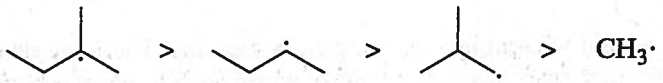
10 RADICAL REACTIONS

SOLUTIONS TO PROBLEMS

10.1



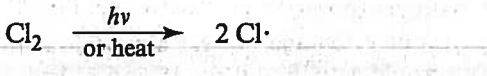
3° > 2° > 1° > Methyl

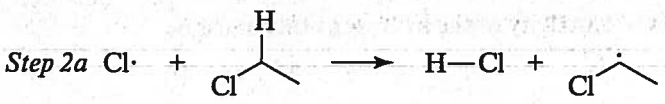
10.2 The compounds all have different boiling points. They could, therefore, be separated by careful fractional distillation. Or, because the compounds have different vapor pressures, they could easily be separated by gas chromatography. GC/MS (gas chromatography/mass spectrometry) could be used to separate the compounds as well as provide structural information from their mass spectra.

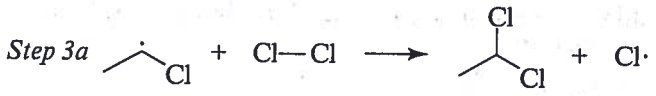
10.3 Their mass spectra would show contributions from the naturally occurring ^{35}Cl and ^{37}Cl isotopes. The natural abundance of ^{35}Cl is approximately 75% and that of ^{37}Cl is approximately 25%. Thus, for CH_3Cl, containing only one chlorine atom, there will be an M^+ peak and an M^++2 peak in roughly a 3 : 1 (0.75 : 0.25) ratio of intensities. For CH_2Cl_2 there will be M^+, M^++2, and M^++4 peaks in roughly a 9 : 6 : 1 ratio, respectively. [The probability of a molecular ion M^+ with both chlorine atoms as ^{35}Cl is (.75)(.75) = .56, the probability of an M^++2 ion from one ^{35}Cl and one ^{37}Cl is 2(.75)(.25) = .38, and the probability of an M^++4 ion peak from both chlorine atoms as ^{37}Cl is (.25)(.25) = 0.06; thus, their ratio is 9 : 6 : 1.] For $CHCl_3$ there will be M^+, M^++2, and M^++4, and M^++6 peaks in approximately a 27 : 27 : 9 : 1 ratio, respectively (based on a calculation by the same method). (This calculation does not take into account the contribution of ^{13}C, ^{2}H, and other isotopes, but these are much less abundant.)

10.4 The use of a large excess of chlorine allows all of the chlorinated methanes (CH_3Cl, CH_2Cl_2, and $CHCl_3$) to react further with chlorine.

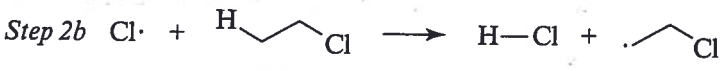
10.5

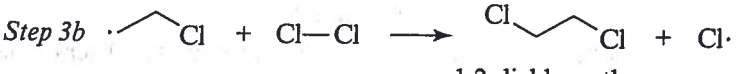






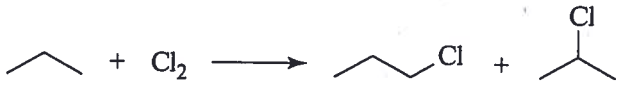
1,1-dichloroethane





1,2-dichloroethane

10.6 (a) There is a total of eight hydrogen atoms in propane. There are six equivalent 1° hydrogen atoms, replacement of any one of which leads to propyl chloride, and there are two equivalent 2° hydrogen atoms, replacement of any one of which leads to isopropyl chloride.



If all the hydrogen atoms were equally reactive, we would expect to obtain 75% propyl chloride and 25% isopropyl chloride:

$$\% \text{ Propyl chloride} = {}^{6}/_{8} \times 100 = 75\%$$

$$\% \text{ Isopropyl chloride} = {}^{2}/_{8} \times 100 = 25\%$$

(b) Reasoning in the same way as in part (a), we would expect 90% isobutyl chloride and 10% *tert*-butyl chloride, if the hydrogen atoms were equally reactive.



$$\% \text{ Isobutyl chloride} = {}^{9}/_{10} \times 100 = 90\%$$

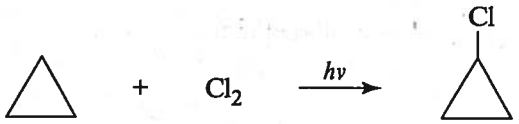
$$\% \textit{ tert}\text{-Butyl chloride} = {}^{1}/_{10} \times 100 = 10\%$$

(c) In the case of propane (see Section 10.5), we actually get more than twice as much isopropyl chloride (55%) than we would expect if the 1° and 2° hydrogen atoms were equally reactive (25%). Clearly, then, 2° hydrogen atoms are more than twice as reactive as 1° hydrogen atoms.

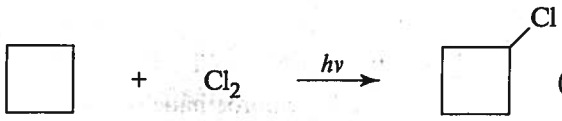
In the case of isobutane, we get almost four times as much *tert*-butyl chloride (37%) as we would get (10%) if the 1° and 3° hydrogen atoms were equally reactive. The order of reactivity of the hydrogens then must be

$$3° > 2° > 1°$$

10.7 The hydrogen atoms of these molecules are all equivalent. Replacing any one of them yields the same product.



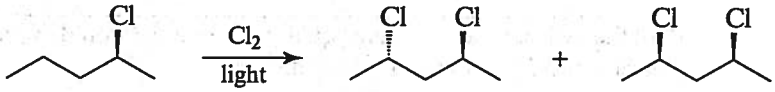
(+ more highly chlorinated products)



(+ more highly chlorinated products)

We can minimize the amounts of more highly chlorinated products formed by using a large excess of the cyclopropane or cyclobutane. (And we can recover the unreacted cyclopropane or cyclobutane after the reaction is over.)

10.8 (a)  (b) 

10.9 (a) 

(*S*)-2-Chloropentane (2*S*,4*S*)-2,4-Dichloropentane (2*R*,4*S*)-2,4-Dichloropentane

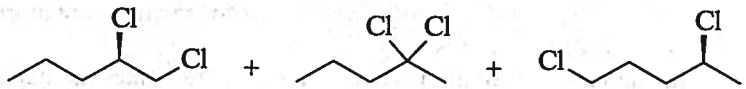
(b) They are diastereomers. (They are stereoisomers, but they are not mirror images of each other.)

(c) No, (2*R*,4*S*)-2,4-dichloropentane is achiral because it is a meso compound. (It has a plane of symmetry passing through C3.)

(d) No, the achiral meso compound would not be optically active.

(e) Yes, by fractional distillation or by gas chromatography. (Diastereomers have different physical properties. Therefore, the two isomers would have different vapor pressures.)

(f and g) In addition to the (2*S*,4*S*)-2,4-dichloropentane and (2*R*,4*S*)-2,4-dichloropentane isomers described previously, we would also get (2*S*,3*S*)-2,3-dichloropentane, (2*S*,3*R*)-2,3-dichloropentane and the following:



(optically active) (optically inactive) (optically active)

10.10 (a) The only fractions that would contain chiral molecules (as enantiomers) would be those containing 1-chloro-2-methylbutane and the two diastereomers of 2-chloro-3-methylbutane. These fractions would not show optical activity, however, because they would contain racemic forms of the enantiomers.