Solutions to Exercises, Chapter 20

20.1

20.2

$$CH_3CH=CH\overset{\bullet}{C}H_2 > CH_3CH_2\overset{CH_3}{\underset{\bullet}{C}}CH_3 > CH_3CH_2\overset{\bullet}{C}HCH_3 > CH_3\overset{CH_3}{\underset{}{C}}H\overset{\bullet}{C}H_2 > H_3C\bullet$$

allylic   tertiary   secondary   primary   methyl
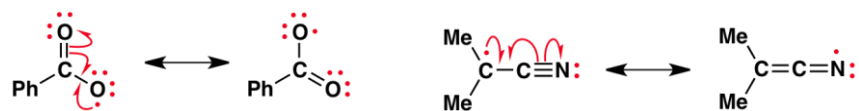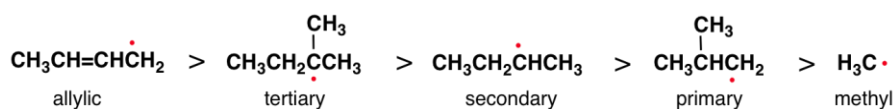
20.3 Concentrations of radicals are small, so the probability of one encountering another is very small (although radical coupling can be one of the steps which terminates a radical chain mechanism). Reaction of the methyl radical with the more abundant Cl_2 to form chloromethane plus a chlorine radical occurs more often; this is one of the chain propagation steps which occurs repeatedly, and is the main reaction to give chloromethane (see Scheme 20.1).
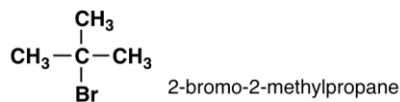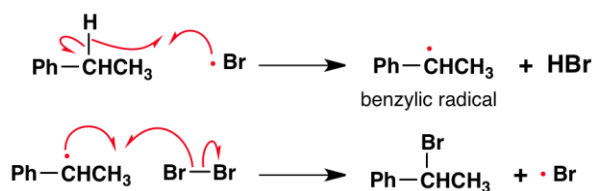
20.4
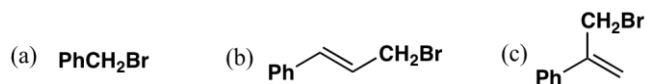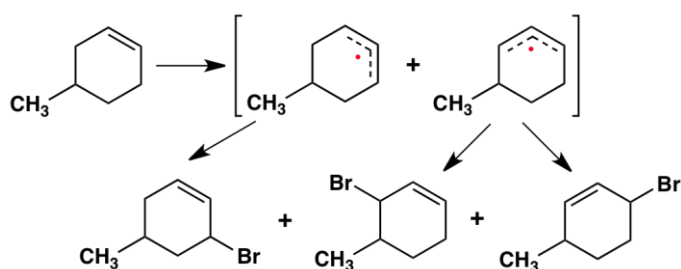

20.5

20.6

2-bromo-2-methylpropane

20.7

benzylic radical

20.8

(a) **PhCH₂Br** (b)   (c)
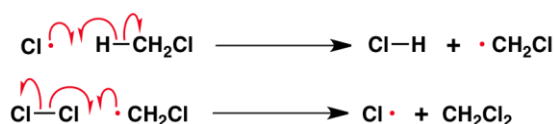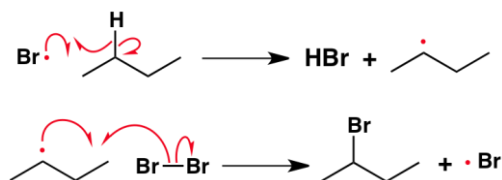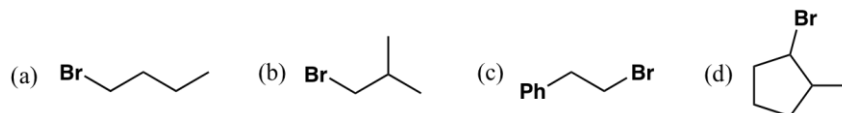
(d) Two allylic radical intermediates are possible which give three products (all of which have *cis* and *trans* isomers).

20.9

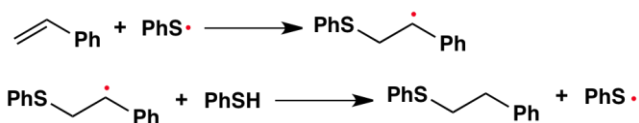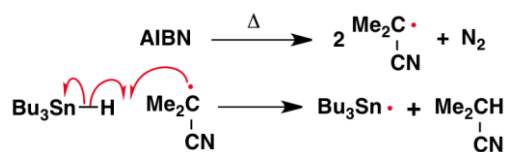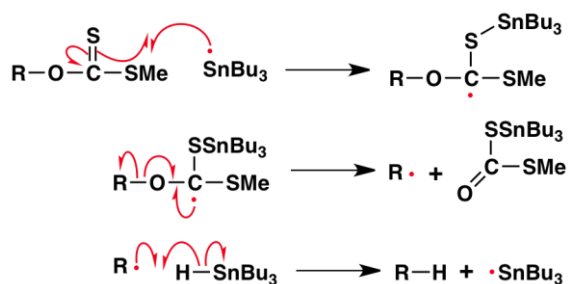(a)   (b)   (c)   (d)

20.10

Initiation:

Propagation:

$$\text{CH}_2=\text{CH-Ph} + \text{PhS}^\bullet \longrightarrow \text{PhS-CH}_2\text{-}{}^\bullet\text{CH-Ph}$$

$$\text{PhS-CH}_2\text{-}{}^\bullet\text{CH-Ph} + \text{PhSH} \longrightarrow \text{PhS-CH}_2\text{-CH}_2\text{-Ph} + \text{PhS}^\bullet$$

20.11

Initiation:

$$\text{AIBN} \xrightarrow{\Delta} 2\ \underset{\text{CN}}{\text{Me}_2\text{C}^\bullet} + \text{N}_2$$

$$\text{Bu}_3\text{Sn-H} \quad \underset{\text{CN}}{\text{Me}_2\text{C}^\bullet} \longrightarrow \text{Bu}_3\text{Sn}^\bullet + \underset{\text{CN}}{\text{Me}_2\text{CH}}$$

Propagation:

$$\text{R-O-C(=S)-SMe} \quad {}^\bullet\text{SnBu}_3 \longrightarrow \text{R-O-}\overset{\text{S-SnBu}_3}{\underset{\bullet}{\text{C}}}\text{-SMe}$$

$$\text{R-O-}\overset{\text{SSnBu}_3}{\underset{\bullet}{\text{C}}}\text{-SMe} \longrightarrow \text{R}^\bullet + \overset{\text{SSnBu}_3}{\underset{\text{O}}{\text{C}}}\text{-SMe}$$

$$\text{R}^\bullet \quad \text{H-SnBu}_3 \longrightarrow \text{R-H} + {}^\bullet\text{SnBu}_3$$

20.12

Initiation:

$$\text{AIBN} \xrightarrow{\Delta} 2\ \underset{\text{CN}}{\text{Me}_2\text{C}^\bullet} + \text{N}_2$$

$$\text{PhS-H} + \underset{\text{CN}}{\text{Me}_2\text{C}^\bullet} \longrightarrow \text{PhS}^\bullet + \underset{\text{CN}}{\text{Me}_2\text{CH}}$$
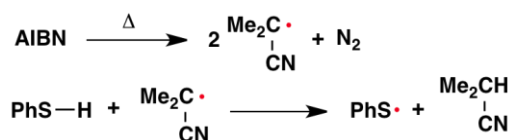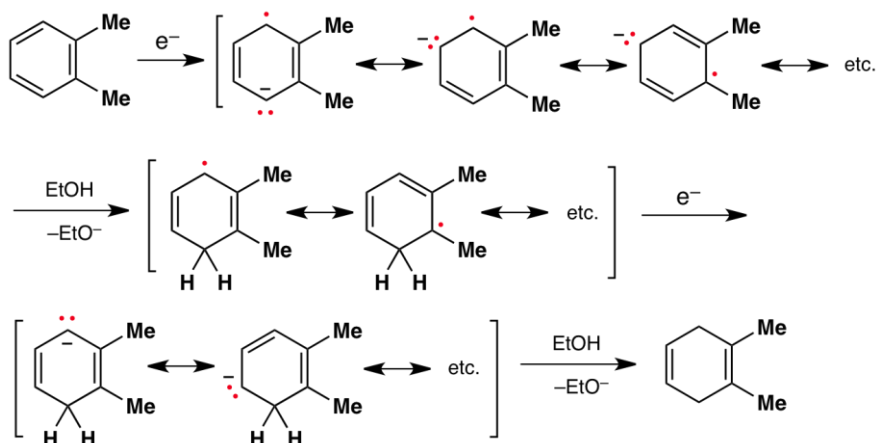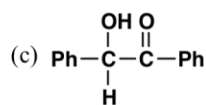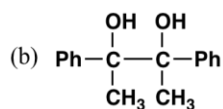
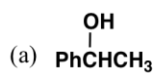Propagation:
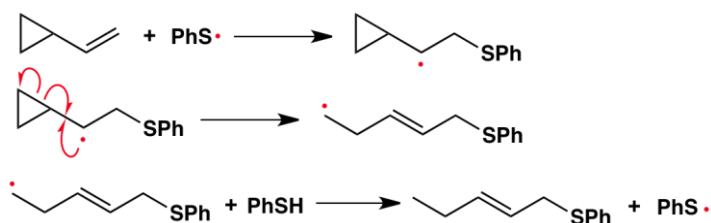
20.13
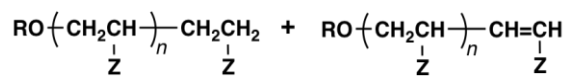
20.14
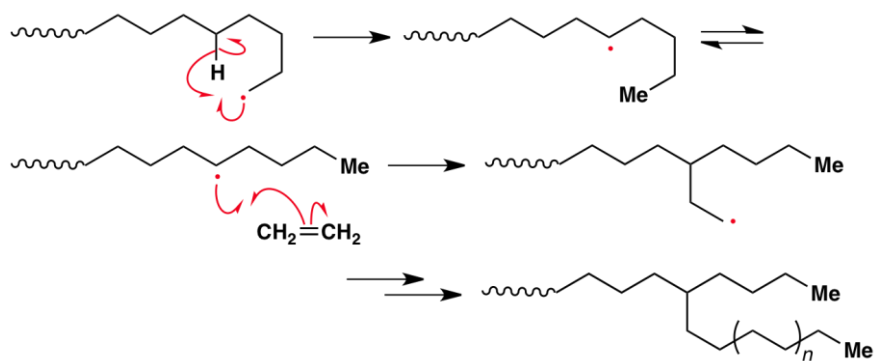
20.15

Following the initial electron transfer to give the delocalized intermediate radical anion, protonation occurs mainly at position 3 *ortho* to a methyl group. Protonation of the cyclohexadienyl anion, formed by the second electron transfer, occurs mainly at the new position 3 (*ortho* to the other methyl group) to give the product shown.
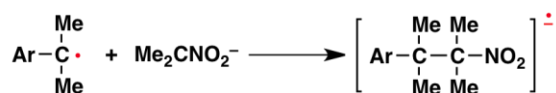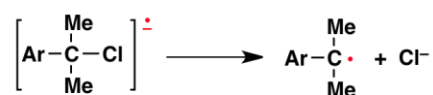
OXFORD
UNIVERSITY PRESS

20.16

(a) PhCHCH₃ with OH above

(b) Ph—C—C—Ph with OH, OH above and CH₃, CH₃ below

(c) Ph—C—C—Ph with OH, O above and H below

20.17

Initiation:

Propagation:

20.18