

CA-II

January 2014

D 53044

- * Between the two tosylates below, which would undergo hydrolysis slower and why?



2. How can the following transformation be effected through condensation?



3. Illustrate the effect of conformation on elimination reactions using suitable examples

- + Using conformational arguments, assess the reaction rate of:

- a) Esterification of menthol, isomenthol, neomenthol and neoisomenthol and
b) CrO₃ oxidation of cyclohexanols with axial and equatorial OH groups.

February 2013

D 34019

1. The rate of solvolysis of the following two compounds are different Why? Which one would undergo faster solvolysis?



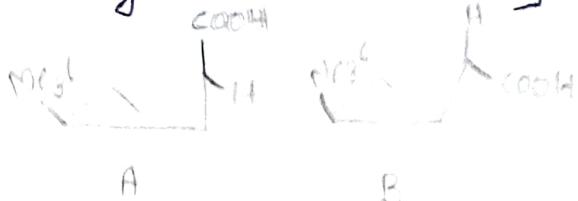
- 2. Explain Cram's rule.
3. Explain the influence of neighbouring group participation in S_N reactions
4. How does the conformation affect the course of C=C formation by H₂O elimination in 2-Phenylcyclohexanols.
5. Briefly discuss dehydrochlorination of menthyl and neomenthyl chlorides.

February 2013

D 33395.

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sololytic re-

1. Which among A and B would esterify faster and why?



2. Illustrate the conformational effect on the hydrolysis of esters of cyclohexyl carboxylic acid.

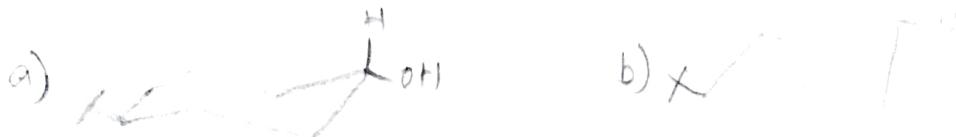
3. With suitable examples, describe the effect of conformation on

- the reaction of MeMgBr on $\text{MeCH}(\text{Ph})\text{-CHO}$.
- HBr elimination of dl and meso $\text{PhCHBr}-\text{CHBrPh}$ and
- Pyrolytic elimination of Ac-OH from cyclohexyl acetates.

January 2012

D 22456

- Methyl xanthate esters of menthol give 3-Menthene whereas neomenthol gives 2-Menthene. Explain.
- Out of the following which one will be oxidised by chromic acid.



- Compare the rates of esterification of isomenthol, neomenthol and isoneomenthol.

January 2011

D 10862.

- Show the preference of antielimination in menthyl and neomenthyl chloride.
- What is the expected product when the following is heated with nitrous acid?

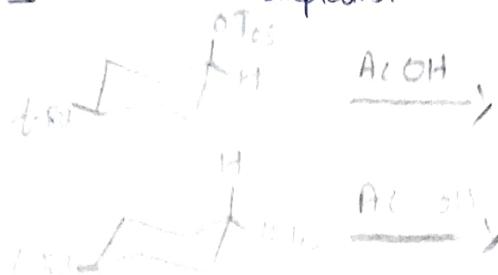


- Discuss the action of MeMgBr on 2-Phenylpropanaldehyde.

November 2010

D 9371

Which of the following pairs of compounds will react faster during the S_N1 solvolytic reactions? Explain:



2. 2,3 -Dibromobutane has both meso and chiral diastereomers. When the meso diastereomer is boiled in acetone with KI, it affords trans - 2 -butene. When the chiral diastereomer is treated in the same way, cis - 2 -butene is obtained. Which process is faster, and why?

November 2009

D 2035

1. Discuss the effect of conformation on (i) debromination of dl - Stilbene by KI and deamination of threo - 1,2o diphenyl - 1 -(p - chlorophenyl) - 2 - ethanol

December 2009

D 2035 A

1. Explain the effect of conformation on the elimination reactions of 2 - Phenylcyclohexanols.
2. Write a brief note on HCl elimination in menthyl and neomenthyl chlorides

January 2007

D 28070

1. To study the rate of saponification of α - COOMe group attached either to axial or to the equatorial position of a cyclohexane ring, one uses a cis or trans 4 - t - butyl derivative of methylcyclohexylcarboxylate. Draw the chair conformations and explain why these are used.
2. Using dehalogenation and dehydrohalogenation reactions as examples, show how conformation influences reactivity.

January 2007

D 21897

1. Among 4 - Methoxybenzyl chloride and 4 - nitrobenzyl chloride, which will undergo S_N1 solvolysis. Why?
2. The t - Bu esters of 2,2 - dimethylpropanoic acid is resistant of alkaline hydrolysis. Why?

January 2006.

D 12419.

- Draw the stereochemistry of the product formed by the add. of bromine to 1-methylcyclohexene.
- Explain why solvolysis of benzylbromide is faster than 2-Phenylbromide.

April 2006
 Explain the
 methyl cation
 Disulphide
 A

January 2006

D 12684

- The rate of hydrolysis of t-butyl chloride and 1-methyl-1-chloro cyclopentane in 4:1 EtOH-H₂O are not the same. Predict which one will hydrolyse faster and explain why?

January 2005

- 1-Phenylpropane on treatment with HCl absorbed on alumina gives a mixture of Z and E-alkene in the ratio 5:1. Write the equation and calculate the free energy change in kJ/mol.
- One isomer of benzene hexachloride (Hexachlorocyclohexane) does not undergo dehydrochlorination easily. Why?
- Predict the product of the S_NA reaction with (i) 2-iodooctene with (ii) bromide ion and (iii) an alkoxide derived from 2-butanol.
- a) Hydrolysis of ethyl 2,4,6-trisopropyl benzoate is difficult under basic conditions. Explain.
b) What is haloketone rule. Based on this comment the conformation of 2-chlorocyclohexanone.
- a) Outline the synthesis of cis-bromostryrene from E-Cinnamic acid.
b) The reduction of 2-butane with magnesium amalgam produces two isomeric glycols. Give its structure.

April 2004

C 35895.

Explain the stereochemistry of HCl elimination of cis-2-chloro-1-methylcyclohexane.

2. Discuss the stereochemistry of S_N2 reactions

April 2003

C 26222

1. Explain the influence of conformation on the reactivity of cyclohexane derivatives.

2. Briefly explain thermal elimination.

February 2003

D 24095

1. Which of the following isomers, cis or trans -4-tertbutylcyclohexyl tosylate will undergo $E2$ reactions faster? Why?

2. Draw the structures of the products formed when (a) meso and enantiomeric 1-bromo-1,2-diphenylpropane is treated with NaOEt and (b) meso and dl-2,3-dibromobutane is treated with KI .

December 2003

D 31259.

1. Which of the following will undergo $E2$ reaction faster? Give the structure of product in each case.



2. Discuss the debromination using KI and dehydrohalogenation using NaOEt of meso and dl 1,2-dibromo-1,2-diphenylethane.

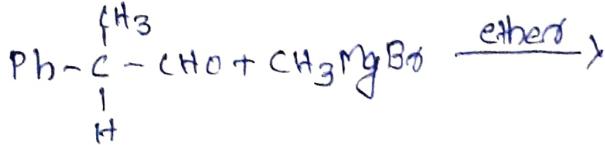
February 2002

C 3072

1. Which of the following, dl-2,3-dibromobutane or meso-2,3-dibromobutane will undergo debromination faster? Why? Show the stereochemistry of products.

2. Why do axial tosylates on cyclohexane rings undergo S_N1 and S_N2 reactions faster than their equatorial isomers? Explain.

3. Predict the stereochemistry of the reaction



4. Draw the stable conformations of cis and trans -4-t-butylcyclohexane and explain which of them will be
- oxidised faster with $\text{CrO}_3/\text{pyridine}$.
 - aerated with acetic anhydride.

April 2002

C 19163

20
Simpler
1. Bromobutyl
Predict the
 C_8H_5

- Show the stereochemistry of the product formed when cis-2-butene is treated with bromine.
- Explain the stereochemistry of the asymmetric carbonyl compounds with LiAlH_4 and RMgX .
- Discuss the stereochemistry of pyrolytic elimination.

April 2002

C 19159.

- During catalytic hydrogenation, hydrogen adds to a double bond in a fashion. Using this information, draw the chair forms of the product in the hydrogenation of 1,2-dimethylcyclohex-1-ene.
- LiAlH_4 reduces RCH_2Cl to RCH_2Z . What would be the product obtained by the reduction of (R)-1-bromo-3-methylheptane? Draw the Fischer projection and determine the configuration.
- (R)- $\text{Me}_3\text{C}-\text{CHBr}-\text{Me}$ is subjected to hydrolysis under SN^1 and SN^2 conditions respectively. Predict the structure of alcohol formed in each case using projection formulae.
- Zaitsev rule is not obeyed when 2-chloro-3-methyl-1-phenylbutane undergoes E_2 elimination. Why? Explain.
- Discuss 1,2-thermal eliminations of carboxylic acids and methyl xanthates.

April 2001

C 12962.

- State an evidence to prove that SN^2 displacement is accompanied by inversion of configuration.
- The dehydrobromination of meso 1,2-dibromo-1,2-diphenylethane gives cis-2-bromostilbene. Explain.
- Give an account of the mechanism leading to the formation of $\text{C}=\text{C}$ by elimination.
- Explain Zaitsev rule with applications.

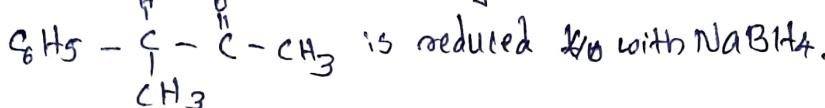
butyl

March 2001

C 12958

1-Bromo-^{2,2,1} heptane is unreactive under S_N1 and S_N2 reaction. Why?

2. Predict the structure of major isomer formed when



3. Discuss the stereochemistry of pyrolytic eliminations citing examples involving eliminations of N-oxides and Xanthates.

April 2001

C 12819

1. Predict tertiary butyl bromide or tertiary butyl chloride will undergo hydrolysis faster. Why?

2. Dehydrohalogenation of both 1-bromo-2-phenyl ethane and 1-bromo-1-phenylethane will give styrene. Which of them give better yield. Explain.

3. Explain the stereoelectronic factors favouring the formation of 4-tert-butyl cyclohexane from cis- or trans- 4-tert butylcyclohexyl tosylate.

4. a) Illustrate and describe the stereoselectivity of addition of bromine to $\text{C}=\text{C}$.
b) How do steric effects and nature of base influence the extent of elimination and substitution reactions?

March 2000

C 1584

1. Among the stable conformations of cis and trans 4-*t*-butylcyclohexanols which of them will react faster

i) with CrO_3 - Pyridine.

ii) with acetic anhydride - pyridine.

2. Explain kinetics and stereochemistry of E_1 , E_2 and $E_{1,2}\text{B}$ mechanisms.

3. Discuss xeno

April 2000

C 1722.

1. Predict the stereochemistry of the product formed when bromine adds to E_2 phenyl-2-butene in presence of acetic acid.

2. Discuss the relationship between conformation and reactivity of cyclohexyl systems.

3. Explain E_2 eliminations are stereospecific with examples.

March 1999

C 5981

predict the
2. Phenyl
among
acid side
R. An

1. Between cis and trans 4-tertbutylcyclohex-1-yl tosylate, which undergoes elimination with $\text{EtO}-\text{HgOH}$? Why?
2. Using projection formulae, show the structure of the products of addition to (i) cis and (ii) trans-2-butene.
3. Explain the effect of neighbouring group participation in S_{N} reactions.

April 1995

C 1989.

1. What conditions on reaction steps would you employ to obtain 1-butene and 2-butene as major product from 2-bromobutane.
2. Explain why the hydrolysis of R-3-bromo-1-butene gives a ~~cyclic~~ 3-hydroxy-1-butene.
3. Draw the structure of R-2-phenylpropionaldehyde and predict the structure of the major product that would arise from it by reaction with MeMgBr and hydrolysis using Clemm's rule.
4. Show that S_{N}^2 displacements are accompanied by inversion at the reaction centre.
5. a) Discuss the stability of 1-chloro-2-methylcyclohexanes. Comment on the rate of dehydrochlorination of these isomers and indicate the orientation of the double bond in the product formed from each isomer.
b) Explain why cis-decalin is conformationally mobile whereas the trans isomer is not.

April 1997

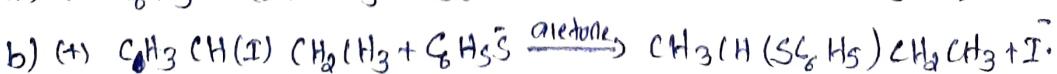
C 31108

1. Write the stereochemical structure of the products obtained by dehydrochlorination of trans and cis 1-chloro-2-methylcyclohexane.
2. The cis-4-t-butylcyclohexanol undergoes faster oxidation by CrO_3 than the trans isomer. Why?

April 1996

C 26409.

1. Predict the stereochemical consequence of the reaction.



S981
alk. alkyl
addition

Predict the structure of the major stereoisomer in the reaction

2-Phenyl propanal + Phenylmagnesium bromide.

Among cis and trans decalin⁻²⁰ which will undergo esterification with acetic acid faster. Why?

1. Answer for the following.

(i) A solution of optically active 2-iodooctane in dry acetone containing dissolved I^- ion, slowly undergoes reionization.

(ii) Acetals, $RCH(O\text{R})_2$, are stable in alkaline medium but are readily hydrolysed in aqueous acid.

5. Whether meso or \pm form of 1,2-dibromo-1,2-diphenylethane will undergo debromination by the action of I^- ion faster. Explain

6. Explain the stereochemical aspects of pyrolytic elimination and outline its mechanism.

April 1995

18116

1. Why does meso-1,2-dibromo-1,2-diphenylethane gives only E-2-bromo stilbene by dehydrobromination

April 1995

18121

1.2. Explain these ones

April 1994

334

1. 1-chloro-1-methoxy ethane reacts with CN^- by $S\text{N}_2$ reaction to form 1-cyano-1-methoxy ethane. Deduce the absolute configuration of this product.

2. Compare the reactivity, in the specified reaction, of the following functional groups in the axial and equatorial position.

(i) Carboxy (esterification)

(ii) halide ($S\text{N}_1$ and E_1)

March 1993

C 6045

1. Two isomeric 2-chloro-trans-decalin, (A) and (B) are available. (A) undergoes dehydrochlorination faster than (B). Identify A and B

2. Explain

(i) A solution of optically active 2-iodooctane in acetone containing some dissolved I^- slowly reionizes.

- 1997
Draw the major
- (i) solvolysis of an alkyl bromide in methanol is catalysed by I^- .
3. Explain croans rule. Using this predict the diastereomers formed by reduction of 3-phenyl-2-butanone by LiAlH_4 .
4. a) Draw the conformations of cis and trans 1-methyl, 2-methyl, 3-methyl cyclohexanols. Compare stabilities.
- b) Draw the conformations of cis and trans 2-methylcyclohexyl chloride. Predict the products of dehydrochlorination of each. Also predict which isomer will undergo dehydrochlorination faster.
- c) Draw the conformations of cis and trans 4-t-butylcyclohexane carboxylic acid. Show
- (i) which is the stronger acid.
 - (ii) which will undergo esterification faster.
5. Draw newman projection to show how cis-2-butene and trans-2-butene are formed in the dehydrobromination of 2-bromo butene.

March 1993

C 5938

1. Among cis and trans 4-t-butylcyclohexyl chloride which will undergo dehydrochlorination faster.
2. Explain why (i) the formation of trans-2-butene is more than cis-2-butene in the acid catalysed dehydration of 2-butanol (ii) compare the rate of esterification of cis and trans 4-t-butylcyclohexane carboxylic acid.
3. Predict the major product of addition of bromine to 4-t-butylcyclohexene.
4. Among the two diastereomers of 1,2-dibromo-1,2-diphenylethane which will undergo debromination faster.
5. Among 2-axial and 2-eq decalin which will undergo dehydration and oxidation by bromic acid faster.

May 1991

C - 5762

1. In the alkaline hydrolysis of optically active-2-butylacetate, do you expect retention, inversion or racemisation.
2. Discuss the mechanism of Xanthate pyrolysis.

May 1990

C 1637.

Draw the conformation of trans-2-methylcyclohexyl bromide and predict the major product of dehydrobromination.

1. Explain why in the dehydrobromination of 3-bromopentene, trans-2-pentene is the major product.
3. Apply croam's rule and explain the stereochemistry of the product obtained by the action of PhMgBr on 2-phenylpropanal.

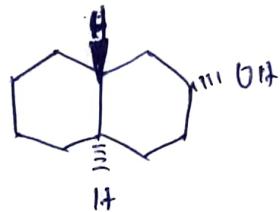
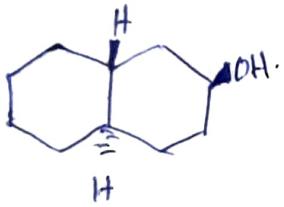
May 1996

C 1575.

1. Which will undergo dehydration faster, cis or trans-4-tert-butylcyclohexanol. Why?
2. With the help of croam's rule suggest a reaction either involves either ~~addition~~ or a Grignard synthesis or a ketone reduction to obtain only trans-3-phenyl-2-butanol as major product.
3. Show how cis-2-methylcyclopentanol can be converted selectively into 3-methylcyclopentane.
4. With the help of projection formulae, show how cis and trans stilbenes are formed by the dehydrobromination of 1,2-diphenyl-1-bromoethane and explain which isomer will be formed preferentially.

June 1989

1. How can cis-4-t-butylcyclohexanol be converted to trans-4-t-butylcyclohexylchloride.
2. Give an account of neighbouring group participation in substitution and elimination reactions.
3. Draw the conformations of the following and show which one will undergo acetylation faster.



4. Solvolysis of (+)-threo-3-phenyl-2-butyl tosylate in acetic acid yielded (\pm)-threo-3-phenyl-2-butyl acetate. Rationalise.