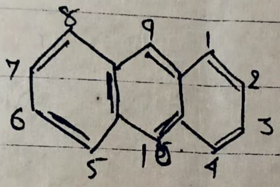
Anthracene -

Extraction from Coal tar → Anthracene occurs in Coal tar (less than 1%.) and is obtained from green oil fraction (b.p. 270°c - 360°c). On cooling this fraction Crude anthracene crystalized out. Crude anthracene contains Phenathreene and Carbazone as impurities.

It is purified by washing it with solvent naphtha (to remove Phenanthrene) and Pyridine (to remove Carbazole). Finally the solid is sublimated to give pure anthracene.

In naming derivatives of anthracene, the numbering system shown below is used.



Classical Structure of anthracene →

(i) It has a molecular formula $C_{14}H_{10}$

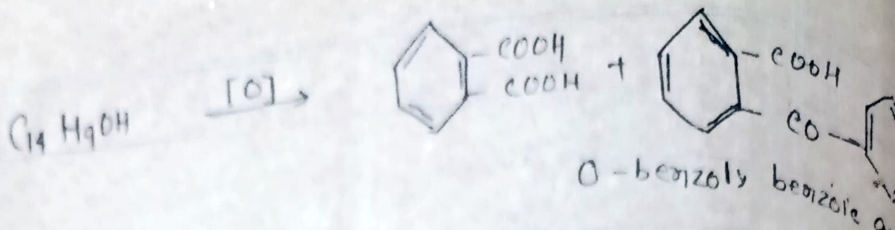
(2) It undergoes the typical aromatic substitution reaction like Sulphonation, nitration, halogenation etc. It shows the aromatic character of anthracene.

(3) Bromination of anthracene gives bromo anthracene, which on fusion with KOH gives hydroxy anthracene.

$$C_{14}H_{10} \xrightarrow{Br_2} C_{14}H_9Br \xrightarrow{KOH} C_{14}H_9OH$$

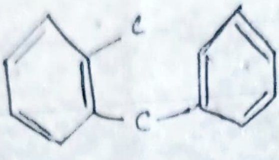
Hydroxy anthracene ($C_{14}H_9$-OH)

On vigrous oxidation gives Phthalic acid and a small amount of o-benzoyl benzoic acid.



O-benzoly benzoic a

This suggests that anthracene contains at least two benzene rings and that its skeleton is as shown.



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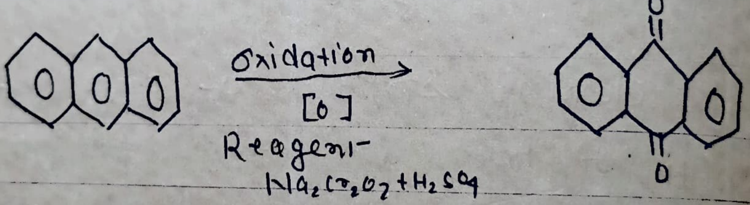
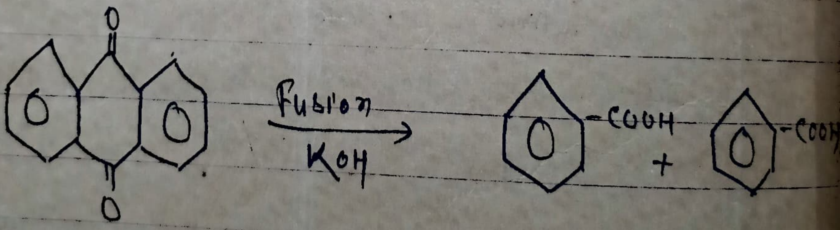
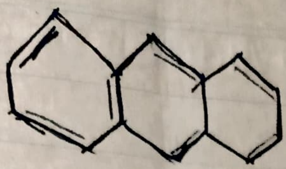
The presence of two benzene ring is confirmed by the fact that on fusion with KOH at 250°c, anthraquinone (which may be obtained from anthracene by direct oxidation) gives two molecules of benzoic acid





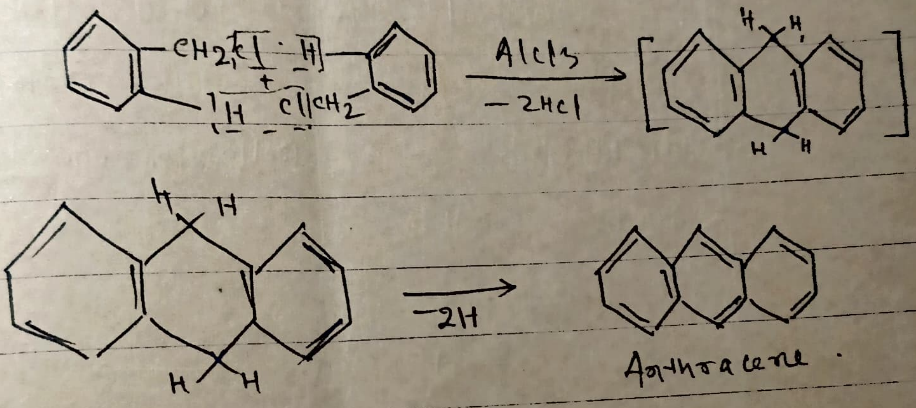
The above reaction confirmed the presence of two benzene rings in anthrac

In skelton I. there are 14 C-atoms. Now, to fit 16 H atoms and to retain the quadrivalency of C-atoms, the middle ring shoud be closed. On taking these facts into consideration following Stru

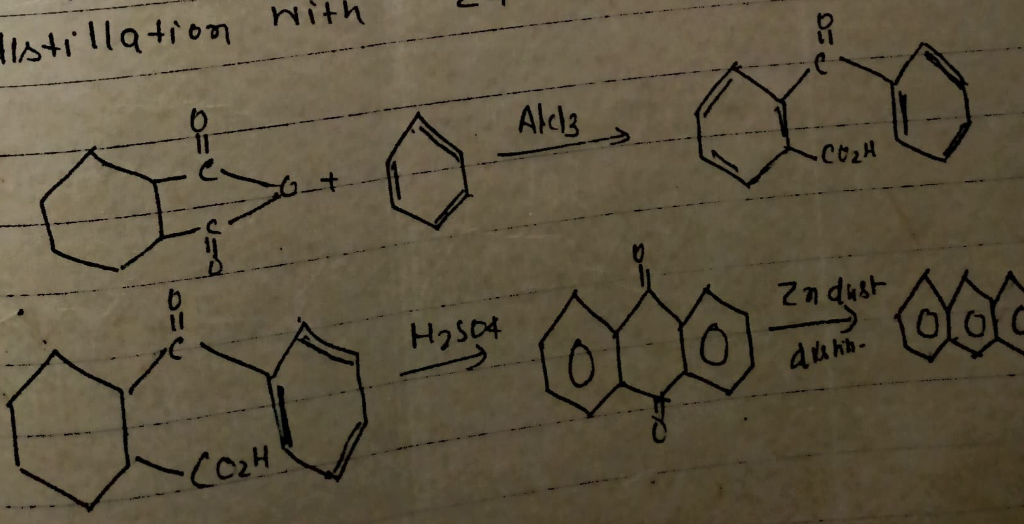


Above Structure has been confirmed by following Synthesis →

(1) By Friedel-Craft reactions → Benzyl chloride reacts with it self to form 9,10-dihydroanthracene which readily loses two H-atoms to yield anthracene.

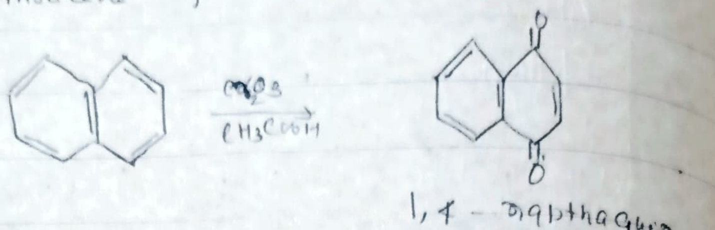


(2) Haworth Synthesis → When Phthalic anhydride in benzene Solution is treated with Alcl3, O-benzoyl Benzoic acid is formed. 3hrs on heating with Conc. H_2SO_4. at 100°c forms 9,10-anthraquinone, which on distillation with Zn dust gives anthracene



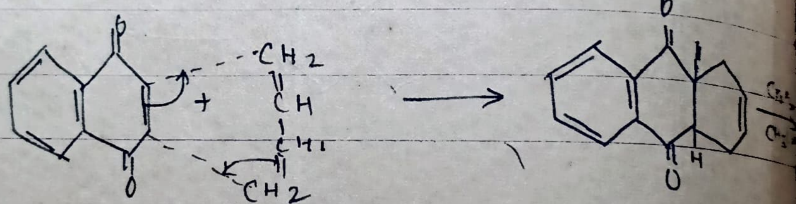
(B) By Diels Alder reaction →

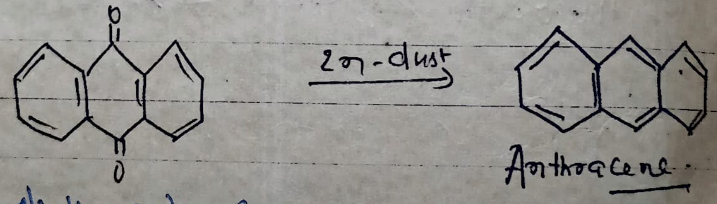
This reaction is used in synthesising anthracene from napthalene.



1,4 - napthaquinone

1,4 - napthaquinone undergoes Diel - Alder - rea with 1,3 - butadiene. The product of this rea is oxidised with Cr_2O_3 in glacial acetic acid to form, 9,10 - anthraquinone, Distillation of anthraquinone With Zn - dust yields anthracene.



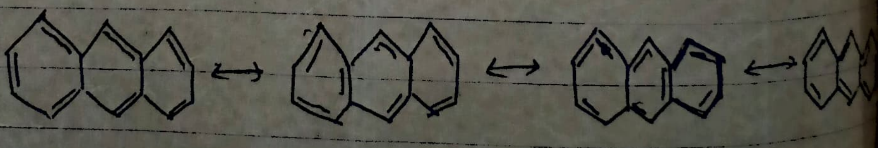


Anthraquinone.

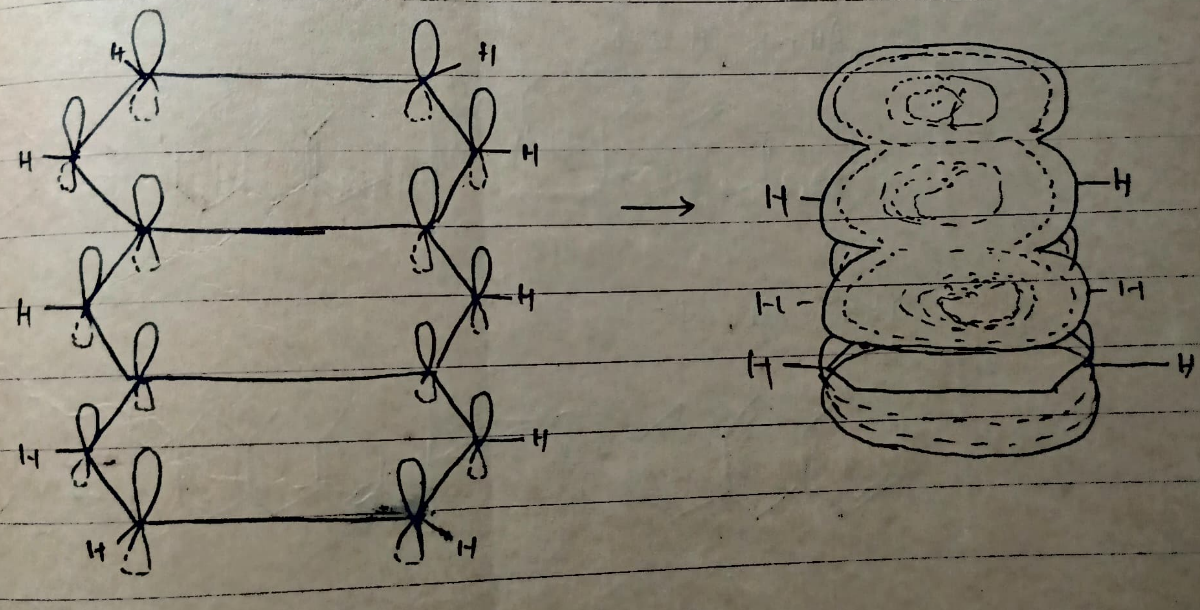
Anthracene.

Resonance hybride Structure →

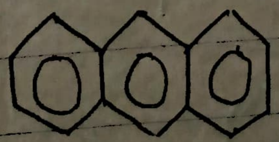
According to resonance theory anthracene is Considered to be the resonance hybride of the following four Canonical forms.



The sp^2 hybride orbitals overlap with each-other and with S- orbitals of the ten H-atoms forming C-C and C-H σ bonds. Since the bonds result from the overlap of trigonal sp^2 orbitals so all the σ-bonds are in one plane. Each C-atom in anthracene possesses an unhybridised P-orbital perpendicular to the plane of σ-bonds, the lateral overlap of these p-orbitals produces a π. M.O. containing 14 electrons one half [illegible] half- of this π. M.O. lies above the plane of bonds and other half lies below the plane of σ bonds.



Now adays Anthracene is represented as.

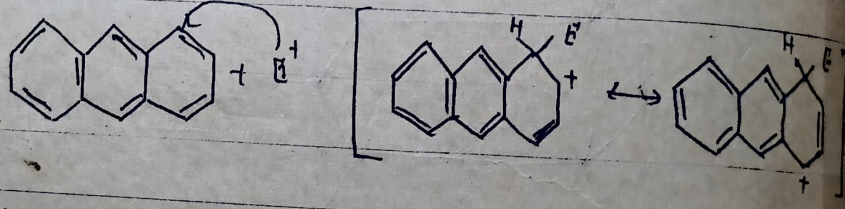


Properties of anthracene → Anthracene is colourless solid. It melts at 218°C and boils at 340°C. It is insoluble in water but dissolves in benzene. It shows a strong fluorescence when exposed to u.v.-light.

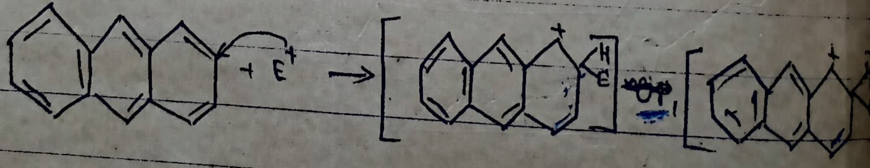
Chemical Properties →

Anthracene undergoes addition and electrophilic substitution reactions. These reactions preferentially occurs at C-9 and C-10 -Positions. This can be understand if we examine the intermediate carbonium ion obtained from attack at C-1, C-2 and C-9. E^+ in the following equations represent an electrophile.

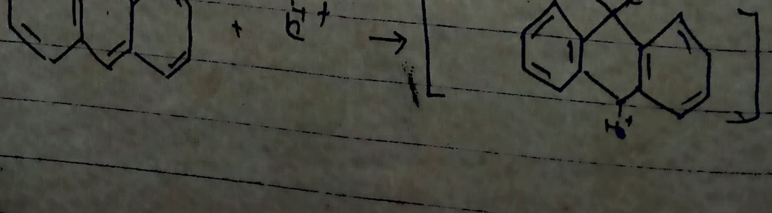
Attack at C-1



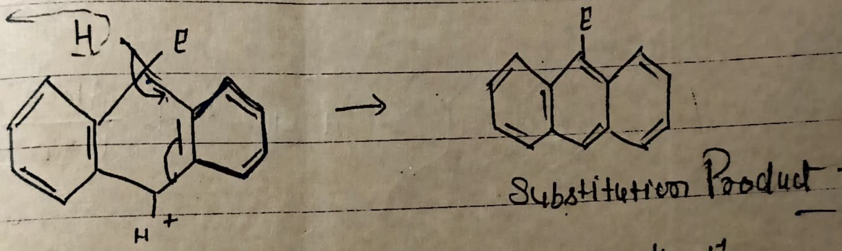
attack at C-2

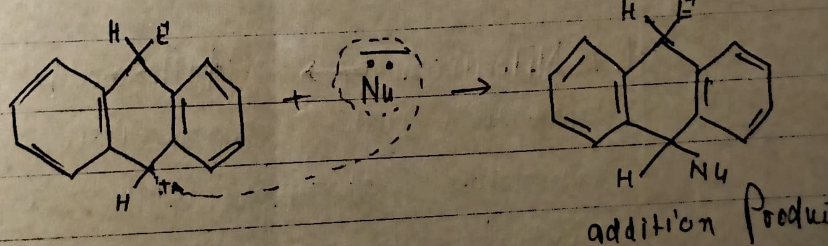


attack at C-9



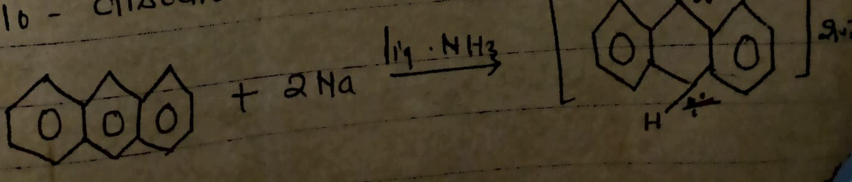
attack at-C-9 → attack at C9 - yields a carbonium ion in which two benzene rings are retained. where as attack at- C-1 or C-2 yields an intermediate in which a napthalene system is retained. The former intermediate is more stable and its formation favoured because resonance energy (2×36=72 K.cal) of two Benzene rings exceeds that of napthalene (61K.cal). This carbonium ion can lose a proton to give the corresponding substitution product, or it can react with a nucleophile to form 9-10 addition product.



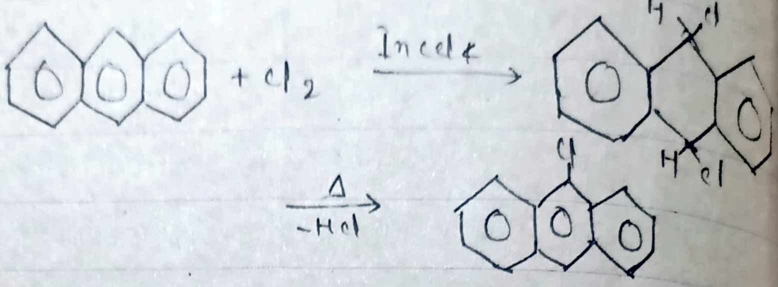


The main chemical Properties of anthracene are described below :->

(i) Reaction with Sodium → Anthracene reacts with metallic sodium in liquid ammonia to form a deep blue solution of 9,10 - disodio anthracene.

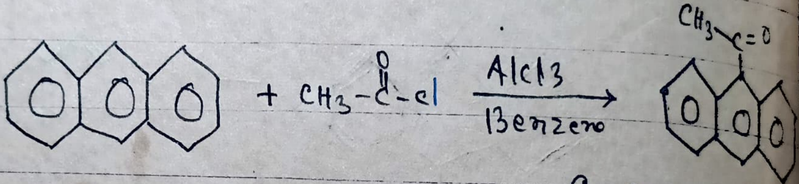


(2) Reaction with halogens → Anthracene reacts with Cl_2 in CCl_4 at room temp. to give 9,10 - dichloro - 9,10 - dihydroxy anthracene. On heating this addition product, is less a molecule of HCl forming 9 - chloro anthracene.



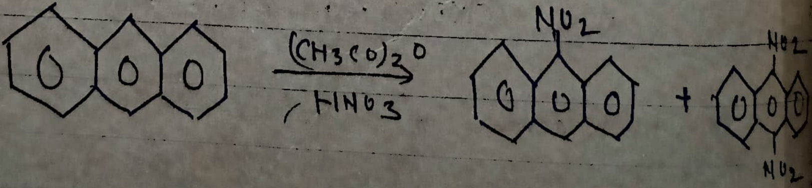
9 - chloroanthracene.

(3) Friedel - Craft - acylation →



9 - acetylanthracene

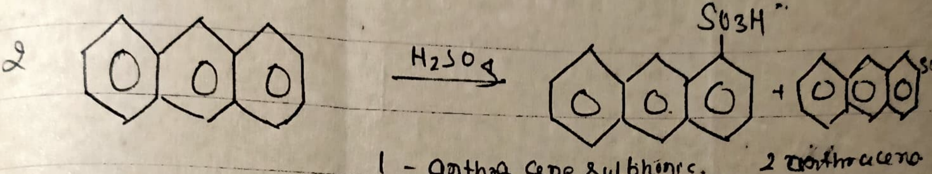
(4) Nitration → Anthracene undergoes nitration with Conc. HNO_3 in acetic anhydride at room temp. to yield a mixture of 9 - anthracene and 9,10 - dinitro anthracene.



The usual nitrating mixture (HNO_3 + H_2SO_4) is not used because it leads to the formation of 9,10 - anthaquinone by oxidation.

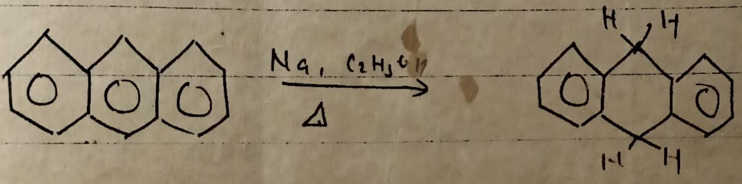
(5) **Sulphonation** → Anthracene undergoes sulphonation with Conc. H_2SO_4 to yield a mixture of 1-anthracene sulphonic acid. and 2-anthracenesulphonic acid.

At a lower temperature former is the major product and at a higher temperature later is the Major Product.

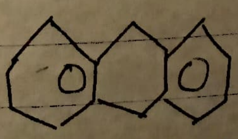


1-anthracene sulphonic acid, 2 anthracene sulphonic acid.

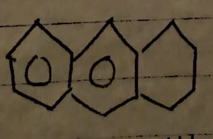
Reduction → Anthracene undergoes reduction with sodium and ethyl alcohol to form 9,-10-dihydro anthracene.



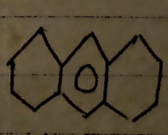
Catlytic reduction using nickel at 225° c first gives 9-10-dihydro anthacene. and on ~~Cooling~~ continued hydrogenation this is converted into 1,2,3,4-tetra hydroanthracene. and 1,2,3,4,5,6,7,8 — Octa hydro anthracene.



9-10. dihydro anthracene,



1,2,3,4-dihydro anthraca



1,2,3,4,5,6,7,8 -octahydro anthracene.

Oxidation → Anthracen undergoes Oxidation with ($Na_2Cr_2O_7 + H_2SO_4$) to form, 9-10-anthraquinone. other Oxidising agent like HNO_3 air in V_2O_5 also led to formation of 9-10-anthraquinone —