5N NaOH
in presence of
air

Ring B becomes aromatic
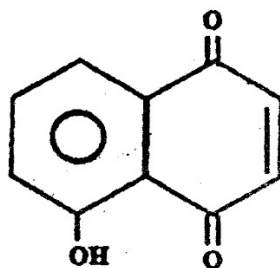Ring A becomes quinonoidal.

Aureonamide

The UV spectrum of this final product is identical with that of 5-hydroxy-1, 4-naphthaquinone.


Aureonamide is given the above structure based on the following evidences.

i) If forms a pentaacetyl derivative by 4 phenolic hydroxyls and by an enolisable carbonyl group.

ii) If forms a 2, 4- dinitrophenyl hydrazone derivative indicating the presence of keto group.

iii) It forms a borate complex with boric acid. The said complex is found to have two boron atoms. '' nce the indicated 4 hydroxyls may be responsible for the complex formation.
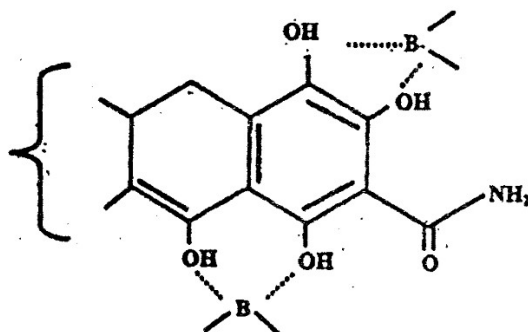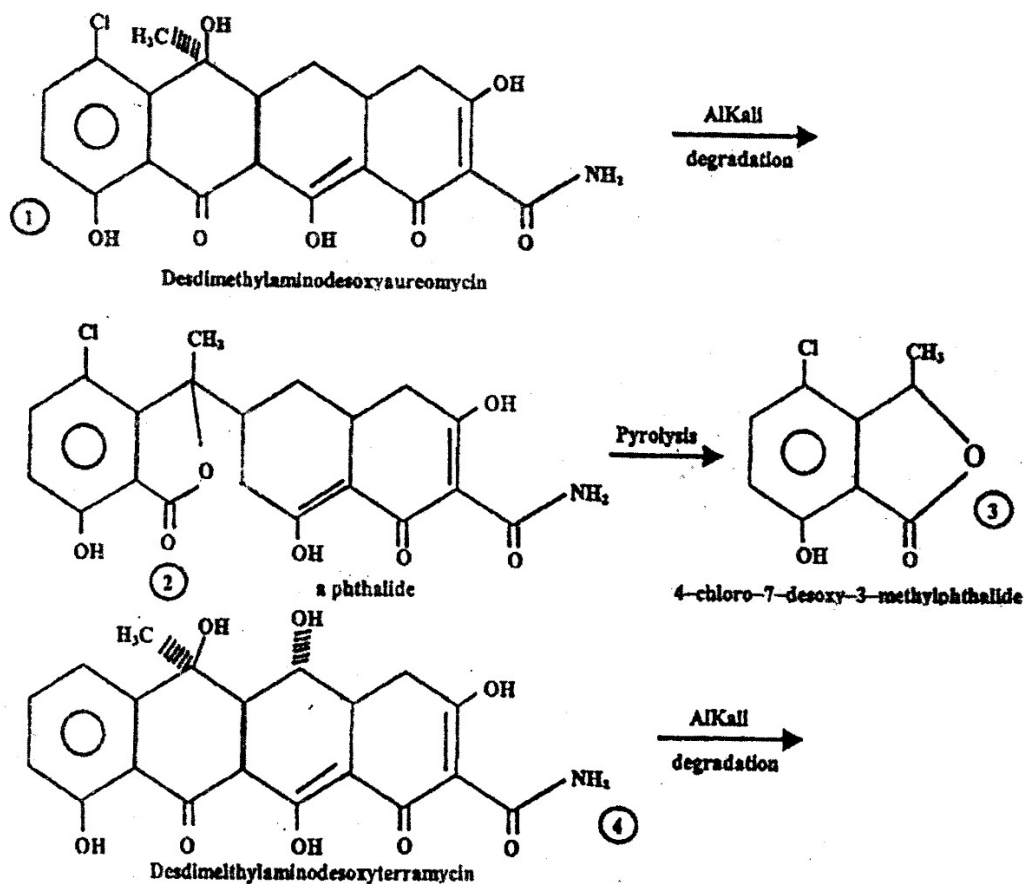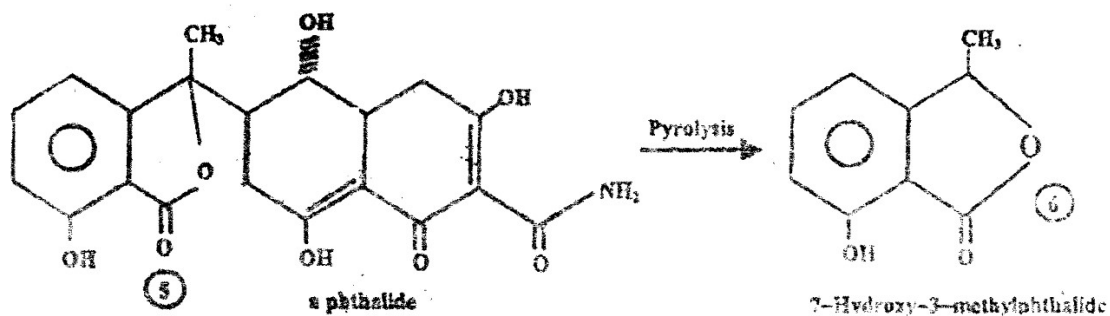
When distilled with Zinc dust aureomycin gives naphthacene which has got a tetracyclic skeleton.

Aureomycin $\xrightarrow[\text{distillation}]{\text{Zn dust}}$

Naphthacene
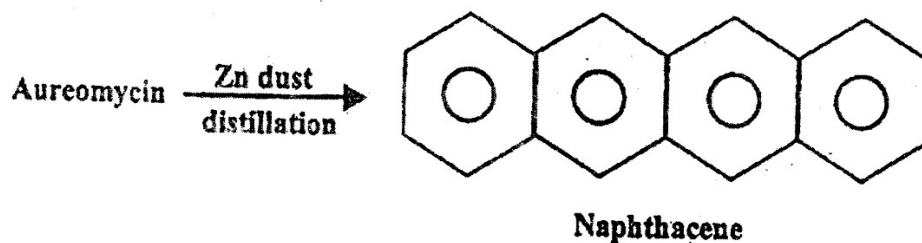
The resemblance of aureomycin to terramycin has been studied through the following spectral comparisons.

a) The desdimethylamino desoxy compound of aureomycin and terramycin has been found to give similar spectra (UV, NMR, IR, etc.,) though aureomycin contains an additional chlorine in ring D.

b) The above compounds have been subjected to the following treatment.

$\xrightarrow[\text{degradation}]{\text{AlKali}}$

Desdimethylaminodesoxyaureomycin (1)

$\xrightarrow{\text{Pyrolysis}}$

a phthalide (2)

4-chloro-7-desoxy-3-methylphthalide (3)

$\xrightarrow[\text{degradation}]{\text{AlKali}}$

Desdimelthylaminodesoxyterramycin (4)

a phthalide   7-Hydroxy-3-methylphthalide

The different curves obtained by subtraction of 3 from 2 and subtraction of 6 from that of 5 are found to be idetical. This suggests that aureomycin and terrmycin have the same chromophoric system.

In a similar manner substraction of the spectrum of Y from that of X gave a spectrum similar to that of a 2, 6 - dihydroxybenzoic acid. Thus the physical, chemical, physiological and UV spectra of aureomycin show a clear resemblance to terramycin which has been already synthesised and the structure confirmed.

* * * *

UNIT – IV
AROMATICITY
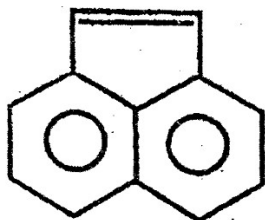### BENZENOID & NON – BENZENOID AROMATIC COMPOUNDS:

Compounds containing at least one benzene ring are termed as benzenoid aromatic compounds. While other compounds that exhibit aromatic behaviour, but do not contain a benzene ring are called non – bezenoid aromatic compounds.

To identify the non – benzenoid aromatic compounds Huckel proposed as follows:

"A cyclic planar conjugated polyene with $4n + 2$ electrons will be aromatic".

Thus, cyclopropenyl cation, cyclopentadienyl anion exhibit aromatic properties.

Of course, Huckel's rule has been found to be strictly valid only for systems with peripheral electrons. So it's applications to condensed poly – cyclic systems may give wrong results. (EX)
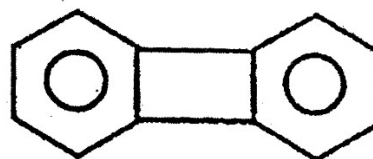
Acenaphthylene   Diphenylene

According to Huckel's rule these compounds should not exhibit aromatic character. But these compounds are definitely aromatic (Benzenoid).

As we have observed, Huckel's rule is of limited applicability as it is concerned. Only with monocyclic systems. The possible aromatic nature of bi – cyclic and polycyclic non – benzenoid hydrocarbons which have classical structures with alternate single and double bonds, has been covered by Craig's rule. This is an empirical rule and proved of value in this connection: but the rule applies only to hydrocarbons in which at least two centers lie on a symmetry axis that converts one kekule – type structure to another.

The structural formula is first labeled with equal numbers of spin symbols α - and β - as far as possible alternately, different symbols being given to the ends of all the double bonds in the kekulae – type structure. The sum is then taken of the number (f) of symmetrically related π - centres not on the symmetry axis. Then the number (g) of interconversions of α - and β - by rotation about the axis is taken.

If this sum, (f+g), is even, the valence bond ground state is symmetric and the compound may be expected to be aromatic. If the sum is odd, the compound may be expected to be non – aromatic.

In pentalene (I) for example, three pairs of centers are related by the symmetry axis, and f=3. upon rotation no interconversion of α - and β -occurs; ie g = 0. Hence, f + g = 3, an odd number, and pentalene should be non – aromatic. Similarly, for heptalene (II) f=5 and g = 0, so f+g=5, and this hydrocarbon too is non – aromatic. For azulene (III), f = 4 and g = 0. So f+g = 4, and the hydrocarbon would be expected to be aromatic.

Fig: 2
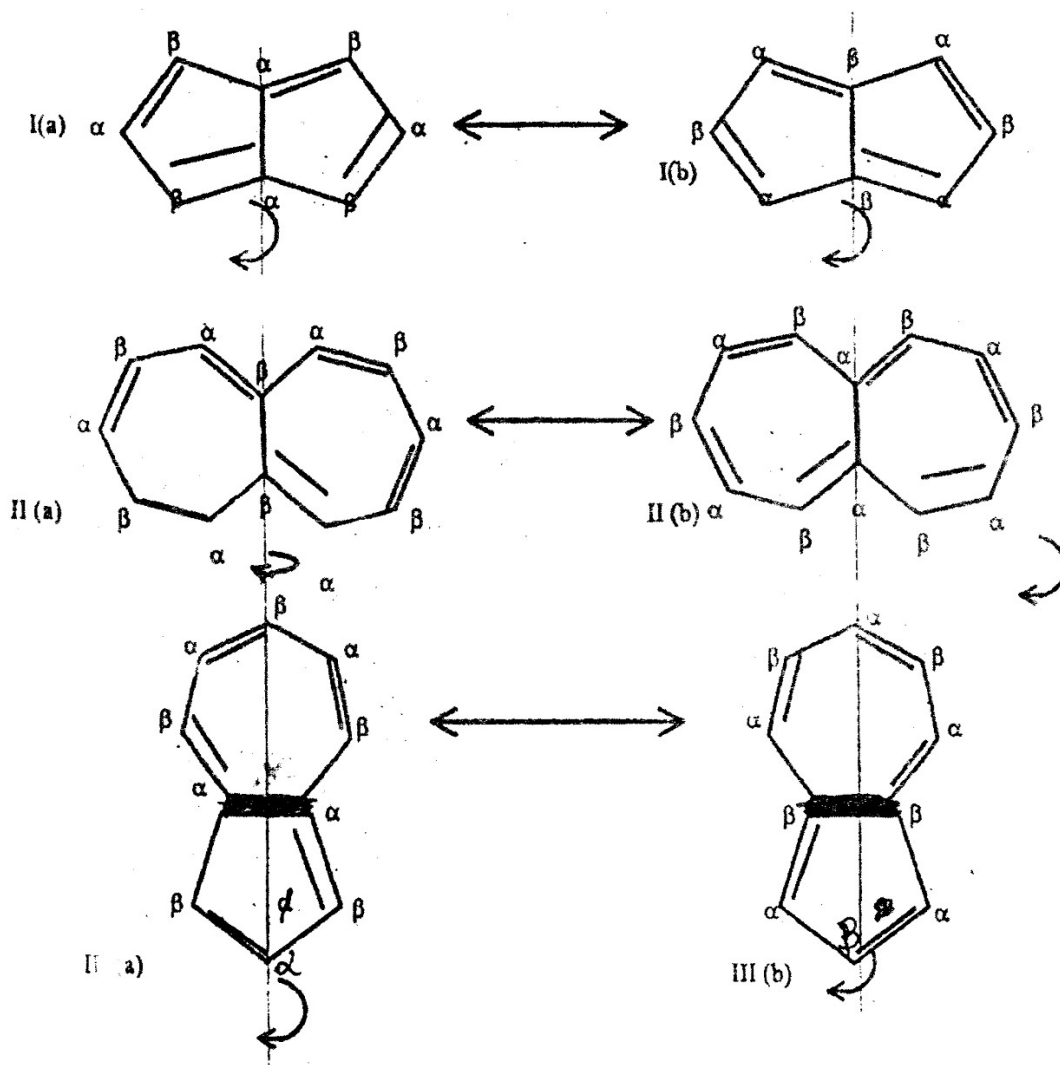
(Experimentally, heptalene has been found to be an unstable non - aromatic hydrocarbon; and azulene is aromatic).

HOMOAROMATCITY

If a compound contains one or more SP³ hybridised carbon atoms in an otherwise conjugated cycle, it is called as homoaromaticity.

Example,

Cyclooctatetraene when dissolved in con. Sulphuric acid gives homotropylium ion by the addition of a proton to one of its double bonds.

Fig : 3
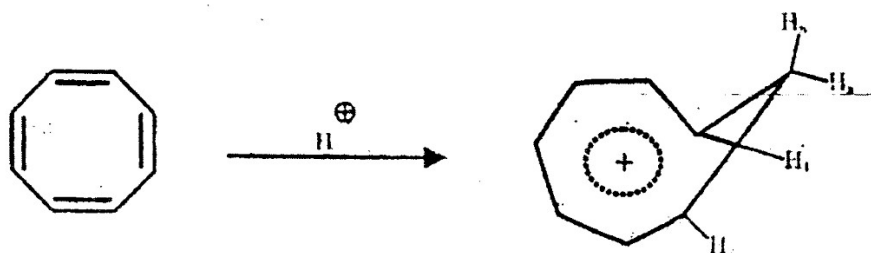
In this ion, an aromatic sextet is spread over seven carbons, as in the tropylium ion. The eight carbon atom is SP³ hybridised, so cannot participate in the cyclic conjugation. This is a case of homoaromaticity.

The effective overlap of the orbitals to form a closed loop is made possible, by forcing the SP³ carbon to be vertically above the aromatic atoms. In this ion, H^b is directly above the aromatic sextet and so is shifted far upfield in the nmr.

ANTI AROMATICITY:

If in a case, the delocalisation of π - electrons leads to instability, then it is called antiaromaticity.
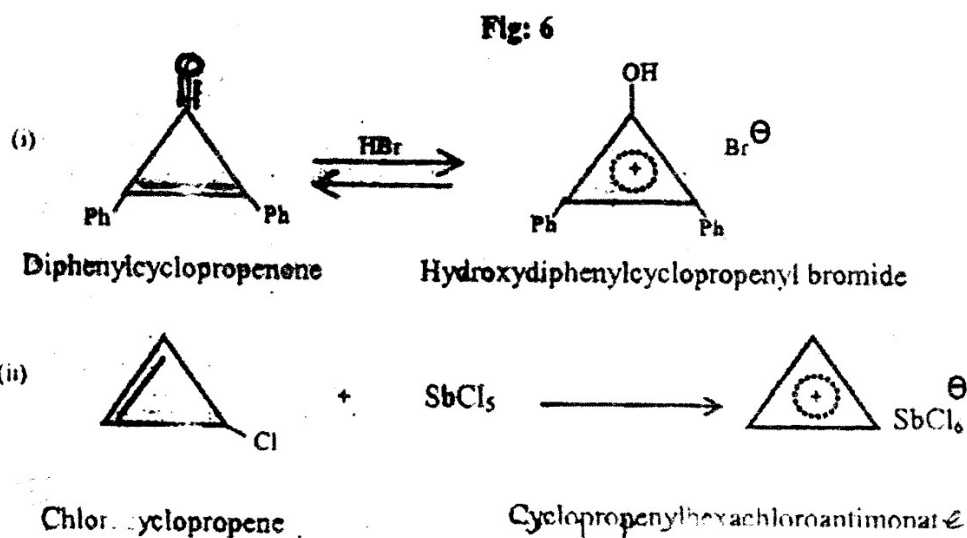
Fig : 4

(Ex)
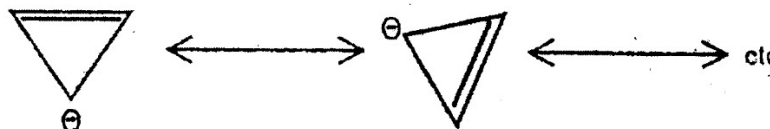
If such compounds lacked aromaticity, one would expect them to be about as stable as similar non – aromatic compounds; but both theory and experiment show that they are in fact much less stable.

SYSTEMS, WITH 2,4,6,8 AND 10 ELECTRONS
THREE – MEMBERD CARBOCYCLIC RINGS

According to Huckel's rule, the simplest aromatic systems (n=0) should only two π electrons. Example, the hypothetical cyclopropenyl cation.

Fig: 5
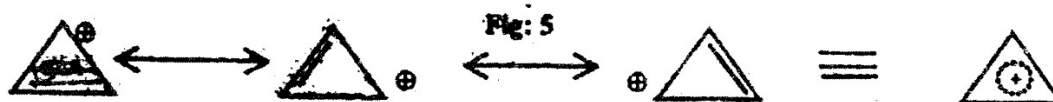
But a number of derivatives cyclopropenyl cation are known Examples are,

Fig: 6

(i)

Diphenylcyclopropenone   Hydroxydiphenylcyclopropenyl bromide

(ii)

Chlor cyclopropene   Cyclopropenylhexachloroantimonate

The stability of triphenylcyclopropenyl cation is so high that it resists addition of bromine and also that of hydrogen over a catalyst. The nmr spectrum of this compound showed only one type of proton, confirming the identity of the three pheyl groups. Moreover, X – ray crystallogrouphic studies have shown that the average carbon –carbon bond length in the three – membered ring is 1.373 +/- 0.005A°.

For methylenecyclopropene or triafulvene both classical and dipolar structures can be written.

The dicyano – derivative, for example, has been found to have a high dipole moment (7.9+/-0.1D) in agreement with the following formulation. Spectral evidences indicate this compound to be a resonance hybrid.

Fig : 7
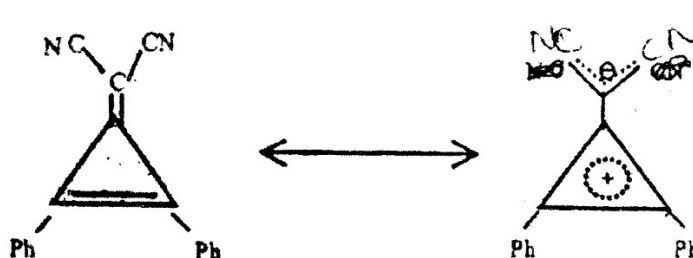
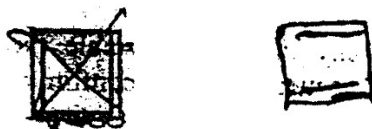Calcicene or cyclopropenylidene cyclopentadiene is also found to exist in resonance forms.

Fig : 8
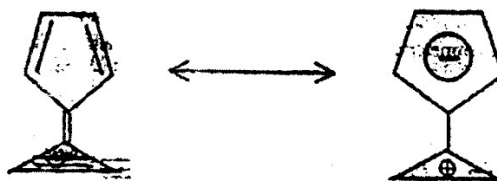
4π - ELECTRON SYSTEMS
Fig :9

Cyclobutadiene is the simplest neutral molecule under this category. According to Huckel's rule, this compound must be non – aromatic. If a planar structure with alternate single and double bonds is visualized, the bond angles would be 90° instead of 120° (SP² hybridisation). i.e., the ring would be considerably strained. Early theoretical studies on butadiene are founds to give conflicting views on the stability, bond lengths and other properties. But most scientists agree that if cyclobutadiene could exist at all would be unstable and non – aromatic.

6π - ELECTRON SYSTEMS

The best 6π electron system is of course, benzene. The behaviour this hydrocarbon is understood by it's "Aromatic Character".

Cyclopentadiene is a typical unsaturated hydrocarbon with two conjugated π bonds. It has a low resonance energy of 3 kcal/mole. When it is treated with a strong base, cyclopentadienyl anion is formed. This according to Huckel's rule must be aromatic, as it has 6 electrons.

Though it is undoubtedly an aromatic system, it shows greater tendency for addition reactions rather than electrophilic substitution reactions.

Electrophilic reagents readily add to it, thereby destroying the aromatic character.

Fig : 10
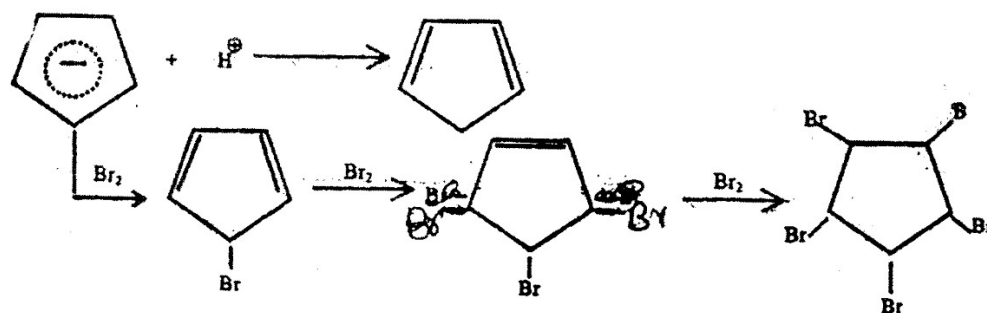
However, it's aromatic character is evidenced by the following facts:

i) The parent hydrocarbon cyclopentadiene 4 π - electrons, but it's anion has 6π electrons. Hence it satifies the (4n + 2) electron rule.

ii). The nmr spectrum of potassium cyclopentadienide anion shows a single sharp signal at δ 5.34. Thus the symmetrical nature of the anion is established. Its resonance energy is 42 Kcal/mole.

Fig : 11
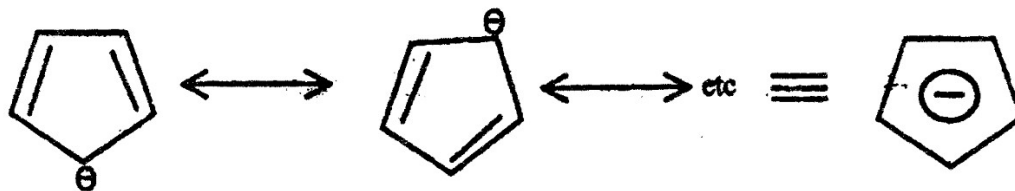
iii) Ferrocene (dicyclopentadienyl iron) is so stable that it undergoes normal aromatic electrophilic substitution reactions. Thus confirming the aromatic character of cyclopentadienyl anion.

FERROCENE

The is a member of π - complexes called, METALLOCENES. These are formed between the cyclopentadienyl anion and transition metals such as, iron, nickel, cobalt etc.

METHODS OF PREPARATION
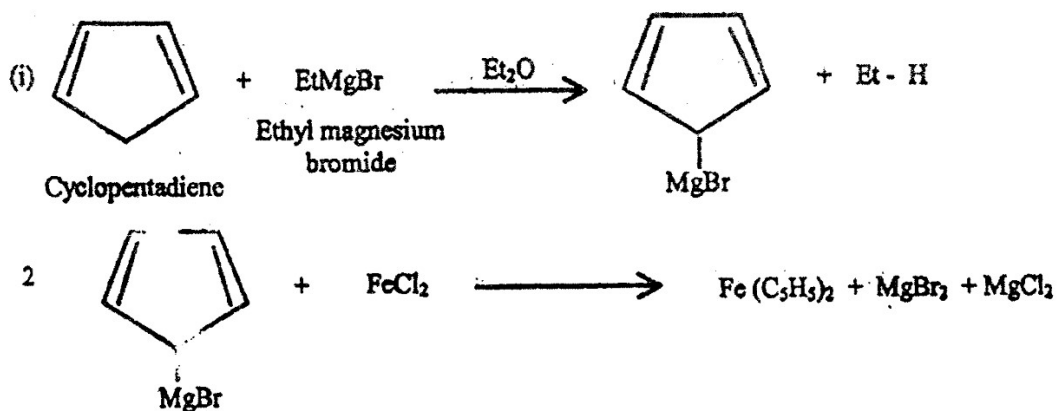
Since in its formation, ferrous salts are partially reduced by Grignard reagent, the product is named as FERROCENE.
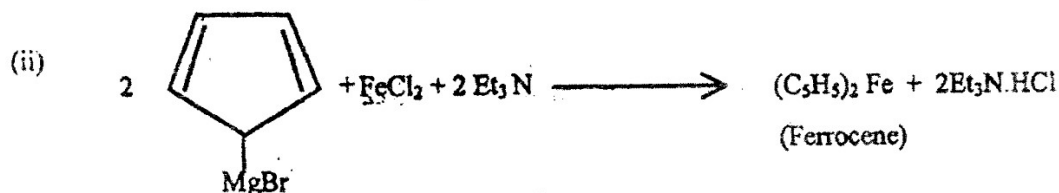
It is a solid. Ferrous ion is sandwiched between two parallel equidistant cyclopentadienyl anion placed 3.41A° apart. C – C bond length is found to be 1.41A°, similar to an aromatic system. The Fe – C distance, 20.3Ao, is equal to the sum of the convalent radii of Fe & C (linked by a single bond).

The dipolemoment of this molecule is zero, indicating the centrosymmetric nature of it. In IR only one C–H stretch value (2075 Cm⁻¹) is observed. Thus all the C-H are equivalent.
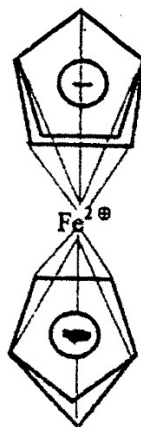
It does not add hydrogen nor do undergoes DAR. Thus it doesn't behave like cyclopentdiene however, it undergoes acylation sulphonation and mercuration (i.e., electrophilic substitutions) more readily than benzene itself. Further it does not undergo halogenation and nitration due to the ease of its oxidation.
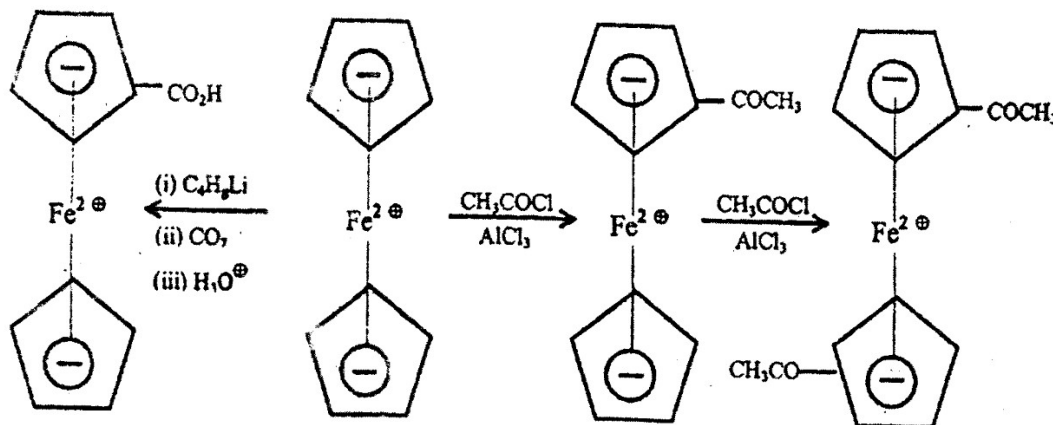
Ferrocene –1-Carboxylic Acid   1-acetyferroceme   1. 1 - Diacetylferrocene   ergoes
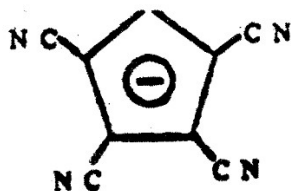
The diazocyclopentadiene shows an UVmax at 298nm and a shoulder around 340nm, with long tailing absorption into the visible region.
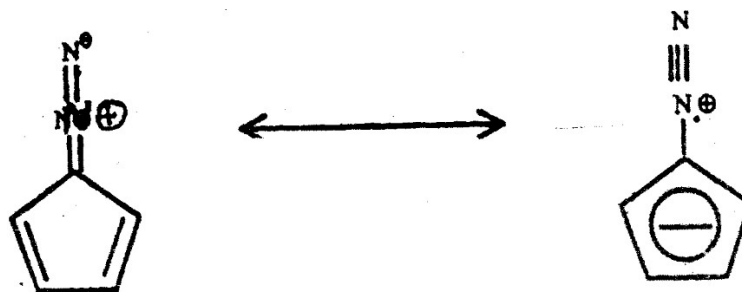
The nmr spectrum for this compound shows two multiples of equal area centred at δ 6.7 and 5.8. the former is attributed to the 3,4 – hydrogens and the latter to 2,5 – hydrogens. Anther interesting example for the 6π - electron systems is cycloheptatrienyl cation or more commonly referred to as tropylium ion. Here 6π -electrons are delocalized over a closed loop of 7 carbon atoms.
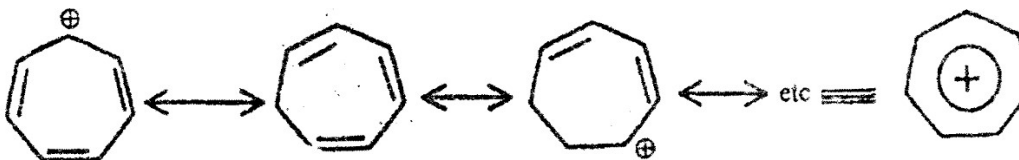
According to Huckel's rule this must be aromatic as it obeys the $(4n+2)$ π-electron rule. The symmetrical nature of the tropylium ion has been established by the following experiment. Labeled trophylium bromide has been prepared from benzene and $^{14}CH_2N_2$. the bromide on treatment with phenylmagnesium bromide ves phenylcycloheptatriene. The benzoic acid, obtained by the oxidation of the latter showed radioactity corresponding to one – seventh of a labeled carbon atom. The phenylmagnesium bromide must therefore, have reacted equally with all seven ring carbon atoms. Thus all the seven carbon atoms are found to be symmetrical.

The C-C bond distance in tropylium cation is 1.40A°. Thus further proving the symmetrical nature of this species. This indeed is a planar molecule with the positive

charge distributed over all the seven carbon atoms. The resonance energy for this molecule is found to be 6.7 Kcal / mole.

The tropylium cation can be obtained by the following methods.

(i) Cycloheptatriene + Bromine → Tropylium bromide

(ii) Cycloheptatriene + $2H_2SO_4$ → Trophyliumbisulphate $HSO_4 + 2H_2O + SO_2$

(iii) Benzene + CH_2X_2 → Tropylium Halide $X^\ominus$
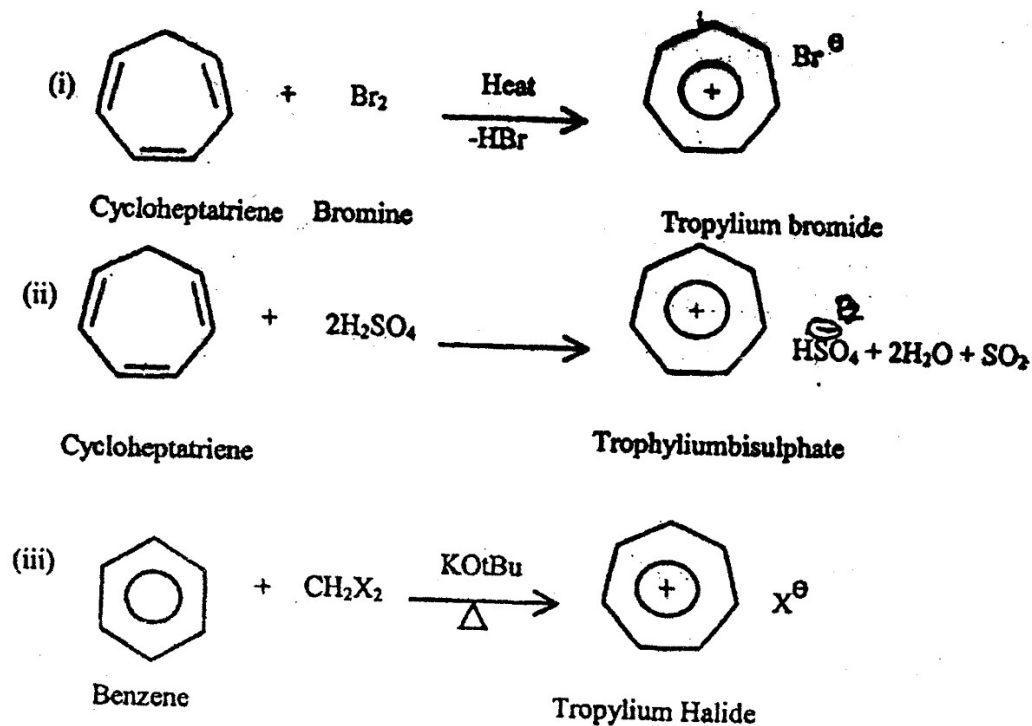
Tropylium ion doesn't undergo electrophilic substitution unlike benzene or ferrocene. Instead it undergoes nucleophilic addition with the formation of the cycloheptatriene system. i.e., the aromatic character will be lost.
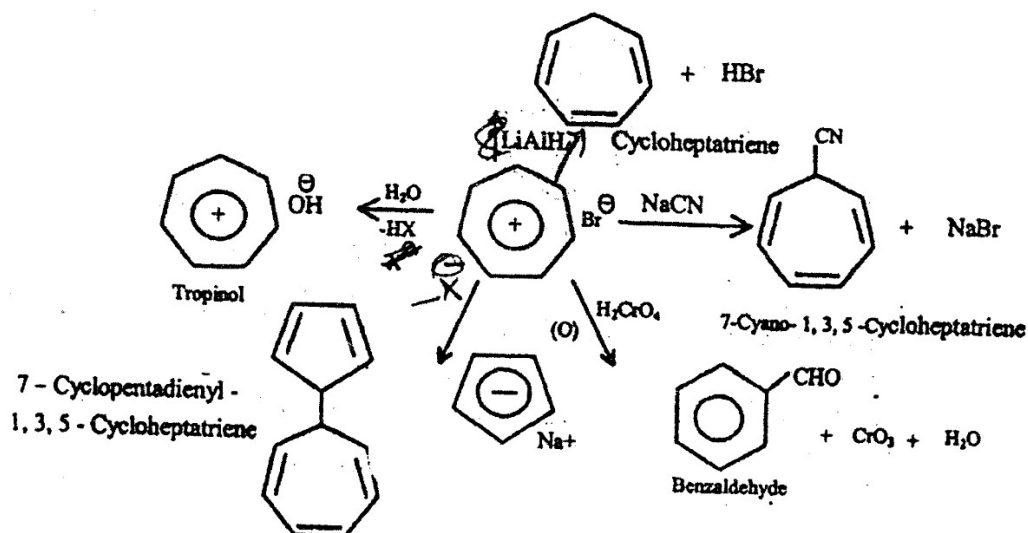
8-π Electron System

Cyeloocatetraene is not planar, but tub – shaped. Therefore it would be expected to be neither aromatic nor anti – aromatic; since both these conditions require overlap of parallel p – orbitals.
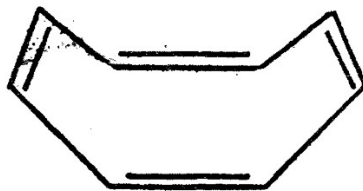
The UV spectrum of cyclo – octatraene shows a maximum at 282nm (log C, 2.4); and the nmr spectrum shows a peak at 5.69 δ, confining the absence of an induced ring current. It seems certain, therefore that cyclooctatetraene is non – planar and non-aromatic.

10-π Electron System
[10] - Annulene :
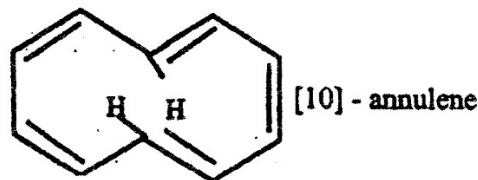
[10] - annulene

Conjugated monocyclic polyenes with the general formula $(C2H2)n$ are termed as annulenes. Annulenes are med as (n) annulenes where 'n' refers to the number of carbon atoms in the ring. For example benzene is a [6] – annulene.
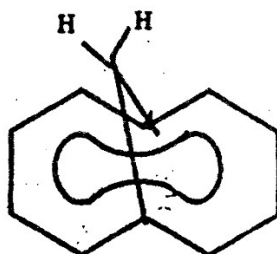
1,6 - Methanocyclodecapentaene

The simplest annulene which may be capable of having a strainless planar ring is [10] –annulene. This compound has trans double bonds. There is interference between 1.6 hydrogen atoms in this compound. Hence it is not planar. i.e., it cannot attain coplanarity and hence does not exhibit aromaticity. But if the 1.6 hydrogens are bridged by a methylenic group, then the resulting compound shows aromatic character. This is possible as the 10 membered ring becomes flattened sufficiently to allow π - electrons delocalization. And the molecule attains aromatic stability as predicated by Huckel's rule. This is a pale yellow solid, stable with a.m.pt. of 29°C.

12π - Electron Systems

This compound does not fall under the category of Huckel's rule. Preliminary works on it indicated it to be an unstable, reactive hydrocarbon. It's trisdehydro compound i.e., trisdehydro [12] annulene is prepared. The 2 electron in the triple bond are contained in a separate π - orbital and is in no way conjugated with the annulene nucleus. Because of the introduction of the triple bonds, the molecule is expected to be planar and strainless. But this does not conform to Huckel's rule and hence is not expected to be aromatic this is confirmed by the nmr spectrum of this compound, which gives a single sharp signal 4.45δ.
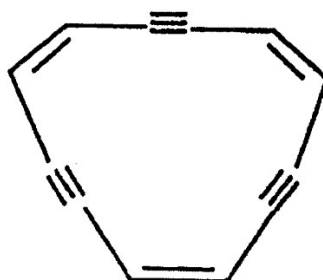
14π - Electron System [14] – Annulene

Cyclotetradecaheptaene or [14] – annulene obeys the $(4n+2)$ π electron rule. Hence it is expected to be aromatic. Models and scale drawings of the compound indicate overlap of the internal hydrogen atoms as in [10] – annulene, but to a lesser degree.
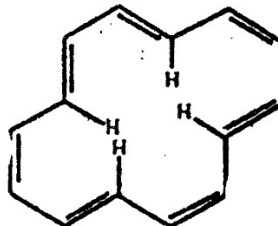
The nmr spectrum, recorded at room temperature, for this compound showed it to be non – aromatic. But at $-60°C$ the spectrum shows broad peaks 7.6δ due to the outer and inner protons. i.e., the compound is diatropic. This compound is completely destroyed by light and air in one day.

X – ray analysis shows that, although there are no alternating single and double bonds, the molecule is not planar. However a number of stable bridged [14] – annulenes have been prepared Example, trans – 15,16 – dimethyldihydropyrene.

This compound is undoubtedly aromatic, the π-perimeter is approximately planar. The C-C bond distance is 1.39 to $1.40A°$. This compound undergoes aromatic substitution and is diatropic. The outer protons are at 8.14 to 8.67δ, while the methyl protons are at -4.25δ.
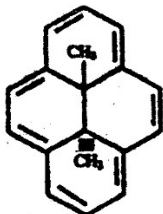
The hydrogen interferences in [14] annulene can be eliminated by introducing one or more triple bonds in the ring. Example, dehydro [14] – annulene. The latter is diatropic and can be nitrated or sulphonated.
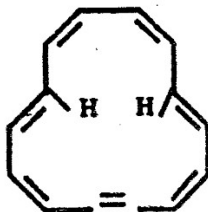

16π - Electron system – [16] – Annulene

This doesn't obey Huckel's rule and hence must be non-aromatic. It can be prepared by the partial hydrogenation of bisdehydo [16]– annulene (or) by irradiation of cyclooctatetrene dimmer. Its physical properties conforms to its non – aromatic nature.
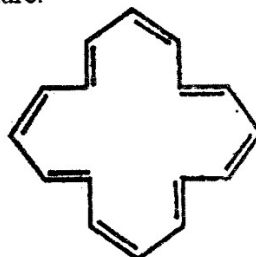
18π - Electrons. (18) – Annulene is diatropic.

In the nmr spectrum, there are two signals, one at 9.0δ and the other and the other at – 3.0δ. The former corresponds to the 12 outer protons and the latter, 6 inner protons. X – ray crystallography shows that this is nearly planar. That means the interference due to the inner hydrogens is not important in annulenes this large. [18] – annulene is reasonably stable; it is can be distilled at low pressures and undergo aromatic substitutions. Though the C – C bond distances are not equal, they do not alternate. There ai . 12 inner bonds of about 1.38A° and 6 outer bonds of about 1.42A°. This molecule is found to have resonance energy of about 37 Kcal/mole, a similar to that of benzene.
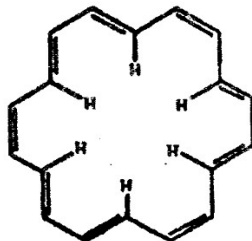
Many of the dehydro [18] – annulenes have been prepared and are found to exhibit aromatic character.

The other annulenes that have been prepared are 20,24,30 – annulenes. The lost one alone satisfies the Huckel's rule. The other two are classified as [4n] – annulenes.

Fulvenes

Fulvenes may be considered as a derivative of the cyclopentadienide anion. It can be prepared by the condensation of cyclopentadiene with aldehydes and ketones in the presence of alkali.

Ylide from dialkyl fulvene
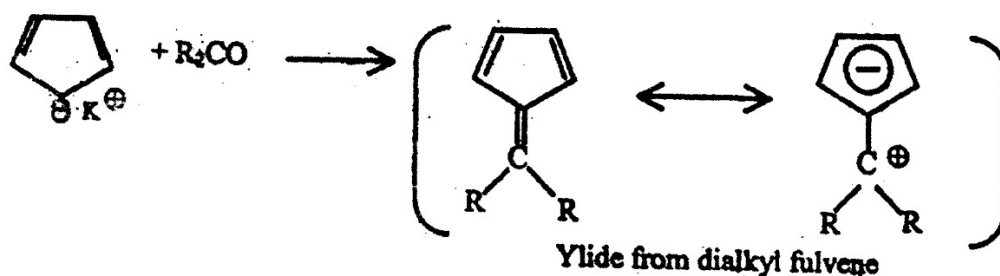
The stable 6 – electron arrangement in the ylide form is due to the movement of the electrons into the ring from the exocyclic double bond.

Measurements of the dipolemoments of fulvene, and of substituted fulvenes, have confirmed the implied separation of charge. Fulvene itself has a dipolemoment of 1D; dialkyl fulvene approximately 1.5D.

The chemical properties of fulvenes suggest that these substances are on the border line between conjugated dienes and true aromatic compounds.

Both addition and substitution reactions occur; and fulvenes readily undergo the DAR.

6,6 - Dimethylfulvene
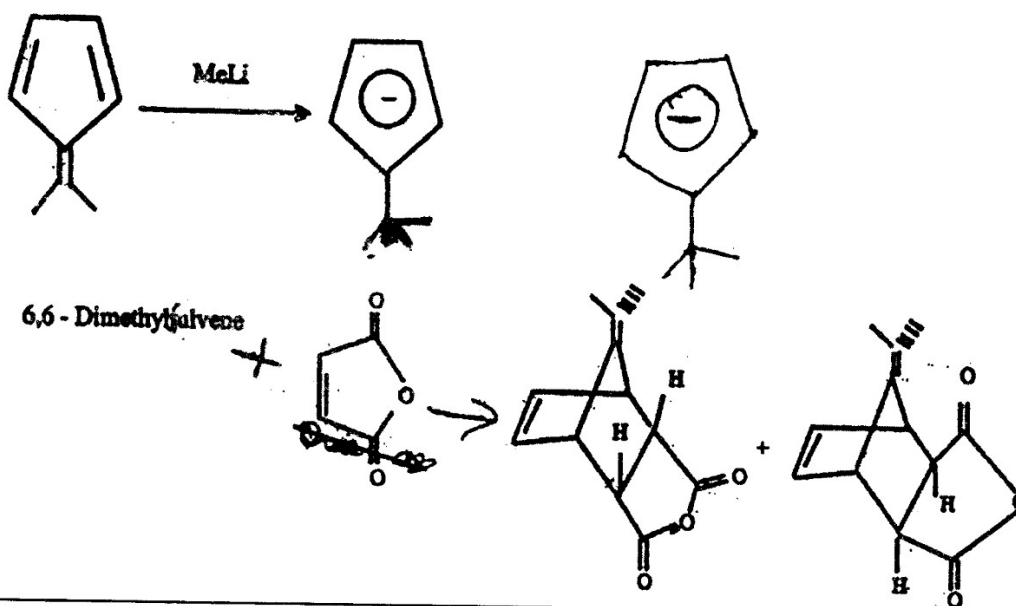
Fulvalenes are a group of molecules related to fulvenes, in which the protons on the exocyclic double bond have been replaced by a second "odd" unsaturated ring having the general formula.
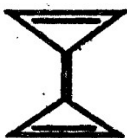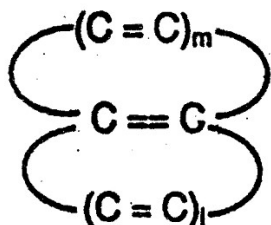
m = l = 1 is called triafulvalene. Neither, this compound nor its derivatives have been prepared.

Next m = 1, l = 2, called triapentaful valene and a number of derivatives of it have been prepared.
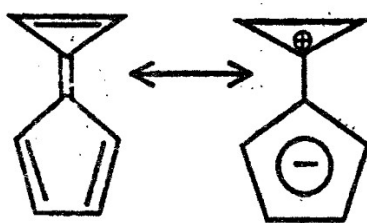
Triapentafulvalene
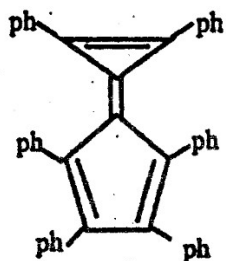
Hexaphenyltriapentafulvalene
$\mu = 6.3$ D

These compounds are otherwise called as calicenes. Next member in the series is fulvalene it self.
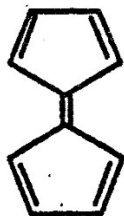
Azulene:

It is a non – alternant hydrocarbon and is found to be aromatic. Its resonance energy is 49 Kcal/ mole. Azulene undergoes a wide variety of electrophilic substitution reactions to give 1 – substituted azulenes, and 1,3 disubstituted azulenes undergo substitution at the 5th position. It can be prepared using a number of methods.

1.

9 - Octalin

2.

Cyclodecane   Azulene   Naphthalene
                                   (20%)   (5%)
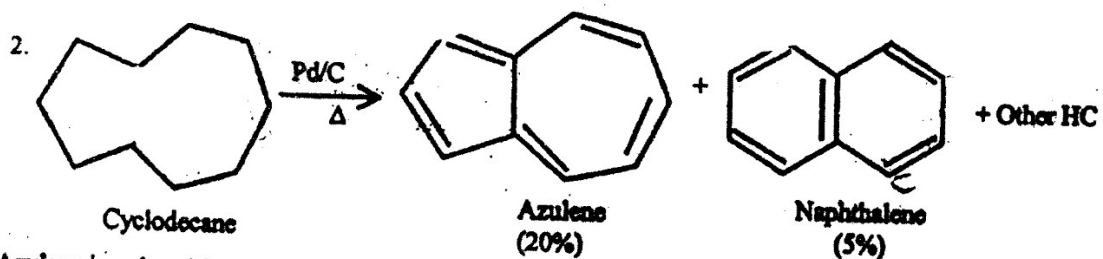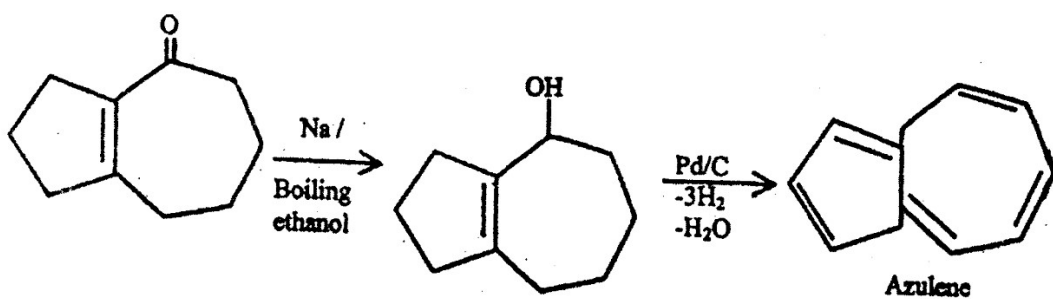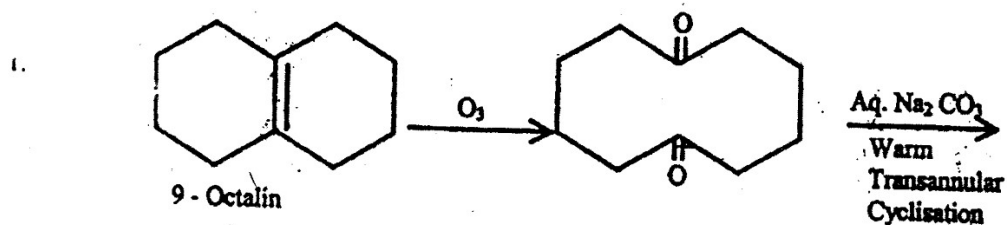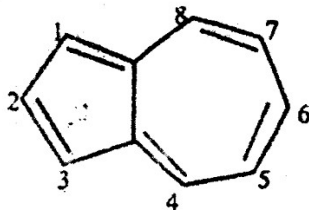
Azulene is a deep blue compound. It is regarded as the resonance hybrid of the following structures.

Azulene   1-acetylazulene   1,3 - Diacetylazulene
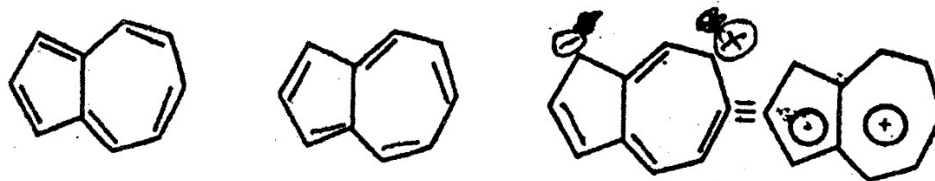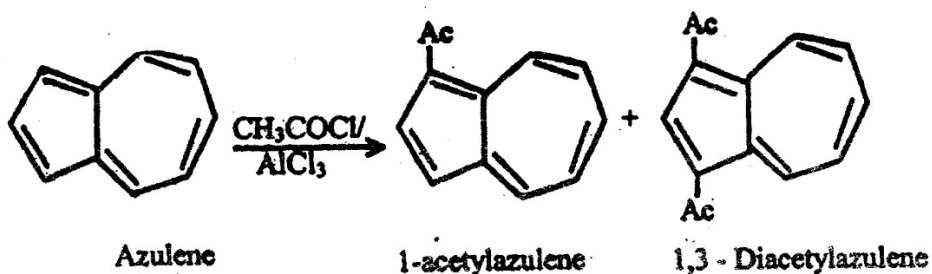
The five membered ring has five and the seven – membered ring has seven π - electrons. (Two π electrons are common to both rings). If one π - electron is transferred from the seven to the five membered ring, each ring will now have a closed shell of six π - electrons. Thus electrophilic subsititution occurs preferentially in the five - membered ring; since this is more electron rich than the seven – membered ring.

Tropolones:

Tropone, tropolones may be termed as "annulenones". The annulenones are cyclic system composed of unsaturated, odd – membered rings in which the "odd" carbon atom is part of an exocyclic unsaturated group) in this care arbonyl group).

Tropone is a resonance hybrid of the classical structure and the tropylium cation structure. Its resonance energy is 29 Keal/mole.
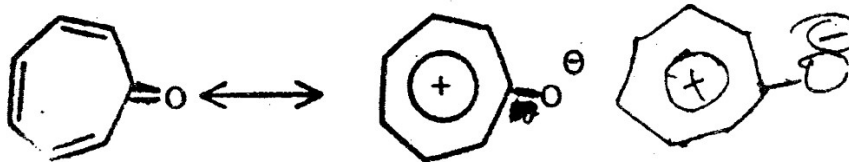
Neverthcless trop - one shows only limited aromatic character. It is readily hydrogenated and rapidly decikiyrused permanganate). Much greater stability, aromatic character are displayed by 2 hydroxytropone or tropolone. The proximity of the carboyl and hydroxyl groups leads to intramolecular H – bonding as well as tautomerism. Some are the methods of preparation are;

Tropone

Tropolone

2.

3.

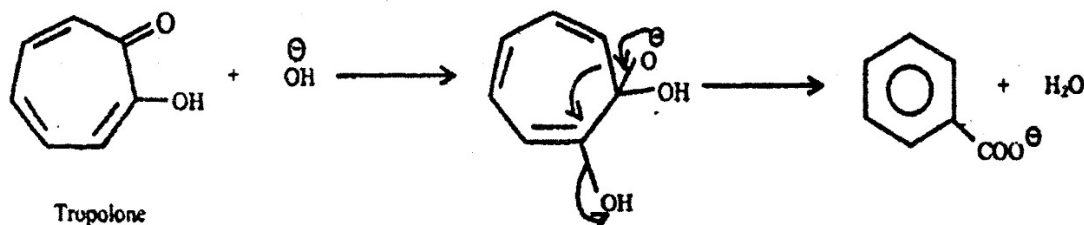Cyclopentadiene   Tetrafluoroethylene
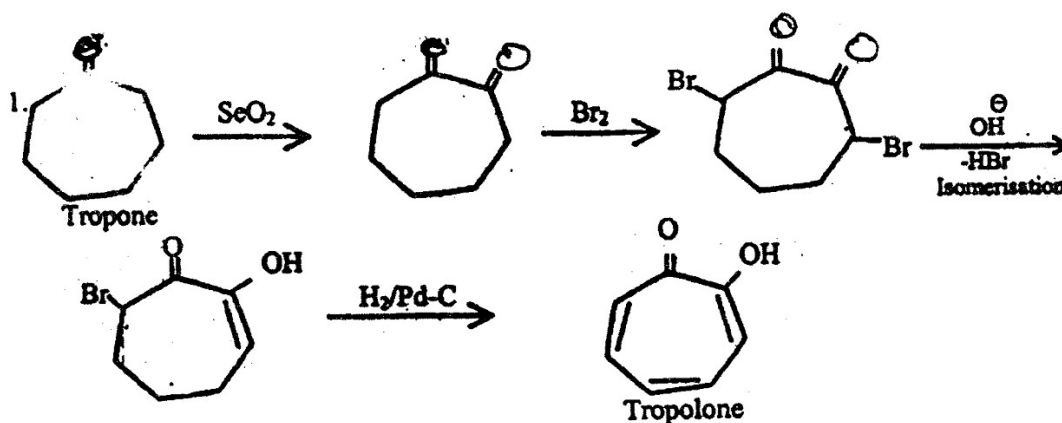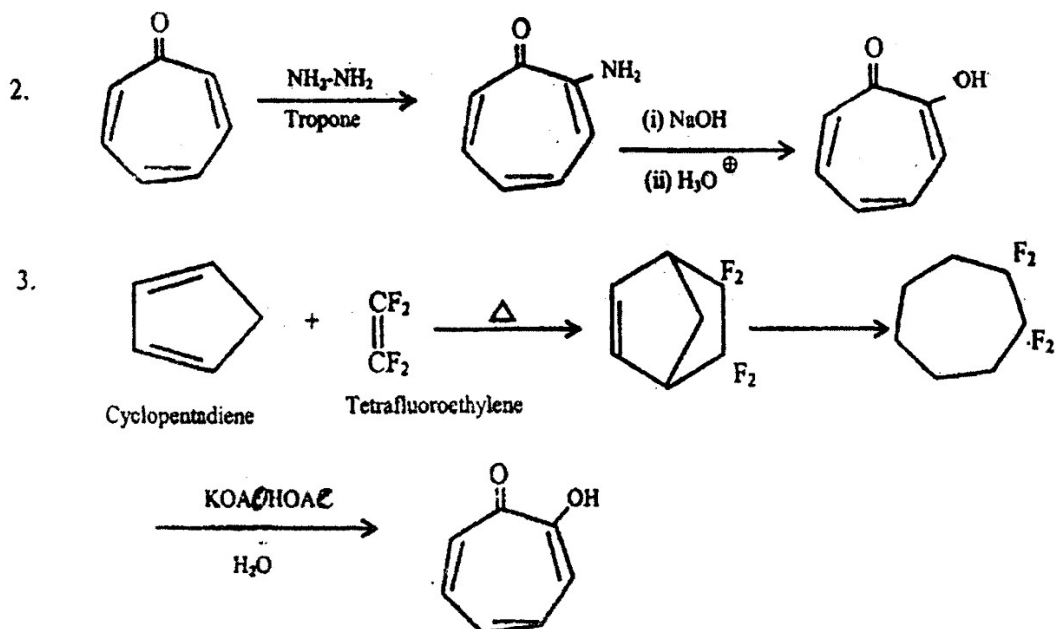
It is a resonance hybrid of the following structures.
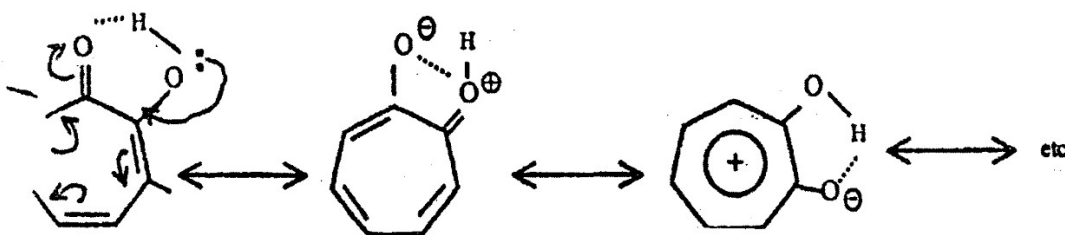
It undergoes a wide variety of electrophilic substitution reactions. It has been found to have a resonance energy of 36 Kcal/mole.

When treated with nucleophilic reagents, say alkali, the tropolones rearrange to derivatives of benzoic acid.
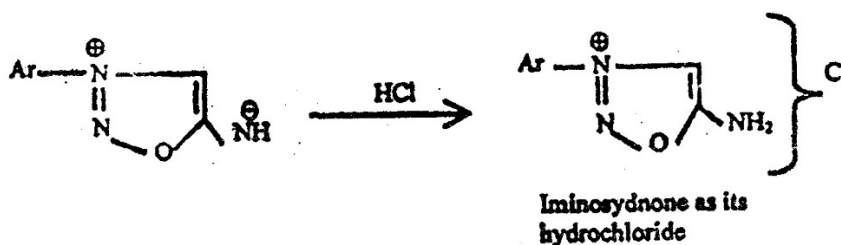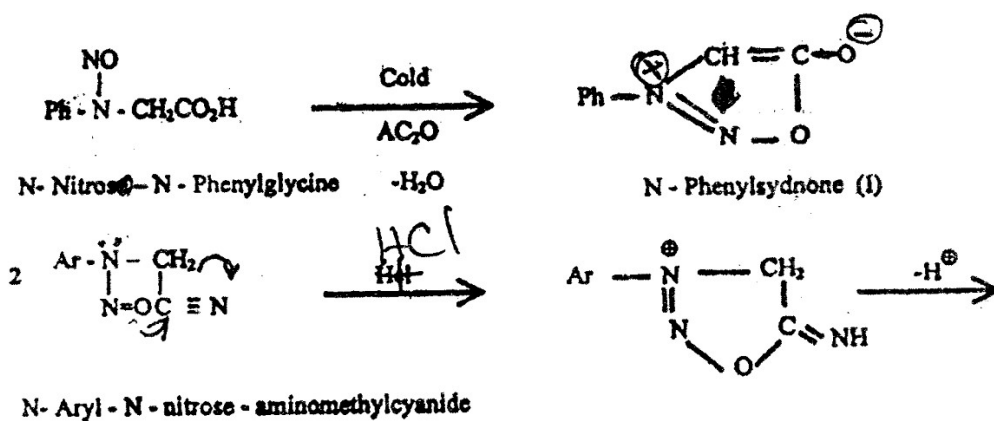

Tropolone

HETEROCYCLIC COMPOUNDS

Sydnones:

Introduction

These are a class of compounds called mesionic compounds. Mesoionic compounds are unsaturated five – membered. Detains with an exocyclic anionic group joined to the ring through a carbon atom. Earl and Mackney in 1935 gave the trivial name 'sydnones' after the university of Sydney in which they were discovered. They are otherwise called as 'inner salts'.

PREPARATION

1. N – phenylsydnone is prepared by treated by treating N – nitros   N phenylglycine with acetic anhydride. The mixed anhydride formed in this reaction is heated to form the heterocycle with the loss of acetic acid.

N- Nitroso– N - Phenylglycine   N - Phenylsydnone (I)

N- Aryl - N - nitrose - aminomethylcyanide

Iminosydnone as its hydrochloride

Properties

3-phenylsydnones readily undergo electrophilic substitution at the 4 position of the phenyl ring. Thus the phenyl sydnones exhibit aromatic character.

4-Nitro derivative

3-phenylsydnone

4-Bromoderivative

4-Chloro derivative
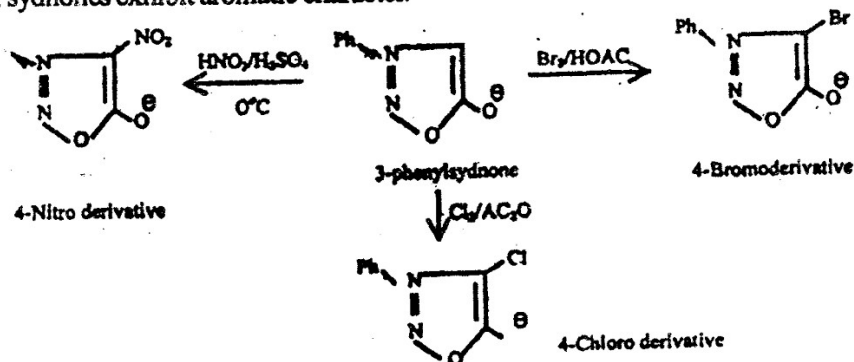
They undergo 1,3 – dipolar cycloaddition reactions with acetylenic type compounds

Structure :

Earl etal represented sydnones by structure (I). This structure is smilar to that of a β lactone. But according to Baker etal sydnones cannot be represented by that structure on the basis of the following objections.

i) This is highly strained system, containing a three – membered ring and a four – membered ring fused together. Such a system cannot be obtained by the dehydration with acetic anhydride.

ii) Many β - lactones are unstable to heat, but sydnones are stable. So, α β - lactone structure is unlikely.

iii) If the β - lactone structure is correct then sydnones should be capable of existing in optically active forms. But when (+) N-nitroso – N – phenylalanine, is convered into a sydnone, the product has been found to be optically inactive.
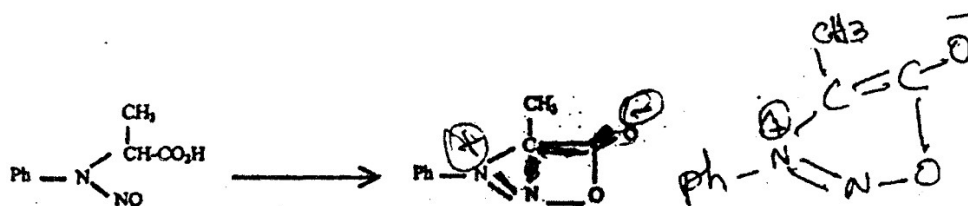
iv) The aryl nucleus in sydnones is very resistant to substitution by eletrophilic reagents. This is to be expected on the basis of the planar nature of sydnones.

So, Baker etal proposed a five – membered ring structure, which cannot be represented by any one purely convalent structure. They put forward a number of charged structures, the sydnones being a resonance hybrid.
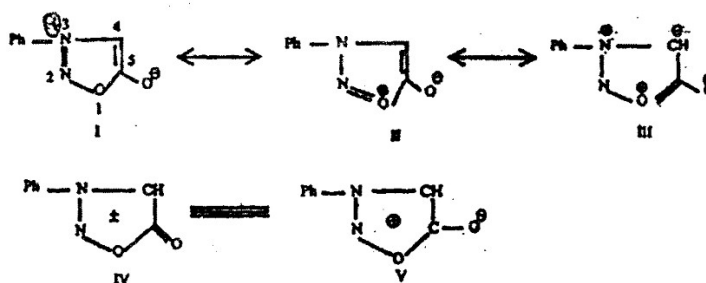
Structures (I) to (III) contribute to the structure of sydnones. Sydnones show large dipolement, N-3 being the positive end. Structures (IV) and then (V) are proposed to explain the larger moments. The form of sydnones represent the meso – ionic compounds.

Recent physical measurement like NMR show that the positive charge is mainly localized on N_3 and the negative charge on the exocyclic oxygen atom. So the sydnones may be considered as the resonance hybrid of the following three structures. (I, VI & VII).
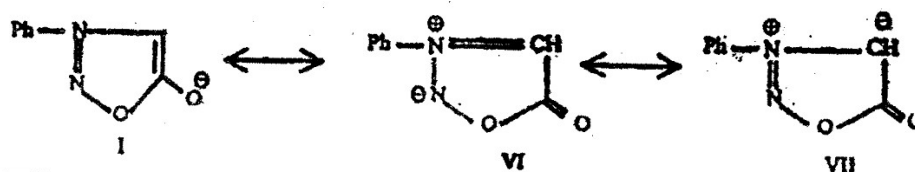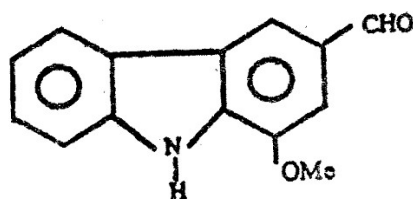
Such a hybrid molecule will be plannar, would not be optically active and accounts for the lack of reactivity of the ring towards electrophilic substitution.
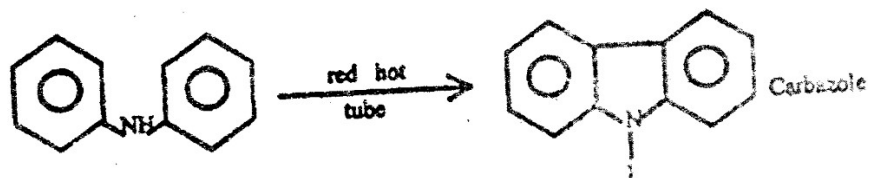
CARBAZOLE
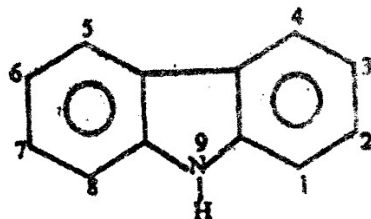
Introduction :

It occurs in coal – tar. Some occur as plant alkaloids. Example, 1 – methoxycarbazole - 3 – carboxaldehyde.
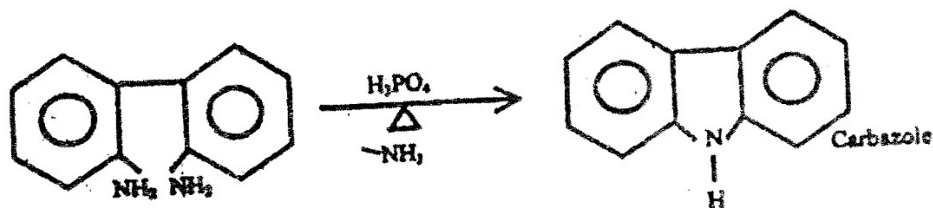

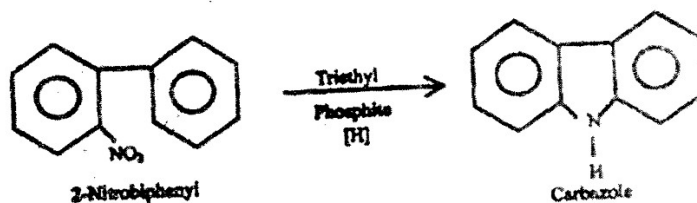Some carbazole derivatives are used as dyestuffs, and N- vinylcarbazole is manufactured as a monomer for plastics.

1. Carbazole is prepared by passing diphenylamine through a red hot tube.

2. It can be prepared by heating 2,2' – diamino – diphenyl with phosphoric acid at 200^0C.

3. It can be prepared by the reduction of 2 – nitrobiphenyl with triethylphosphite.

4. Carbazole is prepared by the decomposition of 1 – phenylbenzotriazole, obtained by the diazotization of 2 – aminodiphenylamine.
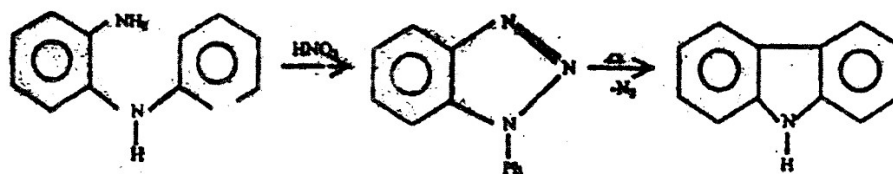
Properties

Electrophilic substitution predominantly takes place at the 3 – position, para to the nitrogen atom. Some residual aromatic character in the five membered ring is indicated by the fact that it is a much weaker base than its acyclic analog, diphenylamine. Carbazole is insoluble in dilute mineral acids. Like pyrrole and indole, carbazole forms alkali metal salts and can be alkylated and a acylated at nitrogen in the presence of bases.

Dicarbazyl
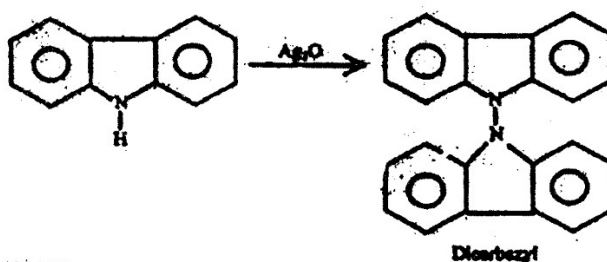
Imidazole : (Iminazole, Glyoxaline)

This is isomeric with pyrazole, and occurs in the purine nucleus and in the amino – acid histidine. Histidine residues are found at the active sites of ribonuclease and of several other enzymes.

4– amino – imidazole – 5 – carboxamide occurs naturally as a riboside. Drugs like metronidazole are active against intestinal infections. Clotrimazole – a broad spectrum antifungal agent.

Preparation

1. It can be prepared by the action of ammonia on glyoxal
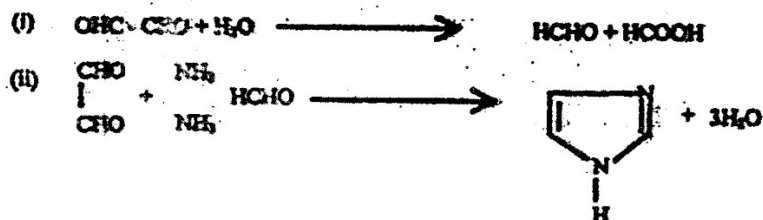
2. By the reaction between an α - dicarbonyl compound, ammonia and formaldehyde, imidazole can be prepared.
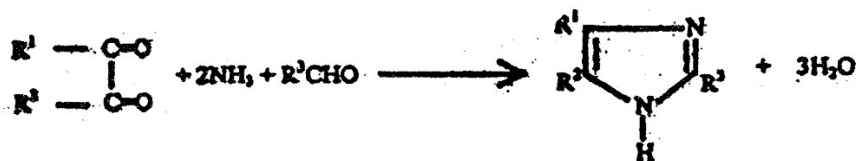
3. imidazole can be prepared by the action of ammonia on a mixture of formaldehyde and tartaric acid dinitrate. The resulting dicarboxylic acid is then heated with quinoline – copper to get imidazole
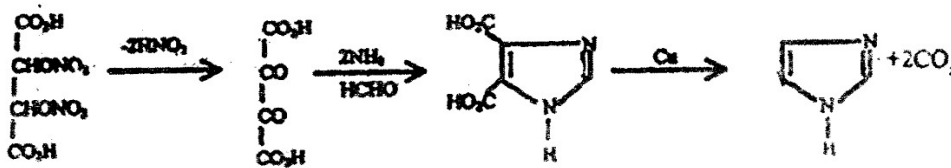
4. By the reaction between α bromoketone and an amidine, imidazole can be prepared.
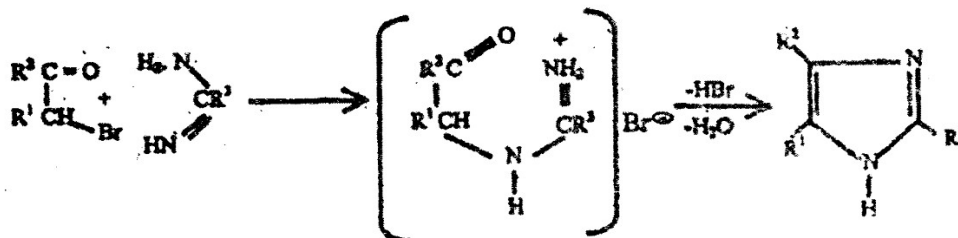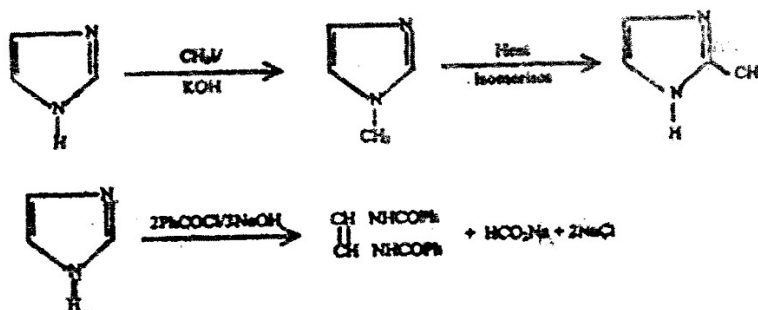

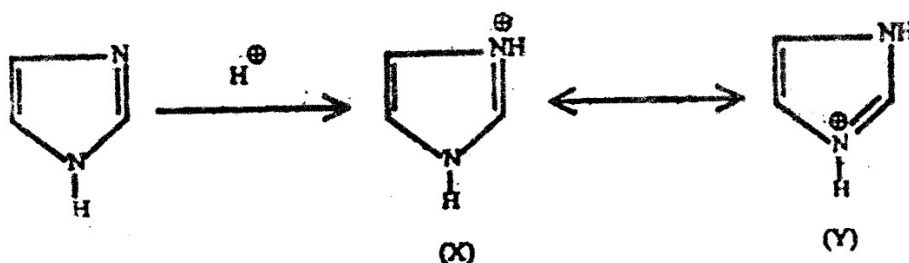A general meth for the preparation of imidazoles is the cyclisation of - acylaminoketones.
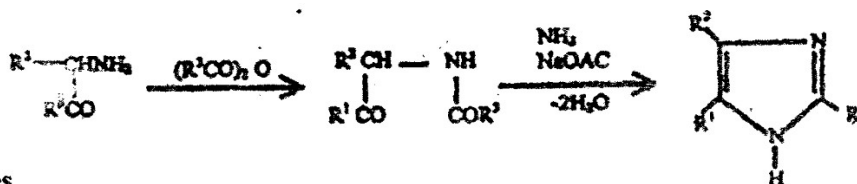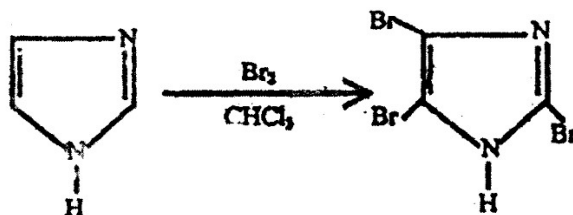

Properties

Imidazole is a weak base, but it is more basic than pyrazole.

3 itration and sulphonation of imidazole produce the 4(5) – derivative. In these reactions the substrate the symmetrical conjugate acid of imidazole.

(X)   (Y)

4. With bromine, imidazole forms 2, 4, 5 – tribromoimidazole.

5. Imidazole undergoes nucleophilioc addition to the dienophiles to give a N_3 – quaternary salt. This then cyclises by nucleophilic addition at C_2.
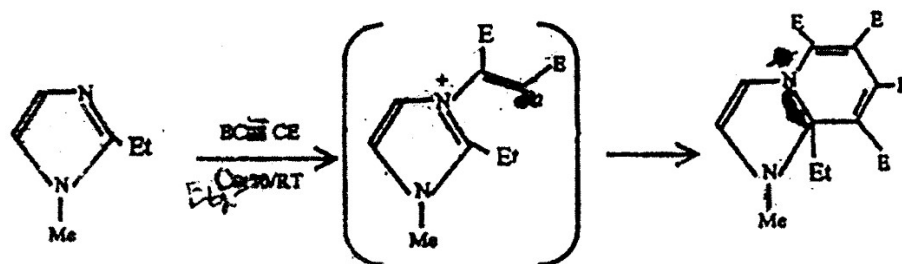

FLAVONES, CYANIN AND QUERCETIN

Introduction

According to Geissman etal all these compounds are called as Flavanoids. This is because the structure of these compounds are based on flavone (2-phenyl – 4 – chromone. Cyanin is an anthocyanin (they are the natural plant pigments) and on the basis of Geissman's classification is one group of flavanoid compounds.

Anthocyanins

They are natural plant pigments; they are glycosides and their aglycons, ie., sugar free pigments are known as the anthocyanidins. The anthocyanins, which are water – soluble pigments, generally occur in the aqueous cell – sap, and are responsible for the large variety of colours in flowers, red – violet – blue. The anthocyanin pigments are amphoteric; their acid salts are usually red, their metallic salts usually blue and in natural solution the anthocyanins are violet. The fundamental nucleus in antocyanidins is benzopyrylium chloride, but the parent compound is, 2 – phenylbenzopyrylium chloride. Example, cyanin chloride.
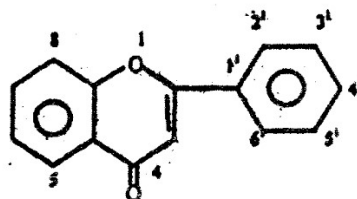

Benzopyrylium
chloride
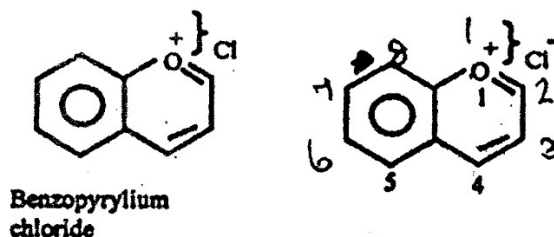
Cyanin Chloride

This is the first anthocyanin to be isolated and its structure determined. The aglycon part of this anthocyanin is cyanidin chloride. It is the 3,3' 4'5,7 – pentahydrxyflavylium chloride. This is present in crimson to blue – red flowers. Examples, deep red dahlia, red roses, blue corn flower etc.,

Chromone

Flavone

Flavone

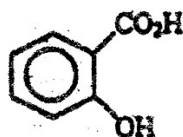This occurs naturally as 'dust' on flowers, leaves etc.

Structure Elucidation

1. On the bais of analytical data and molecular weight determination, the molecular formula of flavones has been found to be $C_{15}H_{15}O_2$.

2. Flavone does not form an acetyl derivative with acetylating agent, suggesting the absence of free hydroxyl group in flavone.

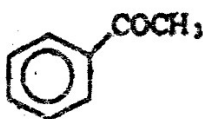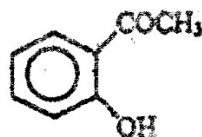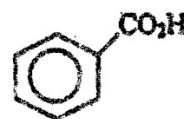3. On fusion with potassium hydroxide, it yields phenol and benzoic acid.

$$C_{15}G_{10}O_2 \rightarrow Phenol + Benzoic\ acid$$
<center>Flavone Fusion</center>

4. On boiling with alcoholic potassium hydroxide, it yield a mixture of four compounds. Salicylic acid (B), acetophenone (C), o – hydroxyacetophenone (D)and benzoic acid (E).
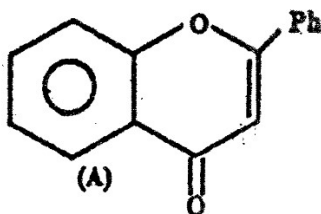

Salicylic Acid (B)   Acetophenone (C)   o-Hydroxyaceto phenone(D)   Benzoic Acid (E)

This formation of these products can be explained if we assume the correct structure of flavones to be (A).


(A)

The formation of these products may be explained, first by the opening of the pyrone ring of flavone to produce o – hydroxydibenzoylmethane (X). The latter then undergoes cleavage in two different ways to give the above said products.

The correct position namely, 5 is ascertained by a synthesis of cyanin chloride, the glucose unit at position 3 is lost during this degradation. So the structure of cycinin chloride should be

G = Glucose unit
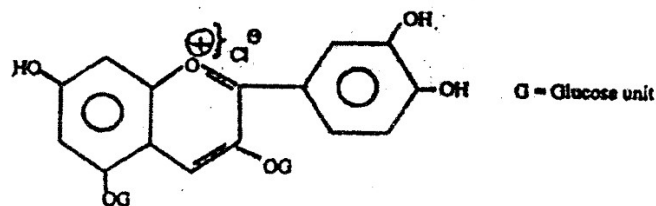
Based on this structure, the above reactions may be formulated as follows :


Cyanin Chloride
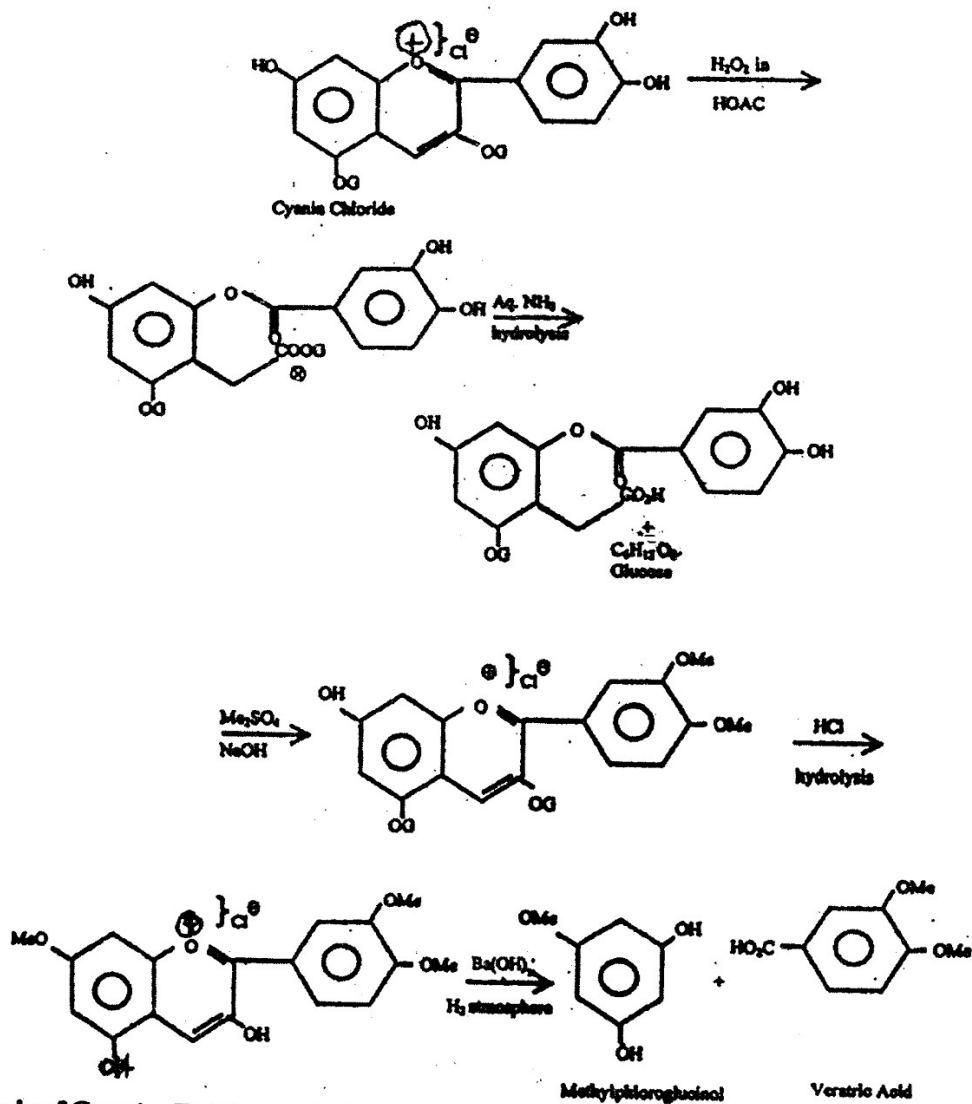
Synthesis of Cyanin (Robinson Etal):

Phloroglucinaldehyde (A) on condensation with tetra – acetyl - π - bromoglucose (B) in acetone solution added with aqueous potassium hydroxide, 2-00-tetracetyl - β - glucosidylphloroglucinadehyde (C) is obtained.

Compound (B) on condensation with ω – hydroxyl – 3,4 – diacetoxy acetophenone (D) in benzene solution gives – ω – o – tetra – acetyl - β - glucosidoxy – 3,4 – discetoxyacetophenone (B). when compounds (C) & (E) are dissolvedi n ethylacetate and the solution saturated with hydrogen chloride, compound (F) is obtained. The latter on treatment with cold aqueous potassium hydroxide followed by treatment with hydrochloric acid gives cyanin chloride.
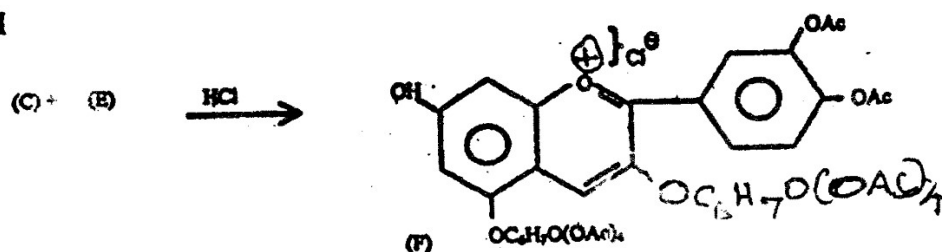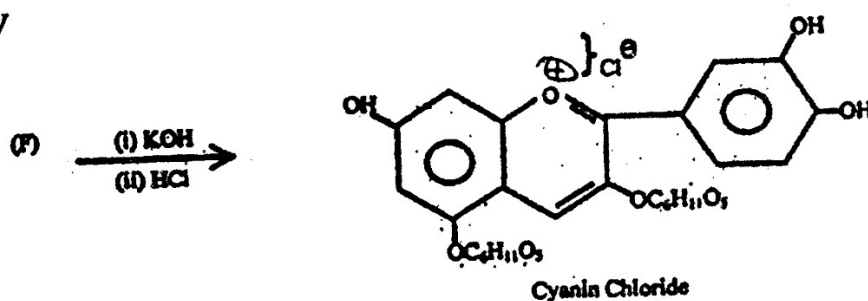
Step I
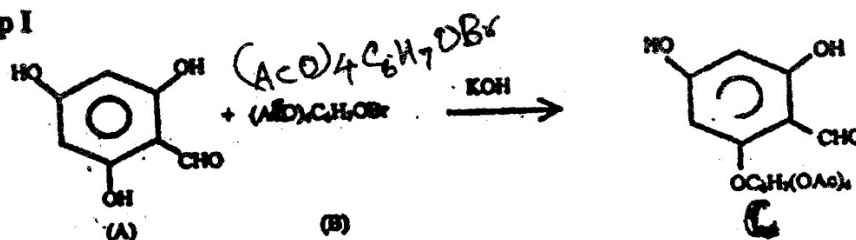
Step II

Step III

Step IV

Cyanin Chloride
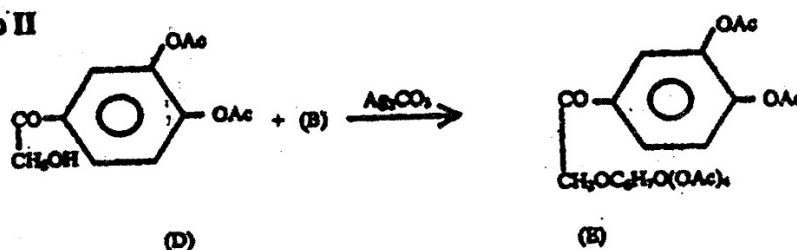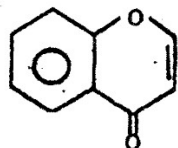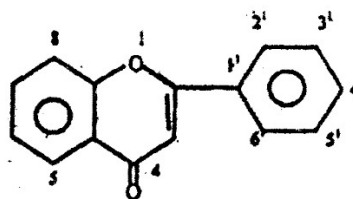
Introduction

The flavones, which are also known as the anthoxanthins, are yellow pigments which occur in the plant kingdom. Flavones occur naturally in the free state, or as glycosides. The aglycon is called as anthoxanthidin, mostly glucose is present as the sugar part. The flavones are the hydroxylated derivatives of flavone (2-phenyl-4-chromon).
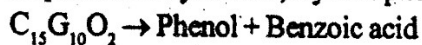
Chromone   Flavone

Flavone

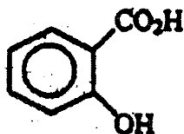This occurs naturally as 'dust' on flowers, leaves etc.

Structure Elucidation

1. On the bais of analytical data and molecular weight determination, the molecular formula of flavones has been found to be $C_{15}H_{15}O_2$.

2. Flavone does not form an acetyl derivative with acetylating agent, suggesting the absence of free hydroxyl group in flavone.

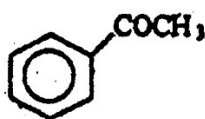3. On fusion with potassium hydroxide, it yields phenol and benzoic acid.

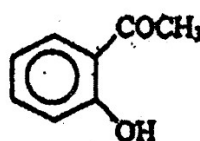$$C_{15}G_{10}O_2 \rightarrow \text{Phenol} + \text{Benzoic acid}$$

Flavone Fusion

4. On boiling with alcoholic potassium hydroxide, it yield a mixture of four compounds. Salicylic acid (B), acetophenone (C), o – hydroxyacetophenone (D)and benzoic acid (E).
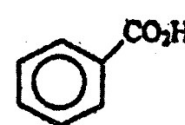

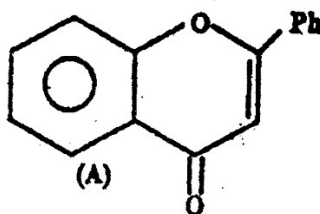Salicylic Acid (B)   Acetophenone (C)   o-Hydroxyaceto phenone(D)   Benzoic Acid (E)

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