(2)The Br2  form a bridgehead

# TOP SIDE ANTI ATTACK

(1) Initial approach of Br2  in a topside, anti attack across trans—cinnamic acid

 because the pi e- initiates attack forces a cascade of e- motion shown below leading to Br-Br bond breakage. The alkene moiety lengthens as the pi system dissolves. The COOH side is favored for reasons discussed in (3)



(3)

(3) Br-Br bond ruptures and the bridgehead dissolves. The Br across the double bond selects the COOH side since this produces a carbocation on the phenyl side, which is stabilizing because of the deolcalization of the aromatic electron. The COOH side flexes downwards away from the Br now sharing its C attachment so that the bonding on that side moves from sp2🡪 sp3 .The remaining Br becomes a bromide ion (Br -) and the carbocation site is sp2 , e.g. it goes flat.



(4) The remaining Br- now attacks from the back (anti side) to neutralize the carbocation. The phen and H flex upwards, and the sp2 hybridization converts to sp3







 (4)

**a**

(5)



(5) rotation of the final product in step (4) to make the rotational isomer with phen and COOH eclipsing each other leads to the final erythro form (3S,2R) Fischer structure. This should melt at ~200oC.

**b**

**TOP SIDE SYN ATTACK**

(1)

(1) syn attack starts with both Br simultaneously donating a single e on the same side of the pi system which evenly divides its pi system in 1 e- transfers. As the Br-C bonds form, the Br-Br bond weakens and the four groups flex down in the same direction.

(3) The final structure in (2) is rotated so that the COOH and phen eclipse each other. This produces the Fischer configuration which is a threo (2R,3R) structure which melts around 95 oC



(3)

(2) Br-Br bond is now entirely broken and the new C-Br bonds have formed. The pi bond is gone and the bond length and the bon length between C2 and C3 is longer. The four groups (H,COOH) and (H,phen) are now in sp3 hybridized form.

(2)





**a**

**bv**

Some style notes:

* Make sure to use a combination of pictures and text with latter being physically close to the former on page; so that a reader can easily see what is being said in words in the accompanying picture. Use the electron pushing `curved’ arrow format wherever possible.
* Make sure critical terms and positions in pictures are well-labeled (as above)
* Use full sentences and be brief. Let the pictures do some of the work

CHEM 4524 LAB NOTES ON ADDITION OF BROMINE TO TRANS-CINNAMIC ACID

 Pictorial summary detailing all four anti attack possibilities

top side, anti attacks bottom side anti attacks









**C2**

**C3**

attack side carbocation configuration\* type

**anti top phen side R,S erythro**

**anti top COOH side S,R erythro**

**anti bottom phen side S,R erythro**

**anti bottom COOH side R,S erythro**

**syn top R,R threo**

**syn bottom S,S threo**

**\***C2,C3 assignments

mp

~200-202o

 90-91o

**1Erythro form is the higher melting form and so the fact that you got the melting points in the 115-160 range is consistent with an impure Erythro compound. The Threo form is not formed –or it is in very low concentration since even pure Threo would not yield mp > 91 C.**

**2syn attack results follow from previous handout detailing the top side mechanism.The bottom side attack will produce the mirror image of top side syn attack.**