

**Organic Chemistry 2**  
**First Examination**  
**February 15/17, 2012**  
**Prof. Malachowski**

Name: \_\_\_\_\_

The examination has eight questions on five pages. The point values for each question are found with the question. Partial credit will be given where appropriate.

Read each question carefully before answering. Be certain you understand everything the question is requesting. Do the easy questions first. If questions appear confusing or exceedingly complex, then you may need to rethink the question. Keep in mind the intended examination topics.

In organic chemistry, hand-drawn pictures convey specific information. Be sure the drawing you have made conveys the essential information required to answer the question. Don't forget to include lone pairs of electrons and formal charges when appropriate.

hydrogen 1 <b>H</b> 1.0079																				helium 2 <b>He</b> 4.0026					
lithium 3 <b>Li</b> 6.941	beryllium 4 <b>Be</b> 9.0122																			boron 5 <b>B</b> 10.811	carbon 6 <b>C</b> 12.011	nitrogen 7 <b>N</b> 14.007	oxygen 8 <b>O</b> 15.999	fluorine 9 <b>F</b> 18.998	neon 10 <b>Ne</b> 20.180
sodium 11 <b>Na</b> 22.990	magnesium 12 <b>Mg</b> 24.305																			aluminum 13 <b>Al</b> 26.982	silicon 14 <b>Si</b> 28.086	phosphorus 15 <b>P</b> 30.974	sulfur 16 <b>S</b> 32.065	chlorine 17 <b>Cl</b> 35.453	argon 18 <b>Ar</b> 39.948
potassium 19 <b>K</b> 39.098	calcium 20 <b>Ca</b> 40.078	scandium 21 <b>Sc</b> 44.956	titanium 22 <b>Ti</b> 47.867	vanadium 23 <b>V</b> 50.942	chromium 24 <b>Cr</b> 51.996	manganese 25 <b>Mn</b> 54.938	iron 26 <b>Fe</b> 55.845	cobalt 27 <b>Co</b> 58.933	nickel 28 <b>Ni</b> 58.693	copper 29 <b>Cu</b> 63.546	zinc 30 <b>Zn</b> 65.39	gallium 31 <b>Ga</b> 69.723	germanium 32 <b>Ge</b> 72.61	arsenic 33 <b>As</b> 74.922	selenium 34 <b>Se</b> 78.96	bromine 35 <b>Br</b> 79.904	krypton 36 <b>Kr</b> 83.80								
rubidium 37 <b>Rb</b> 85.468	strontium 38 <b>Sr</b> 87.62	yttrium 39 <b>Y</b> 88.906	zirconium 40 <b>Zr</b> 91.224	niobium 41 <b>Nb</b> 92.906	molybdenum 42 <b>Mo</b> 95.94	technetium 43 <b>Tc</b> [98]	ruthenium 44 <b>Ru</b> 101.07	rhodium 45 <b>Rh</b> 102.91	palladium 46 <b>Pd</b> 106.42	silver 47 <b>Ag</b> 107.87	cadmium 48 <b>Cd</b> 112.41	indium 49 <b>In</b> 114.82	tin 50 <b>Sn</b> 118.71	antimony 51 <b>Sb</b> 121.76	tellurium 52 <b>Te</b> 127.60	iodine 53 <b>I</b> 126.90	xenon 54 <b>Xe</b> 131.29								
cesium 55 <b>Cs</b> 132.91	barium 56 <b>Ba</b> 137.33	57-70 *	lutetium 71 <b>Lu</b> 174.97	hafnium 72 <b>Hf</b> 178.49	tantalum 73 <b>Ta</b> 180.95	tungsten 74 <b>W</b> 183.84	rhenium 75 <b>Re</b> 186.21	osmium 76 <b>Os</b> 190.23	iridium 77 <b>Ir</b> 192.22	platinum 78 <b>Pt</b> 195.08	gold 79 <b>Au</b> 196.97	mercury 80 <b>Hg</b> 200.59	thallium 81 <b>Tl</b> 204.38	lead 82 <b>Pb</b> 207.2	bismuth 83 <b>Bi</b> 208.98	polonium 84 <b>Po</b> [209]	astatine 85 <b>At</b> [210]	radon 86 <b>Rn</b> [222]							
francium 87 <b>Fr</b> [223]	radium 88 <b>Ra</b> [226]	89-102 * *	lawrencium 103 <b>Lr</b> [262]	rutherfordium 104 <b>Rf</b> [261]	dundium 105 <b>Db</b> [262]	seaborgium 106 <b>Sg</b> [266]	bohrium 107 <b>Bh</b> [264]	hassium 108 <b>Hs</b> [269]	meitnerium 109 <b>Mt</b> [268]	unnilium 110 <b>Uun</b> [271]	ununium 111 <b>Uuu</b> [272]	unbibium 112 <b>Uub</b> [277]		ununquadium 114 <b>Uuq</b> [289]											

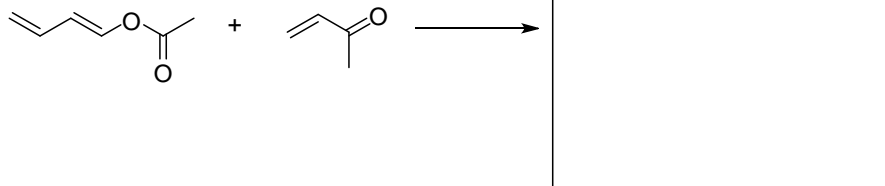
\* Lanthanide series

lanthanum 57 <b>La</b> 138.91	cerium 58 <b>Ce</b> 140.12	praseodymium 59 <b>Pr</b> 140.91	neodymium 60 <b>Nd</b> 144.24	promethium 61 <b>Pm</b> [145]	samarium 62 <b>Sm</b> 150.36	europium 63 <b>Eu</b> 151.96	gadolinium 64 <b>Gd</b> 157.25	terbium 65 <b>Tb</b> 158.93	dysprosium 66 <b>Dy</b> 162.50	holmium 67 <b>Ho</b> 164.93	erbium 68 <b>Er</b> 167.26	thulium 69 <b>Tm</b> 168.93	ytterbium 70 <b>Yb</b> 173.04
actinium 89 <b>Ac</b> [227]	thorium 90 <b>Th</b> 232.04	protactinium 91 <b>Pa</b> 231.04	uranium 92 <b>U</b> 238.03	neptunium 93 <b>Np</b> [237]	plutonium 94 <b>Pu</b> [244]	americium 95 <b>Am</b> [243]	curium 96 <b>Cm</b> [247]	berkelium 97 <b>Bk</b> [247]	californium 98 <b>Cf</b> [251]	einsteinium 99 <b>Es</b> [252]	fermium 100 <b>Fm</b> [257]	mendelevium 101 <b>Md</b> [258]	nobelium 102 <b>No</b> [259]

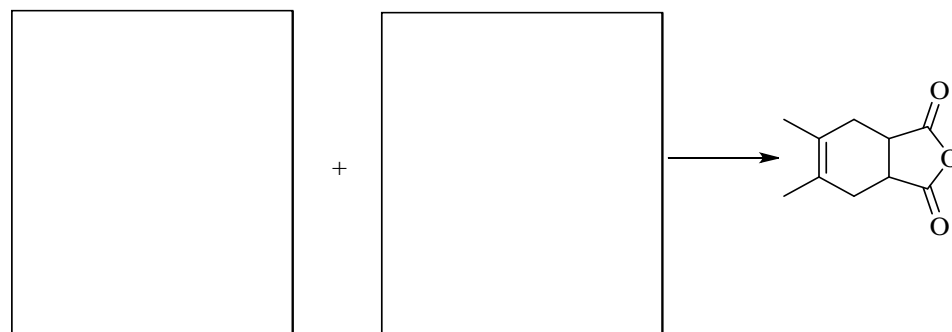
\*\* Actinide series

1. Provide the necessary information, product(s) or starting materials, to complete the following reactions. (5 pts. each)

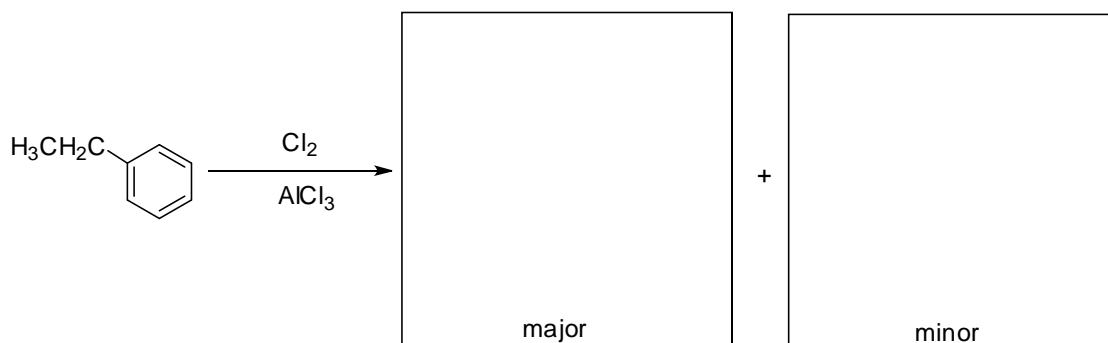
a)



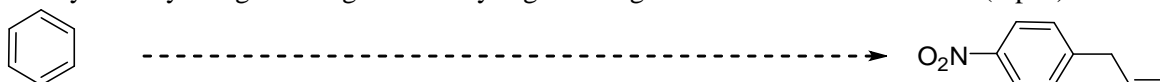
b)



c)

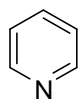


2. Suggest a series of reactions to take the starting material on the left to the product on the right. This will require two or three steps. You may use any inorganic reagent and any organic reagent of seven carbons or less. (6 pts.)

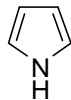


3. Rank the following structures in order of their reactivity in electrophilic aromatic substitution reactions. (3 pts. each)

a)



a

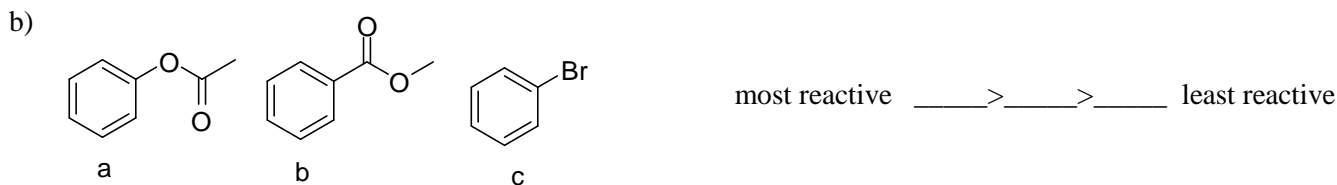


b



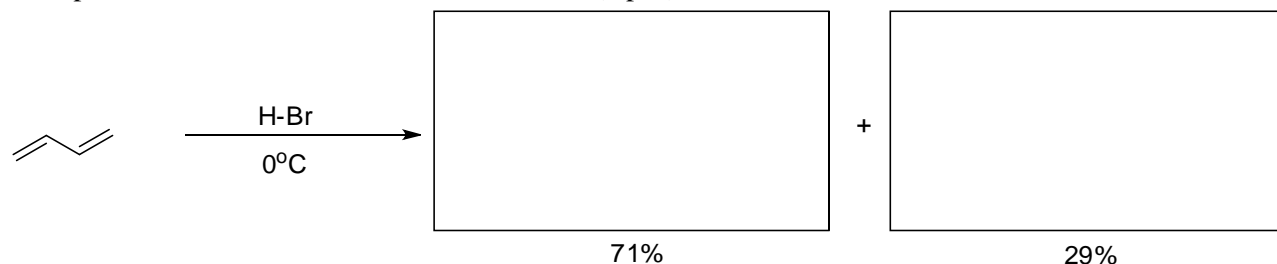
c

most reactive \_\_\_\_\_ > \_\_\_\_\_ > \_\_\_\_\_ least reactive

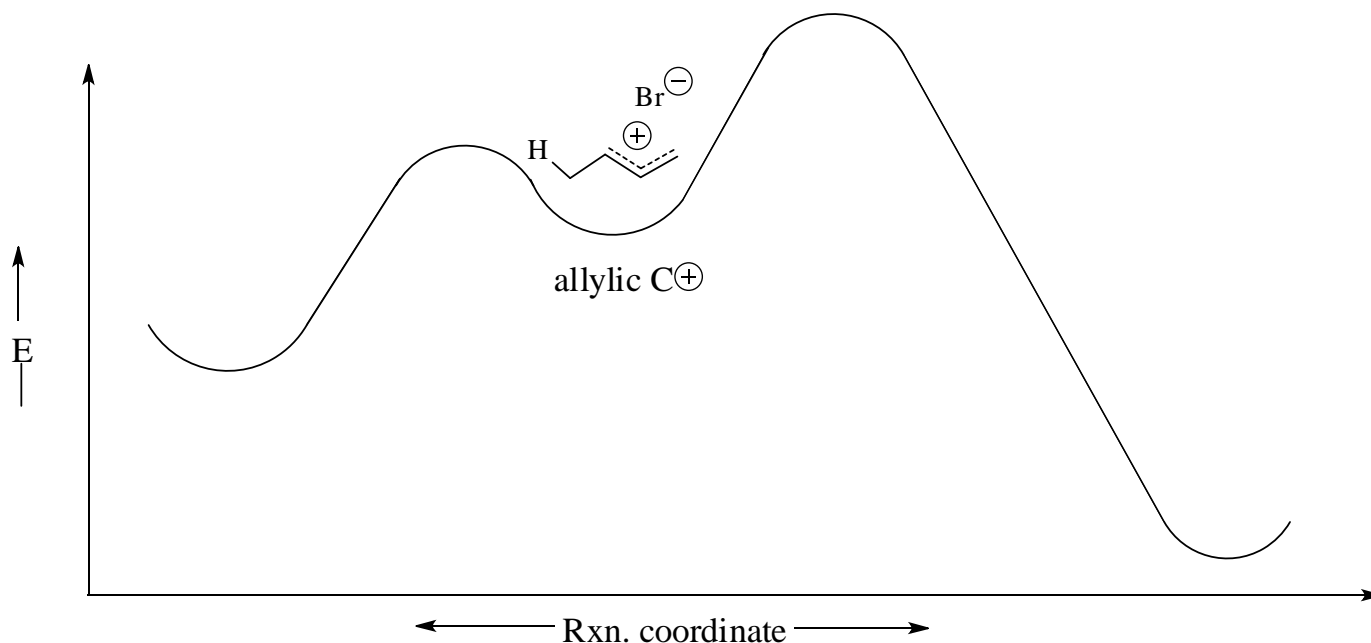


4. Answer the following questions about the reaction of 1,3-butadiene with HBr.

a) Draw the products of the reaction in the boxes below. (6 pts.)

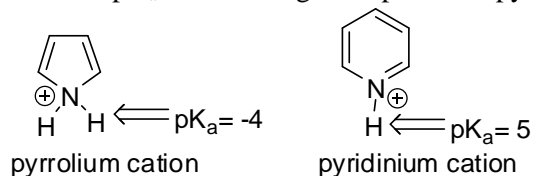


b) The energy diagram for the second step in the reaction is shown below. Label or place the following items on the diagram: energy of activation ( $E_a$ ) for the 1,2-product;  $E_a$  for the 1,4-product; structure and location of the kinetic product; structure and location of the thermodynamic product. (9 pts.)



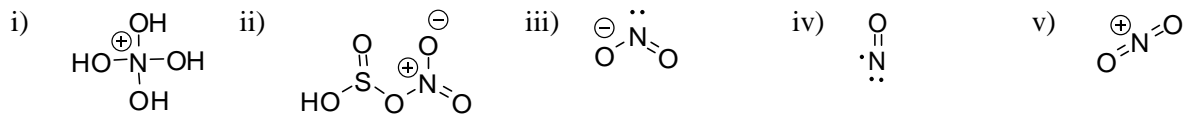
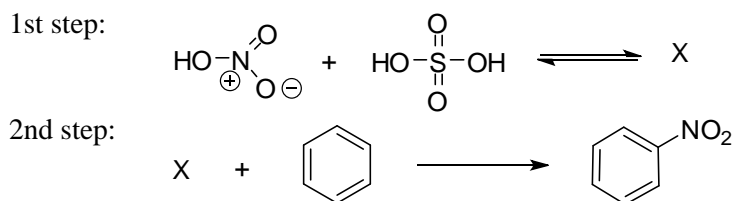
5. Multiple choice questions. (5 pts. each)

a. Which answer best explains the difference in  $pK_a$  for the designated proton in pyrrolium and pyridiniumcation?

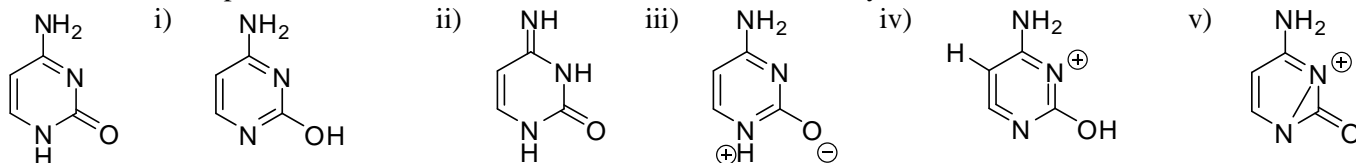


- i) Pyrrole is a stronger conjugate acid than pyridine.
- ii) Pyrrole loses aromaticity when it protonates to form the pyrrolium cation.
- iii) Pyrrole is a more electron rich aromatic ring than pyridine.
- iv) Pyridiniumcation distributes the cation charge around the ring better.
- v) Pyridine has more stable molecular orbitals and a smaller HOMO-LUMO energy gap.

b. Circle the structure of the intermediate X that forms in the following reaction sequence.

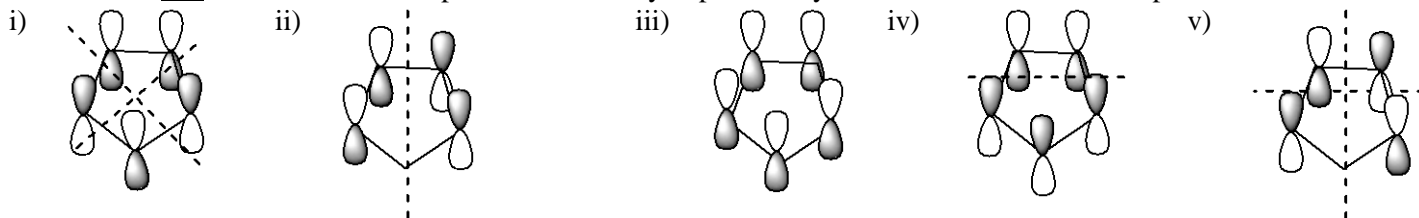


c. Which structure represents an aromatic tautomer or structural isomer of cytosine?



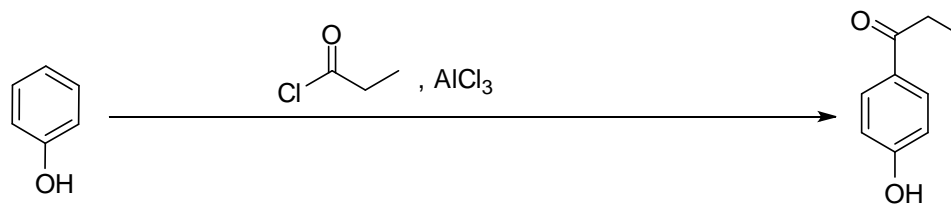
cytosine(C)

d. Circle the *two* molecular orbital representations of cyclopentadienyl anion shown below that represent HOMO orbitals.



6. Provide the necessary information about the reaction shown below.

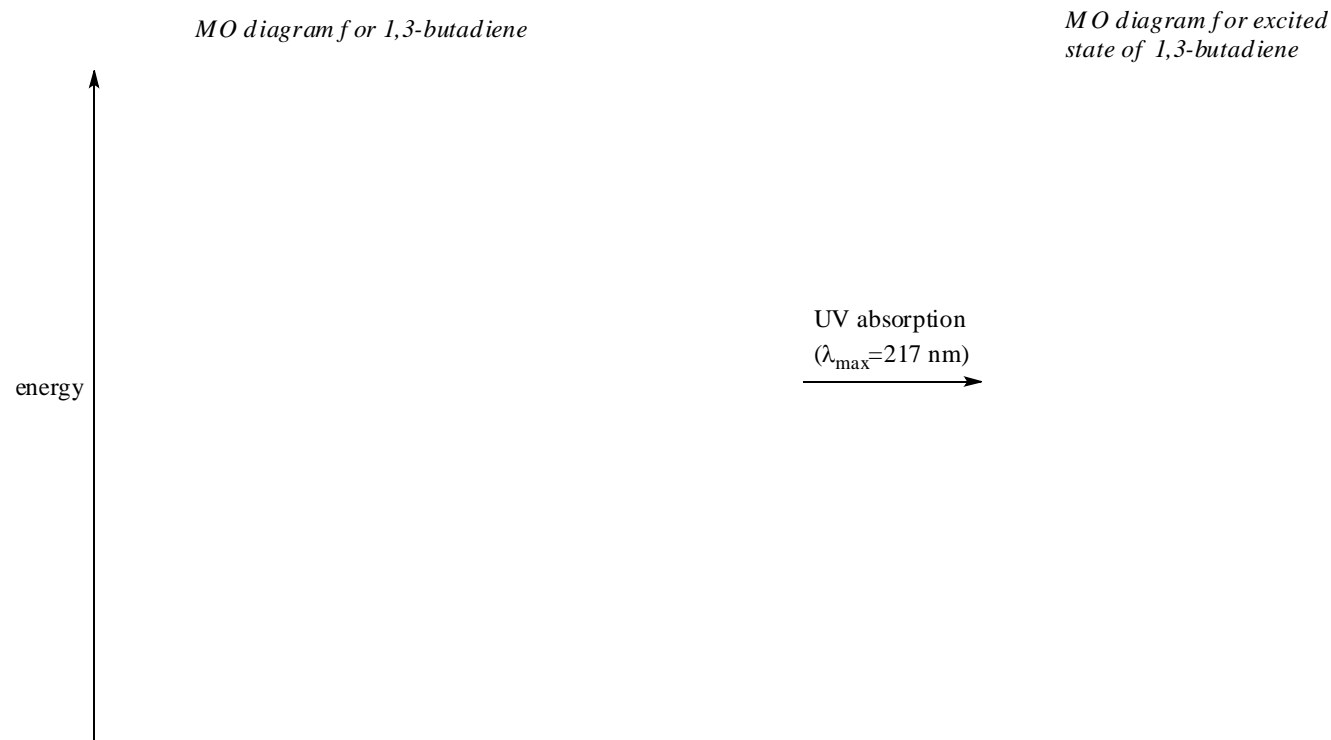
a) Draw the mechanism of the reaction. You do NOT need to include resonance structures. You should include all formal charges and curved electron flow arrows. (9 pts.)



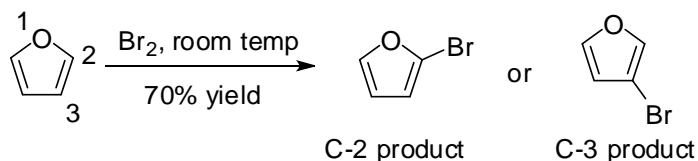
b) Show all the important resonance contributors of the key ring intermediate in the reaction. Be sure to include formal charges and curved electron flow arrows to indicate all electron movement. (6 pts.)

7. a) Draw the molecular orbital diagram for 1,3-butadiene in the space below. Include orbital phase and node information. Label the bonding and antibonding orbitals. Identify the HOMO and LUMO orbitals. (10 pts.)

b) To the right of your diagram, show the effect of UV absorption at 217 nm. Draw the energy diagram for the excited state of 1,3-butadiene that results from this absorption. Assume the absorption is a  $\pi$  to  $\pi^*$  transition. You do not need to redraw the molecular orbital pictures with the phases. (3 pts.)



8. As shown below, the bromination of furan can in theory afford two possible products, the C-2 or the C-3 isomer. (10 pts.)



a) Draw the carbocation intermediate for the reaction of both possible products. Draw all the important resonance forms for each carbocation intermediate. Be sure to include electron flow arrows, lone pairs and formal charges where appropriate.

b) Which product is favored, the C-2 or C-3? Briefly explain why.

c) The bromination with furan occurs at room temperature, while that for benzene needs a Lewis acid catalyst and considerable heating. Circle the answer that best explains this reactivity difference.

- i) Five member rings are always more electron rich than six member rings.
- ii) Benzene has special stability from its aromatic system and furan is non-aromatic which is a more reactive state.
- iii) Furan has six  $\pi$  electrons controlled by 5 nuclei, while benzene has the same number of  $\pi$  electrons and one more nucleus.
- iv) The HOMO-LUMO gap for benzene is smaller which makes the pi electrons of benzene less stable.
- v) Furan comes from the Latin word furfur which means bran and so it has the same explosive reactivity that too much bran in your diet can have.