

NAME: _____ Section: _____ Student Number: _____

Spring 2020

Chemistry 2500 Midterm #1A

_____/ 70 marks

- INSTRUCTIONS:
- 1) Please read over the test carefully before beginning. You should have 7 pages of questions and a data/periodic table sheet.
 - 2) Unless otherwise stated in the question, explain all of your answers fully. Use diagrams where appropriate. When invoking any argument based on resonance, you must draw all relevant resonance structures.
 - 3) ALL structures must be drawn showing lone pairs, non-zero formal charges and reasonable bond angles – regardless of whether they are expanded, condensed or line-bond. Marks will be deducted for poorly drawn structures.
 - 4) Marks will be deducted for incorrect information added to an otherwise correct answer.
 - 5) If your work is not legible, it will be given a mark of zero.
 - 6) Calculators are not allowed. You are not permitted to have any electronic devices with you during the exam unless authorized by the instructor.
 - 7) You may use a molecular model kit.
 - 8) You have 2 hours to complete this test.

Confidentiality Agreement:

I agree not to discuss (or in any other way divulge) the contents of this exam until after 8:00 pm Mountain Time on Thursday, February 13th, 2020. I understand that breaking this agreement would constitute academic misconduct, a serious offense with serious consequences. The minimum punishment would be a mark of 0/70 on this exam and removal of the “overwrite midterm mark with final exam mark” option for my grade in this course; the maximum punishment would include expulsion from this university.

Signature: _____

Date: _____

Course: CHEM 2500 (Organic Chemistry I)

Semester: Spring 2020

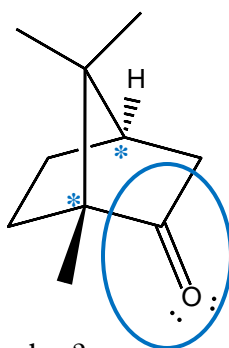
The University of Lethbridge

Question Breakdown

Q1	/ 7
Q2	/ 5
Q3	/ 8
Q4	/ 10
Q5	/ 12
Q6	/ 10
Q7	/ 10
Q8	/ 8
Total	/ 70

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1. The molecule below is camphor, one of the main ingredients in Buckley's original cough syrup and Vick's Vaporub: [7 marks]

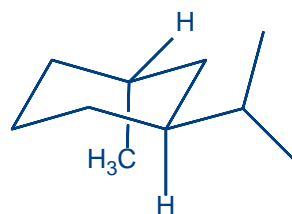
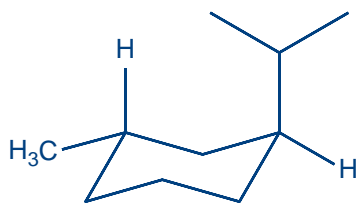


- (a) What is the molecular formula for camphor? [1 mark]
 $C_{10}H_{16}O$
- (b) Circle and name the functional group in camphor. [2 marks]
ketone
- (c) Draw a * at each chirality center in camphor. [2 marks]
Marks will be deducted for extra * on atoms that aren't chirality centers.
- (d) What is the definition of a chiral molecule? According to this definition, is camphor chiral or achiral? [2 marks]

A chiral molecule is non-superimposable with its mirror image.

In plain language, a chiral molecule is different from its mirror image. If you build a model of a chiral molecule and another model of its mirror image, it will be impossible to make the two models identical without breaking at least one bond – no matter how much you rotate either model as a whole (or rotate about single bonds within either model).

2. Draw both chair conformers of *trans*-1-isopropyl-3-methylcyclohexane. Write "more stable" under the more stable of the two conformers. [5 marks]



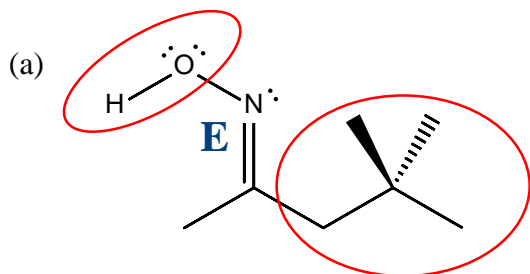
more stable
(larger group at equatorial site)

*One of the more common errors was drawing one conformer of the *trans* isomer then the both-groups-equatorial conformer of the *cis* isomer. Those are isomers not conformers.*

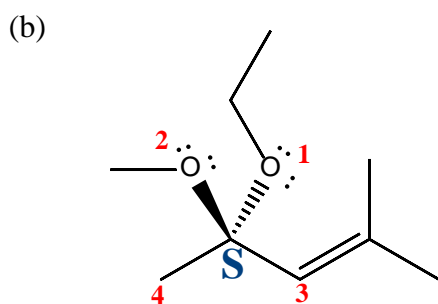
Also, please be careful that your axial bonds look vertical (as in the pictures above) and that your equatorial groups point "out" of the molecule (as in the pictures above). You MUST draw both groups attached to a carbon in order for it to be clear which is axial and which is equatorial. Also, if you explicitly draw a C, you must draw all groups attached to it, and if you draw a bond to H, you must write the H at the end of the bond.

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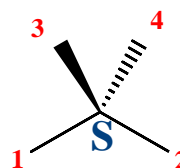
3. For each of the molecules below, assign the stereochemical configuration(s) as *E*, *Z*, *R* or *S*.
 For full marks, you must show the priority numbers you used to assign each configuration and it must be clear what part of the molecule is being described as *E*, *Z*, *R* or *S*. [8 marks]



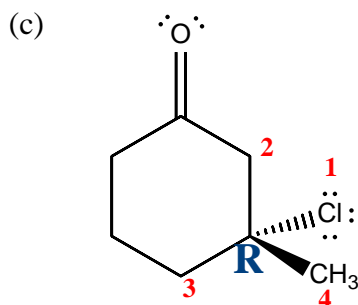
The C=N double bond is *E*.
 There is no chirality centre in this molecule.



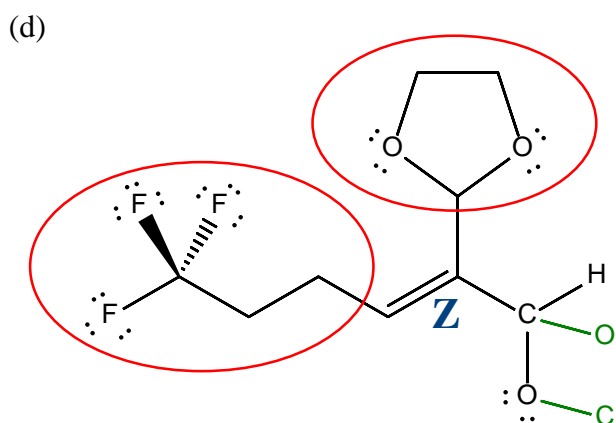
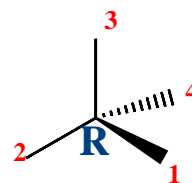
Rearranging groups to put lowest priority group pointing away from the viewer gives:



Remember that switching one pair of groups at a chirality centre gives the enantiomer but switching two pairs of groups gives back the same configuration.



Rearranging groups to put lowest priority group pointing away from the viewer gives:



The C=C double bond is *Z*.
 There is no chirality centre in this molecule.

Phantom atoms are necessary to distinguish between the aldehyde and acetal groups. These are shown in green on the diagram.

1. C vs. C
2. O, O, H vs. O, O, H
3. C, C vs. C (since the second C is bigger than nothing, the top group is assigned higher priority)

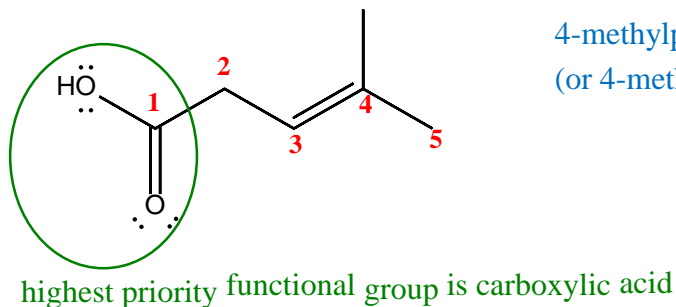
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4. Name each of the following molecules according to IUPAC rules. [10 marks]
You do not need to explain your names.

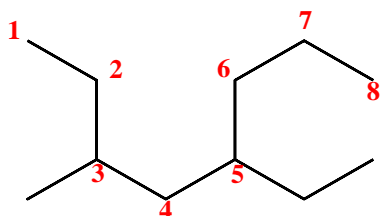
- (a) 3-aminopropane-1-thiol



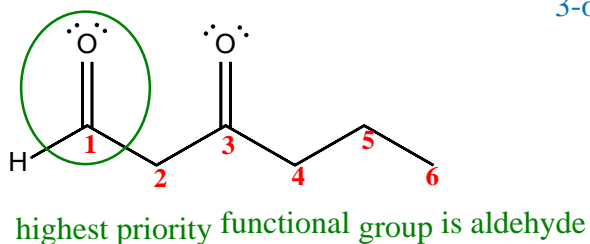
- (b) 4-methylpent-3-enoic acid
(or 4-methyl-3-pentenoic acid)



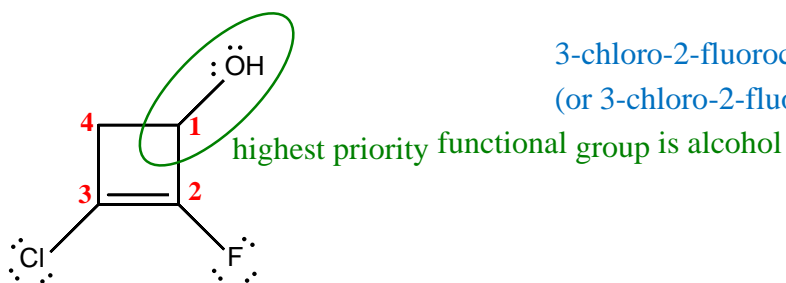
- (c) 5-ethyl-3-methyloctane



- (d) 3-oxohexanal



- (e) 3-chloro-2-fluorocyclobut-2-enol
(or 3-chloro-2-fluoro-2-cyclobutenol)



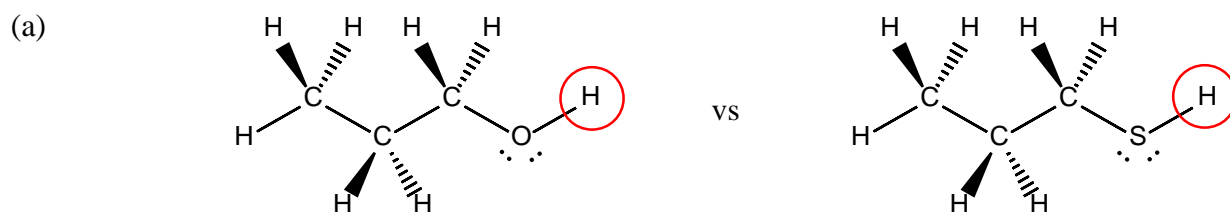
5. For each of the following pairs of molecules: [12 marks]

- circle the most acidic hydrogen atom(s) on each molecule, (0.5 mark per molecule)
- identify the stronger acid, and (1 mark per pair)
- explain why it is the stronger acid (in terms of chemical structure(s); I am looking for more than numbers from a table) (2 marks per pair)

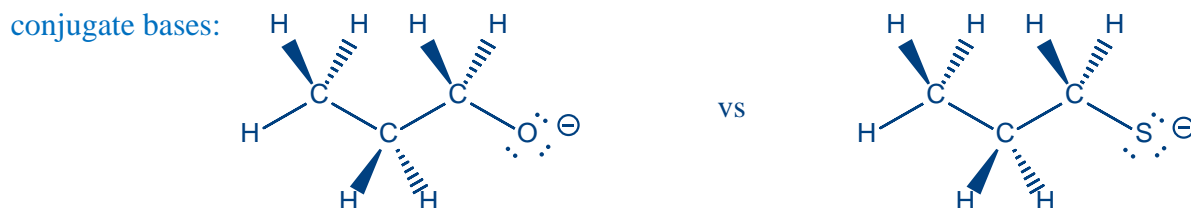
When you are comparing two neutral acids, always start by drawing the conjugate base of each. Both conjugate bases will be anions so look for factors that would differentiate between their stability. The more stable anion will be more readily formed, so a stronger acid has a more stable conjugate base.

When you are comparing acidity of two cations, both conjugate bases will be neutral (and therefore presumably stable). So, look at factors that would differentiate between the reactivity of the cations.

In this context, less stable = more reactive and more stable = less reactive.

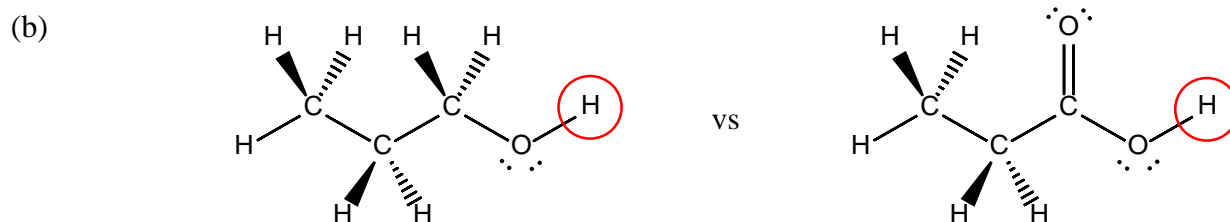


stronger acid

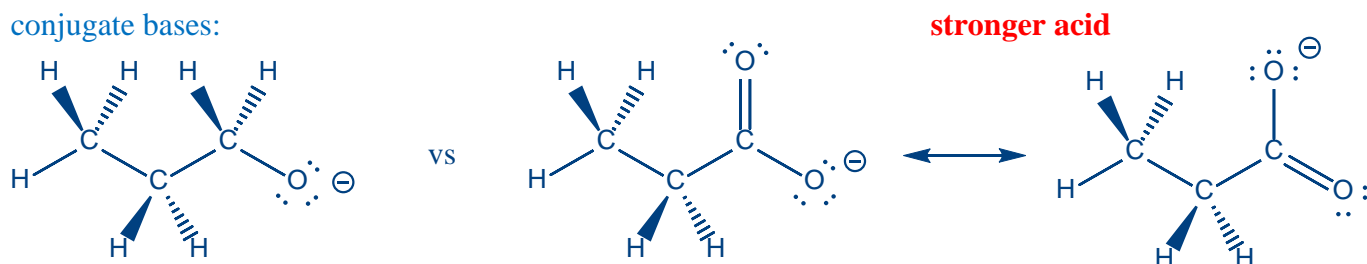


Sulfur is a larger atom than oxygen therefore S^- has a lower charge density than O^- .

As such, we expect the conjugate base of the thiol to be more stable than the conjugate base of the alcohol, making the thiol a stronger acid than the alcohol.



stronger acid



The negative charge of the conjugate base of the carboxylic acid is delocalized over two oxygen atoms. As such, we expect it to be more stable than the conjugate base of the alcohol, making the carboxylic acid a stronger acid than the alcohol.

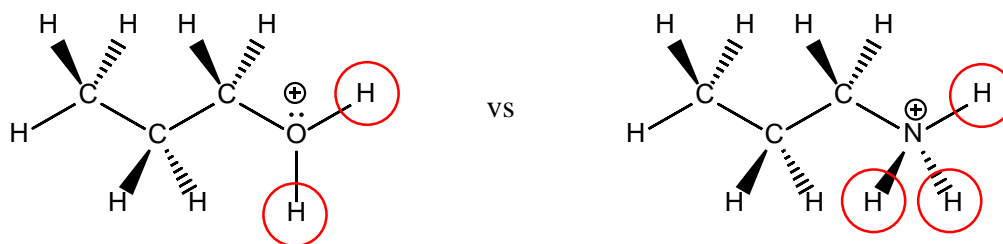
Resonance structures required for full marks.

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(c)

**stronger acid**

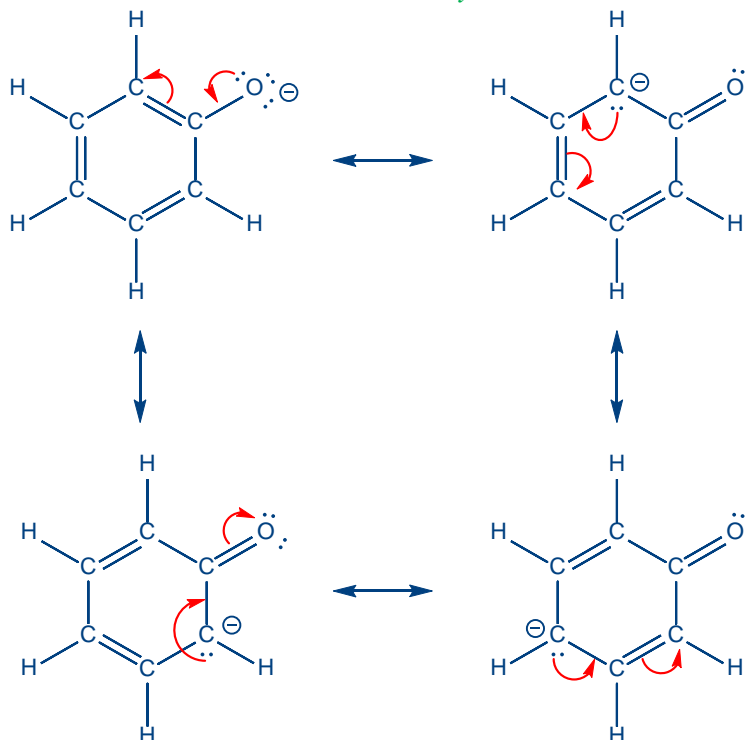
Oxygen is more electronegative than nitrogen, and it is generally unfavourable to have positive charges on electronegative elements.. As such, the acid containing O^+ will be more reactive than the one containing N^+ .

6. Carbonate ions (CO_3^{2-}) are strong enough bases to deprotonate phenols but not aliphatic alcohols like methanol, ethanol or propanol. **[10 marks]**

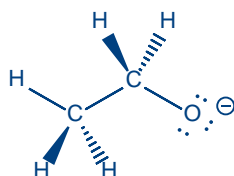
(a) Draw resonance structures that demonstrate why phenol is a stronger acid than ethanol.

[4 marks]

As in question 5, strength of a neutral acid is determined by stability of its conjugate base. Start by drawing the conjugate base of phenol. Then draw resonance structures of that conjugate base that show how the negative charge is delocalized across several atoms. Resonance structures that don't delocalize charge do NOT contribute to an ion's stability!



For comparison, the conjugate base of ethanol is not resonance stabilized; the charge is fully localized on one oxygen atom:

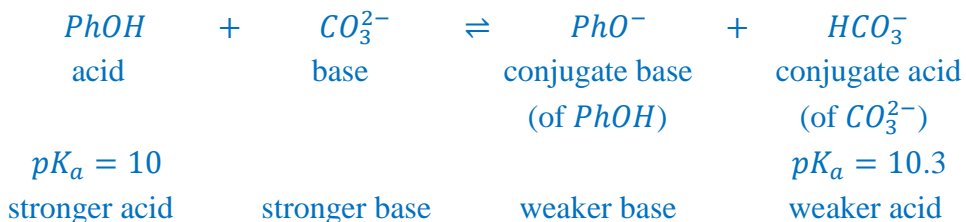


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pK_a values measure the strength of an acid. Bases do not have pK_a values. You can, however, use the pK_a value of the conjugate acid of a base to assess the strength of the base (since stronger bases have weaker conjugate acids and weaker bases have stronger conjugate acids).

Also, please be careful using the terms “strong acid” or “strong base”. There were no strong acids (acids with negative pK_a values) in this question – only stronger acids and weaker acids.

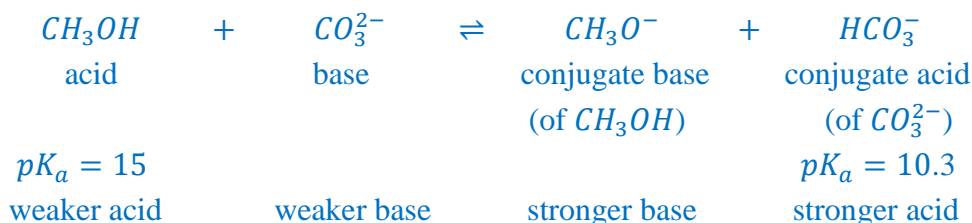
- (b) Use pK_a values to explain why a carbonate ion can deprotonate a significant fraction of molecules in a sample of phenol. Your answer should include a balanced reaction equation. [3 marks]



The pK_a of phenol is slightly lower than the pK_a of bicarbonate (the conjugate acid of carbonate), so phenol is a slightly stronger acid than bicarbonate. Since the strength of a base is inversely related to the strength of its conjugate acid, carbonate is a slightly stronger base than phenoxide (the conjugate base of phenol).

Since the stronger acid and stronger base lie on the reactants side of this reaction equation, the equilibrium lies toward the product side. As such, we'd expect a significant fraction of phenol molecules to be deprotonated by carbonate.

- (c) Use pK_a values to explain why a carbonate ion will **NOT** deprotonate a significant fraction of molecules in a sample of methanol. Your answer should include a balanced reaction equation. [3 marks]

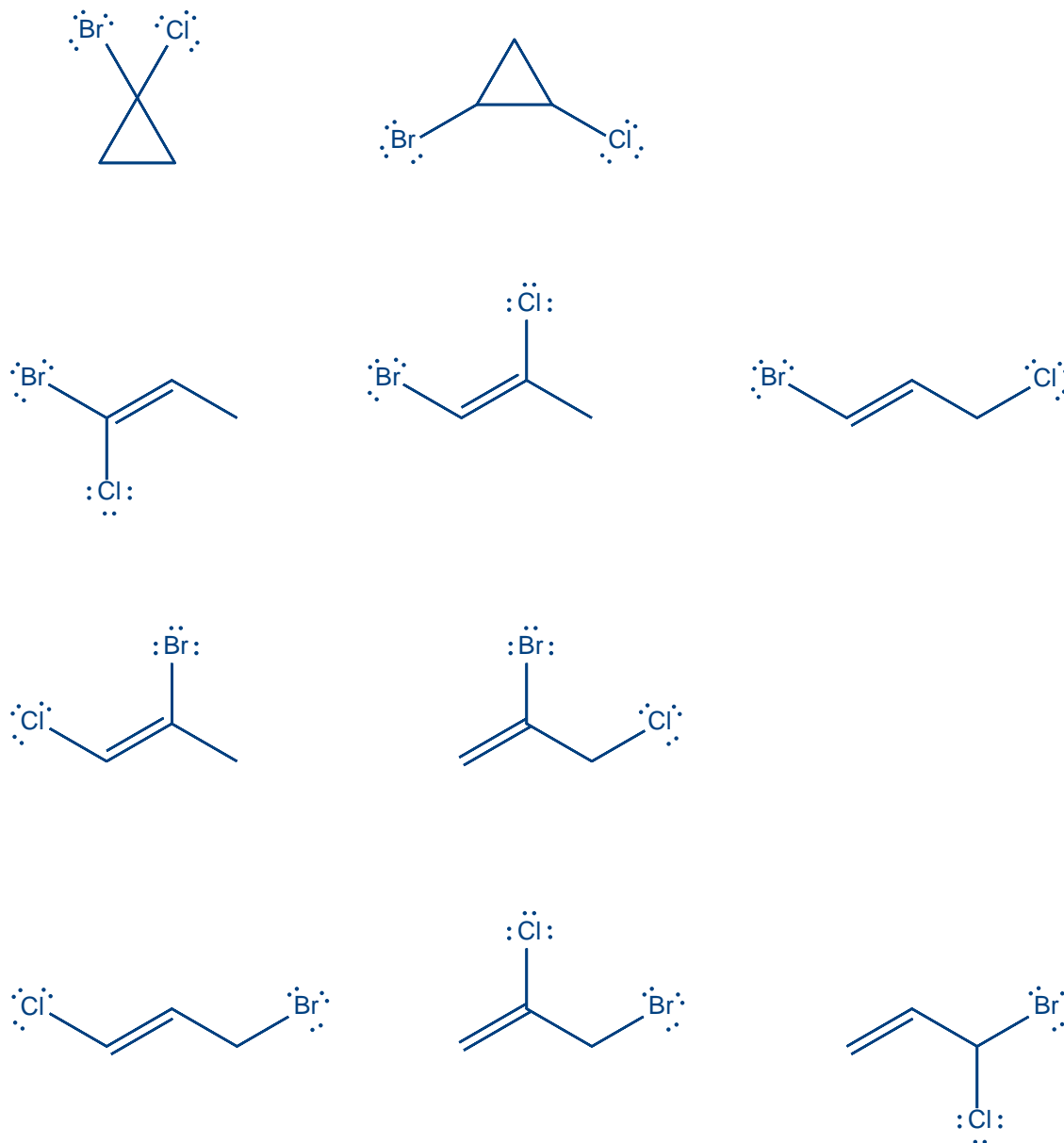


The pK_a of methanol is 5 units higher than the pK_a of bicarbonate (the conjugate acid of carbonate), so bicarbonate is a stronger acid than methanol (by a factor of 10⁵ = 100,000). Since the strength of a base is inversely related to the strength of its conjugate acid, methoxide (the conjugate base of methanol) is a stronger base than carbonate.

Since the stronger acid and stronger base lie on the products side of this reaction equation, the equilibrium lies toward the reactant side. As such, we do NOT expect a significant fraction of methanol molecules to be deprotonated by carbonate.

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7. Draw all **structural** isomers with the molecular formula C_3H_4BrCl . [10 marks]
Marks may be deducted if the same isomer is drawn multiple times.



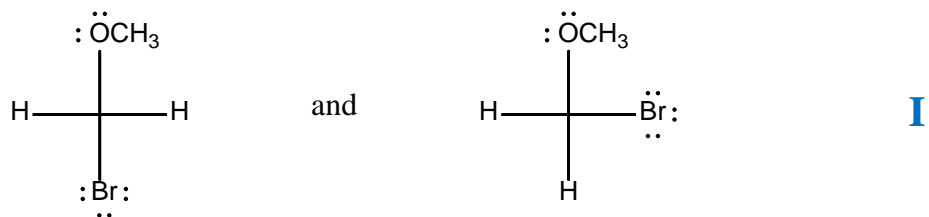
The trick to finding all ten structural isomers is to be methodical. In the answer above, I locked in the position of Br in each row and drew each possible position of Cl to make sure I got them all.

8. What is the relationship between each of the following pairs of molecules? [8 marks]

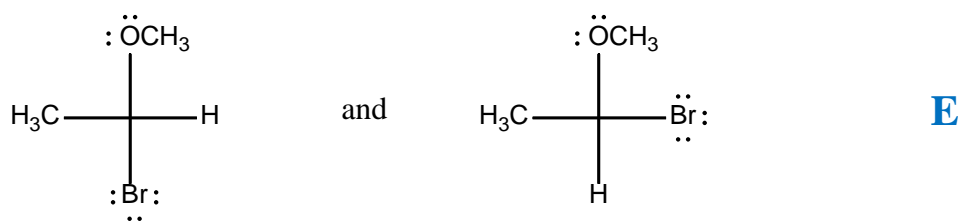
For each pair, indicate whether they are:

- C – conformers,
- D – diastereomers,
- E – enantiomers,
- SI – structural isomers, or
- I – identical molecules

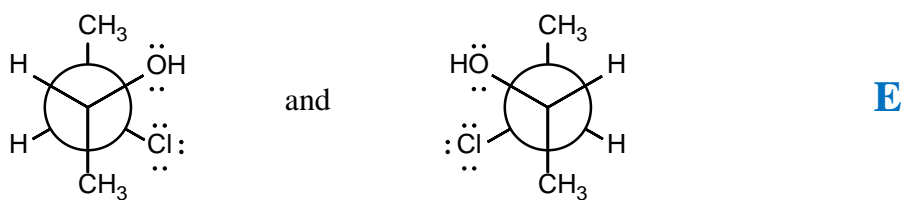
(a)



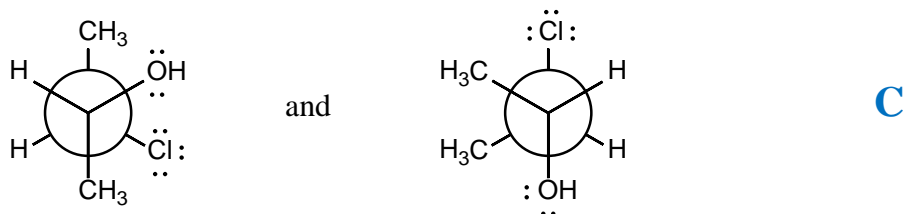
(b)



(c)



(d)



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Some Useful Data**Principal Functional Group Priority List**

Carboxylic acid

Sulfonic acid

Ester

Acid chloride

Amide

Nitrile

Aldehyde

Ketone

Alcohol

Thiol

Amine

1 **Chem 1000 Standard Periodic Table** **18**

1.0079 H 1																	4.0026 He 2	
6.941 Li 3	9.0122 Be 4												10.811 B 5	12.011 C 6	14.0067 N 7	15.9994 O 8	18.9984 F 9	20.1797 Ne 10
22.9898 Na 11	24.3050 Mg 12	3	4	5	6	7	8	9	10	11	12	26.9815 Al 13	28.0855 Si 14	30.9738 P 15	32.066 S 16	35.4527 Cl 17	39.948 Ar 18	
39.0983 K 19	40.078 Ca 20	44.9559 Sc 21	47.88 Ti 22	50.9415 V 23	51.9961 Cr 24	54.9380 Mn 25	55.847 Fe 26	58.9332 Co 27	58.693 Ni 28	63.546 Cu 29	65.39 Zn 30	69.723 Ga 31	72.61 Ge 32	74.9216 As 33	78.96 Se 34	79.904 Br 35	83.80 Kr 36	
85.4678 Rb 37	87.62 Sr 38	88.9059 Y 39	91.224 Zr 40	92.9064 Nb 41	95.94 Mo 42	(98) Tc 43	101.07 Ru 44	102.906 Rh 45	106.42 Pd 46	107.868 Ag 47	112.411 Cd 48	114.82 In 49	118.710 Sn 50	121.757 Sb 51	127.60 Te 52	126.905 I 53	131.29 Xe 54	
132.905 Cs 55	137.327 Ba 56	La-Lu	178.49 Hf 72	180.948 Ta 73	183.85 W 74	186.207 Re 75	190.2 Os 76	192.22 Ir 77	195.08 Pt 78	196.967 Au 79	200.59 Hg 80	204.383 Tl 81	207.19 Pb 82	208.980 Bi 83	(210) Po 84	(210) At 85	(222) Rn 86	
(223) Fr 87	226.025 Ra 88	Ac-Lr	(265) Rf 104	(268) Db 105	(271) Sg 106	(270) Bh 107	(277) Hs 108	(276) Mt 109	(281) Ds 110	(280) Rg 111	(285) Cn 112	(284) Nh 113	(289) Fl 114	(288) Mc 115	(293) Lv 116	(294) Ts 117	(294) Og 118	
138.906 La 57	140.115 Ce 58	140.908 Pr 59	144.24 Nd 60	(145) Pm 61	150.36 Sm 62	151.965 Eu 63	157.25 Gd 64	158.925 Tb 65	162.50 Dy 66	164.930 Ho 67	167.26 Er 68	168.934 Tm 69	173.04 Yb 70	174.967 Lu 71				
227.028 Ac 89	232.038 Th 90	231.036 Pa 91	238.029 U 92	237.048 Np 93	(240) Pu 94	(243) Am 95	(247) Cm 96	(247) Bk 97	(251) Cf 98	(252) Es 99	(257) Fm 100	(258) Md 101	(259) No 102	(262) Lr 103				

Developed by Prof. R. T. Boeré (updated 2016)