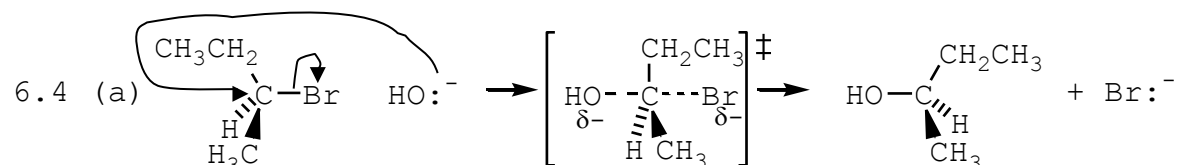


Answers to Puzzles of Chapter 6
Substitution Reactions of Alkyl Halides

6.1 1-chlorobutane has the higher bp because it is less branched than its constitutional isomer, 2-chloro-2-methylpropane, and so has more surface area and more dispersion forces.

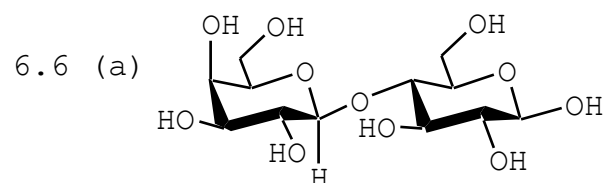
6.2 (a) With larger surface area & dispersion forces, trichlorofluoromethane has a higher bp.
(b) Larger surface area & dispersion forces give 1,1-dichloro-2,2,2-trifluoroethane a higher bp.

6.3 (a) The rate would increase by a factor of $3 \times 3 = 9$.
(b) The rate would change by a factor of $(1/2)(1/2) = 1/4$



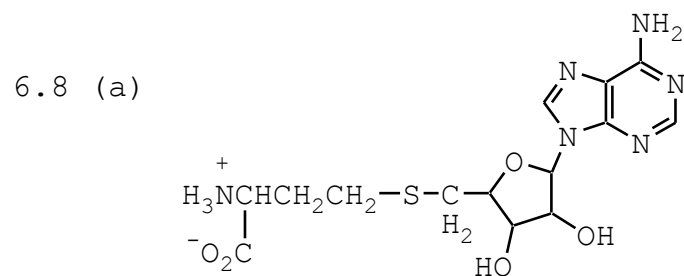
(b) (*R*)-2-butanol (c) identical since enantiomers have the same energy

6.5 good S_N2 leaving groups: (a) & (c)



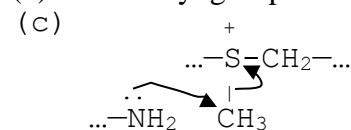
(b) Because its conjugate acid is strong, UDP is a weak base and a good leaving group.

6.7 (a) OK: good I^- leaving group, methyl C skeleton (b) poor: poor ^-OH leaving group
(c) poor: poor H^- leaving group (d) OK: good Br^- leaving group, 1° skeleton
(e) poor: poor H^- leaving group (f) poor: poor $^-C\equiv N$ leaving group
(g) OK: good Cl^- leaving group, 2° skeleton (h) poor: 3° skeleton
(i) poor: poor RO^- leaving group (j) poor: poor H^- leaving group, 3° skeleton



Its conjugate acid has a positive charge and so is stronger than H_2S , which is a borderline strong acid. Therefore, the leaving group is a weak base and a good leaving group.

(b) The methyl group is smaller with less steric hindrance.



6.9 (a) OK: strong base (b) OK: strong base (c) poor: weak base (d) OK: strong base

(e) OK: soft (f) poor: weak base (g) poor: too bulky

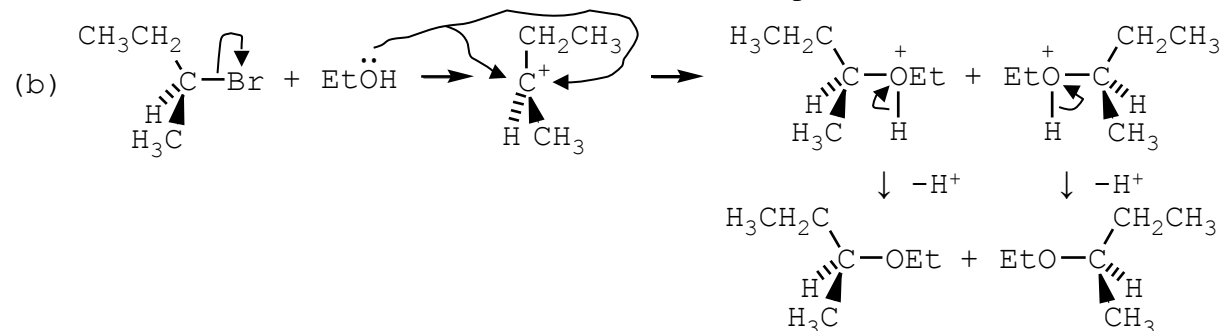
6.10 Its base e's, being on the less EN N, are less stable, more basic, and so more nucleophilic.

6.11 (a) increase rate by a factor of 2 (b) no change

6.12 Good S_N1 leaving groups: (a) & (c), same as good S_N2 leaving groups

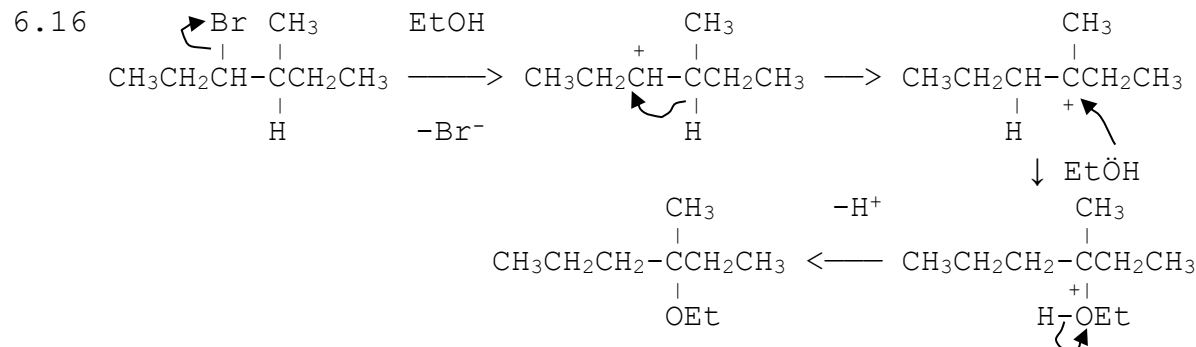
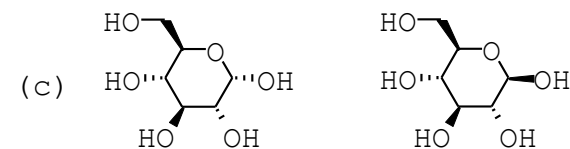
6.13 (a) poor: Me skeleton (b) poor: poor HO⁻ leaving group (c) poor: poor H⁻ leaving group
(d) poor: 1° skeleton (e) poor: poor H⁻ leaving group (f) poor: poor N≡C⁻ leaving group
(g) OK: good Cl⁻ leaving group, 2° (h) OK: good Br⁻ leaving group, 3°
(i) poor: poor RO⁻ leaving group (j) poor: poor H⁻ leaving group

6.14 (a) S_N1 because ethanol is a weak base and weak nucleophile

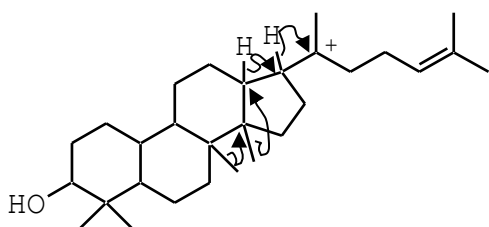


6.15 (a) glucose is a good leaving group because its alcohol group leaves as a weak base.

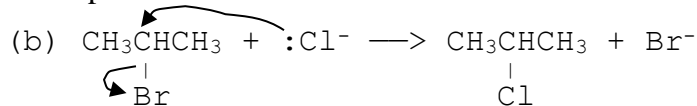
(b) Resonance stabilizes it:



6.17



6.18 (a) S_N2 because the aprotic solvent propanone and the strong nuc Cl^- favor S_N2 . The 2° elie is compatible with S_N2 .



6.19 (a) Suitable for S_N1 because it is a weak, hard base and so too weak of a nucleophile for S_N2 .

(b) S_N1 because it is a weak, hard base and so too weak of a nucleophile for S_N2 .

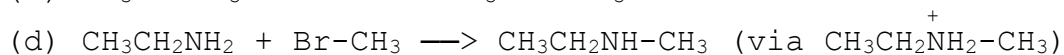
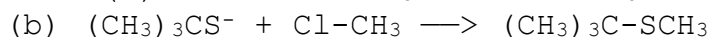
(c) S_N1 because there is no strong nucleophile.

(d) Ethanol is a preferred S_N1 solvent because it is protic. (e) 3° (f) methyl & 1°

(g) $R\text{-NO}_3$ & $R\text{-OCH}_2\text{CH}_3$

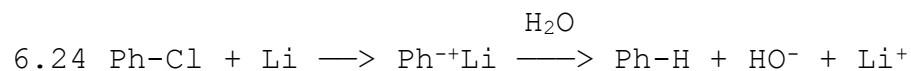
6.20 (a) [nucleophile] \uparrow (b) nucleophilicity \uparrow (c) aprotic solvent if the nuc is an anion

6.21 (a) [nucleophile] \downarrow (b) nucleophilicity \downarrow (c) protic solvent if the electrophile is uncharged



6.23 (a) $[\text{H}^+] \cong 10^{-9}$ so that it has a nucleophilic ^-S group, but a nonnucleophilic H_3N^+ group.

(b) e.g., $\text{CH}_3\text{CH}_2\text{Br}$



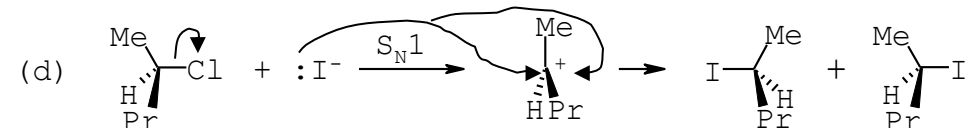
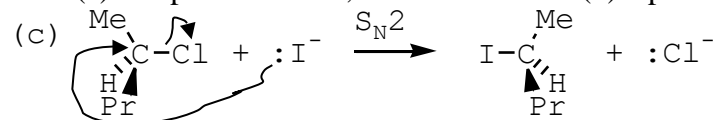
6.25 (a) BrCH_2CH_3 ; more dispersion forces (b) $\text{CH}_3\text{CHClCH}_3$; dipole-dipole forces

(c) $\text{ICH}_2\text{CH}_2\text{CH}_2\text{CH}_3$; more dispersion forces (d) $\text{CH}_3\text{CHICH}_3$; more dispersion forces

6.26 (a) reduce rate of S_N2 by a factor of $2 \times 2 = 4$; reduce rate of S_N1 by a factor of only 2

(b) Diluting the reactants favors S_N1 over S_N2 as shown in part a.

6.27 (a) an aprotic solvent, such as DMSO (b) a protic solvent, such as methanol



6.28 (a) CH_3Br is feasible because it is \ominus ctet and H_2O is a weak base & good leaving group.

$\text{CH}_3\text{OH}_2\text{Br}$ is not feasible because too many (10) e's surround O.

CH_3OHBr^+ is not feasible because H^- is a very strong base & impossible leaving group.

BrOH_2^+ is not feasible because $^-CH_3$ is a very strong base & impossible leaving group.

HBr is not feasible because HBr is a stronger acid than CH_3OH_2^+ .


(b) No, because stable products don't result.

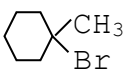
6.29 (a) 2nd reaction is faster because HS^- is a stronger base and therefore a stronger nuc than Cl^-

(b) 1st reaction is faster because Br^- is a weaker base and so a better leaving group than HO^-

(c) 2nd reaction is faster because CH_3Br is a methyl elie and therefore less sterically hindering.

(d) 1st reaction is faster because the aprotic solvent $(\text{CH}_3)_2\text{S}=\text{O}$ solvates the anion nuc less.

6.30 (a)  because it is the only 1° elie for the $\text{S}_{\text{N}}2$.

(b)  because it is the only 3° elie for the $\text{S}_{\text{N}}1$ reaction.

6.31 (a) $\text{S}_{\text{N}}1$ because ^-SH is a strong nucleophile, which would speed up an $\text{S}_{\text{N}}2$ reaction.

(b) $\text{Me}_3\text{C}-\text{OH} + \text{Me}_3\text{C}-\text{SH}$ are organic products

6.32 (a) $\text{Et}-\text{Br}$ (b) $\text{Et}-\text{OH}$ (c) no reaction (d) no reaction (e) no reaction (f) $\text{Et}-\text{NHMe}$

(g) $\text{Et}-\text{OMe}$ (h) no reaction (i) $\text{Et}-\text{C}\equiv\text{CMe}$ (j) $\text{Et}-\text{C}\equiv\text{N}$ (k) $\text{Et}-\text{SH}$ (l) $\text{Et}-\text{SMe}$ (m) $\text{Et}-\text{PPh}_3^+$

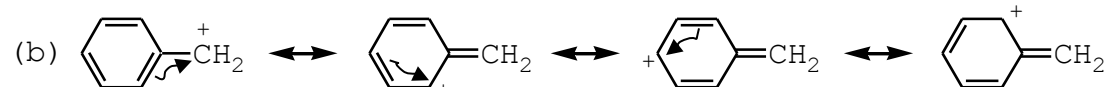
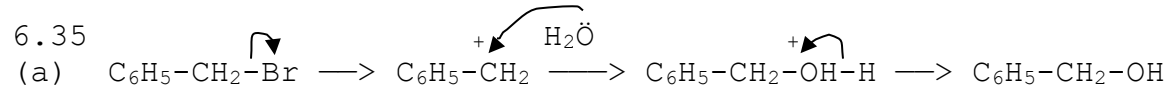
6.33 (a) $\text{Me}_3\text{C}-\text{Br}$ (b) $\text{Me}_3\text{C}-\text{OH}$ (c) $\text{Me}_3\text{C}-\text{OH}$ (d) no reaction (e) no reaction

(f) $\text{Me}_3\text{C}-\text{NHMe}$ (g) $\text{Me}_3\text{C}-\text{OMe}$ (h) $\text{Me}_3\text{C}-\text{OMe}$ (i) $\text{Me}_3\text{C}-\text{C}\equiv\text{CMe}$ (j) $\text{Me}_3\text{C}-\text{CN}$

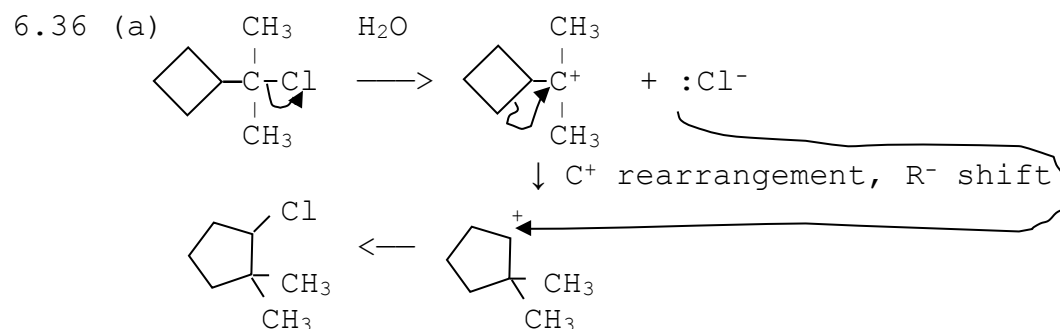
(k) $\text{Me}_3\text{C}-\text{SH}$ (l) $\text{Me}_3\text{C}-\text{SMe}$ (m) $\text{Me}_3\text{C}-\text{PPh}_3^+$

6.34 (a) Not $\text{S}_{\text{N}}2$ because it is 3° and blocks back approach.

(b) Not $\text{S}_{\text{N}}1$ because a planar carbocation could not form at the vertex of a cube.



resonance stabilizes it enough.



(b) This C^+ rearrangement is unusual because a 3°C^+ becomes a 2°C^+ , normally less stable. But the 3°C^+ is actually less stable because it has much more ring strain.

6.37 (a) first, 2° elie faster in $\text{S}_{\text{N}}2$; second, 3° elie faster in $\text{S}_{\text{N}}1$

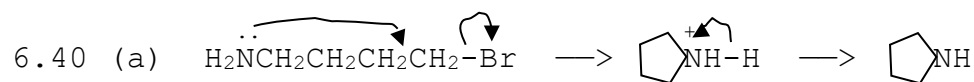
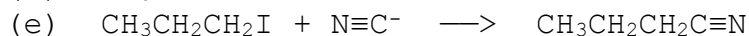
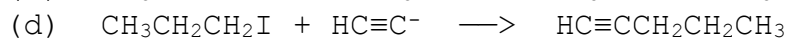
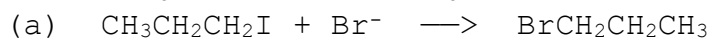
(b) second with weaker base I^- leaving group faster in $\text{S}_{\text{N}}2$ & $\text{S}_{\text{N}}1$

(c) aprotic solvent DMSO faster for $\text{S}_{\text{N}}2$; protic solvent ethanol faster for $\text{S}_{\text{N}}1$

6.38 (a) e.g., $\text{Cl}-\text{CH}_2\text{CH}_3 + ^-\text{OH} \longrightarrow \text{HO}-\text{CH}_2\text{CH}_3 + \text{Cl}^-$

(b) $\text{HO}-\text{CH}_2\text{CH}_3$ is very soluble in water because it is very polar, like water.

(c) The product has a higher boiling point because it has hydrogen "bonds".



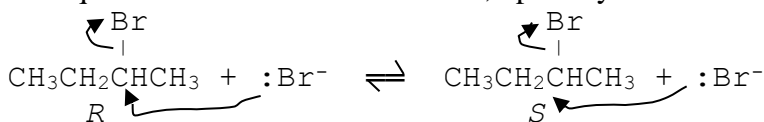
(b) $\text{rate} = k[\text{amine}]$ (c) $\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{-NHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{-Br}$ (d) $\text{rate} = k[\text{amine}]^2$

(e) dilute the amine

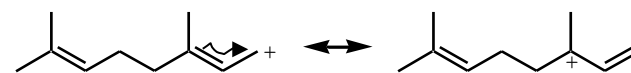
6.41 (a) good leaving group because it's a weak base (b) $\text{CH}_3\text{CH}_2\text{-C}\equiv\text{N} + ^-\text{O}_3\text{S-C}_6\text{H}_4\text{-CH}_3$

6.42 from $^-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$ by an intramolecular $\text{S}_{\text{N}}2$

6.43 Equilibrium establishes a racemic, optically inactive mixture of *R* and *S* 2-bromobutane:



6.44 (a) resonance stabilizes:



(b) resonance indicates that a full double bond does not exist between the second and third carbons, so it can rotate around that C-C bond:

