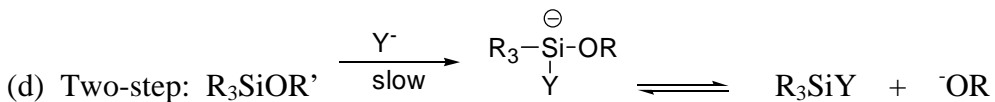
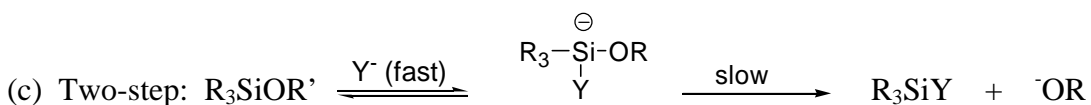
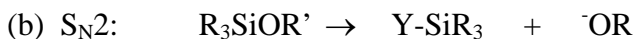


CHE 450 Homework 7  
Due Friday April 8, 2005

1. Question 3 in chapter 8 of your textbook (page 543).

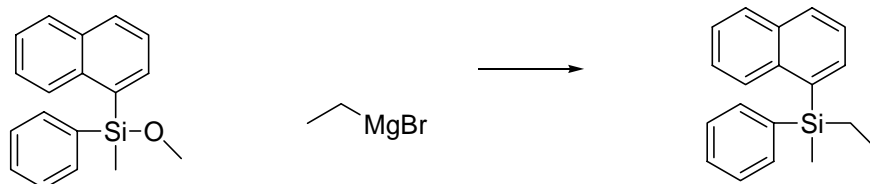
2. Silicon compounds of the type  $R_3SiOR$  undergo nucleophilic substitution. From the following experimental observations, decide which of the mechanisms shown is most likely.



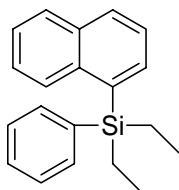
Experimental observations:

(a) Substitution almost always proceeds with retention or inversion--never with racemization.

(b) The reaction shown below gives only the product depicted:

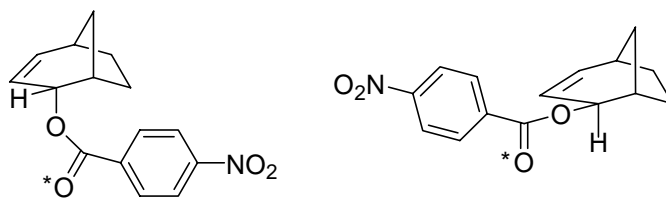


None of this product is formed.



(c) Acyloxysilanes (leaving group  $R'CO_2^-$ ) are considerably more reactive than alkoxy silanes.

3. Consider the solvolysis of the two isomeric chiral p-nitrobenzoates shown below.



- (a) Draw the structure of the free ion that would be formed by complete dissociation. What would be the stereochemistry of product formed from this ion?
- (b) The compounds labeled with  $^{18}\text{O}$  as indicated racemize during solvolysis;  $^{18}\text{O}$  equilibration is also observed. For the isomer on the left,  $k_{eq} = k_{rac}$ . What does this result imply about the structure of the ion pair?
- (c) For the isomer on the right,  $k_{eq} > k_{rac}$ . What does this result imply about the structure of the ion pair?
- (d) Propose a reason for the difference of behavior of the two isomers.