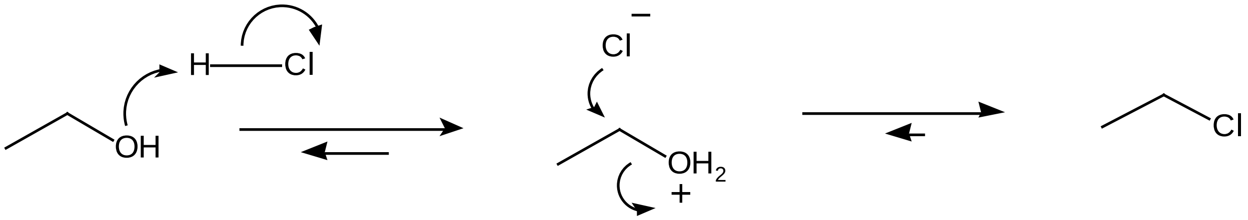
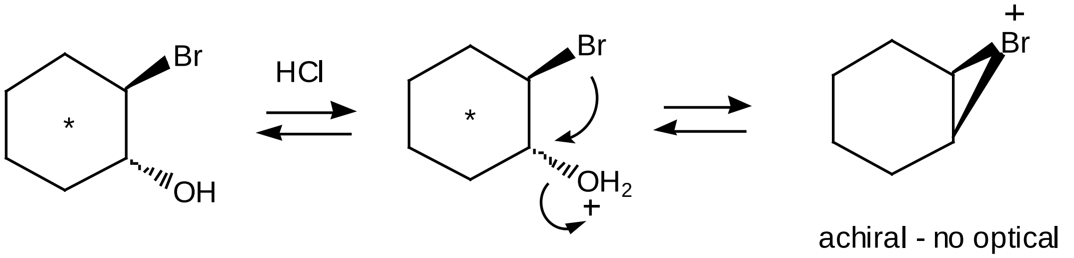
Answers to Hour Examination #3, Chemistry 302-302A, 2005

1. Part (a) better be easy......



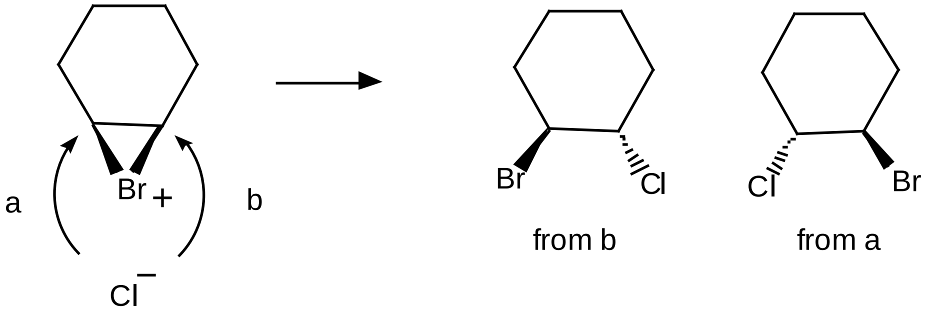
(b) Odd stereochemical result? Must be a Neighboring Group Problem. What's the internal nucleophile? Got to be that Br. The rest is easy.



1

* = optically active

achiral - no optical
activity possible beyond
this point

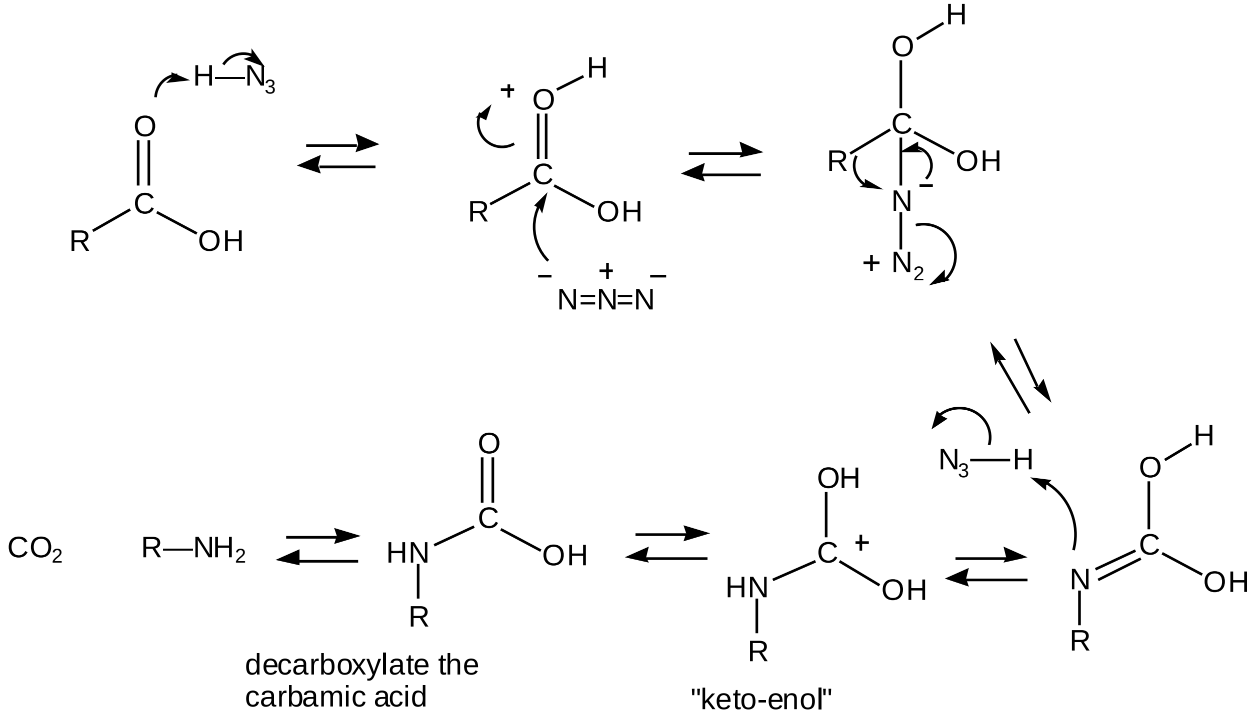


from b

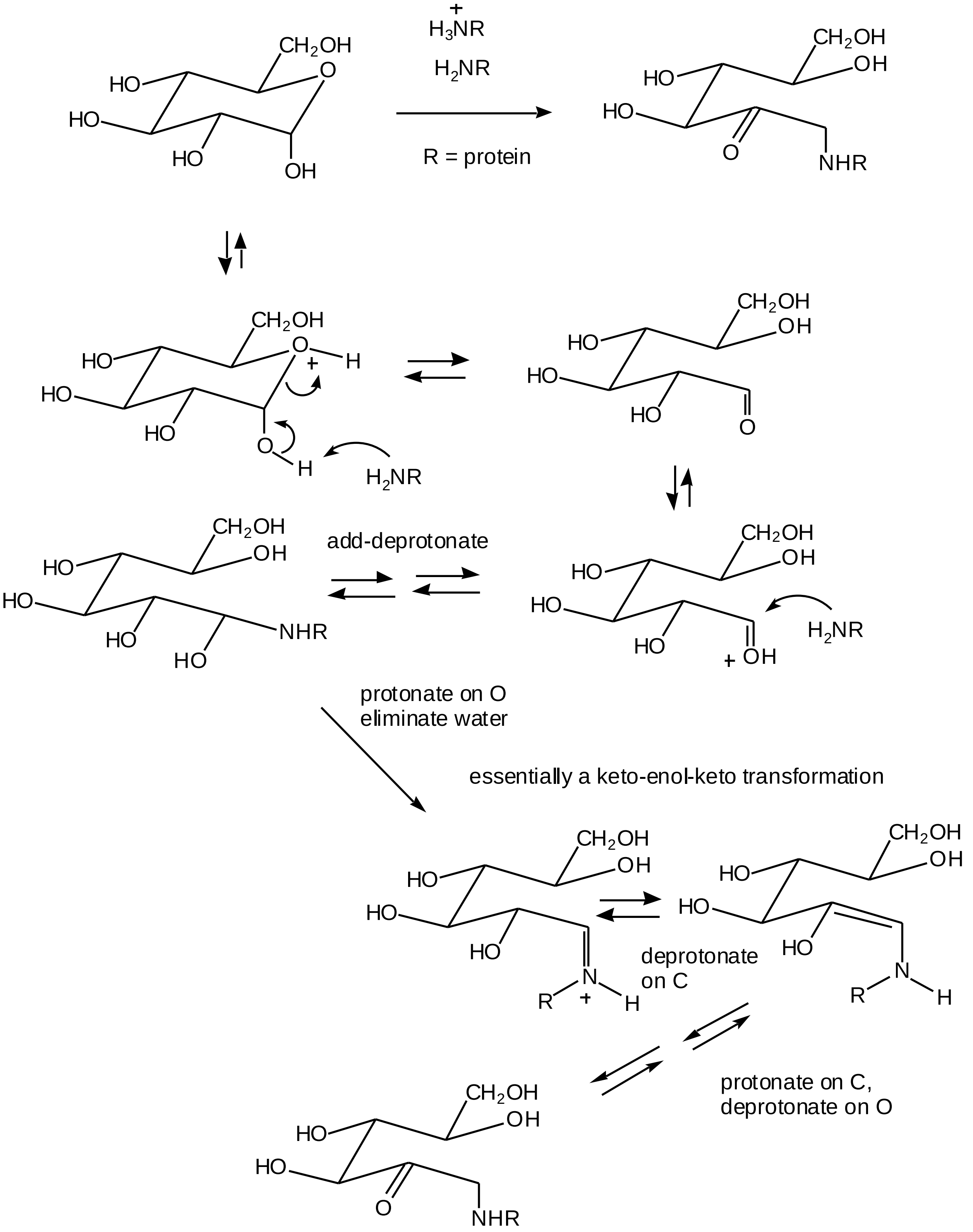
from a

2a (racemic)

2. A mechanism involving an initial acylium ion is also acceptable, but addition - elimination (with OH as leaving group) to give a Curtius - like process is not a good answer.



3. This problem is just an exercise in proton pushing, and doing keto-enol transformations.



4. There are two general non-oxidative ways of making ketones. One is to let carboxylic acids react with alkyllithiums. That answer is not allowed here, so the other general way, the acetoacetic ester synthesis must be it.
(a)

1. LDA, then CH_3I (alkylate alpha position)

2. full eq. of ethoxide (Claisen)

3. H_3O^+/H_2O (hydrolysis and decarboxylation)

(b)

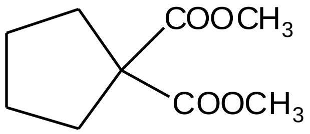
1. ethyl acetate plus a full equivalent of ethoxide (Claisen to anion)

2. Ethyl iodide (alkylation)

3. H_3O^+/H_2O (hydrolysis and decarboxylation).

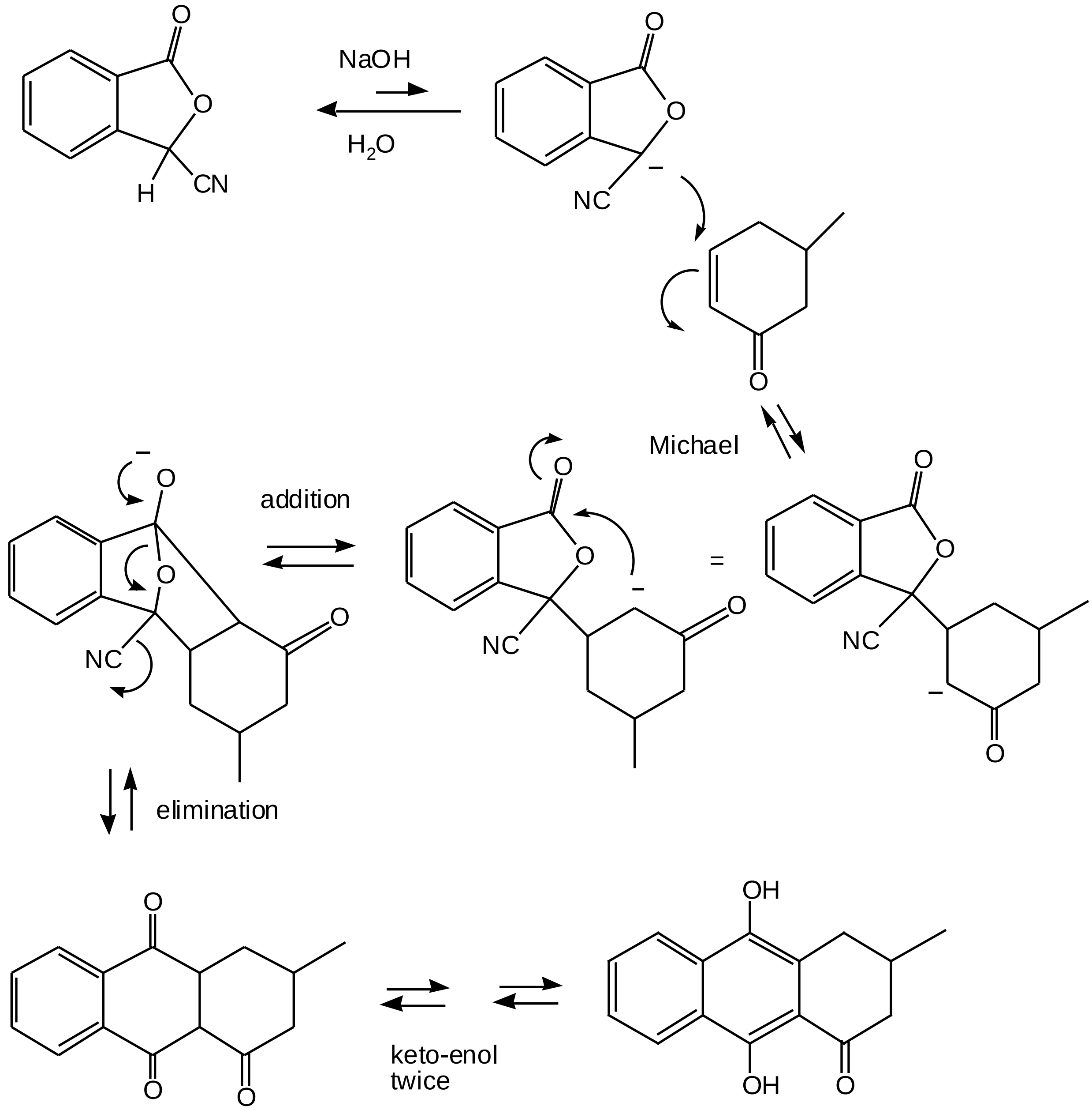
(c)

a. Two eq. methoxide with dimethyl malonate/1,4-dibromobutane does a double S_N2 to make

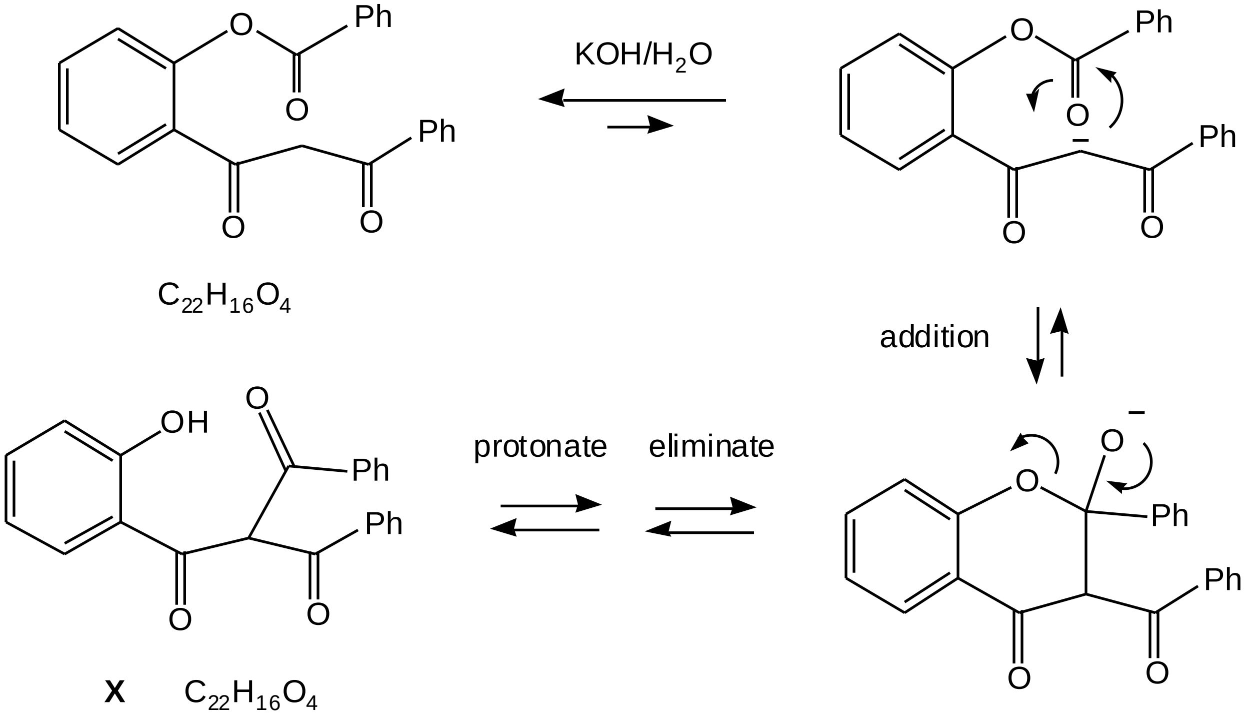


b. H_3O^+/H_2O and heat decarboxylates to the product.

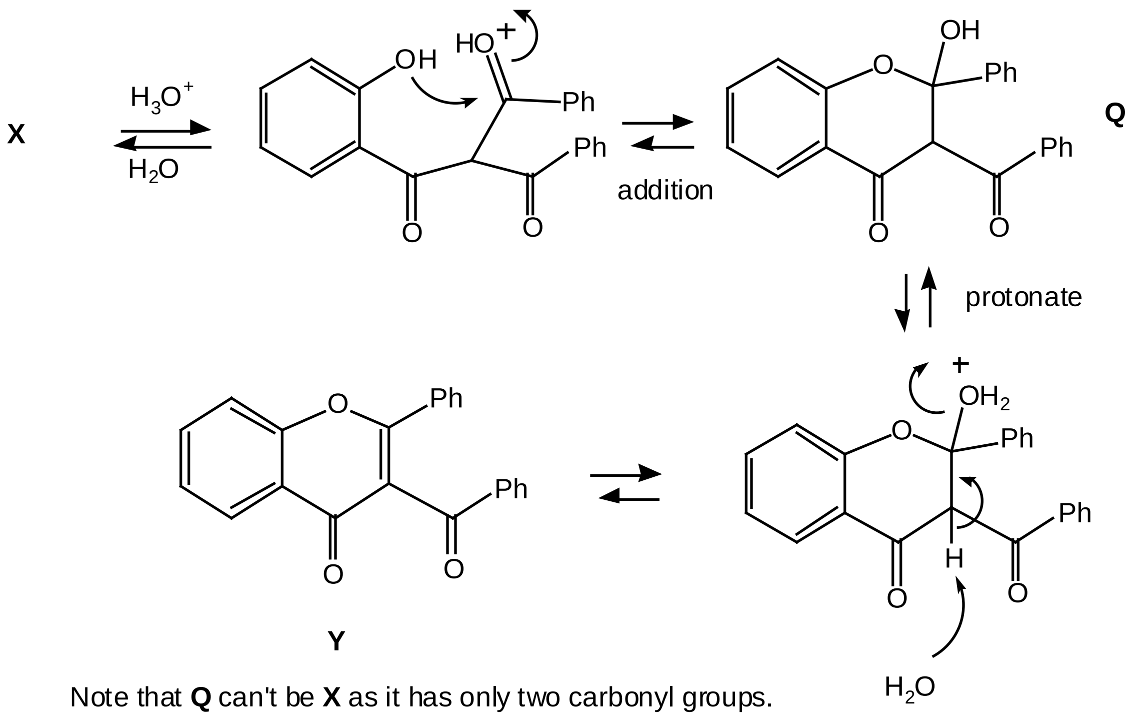
5. Remove the alpha hydrogen, do a Michael, then addition-elimination.



6. The first conversion, starting material **--->** **X** is easy. Addition-elimination. Now there is an OH (3350 cm^{-1}), and three conjugated C=O groups.

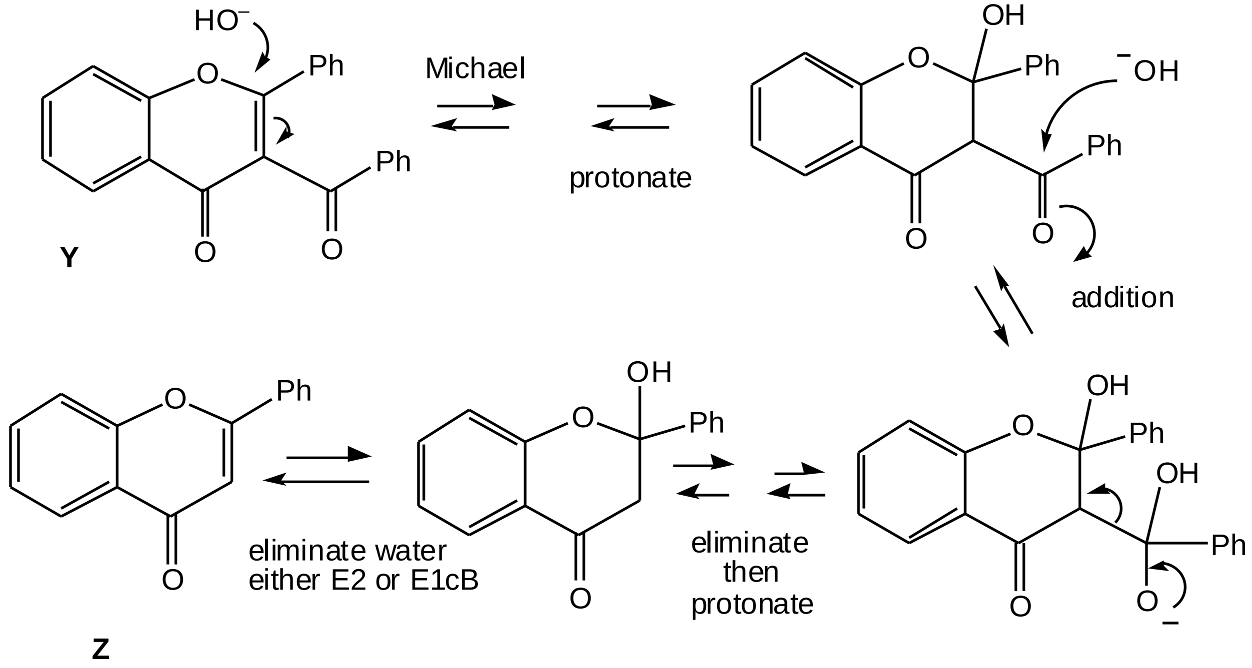


Now another addition- elimination sequence, this time in acid, gives **Y.**



Note that **Q** can't be **X** as it has only two carbonyl groups.

The sequence from **Y** to **Z** is the only hard one. That double bond has to be temporarily removed (by a Michael reaction) before the benzoyl group can be taken off (addition-elimination again).



We might go directly to **Z** from the eliminated enolate **W** shown below: