# **Alkyl Halides**

**PROBLEM 850** Considering that following reaction proceed by  $S_N 2$  mechanism, select the faster reaction of each pair and explain your reasoning :

(a) Reaction of cyanide ion with *n*-iodoheptane or *n*-chloroheptane.

(b) Reaction of ethanol or sodium ethoxide with *n*-butyl bromide

(c) Reaction of azide ion with 1-butyltosylate or 2-butyltosylate.

(d) Reaction of tertiary butoxide with ethyl bromide or reaction of ethoxide with tertiary butyl bromide.

(e) Reaction of cyanide ion with 2-bromopentane or  $CH_3CH_2CH$ — $CH(CH_3)_2$ 

ĊH<sub>2</sub>Br

**PROBLEM 851** Explain the following observations :



**PROBLEM 852** An organic compound *A* has molecular formula  $C_7H_{15}Cl$  and it can be resolved into enantiomers as well as diastereomers. *A* on treatment with alcoholic solution of KOH yields three isomeric alkenes *B*, *C* and *D* having molecular formula  $C_7H_{14}$ , all of them can be resolved into enantiomers. Treating either *B* or *C* with acidic solution of KMnO<sub>4</sub> yield  $E(C_5H_{10}O_2)$  and ethanoic acid. *E* is still resolvable. Heating *E* with soda lime (NaOH/CaO) yields  $C_4H_{10}$  which is non-resolvable. Identify *A* to *E*.

**PROBLEM 853** A organic compound A has molecular formula  $C_6H_{13}Cl$  and it can be resolved into enantiomers. A on treatment with alcoholic solution of KOH yield four alkenes B, C, D and E, none of them can be resolved into enantiomers. B and C are stereoisomers and treatment of either B or C with  $Cl_2$  yields racemic mixture of  $C_6H_{12}Cl_2$ . On the other hand D and E are stereoisomers and D on treatment with  $Cl_2$  yields a meso compound  $C_6H_{12}Cl_2$  while E on similar treatment yield a racemic mixture of  $C_6H_{12}Cl_2$ . Also B has greater heat of hydrogenation than C. Deduce structures of A to E.

**PROBLEM 854** Give reason:

(a) Hydrolysis of methylbromide takes place much faster in presence of NaI.

(b) When tertiary butyl chloride undergo hydrolysis in aqueous NaOH, the rate of formation of tertiary butyl alcohol does not increase appreciably as OH<sup>-</sup> concentration is increased, however a marked decrease in concentration of *t*-butyl chloride is observed.

(c) When methyl bromide reacts with NaCN, major product is CH<sub>3</sub>CN, whereas when CH<sub>3</sub>Br reacts with AgCN, major product is CH<sub>3</sub>NC.

**PROBLEM 855** Explain the mechanism of following reactions:



**PROBLEM 856** Account for the following observations:

- (a) *t*-BuF is solvolysed only in very acidic solution.
- (b) *t*-BuCl is solvolysed more slowly than 2-chloro-2,3,3-trimethylbutane.
- (c) *t*-BuCl is solvolysed much faster than 2-chloro-1,1, 1-trifluoro-2-methy-lpropane.

**PROBLEM 857** Explain the following observations in  $S_N$  1 reactions:

- (a) AgNO<sub>3</sub> increases the rate of solvolysis
- (b) the more acidic the nucleophilic solvent, the faster is the rate of solvolysis.

**PROBLEM 858** Complete the following reaction sequence, showing the major product you expect for each stage. Also indicate stereo-chemistry where possible.

(a) 
$$CH_3CHCH_3 \xrightarrow{TsCl} A \xrightarrow{NaN_3} B$$
  
OH

(b) 
$$CH_2CH_2CH_2OCH_3$$
  
 $H_3C$  Br  $CH_3SNa$ 

**PROBLEM 859** Explain the relative rate of *E*-2 reaction of the following compounds:



**PROBLEM 860** Explain the followings:

(a) When  $CH_3Br$  is dissolved in ethanol, no reaction occurs at 25°C. When excess of  $C_2H_5ONa$  is added, a good yield of ethyl-methyl ether is obtained.

(b) Explain the role of solvent in the reaction of potassium ethanoate with ethyl iodide.

(c) Which nucleophile reacts more rapidly with  $CH_3I$ :  $Et_3N$  or  $Et_3P$ ?

**PROBLEM 861** Predict product in the following reaction:



**PROBLEM 862** In attempting to synthesize 1-methylcyclohexene, you are trying reaction of trans-1-iodo-2-methyl cyclohexane with potassium tri-tertiary butoxide. The reaction fails to produce the desired product and the isolated product is 3-methylcyclohexene. Using a detailed mechanistic analysis, explain why this alternative product is formed?

**PROBLEM 863** The two tosylate shown below react differently under identical conditions. One will undergo a facile  $S_N 2$  reaction while other will easily eliminate via *E*-2 mechanism. Draw structures of major product for each reaction and provide mechanistic explanation for them:



**PROBLEM 864** When piperidine undergoes the indicated series of reactions, 1,4-pintadiene is obtained as product.



When four different methyl substituted piperidine is subjected to same series of reactions, each forms a different dienes-1,5-hexadiene, 1,4-pentadiene, 2-methyl-1,4-pentadiene and 3-methyl-1,4-pentadiene. Which methyl substituted piperidine yields which diene?

**PROBLEM 865** Give substitution product mentioning their stereochemistry:



**PROBLEM 866** In the following pair of reactions, which will occur at faster rate-explain your choice:



**PROBLEM 867** Propose mechanism:



**PROBLEM 868** Explain the following observations:

(a) Azide ion  $(N_3^-)$  react with 2-bromopentane thousand times faster than with neopentyl bromide in a  $S_N^2$  reaction though former is a secondary halide while latter is primary.

(b) What will happen to the stereochemistry of product of the following reaction:

$$H \xrightarrow{Br}_{D} CH_3 + N_3^- \xrightarrow{S_N^2} \blacksquare$$

- (c) What will happen to the rate if the concentration of alkyl bromide in (b) is doubled?
- (d) What will happen to the rate if the concentration of azide ion in (b) is doubled?
- (e) How the sign of optical rotation of reactant and product are related in (b)
- (f) When allowed to stand in dilute  $H_2SO_4$ , laevo-rotatory 2-butanol slowly loses optical activity.

**PROBLEM 869** Assuming that the following reaction takes place by  $S_N 2$  mechanism, select the faster reaction in each pair and explain reason for your choice:

- (a) Reaction of cyanide ion with *n*-iodoheptane or *n*-chloroheptane.
- (b) Reaction of ethanol or  $C_2H_5ONa$  with *n*-butyl bromide.
- (c) Reaction of azide ion  $(N_3^{-})$  with *n*-butyl tosylate or *s*-butyl tosylate.
- (d) Reaction of isopropoxide with ethyl bromide or reaction of ethoxide with 2-bromopropane.

**PROBLEM 870** Synthesize the following compounds from indicated starting material:



**PROBLEM 871** Explain why allyl bromide (CH<sub>2</sub>=CHCH<sub>2</sub>Br) undergoes rapid substitution under either  $S_N 1$  or  $S_N 2$  reaction condition.

**PROBLEM 872** Following reactions are not feasible as indicated. Briefly explain the reason for their failure:



**PROBLEM 873** Provide mechanism:



**PROBLEM 874** Arrange the following in the increasing order of their ability as a leaving group: (a)  $CH_3S^-$ ,  $CH_3O^-$ ,  $CF_3^-$  and  $F^-$  (b)  $CF_3SO_3^-$ ,  $CH_3SO_3^-$  and  $CH_3COO^-$ 

**PROBLEM 875** An organic compound *A* has molecular formula  $C_6H_{11}Br$ . *A* decolorizes brown colour of bromine water but it can't be resolved into enantiomers. *A* on treatment with HBr produces  $B(C_6H_{12}Br_2)$  which is still non-resolvable. Also *A* on treatment with HBr in presence of a peroxide  $(R_2O_2)$  yields *C*-an isomer of *B*, but it is resolvable. *B* on heating with Zn-metal yields  $D(C_6H_{12})$  which on treatment with ozone followed by hydrolysis of product in presence of Zn-powder yield acetone as the only organic compound. Also *A* on treatment with ethanolic KOH solution yields  $E(C_6H_{10})$ 

as only possible product. *E* on treatment with excess of  $HBr/R_2O_2$  in cold produces isomeric *F* and *G* with their molecular formula  $C_6H_{12}Br_2$ , in which *F* is a meso compound while *G* is resolvable. Also *F* on hydrolysis in aqueous NaOH yield a diol  $C_6H_{14}O_2$  which on refluxing with dilute  $H_2SO_4$  yields the adjoining compound.

Deduce structures of A to G.

**PROBLEM 876** An organic compound is optically active and has molecular formula  $C_{14}H_{23}Br$ . *A* does not decolourise cold, dilute and alkaline solution of KMnO<sub>4</sub>. *A* on treatment with potassium tertiary butoxide in tertiary butanol yields  $B(C_{14}H_{22})$  as the major product. *B* on treatment with acidified permanganate solution yields  $C(C_{14}H_{22}O_4)$ . *C* on heating with sodalime yields  $D(C_{12}H_{22})$  which can also be formed by dissolving cyclohexyl bromide in etheral solution of Mg. Identify *A* to *D*.

**PROBLEM 877** An optically active organic compound A has molecular formula  $C_7H_{16}O$ . A neither changes the colour of bromine water nor evolve any gas on reacting with MeMgBr. A on refluxing with dilute  $H_2SO_4$  produces  $B(C_3H_8O)$  and  $C(C_4H_{10}O)$ . B is non-resolvable and gives yellow precipitate with

NaOH/I<sub>2</sub> while *C* is resolvable. *C* on heating with concentrated solution of H<sub>2</sub>SO<sub>4</sub> yield stereo-isomeric compounds *D* and *E* with their molecular formula C<sub>4</sub>H<sub>8</sub>. *D* on treatment with Br<sub>2</sub>/CCl<sub>4</sub> yields a meso dibromide while *E* on similar treatment yields racemic mixture of products. Identify *A* to *E*.

**PROBLEM 878** An organic compound  $A(C_5H_{11}Cl)$  is optically active and on treatment with ethanolic KOH solution yields  $B(C_5H_{10})$  as major product which does not show stereo-isomerism. Also A on treatment with  $(CH_3)_2Cu$  yields  $C(C_6H_{14})$  which is optically inactive. Deduce structures of A to C.

**PROBLEM 879** An organic compound *A* has molecular formula  $C_{10}H_{17}Br$  and it is non-resolvable. *A* does not decolourise brown colour of bromine water solution. *A* on treatment with  $(CH_3)_3COK/(CH_3)_3COH$  yields  $B(C_{10}H_{16})$  as major product. *B* on treatment with  $H_2/Pt$  yields  $C_{10}H_{18}$  which on treatment with  $Cl_2/hv$  yields three monochloro derivative. Also *B* on boiling with acidic permanganate solution yields  $C(C_{10}H_{16}O_3)$ . *C* on heating with soda-lime yields  $D(C_9H_{16}O)$ . *D* on reducing with LiAlH<sub>4</sub> followed by heating the product with concentrated  $H_2SO_4$  yields  $E(C_9H_{16})$  as major product. *E* on treatment with ozone followed by work-up with Zn-H<sub>2</sub>O yields 6-keto nonanal. Deduce structures of *A* to *E*.

**PROBLEM 880** An organic compound *A* has molecular formula  $C_5H_{10}O$  and it neither decolourise bromine water solution nor evolve any gas on heating with Na-metal. *A* on refluxing with aqueous HI yields  $B(C_5H_{10}I_2)$  which is non-resolvable. *B* on treatment with NaCN in acetone yield  $C(C_6H_{10}IN)$  in significant amount while *B* on treatment with aqueous Ag<sub>2</sub>O yields  $D(C_5H_{11}IO)$  in significant amount. *D* does not change the orange colour of acidic dichromate solution. Deduce structures of *A* to *D*.

**PROBLEM 881** An optically active organic compound *A* has molecular formula  $C_{11}H_{16}O$  and it gives off a colourless gas on treatment with  $CH_3MgBr$ . *A* on heating with concentrated  $H_2SO_4$  yields  $B(C_{11}H_{14})$  which does not show stereo-isomerism. *B* on treatment with HBr in absence of a peroxide yields  $C(C_{11}H_{15}Br)$  which is resolvable while addition of HBr on *B* in presence of a peroxide yields *D*, an isomer of *C* but it is non-resolvable. Also *B* on treatment with ozone followed by work-up with Zn-H<sub>2</sub>O yields  $C_8H_8O$  and  $C_3H_6O$  in which former can also be obtained by Friedal Craft's acylation reaction of benzene. Both these ozonolysis products gives yellow precipitate on treatment with NaOH/I<sub>2</sub>. Deduce structures of *A* to *D*.

**PROBLEM 882** Bring about the following transformations:

- (a)  $C_6H_5CH_2OH \longrightarrow C_6H_5CH_2SCH_2CH_3$
- (b) *n*-pentanol  $\longrightarrow$  *n*-pentyl iodide
- (c)  $C_6H_5SH \longrightarrow C_6H_5SCH_2CH_2C_6H_5$
- (d) *n*-butyl bromide  $\longrightarrow$  2-heptyne



**PROBLEM 883** Both mesylates and triflates are good leaving groups. However, triflate displacements proceed about 5000 times faster than mesylate displacements. Explain why triflate is a better leaving group than mesylate.

**PROBLEM 884** Upon treatment with  $Ag^+$  ions, on  $\alpha$ -halo-ether undergo substitution via SN-1 mechanism. Consider the following two reactions and explain why 1 produces a mixture of two possible stereoisomers while 2 provides only one.



**PROBLEM 885** For each of the following of substrate, indicate with reasoning, which will react at faster rate under the given reaction conditions. In addition, indicate whether you expect each reaction to follow SN-1 or SN-2 pathways.



**PROBLEM 886** Write products in the following reactions explaining mechanism of their formations:





**PROBLEM 887** Write products in the following reactions indicating their stereochemistry:





(g) 
$$CH_2 = CH - CH_2 - CH - CH - CH_3 \xrightarrow{KOH} E-2$$

**PROBLEM 888** Write mechanism for the following reaction:

$$CH_{2} = C - CH_{2} - CH - CH_{3} + CH_{3}OH \xrightarrow{heat} CH_{2} = C - CH - CH_{2}CH_{3}$$

$$CH_{2} = C - CH_{2} - CH - CH_{3} + CH_{3}OH \xrightarrow{heat} CH_{2} = C - CH - CH_{2}CH_{3}$$

**PROBLEM 889** Bring about the following transformations:



**PROBLEM 890** Write major products in the following reaction and discuss their stereochemistry:



**PROBLEM 891** 5-Bromononane on treatment with potassium tertiary butoxide in ethanol produces a mixture of *cis*-4-nonene (23%) and *trans*-4-nonene (77%). Draw Newman's projections of 5-bromononane, looking down the C5–C6 bond showing the conformational forms that lead to *cis*-4-nonene and *trans*-4-nonene respectively. Based on conformational analysis, suggest reason why transform of product predominate.

**PROBLEM 892** Give stereochemical structures of product formed in the following reactions:



**PROBLEM 893** An alkyl bromide *A* has molecular formula  $C_8H_{17}$ Br and four different structures can be drawn for it, all optically active. *A* on refluxing with ethanolic KOH solution yields only one elimination product  $B(C_8H_{16})$  which is still enantiomeric. *B* on treatment with  $H_2$ /Pt yields  $C(C_8H_{18})$  which does not rotate the plane polarized light. *B* on ozonolysis followed by work-up with  $H_2O_2$  yields  $D(C_7H_{14}O)$  as one product which is still resolvable. Deduce structures of *A* to *D*.

**PROLBEM 894** Provide missing products, starting material or reagents/conditions, for each of the following reactions:



**PROBLEM 895** Propose mechanism of the following reaction:



**PROBLEM 896**  $S_N^2$  reaction of simple carboxylate ions with haloalkanes in aqueous medium generally do not gives good yields of esters, explain. Reactions of 1-iodobutane with sodium acetate gives an excellent yield of ester if carried out in acetic acid medium. Why acetic acid is a better solvent for this process than water?

**PROBLEM 897** Provide major substitution product in the following reaction:

(a) 2-butanol + HBr  $\xrightarrow{\text{heat}}$  (b) 3,3-dimethyl-2-butanol + HBr  $\xrightarrow{\text{heat}}$ (c)  $\bigvee$  OH + HCl  $\xrightarrow{\text{Heat}}$  (d)  $\bigvee$  OH + HCl  $\xrightarrow{\text{Heat}}$ 

**PROBLEM 898** Provide structure of major product in the following reaction indicating stereochemistry where appropriate:

(a) 
$$C_{H_3} \xrightarrow{D}_{H} \xrightarrow{TsCl} \xrightarrow{NaCN}$$
 (b)  $C_{H_3} \xrightarrow{D}_{H} \xrightarrow{HBr} \xrightarrow{NaCN}$ 

**PROBLEM 899** How 1-butanol can be converted efficiently into:

(a) 1-iodobutane (b) N-ethylethanamine (c) Butylpropanoate (d) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SH (e) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>

**PROBLEM 900** Which of the following alkyl halide could be successfully used to synthesize Grignard reagent and why other fail?



**PROBLEM 901** Propose mechanism of the following reactions:



**PROBLEM 902** Explain mechanism of formation of products in the following reactions:



**PROBLEM 903** Discuss the relative reactivity of reactants in the following pairs:



**PROBLEM 904** (a) Give structures of products obtained from the reaction of both enantiomers of cis-1-chloro-2-isopropyl cyclopentane with CH<sub>3</sub>ONa.

(b) Are all the products obtained chiral?

(c) How would products differ if the starting material were *trans* isomer?

(d) Which pair of structure (enantiomers) form substitution product more rapidly-*cis* or *trans* and why?

(e) Which pair of products form elimination product more rapidly *cis* or *trans?* 

**PROBLEM 905** Write elimination products in the following reaction and compare their relative reactivity:



**PROBLEM 906** Compare the following compound for their reactivity in SN-1 reaction:



**PROBLEM 907** Propose mechanism of the following reaction:



# **Solutions**

# ALKYL HALIDES

- **850.** (a) *n*-iodoheptane since iodide ion is a better leaving group.
  - (b) Sodium ethoxide since it is a stronger nucleophile than ethanol
  - (c) 1-butyltosylate, due to less steric hinderence.
  - (d) triarylbutoxide with ethyl bromide.
  - (e) with-2-bromopentane.
- **851.** Both the reactions are examples of  $S_N 2$  reaction. Since aniline is a weaker nucleophile than cyclohexylamine, former undergoes slower substitution reaction.



- **854.** (a) Methylbromide undergo halogen exchange with NaI forming methyl iodide. Iodide being a better leaving group then bromide, rate of hydrolysis is increased.
  - (b) The predominant reaction in this case is elimination (E-2) which depends on concentration of both alkyl halide and base. Increasing concentration of base increases the rate of E-2 reaction decreasing concentration of alkyl halide.
  - (c) NaCN is ionized completely giving ambident (CN<sup>-</sup>) nucleophile. Since carbon is better electron donor than nitrogen, bonding occurs from carbon side. AgCN being covalent, CN<sup>-</sup> is not totally free for attack and attack primarily occurs from nitrogen side giving isocyanide.



- 856. (a) C—F bond is the strongest carbon-halogen bond, undergo very difficult heterolysis.
  - (b) Latter forms a more stable carbocation.
  - (c) *t*-butylchloride form a more stable carbocation.
- **857.** (a) AgNO<sub>3</sub> forms insoluble AgX driving reaction in forward direction.
  - (b) More acidic solvent increases the rate of heterolysis facilitating formation of carbocation.



- **859.** III < II < I
- **860.** (a) Ethanol being a very weak nucleophile can't activate  $S_N 2$  reaction, and  $CH_3Br$  being very less reactive in  $S_N 1$  reaction, neither  $S_N 1$  nor  $S_N 2$  take place. Adding excess of  $C_2H_5ONa$  involve  $S_N 2$  reaction and ether is formed.
  - (c)  $Et_3P$  is a better nucleophile than  $Et_3N$ .



**862.** Tertiary butyl being a bulky base abstract H-from less hindered  $\beta$ -carbon giving this alternative product.

Solutions



**868.** (a) Though neopentylbromide is primary, bulky tertiary butyl group poses very large steric hindrance to the attack of bulky nucleophile  $N_3^-$ .

(b) 
$$H \xrightarrow{Br} CH_3 + N_3^- \xrightarrow{S_N 2} CH_3 \xrightarrow{N_3} H$$
  
D D

- (c) Rate will double (d) Rate will double (e) not related
- (f) Racemization occur through carbocation intermediate.
- **869.** (a) *n*-iodoheptane (b)  $C_2H_5ONa$  (c) *n*-butyltosylate (d) isoproposide with  $C_2H_5Br$ .

**870.** (a) HO 
$$\longrightarrow$$
 OH  $\xrightarrow{\text{NaOH}} \xrightarrow{\text{CH}_3\text{I}}$  Product

(b) 
$$C_6H_5CH_2OH \xrightarrow{TsCl} \xrightarrow{NH_3}$$
 Product.

(c) 
$$C_6H_5OH \xrightarrow{TsCl} \xrightarrow{CH_3CH_2CH_2SNa}$$
 Product.  
(d)  $Cl \xrightarrow{B_2H_6} \xrightarrow{KOH}$  Product.

- 871. Allyl bromide produces a resonance stabilized carbocation justifying its greater reactivity in  $S_N 1$  reaction. Also carbon  $\beta$  to Br has an empty *p*-orbital which share some of the shared electron pairs of pentavalent transition state formed in  $S_N 2$  reaction, increasing its stability and hence reactivity.
- **872.** (a)  $CN^-$  being weaker nucleophile than  $H^-$ .
  - (b)  $3^{\circ}$  carbocation is more stable than  $1^{\circ}$ .
  - (c) Geminal diols are unstable.



**874.** (a)  $CF_3^- < CH_3O^- < CH_3S^- < F^-$  (b)  $CH_3COO^- < CH_3SO_3^- < CF_3SO_3^-$ 







In both mesylate and triflate, the leaving group anion is stabilized by resonance. In the case of triflate, the three fluorides provide additional stabilization to the anion via electron withdrawing inductive effect.







**890.** Since, the tosylate is tertiary, E-2 and  $S_N 1$  are equally probable:



Solutions



Problems in Chemistry



- **896.** Esters are usually water insoluble, if acetic acid is used, it gives homogeneous medium driving reaction in forward direction.
- 897. (a) 2-chlorobutane,
  - (b) 2-chloro-2,3-dimethylbutane,
  - (c) 1-methylchlorocyclopentane,
  - (d) 1-ethyl-2-methyl chlorocyclohexane.



**900.** Only II can be used for successful synthesis of Grignard reagent, rest all contain acidic proton and will react with  $R^-$  (from Grignard reagent) forming alkane.



Solutions



- **903.** (a)  $(CH_3)_3CI$  is more reactive since I<sup>-</sup> is a better leaving group than Cl<sup>-</sup>.
  - (b) I is more reactive since  $\beta$ —H is less sterically hindered compared to II.



(b) As shown in (a), the predominant elimination product is achiral.



#### Problems in Chemistry



II is more reactive towards elimination reaction since the bulky base will abstract a H from side of least steric crowding giving more stable alkene.



906. (a) First is more reactive since it produces a more stable carbocation:

(b) Second is more reactive since it produces a resonance stabilized allylic carbocation.

- (c) First is more reactive since it produces a more stable benzylic carbocation.
- (d) Second is more reactive due to the same reason as with (b).

(e) Second is more reactive due to the same reason as with (a).

