

REACTION REVIEW

A STUDENT WHO HAS MASTERED THIS MATERIAL SHOULD BE ABLE TO PREDICT PRODUCTS, IDENTIFY REACTANTS, GIVE REACTION CONDITIONS, PROPOSE SYNTHESSES, AND PROPOSE MECHANISMS (AS LISTED BELOW) USING THESE:

Substitution Reactions

S_N2 (proceeds with inversion). R must be methyl or primary if the nucleophile is a strong base; it may also be secondary if the nucleophile is a weak base. The bulky strong base $(CH_3)_3COK$ gives elimination even if the substrate is primary (see below). A knowledge of the mechanism is important. An acid-base reaction is sometimes necessary to prepare the nucleophile before the S_N2 reaction proper can be performed.

S_N1 (proceeds with racemization). R must be tertiary, the solvent should be polar and protic, and the nucleophile must be a weak base for this reaction to occur reliably. A knowledge of the mechanism is important. The reaction of alcohols with hydrogen halides is S_N1 in tertiary substrates and S_N2 in primary substrates.

Alkyl halide syntheses: The reactions of alcohols with hydrogen halides, $SOCl_2$, and PBr_3

Carboxylate ester synthesis: Acid chlorides plus alcohols. To make the acid chloride, react the corresponding carboxylic acid with $SOCl_2$.

Free Radical Halogenation with Cl_2 and Br_2 ; F_2 is overactive, and I_2 is unreactive. Br_2 is more selective than Cl_2 . A knowledge of the mechanism is important.

Elimination Reactions:

$E2$, usually dehydrohalogenation (*anti* elimination). Most $E2$ reactions give the more stable alkene as the major product; the starting substrate must be secondary or tertiary. Strong, bulky bases (typically potassium *tert*-butoxide) attack less sterically hindered protons and give elimination when the alkyl halide is primary. A knowledge of the mechanism is important.

Dehydration. This reaction of alcohols gives the more stable alkene as the major product; rearrangements occur when favored by energy considerations. A knowledge of the mechanism is important.

Addition Reactions:

Hydrogenation of alkenes and alkynes with the usual metal catalysts (Pt, Pd, Ni) to give alkanes, and the hydrogenation of alkynes to give both *cis* and *trans* alkenes.

Markovnikov addition: Addition of HX (that is, HF, HCl, HBr (no peroxides), HI, H_2SO_4 , etc.) to alkenes and alkynes. A knowledge of the mechanism is important.

Addition of water: Hydration, oxymercuration-demercuration (Markovnikov addition, no rearrangements), and hydroboration-oxidation (anti-Markovnikov, overall *syn* addition)

Anti-Markovnikov addition of HBr. Knowledge of the mechanism is important.

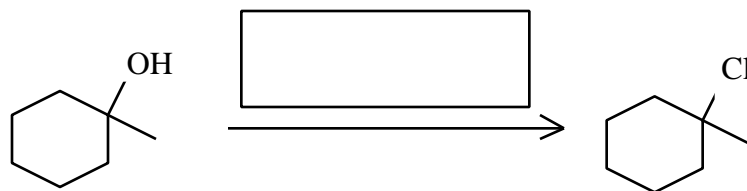
Addition of halogens (Br_2 and Cl_2), *anti* addition. A knowledge of the mechanism is important.

Glycols: Addition of $KMnO_4$ (cold) to make glycols (*syn* addition); epoxidation followed by hydrolysis of the epoxide (*syn* addition in the first step followed by inversion; overall *anti* addition). Knowledge of the mechanisms of the hydrolysis reaction is important.

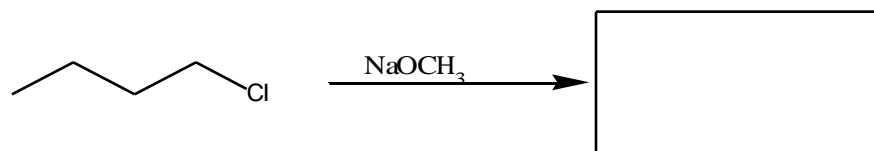
Degradation Reactions, using both ozonolysis and potassium permanganate

1. Supply the missing reactant, conditions, or product.

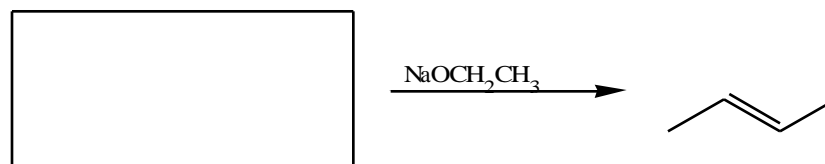
a)



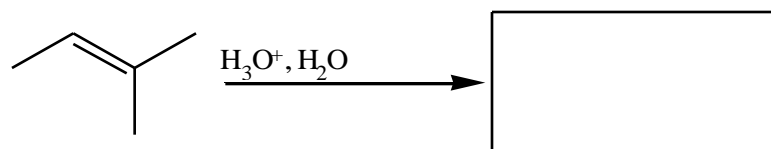
b)



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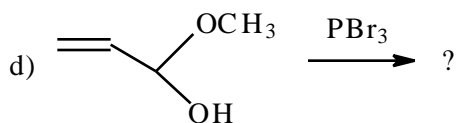
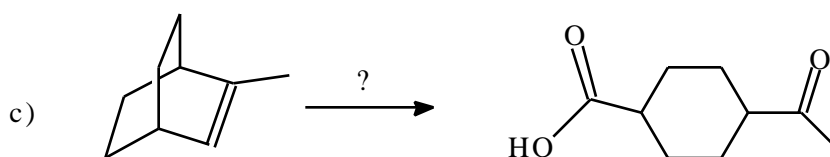
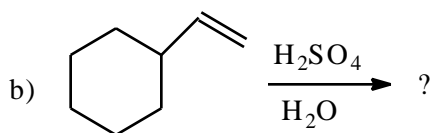
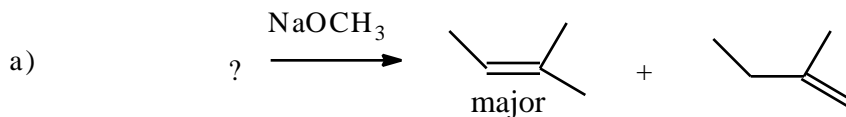


d)



2. Suggest a synthesis of cyclopentene from cyclopentane. *Hint: this takes more than one step!*

1. Give the structure of the major organic product(s) or supply the missing reactant/conditions or starting material. Show the stereochemistry of the products or starting material, if applicable.



2. Suggest an efficient synthesis of the following compounds:

a) Butylcyclohexane from ethane

b) *Trans*-2-butene from 2,3-dibromobutane

3. Propose a curved-arrow mechanism for the following reaction:

