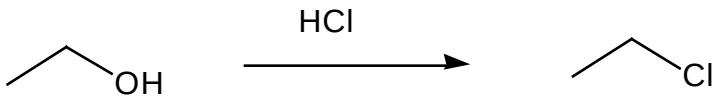
Hour Examination #3, Chemistry 302-302A, April 28, 2005

"Chemiftry is the art of decompounding bodies...."

Thomas Southwell, M.D. London, 1764.

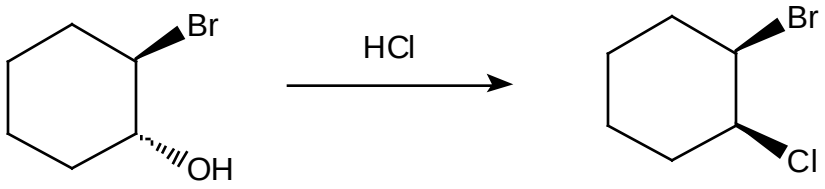
1 (20 points). Alcohols, R-OH, are generally converted into halides, R-X, on reaction with HX.

Thus:



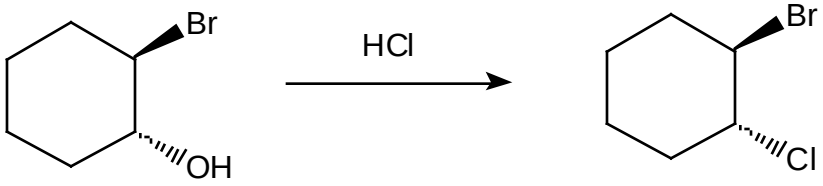
(a) Write a mechanism for this change.

(b) Professor Les Gometz, ever the generalist, expected that optically active alcohol **1** would follow a similar path. Also, being very sophisticated mechanistically, Les was confident that the stereochemistry of the product **2** would be as shown, and that **2** would still be optically active.



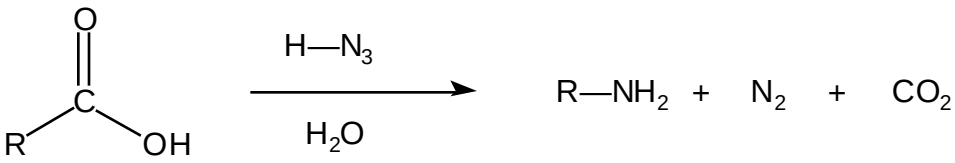
1 (optically active) **2** (optically active)

Imagine his surprise when the product turned out to be racemic **2a**. Explain mechanistically.

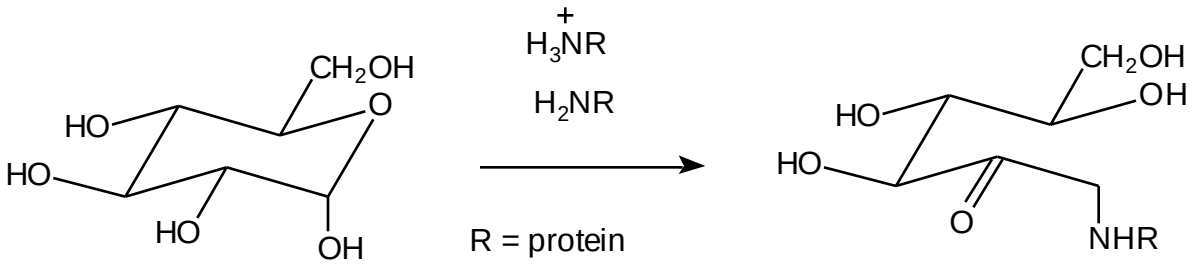


1 (optically active) **2a** (racemic)

2 (15 points). Provide a mechanism for the Schmidt reaction, shown below. Please note - the reagent really is hydrazoic acid, HN_3, not ammonia NH_3.



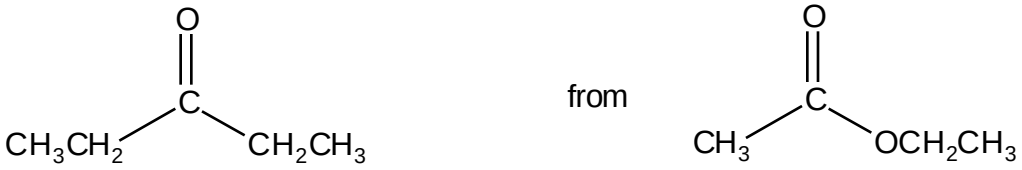
3 (15 points). The characteristic brown color of toast (and roast chicken) is the result of the Amadori reaction shown below. Provide a mechanism for this transformation:



4 (15 points). Provide syntheses of the following molecules from the indicated starting materials. No mechanisms are necessary and you may use inorganic reagents of your choice as well as LDA, LSD, LUMO, LSMFT, alcohols and alkyl halides containing no more than two carbons, and the tears of Hagga from Hagga's Hill (identify the cultural reference and you get 0.25 points).

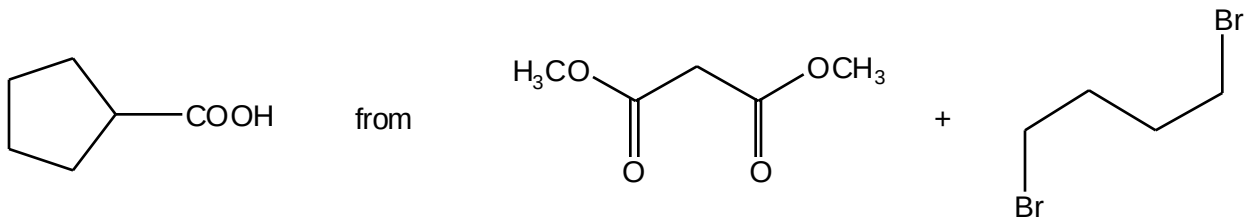
Please note that Princeton University has prohibited the use of any organolithium or Grignard reagents. They must cost too much.

(a)

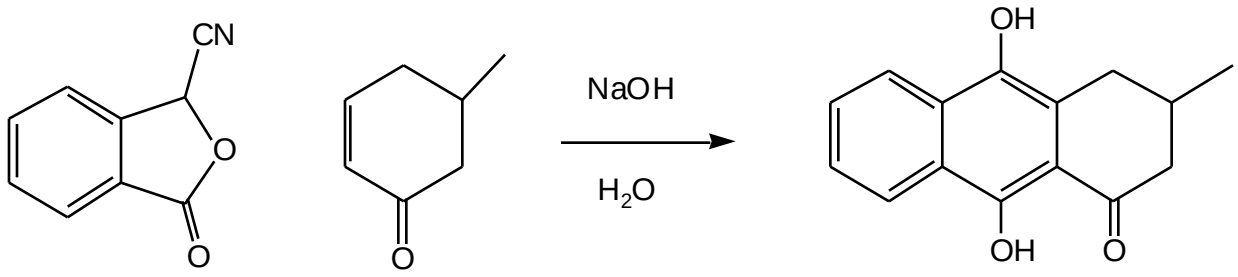


(b)

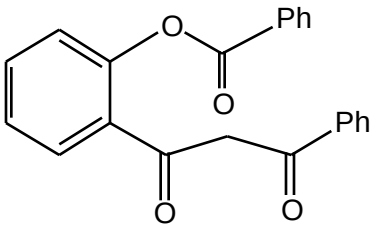
(c)



5 (15 points). The following transformation was important in the synthesis of pacybasin. Provide us with a good mechanism.



6 (20 points). The Baker-Venkataraman synthesis depends on transformations of the following kinds. Provide a structure for **X** and mechanisms for all transformations. Yes, we know this question is perilously close to a repeat, but this year we go further.....



$C_{22}H_{16}O_4$

KOH/H_2O

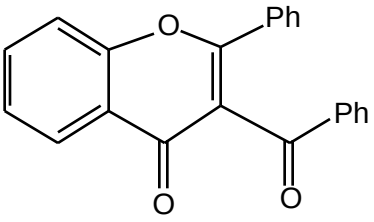
X $C_{22}H_{16}O_4$

IR: three strong peaks at ca. 1685 cm^{-1}, a broad peak at 3350 cm^{-1}.
Three signals in the ^{13}C NMR spectrum at ca. 190 ppm.

X

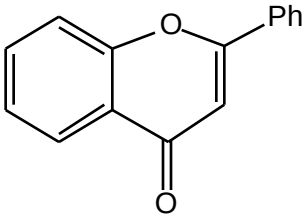
H_3O^+

H_2O



Y

KOH/H_2O



Z

"I pledge that I have not violated the Honour Code on this examination."