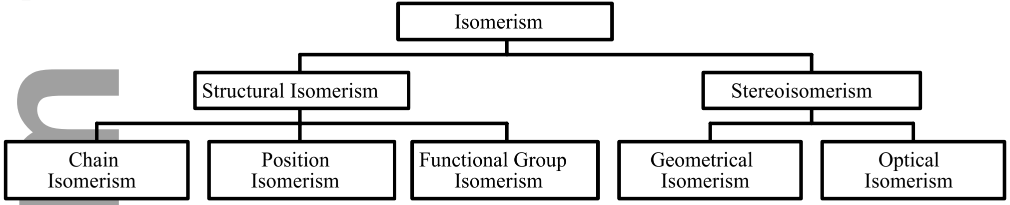
Test Covers: Isomerism, Benzene and Haloalkanes

Isomerism

Pp. 871-75, 930-32, 939-41, 968-71



- **Isomers:** Are two or more compounds having the same formulas but different structures and therefore different chemical/physical properties.
- **Ligands:** The groups that are coordinated (bonded) to the central atom in a complex.
- **Structural Isomerism:** Differ in basic structure or bond type. (Connectivity is different)
- **Stereo-Isomerism:** Differ because of the spatial arrangement (configurations) of the bonds. (Connectivity is the same)

Table 1: Structural Isomers

Chain Isomerism	Rearrangement of hydrocarbon chain.	As branching increases, b.pt. decreases as the van-der-wall's forces are weaker because of the smaller effective surface area.
Position Isomerism	1. Functional group has different position. 2. Functional group forms part of chain.	These isomers are chemically similar because they possess the same functional group.
Functional Group Isomerism	Atoms arranged to give different functional groups. Belong to different homologous series'.	Both physical and chemical properties are quite different. Alcohols isomeric with ethers. Aldehydes isomeric with ketones. Acids isomeric with esters.

Table 2: Stereo-Isomerism

Geometrical Isomerism	• If bond cannot rotate → Two spatial arrangements are possible. • Example C=C cannot rotate because it would involve breaking a π; Thus there are multiple isomers. • ***cis:*** like groups on one side • ***trans:*** if same groups on dif sides • There is a temperature above which geometric isomers can change from one to another (enough energy to break π bond).	***cis:*** more reactive, lower melting point, less stable, more soluble. Why? Because the large substituent groups have a greater separation from one another in the trans form and are thus less likely to interfere with one another than in the cis form. May be separated through fractional distillation or fractional crystallization. Ring strain in cycloalkanes (less than 5 Carbons) leads to less stability.
Optical Isomerism	• Optical Activity: Ability to rotate the plane of polarization of polarized light to right/left. • Detected with a polarimeter. • Dextrarotatory: Analyzer clockwise. • Lavorotatory: Analyzer anti-clockwise. • Amount of rotation depends on: compound, concentration, length of beam, solvent, temperature, wavelength. • Only in asymmetric molecules. • Chiral Centre: Asymmetric C-atom. • Enantiomers: Mirror-image	Enantiomers: • Same physical properties • Same chem. properties except to optically active reagents. Racemic Mixtures • Rotation of light zero; equal amounts of enantiomers (racemic mixture) • Normal methods of separation will not separate mixtures; identical physical properties. • Resolution of a racemic mixture: React with an optically active compound; products that are not enantiomers can be separated by usual methods (physical properties). Then the orignal enantiomers

		may be regenerated.

Further Organic Question

H1. Bromine can react with benzene by an electrophilic substitution mechanism

(a) Give the chemical equation for the formation of bromobenzene from benzene and bromine. [1]

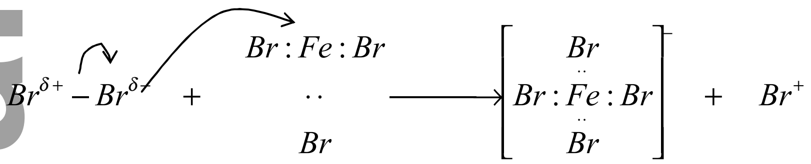
$Br_2 + C_6H_6 \longrightarrow C_6H_5Br + HBr$

(b) State the necessary conditions for this reaction to take place. [1]

A halogen carrier, either $FeBr_3$ or $AlCl_3$ must be present.

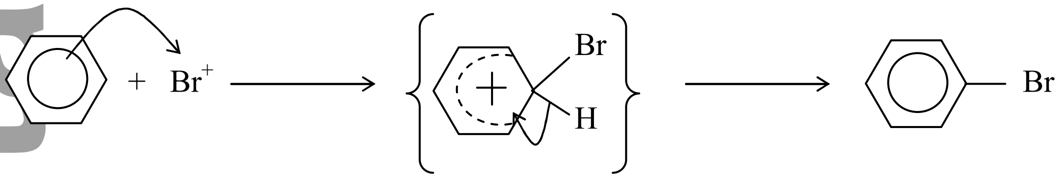
(c) Identify the species which acts as the electrophile and show how it is formed. [2]

Br_2 reacts with a halogen carrier (e.g. $FeBr_3$) to form a brominium ion (Br^+) and the anion $FeBr_4^-$. This process takes place because the Lewis acid $FeBr_3$ molecule induces a dipole in the Bromine molecule as it approaches. The Lewis acid then withdraws electrons from the bond between the bromine atoms in a heterolytic process. The negatively charged bromide ion bonds with the Lewis acid and the positively charged electrophilic brominium ion attacks the π - delocalized electron cloud in the benzene ring.



$$Br^{\delta+} - Br^{\delta-} + \begin{matrix} Br : Fe : Br \\ \cdot\cdot \\ Br \end{matrix} \longrightarrow \left[\begin{matrix} Br \\ Br : \overset{\cdot\cdot}{\underset{\cdot\cdot}{Fe}} : Br \\ Br \end{matrix} \right]^- + Br^+$$

(d) Give the mechanism for the reaction between bromine and benzene, clearing showing the structural formula of the organic intermediate formed. [2]

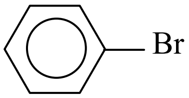


The electrophilic brominium ion attacks the electron cloud of the benzene ring, forcing the benzene ring to donate a pair of electron, forming a C-Br bond and leaving a positive charge on the carbon atom. The carbocation formed, often referred to as the Wheland intermediate, is resonance stabilized, but expels a proton (H^+) to regenerate the aromatic ring (the Brominium ion disrupted the aromatic character of benzene).

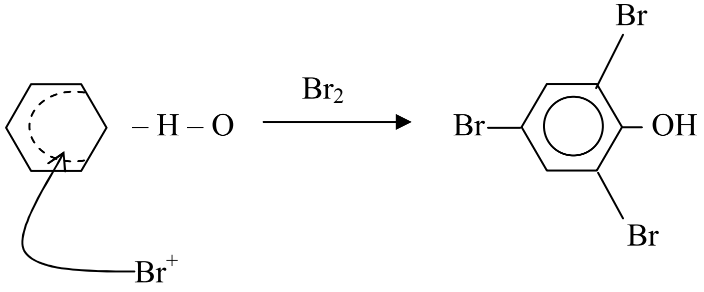
(e) Describe and explain how the reactivity of phenol with bromine compares with that of benzene and bromine. Your answer should include any difference in the reaction conditions and include the structural formula of the main product formed. [4]

The halogenation of phenol and benzene are very different processes. In the halogenation of benzene, the benzene ring will be attacked by an electrophilic halogenium. The reaction of $C_6H_6 + Br_2$ is difficult, as it requires the presence of a halogen carrier (i.e. a Lewis acid) such as $AlCl_3$ or $FeCl_3$ in order to form a more substituted product – bromobenzene. Conversely, the halogenation of a phenol is very easy, taking place at room temperature – forming the product 2,4,6-tribromophenol – because the O-atom of the –OH on phenol activates the C_6H_6 ring by the conjugative effect. The rate of reaction may then be increased with an electrophile such as Br_2.

Benzene and Bromine: The reaction takes place as delineated in part d.



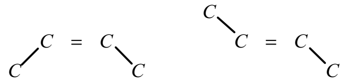
Phenol and Bromine: An electrophilic attack facilitated by the C_6H_6 ring is activated by the conjugation of the lone pair of electrons on the O-atom into the $\pi-$electron cloud of the ring. 2,4,6-tribromophenol immediately appears as a white precipitate at room temperature.



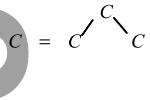
H2.

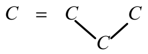
(a) Explain why but-2-ene can exist as two geometric isomers whereas but-1-ene cannot. [2]

But-2-ene can exist as two geometric isomers because of the position of its double bond:



Namely, cis-2-butene and trans-2-butene can be formed. This is due to the fact that the π-bond in the but-2-ene double bond restricts rotation between the 2nd and 3rd carbon atoms. In contrast, but-1-ene does not have any isomers, as the molecule may simple be rotated to give, what might have been considered, its isomer.





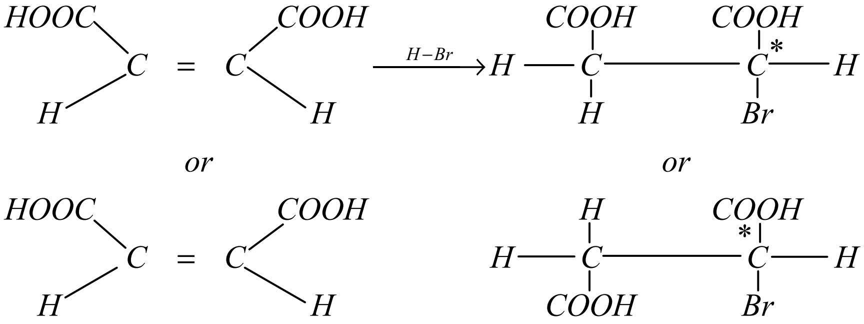
(b)

(i) When HBr is added to both of the geometric isomers of but-2-ene-1,4-dioic acid, HOOCCHBrCH$_2$COOH is produced. Give the structural formulas of the two stereoisomers of this product, showing clearly how the structures differ. [2]

i)

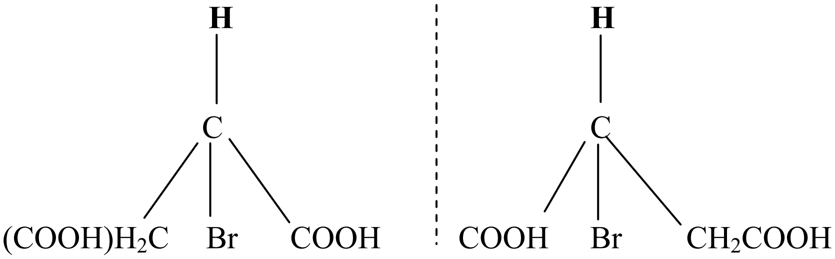
Left: trans-1,4-dioic acid
Right: cis-1,4-dioic acid

(ii) State the difference in the physical properties of these to stereoisomers and identify the features of these molecules which is responsible for this property. [2]



Note that Markovnikov's rule is not required since symmetrical molecule.

The difference in physical properties of these to stereoisomers is caused by the chiral centre carbon present (*) which causes optical activity.

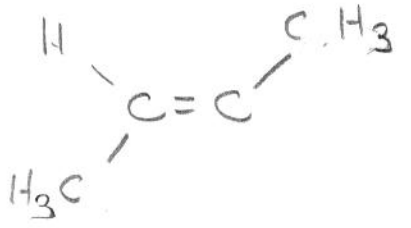


Physical properties identical except they will rotate plane polarized light equal in magnitude but opposite direction.
The feature that is responsible in these molecules is the chiral carbon center (i.e. → a c-atom attached to different groups of an asymmetric c-atom).

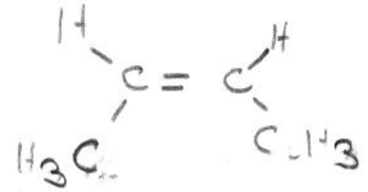
H1. This question is about isomers with the general formula C_nH_{2n}.

(a)

(i) Draw the structures of the two geometrical (cis/trans) isomers of C_4H_8, giving their full names. [3]

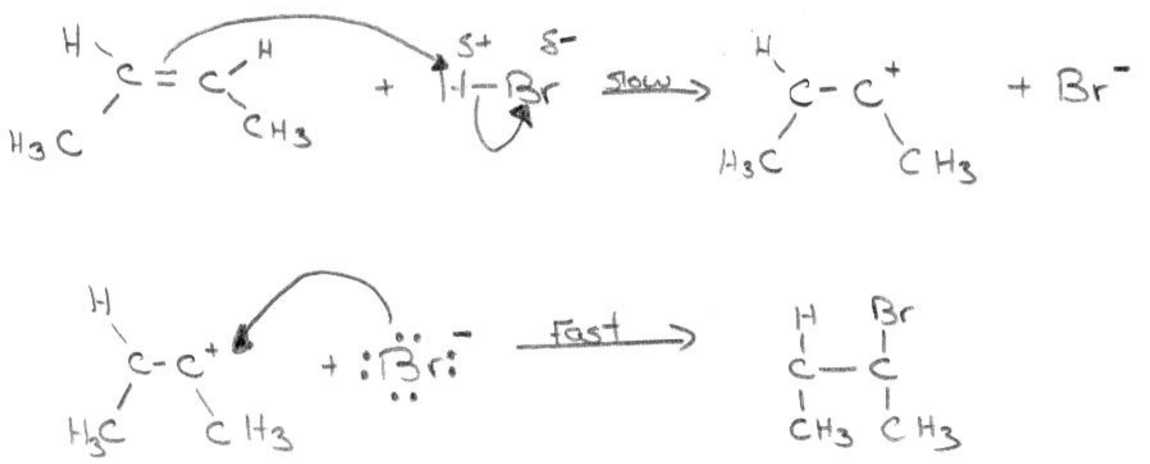


trens-but-2-ene



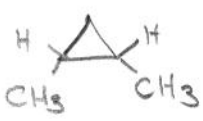
cis-but-2-ene

(ii) Write the mechanism for the reaction of the cis isomer of C_4H_8 with bromine (dissolved in a non-polar solvent). [2]

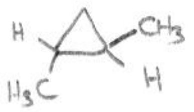


(b)

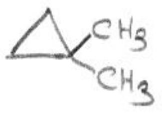
(i) There are four isomers with the formula C_5H_{10} which contain a three-membered carbon ring. Draw the isomers and label them A, B, C and D. [4]



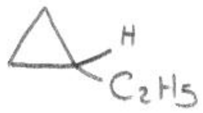
A



B



C



D

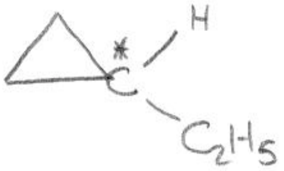
A: cis-1,2-dimethylcyclopropane.
B: trans-1,2-dimethylcyclopropane
C: 1,1-dimethylcyclopropane
D: 1-diethylcyclopropane

(ii) Indicate, by writing two letters (chosen from A, B, C and D) a pair of isomers that are structural isomers and a pair that are geometrical isomers. [2]

Geometric: A, B
Structural: C, D

(iii) From the four isomers A, B, C and D, draw the structure of an isomer that shows optical isomerism and mark the chiral centre with an asterick (*). [2]

D



(c) Use the examples from parts (a) and (b) to explain the existence of geometrical isomers.

Geometrical isomers exist as a result of a carbon-carbon double bond (C=C). Explicitly, the C=C bond does not allow free rotation because it would involved breaking a π bond (geometric isomerism). In C-C and C≡C bonds, this is not case, and the bond may rotate. Accordingly, when a C=C bond exists, each side of the C=C can vary in the sense that both A and B are possible. When a C-C exists, the bonds could rotate to produce either.

(d) Suggest a reason why compounds containing three-membered carbon rings are less stable than those containing four-membered rings.

Three-membered carbon rings are less stable than four-membered rings because of the resultant bond angles. If a ring contains three carbons, the bond angles are 60˚. If a ring contains four carbons, the bond angles are greater. Shrinking the bond angle places strain on the molecule, which diminishes its stability. Accordingly, a three-membered carbon ring with 60˚ bond angles is more strained and hence less stable than a four-membered carbon ring with 90˚ bond angles.