

CHEM 222 section 01

LECTURE #03

Tues., Sept.11, 2007

Lecture topics & readings

Today's class

- continue reactions of alcohols

Before next class

- read ROH material: 10.1 - 10.4

Next class

- elimination of alcohols
- oxidation of alcohols
- overview of ethers & other Ch.10 rxns

(1)

10.1 Nucleophilic substitution of alcohols *continued...*

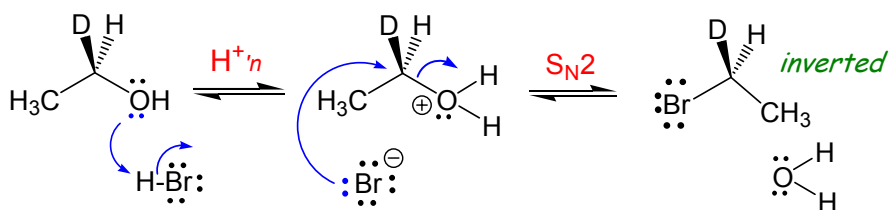
General mechanism: Activation (make good LG) + Substitution (Nu replaces LG)

1a) 3° ROH + HX: activation ($H^+ \cdot n$) + S_N1 ←*did example on board*

1b) 2° ROH + HX: $H^+ \cdot n$ + S_N1 ...with rearrangement? ←*on own...*

1c) 1° ROH + HX: $H^+ \cdot n$ + S_N2

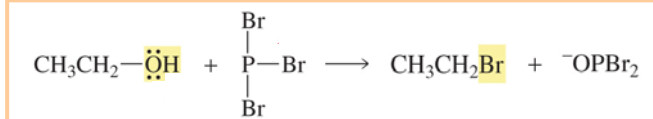
- Simple & fast with HI, HBr :



(2)

ROH Rxn Type 2: Other ways to replace OH with a good LG

b) Phosphorus
Trihalides
PX₃



Mechanism:
p.434

(5)

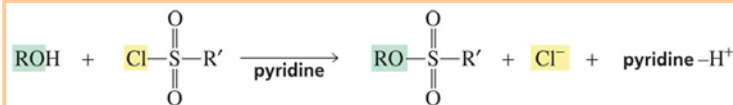
ROH Rxn Type 2: Summary - replacing OH with halide X

TARGET ROH → ?	REAGENTS TO USE (see Table 10.1)		
	1°	2°	3°
RCI	HCl / ZnCl ₂ (S _N 2) SOCl ₂ (S _N 2) PCl ₃ / py (S _N 2)	HCl (S _N 1) SOCl ₂ (S _N 2) PCl ₃ / py (S _N 2)	HCl (S _N 1)
RBr	HBr (S _N 2) PBr ₃ / py (S _N 2)	HBr (S _N 1) PBr ₃ / py (S _N 2)	HBr (S _N 1)
RI	HI (S _N 2) PI ₃ / py (S _N 2)	HI (S _N 1) PI ₃ / py (S _N 2)	HI (S _N 1)

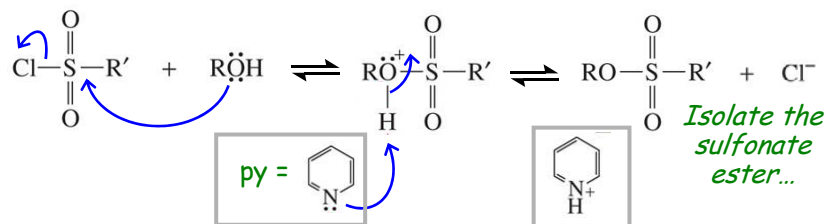
When possible: avoid S_N1, if foresee rearrangements...

(6)

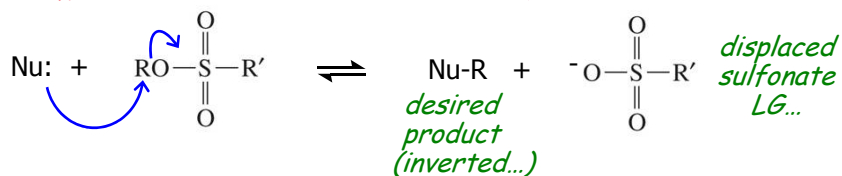
c) Sulfonyl chlorides
(Bruice 10.3)



Activation of ROH:



THEN S_N2 substitution: with whatever Nu you like...

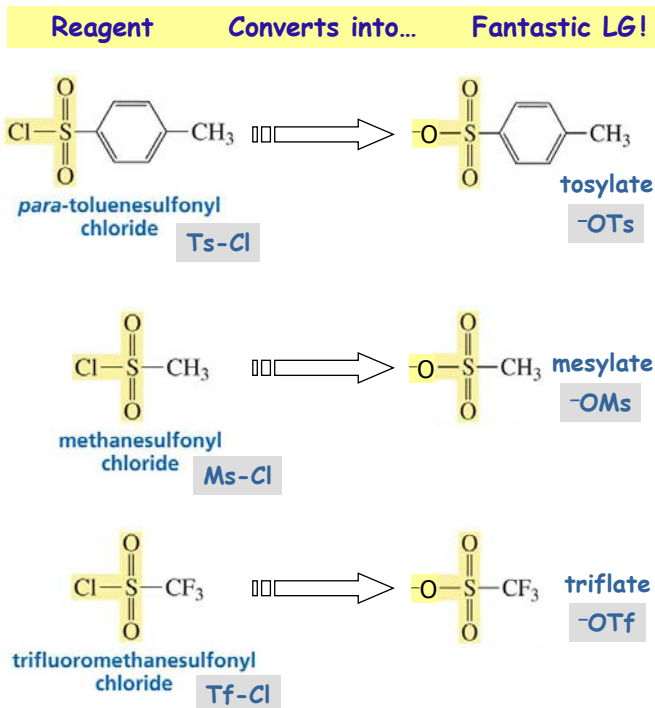


Sulfonate esters = great substitution substrates

(i) easy to make

(ii) great LG

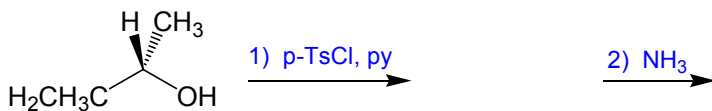
(iii) tolerate basic conditions



Why so great?
(~100x > Cl-...)

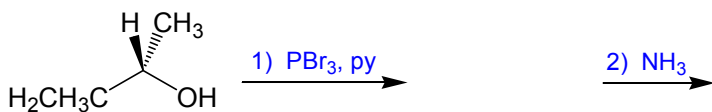
Converting alcohols into better substitution substrates:
sulfonate esters vs. halides... (compare p.437)

Note stereochemistry of products vs. original ROH:



(S)-2-butanol

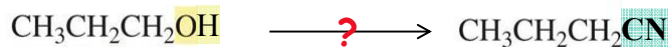
*PRACTICAL TIP:
Wash with dilute base
to liberate free amine*



(9)

Review the possibilities for this 2-step transformation

Try (a) via a sulfonate
(b) via a halide



(10)