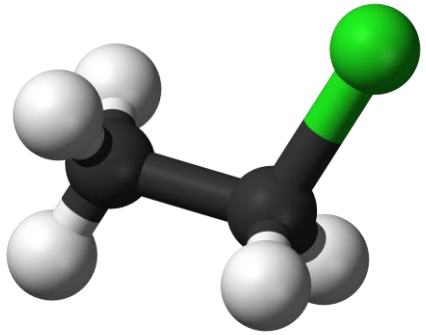
2302263 – Organic Chemistry I – Part III

Lecture 1-1

Alkyl Halides - Structures Properties Preparations



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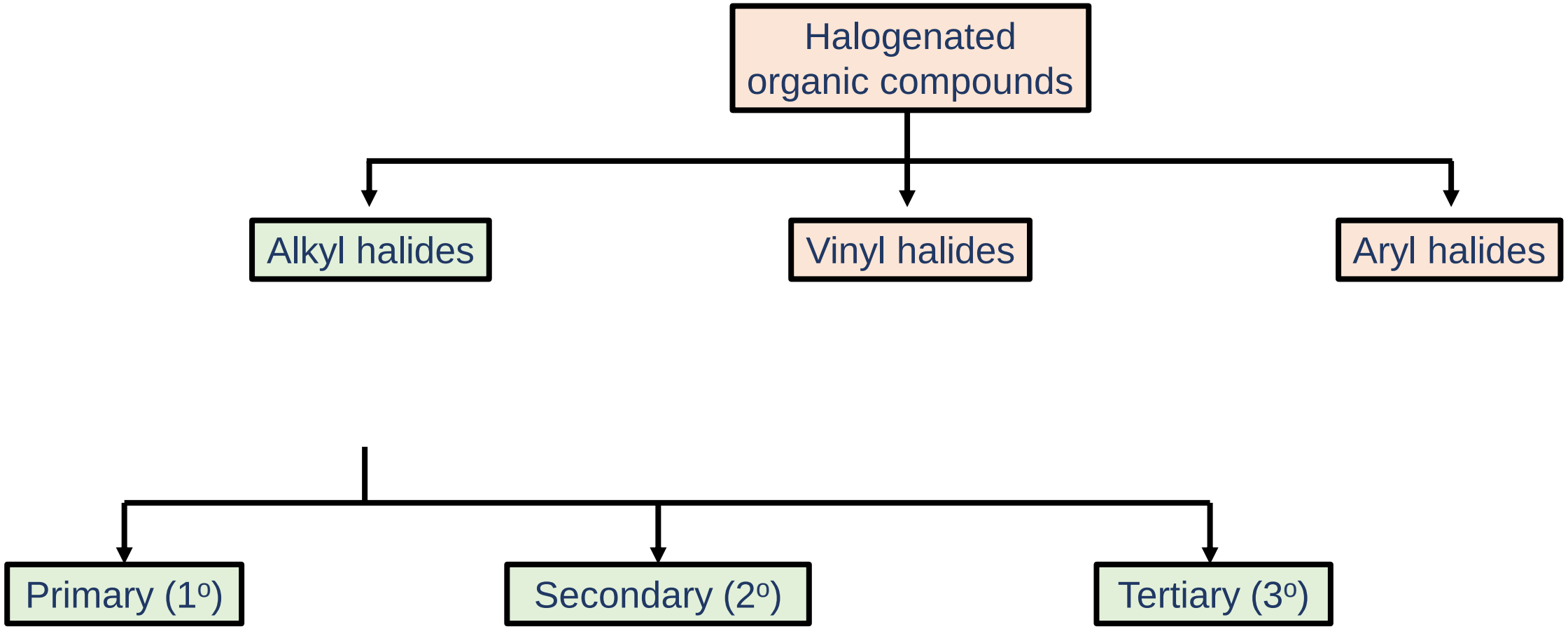
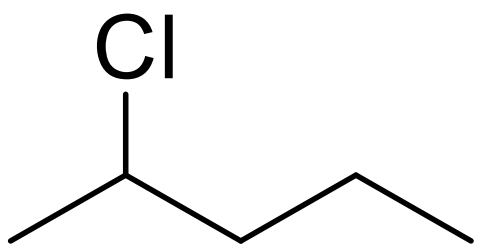
Recommended Textbook:

Chapter 6 in *Organic Chemistry*, 8th Edition, L. G. Wade, Jr., **2010**, Prentice Hall (Pearson Education)

What is alkyl halide?



IUPAC Nomenclature



2-chloropentane

Prefixes

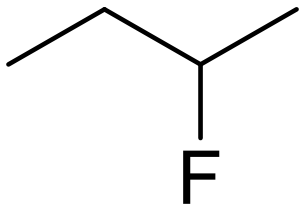
F =

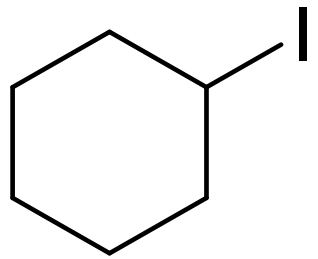
Cl =

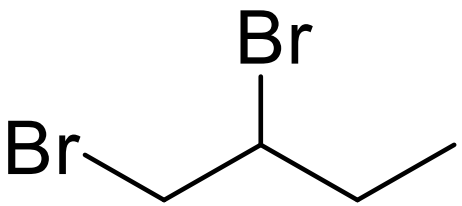
Br =

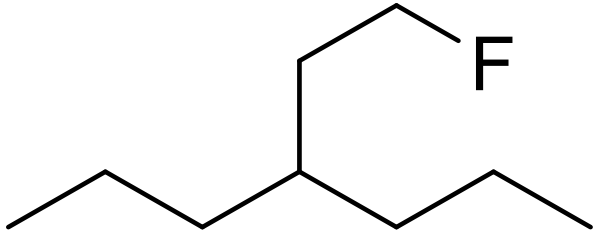
I =

IUPAC Nomenclature









Common Uses

1) Solvents

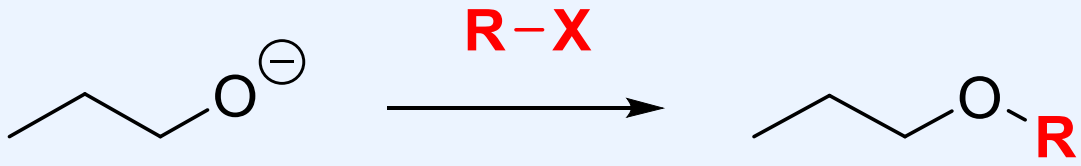
CH_2Cl_2
dichloromethane

$CHCl_3$
trichloromethane

CCl_4
tetrachloromethane

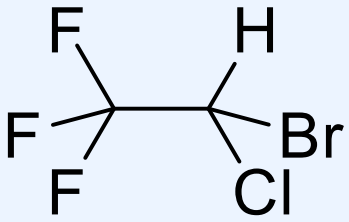
CH_3CCl_3
1,1,1-trichloroethane

2) Reagents



3) Anesthetics

$CHCl_3$
trichloromethane



2-bromo-2-chloro-1,1,1-trifluoroethane

Common Uses

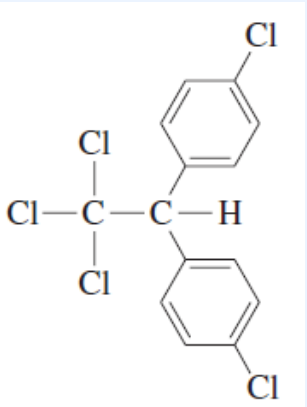
4) Refrigerants & Foaming Agents

freons / chlorofluorocarbons

CF_2Cl_2
dichlorodifluoromethane

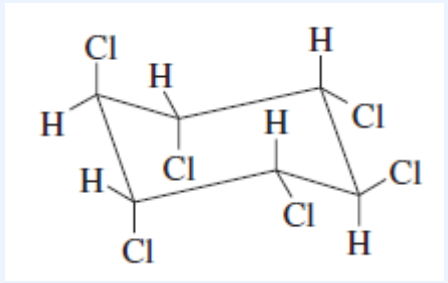
$CHFCl_2$
dichlorofluoromethane

5) Pesticides



DDT (**D**ichloro**D**iphenylTrichloroethane)

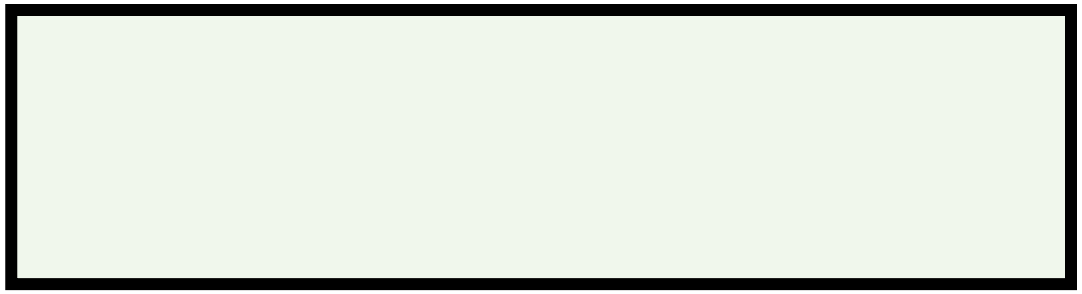
1,1,1-trichloro-2,2-bis-(*p*-chlorophenyl)ethane

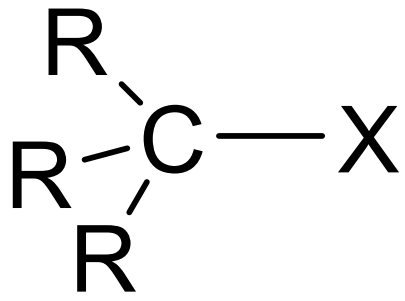


lindane

Structure – Dipole moment (μ)

Unit = debyes (*D*)





δ is the amount of charge separation

	I	<	Br	<	Cl	<	F
electronegativity:	2.7		3.0		3.2		4.0

d is the bond length.

	C—F	<	C—Cl	<	C—Br	<	C—I
bond length:	1.38 Å		1.78 Å		1.94 Å		2.14 Å

	C—I	<	C—Br	<	C—F	<	C—Cl
dipole moment, μ:	1.29 D		1.48 D		1.51 D		1.56 D

Structure – Dipole moment (μ)

Molecular dipole moments

X	CH_3X	CH_2X_2	CHX_3	CX_4
F	1.82 D	1.97 D	1.65 D	0
Cl	1.94 D	1.60 D	1.03 D	0
Br	1.79 D	1.45 D	1.02 D	0
I	1.64 D	1.11 D	1.00 D	0

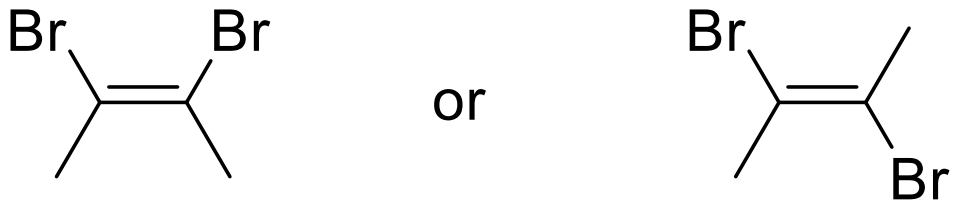
Structure – Dipole moment (μ)

Example 1

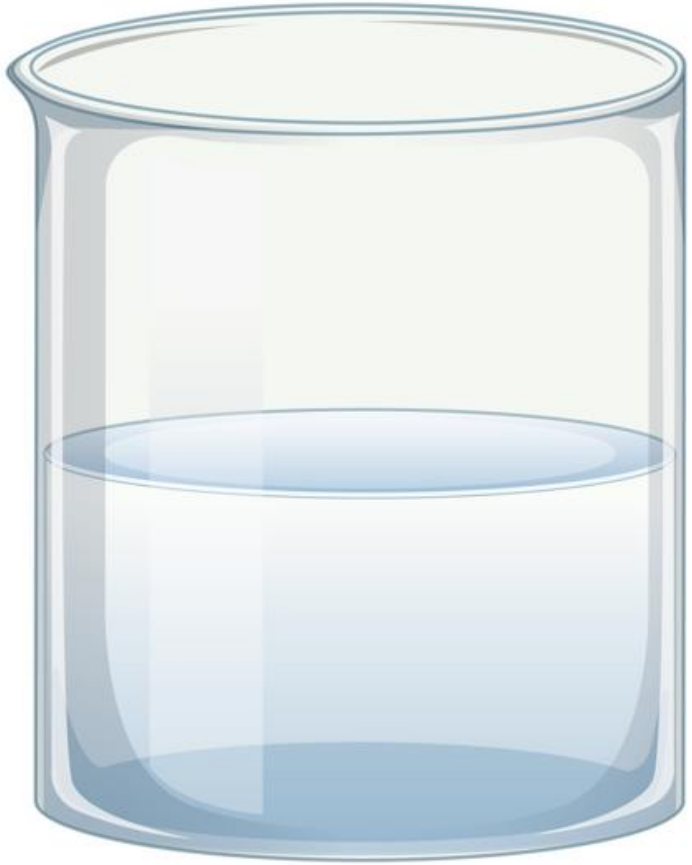
For each pair of compounds, predict which one has the higher molecular dipole moment

(a) chloroethane or iodoethane

(b) 1-bromopropane or cyclopropane

(c) 

Physical Properties – Boiling Points



Intermolecular forces

1) London force

2) Dipole-dipole attractions

3) Hydrogen bonding

Physical Properties – Boiling Points

ethyl fluoride, bp –38 °C

ethyl chloride, bp 12 °C

ethyl bromide, bp 38 °C

ethyl iodide, bp 72 °C

Halogen	van der Waals Radius (10^{-8} cm)
F	1.35
Cl	1.8
Br	1.95
I	2.15
H (for comparison)	1.2

Physical Properties – Boiling Points

Compound	Molecular Weight	Boiling Point (°C)
$CH_3—F$	34	−78
$CH_3—Cl$	50.5	−24
$CH_3—Br$	95	4
$CH_3—I$	142	42
CH_2Cl_2	85	40
$CHCl_3$	119	61
CCl_4	154	77
$CH_3CH_2—F$	48	−38
$CH_3CH_2—Cl$	64.5	12
$CH_3CH_2—Br$	109	38
$CH_3CH_2—I$	156	72

Compound	Molecular Weight	Boiling Point (°C)
$CH_3CH_2CH_2—F$	62	3
$CH_3CH_2CH_2—Cl$	78.5	47
$CH_3CH_2CH_2—Br$	123	71
$CH_3CH_2CH_2—I$	170	102
$(CH_3)_2CH—Cl$	78.5	36
$(CH_3)_2CH—Br$	123	59
$(CH_3)_2CH—I$	170	89
$CH_3CH_2CH_2CH_2—F$	76	33
$CH_3CH_2CH_2CH_2—Cl$	92.5	78
$CH_3CH_2CH_2CH_2—Br$	137	102
$CH_3CH_2CH_2CH_2—I$	184	131
$(CH_3)_3C—Cl$	92.5	52
$(CH_3)_3C—Br$	137	73
$(CH_3)_3C—I$	184	100

Physical Properties – Density

Compound	Density (g/mL)
$CH_3—F$	
$CH_3—Cl$	0.92
$CH_3—Br$	1.68
$CH_3—I$	2.28
CH_2Cl_2	1.34
$CHCl_3$	1.50
CCl_4	1.60
$CH_3CH_2—F$	0.72
$CH_3CH_2—Cl$	0.90
$CH_3CH_2—Br$	1.46
$CH_3CH_2—I$	1.94

Compound	Density (g/mL)
$CH_3CH_2CH_2—F$	0.80
$CH_3CH_2CH_2—Cl$	0.89
$CH_3CH_2CH_2—Br$	1.35
$CH_3CH_2CH_2—I$	1.75
$(CH_3)_2CH—Cl$	0.86
$(CH_3)_2CH—Br$	1.31
$(CH_3)_2CH—I$	1.70
$CH_3CH_2CH_2CH_2—F$	0.78
$CH_3CH_2CH_2CH_2—Cl$	0.89
$CH_3CH_2CH_2CH_2—Br$	1.28
$CH_3CH_2CH_2CH_2—I$	1.62
$(CH_3)_3C—Cl$	0.84

Physical Properties

Example 2

For each pair of compounds, predict which compound has the higher boiling point.

(a) 2-bromopropane and 1-bromobutane

(b) 2-chlorooopropane and 2-bromo-2-methylpropane

(c) 1-bromobutane and 1-chlorobutane

Physical Properties

Example 3

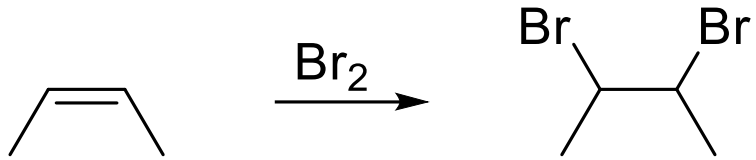
- When water is shaken with hexane, the two liquids separate into two phases. Which compound is present in the top phase, and which is present in the bottom phase?
- When water is shaken with chloroform, a similar two-phase system results. Again, which compound is present in each phase?
- What do you expect to happen when water is shaken with ethanol (CH_3CH_2OH)?



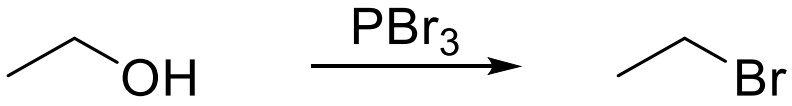
Synthesis of Alkyl Halides

(a) from alkanes: Free-Radical Halogenation
(revision)

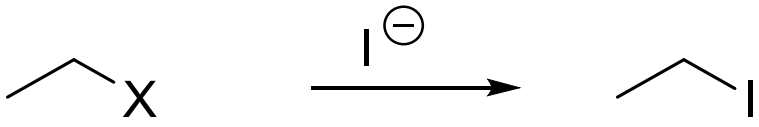
(b) from alkenes & alkynes: Addition
(in the following topic)



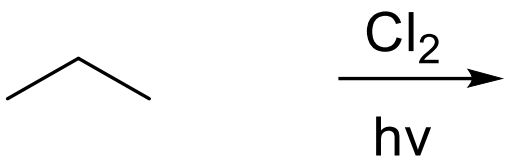
(c) from alcohols: Substitution
(in the following topic)



(d) from other halides: Substitution
(in the Synthesis part)



Synthesis - Free-Radical Halogenation



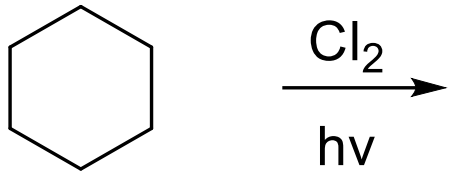
- **Poor selectivity**
- **Multiple substitution**

} **Mixture of products** → **Poor yield**

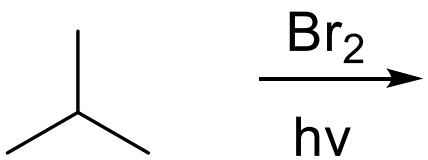
Synthesis - Free-Radical Halogenation

Successful reactions:

- Equivalent hydrogens



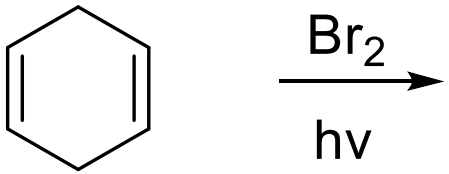
- Tertiary free-radical intermediate

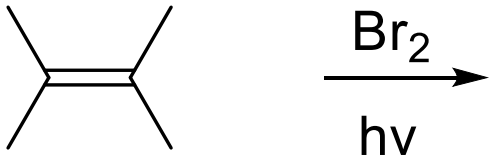


Synthesis - Free-Radical Halogenation

Successful reactions:

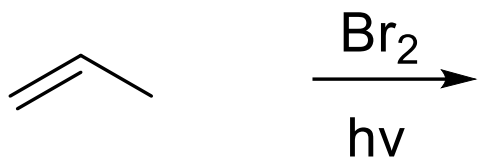
- Allylic bromination



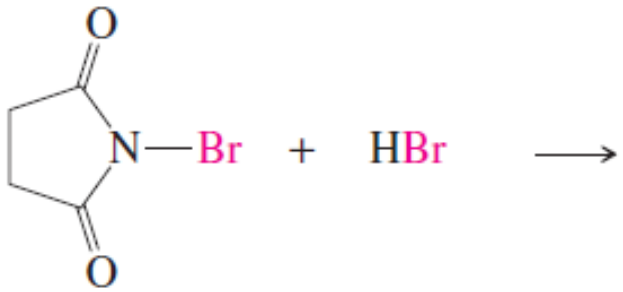


Synthesis - Free-Radical Halogenation

- Allylic bromination – side reactions



- Solution: using *N*-bromosuccinimide (NBS)

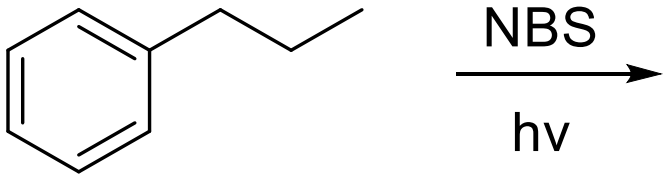


N-bromosuccinimide (NBS)

Synthesis - Free-Radical Halogenation

Successful reactions:

- Benzylic bromination



Synthesis - Free-Radical Halogenation

Example 4

Show how free-radical halogenation might be used to synthesize the following compounds. In each case, explain why we expect to get a single major product.

(a) 1-chloro-2,2-dimethylpropane

(b) 2-bromo-2-methylbutane

(c)