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University, Kanpur

**Answer Script Details**

**Barcode** 1246440

**Roll No.** 24063001034

**Exam** MASTER OF SCIENCE\_ODD EXAM-DEC-24

**Total Mark** 57/75.00

**Subject** B020702T - ORGANIC CHEMISTRY - I

**Question wise Mark Summary**

**Q.No Mark Q.No Mark Q.No Mark Q.No Mark**

1A 4/5

1B 4/5

1C 4/5

1D 4/5

1E 2/5

1F 4/5

1G 4/5

1H 4/5

1I 4/5

2 12/15

3 0/15

4 0/15

5 0/15

6 0/15

7 11/15

8 0/15

9 0/15



### INSTRUCTIONS TO THE CANDIDATE FOR FILLING PART-I

1. Read the instructions carefully given on the answer script and admit card.
2. Write Date of Exam, Shift, Paper Code & Name of Subject Correctly.
3. Write Name & Roll No. Correctly.
4. Write Semester & Branch Correctly.

### INSTRUCTIONS TO THE CANDIDATE FOR FILLING PART-III

1. Use blue or black ball point pen for writing alphabets & numerals in  Boxes.
2. Carefully study the example before you start marking.
3. As shown in the example below blacken the circles completely.



4. Make no Stray marks on this sheet.
5. **DO NOT WRITE OR MARK ON THE BAR CODE.**

### IN ORDER TO AVOID UFM (UNFAIR MEANS):

1. The Roll No. and Answer Book no. found elsewhere or any other symbol found in the answer book will be treated as unfair means.
2. Any tempering of Bar Code and Booklet no shall be treated as Unfair Means.
3. Do Not bring the materials like slip of paper/mobile/digital diaries/ study material/ revision notes in examination hall. Possession of the mobiles/ digital diaries/ electronic watch and any other electronic gadget except memory less scientific calculator shall be considered as UFM case.
4. Do not keep or paste currency note in answer script it shall be consider as UFM.

### अनुचित साधन से बचने हेतु:

1. उत्तर पुस्तिका के निर्देशित स्थान को छोड़कर अनुक्रमिक एवं उत्तरपुस्तिका का क्रमांक कहीं और न लिखें तथा कोई भी किताब न बनायें क्योंकि यह अनुचित साधन प्रयोग की परिधि में आता है।
2. उत्तर पुस्तिका के शरकोक अथवा उत्तर पुस्तिका सख्या पर छेद करने पर अनुचित साधन प्रयोग माना जायेगा।
3. परीक्षा कक्ष में किम्ब वस्तुएं साथ न लायें, जैसे लिखे हुए कागज के टुकड़े, मोबाइल, डिजिटल कायरी, कोपी, पुस्तक वह सभी वस्तुएं जो अनुचित साधन के अन्तर्गत आती हैं। केवल संबंधित प्रश्नपत्र में ही मेमोरी लेस साइटफिक कैल्कुलेटर ले जाने की अनुमति होगी।
4. उत्तर पुस्तिकाओं में रूपरे न रखें न ही उत्तर पुस्तिका में किताबरी। ऐसा करना अनुचित साधन प्रयोग की परिधि में आता है।

### परीक्षार्थी के लिए निर्देश

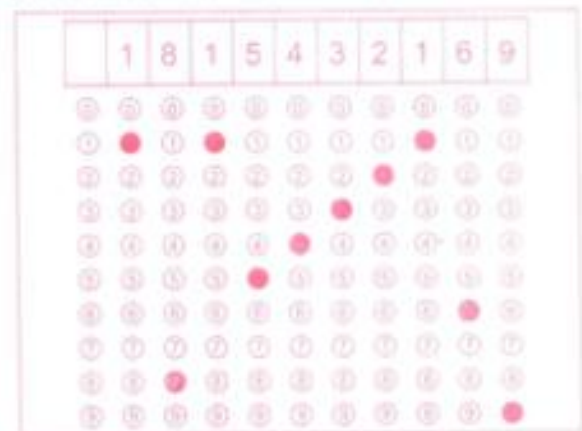
1. प्रवेश पत्र एवं उत्तर पुस्तिका पर दिये गये निर्देशों को ध्यान से पढ़ें।
2. कवर पृष्ठ के दूसरी तरफ कुछ न लिखें।
3. उत्तर पुस्तिका के पृष्ठों पर दामो तरफ लिखें।
4. प्रश्न पत्र पर अपने अनुक्रमांक को अतिरिक्त कुछ न लिखें।
5. प्रश्न पत्र कोड एवं प्रश्न पत्र कोड सावधानी पूर्वक लिखें।
6. अपनी स्थिति स्पष्ट लिखें।
7. उत्तर पुस्तिका के पृष्ठों की संख्या देखें। अगर उत्तर पुस्तिका में पृष्ठ (1-24) से कम है या कटे हुए हैं, तो परीक्षा शुरू होने के पूर्व दूसरी उत्तर पुस्तिका ल लें।
8. प्रश्नपत्र को देखें, यदि प्रश्नपत्र में विषय कोड, विषय का नाम तथा प्रश्न में कोई त्रुटि है तो उत्तर परीक्षा शुरू होने के 30 मिनट के अन्दर क निरीक्षक को तत्काल सूचित करें, उसके बाद विश्वविद्यालय द्वारा क कार्यवाही नहीं की जायेगी।
9. प्रश्नों के उत्तर लिखने के लिये पैसिल का प्रयोग न करें।
10. **किसी भी अतिरिक्त माफ नहीं दिया जायेगा।**

### INSTRUCTIONS TO THE CANDIDATE

1. Read the instructions carefully given on the Question Paper, Admit Card & Answer Script.
2. Do not write anything on back side of the cover page.
3. Write on both sides of pages of answer book.
4. Do not write anything on question paper except Roll Number.
5. Write Paper Code & Question Paper Id carefully.
6. CHECK the number of pages (1-32) or any other kind of damage in your answer script, if found than change the answer scri immediately before the commencement of examination.
7. CHECK the Question Paper for any kind of discrepancy e.g. Subject Code, Subject Name and Question of the Question Paper during first THIRTY MINUTES of the commencement of the exam, so that it can be corrected in TIME. After that no corrections shall be entertained by the university.
8. Do not use pencil for answering the question.
9. Write status correctly e.g. those appearing in carry over paper should fill in status as Carry Over. Those appearing as E Students should fill in status as ex.
10. No supplementary answer book & graph paper will be provided.

### INSTRUCTIONS TO THE CANDIDATE FOR FILLING PART-IV

1. Use blue or black ball point pen for writing alphabets & numerals in  Boxes.
2. Use blue or black ball point pen for filling the circles.



Note - if your Roll No. is of 10 digits. Please leave first three columns

Section-C

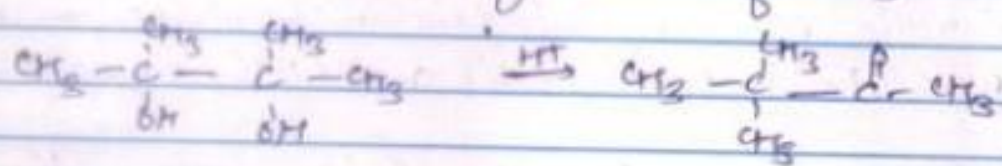
2. Rearrangement reactions the molecules undergo a structural rearrangement, often involving a shift of atoms or groups within a molecule, to form a new product. These reactions often occur via intermediates, such as carbocations, radicals and so on.

Types of rearrangement reaction are as follows:-

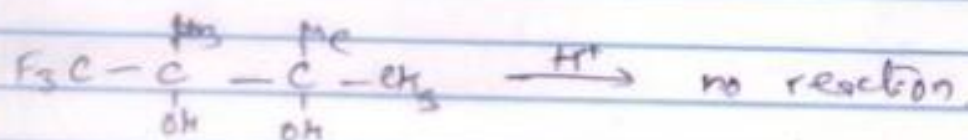
- Sigmatropic rearrangement.
- Electrocyclic rearrangement.
- Pericyclic rearrangement.
- Conventional rearrangement.

Pinacol-pinacolone rearrangement:-

Pinacols are ditertiary 1,2-diols. The simplest member is  $\text{Me}_2\text{C}(\text{OH})\cdot\text{C}(\text{OH})\text{Me}_2$ . When this is treated with dilute or concentrated  $\text{H}_2\text{SO}_4$ , a rearrangement reaction takes place which leads to the formation of  $\text{Me}_2\text{C}-\text{CO}-\text{Me}$  (pinacolone).



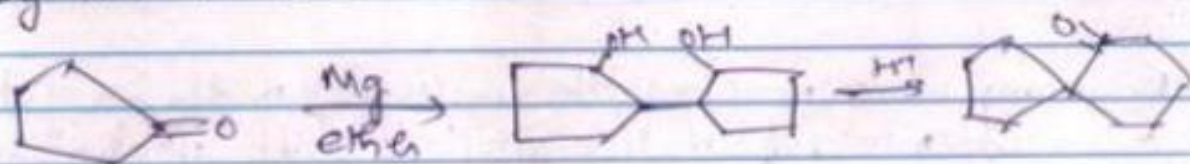
1,2-diols containing substituents with strong -I effect do not undergo the pinacol-pinacolone rearrangement reaction.



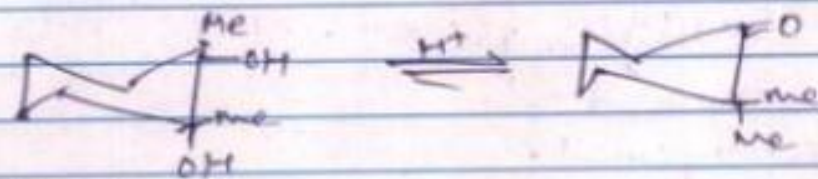
Spiroenes and their derivatives can be easily prepared



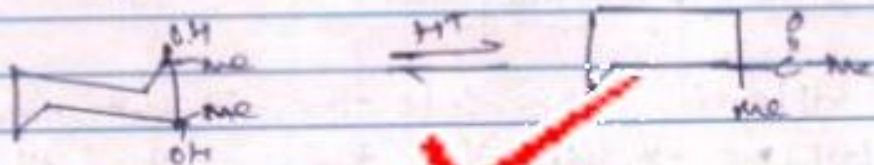
by this reaction.



It has been found that - In the alicyclic system that a group trans to the leaving group usually migrates in pinacol-rearrangement reaction.



(cis-form)



(trans-form)

In sigmatropic rearrangement reaction the rearrangement takes place in  $[1,3]$ ,  $[5,5]$  and  $[3,3]$  rearrangement position.

When the rearrangement takes place in  $[1,3]$  position through the substitution of one group with other the result formation of product in  $[1,3]$  position.



### Section-B.

2. The theory is based on their polarizability, charge density, and the type of interactions they prefer.

#### Hard and Soft Nucleophiles:

- Have high charge density (small and compact size).
- Low polarizability (difficult to distort electron cloud).
- Tend to react with hard electrophiles (ionic or electrostatic interactions dominate).

E.g.  $\text{OH}^-$ ,  $\text{NH}_3$ ,  $\text{F}^-$ ,  $\text{RO}^-$

#### Soft Nucleophiles:

- Have low charge density (large more diffuse).
- High polarizability (easier to distort electron cloud).
- Tend to react with soft electrophiles (covalent interactions dominate).

E.g.  $\text{I}^-$ ,  $\text{RS}^-$ ,  $\text{CN}^-$ ,  $\text{C}=\text{C}$

#### Hard and Soft Electrophiles

Electrophiles are electron deficient species that accept electrons to form a bond.

#### Hard Electrophiles:

- Small and have high positive charge density.



- Low polarizability.
- Prefer ionic or electrostatic interactions.

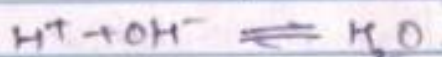
E.g.  $\text{H}^+$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ .

### Soft Electrophiles

- Large, with low positive charge.
- High polarizability.
- Prefer covalent bonding  with soft nucleophiles.

E.g.  $\text{Hg}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{I}_2$ .

- Hard and hard interactions - strong and stable due to ionic character.
- E.g.  $\text{OH}^-$  reacting with  $\text{H}^+$



- Soft-soft interactions - strong and stable due to covalent character.

E.g.  $\text{RS}^-$  reacting with  $\text{CH}_3\text{I}$ .

### Applications of HSAB:

1. Reaction Prediction - helps in predicting with nucleophile will attack which electrophile.
2. Selectivity in organic reactions - soft electrophile will react with nucleophile like hard



electrophile will react with hard nucleophile.

2. Complex formation - It predicts which metal ion binds preferentially to specific ligands in coordination chemistry.

e.g.  $Cu^{2+}$  forms a stable complex with  $CN^-$ .

4. Solubility and Precipitation - It is used to understand the solubility of compounds. Hard-soft interactions lead to more insoluble compounds.

e.g.  $Mg^{2+}$  forms an insoluble salt with  $CO_3^{2-}$  i.e.  $MgCO_3$ .

5. Catalysts - It explains the catalysis of reactions with reactants in both homogeneous and heterogeneous catalysis.

6. Biological Chemistry - It explains metal ion selectivity in enzymes and biological systems.

e.g.  $Zn^{2+}$  binds to S-containing amino acids like cysteine in enzymes.

7. Environmental Chemistry - Explains the mobility of metal ions in the environment.

Section - A

1. (a) Carbocations are organic carbon compounds having vacant p-orbital. Its hybridization is  $sp^3$ .

The general stability trend is

Tertiary > Secondary > Primary > Methyl.

• Inductive Effect - Alkyl groups are electron donating via the inductive effect, which reduces the positive charge on the carbocation. Therefore, tertiary carbocations have more electron donating capacity compared to secondary and primary. ✓

• Resonance Stabilization - Carbocations stabilized by resonance are highly stable.

e.g. Benzyl carbocation and allylic carbocation are more stable than tertiary one.

• Hyperconjugation - Alkyl groups stabilize carbocation through hyperconjugation, where electrons from adjacent C-H bonds delocalize into the empty p-orbital of the carbocation.

• Aromaticity - Aromatic carbocations such as the ~~anti~~ cyclopropyl methyl carbocation gain extra stability due to aromatic resonance.



Thus the stability of carbocation is determined by how effectively the positive charge is delocalised.

\*) Aromaticity of a compound is determined basically by Huckel's Rule.

The features of an aromatic compound are:-

- The structure must be cyclic.
- Each atom in the ring must have an unhybridised p-orbital.
- These p-orbitals must be parallel.
- The overlapping  $\pi$ -system must have  $4n+2$  electrons.
- Delocalisation of  $\pi$ -electrons in the ring must lower the electronic energy.

It states that a molecule is aromatic if it contains a planar geometry, cyclic structure with a number of  $\pi$  electrons that follows the formula of  $4n+2$  integer.

Some of the examples of aromatic compounds are:-

Benzene. — It is planar, cyclic and follows the Huckel rule.



→  $4n+2$  - Rule.

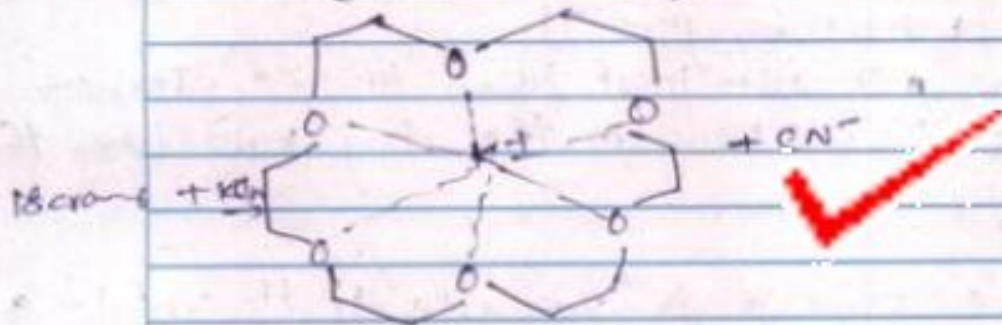
Here  $n=3$ .



- a) A group of large-ring polyethers, because of 3-D shapes are called crown ethers. The compounds are cyclic polymers of ethylene glycol.

Crown ethers are able to complex various metal ions through ion-dipole involving the unshared pair of electron on oxygen atom. A crown ether complexes effectively that particular cation which fits well into the cavity of the crown.

e.g. 18-crown-6 forms strong compound with  $K^+$  ion (diameter 2.66 Å).



18-crown-6

The new cation is lipophilic on outside and has positive charge buried within the molecule. The lipophilicity makes it soluble in organic solvents of low polarity.

When it enters in organic solvent, it gets the anion into it. The anion is shielded from the positive charge on the  $K^+$  by the bulky side of the crown, thus forming only loose ion pairs and is highly reactive.



4) Static Inhibition of Resonance refers to a phenomenon in which bulky groups attached to a molecule prevent effective resonance due to steric hindrance. This occurs when the bulky substituents distort the planarity required to conjugate between a  $\pi$ -system and a lone pair or another  $\pi$ -system. With proper overlap of orbitals, resonance is either reduced or completely inhibited.

Key factors of static inhibition of resonance:

- Planarity Disruption - Bulky groups can twist or distort the molecular geometry, forcing the orbitals out of alignment.
- Steric Hindrance - Large substituents can repel each other, creating strain and preventing the molecule from adopting the planar structure which leads to resonance destabilization.

The static inhibition can lead to resonance destabilization of a compound.

5) Optical activity of allenes:

The optical activity of a compound undergoes specific structural condition. Optical activity refers when a molecule is chiral, meaning it lacks a plane of symmetry or a centre of symmetry and cannot be superimposed on its mirror image.

Chirality in Allenes:

Allenene compounds with the general structure  $C=C=C$ .



where the central carbon is  $sp$ -hybridized, and the two terminal carbons are  $sp^2$ -hybridized. The chirality in allenes depends on the following conditions:-

1. Perpendicular Plans of Substituents - Due to linear structure of the central carbon and the perpendicular arrangement of the  $p$ -orbitals, the substituents on one terminal C lie in a plane perpendicular to the substituents on the other terminal C.

### Conditions for Optical Activity in Allenes

- The two substituents on each terminal carbon must be different from each other.

e.g.  $CH=C=C(CH_3)R$ , where  $R \neq CH_3$ .

- The substituents on one terminal carbon must also differ from those on the other terminal carbon.

e.g.  $CH=C=C(CH_3)(Cl)$ .

### 2) Singlet Methylene ( $^1CH_2$ )

- Electronic Configuration -

both valence electrons on C are paired in the same  $sp^2$ -hybridized orbital.

The electronic configuration is  $(sp^2)^2(p_z)^0$ .

- Spin state -

spin multiplicity is 1. It is diamagnetic species.



Geometry - Singlet methylene has a bent structure with an approximate bond angle of  $102^\circ$  due to  $sp^2$  hybridization.

Reactivity - Highly reactive and often acts as an electrophile due to empty  $p_z$  orbital.

### Triplet Methylene ( $^3CH_2$ )

• Electronic Configuration - Two unpaired electrons occupy separate orbitals. The electronic configuration is  $(sp^2)^2(p_z)^1$ .

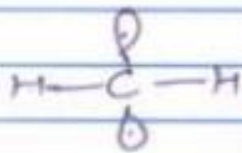
• Spin state - Spin multiplicity is 3. It is a paramagnetic species.

• Geometry - Triplet-methylene has a linear structure with a bond angle of  $180^\circ$  as the unpaired electrons in orthogonal orbitals minimize repulsion.

• Reactivity - Less reactive than singlet methylene and typically acts as a diradical in reactions.



Singlet methylene



Triplet methylene.

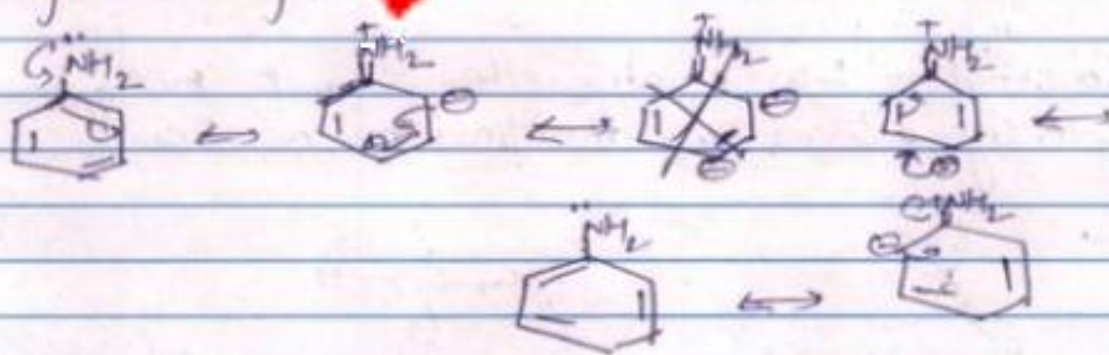


b) Aniline is more reactive than acetanilide in electrophilic substitution reactions due to the difference in electron-donating ability of  $-NH_2$  group in aniline compared to  $-NHCOCH_3$  group in acetanilide.

### ii. Electron Donating Ability -

In aniline  $-NH_2$  group directly donates its lone pair of electrons to the benzene ring through resonance increasing the electron density in the ring. On the other hand, in acetanilide, the lone pair of electrons on N atom is partially delocalized into the carbonyl system of the ring which results in the formation of the ring substituents.

a. Resonance stabilisation - The resonance stabilisation of the aniline leads to the formation of a complex compound.





!! Tautomerism is the rearrangement of atoms in the compounds which leads to formation of rearranged products. If the compound is generally reactive in nature, it leads to formation of compounds which are chiral active. The activity of compounds can result in formation of compounds which are active +

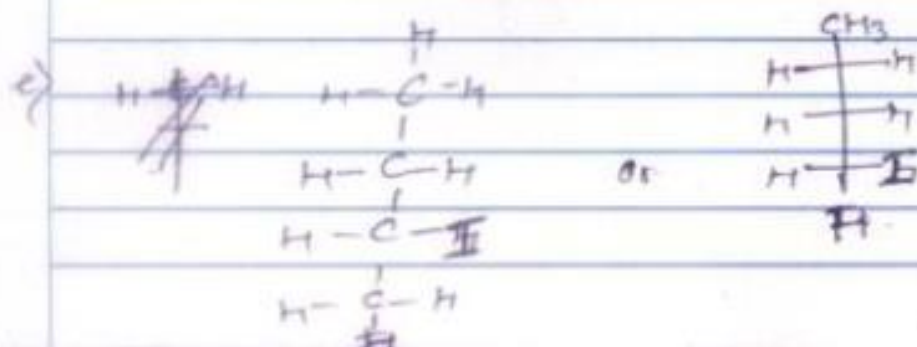
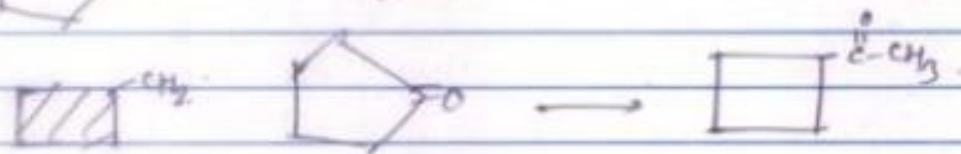
Some of the features of this compound are as follows:-

- The compound has similar structural formula but different geometries. The molecule or the compound rearranges to form a tautomer.
- The chiral activity of a compound leads to ~~form~~ same in both the tautomers.

eg. The cis and trans form of the compound leads to same result in all chemical reactions.

Examples of tautomerism are as follows:-

 rearranges in the same manner as it does.

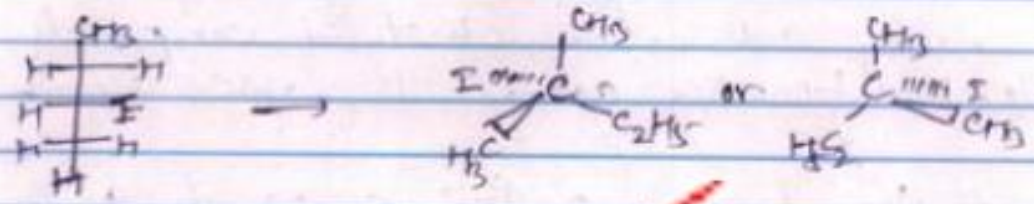




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The conversion of <sup>from Fischer</sup> 2-iodobutane to flying wedge formula is as follows:



Fischer Projection  
(2-iodobutane)

Wedge formula  
(2-iodobutane)



Paper Code

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15





Paper Code

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16





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