiment with phenalenium perchlorate showed 85% deuteration in the phenalene molecule.

It is known that phenalenium perchlorate (56) on hydrolysis gives phenalene (6) and phenalen-1-one (45) approximately in the ratio 1:1. Reid[41] suggested two possible intermediates by which these two products arise from the hydrolysis of phenalenium cation, although none of the two intermediates was isolated. The two intermediates are the carbinol (68a) and the ether (68b); both are capable of giving rise to phenalene (6) and phenalenone (45) by hydride transfer as shown below:

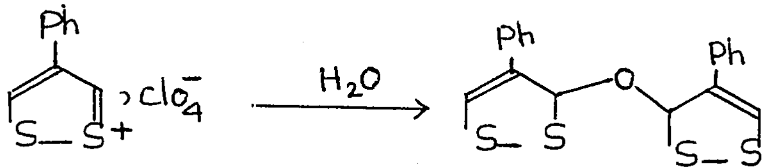


Honen[37] reported the isolation of the ether (68b) by the rapid hydrolysis of phenalenium tetrafluoroborate. Reid et al.[125] and Newman[126] reported that the hydrolysis of the perchlorates (69) and (70) yielded the ether (71) and (72) respectively.



69

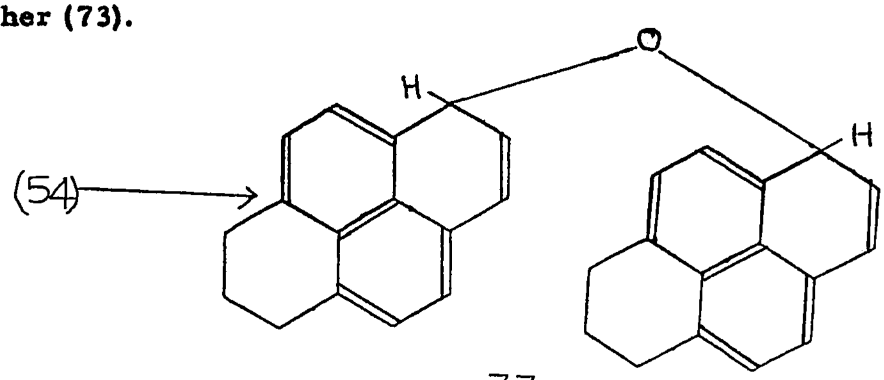
71



70

72

The hydrolysis of 1, 2, 3-trihydropyrenium perchlorate (54) solution in acetonitrile with water, yielded neither tetrahydropyrenes (2 and 3) nor any ketones, but a green solid which we suppose to be a di-tetrahydropyrenyl ether (73).



73

The ether (73) showed a U. V. spectrum very similar to that of tetrahydropyrenes (2 and 3) with e_{max} almost double that of ℓ_{max} for tetrahydropyrenes. The I. R. spectrum of the ether showed a characteristic ether absorption at 1085 cm^{-1}. The green solid (73) resisted all attempts to purify it. It decomposed to black tar in chromatography-column and was insoluble in almost all solvents, except chloroform, in which it was very unstable. The impure ether (73) gave an elemental analysis for C and H within 1% error. This ether was extremely paramagnetic substance; no NMR spectrum was possible. When dehydrogenated with 5% Pd/c at 360° under a nitrogen atmosphere, it gave 70% pyrene (calculated with respect to ether, 73).

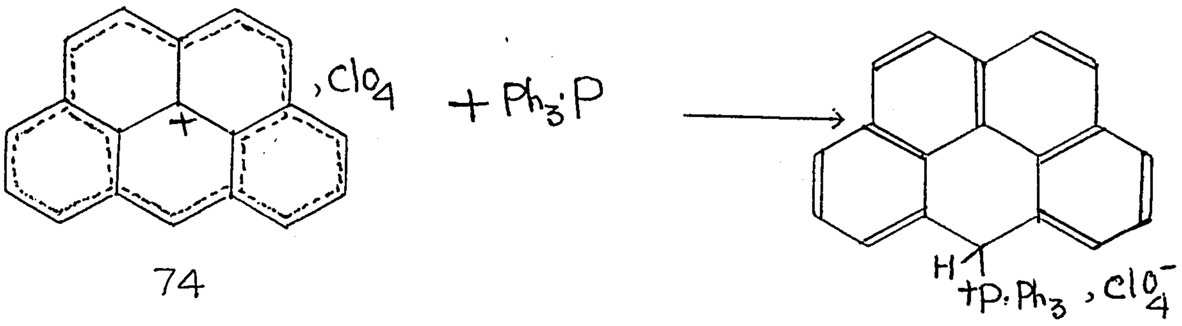
Further proof of the structure of ether (73) came from its cleavage into 1, 2, 3-trihydropyrenium perchlorate (54) with 72% perchloric acid in chloroform solution, in 75% yield.

$$[\ 73\ ] \xrightarrow[\text{in } CHCl_3]{HClO_4} \underset{75\%}{(\ 54\ )}$$

Some Attempted Reactions of 1, 2, 3-Trihydropyrenium Perchlorate (54):

The first attempted reaction was the reaction of methyl lithium on the perchlorate salt (54). The reaction was carried out under a nitrogen atmosphere and in dry ether. From this reaction, lithium perchlorate was isolated as white needles. The mother liquor of lithium perchlorate gave a viscous liquid from which only 10% tetrahydropyrenes (2 and 3) were recovered by column chromatography. The remaining material when dehydrogenated with 5% Pd/C, gave (≈1.0%) solid and the rest was an unidentified tar. The solid material was found to be a mixture of pyrene and mono-methylpyrene; a small amount of dimethylpyrene was also present in the mixture (as detected by mass spectrograph). A similar attempt was made by Pettit[14] to prepare a methyl phenalene from phenalenium perchlorate with methyl lithium or with methyl magnesium bromide. Although a reaction appeared to take place, in neither case any identifiable product was isolated.

A second reaction was attempted with 1, 2, 3-trihydropyrenium perchlorate and pyridine. This reaction gave pyridine perchlorate as the only isolable product; the remainder was an unidentified tarry material. Reid and Bonthrone[43] reported the compound (75), which was formed by the action of triphenylphosphine on benzo[cd]pyrenium cation (74).



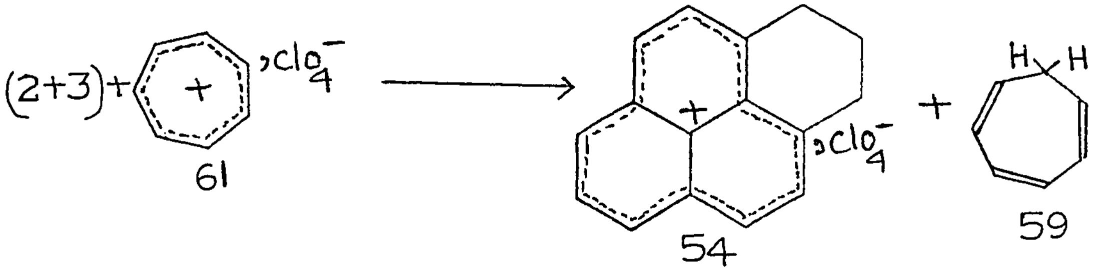
74

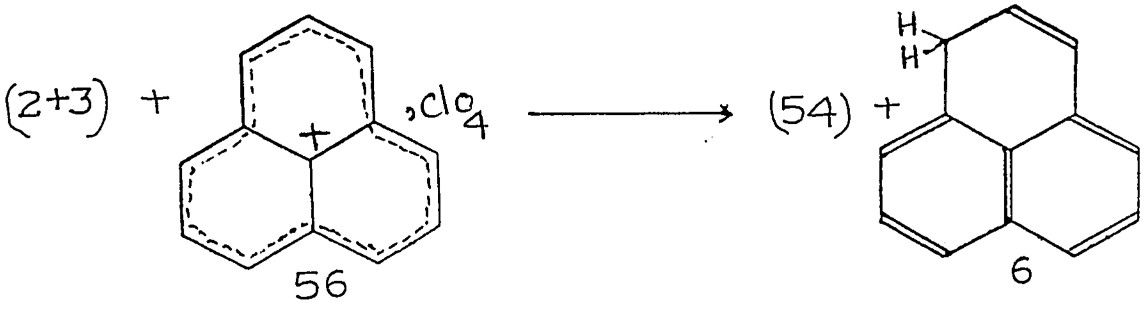
75

Accordingly, we attempted a similar reaction between 1, 2, 3-trihydropyranium perchlorate and triphenyl phosphine. We obtained a viscous liquid which turned to a foamy solid under a vacuum. We were unable to identify the material either by NMR or by other means.

Hydride Exchange between (i) Tetrahydropyrenes (2 and 3) and Phenalenium Perchlorate and (ii) Tetrahydropyrenes and Tropenium Perchlorate

1, 2, 3,-Trihydropyrenium cation was found to be more stable than phenalenium or tropenium cation. When phenalenium and tropenium perchlorates in acetonitrile solution were mixed with an equivalent amount of tetrahydropyrenes, 1, 2, 3-trihydropyrenium perchlorate (54) was isolated in 85% and 90% yield respectively and from the mother liquor of the perchlorate the corresponding hydrocarbon, phenalene and cycloheptatriene was also recoverable.



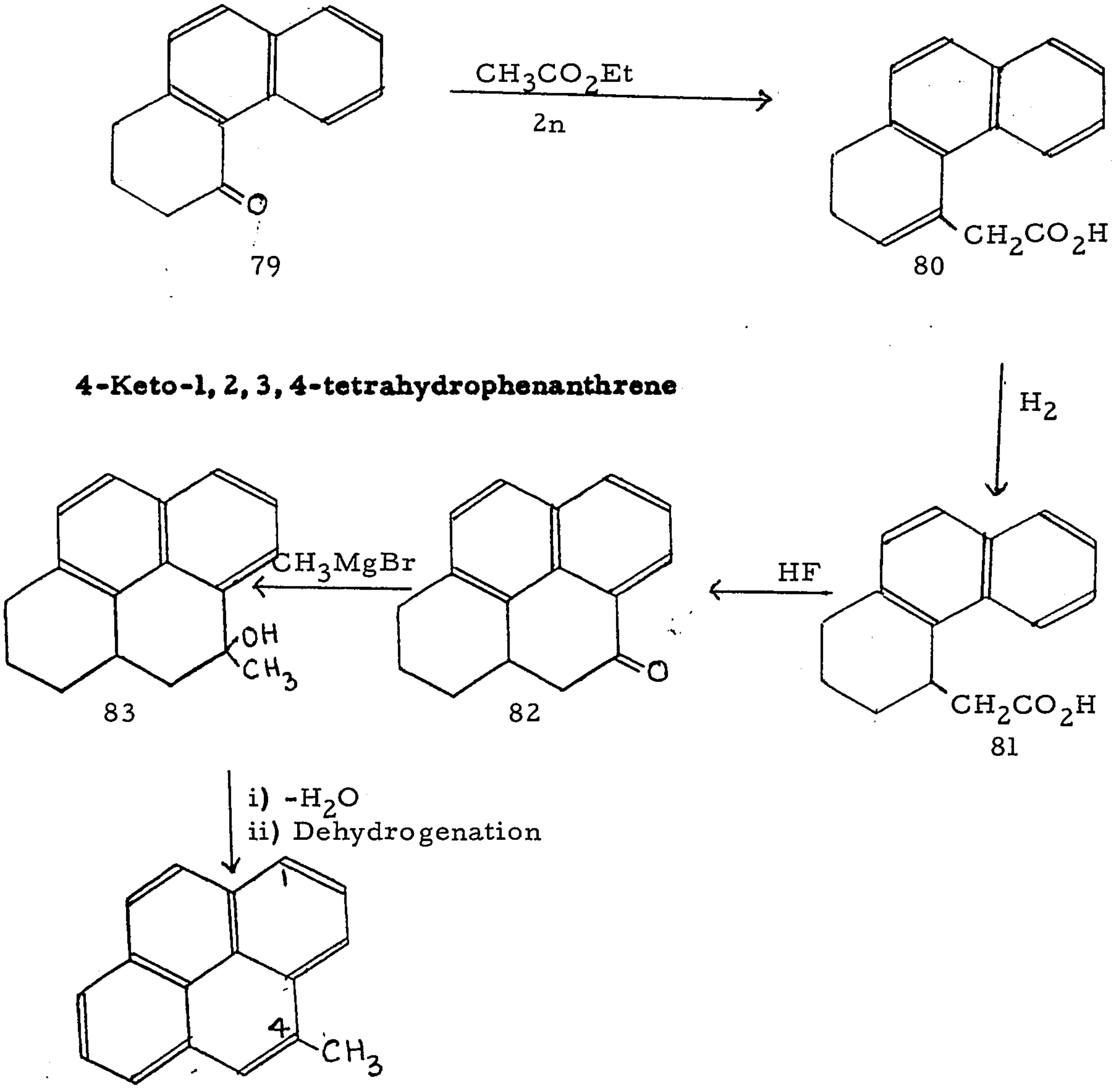


Methylation of the Tetrahydropyrene Anion

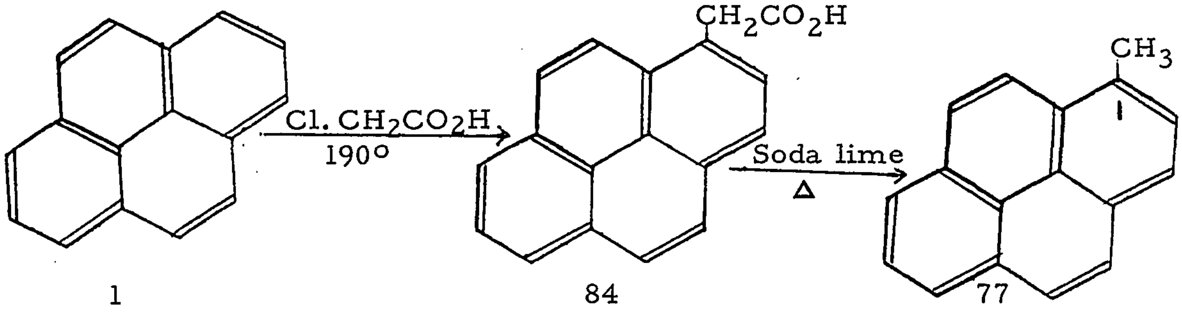
Tetrahydropyrenes (2 and 3) gave a red anion when treated with n-BuLi in dry ether. The methylation of this anion with methyl iodide gave a viscous liquid which showed two components when analysed by VPC. This mixture of methylated compounds was dehydrogenated under a nitrogen atmosphere with 5%, Pd/C and gave two methyl-pyrene isomers. These two isomers were separated by fractional crystallization in ethanol. The major isomer (75%) was identified as 4-methyl pyrene (76) since its mp agreed with the reported[127, 128] mp for the same isomer. The minor isomer (25%) was identified as 2-methyl pyrene (78); mp agreed with the reported[129] mp for 2-methyl pyrene.

There are three possible isomers of methyl pyrene ; 4-methyl, 1-methyl and 2-methyl pyrenes. The structures of three isomers have been confirmed by synthesis:

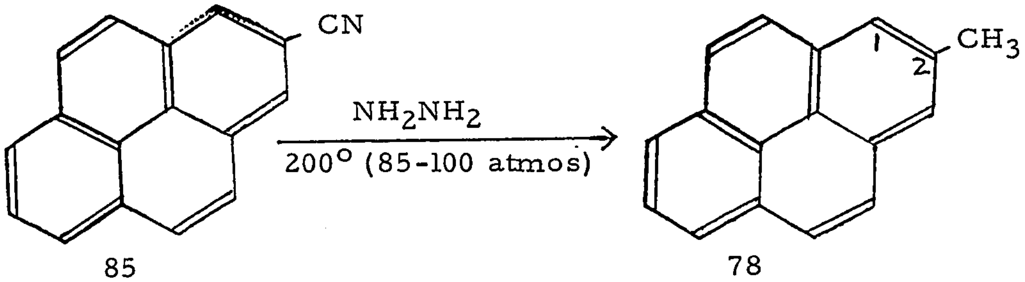
Synthesis of 4-methyl pyrene (Newman)[127]



Synthesis of 1-methyl pyrene (Vollmann)[129]



Synthesis of 2-methyl pyrene (Vollmann)[129]



In a recent paper, Clar et al.[130] reported that the 4,5-double bond of pyrene molecule behaves as an olefinic double bond and the 'methyl' signal for 4-methyl-pyrene in NMR spectrum shows a doublet at 7.15τ with a coupling of 1.3 cps; whereas 1-methyl or 2-methyl pyrene gives rise to a single methyl peak as they represent a methyl group, substituted in a fully aromatic ring. Our major isomer (76) gave an NMR spectrum (Fig. 22) identical to that reported for 4-methyl pyrene and the minor isomer (78) gave a singlet for its methyl group (Fig. 23).

In another experiment, tetrahydropyrene anion was treated with carbon dioxide. A yellow, water soluble solid was obtained. The NMR spectrum of the solid in D_2O was not successful because of the extremely paramagnetic property of the yellow solid. This yellow solid, when acidified with sulfuric acid, gave a green solid which showed a carbonyl band at 1680 cm^{-1} in I.R. But this acid also was found to be extremely paramagnetic and all attempts to crystallize it failed. So no structural assignment to the acid was possible. This acid, on dehydrogenation with 5% Pd/C, yielded about 10% pyrene; the remainder was an unidentified tar.

A similar experiment was reported by Boekelheide[1] with phenalene anion and carbon dioxide. He isolated a green solid, on acidification of which yielded a red solid of unknown constitution.

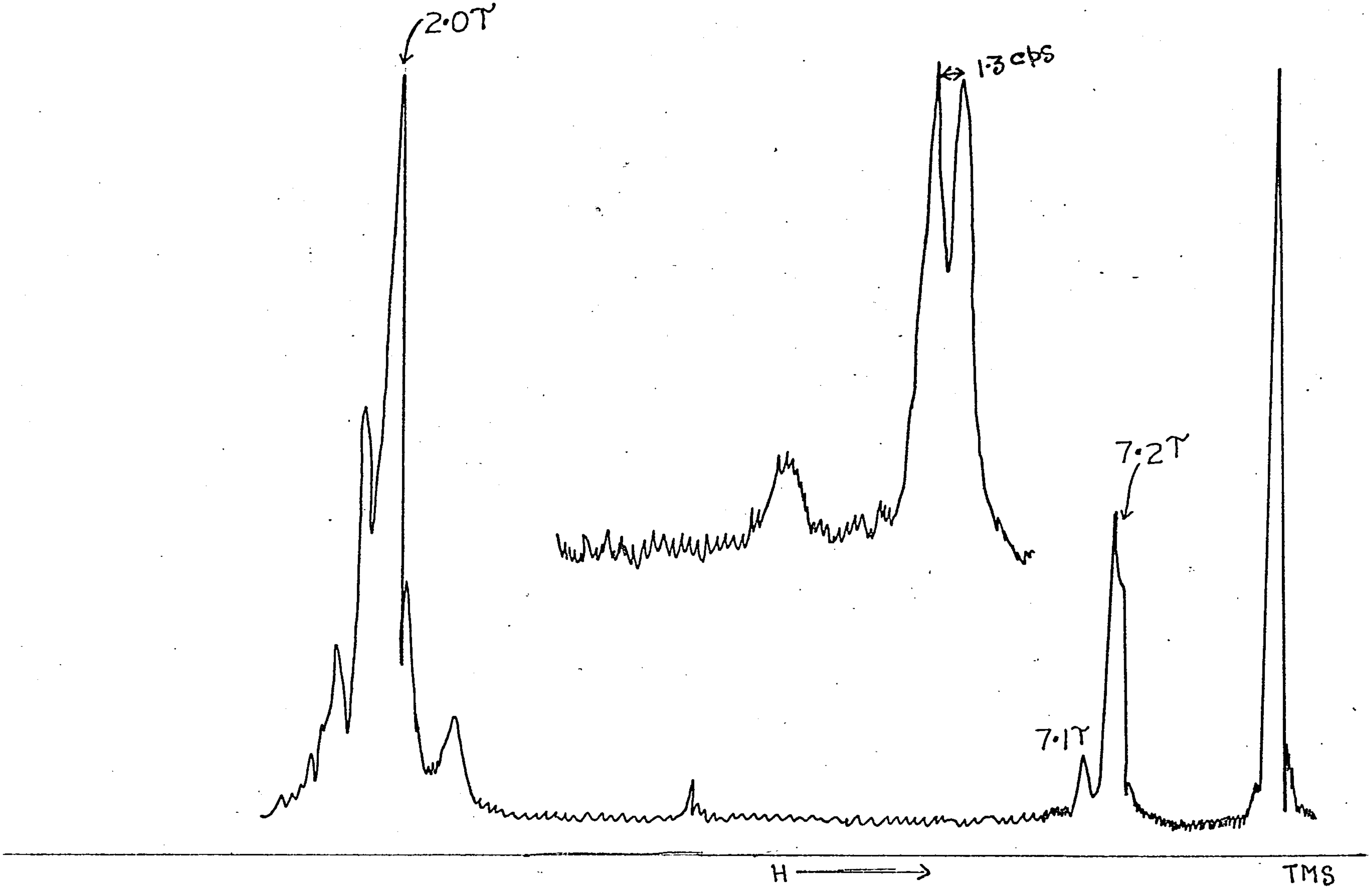
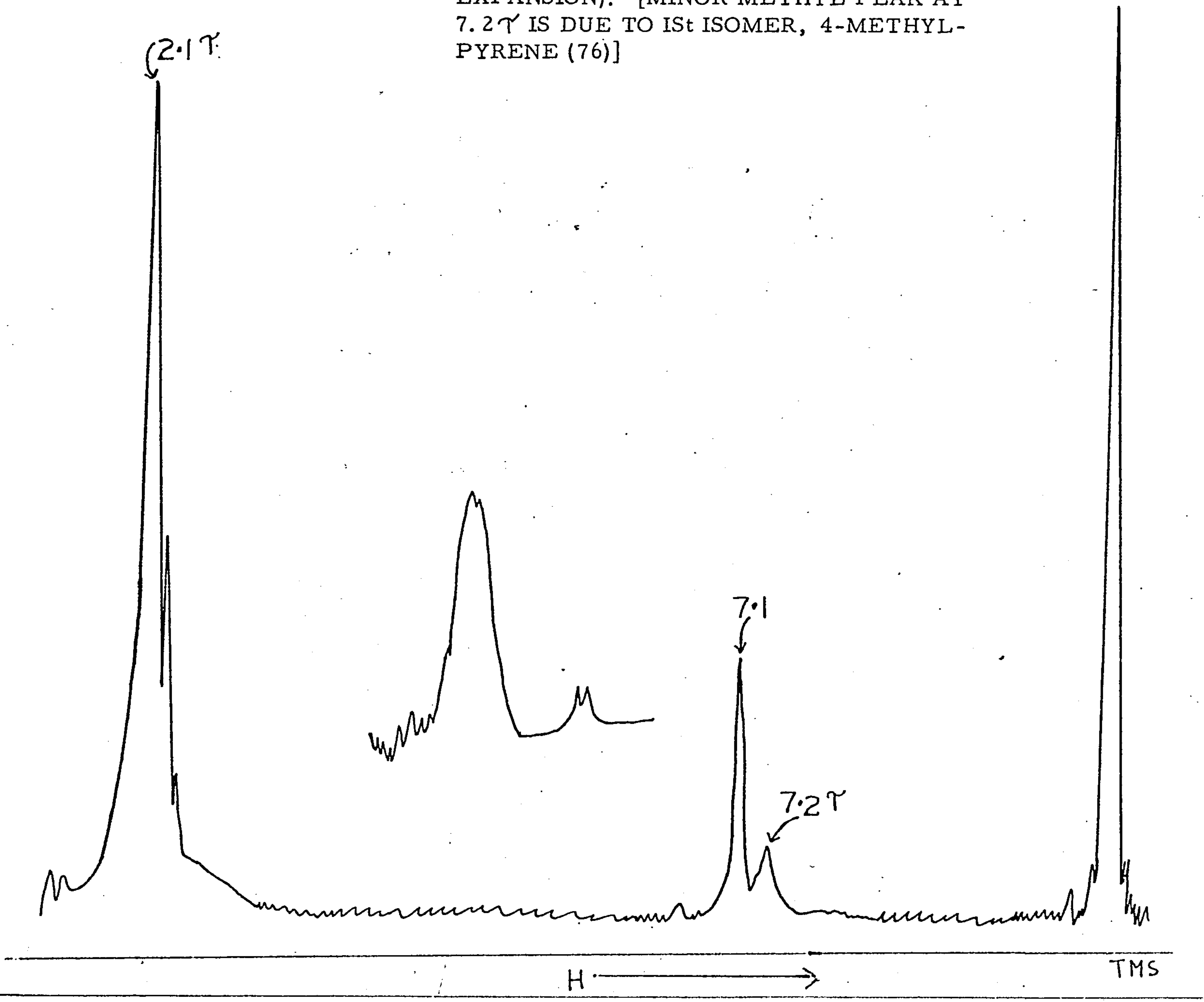


FIG. 22. NMR SPECTRUM OF 4-METHYLPYRENE (76) IN DEUTEROCHLOROFORM (WITH 6 TIMES EXPANSION. [Minor methyl peak at 7.10τ is due to 2nd isomer, 2-methylpyrene (78)].

FIG. 23. NMR SPECTRUM OF 2-METHYLPYRENE (78) IN DEUTEROCHLOROFORM (WITH 6 TIMES EXPANSION). [MINOR METHYL PEAK AT 7.2τ IS DUE TO ISt ISOMER, 4-METHYLPYRENE (76)]



1, 2, 3-Trihydropyrenyl Radical (86)

The radical (86) was generated by the action of chloranil on tetrahydropyrenes (2 and 3) in carbon tetrachloride solution. This radical was then oxidised to 1, 2, 3-trihydropyrenium perchlorate (54) and 1, 2, 3-trihydropyrenium tri-iodide by the action of silver perchlorate and iodine respectively on the radical. The perchlorate and the tri-iodide salts were identical to the corresponding salt, obtained from 1, 2, 3-trihydropyrenium cation.

Compounds (2 and 3) are substituted phenalenes and, like phenalene itself[28], readily lose one hydrogen from the lone methylene group, presumably by air oxidation. A carbon tetrachloride solution of tetrahydropyrenes (2 and 3) gave a well resolved e. s. r. spectrum. The 1, 2, 3-trihydropyrenyl radical (86) is given the name 1, 9-trimethylene phenalenyl radical. (This name was used for convenience in comparison with phenalenyl radical). The 'g' value of the radical in carbon tetrachloride is 2. 00269, close enough to suggest[131] a neutral hydrocarbon radical; this value is only 0. 00002 higher than that of phenalenyl[132].

Most of the spectrum (Fig. 24) can be readily analyzed (mesitylene as solvent at room temperature) in terms of a quintet from 4 protons with a coupling constant of 6. 092 gauss, a quartet from 3 protons with 1. 745 gauss and a triplet from 2 protons with 0. 449 gauss. As seen in Table 10 the first two constants are very similar to those of phenalenyl in toluene[133-135] and are obviously the aromatic protons. The remainder of the spectrum is described

FIGURE 24.

E.S.R. SPECTRUM OF 1,2,3-TRIHYDROPYRENYL RADICAL (86) AT +20° AND -70°.

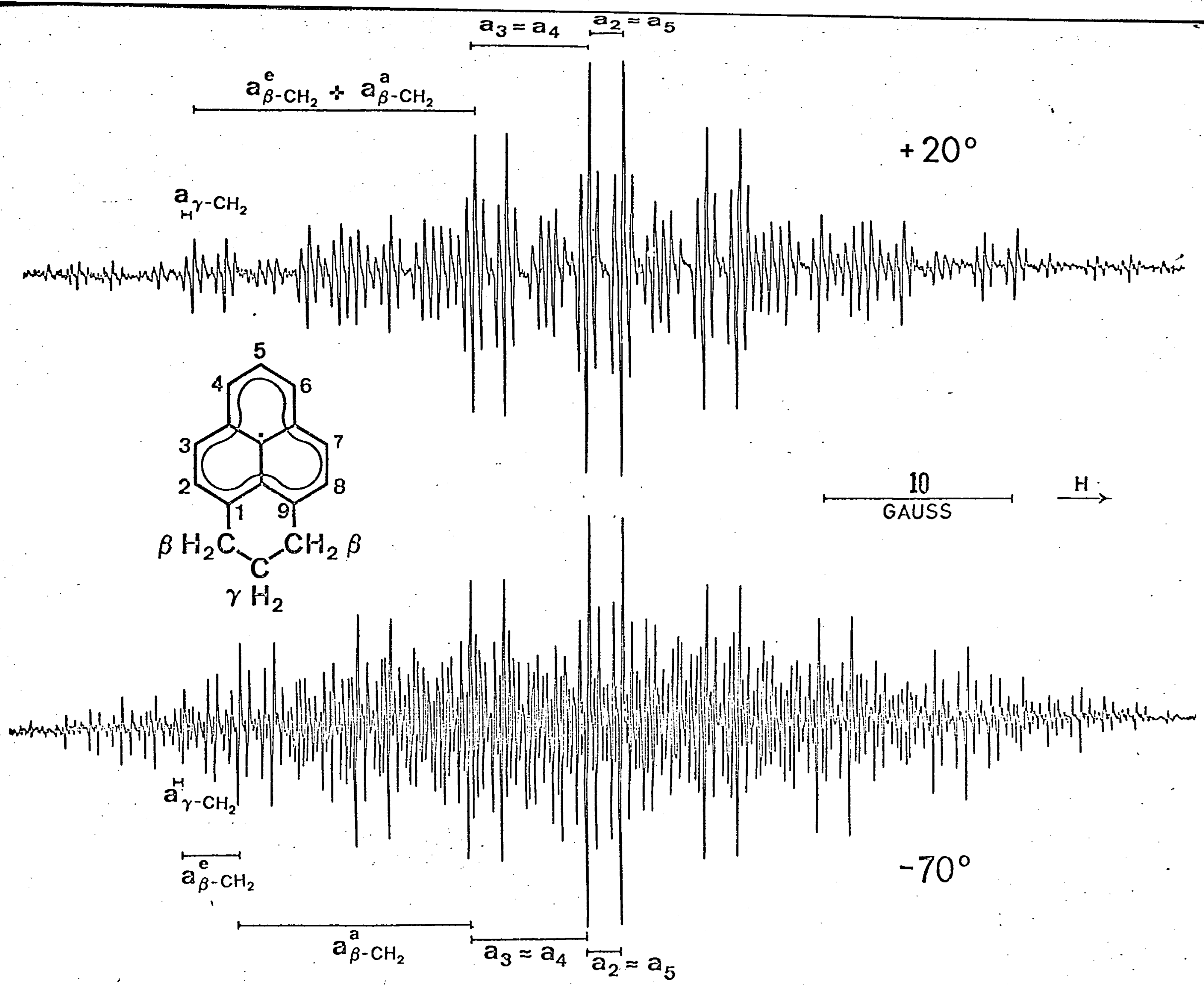

a3 = a4
a2 = a5
$a^{e}_{\beta\text{-CH}_2}$ + $a^{a}_{\beta\text{-CH}_2}$
+20°
$a^{H}_{\gamma\text{-CH}_2}$
5
4
6
3
7
2
8
1
9
β H2C
CH2 β
C
γ H2
10
GAUSS
H
$a^{H}_{\gamma\text{-CH}_2}$
$a^{e}_{\beta\text{-CH}_2}$
-70°
$a^{a}_{\beta\text{-CH}_2}$
a3 = a4
a2 = a5

Table 10

Proton coupling constants at room temperature*

Radical Solvent	1,9-Trimethylenephenalenyl mesitylene		phenalenyl toluene
$a_{3,4,6,7}$	6.092 g	$a_{1,3,4,6,7,9}$	6.308
$a_{2,5,8}$	1.745	$a_{2,5,8}$	1.820
$a_{\beta}^{a} + a_{\beta}^{e}$	14.77		
a_{γ}	0.449		

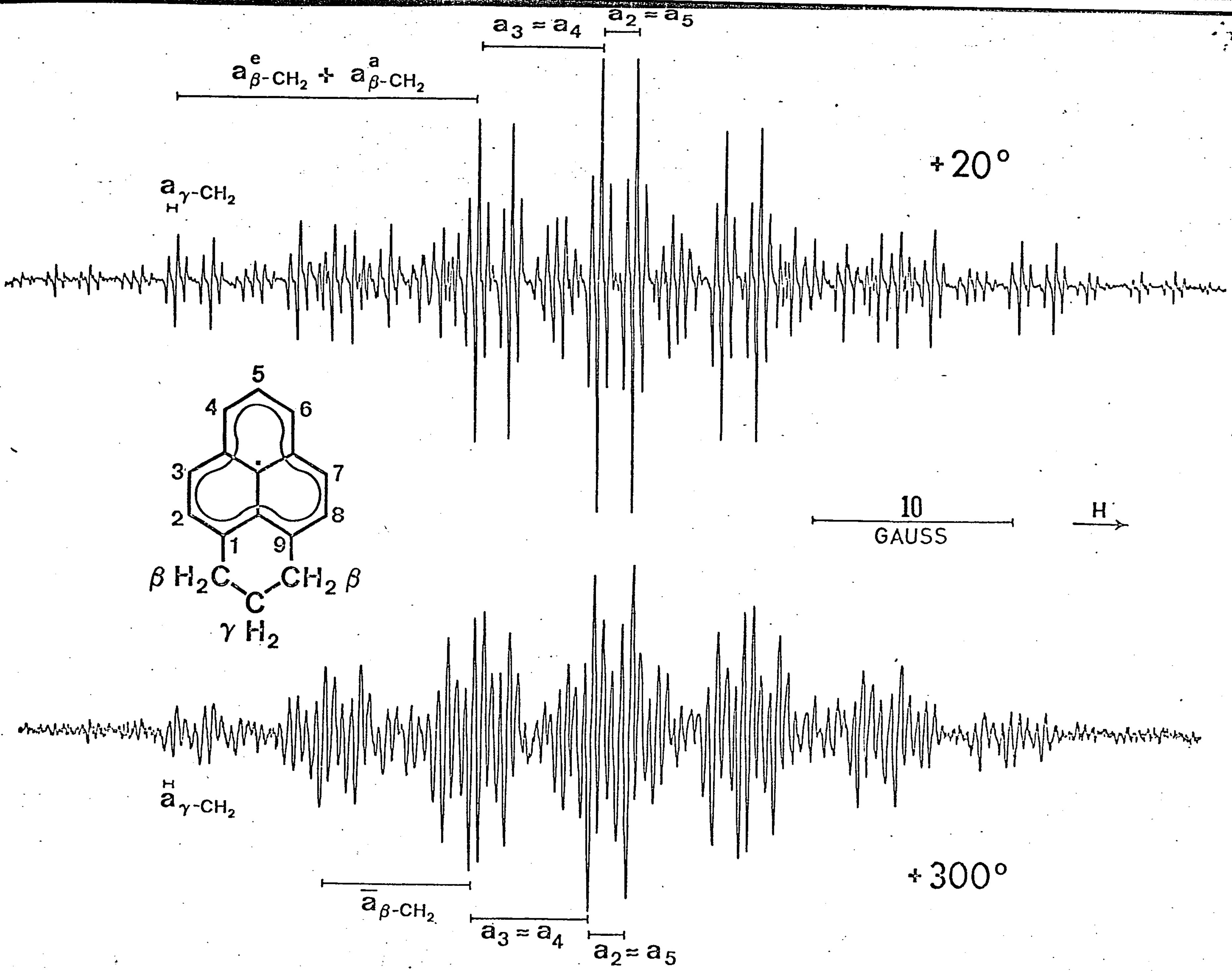
*Accuracy ±0.003 G except for $a_{\beta}^{a} + a_{\beta}^{e}$ where ± 0.01 G.

by a triplet splitting with intensities 1:4:1 and spacing 14.77 gauss. The two triplets are interpreted by analogy with the results of Boer and Praat[136] and Iwaizumi and Isobe[137] for the related ion radicals of 1,2,3,6,7,8-hexahydropyrene. The small triplet is assigned to the central methylene group and the large triplet results from rapid conformational interconversion of the remaining four methylene protons between axial and equatorial positions. This causes an alternating line width where the second and fourth lines of a 1:4:6:4:1 quintet, which would arise in the limit of very rapid interconversion, as well as 1/3 of the central line are broadened beyond detection, leaving a 1:4:1 triplet. The spacing of the triplet is then the sum of the axial and equatorial proton coupling constants.

To provide further evidence of the interconversion the spectrum was examined at -70° in 1,2-dimethoxyethane (Fig. 24) and at 300° in 1-bromonaphthalene (Fig. 25). The coupling constants are given in Table 11. At -70° the interconversion rate has decreased to the point that the spectrum is that of a static conformation with all the expected lines present. The axial and equatorial coupling constants can be separately measured and the sum is in agreement with the room temperature value, making allowance for temperature and solvent variations[138]. On the other hand, at + 300° the rate has become so rapid that the spectrum represents the average conformation in which the four β-protons are equivalent with a coupling constant which is one half the sum of the axial and equatorial values, again allowing for temperature and solvent effects. These results, which are comparable to those of

FIGURE 25.

E. S. R. SPECTRUM OF 1, 2, 3-TRIHYDROPYRENYL RADICAL (86) AT +20° AND + 300°.



$a_2 = a_5$
$a_3 = a_4$
$a^e_{\beta\text{-CH}_2} + a^a_{\beta\text{-CH}_2}$
$a^H_{\gamma\text{-CH}_2}$
+20°
5
4
6
3
7
2
8
1
9
$\beta\ H_2C$
$CH_2\ \beta$
C
$\gamma\ H_2$
10
GAUSS
H
$\overset{H}{a}_{\gamma\text{-CH}_2}$
+300°
$\bar{a}_{\beta\text{-CH}_2}$
$a_3 = a_4$
$a_2 = a_5$

Table 11

Proton coupling constants of 1,9-trimethylenephenalenyl at various temperatures

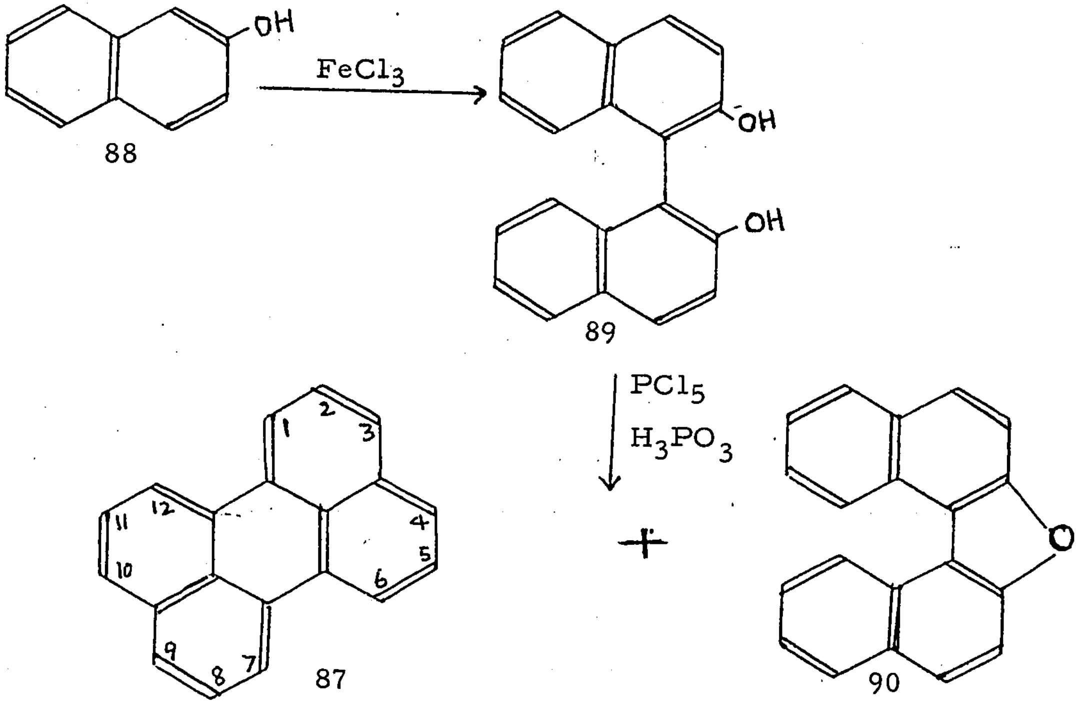
Solvent	1,2-dimethoxyethane		1-bromonaphthalene	
Temperature	-70°C	+20°C	+20°C	+300°C
$a_{3,4,6,7}$	6.14 g	6.12	5.99	5.90
$a_{2,5,8}$	1.74	1.73	1.72	1.72
a_β^a	11.97	-	-	-
a_β^e	2.99	-	-	-
$\tilde{a}_\beta$	-	-	-	7.19
$a_\beta^a + a_\beta^e$	14.96	14.86	14.60	14.38
a_γ	0.47	0.45	0.44	0.43
accuracy	1%	1%	1%	2%

Iwaizumi and Isobe for the 4, 5, 9, 10-tetrahydropyrene anion radical, help to confirm the analysis of the spectrum and the presence of the conformational interconversion. These spectra are unusually wide, 60 gauss. This is partly caused by the phenalenyl nucleus, which, being an odd alternant hydrocarbon[139], has considerable negative spin density as well as enhanced positive spin densities. The aliphatic substituent further increases the width because it provides axial protons adjacent to positions of high spin density.

The effect of the substitution on the phenalenyl radical can be seen in Table 10, where the aromatic proton coupling constants have been reduced by about 4%. On the other hand, although the symmetry has been reduced from threefold to twofold, those protons which were equivalent in phenalenyl appear to remain equivalent on substitution. There is no evidence of line splitting, although the lines are only 70 miligauss wide peak-to-peak. These results may be compared with those of Rabold et al.[140] who reported coupling constants of 6.21 and 1.68 gauss for 1-hydroxyphenalenyl radical. These again are only slightly different from those of phenalenyl radical.

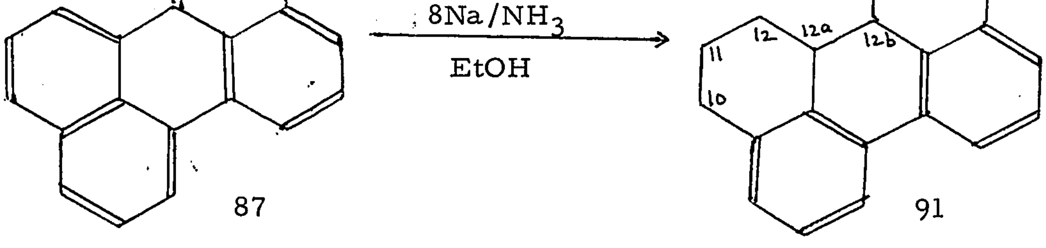
Synthesis of Perylene (87)

The synthesis of perylene (87) was performed according to the method of Zinke et al.[141]. β-Naphthol (88) was oxidized to β-dinaphthol (89) with ferric chloride[142], which was cyclized on heating with phosphorus pentachloride and ortho-phosphorous acid to perylene (87) in 25% yield. Another major product of the reaction was β-dinaphthylene oxide (90), 30% yield.



Birch Reduction of Perylene (87) (Method A):

The reduction of perylene with sodium (8 equivalents) in liquid ammonia in the presence of ethanol, gave only one product, an octahydroperylene in 97% yield. The structure of the octahydroperylene was assigned as 1, 2, 3, 10, 11, 12, 12a, 12b-octahydroperylene (91) as its mp was the same as the reported[143] mp for the same compound.

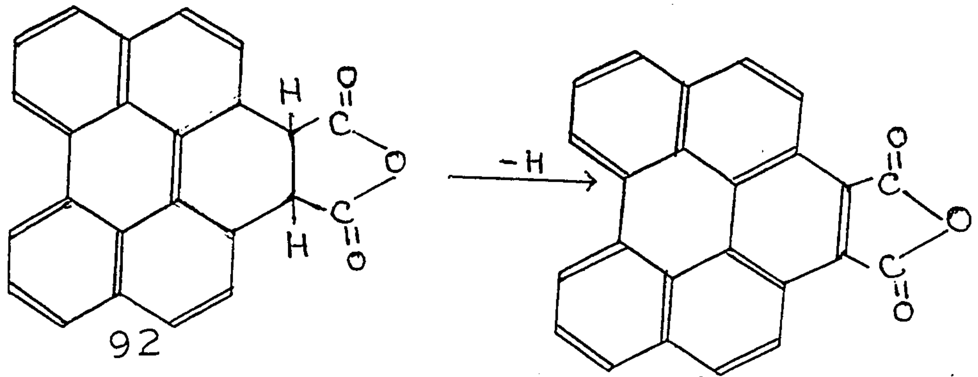


Further proofs for the structure (91) were obtained from its U. V. and NMR spectra. The U. V. spectrum of the compound was similar to that of biphenyl (l_{max} 41,000), and the l_{max} for (91) is (40,000). The NMR spectrum (Fig. 26) of (91) showed three multiplets at 8.0, 7.3 and 6.6 (14H) and another multiplet at 2.9 (6H). Elemental analysis and mass spectrum of the compound agreed with a molecular formula of $C_{20}H_{20}$ (octahydroperylene).

The reduction of perylene with four equivalents of sodium under the same experimental conditions gave 45% of the same octahydroperylene (91) and 55% unreacted perylene.

Dehydrogenation of 1,2,3,10,11,12,12a,12b-Octahydroperylene (91) with Chloranil in the Presence of Perchloric Acid

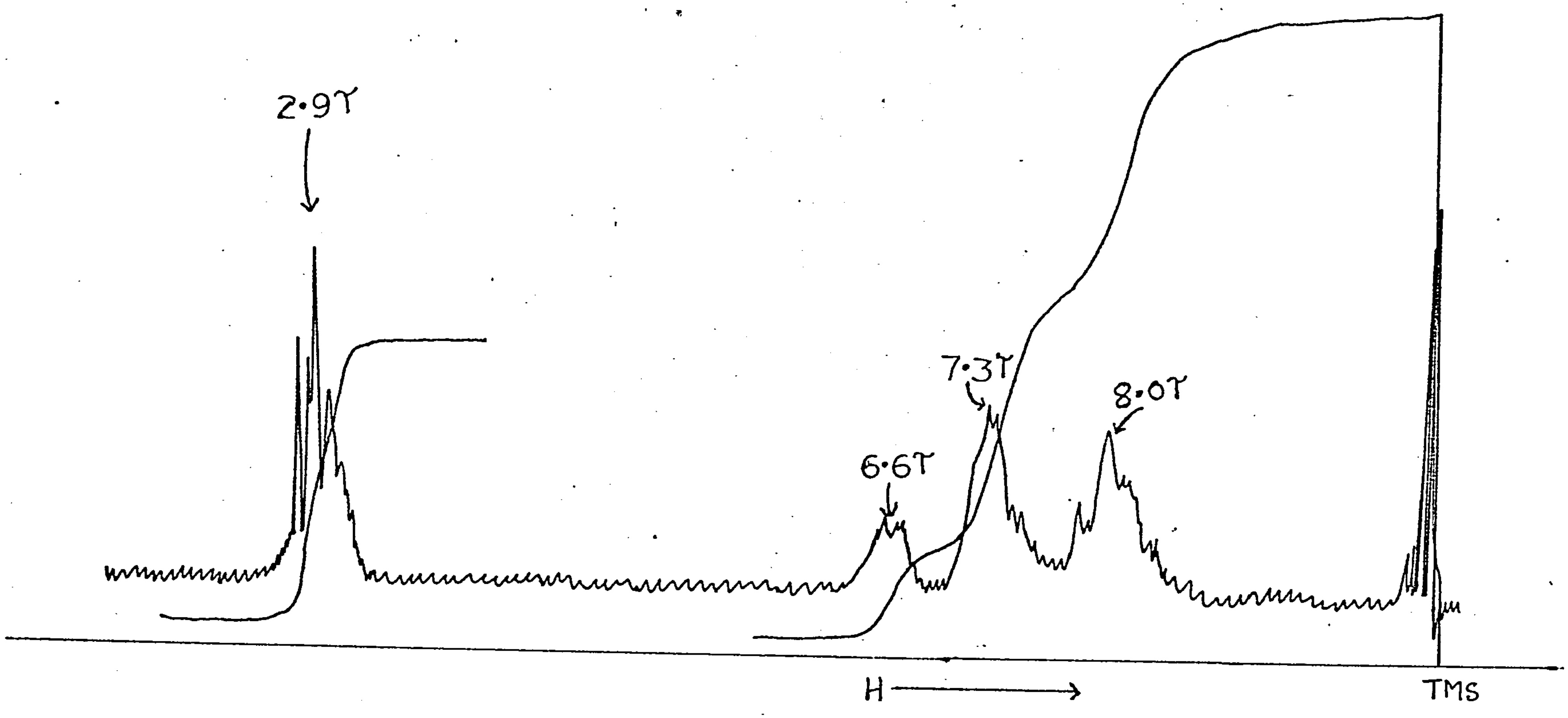
We attempted an experiment with octahydroperylene (91) to test whether it contains a phenalene structural unit. When (91) was treated with chloranil in the presence of perchloric acid, we observed a clean dehydrogenation reaction. We mentioned in an earlier chapter that α quinone can act as an efficient hydride acceptor and it can easily dehydrogenate 1,2-dihydro- and 1,4-dihydronaphthalenes to naphthalene[110-112]. The dehydrogenation of the compound (92) with chloranil was reported by E. Clar[145].



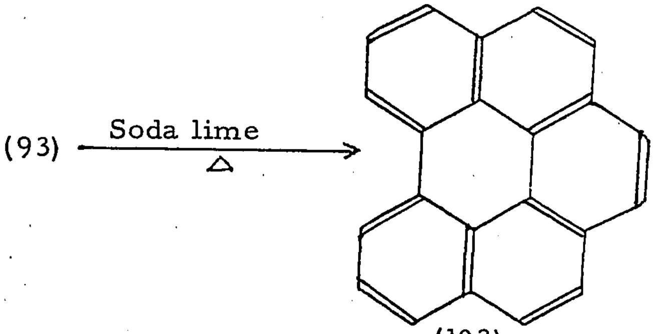
92

93

FIG. 26. NMR SPECTRUM OF 1, 2, 3, 10, 11, 12, 12a, 12b-OCTAHYDROPERYLENE (91) IN CARBON TETRACHLORIDE

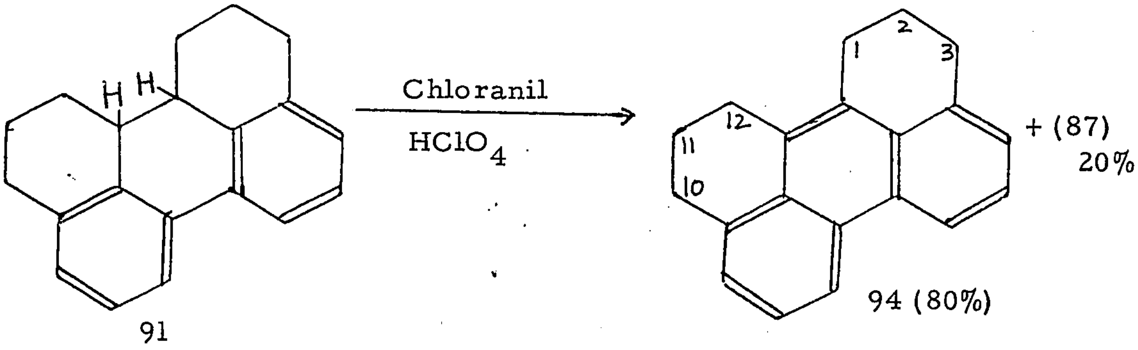


Decarboxylation of (93) with soda lime gave 1,12-benzoperylene (103).



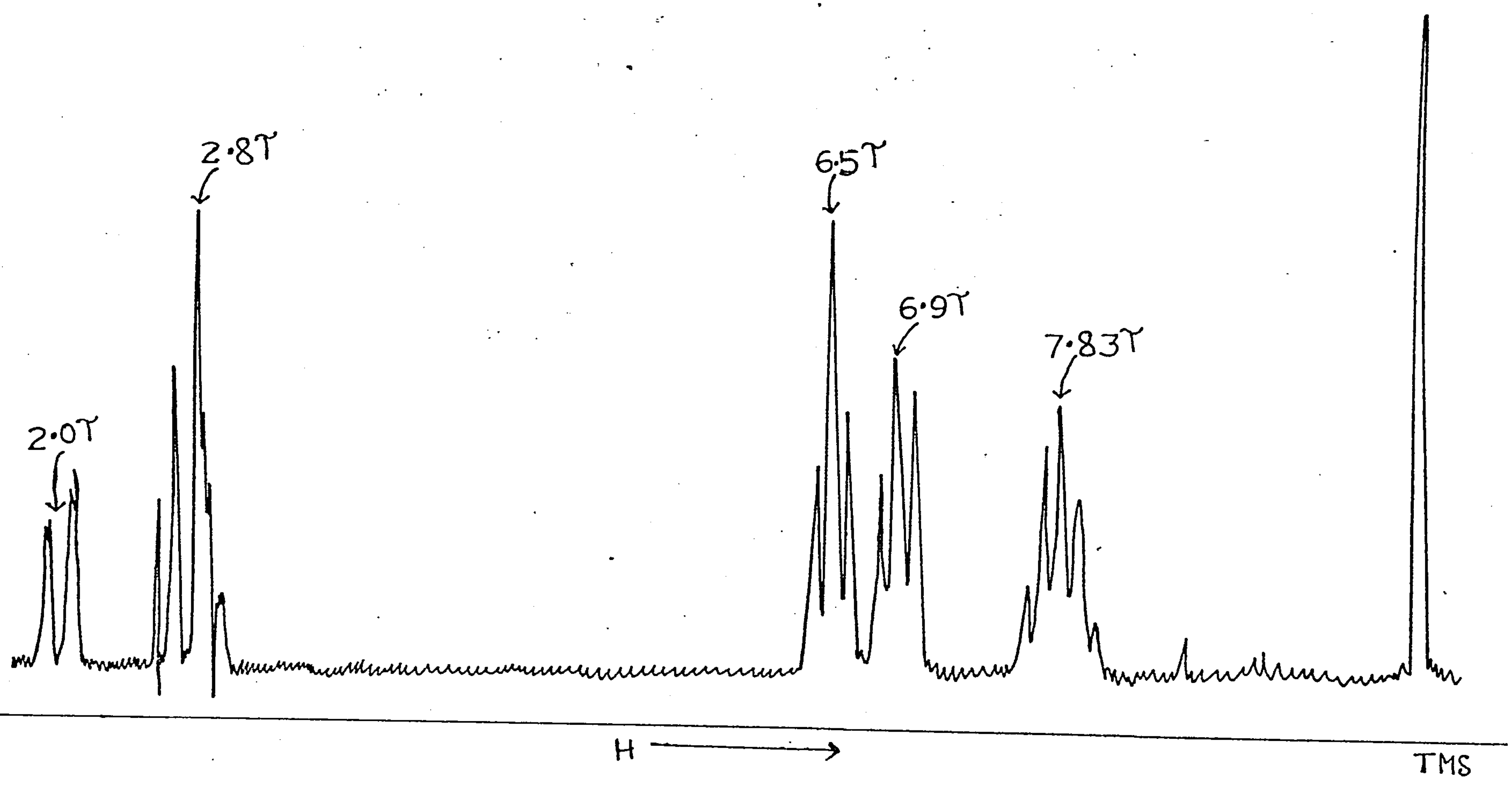
(103)

The dehydrogenation of (91) with chloranil in the presence of perchloric acid gave a hexahydroperylene (94) in 80% yield and perylene (87) in 20% yield. The hexahydroperylene (94) was assigned the structure as 1, 2, 3, 10, 11, 12-hexahydroperylene (94), since its mp agreed with the reported[146] mp for the same compound.



The above structure (94) for the hexahydroperylene has been confirmed by several authors[147-149]. Further proof of the structure (94) came from its NMR spectrum (Fig. 27), which

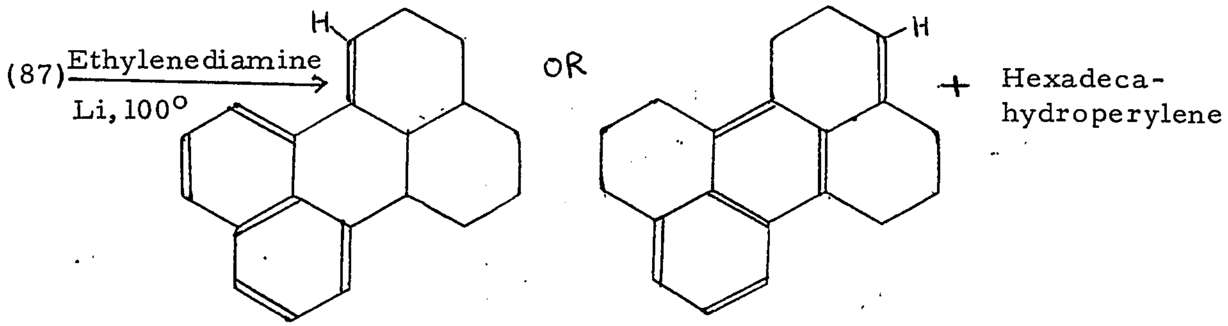
FIG. 27. NMR SPECTRUM OF 1, 2, 3, 10, 11, 12-HEXAHYDROPERYLENE (94) IN DEUTEROCHLOROFORM



showed a multiplet at 7.83 τ (4H), two triplets at 6.9 and 6.5 τ (8H) and two multiplets at 2.8 and 2.0 τ (6H). Mass spectrum and analysis of the compound agreed with the molecular formula $C_{20}H_{18}$ (hexahydroperylene).

Reduction of Perylene (87) (Method B):

The reduction of perylene with lithium (16 equivalents) in ethylenediamine gave an octahydroperylene in approximately 90% and a hexadecahydroperylene in 10% yield. Brooks et al.[96] also reported these two compounds from the reduction of perylene using the same reagents and experimental conditions. On the basis of I.R. and U.V. spectral data, they assigned either of the two structures (95 or 96) to the octahydroperylene.

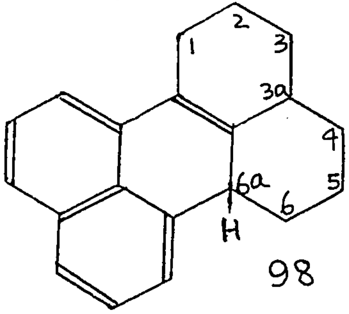


95 96 97

However, we found that both the proposed structures were in error for the following reasons:

1. The NMR spectrum (Fig. 28) of the octahydroperylene showed no vinylic proton to be present, but a tertiary aliphatic proton at 6.4 (broad peak), 13 aliphatic protons centered at 8.2 and 7.6 and six aromatic protons at 2.65 .
2. The I. R. and U. V. spectra of the compound were almost identical to those of phenalene (6) or tetrahydropyrenes (2 and 3).
3. The octahydroperylene gave a cation (isolated as perchlorate) with chloranil and perchloric acid and showed an e. s. r. signal similar to that of a substituted phenalenyl radical. This evidence showed that the compound contains a phenalene skeleton.

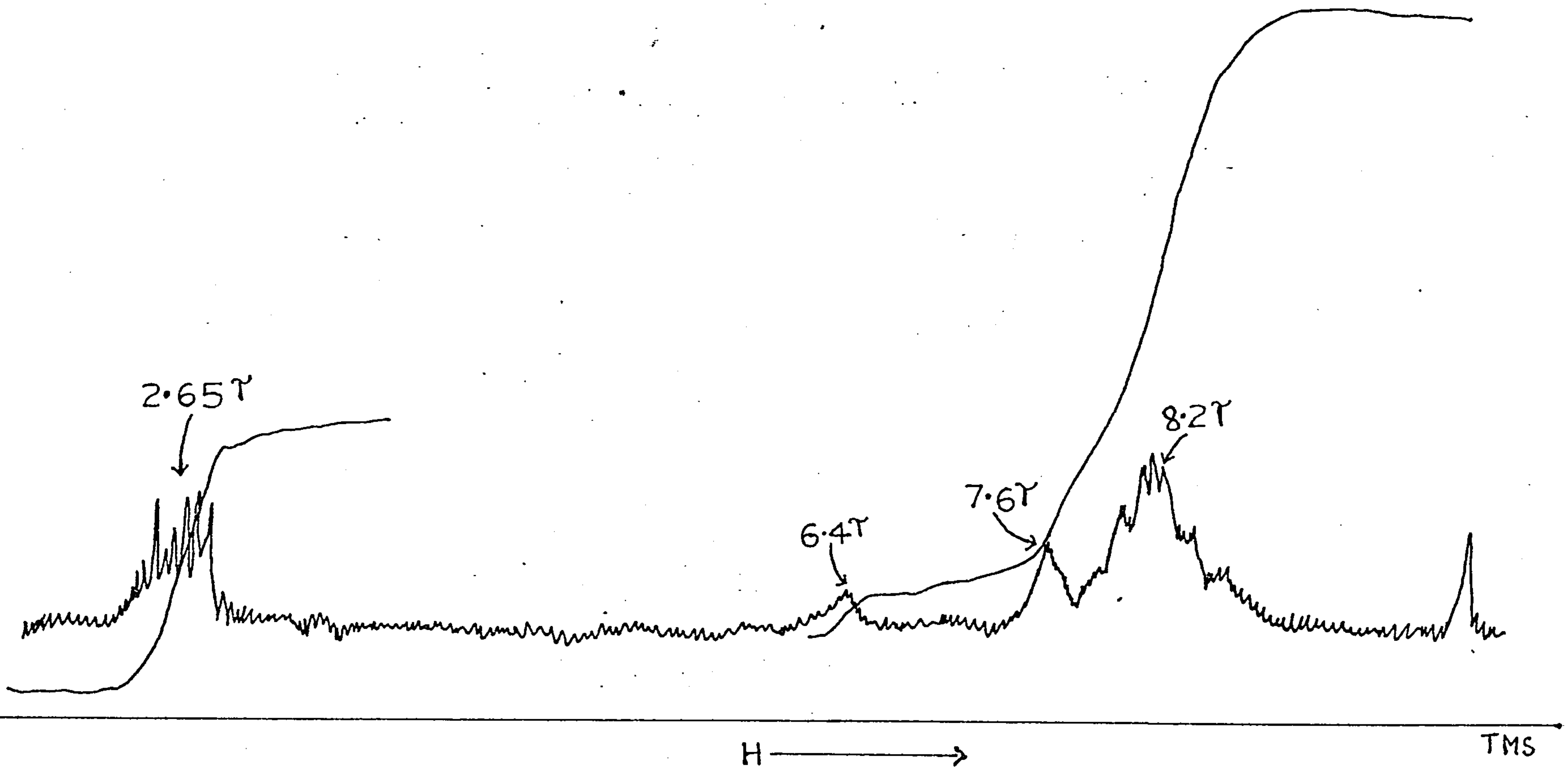
On the basis of the above facts, we have assigned the structure to the octahydroperylene as 1, 2, 3, 3a, 4, 5, 6, 6a-octahydroperylene (98) as shown below.



98

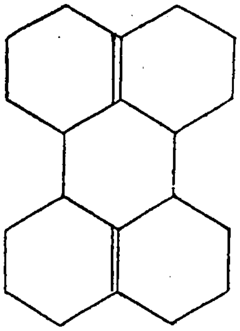
No positive structural assignment was possible for the hexadecahydroperylene (97), mass spec. 268 (mol. wt. of a hexadecahydroperylene 268.444).

FIG. 28. NMR SPECTRUM OF 1, 2, 3, 3a, 4, 5, 6, 6a-OCTAHYDROPERYLENE (98) IN CARBON TETRACHLORIDE

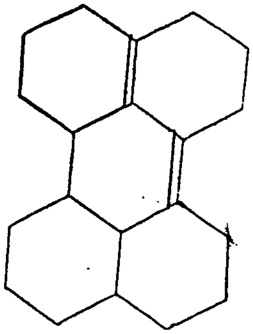


The NMR spectrum of this hexadecahydroperylene showed (Fig. 29) a complex multiplet for the aliphatic protons; no aromatic or vinylic proton signals were observed. The I.R. spectrum of the compound showed a weak band at 1650 cm^{-1} (the presence of a tertiary double bond) and the U.V. spectrum showed only one absorption band at 219 mμ (ϵ 11,000).

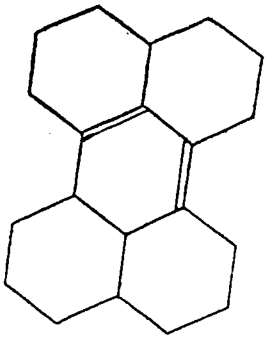
The following possible structures may be given to this hexadecahydroperylene (97) on the basis of the NMR evidence:



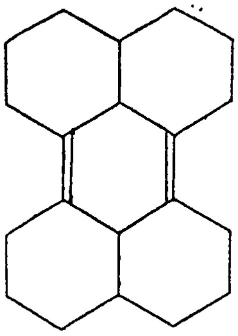
A



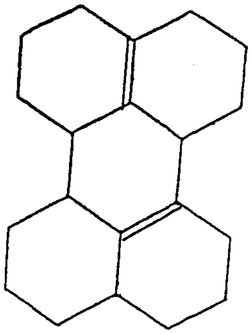
B



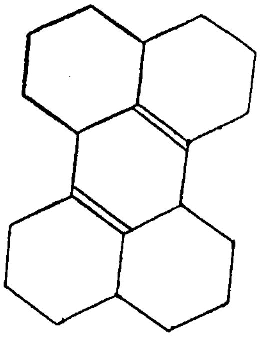
C



D

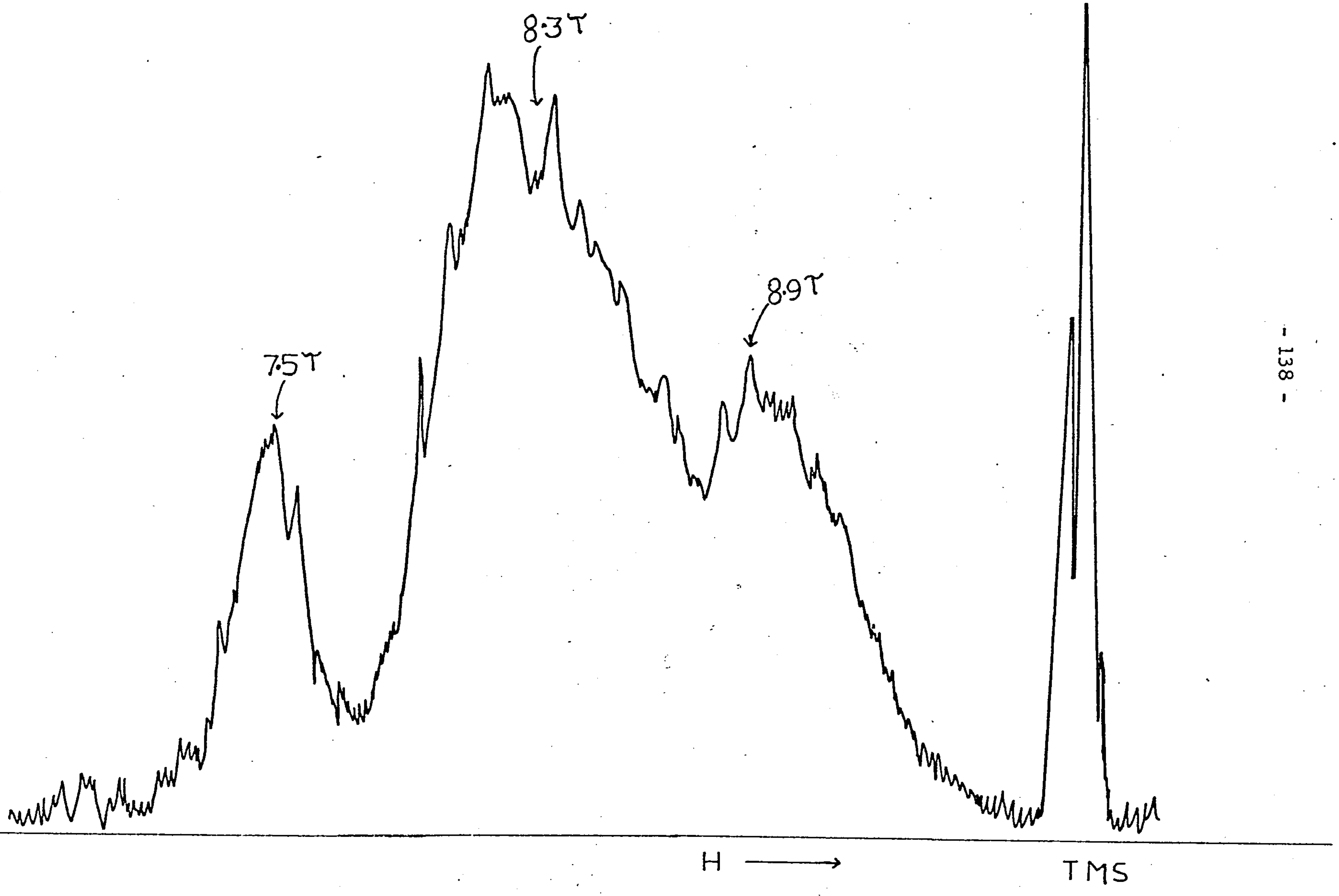


E



F

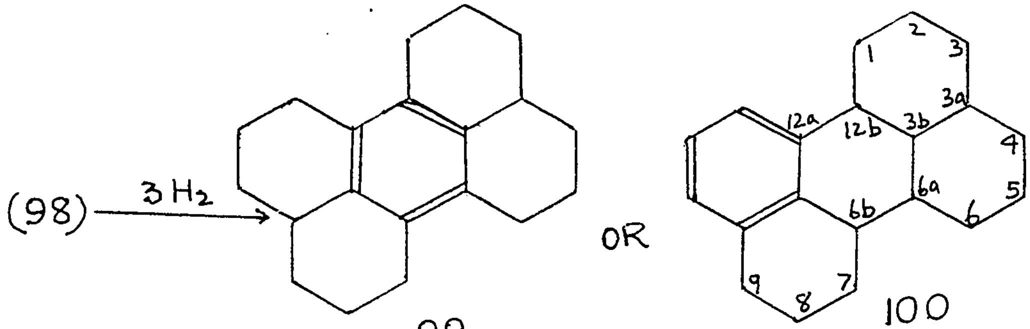
FIG. 29. NMR SPECTRUM OF HEXADECAHYDROPERYLENE (97) OF UNKNOWN STRUCTURE IN CARBON TETRACHLORIDE



From the U. V. evidence we may rule out the cis-and trans-conjugated dienes B and C, since these will absorb at a much higher wavelength. This leaves us in the uncomfortable position of having a non-conjugated diene which shows an absorption above 200 mμ. Examination of the literature indicates that this is not a unique case. For example, bicyclohepta-diene, a non-conjugated diene, has maxima at 205, 214 and 220 mμ. Models of possible configurations of the other non-conjugated dienes (A, D, E and F) do not give any clear-cut choice of structure for the unknown hexadecahydroperylene. We feel that without further work, the structure of (97) is not assignable.

Hydrogenation of 1, 2, 3, 3a, 4, 5, 6, 6a-Octahydroperylene (98)

Octahydroperylene (98) took three moles of hydrogen on hydrogenation at atmospheric pressure of hydrogen and in the presence of 5% Pd/C. The hydrogenation product was found to be a tetradecahydroperylene (mol. wt. of $C_{20}H_{26}$ 266.428, found by mass spec. 266). It had a U. V. spectrum similar to that of benzene (ε_{max} 75,000). Two possible structures can be written for the tetradecahydroperylene:



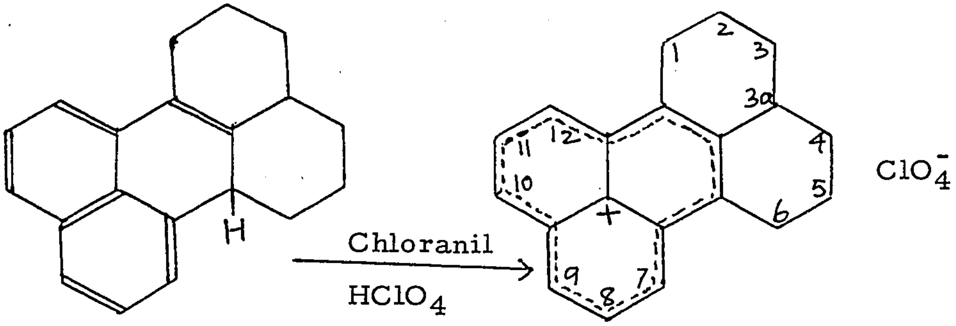
99

100

The NMR spectrum (Fig. 30) of the compound showed two multiplets at 2.84 and 2.3 τ (3, aromatic protons) and another two multiplets at 8.0 and 7.15 τ (23 aliphatic protons) which agrees with the formula (100).

1, 2, 3, 3a, 4, 5, 6-Heptahydroperylenium Perchlorate (101)

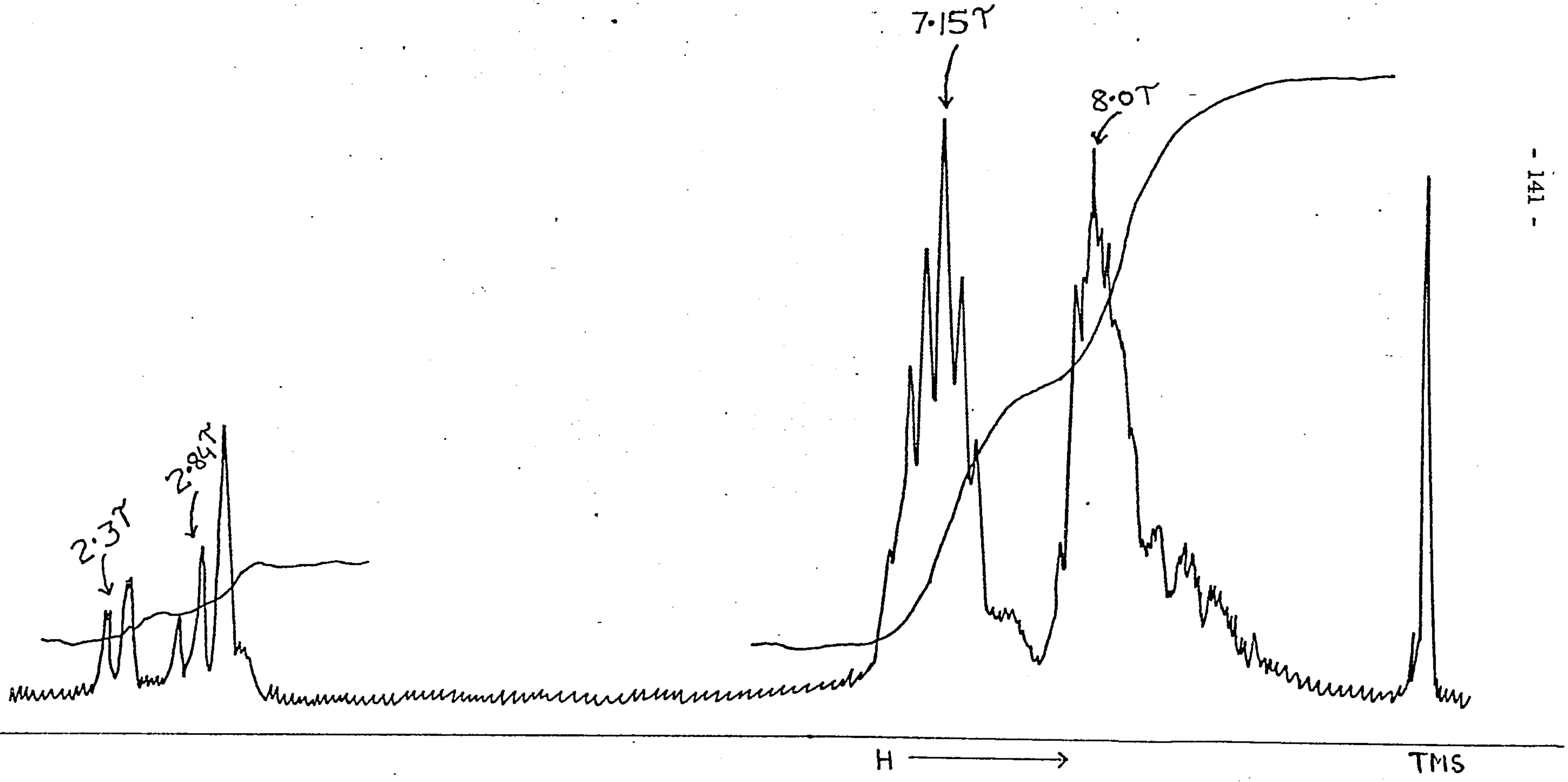
The perchlorate salt (101) was prepared from octahydroperylene (98) in the presence of chloranil and perchloric acid at room temperature in 86% yield.



98 101

The I.R. and U.V. spectra of (101) are similar to those of 1, 2, 3-trihydropyrenium perchlorate (54). The NMR spectrum of the salt (101) in 98% sulfuric acid gave a poorly resolved spectrum with a broad peak between 7.5 and 6.6 τ (13H), two multiplets at 1.93 τ and 1.5 τ (6H) (Fig. 31). The 'τ' values of a few cations are compared in Table 12.

FIG. 30. NMR SPECTRUM OF 1, 2, 3, 3a, 3b, 4, 5, 6, 6a, 6b, 7, 8, 9, 12b-TETRADECAHYDROPERYLENE (100) IN CARBON TETRACHLORIDE



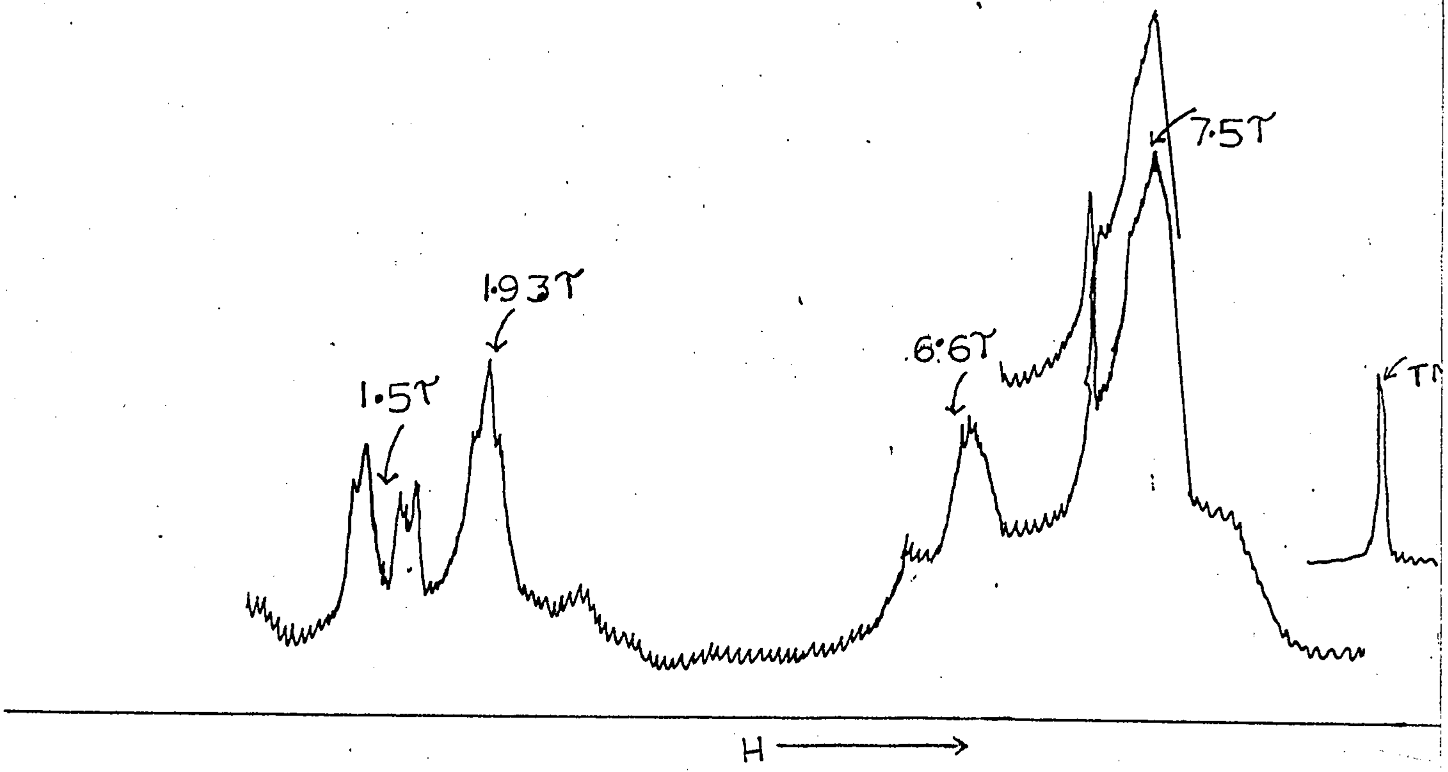


FIG. 31. NMR SPECTRUM OF 1, 2, 3, 3a, 4, 5, 6-HEPTAHYDRO-PERYLENIUM PERCHLORATE (101) IN 98% SULFURIC ACID (EXTERNAL TMS)

TABLE 12

NUCLEAR MAGNETIC RESONANCE POSITIONS OF A FEW CATIONS - RELATIVE TO TMS AS 10.

Cation	Solvent	τ Values
Tropenium[37]	CH_3CN	.75
	D_2SO_4	1.01
Triphenylmethyl[37]	CH_3CN	1.77, 1.94, 2.07, 2.17
	D_2SO_4	2.87, 3.0, 3.14, 3.28
Phenalenium[37]	D_2SO_4	1.46, 2.21
1, 2, 3-Trihydro-pyrenium	H_2SO_4	1.06, 1.85
1, 2, 3, 3a, 4, 5, 6-Heptahydroperylenium	H_2SO_4	1.5, 1.93

1, 2, 3, 3a, 4, 5, 6-Heptahydroperylenium perchlorate (101) is less stable than 1, 2, 3-trihydropyrenium perchlorate (54). The brown perchlorate salt (101) turns to a black mass on exposure to air. The acetonitrile solution of the salt (101), when hydrolyzed with water, gave a green solid, which showed an ether absorption band at 1085 cm^{-1} in I. R. The compound had the same physical properties as those reported for di-tetrahydropyrenyl ether (73). Hence, we believe this compound to be a di-octahydroperylenyl ether (102).

This ether, on dehydrogenation with Pd/C, afforded 60% perylene (calculated with respect to ether, 102) and cleavage with perchloric acid, gave 70% heptahydroperylenium perchlorate (101)

The perchlorate salt (101), on reduction with lithium aluminum hydride, gave 65% octahydroperylene (98), identical in all respects with an authentic sample. The remainder of the reduction product was an unidentified tar.

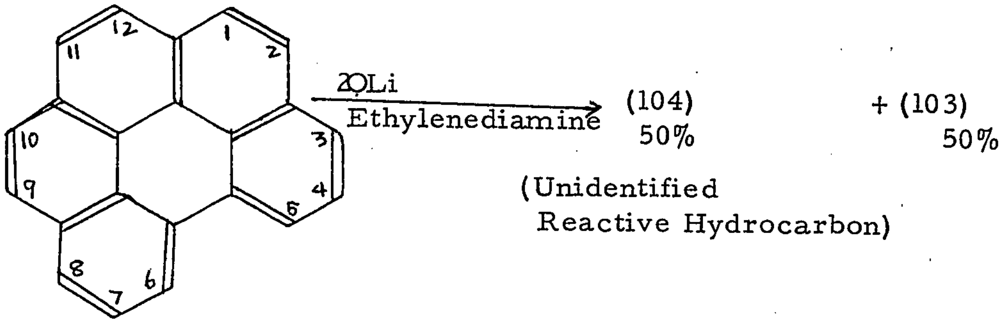
Octahydroperylene (98) also gave a red anion when treated with n-BuLi. This anion, on methylation, gave a viscous liquid which showed a mass of 274 (by mass spec.) which corresponded to a mono-methylated octahydroperylene. This viscous liquid, however, gave only perylene (87) on dehydrogenation with Pd/C at 360°.

The hydrocarbon (98) also showed an e. s. r. signal in carbon disulfide solution. The spectrum is quite complicated, due to the aliphatic part of the radical. The analysis of the spectrum is not yet complete and further work is in progress.

Reduction of 1,12-Benzoperylene or Benz-[ghi]-perylene (103) and Coronene (105)

The possibility arose in our mind that the reduction of the higher members of the polycyclic family might also give rise to compounds containing a phenalene structural unit.

1, 12-Benzoperylene on reduction with 20 equivalents of lithium in ethylenediamine, gave a very reactive hydrocarbon ($\approx$ 50%), (50% unreacted benzoperylene was recovered). This reactive hydrocarbon decomposed very fast on exposure to air or in an attempt to chromatograph the crude product.



103

The hydrocarbon (104) gave a brown perchlorate salt with chloranil and perchloric acid. The perchlorate salt had a characteristic perchlorate ion absorption band at 1120 cm^{-1} in I. R. and had a definite mp (144-146°).

The NMR spectrum of the crude reactive hydrocarbon (104) (Fig. 32) in a degassed carbon disulfide solution gave no conclusive evidence regarding the structure of the hydrocarbon. The hydrocarbon spectrum did, however, show a methylene signal at 6.0τ , characteristic signal for a phenalene-type 'methylene group'. The hydrocarbon in

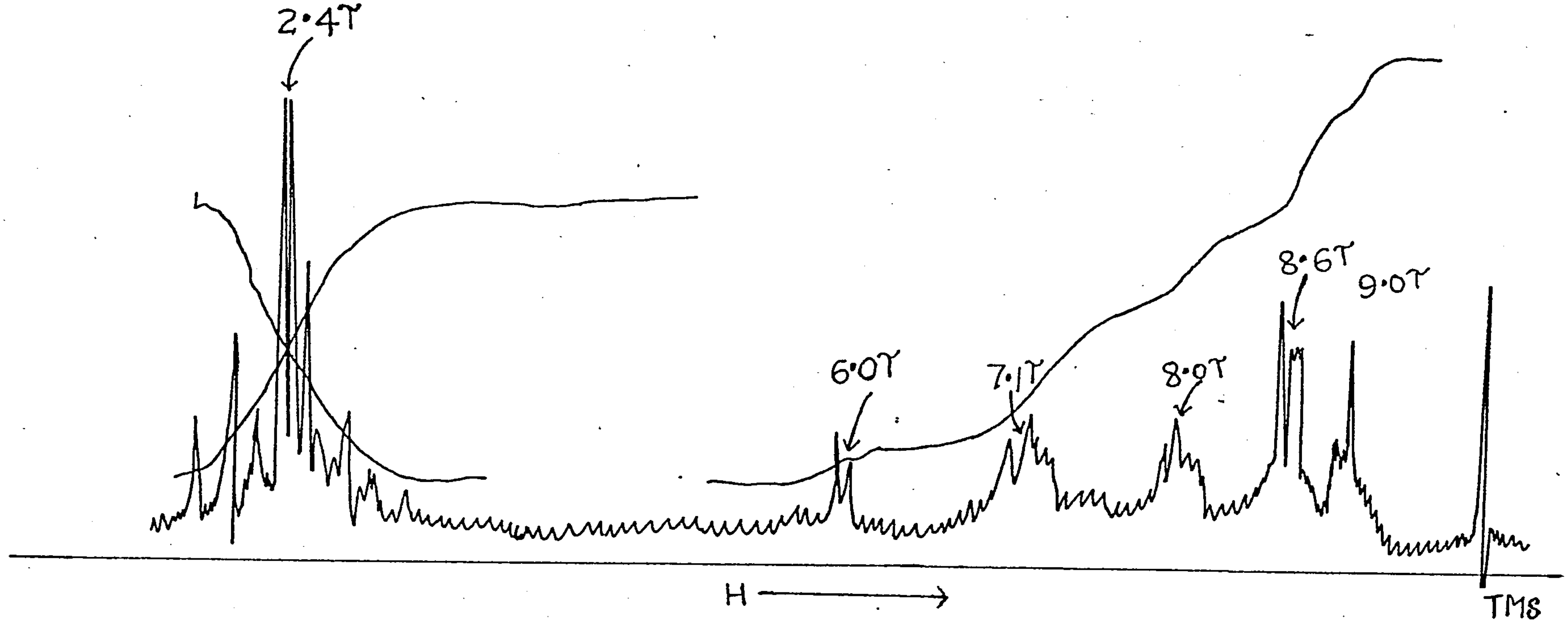


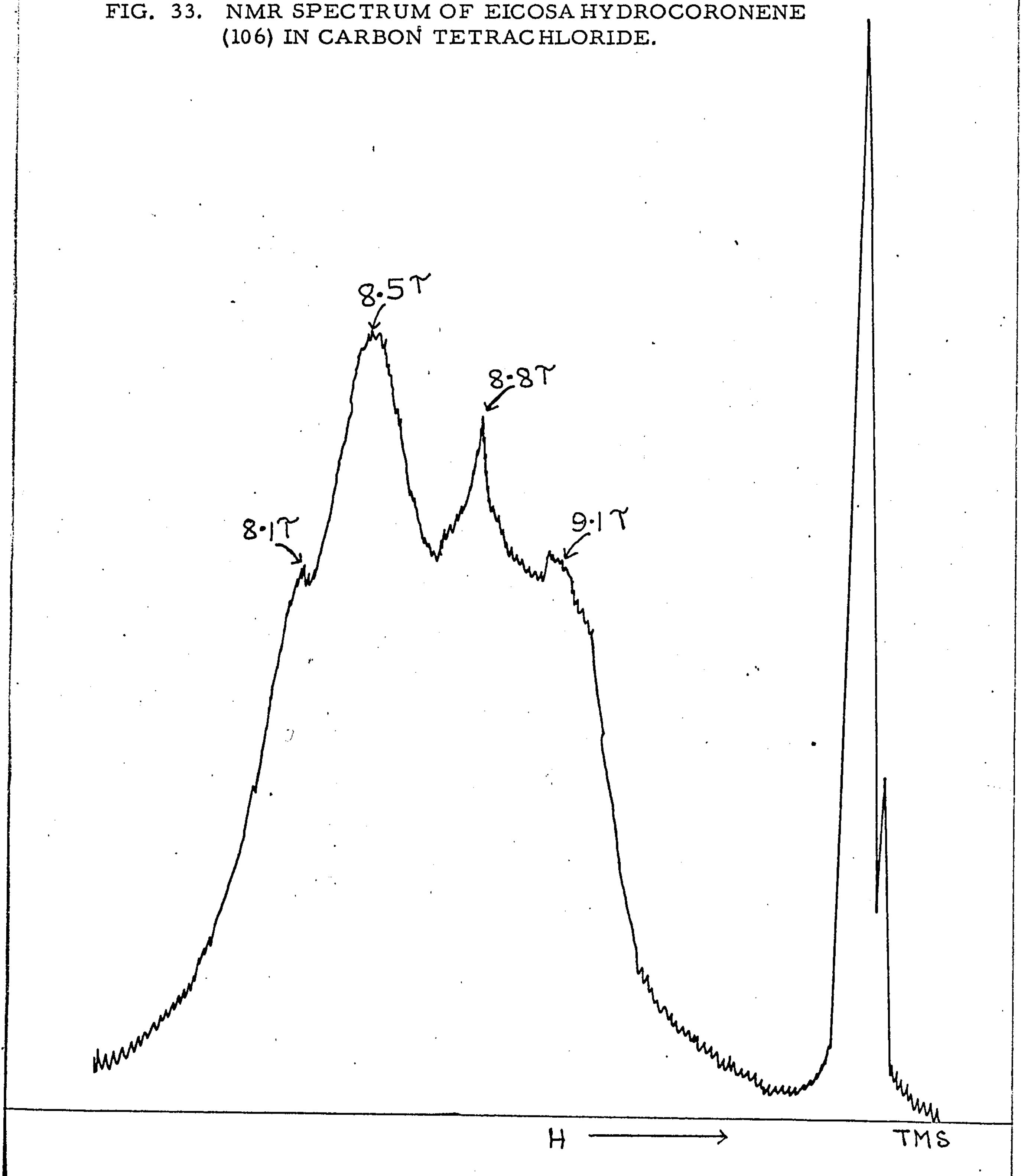
FIG. 32. NMR SPECTRUM OF BIRCH REDUCTION PRODUCT OF 1,12-BENZOPERYLENE (CRUDE) IN CARBON DISULFIDE.

carbon disulfide also showed a complex e. s. r. signal for a substituted phenalenyl radical. Due to the extreme reactivity of the reduced hydrocarbon (104) and the lack of benzoperylene, we are unable to make a choice between the possible isomers containing a phenalene structure.

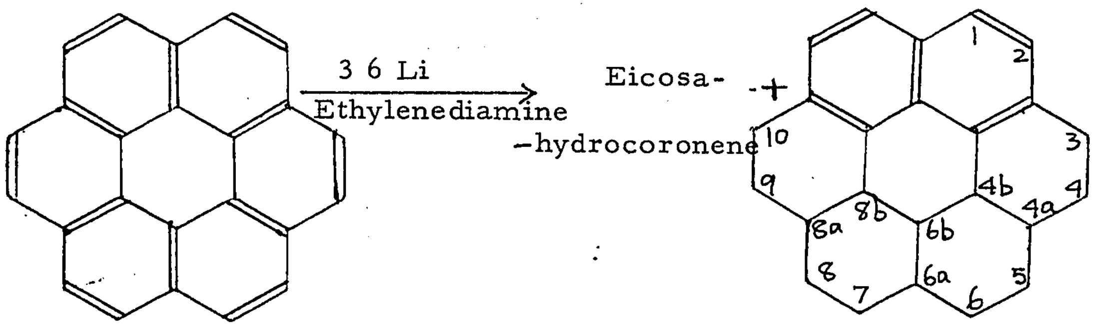
Coronene (105), on similar reduction with 36 equivalents of lithium in ethylene diamine, yielded two reduced hydrocarbons. The major product (70%) was a needle-shaped white crystalline solid, which corresponded to a eicosahydrocoronene (106) ($C_{24}H_{32}$ mol. wt. 320.5, found: 320 by mass spec.). Completely saturated coronene would be 324. The NMR spectrum (Fig. 33) of the hydrocarbon (106) showed no aromatic or vinylic proton absorptions. This indicates two tertiary double bonds. Further substantiation of this conclusion came from the I. R. spectrum which showed an absorption at 1645 cm^{-1}. The U. V. spectrum was very similar to that of hexadecahydroperylene (97) (λ_{max} 220 mμ , ϵ12,000), indicating a possible similar geometry for the two double bonds in both compounds. Without the benefit of further evidence we are again unable to assign the structure of compound (106).

The minor hydrocarbon (107) (30%) showed a U. V. spectrum similar to that of naphthalene. The I. R. spectrum indicated only aromatic and aliphatic absorption bands. This compound does not possess any phenalene structural unit (I. R. and U. V. spectra are different from those of phenalene), as

FIG. 33. NMR SPECTRUM OF EICOSA HYDROCORONENE (106) IN CARBON TETRACHLORIDE.

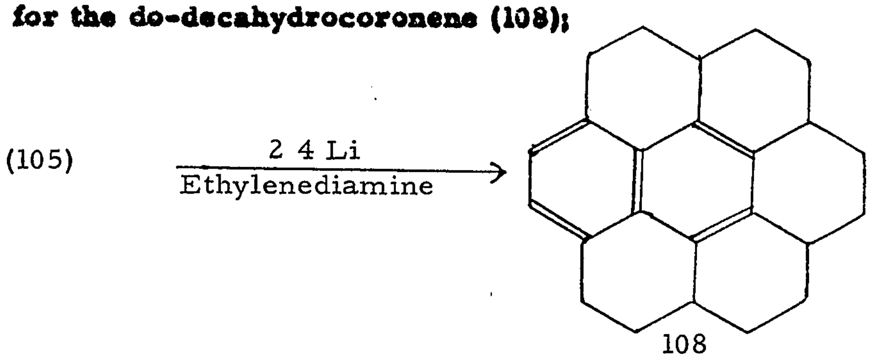


indicated by its inability to form a perchlorate salt with chloranil and perchloric acid. The molecular weight of this material was 314 as determined by mass spectrometry which corresponded to a tetradecahydrocoronene. The NMR spectrum (Fig. 34) of the tetradecahydrocoronene (107) showed absorptions for four aromatic protons at 3.0 τ and 22 aliphatic protons at 8.1 and 7.1 τ. The possible structure of the tetradecahydrocoronene is shown below (107).



105 106 107

Brooks et al.[96] reported that coronene gave a do-decahydrocoronene (108) on similar reduction, using 24 equivalents of lithium in ethylene diamine. On the basis of I. R. and U. V. spectral data they assigned the following structure for the do-decahydrocoronene (108);



108

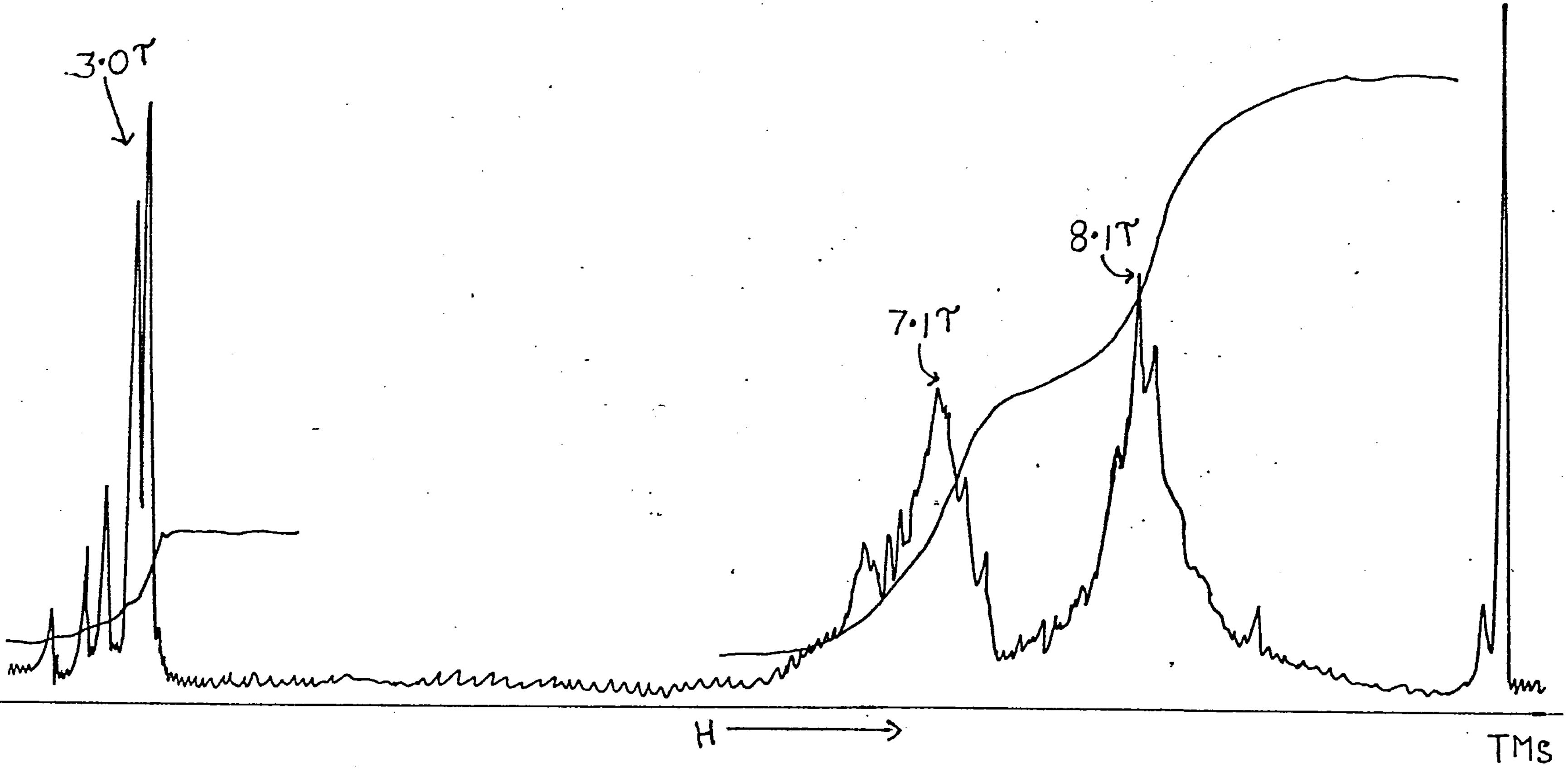


FIG. 34. NMR SPECTRUM OF TETRADECAHYDROCOCONENE (107) IN DEUTEROCHLOROFORM

Coronene was reduced with an excess of lithium in ethylenediamine by Reggel *et al*.[150], who obtained a completely hydrogenated coronene.

We believe a phenalene structural unit can be formed in coronene molecule also, under a suitable reaction condition. Reported[96] do-decahydrocoronene (108) possesses a vinyl-naphthalene structural unit as shown from its I. R. and U. V. spectra. Since these workers had no NMR spectrum of the compound, the evidence for the proposed structure is not very strong. In the light of our experience in other peri-condensed aromatic systems, we have reservations in accepting the findings of Brooks.

Due to rather a high price ($100 per gram) of coronene or an alternative tedious synthesis, we did not carry out any further study of this system.

EXPERIMENTAL

Melting points were determined with a Leitz Wetzlar microscopic apparatus and are uncorrected.

All evaporations were done in vacuo at room temperature unless otherwise stated.

Infrared spectra were measured in Nujol mull or in chloroform solution (solvent compensated) on a Perkin-Elmer Infracord instrument and Beckman IR 8 spectrophotometer.

The proton magnetic resonance spectra were measured with a Varian V-4302 spectrometer operating at 60 MC/sec. When spectra were taken in carbon tetrachloride, carbon disulfide and deuterochloroform they were calibrated with reference to tetramethylsilane (TMS) as an internal standard. However, they were calibrated with reference to external (TMS) when taken in sulfuric acid, deuterosulfuric acid and perchloric acid.

Abbreviations used are:
s (singlet: d (doublet); t (triplet), and m (multiplet).

Mass spectra were taken using a Hitachi Perkin-Elmer RMV-6D-2 with a direct inlet system. Ultraviolet and visible spectral data were taken on a Perkin-Elmer Model 202 spectrometer.

Analyses were done by Midwest Microlab Inc., and Dr. A. B. Bernhardt, Germany.

Gas chromatographic analyses were carried out using a Beckman/GC-2 instrument having a column of 18 ft. x 1/4 inch, packed with either 60/80 glass beads with 0.2% apiezon as stationary phase or 60/80 chromosorb with 1% apiezon as stationary phase.

The e.s.r. spectra were run on a Varian spectrometer with 100 KC modulation. All samples were thoroughly degassed and sealed in U tubes under high vacuum with the exception of those in 1-bromonaphthalene. In this case, the deoxygenated samples were sealed under a nitrogen atmosphere.

All solvents were employed as supplied commercially unless a dry solvent was desired. Ethanol was dried by refluxing it with iodine and magnesium and finally distilled. Ether was dried on sodium wire and stored in an amber-coloured bottle in the dark. Ethylene diamine was first dried over potassium hydroxide pellets, then on sodium metal and finally distilled over sodium. Acetonitrile was dried over phosphorus pentoxide and distilled over it.

Pyrene (pure grade, K and K Laboratories) was zone refined[151] by passing three times through a sixteen stage zone refiner. Perylene was synthesized in this laboratory starting with β-naphthol, following the procedure of Hansgirg et al.[141].

Birch Reduction of Pyrene (Method A)

The procedure used for the reduction was that reported by Otto Neunhoeffer *et al.*[3] in supposedly making 1, 6- or 1, 8-dihydropyrene. Pure pyrene (1), mp 149-150° (reported[151] 149.5°-150°), 14.157 g (0.07 mole) was dissolved in 300 ml of dry ether and 50 ml of freshly distilled absolute ethanol. This solution was added to 500 ml of liquid ammonia in a three-necked flask (2 l) equipped with a dry ice condenser and nitrogen inlet and outlet tubes. The whole assembly was flushed with pure and dry nitrogen and a constant flow of nitrogen was maintained until the end of the reaction. Small pieces of pure reagent grade sodium, 7.0 g (0.3043 g-atom, 4 equivalents) were added quickly into the stirred reaction mixture and the reaction was allowed to proceed (at -30°) for 4 hr. After the addition of sodium, a deep, persistent red colour appeared. If all the reagents are not pure and dry, or if the assembly is not airtight, the solution becomes blue to blue-green. After 4 hr. of refluxing, the ammonia was allowed to evaporate slowly at room temperature. After complete evaporation of ammonia the red reaction mixture turned pale yellow. A 500 ml portion of ether and 300 ml of water was added to the reaction mixture. The ether layer was washed several times with water, followed by shaking with 200 ml of 10% sulfuric acid and finally water washed. The ether solution was dried by filtering through anhydrous sodium sulfate. All the operations were carried out as far as possible under a nitrogen atmosphere. The ether solution was concentrated *in vacuo* to give 13.5 g of crude reduction product. The product was stored at -30° under a vacuum.

The crude reduction product was analyzed using a Beckman/GC-2 gas chromatograph (at 220°), having a column of 18 ft. x 1/4 in., packed with 60/80 glass beads with 0.2% apiezon as stationary phase. Two major and two minor peaks were recorded. The two major peaks corresponded to two isomeric tetrahydropyrenes 2 and 3 (1,2,3,6- and 1,2,3,5-) approximately in the ratio 2:1 respectively and constituted 89% of the total reduction product. The other two minor peaks were identified as 1,2,3,3a,4,5,5a,6,7,8-decahydropyrene (5) (8%) and unreacted pyrene (3%) respectively (Fig. 10).

A chloroform solution containing 2.0 g of crude reduction product was chromatographed on freshly activated (210°, 48 hr.) Woelm alumina (1.5 x 30 cm column slurry packed with petroleum ether, bp 30-60°) and eluted with the same solvent. The first 200 ml of petroleum ether fraction afforded 0.50 g of white 1,2,3,6- and 1,2,3,5-tetrahydropyrenes (2 and 3) which turned yellow slowly and ultimately to black tar on exposure to air; mp 54-56°.

U.V. $\lambda_{max}^{cyclohexane}$: 204 mu (e 16,500), 218 mu (e 16,000), 241 mu (e 33,000), 275 mu (e 1,500), 324 mu (e 9,700), 327 mu (e 9,600), 337 mu (e 9,000), 341.5 mu (e 8,000) and 357 mu (e 7,400). (Fig. 12).

I.R. (chloroform): 3040 cm^{-1}, 2925 cm^{-1}, 2842 cm^{-1}, 1640 cm^{-1}, 1580 cm^{-1}, 1443 cm^{-1} and 845 cm^{-1}. (Fig. 11).

NMR (carbon disulfide): 8.15, 7.65 and 7.20 τ (m, 6H). 6.18 τ (s, 2H). 4.35 τ (m, 1H). 3.20 and 3.52 τ (t, 0.70H) and 3.0 τ (m, 4.30H). (Fig. 13).

Mass spec: 206 (mol. wt. of tetrahydropyrene, 206.288).

The subsequent fractions collected from the chromatographic column contained a less pure mixture of the two isomers, probably contaminated by the decomposition products of tetrahydropyrenes. The separation of decahydropyrene and unreacted pyrene from the reduction product was achieved by another method which will be described later.

The experiment was repeated under the same experimental conditions but with dry and purified ammonia (ammonia was passed through barium oxide and glass wool); the same reduction products were observed as in the previous experiment.

Birch reduction of pyrene with two equivalents of sodium under the same experimental condition as before gave 45% tetrahydropyrenes (2 and 3), 2% decahydropyrene (5) and the balance was unreacted pyrene.

Separation of 1, 2, 3, 3a, 4, 5, 5a, 6, 7, 8-Decahydropyrene (5) and Unreacted Pyrene from Tetrahydropyrenes

Crude reduction products (2.06 g) from the Birth reduction of pyrene were dissolved in 20 ml of acetic acid and to this a solution of chloranil (2.46 g) and 3 ml of 72% perchloric acid in 400 ml of acetic acid was added. 1, 2, 3-Trihydropyrenium perchlorate was precipitated, which was separated by filtration. The mother liquor of the perchlorate salt was extracted with ether and the ether layer was washed with water to free it from acetic acid. The ether extract was then treated with 10% aqueous sodium hydroxide to remove quinol. After separation of quinol, the ethereal solution was evaporated *in vacuo*. The residue thus obtained, (0.230 g) was dissolved in a minimum amount of ethanol and added to a saturated solution of an equivalent amount of picric acid, also dissolved in ethanol. Long red needles of pyrene picrate precipitated out. This was filtered, washed with cold ethanol and dried; 0.120 g., mp 221-222° (reported[154] 222°). This red picrate of pyrene was decomposed in benzene with aqueous sodium carbonate solution into pyrene, which was crystallized from ether-ethanol, 0.60 g (3%), mp 149-150°, mixed mp with an authentic sample 149-151°.

The filtrate of the pyrene picrate was concentrated in vacuo and the residue was triturated with petroleum ether, bp 30-60°, which removed only decahydropyrene. After evaporation of the petroleum ether, a viscous liquid was obtained which was dried under vacuum: yield 0.16 g (8.0%). The crude decahydropyrene (5) was chromatographed on freshly activated alumina (1.5 x 20 cm column slurry packed with petroleum ether, bp 30-60°) and eluted with the same solvent. The first 300 ml of petroleum ether fraction after evaporation of the solvent gave 0.14 g of viscous oil. This oil showed only one spot in TLC and one peak by VPC. The oil was further purified by molecular distillation at 150-151°/12 mm. The oil crystallized when kept in freezer; mp 32-34° (reported[98] mp 34°; bp 151-152°/12 mm).

U.V. $\lambda_{max}^{cyclohexane}$: 222 mμ (e 14,000) and 270 mμ (e 400).

NMR (deuterochloroform): 8.7, 8.2, 733 τ (m, 18H) and 3.3 τ (s, 2H). (Fig. 14).

Mass Spec.: 212 (mol. wt. of decahydropyrene 212.336).

Anal. Calcd. for $C_{16}H_{20}$: C, 90.506; H, 9.494.

Found: C, 90.37; H, 9.59.

Protonation of Pyrene Anion with Ethanol

Pure pyrene (1), 4.04 g (0.02 mole), dissolved in 100 ml of dry ether was added to 200 ml of liquid ammonia. Pure sodium in small pieces, 1.0 g (0.045 g-atom) was added to the pyrene solution and the reaction was allowed to proceed at -30° for 4 hr. under a nitrogen atmosphere. Dry ethanol (10 ml) was added quickly to the red pyrene anion. The red colour persisted even after the addition of ethanol and disappeared only after complete evaporation of ammonia. After the addition of ethanol, ammonia was evaporated as quickly as possible and the reaction product was extracted with ether. The ether layer was washed thoroughly with water, 10% sulfuric acid and then again with water, dried over anhydrous sodium sulfate and the solvent was removed in vacuo. The product when analyzed by VPC showed 30% tetrahydropyrenes (2 and 3), 10% 4, 5-dihydropyrene (12) and 55% unreacted pyrene (1). In addition, 5% unidentified tar was also recovered. In another, similar experiment, the anion was protonated after the evaporation of ammonia. The solution remained red even after the evaporation of ammonia, but when protonated with ethanol the red colour was immediately discharged. In both the protonation experiments, the products were the same. The protonation experiment was repeated with t-BuOH as protonating agent and the products in this case were the same as in the protonation with ethanol.

Separation of 4, 5-Dihydropyrene (12)

The crude protonation product (2g) was dissolved in 30 ml of acetic acid and this was added to a solution of chloranil (1. 0 g) in 100 ml of acetic acid and 1. 0 ml of 72% perchloric acid. 1, 2, 3-Trihydropyrenium perchlorate (54) was precipitated and dry ether (100 ml) was added to make the precipitation of the perchlorate salt complete. The perchlorate salt was separated and the mother liquor was diluted with more ether. The ether layer was washed free from acetic acid and extracted with 10% sodium hydroxide. The aqueous alkaline solution gave (0. 6 g) hydroquinone on acidification with hydrochloric acid. The ether layer, after removal of solvent gave a mixture of 1. 3 g of pyrene (1) and 4, 5-dihydropyrene (12). The mixture of (1) and (12) in ethanol was treated with an equimolecular quantity of picric acid. The picrate of pyrene was precipitated as red needles and that of 4, 5-dihydropyrene was soluble in ethanol. The ethanol solution was taken and treated with aqueous sodium bicarbonate solution; 4, 5-dihydropyrene precipitated and crystallized from ethanol; white plates (0. 10 g), mp 131-132° (reported[99] 132°).

U. V. $\lambda_{max}^{cyclohexane}$: 250 mu (e 28, 000), 257 mu (e 44, 700), 263 mu (e 29, 500), 280 mu (e 11, 500), 286 mu (e 11, 000), 295 mu (e 8, 200), 298 mu (e 12, 600), 311 mu (e 1, 600), 317. 5 mu (e 1, 400), 323 mu (e 1, 600), 327 mu (e 1, 500), 331 mu (e 1, 500), 338 mu (e 1, 400), 342 mu (e 1, 300), 345 mu (e 1, 300) and 350 mu (e 400).

I. R. (chloroform): 3042 cm^{-1}, 2930 cm^{-1}, 2840 cm^{-1}, 1600 cm^{-1}, 1445 cm^{-1} and 840 cm^{-1}.

NMR (carbon tetrachloride): 6.75 τ (s, 4H) and 2.5 τ (m, 8H), (Fig. 15).

Mass spec.: 204 (mol. wt. of dihydropyrene 204.288).

Anal. Calcd. for $C_{16}H_{12}$: C, 94.08; H, 5.92.

Found: C, 93.84; H, 6.13.

Protonation of Pyrene Anion with Water

Pure pyrene, 4.04 g (0.02 mole) in 100 ml of dry ether was added to 200 ml. of liquid ammonia and to this solution small pieces of sodium, 1.0 g (0.045 g-atom) were added under a nitrogen atmosphere. The reaction was allowed to proceed for 4 hr. at -30°. The red anion was then protonated with water (10 ml). The red colour was discharged in 1-2 minutes. Ammonia was evaporated and the product was extracted with ether. The product was identified by NMR, TLC and VPC and was found to be a mixture of pyrene (40%) and 1,2-dihydropyrene (16) (55%) and about 5% 4,5-dihydropyrene (12). Dihydropyrene (16) was separated from pyrene and 4,5-dihydropyrene (12) by fractional crystallization ffom ethanol, mp 110-113°.

U.V. $\lambda_{max}^{cyclohexane}$: 215 mu (e 108,000), 231 mu (e 100,000), 238 mu (e 66,000), 259 mu (e 26,000), 270 mu (ϵ 30,000), 322 mu (e 20,000), 340 mu (e 28,000) and 362 mu (e 14,200).

I.R. (chloroform): 3040 cm^{-1}, 3010 cm^{-1}, 2920 cm^{-1}, 2870 cm^{-1}, 1600 cm^{-1}, 1580 cm^{-1}, 1500 cm^{-1}, 1440 cm^{-1} and 830 cm^{-1}.

NMR (carbon tetrachloride): 6.3 and 6.1 τ (m, 4H), 4.3 and 4.1 τ (m,t,2H), 3.9 and 3.7 τ (t, 1H) and 2.9 τ (m, 5H). (Fig. 16).

Mass Spec.: 204 (mol. wt. of dihydropyrene 204.288).
Anal. Calcd. for $C_{16}H_{12}$: C, 94.08; H, 5.92.
Found: C, 93.80; H, 6.22.

The protonation experiment with water was repeated under the following conditions:

(i) Adding water after the evaporation of ammonia, and
(ii) Using dry and pure ammonia (by passing commercial ammonia through barium oxide and glass wool).

In both these cases the products were the same as before. In another experiment pyrene anion was made from pyrene with two equivalents of sodium in boiling THF and protonation of this anion with water also gave the same dihydropyrenes as in the previous experiment.

Hydrogenation of 1,2-Dihydropyrene (16):

1,2-Dihydropyrene, 0.51 g (0.0025 mole), dissolved in 20 ml of cyclohexane was hydrogenated at room temperature and under one atmospheric pressure of hydrogen, using 1.0 g of 5% Pd/C catalyst. A total of 110 ml of hydrogen (0.005 mole) was taken up in one hour and after that there was no further uptake of hydrogen. The hydrogenation product, after extracting with ether, yielded 0.490 g of 1,2,3,3a,4,5-hexahydropyrene (18), crystallized from ethanol, white leaflets, mp 104-105°. The hexahydropyrene (18) thus obtained was identical in all respects with an authentic sample. [The data for hexahydropyrene (18) are given in a later experiment].

Birch Reduction of 1, 2-Dihydropyrene (16)

1, 2-Dihydropyrene, 2.04 g (0.01 mole) was dissolved in 50 ml of dry ether and 8 ml of absolute ethanol and was added to 150 ml of liquid ammonia. Small pieces of sodium, 0.5 g (0.023 g-atom) were added to this solution under a nitrogen atmosphere and the solution turned red. The reaction was allowed to proceed for 4 hr. and after that time, ammonia was evaporated. The reduction product, after extracting with ether, yielded 1.9 g of tetrahydropyrenes (2 and 3) in the ratio 2:1 respectively. The tetrahydropyrenes obtained in this experiment were identical in all respects with an authentic sample.

Methylation of Pyrene Anion

The pyrene anion, prepared by adding a solution of 4.04 g (0.02 mol) of pyrene in dry ether (100 ml) to a solution of 1.0 g of sodium (0.045 g-atom) in 200 ml of liquid ammonia under a nitrogen atmosphere, was methylated with methyl iodide (6 g., 2 equivalents). After the addition of methyl iodide, the red colour of the anion was discharged in three minutes. Ammonia was evaporated and the product was isolated by extracting with ether. The methylated product was chromatographed on activated alumina (1.5 x 20 cm column slurry packed with petroleum ether, bp 30-60°) and eluted with the same solvent. The first fraction contained methylated hydrocarbons, 1.25 g (60%) and the latter fractions, unchanged pyrene, 0.73 g (40%). The methylated products were dehydrogenated under a nitrogen atmosphere by heating with 1.0 g of 5% Pd/C at 350° for 3 hr., affording a mixture of 0.96 g of

4-methylpyrene (76) and 2-methylpyrene (78) in the ratio 3:1 respectively. The two isomers were separated by fractional crystallization from ethanol. The two isomers were identical with respective authentic samples.
[The data for the two isomers are given in a later experiment].

Reduction of Pyrene (Method B)

A modified procedure of Silberman et al.[96] was used. Pure pyrene (1), 4.05 g (0.02 mole) was suspended in 80 ml of pure and dry ethylenediamine. The suspension was stirred at 90-100° under a nitrogen atmosphere and small pieces of pure lithium, 1.11 g (0.16 g-atom) were added over a period of 2 hr. After the addition of lithium, the reaction was heated for another hour. On the addition of lithium the solution turned red and this red colour persisted throughout the reaction time. The reaction mixture was cooled to ice temperature and 3 ml of ethanol added to destroy any unreacted lithium. The reaction mixture was diluted with 300 ml of ether and the ether layer was thoroughly washed first with water, then with 10% sulfuric acid and finally with water. The ether layer was dried over anhydrous sodium sulfate and the solvent removed *in vacuo* to give 3.92 g of crude reaction product. The crude reaction product was analyzed by VPC on an 18 ft. column packed with 60/80 glass beads with 0.2% apiezon as stationary phase. The two major peaks recorded corresponded to two isomeric tetrahydropyrenes (2 and 3) in the ratio 2:1. A minor peak (8%) of pyrene was also recorded but this arose from a slight decomposition of the tetrahydropyrenes in the chromatographic column. (No pyrene was detected by TLC on alumina or in the mother liquor from the perchlorate salt preparation).

Tetrahydropyrenes (2 and 3) obtained by this method were identical to those obtained from Birch reduction.

Hydrogenation of Tetrahydropyrenes (2 and 3)

Freshly chromatographed tetrahydropyrenes, 0.505 g (2.45 m moles), dissolved in 20 ml of ethanol, were hydrogenated at room temperature and atmospheric pressure, using 0.50 g of 5% Pd/C catalyst. A total of 52 ml of hydrogen was taken (2.40 m moles) in 1 hr. The reaction was continued for an additional hour but there was no further uptake of hydrogen. The content of the flask was extracted first with boiling ethanol and then with ether. The combined extracts were decolourized with 0.50 g of active charcoal, filtered and the filtrate evaporated in vacuo to give 0.450 g of crude hexahydropyrenes.

The VPC of the reaction product, using a column of 18 ft. x 1/4 in., packed with 60/80 glass beads with 0.2% apiezon at 220°, showed two components. These were identified as two isomeric hexahydropyrenes, 1, 2, 3, 6, 7, 8-hexahydropyrene (17) and 1, 2, 3, 3a, 4, 5-hexahydropyrene (18) in the ratio 3:1 respectively. The reaction product was crystallized from ethanol. The first crop of crystals were long white needles of 1, 2, 3, 6, 7, 8-hexahydropyrene (17), mp 131-132° (reported[106] 132-133°), yield 0.308 g (61.4%).

The mother liquor from the above crystallization was evaporated to dryness, weighed 0.165 g and dissolved in a minimum quantity of 99% ethanol. This was mixed with a saturated solution of picric acid (1:1) also dissolved in ethanol. A reddish brown picrate was obtained which was triturated with petroleum ether, bp 30-60°. The petroleum ether washings were evaporated and the residue crystallized from ethanol, giving 0.015 g (3%) of 1, 2, 3, 6, 7, 8-hexahydropyrene (17). This was combined with previously obtained hexahydropyrene, giving a total yield of 64.4%.

U. V. $\lambda_{max}^{methanol}$: 231 mu (e 60, 300), 296 mu (e 7, 600), 316 mu (e 4, 000), 326 mu (e 1, 300) and 332 mu (e 3, 300).

NMR (carbon tetrachloride): 7.9 τ (m, 4H), 6.9 τ (t, 8H) and 2.98 τ (s, 4H). (Fig. 17).

Mass Spec.: 208 (mol. wt. of hexahydropyrene 208.304).

<u>Anal.</u> Calcd. for $C_{16}H_{16}$: C, 92.257; H, 7.743.

<u>Found:</u> C, 92.15; H, 8.06.

The picrate of 1, 2, 3, 3a, 4, 5-hexahydropyrene was decomposed in benzene with aqueous sodium carbonate solution. The free hydrocarbon (18) was crystallized from ethanol; colourless leaflets, 0.110 g (22%), mp 104-105° (reported[106] 105-105.5°).

U. V. $\lambda_{max}^{methanol}$: 231.5 mu (e 59, 800), 283 mu (e 10, 800), 295 mu (e 8, 000), 311 mu (e 3, 600), 321 mu (e 1, 500) and 326 mu (e 3, 500).

NMR (carbon disulfide): 8.1 and 7.1 τ (m, 11H) and 2.7 τ (m, 5H). (Fig. 18).

Mass Spec.: 208 (mol. wt. of hexahydropyrene 208.304).
Anal. Calcd. for $C_{16}H_{16}$: C, 92.257; H, 7.743.
Found: C, 92.43; H, 7.77.

The hydrogenation experiment was repeated using cyclohexane, a less polar solvent than ethanol, to see if there was any change in the ratio of the two hexahydropyrenes (17 and 18). But no change in the ratio of the two hexahydropyrenes was observed.

Oxidation of Tetrahydropyrenes (2 and 3) with Sodium Dichromate

The procedure followed for the oxidation of tetrahydropyrenes was the one used by Boekelheide and Larrabee[1] for the oxidation of phenalene. We found it necessary to slightly modify the procedure.

To a solution of 24.7 g (0.06 mole) of sodium dichromate dihydrate in 100 ml of glacial acetic acid and 10 ml. of conc. sulfuric acid was added slowly a solution of tetrahydropyrenes, 2.06 g (0.01 mole) in 40 ml of glacial acetic acid. After the addition of the whole of the tetrahydropyrenes solution, the reaction mixture was heated on a steam bath for a period of 3 hr. with occasional shaking. The mixture was then cooled to room temperature and poured into 1 ℓ. of cold water, giving a brown precipitate, which was filtered. The residue was extracted with 1 ℓ. of warm chloroform (most of the residue did not go into solution). The extract was concentrated in vacuo and chromatographed on alumina (2.5 x 45 cm. column slurry packed with petroleum ether, bp 30-60°). Elution with solvent mixtures varying from pure petroleum ether to pure ether gave no eluted products. Finally, the chromatogram was eluted with pure chloroform and the eluent on removal of solvent gave a red brown solid of 1, 8-pyrene quinone (48) which was crystallized from acetic acid, long needles, mp 270-271° (reported[107]: 270°); yield 0. 610 g (30%).

I. R. (chloroform): 3030 cm^{-1}, 1635 cm^{-1}, 1600 cm^{-1}, 1575 cm^{-1}, 860 cm^{-1} and 840 cm^{-1}.

Mass Spec.: 232 (mol. wt. of pyrene quinone 232. 240).

The chloroform insoluble residue resisted all attempts to identify it, mainly because of its insolubility in almost all organic solvents except DMSO. But DMSO solution was found to be extremely paramagnetic when it was attempted to take the NMR spectrum of the solution. The oxidation experiment was repeated in the absence of conc. sulfuric acid and also by increasing the proportion of sulfuric acid. In the former case, only 10% 1, 8-quinone (48) was obtained and in the latter, the % yield of quinone was the same as before.

The oxidation of tetrahydropyrenes (2 and 3) was attempted with alkaline permanganate [106] and osmium tetroxide + sodium metaperiodate[152]; in neither case was any identifiable material isolated. The black tarry materials obtained in these experiments showed two carbonyl absorptions at 1665 cm^{-1} and 1637 cm^{-1} in I. R. Oxidations with various oxidizing agents such as H_2O_2, O_3, SeO_2, NaOCl etc. failed to give any isolable products.

1, 2, 3-Trihydropyrenium Perchlorate (54) (Method A)

The procedure of D. H. Reid and R. G. Sutherland[2] for the synthesis of phenalenium perchlorate was used. Pure tetrahydropyrenes (2 and 3), 2.06 g (0.01 mole) dissolved in 60 ml of acetic acid were added at room temperature to a solution of 2.460 g (0.01 mole) of purified chloranil and 3 ml of 72% perchloric acid in 400 ml of acetic acid. 1, 2, 3-Trihydropyrenium perchlorate (54) immediately precipitated as yellow needles. Dry ether (300 ml) was added to the reaction mixture to complete the precipitation of the perchlorate salt. The slurry was filtered under suction in a dry nitrogen atmosphere and then washed with another 100 ml of dry ether. The perchlorate salt was stored under a vacuum; yield 2.50 g (90%), mp 160-161°. This perchlorate salt is very stable and can be stored for months under a vacuum at room temperature.

U. V. $\lambda_{max}^{acetonitrile}$: 227 mu (e 32,500), 263 mu (e 13,000), 274 mu (e 17,000), 308 mu (e 3,000), 322 mu (e 5,000), 337.5 mu (e 8,500) and 408 mu (e 35,000).

I. R. (Nujol): 1120 cm^{-1} (very broad band, characteristic absorption of perchlorate ion).

NMR (72% perchloric acid): 7.64 τ (broad, 2H), 6.5 τ (broad, 4H), 1.85 τ (m, 3H) and 1.06 τ (m, 4H). (Fig. 19b).

NMR (98% sulfuric acid): 7.64 τ (broad, 2H), 6.5 τ (broad, 4H), 1.85 τ (broad 't', 3H) and 1.06 τ (broad 'd', 4H). (Fig. 19A).

Anal. Calcd. for $C_{16}H_{13}ClO_4$: C, 63.063; H, 4.300; Cl, 11.635. Found: C, 63.42; H, 4.300; Cl, 11.95.

Recovery of 2, 3, 5, 6-Tetrachloroquinol (55)

The filtrate of the perchlorate salt from the above experiment was diluted with more ether and the ether layer was washed thoroughly with water to free it from acetic acid. The ether layer was then extracted exhaustively with 10% aqueous sodium hydroxide and the aqueous phase acidified with conc. hydrochloric acid. The precipitated quinol (55) was filtered, washed with water and dried in vacuo. Recrystallization from acetic acid gave white needles, 2.20 g (98%); mp 231-232° (recorded[153], 232°).

1, 2, 3-Trihydropyrenium Fluoroborate

Tetrahydropyrenes (2 and 3), 2.06 g (0.01 mole) dissolved in 70 ml of glacial acetic acid were added to a solution of 2.46 g (0.01 mole) of chloranil in 400 ml of glacial acetic acid. To this solution, 5 ml of 48-50% tetrafluoroboric acid was added at room temperature. The fluoroborate salt immediately precipitated as yellow needles. Dry ether (300 ml) was added to this to complete the precipitation. The slurry was filtered through a sintered glass funnel and the salt was washed with an additional 100 ml of dry ether; the fluoroborate salt was stored under a vacuum; yield 2.12 g (85%); mp 120-121°.

I. R. (Nujol): 1060 cm^{-1} (broad band, characteristic absorption of fluoroborate ion).

The fluoroborate salt is much more unstable than the corresponding perchlorate salt. A few minutes' exposure to air turns the salt to a black tar.

Anal. Calcd. for $C_{16}H_{13}BF_4$: F, 26.02.
Found: F, 25.51.

1, 2, 3-Trihydropyrenium Tri-iodide

A 2.06 g (0.01 mole) sample of crude tetrahydropyrenes (2 and 3) was dissolved in 70 ml of glacial acetic acid at room temperature. To this was added a solution of 2.46 g (0.01 mole) of chloranil in 400 ml of glacial acetic and 8 ml (0.03 mole) of 50% hydriodic acid. After the addition, a blue-black solid appeared in the form of microneedles. Dry ether (300 ml) was added to complete the precipitation of the iodide. The salt was filtered immediately through a sintered glass funnel and the residue washed thoroughly with additional dry ether (100 ml); yield 4.75 g (88%); mp 104-105°. This iodide can be stored for months in a evacuated flask. The analysis of iodide salt showed that the salt was a tri-iodide.

Anal. Calcd. for $C_{16}H_{13}I_3$: C, 32.794; H, 2.36; I, 64.97.
Found: C, 32.93; H, 2.23; I, 65.18.

1, 2, 3-Trihydropyrenium Perchlorate (54) in the Presence of Azobenzene (Method B)

Tetrahydropyrenes (2 and 3) 1.03 g (0.005 mole) dissolved in 40 ml of glacial acetic acid, were added to a solution of 0.91 g (0.005 mole) of azobenzene in 20 ml of acetic acid at room temperature. To this mixture, 5 ml of 72% perchloric acid was added. A yellow precipitate formed immediately and dry ether (300 ml) was added to complete the precipitation of the perchlorate. The precipitated perchlorate salt was filtered, washed thoroughly with dry ether and dried in vacuo; yield 2.74 g, mp (some melted at 160-170° and some decomposed above 300°). The perchlorate salt was identified as a mixture of 1, 2, 3-trihydropyrenium and benzidine perchlorates.

I.R. (Njuol): 1120 cm^{-1} (broad band, characteristic absorption of a perchlorate ion) and 3100 cm^{-1}, 1610 cm^{-1}, 1490 cm^{-1} (characteristic absorptions of a NH_3^+ ion).

NMR (98% sulfuric acid): 7.64, 6.5, 2.7, 2.5, 2.4, 2.2, 1.9 and 1.05 τ .

NMR of pure 1, 2, 3-trihydropyrenium perchlorate (in 98% H_2SO_4): 7.64, 6.5, 1.85 and 1.06 τ.

NMR of pure benzidine perchlorate (in 98% H_2SO_4): 2.7, 2.5, 24 and 2.2 τ .

The perchlorate salts obtained from the above experiment (1.93 g) were reduced with 0.65 g of lithium aluminum hydride. The reduction products were triturated with petroleum ether (bp 30-60°) in which only tetrahydropyrenes dissolved. Tetrahydropyrenes (2 and 3) thus obtained (0.52g)

were identical in all respects with an authentic sample. Petroleum ether-insoluble portion was crystallized from ethanol, giving 0.58 g of p-benzidine (58), mp 126-128° (reported[119]: 128°).
I.R. (chloroform): 3480 cm^{-1}, 3400 cm^{-1}, 3010 cm^{-1}, 1620 cm^{-1}, 1500 cm^{-1}, 1270 cm^{-1} and 810 cm^{-1}.
NMR (deuterochloroform): 6.4 τ (broad s, 4H), 3.3 and 2.65 τ (m, 8H). (Fig. 20).

Phenalenium Perchlorate (58) in the Presence of Azobenzene

To a solution of 0.5 g (3 m moles) of phenalene (6) dissolved in 20 ml of acetic acid was added a solution of azobenzene (0.55 g) (3 m moles) also dissolved in acetic acid (15 ml). Perchloric acid (4 ml, 72%) was added to this mixture at room temperature. The mixture was then diluted with 300 ml of dry ether. The precipitated perchlorate salts were filtered, washed thoroughly with dry ether and dried *in vacuo;* yield 1.65 g.
I.R. (Njuol): 3100 cm^{-1}, 1610 cm^{-1}, 1490 cm^{-1} and 1120 cm^{-1}.

The perchlorate salts, 1.30 g, were reduced with lithium aluminum hydride in dry ether. The reduction products were triturated with pentane (200 ml). The pentane fraction afforded 0.30 g of phenalene (6)mp 84-85°; identical in all repects with an authentic sample.

The pentane-insoluble residue, on crystallization from ethanol, afforded 0.40 g of p-benzidine, mp 125-127°; mixed mp 126-128°.

Action of Perchloric Acid on Tetrahydropyrenes (2 and 3)

Freshly chromatographed tetrahydropyrenes (2 and 3) 1.03 g (0.005 mole) were dissolved in 30 ml of glacial acetic acid or in 25 ml of dry acetonitrile. Five ml of 72% perchloric acid was added to this solution of tetrahydropyrenes at room temperature. The solution immediately turned greenish-yellow. To this, 200 ml of dry ether was added, to precipitate the perchlorate salt (54). The precipitate was filtered in a sintered glass funnel with thorough washing with more dry ether (100 ml). The perchlorate salt was dried *in vacuo*; yield 0.685 g (45%); mp 161-162°. The perchlorate obtained in this experiment was identical in all respects with an authentic sample.

Anal. Calcd. for $C_{16}H_{13}ClO_4$: C, 63.063; H, 4.30; Cl, 11.635. *Found:* C, 62.64; H, 4.27; Cl, 11.61.

The mother liquor of the perchlorate salt from the above experiment was diluted with more ether and the ether layer washed thoroughly with water until it was free from acetic acid. The ether layer was dried over anhydrous sodium sulfate and concentrated in a rotary evaporator. The residue was dissolved in a minimum quantity of chloroform and chromatographed over freshly activated alumina (2.5 x 30 cm column slurry packed with petroleum ether, bp 30-60°). The first 300 ml petroleum ether fraction gave 0.40 g of 1, 2, 3, 3a, 4, 5-hexahydropyrene (18) and the subsequent fractions gave 0.045 g of some hexahydropyrene. The products obtained in the different fractions were the same as shown by melting point, TLC and VPC. All the fractions were combined together and crystallized from ethanol; white leaflets, yield 0.420 g (40%), mp 105-106°, identical with an authentic sample. The mother liquor of the perchlorate salt contained only one hexahydropyrene [1, 2, 3, 3a, 4, 5-hexahydropyrene (18)], as shown by VPC analysis.

A similar experiment was performed using deuteroperchloric acid ($d_1 \approx 96\%$). The hexahydropyrene (18) thus obtained gave the following data:

NMR (carbon disulfide): 8. 2 and 7. 2 τ (m, 10. 7H) and 2. 7 τ (m, 4. 7 H). (Deuterium was present in both aliphatic and aromatic parts of the molecule).

Mass Spec.: 209 (mol. wt. of mono-deuterated hexahydropyrene 209. 304). Deuterium found: 60% (by mass spectrometry).

1, 2, 3-Trihydropyrenium perchlorate (54) obtained in this experiment was reduced to the corresponding hydrocarbons (2 and 3), which contained 10 ~ 12% d_1 as determined by mass spectrometry

Action of Concentrated Sulfuric Acid on Tetrahydropyrenes (2 and 3)

Since cycloheptatriene (56) and phenalene (6) dissolve in 98% sulfuric acid to yield tropenium ion[39] and phenalenium ion[37] respectively, it was of interest to determine whether or not a similar conversion of tetrahydropyrenes was possible. Honen[37] reported the yield of 22. 5% tropenium ion (57) and 51. 1% of phenalenium ion (58) as determined by ultra-violet spectrometry. Accordingly, samples of pure tetrahydropyrenes were treated with 98% H_2SO_4 and the quantitative U. V. spectra of the resulting solutions determined. The spectrum of tetrahydropyrenes in 98% H_2SO_4 is quite similar to that of 1, 2, 3-trihydropyrenium cation in the same solvent. The following spectral yields of 1, 2, 3-trihydropyrenium cation were obtained.

	Absorption Intensity (e) 408 mμ peak		% Yield of Cation
	17,000		48.57
	17,500		50.0
	16,500		47.99
Average	17,000	Average	48.8

(Based on the 408 mμ absorption intensity of the cation, e 35,000).

The NMR spectrum of tetrahydropyrenes in 98% H_2SO_4 was identical to that of 1,2,3-trihydropyrenium perchlorate in the same solvent.

NMR (1,2,3-trihydropyrenium perchlorate in 98% H_2SO_4): 7.64 and 6.5 τ (m, 6H), 1.85 and 1.06 τ (m, 7H). (Fig. 19A).

NMR (tetrahydropyrenes in 98% H_2SO_4): 7.64 and 6.5 τ (m, 10H), 1.85 and 1.06 τ (m, 7H). (Fig. 21).

In another experiment tetrahydropyrenes, 0.51 g (0.0025 mole) were dissolved in 20 ml of acetic acid and to this solution one ml of 98% H_2SO_4 was added. A greenish yellow solid precipitated after the solution was diluted with 100 ml of dry ether. The precipitated salt was very unstable and decomposed to a black tar within a minute. The mother liquor of the salt after working-up as usual, gave also an unidentified tarry residue. No unsymmetrical or 1,2,3,3a,4,5-hexahydropyrene (18) was isolated from the mother liquor.

Reduction of 1, 2, 3-Trihydropyrenium Perchlorate (54) with Lithium Aluminum Hydride

The perchlorate salt, 1.524 g (0.005 mole) was added quickly to a solution of lithium aluminum hydride, 0.228 g (0.006 mole) in 100 ml of dry ether under a nitrogen atmosphere. Stirring was continued for 1.5 hr., while the perchlorate salt gradually dissolved giving a pale yellow solution. The mixture was diluted with water and 300 ml of ether and the ether phase was washed three times with water and dried over anhydrous sodium sulfate. Solvent was removed in a rotary drier and the residue was dried *in vacuo*. Yield: 0.93 g (91%). The crude product was analyzed by VPC using the same column and condition as previously mentioned in the case of the analysis of tetrahydropyrenes. Two major peaks were recorded corresponding to two isomeric tetrahydropyrenes (2 and 3) in the ratio 2:1. There was another minor peak corresponding to pyrene (8%) which arose from the decomposition products of the tetrahydropyrenes in the VPC column.

The reduction product of the perchlorate salt was chromatographed on freshly activated (210°, 48 hr.) Wolem alumina (1.5 x 30 cm column slurry packed with petroleum ether, bp 30-60°) and eluted with the same solvent. The first 300 ml eluent yielded 0.510 g of tetrahydropyrenes (2 and 3), identical with an authentic sample.

The reduction of the perchlorate (54) was repeated with $LiAlD_4$. The deuterated hydrocarbons (2 + 3) thus obtained gave the following data:

NMR (carbon disulfide): 8.15, 7.65 and 7.20 τ (m, 6H), 6.18 τ (s, 1.52 H), 4.35, 3.20, 3.52 and 3.0 τ (5.71 H). The deuterium content was 82%; active methylene contained 48% and the remainder was spread over the vinylic and aromatic part of the molecule.

Mass Spec.: 207 (mol. wt. of mono-deuterated tetrahydropyrenes 207.288).

Hydrolysis of 1, 2, 3-Trihydropyrenium Perchlorate (54)

A sample of freshly prepared perchlorate salt, 1.22 g (0.004 mole) was dissolved in 40 ml of acetonitrile under a nitrogen atmosphere. Within ten minutes the salt dissolved completely, giving a dark greenish-yellow solution. The salt solution was then hydrolyzed with 10 ml of water with constant stirring. After half an hour the solution was diluted further with approximately 100 ml of water. A green substance immediately precipitated out. The precipitate was filtered and dried; yield 0.655 g (95%), mp 80-85°. This green solid was only sparingly soluble in all common organic solvents except chloroform. In chloroform, it decomposed to black tar in a few minutes. All attempts to crystallize it failed and purification by chromatography was also not possible, since it decomposed in the chromatographic column.

The following are the spectral data of the green solid (73):

U. V. $\lambda_{max}^{cyclohexane}$: 234 mu (e 58,000), 242 mu (e 80,000), 264 mu (e 34,500), 274.5 mu (e 35,000), 308 mu (e 15,500), 322 mu (e 28,000), 332 mu (e 27,500), 337 mu (e 40,000) and 361 mu (e 16,500).

I. R. (chloroform): 3040 cm^{-1}, 3010 cm^{-1}, 2935 cm^{-1}, 2865 cm^{-1}, 1620 cm^{-1}, 1580 cm^{-1}, 1440 cm^{-1}, 1085 cm^{-1} and 830 cm^{-1}.

Anal. Calcd. for $C_{32}H_{26}O$ (di-tetrahydropyrenyl ether):
C, 90.105; H, 6.144.
Found: C, 89.1; H, 5.4.

Dehydrogenation of Di-tetrahydropyrenyl Ether (73)

Di-tetrahydropyrenyl ether, 2.13 g (5 m moles) obtained from the hydrolysis of the perchlorate salt was mixed thoroughly with 2.0 g of 5% Pd/C and heated at 360° under a nitrogen atmosphere for 8 hr. After cooling to room temperature, the dehydrogenation product was extracted with 300 ml of ether and then with 200 ml of chloroform. The ether fraction yielded 1.425 g of pyrene (1) (70%), crystallized from ethanol, mp 149-150°. The chloroform fraction gave (020 g) of a tarry material which was unidentified.

Cleavage of Di-tetrahydropyrenyl Ether (73) with Perchloric Acid

Perchloric acid (1 ml) was added to a solution of the ether (73), 0.852 g (0.002 mole) in chloroform (20 ml.). The solutinn was boiled for 1 min. and cooled to room temperature. Dry ether, 50 ml was added to this solution and 1, 2, 3-trihydropyrenium salt (54) precipitated, 0.910 g (75%), identical with an authentic sample of 1, 2, 3-trihydropyrenium perchlorate.

Reaction of 1, 2, 3-Trihydropyrenium Perchlorate (54) with Methyl Lithium

The perchlorate salt (54), 1.83 g (0.006 mole) was stirred in 50 ml of dry ether under a nitrogen atmosphere at room temperature with 3.5 ml of 5.2% methyl lithium (0.008 mole) solution in diethyl ether. The perchlorate salt dissolved completely within ten minutes, giving a red solution. The stirring was continued for an additional hour. The reaction mixture was diluted with 200 ml of water and extracted with ether. The ether layer was washed thoroughly with water, dried over anhydrous sodium sulfate and evaporated in vacuo to give a black viscous liquid (1.20 g). This was dissolved in a minimum amount of chloroform and chromatographed on freshly activated Wolem alumina (1.5 x 30 cm column slurry packed with petroleum ether, bp 30-60°) and eluted with the same solvent. The first 300 ml of petroleum ether fraction gave 0.125 g (10%) of tetrahydropyrenes (2 and 3), mp 54-56°, having the same IR and UV spectraas those of an authentic sample. The subsequent fractions (in 50-50 petroleum ether-ether) gave a black tarry product (1.10g). This was dehydrogenated with one gram of 5% Pd/C at 350° under a nitrogen atmosphere. The heating was continued for 4 hr. The reaction mixture was cooled and extracted thoroughly first with 200 ml of ether and then with 300 ml of chloroform. The ether fraction gave 0.012 g (1.0%) of white residue, mp 115-120°. Thin layer chromatography on alumina showed three spots and one of them was identified as pyrene. Mass spectrum of the crude material showed mass at 202 (pyrene), 216 (monomethylpyrene) and a very weak peak at 230 (dimethylpyrene). Because of the very low yield of the methylated pyrenes no attempt was made to separate and identify them.

The chloroform fraction afforded an unidentifiable tar (0.950 g).

Hydride Exchange Between Tetrahydropyrenes (2 and 3) and Phenalenium Perchlorate(58)

Freshly prepared phenalenium perchlorate, 0.263 g (0.001 mole) was dissolved in 20 ml of acetonitrile. A solution of tetrahydropyrenes (2 and 3), 0.206 g (0.001 mole) in 20 ml of acetonitrile was added quickly to the perchlorate solution under a nitrogen atmosphere. Immediately a precipitation of yellow 1, 2, 3-trihydropyrenium perchlorate (54) occurred in the form of fine needles. Dry ether (200 ml) was added to complete the precipitation of the salt. The perchlorate salt was filtered and dried *in vacuo*; yield 0.260 g (85%), mp 159-160°, mixed mp with an authentic sample 159-161°. The perchlorate salt obtained by this method had I. R. and U. V. spectra identical to those of an authentic sample.

The mother liquor of the perchlorate salt was diluted with more ether and was washed with water. The ether layer was separated, dried over anhydrous sodium sulfate and the solvent removed in vacuo. The residue was chromatographed over basic alumina and eluted with pentane. The first 300 ml of pentane fraction gave a white residue of phenalene (6), which was crystallized from pentane; yield 0.115 g (70%), mp 84-85° (reported[1] 86°). The I.R. and U.V. spectra were identical to those of an authentic sample of phenalene.

Hydride Exchange Between Tetrahydropyrenes (2 and 3) and Tropenium Perchlorate (37)

Tropenium perchlorate (obtained from cycloheptatriene, perchloric acid in the presence of chloranil), 0.190 g (0.001 mole) was dissolved in 10 ml of acetonitrile. Tetrahydropyrenes 0.206 g (0.001 mole) in 20 ml of acetonitrile were added to this solution with stirring under a nitrogen atmosphere. The solution turned greenish-yellow and 1, 2, 3-trihydropyrenium perchlorate precipitated slowly. Dry ether (200 ml) was added to this solution to complete the precipitation of the perchlorate salt. The precipitate was filtered, washed thoroughly with dry ether and dried in vacuo; yield 0.271 g (90%), mp 159-160°. The 1, 2, 3-trihydropyrenium perchlorate so obtained had the same I.R. and U.V. spectra as those of an authentic sample.

The perchlorate mother liquor was diluted with more ether and the ether layer washed with water. The ether layer was dried over anhydrous sodium sulfate and the solvent was removed in vacuo. The residue was chromatographed on alumina (1.5 x 10 cm column slurry packed with petroleum ether, bp 30-60°) and eluted with the same solvent. The pure cycloheptatriene (56) thus obtained weighed 0.740 g (80%) and was identified by comparing its I.R. spectrum with that of an authentic sample.

Methylation of Tetrahydropyrene Anion

Pure tetrahydropyrenes (2 and 3) 1.03 g (5 m moles) were dissolved in 30 ml of dry ether in a flask (250 ml). The flask was equipped with a nitrogen inlet and outlet tube and a rubber septum for injecting n-butyl lithium. By means of a syringe, 3.0 ml of 2.33M n-butyl lithium in hexane was injected into the reaction mixture. Immediately after the addition of the base, the colour of the solution turned deep red. After ten minutes of stirring, 1.0 g (0.0071 mole) of methyl iodide in 10 ml of dry ether was added slowly to the blood red reaction mixture. The addition of methyl iodide was completed in 0.5 hr. The blood red colour of the solution slowly turned pale yellow with the addition of methyl iodide. After the addition of all the methyl iodide, the reaction was allowed to continue for an additional 0.5 hr. The reaction mixture was diluted with water, extracted with ether and the ether layer separated and dried over anhydrous sodium sulfate. Removal of the solvent in vacuo afforded 1.02 g of thick liquid. This liquid showed two peaks in the ratio 3:1, when analyzed by VPC using a column of 18 ft. packed with 60/80 chromosorb with 1% apiezon as stationary phase.

Mass Spec. of the liquid: 220 (mol. wt. of monomethyl tetrahydropyrene 220.31).

Dehydrogenation of Methylated Tetrahydropyrenes

Crude methylated tetrahydropyrenes from the above experiment, 2.20 g (0.01 mole) were heated with 2.0 g of 5% Pd/C at 350° under a nitrogen atmosphere and the heating was continued for 4 hr. The dehydrogenation product was extracted with 200 ml of ether and 100 ml of chloroform. The two extracts were combined and decolourized with active charcoal. The filtrate was concentrated in vacuo giving a solid residue, 1.32 g (61%). The residue showed two peaks in the ratio 3:1 when analyzed by VPC. The two isomers were separated by fractional crystallization from ethanol and identified as 4-methylpyrene (76) and 2-methylpyrene (78).

4-Methylpyrene (major isomer, 75%); mp 145-147° (reported[127] : 149°; 146-147°.

NMR (deuterochloroform): 7.20 τ (d, 3H) and 2.0 τ (m, 9H). (Fig. 22)

Mass Spec.: 216 (mol. wt. of monomethylpyrene 216.28).

Anal. Calcd. for $C_{17}H_{12}$: C, 94.407; H, 5.593.
Found: C, 94.21; H, 5.65.
2-Methylpyrene (minor isomer, 25%); mp 140-143° (reported[129]: 143-143.5°).
NMR (deuterochlorcform): 7.10 τ (s, 3H) and 2.1 τ (m, 9H). (Fig. 23).
Mass Spec.: 216 (mol. wt. of monomethylpyrene 216.28).
Anal. Calcd. for $C_{17}H_{12}$: C, 94.407; H, 5.593.
Found: C, 94.67; H, 5.69

Reaction of Tetrahydropyrene Anion with CO_2

Tetrahydropyrenes (2 and 3) 1.03 g (5 m moles), dissolved in 30 ml of dry ether, were treated with 3 ml of 2.33M n-butyl lithium in hexane under a nitrogen atmosphere. After the addition of the base, pure and dry carbon dioxide gas was bubbled through the red solution for 20 minutes. The red colour was discharged and a yellow solid precipitated out. The precipitate was filtered, washed thoroughly with dry ether and dried; yield 1.06 g (87%). This yellow solid was soluble in water. An attempt to obtain an NMR spectrum in D_2O failed, as the substance was found to be extremely paramagnetic.

The yellow solid which was supposed to be the lithium salt of tetrahydropyrene carboxylic acid was dissolved in a minimum amount of water and acidified with 50% sulfuric acid. A green solid was precipitated, which was filtered and dried. All attempts to crystallize it failed. In solution, the acid turned to a tarry black mass and this was also found to be extremely paramagnetic. On heating, the free acid started to turn black from 90-100° and melted to dark dense liquid at 115-120°. In I. R. it showed a carbonyl absorption band at 1680 cm^{-1}.

Free acid (1. 0 g) was dehydrogenated with 0. 50 g of 5% Pd/C at 250° under a nitrogen atmosphere. The dehydrogenated product was extracted with 200 ml of ether and 100 ml of chloroform, from the ether fraction; on removal of solvent *in vacuo*, 0. 080 g of pyrene (1) was obtained, after crystallization from ethanol melted at 148-150°, mixed mp 149-150°. The I. R. spectrum was identical to that of pure pyrene. The chloroform ffaction gave a black tar (0. 250 g) which was not identified.

1, 2, 3-Trihydropyrenium Tri-iodide from 1, 2, 3-Trihydropyrenyl Radical (86)

The procedure employed for the preparation of the radical is that described by Reid[30] for the preparation of the phenalenyl radical. Tetrahydropyrenes (2 and 3) 1. 03 g (5 m moles), dissolved in 10 ml of carbon tetrachloride, were added to a solution of 0. 62 g (2. 5 m moles) of chloranil also dissolved in carbon tetrachloride (20 ml). To this solution, 3. 81 g (15 m moles) of iodine in 50 ml of carbon tetrachloride was slowly added. The reaction was allowed to continue for half an hour and the blue-black tri-iodide salt slowly precipitated. Dry ether (200 ml) was added to this mixture to complete the precipitation of the tri-iodide salt. The precipitate was filtered, washed thoroughly with dry ether and dried *in vacuo*; yield 1. 45 g (50%), mp 103-104°, mixed mp with an authentic sample 103-105°.

Found: I, 64. 90 and 65. 01.

$C_{16}H_{13}I_3$ requires: I, 64. 97.

The mother liquor of the tri-iodide salt was diluted with 200 ml of ether and the ether layer washed several times with water. The ether layer was extracted with 10% sodium hydroxide solution (200 ml) and the alkaline extract acidified with conc. hydrochloric acid. The precipitated quinol (55) was crystallized from acetic acid; yield 0.240 g (45%), mp 230-231°. The ether fraction contained 0.430 g of unchanged tetrahydropyrenes, contaminated with the decomposition products of tetrahydropyrenes.

1, 2, 3-Trihydropyrenium Perchlorate (10) from 1, 2, 3-Trihydropyrenyl Radical (86)

Tetrahydropyrenes (2 and 3), 1.03 g (5 m moles) were dissolved in 10 ml of carbon tetrachloride and to this a solution of 0.62 g (2.5 m moles) of chloranil in 20 ml of carbon tetrachloride was added slowly with constant stirring. To the stirred solution, 1.04 g (5 m moles) of anhydrous silverperchlorate in 50 ml of carbon tetrachloride was added and the stirring was continued for an hour. Dry ether (300 ml) was added and the precipitate filtered. The precipitate was dissolved in 20 ml of acetonitrile and the undissolved silver was separated by filtration. The perchlorate salt (54) was reprecipitated from the filtrate by adding dry ether (200 ml). The precipitate was filtered and dried in vacuo; yield 1.0 g (60%), mp 158-160°, mixed mp 159-160°. I.R. (Nujol): 1120 cm^{-1} (broad band, characteristic absorption of perchlorate ion).

Found: ClO_4; 32.364 and 32.42.

$C_{16}H_{13}ClO_4$ requires: ClO_4; 32.636.

The perchlorate mother liquor was treated in the same way as in the previous experiment to yield 0.38 g (65%) of quinol (55), mp 229-230°. The ether fraction afforded 0.310 g of unchanged tetrahydropyrenes contaminated with the decomposition products of tetrahydropyrenes.

E.S.R. of 1,2,3-Trihydropyrenyl Radical (86)

Pure tetrahydropyrenes (2 and 3) 0.100 g, dissolved in a minimum amount of carbon tetrachloride was degassed and sealed under vacuum in an e.s.r. sample tube. A well resolved e.s.r. spectrum was obtained. The 'g' value of the radical in carbon tetrachloride is 2.00269 compared to 2.00267 for the phenalenyl radical. The e.s.r spectrum of the radical was studied in mesitylene at room temperature (Fig. 24). To provide evidence for the rapid conformational interconversion of the methylene protons between axial and equatorial positions, the spectrum was also examined at -70° inl, 2-dimethoxyethane (Fig. 24) and at + 300° in 1-bromonaphthalene (Fig. 25).

Synthesis of Perylene (87)

For the preparation of perylene from β-dinaphthol, the method of Zinke[141] was followed. Dry β-dinaphthol (obtained by the oxidation[142] of β-naphthol with aqueous $FeCl_3$ solution), 57.2 g (0.2 mole) was thoroughly mixed with 57.4 g (0.7 mole) of dry orthophosphorous acid and 58.24 g (0.28 mole) of phosphorus pentachloride. The mixture was heated slowly under a nitrogen atmosphere. The nitrogen outlet of the reaction flask was connected to an empty trap, which was connected to a second trap containing water. The outgoing gases were burnt in a Meeker burner flame. The temperature of the reaction wa s kept constant at 360° and the heating was continued for 4 hr. The reaction mixture was then cooled to the room temperature and the reaction flask thoroughly flushed with nitrogen before opening the flask to the atmosphere (a fire hazard exists unless the phosphines are first removed). After the experiment, all the tubings used in the safety traps were thoroughly rinsed with 10% sodium hypochlorite solution, before exposing them to the atmosphere or before washing with water, otherwise the deposited phosphorus catches fire in contact with air or water. The cantent of the reaction flask was extracted by refluxing with 3l of chloroform. Removal of the chloroform gave a solid residue that was then extracted with 1 ℓ. of ether. The ether extract, after evaporation of the solvent, was crystallized from ether-ethanol (1:1), giving yellow plates of β-dinaphthylene oxide, 16.0 g (30%), mp 155-157° (reported[155]; 158.5°). The residue, which did not dissolve in ether was crystallized from xylene to give large golden yellow plates of perylene (87); yield 12.5 g (25%); mp 272-274°. (reported[156]: 273-274°).

[β-Dinaphthol, phosphorous acid and phosphorus pentachloride all should be very dry, otherwise the yield of preylene drops to 5% and the yield of β-dinaphthylene increases to 50%].

Birch Reduction of Perylene (87) (Method A)

Pure perylene, 5.04 g (20 m moles) was suspended in 200 ml of dry ether and 25 ml of freshly distilled absolute ethanol. In a three-necked (1 ℓ) flask fitted with a dry ice condenser, 200 ml of liquid ammonia was collected. To this ammonia, the suspension of perylene was added. Small pieces of sodium, 3.7 g (0.16 g-atom) were added quickly to the reaction mixture while the reaction flask was flushed with nitrogen. The reaction was stirred for 2 hr. under a nitrogen atmosphere. After the addition of sodium the reaction mixture turned deep blue, but after 30-40 minutes the blue colour disappeared and the reaction mixture became completely colourless. After 2 hr., the ammonia was evaporated and the reaction mixture diluted with more ether. The ether layer was washed thoroughly with water, 10% sulfuric acid and then again with water, dried over anhydrous sodium sulfate and the solvent removed <u>in vacuo</u>. The crude reduction product, 5.0 g, was dissolved in a small amount of chloroform and was chromatographed over activated alumina on a 3.5 x 60 cm column slurry packed with petroleum ether, bp 30-60°. The first three 200 ml of petroleum ether fractions yielded 4.8 g of white 1, 2, 3, 10, 11, 12, 12a, 12b-octahydroperylene (91). The subsequent fractions gave no other products. The chromatographed product was crystallized from ethanol; long white needles, 4.7 g (97%), mp 118-120° (reported[143]: 119-121°).

U. V. $\lambda_{max}^{cyclohexane}$: 216 mu (e 40,000) and 266 mu (e 900).
I. R. (chloroform): 3060 cm^{-1}, 2940 cm^{-1}, 2850 cm^{-1}, 1600 cm^{-1}, 1480 cm^{-1}, 1440 cm^{-1}, 820 cm^{-1} and 710 cm^{-1}.
NMR (carbon tetrachloride): 8.0, 7.3 and 6.6 τ (m, 14H) and 2.9 τ (m, 6H). (Fig. 26).
Mass Spec.: 260 (mol. wt. of octahydroperylene 260.38).
Anal. Calcd. for $C_{20}H_{20}$: C, 92.258; H, 7.742.
Found: C, 91.92; H, 7.92.

The experiment was repeated using THF + ethanol, as solvent in place of ether + ethanol, under the same experimental conditions as stated previously, but the same octahydroperylene (91) was obtained.

Using the above procedure, the reduction of perylene was done with only 4 equivalents of sodium. Separation of the products by column chromatography gave 45% 1, 2, 3, 10, 11, 12, 12a, 12b-octahydroperylene (91) and 55% unreacted perylene (87).

Dehydrogenation of 1, 2, 3, 10, 11, 12, 12a, 12b-Octahydroperylene (91) with Chloranil in Perchloric Acid

Pure octahydroperylene, 2.60 g (10 m moles), dissolved in 50 ml of acetic acid was added to a solution of 4.92 g (20 m moles) of chloranil in 600 ml of acetic acid and 5 ml of 72% perchloric acid. The solution was allowed to stand for 8 hr. at room temperature (or warmed to 80° for half an hour). Ether(400 ml) was added to the mixture and the ether layer then washed thoroughly with water until it was free from acetic acid. The ether solution was then treated with 10% sodium hydroxide solution to remove quinol. After removal of the solvent, the ether layer gave a solid residue which was chromatographed over active alumina on a 3.5 x 60 cm column slurry packed with petroleum ether, bp 30-60°. The first three 200 ml petroleum ether fractions gave a yellow solid residue that was crystallized from ethanol as long, yellow needles of 1,2,3,10,11,12-hexahydroperylene (94), 2.06 g (80%), mp 188-189° (reported[146] 189°).

U.V. $\lambda_{max}^{cyclohexane}$: 227 mμ (e 10,700), 233 mμ (e 10,000), 258 mμ (e 76,500), 265 mμ (e 107,000), 348 mμ (e 5,000), 365 mμ (e 6,000) and 388 mμ (e 11,500).

NMR (deuterochloroform): 7.83 τ (m, 4H), 6.9 τ (t, 4H), 6.5 τ (t, 4H), 2.8 and 2.0 τ (m, 6H). (Fig. 27).

Mass Spec.: 258 (mol. wt. of hexahydroperylene 258.364).

Anal. Calcd. for $C_{20}H_{18}$: C, 92.978; H, 7.022.

Found: C, 93.07; H, 7.15.

The latter fractions (eluted with chloroform) gave 0.50 g (20%) of perylene, which was crystallized from xylene as large yellow plates, mp 271-273°, mixed mp with an authentic sample 272-273°. The I.R. spectrum was identical to that of a pure perylene (87).

The aqueous alkaline extract was acidified with concentrated hydrochloric acid and the percipitated quinol (55) was recrystallized from acetic acid as white needles, 4.46 g (90%), mp 231-233°.

Reduction of Perylene (Method B)

The procedure of Silberman *et al.*[76] was used. Pure perylene, 5.04 g (20 m moles) was stirred in 100 ml of dry ethylenediamine at 90-100° under a nitrogen atmosphere in a three-necked flask (0.5 l) equipped with a reflux condenser. Small pieces of pure lithium, 2.24 g (0.32 g-atom) were added over a period of 2 hr. On addition of lithium, the solution initially turned blue and then red. The red colour persisted throughout the time of the reaction. The stirring was continued for an additional hour. The reaction mixture was cooled to ice temperature and to the cooled solution about 4-5 ml of ethanol was added to destroy any unreacted lithium. This was followed by the addition of 300 ml of ether and 100 ml of water. The ether layer was washed thoroughly with water, 10% sulfuric acid and then again with water to make it completely free from ethylenediamine. The ethereal solution, after drying over anhydrous sodium sulfate, was concentrated *in vacuo* to give 4.96 g of crude product. The crude reaction product (1.0 g) was chromatographed over activated alumina on a 2.5 x 30 cm column slurry packed with normal hexane and eluted with the same solvent. The first two 200 ml hexane fractions gave 0.102 g (10.2%) of oily product which became solid on evacuation. This material was crystallized from ethanol as white needles of a hexadecahydroperylene (97), mp 118-120°.

U.V. $\lambda_{max}^{cyclohexane}$: 219 mμ (e 11,000).

I.R. (chloroform): 2925 cm^{-1}, 2842 cm^{-1}, 1650 cm^{-1}, 1445 cm^{-1} and 820 cm^{-1}.

NMR (carbon tetrachloride): 8.9, 8.3 and 7.5 τ (Fig. 29).

Mass spec.: 268 (mol. wt. of hexadecahydroperylene 268.444).

Anal. Calcd. for $C_{20}H_{28}$: C, 89.486; H, 10.514.

Found: C, 89.20; H, 10.29.

No positive structural assignment was possible with the above data.

The next two 300 ml of (1:1) benzene-hexane fractions gave 0.85 g (89.8%) of light yellow solid of 1, 2, 3, 3a, 4, 5, 6, 6a-octahydroperylene (98) which was crystallized from 1:2 hexane-benzene mixture as coarse needles, mp 145-147° (reported[96]: 148°). This material was air unstable.

U.V. $\lambda_{max}^{cyclohexane}$: 234 mμ (e 40,800), 241 mμ (e 43,500), 252 mμ (e 17,000), 262 mμ (e 11,600), 304 mμ (e 10,500), 31y mμ (e 17,000), 333 mμ (e 19,000) and 352 mμ (e 1,600).

I.R. (chloroform): 3040 cm^{-1}, 2930 cm^{-1}, 2840 cm^{-1}, 1645 cm^{-1}, 1585 cm^{-1}, 1446 cm^{-1} and 850 cm^{-1}.

NMR (carbon tetrachloride): 8.2, 7.6 τ (m, 13H), 6.4 τ (broad, 1H) and 2.65 τ (m, 6H). (Fig. 28).

Mass Spec.: 260 (mol. wt. of octahydroperylene 260.38).

Hydrogenation of 1, 2, 3, 3a, 4, 5, 6, 6a-Octahydroperylene (98)

Pure octahydroperylene, 0.260 g (1 m mole), dissolved in 30 ml of ethanol, was hydrogenated at room temperature and atmospheric pressure in the presence of 0.20 g of 5% Pd/C. A total of 65 ml of hydrogen (3 m moles) was consumed in 4 hr. The reaction mixture was extracted with ether, water washed, dried over anhydrous sodium sulfate and concentrated in vacuo. The white solid residue was crystallized from ether-ethanol as large white needles of 1, 2, 3, 3a, 3b, 4, 5, 6, 6a, 6b, 7, 8, 9, 12b-tetradecahydroperylene (100), 0.215 g (81%), mp 100-102°.

U. V. $\lambda_{max}^{cyclohexane}$: 233 mμ (e 53, 500), 241 mμ (e 75, 000), 267 mμ (e 5, 500), 290 mμ (e 8, 700), 302 mμ (e 9, 500) and 312 mμ (e 7, 500).

Mass Spec.: 266 (mol. wt. of tetradecahydroperylene 266.43).

NMR (carbon tetrachloride): 8.0, 7.15 τ (m, 23H), 2.84 and 2.3 τ (m, 3H). (Fig. 30).

Anal. Calcd. for $C_{20}H_{26}$: C, 90.163; H, 9.84.

Found: C, 89.86; H, 10.17.

1, 2, 3, 3a, 4, 5, 6-Heptahydroperylenium Perchlorate (101)

To 2.60 g (10 m moles) of crude octahydroperylene (98) dissolved in 100 ml of acetic acid at room temperature, a solution of 2.46 g (10 m moles) of chloranil and 3 ml of 72% perchloric acid in 300 ml of acetic acid was added. A brownish perchlorate salt immediately precipitated out. Dry ether (300 ml) was added to complete the precipitation of the salt. The salt was filtered, washed thoroughly with ether and dried in vacuo, yield 2.62 g (86%), mp 140-142°.

U.V. $\lambda_{\text{max}}^{\text{acetonitrile}}$: 226 mu (e 25,000), 253 mu (e 17,500), 265 mu (e 14,000), 365 mu (e 7,900), 389 mu (e 8,700), 410 mu (e 39,300) and 436 mu (e 5,600).

I.R. (Nujol): 1120 cm^{-1} (broad absorption band, characteristic of perchlorate ion).

NMR (98% sulfuric acid): 7.5, 6.6 (bread, 13H) and 1.93, 1.5 (m, 6H). (Fig. 31).

Anal. Calcd. for $C_{20}H_{19}ClO_4$: C, 67.224; H, 5.337; Cl, 9.88.

Found: C, 67.46; H, 5.09; Cl, 9.58.

The mother liquor of the perchlorate salt was diluted with more ether. The ether layer was washed thoroughly with water and extracted exhaustively with 10% sodium hydroxide solution. The ether extract gave a white residee, which was crystallized from ethanol to yield 0.264 g (10%) of a hexadecahydroperylene (97), mp 118-120°.

The alkaline extract, after acidification with conc. hydrochloric acid and crystallization from acetic acid, gave 1.985 g (80%) of hydroquinone (55), mp 230-232°.

Reduction of 1, 2, 3, 3a, 4, 5, 6-Heptahydroperylenium Perchlorate (101) with Lithium Aluminum Hydride

The heptahydroperylenium perchlorate, 0.358 g (1 m mole) was stirred in 30 ml of dry ether under a nitrogen atmosphere with 0.57 g (1.5 m moles) of lithium aluminum hydride for 90 minutes. All the perchlorate salt went into solution. Water (100 ml) was added to destroy any excess lithium aluminum hydride. The product was extracted with ether and the ether layer was thoroughly washed with water, dried over anhydrous sodium sulfate and concentrated *in vacuo*. The residue was chromatographed over alumina on a 2.5 x 30 cm column slurry packed with 1:1 benzene-hexane and eluted with the same solvent. The first 300 ml of benzene-hexane fraction gave 0.114 g (55%) of octahydroperylene (98), mp 144-146°, mixed mp 145-147°. The subsequent fractions gave a tarry material (0.080 g) which was not further investigated.

Hydrolysis of 1, 2, 3, 3a, 4, 5, 6-Heptahydroperylenium Perchlorate (101)

A solution of perchlorate salt, 0.358 g (1 m mole) in 15 ml of acetonitrile was hydrolyzed by the addition of 10 ml of water. The hydrolysis was done under a nitrogen atmosphere. After the addition of water, a green solid (102) was precipitated out. The precipitate was filtered, washed with water and dried; 0.240 g (91%). All attempts to crystallize the green material failed: mp 200-205° (decomposes to black tar).

I.R. (chloroform): 3040 cm^{-1}, 3015 cm^{-1}, 2940 cm^{-1}, 2860 cm^{-1}, 1620 cm^{-1}, 1580 cm^{-1}, 1440 cm^{-1}, 1085 cm^{-1} (broad absorption band characteristic of ether) and 835 cm^{-1}.

The green material, 0.270 g, was dehydrogenated by heating it for 4 hr. with 0.20 g of 5% Pd/C at 360°, under a nitrogen atmosphere. The dehydrogenated product was extracted with chloroform to give 0.150 g (60%) of perylene (87), which was crystallized from xylene as large plates, mp 270-272°, mixed mp 271-273°.

The ether (102) was cleaved into heptahydroperylenium perchlorate (101) in 60% yield by heating it with 72% perchloric acid in chloroform solution.

Reduction of 1,12-Benzoperylene (103) with Lithium-ethylenediamine

Pure 1,12-benzoperylene (synthesized according to Clar's method[145]) 1.035 g (3.75 m moles) was stirred in 20 ml of pure and dry ethylenediamine at 90-100° under a nitrogen atmosphere in a 100 ml flask, equipped with a reflux condenser. Small pieces of pure lithium, 0.50 g (0.0750 g-atom) were added in portions for 2 hr. During the addition of lithium the solution turned blue and finally to a persistent red colour. The stirring was continued for an additional hour. The reaction mixture was cooled to ice temperature, diluted with water and extracted with 300 ml of chloroform. The chloroform layer was washed thoroughly with water, 10% sulfuric acid and then again with water, dried over anhydrous sodium sulfate and concentrated in vacuo to give 0.92 g of yellow reaction product. A 0.5 g portion of the reduction product waschromatographed over activated alumina on a 1.5 x 20 cm column slurry packed with petroleum ether, bp 30-60° and eluted with the same solvent. The reduction product decomposed completely in the chromatographic column, giving only black tar on elution. The benzene fractions gave 0.25 g (50%) of unreacted benzoperylene.

The preparation of perchlorate salt was attempted with the remaining 0.42 g of crude reduction product following the usual procedure (in acetic acid in the presence of chloranil and perchloric acid). A brown perchlorate salt, 0.225 g (40%) was obtained; mp 144-145°.

I. R. (Nujol): Broad absorption band at 1120 cm^{-1}.

The above perchlorate salt was reduced with lithium aluminum hydride and the hydrocarbon thus produced was very unstable. An NMR spectrum of this hydrocarbon in a degassed carbon disulfide solutinn gave no conclusive evidence regarding the structure of the hydrocarbon. The hydrocarbon spectrum did, however, show a methylene signal at 6.0 τ characteristic of a phenalene type methylene group (Fig. 32). The hydrocarbon in carbon disulfide also showed a complex e.s.r. signal for a substituted phenalenyl radical.

Reduction of Coronene (105) with Lithium in Ethylenediamine

Pure coronene (synthesized according to Clar's[145] method) 0.450 g (0.0015 mole) was stirred with lithium, 0.324 g (0.054 g-atom) in 10 ml of ethylenediamine at 95°. The reactinn was allowed to proceed for 3 hr. and then worked up in the same way as described in the previous experiment. The crude reduction product, 0.40 g was chromatographed over activated alumina on a 1.5 x 20 cm column slurry packed with petroleum ether, bp 30-60° and eluted first with the same solvent and then with benzene. The petroleum ether fraction gave 0.280 g (70%) of white solid of an eicosahydrocoronene (106), crystallized from ethanol as white needles, mp 240-242° (decomposes).

U. V. $\lambda_{max}^{cyclohexane}$: 220 mμ (e 12,000).

I. R. (chloroform): 2930 cm^{-1}, 2845 cm^{-1}, 1645 cm^{-1}, 1450 cm^{-1}, and 815 cm^{-1}.

NMR (carbon tetrachloride): 9.1, 8.8, 8.5 and 8.1 τ (Fig. 33).

Mass Spec.: 320 (mol. wt. of an eicosahydrocoronene 320).

No structural assignment was possible from the above data.

The benzene fraction yielded 0.115 g (30%) of light yellow solid of a tetradecahydrocoronene (107) crystallized from benzene-ethanol, mp 170-172.°

U. V. $\lambda_{max}^{cyclohexane}$: 218 mμ (e 36,000), 252 mμ (e 24,000), 270 mμ (e 50,000), 284 mμ (e 10,000), 335 mμ (e 6,000), 353 mμ (e 8,000) and 371 mμ (e 4,000).

I. R. (chloroform): 3030 cm^{-1}, 2930 cm^{-1}, 2840 cm^{-1}, 1500 cm^{-1}, 1440 cm^{-1} and 840 cm^{-1}.

NMR (deuterochloroform): 8.1 τ, 7.1 τ (m, 22H) and 3.0 τ (m, 4H). (Fig. 34).

Mass Spec.: 314 (mol. wt. of a tetradecahydrocoronene 314).

Anal. Calcd. for $C_{24}H_{26}$: C, 91.67; H, 8.33.

Found: C, 91.88; H, 8.04.

From the above data the structure of the tetradecahydrocoronene may be given as 3, 4, 4a, 4b, 5, 6, 6a, 6b, 7, 8, -8a, 8b, 9, 10-tetradecahydrocoronene (107).

CLAIMS TO ORIGINAL RESEARCH

1. Birch reduction of pyrene afforded two new tetrahydropyrenes, 1, 2, 3, 6-tetrahydropyrene and 1, 2, 3, 5-tetrahydropyrene respectively, in the ratio 2:1.

2. The structures of the two tetrahydropyrenes were determined by proton magnetic resonance studies and by comparing their physical and chemical properties with those of phenalene.

3. 1, 2, 3-Trihydropyrenium cation, a substituted phenalenium cation of this type is reported for the first time. The cation was isolated as stable perchlorate, fluoroborate and tri-iodide salts.

4. 1, 2, 3-Trihydropyrenium cation was found to be more stable than triphenylmethyl, phenalenyl and tropenium cations.

5. We isolated di-tetrahydropyrenyl ether, the hydrolysis product of 1, 2, 3-trihydropyrenium cation. Such an ether was assumed as an intermediate in the hydrolysis of phenalenium cation.

6. We isolated 1, 2, 3-trihydropyrenium cation from tetrahydropyrenes with $HClO_4$, even in the absence of any hydride acceptors with the concomitant formation of 1, 2, 3, 3a, 4, 5-hexahydropyrene, formed by intermolecular hydride transfer.

7. We have reported 1, 2, 3-trihydropyrenyl or 1, 9-trimethylenephenalenyl radical, a stable neutral radical. Its structure has been determined by electron spin resonance studies in various solvents and at various temperatures.

8. Birch reduction of perylene afforded 1, 2, 3, 10, 11, 12, 12a, 12b-octahydroperylene as an absolute product in essentially a quantitative yield (96%), free from other reduction products of perylene.

9. Dehydrogenation of 1, 2, 3, 10, 11, 12, 12a-octahydroperylene with chloranil in the presence of $HClO_4$ afforded 1, 2, 3, 10, 11, 12-hexahydroperylene in 80% yield, free from other reduction products of perylene.

10. The reduction of perylene with lithium in ethylenediamine afforded 1, 2, 3, 3a, 4, 5, 6, 6a-octahydroperylene a reactive hydrocarbon having a phenalene structural unit in it.

11. We isolated 1, 2, 3, 3a, 4, 5, 6-heptahydroperylenium cation, another substituted phenalenium cation. We have also detected the corresponding radical by e. s. r.

12. We have pointed out for the first time that Birch reduction or its modified method (Li + ethylenediamine) is a potential method for creating a reactive phenalene structural unit in a suitable polycyclic aromatic hydrocarbon.

13. The following new compounds are reported:
a) 1, 2, 3, 6-Tetrahydropyrene;
b) 1, 2, 3, 5-Tetrahydropyrene;
c) 1, 2-Dihydropyrene;
d) 1, 2, 3-Trihydropyrenium cation;
e) 1, 2, 3-Trihydropyrenyl radical;
f) 1, 2, 3, 3a, 4, 5, 6, 6a-Octahydroperylene;
g) 1, 2, 3, 3a, 4, 5, 6-Heptahydroperylenium cation and radical;
h) 1, 2, 3, 3a, 3b, 4, 5, 6, 6a, 6b, 7, 8, 9, 12b-Tetradecahydroperylene;
i) An eicosahydrocoronene (structure not known);
j) 3, 4, 4a, 4b, 5, 6, 6a, 6b, 7, 8, 8a, 8b, 9, 10-Tetradecahydrocoronene.

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