Department of Chemistry
SUNY/Oneonta

Chem 221 - Organic Chemistry I

Examination #4 - December 7, 1998*

INSTRUCTIONS ---

This examination is in multiple choice format; the questions are in this Exam Booklet and the answers should be placed on the "Test Scoring Answer Sheet" which must be turned in and will be machine graded.

On the Test Scoring Answer Sheet, using a soft pencil, enter the following data (in the appropriate places): your name, instructor's name, your student (Social Security) number, course number (30022101) and the test number (04); darken the appropriate bubbles under the entries, making dark black marks which fill the bubbles.

You may use a set of molecular models, but no other aids, during the exam.

Answer all questions; they are worth 1.81818... points each.

You have 90 minutes. Good luck!

* "... a day which shall live in infamy ..." – F. D. Roosevelt

1. The term S_N2 means

(A) substance, nice, squared. (B) stupid, nitwit, squared. (C) substitution, nucleophilic, second order. (D) substitution, nucleophilic, bimolecular. (E) substitution on an sp^2 hybridized nitrogen.

In questions 2-8 select the mechanism(s) [there may be more than one] that fit the description provided, from the list of mechanisms below. The substrate would be an alkyl halide or tosylate.
List of mechanisms: (A) S_N1, (B) S_N2, (C) E1, (D) E2, (E) S_N1 & S_N2, (F) E1 & E2, (G) S_N1 & E1, (H) S_N2 & E2

2. This reaction mechanism is characterized by inversion of stereochemistry at a stereogenic reaction center and exhibits second-order kinetics.

3. This reaction mechanism is characterized by partial or complete racemization at a stereogenic reaction center and exhibits first-order kinetics.

4. This reaction mechanism is characterized by a carbocation intermediate.

5. This reaction mechanism is characterized by the requirement that the leaving group and a hydrogen on an adjacent carbon be periplanar and preferably anti-periplanar.

6. This reaction mechanism is favored by 3° substrates, high temperatures, and a strong base.

7. This reaction mechanism is favored by 3° substrates, low temperatures, polar solvents, and low concentrations of very weak bases.

8. These mechanisms will both operate if a 2° substrate is reacted with a high concentration of strong base/nucleophile.

9. Which of the following mechanism types is(are)*likely* in this reaction:
$CH_3I + KOH \rightarrow CH_3OH + KI$

(I) S_N1, (II) S_N2, (III) E1, (IV) E2

(A) I&II, (B) III&IV, (C) I, (D) II

10. Which of the following mechanism types is(are) *highly unlikely* in this reaction:
$CH_3I + KOH \rightarrow CH_3OH + KI$

(I) S_N1, (II) S_N2, (III) E1, (IV) E2

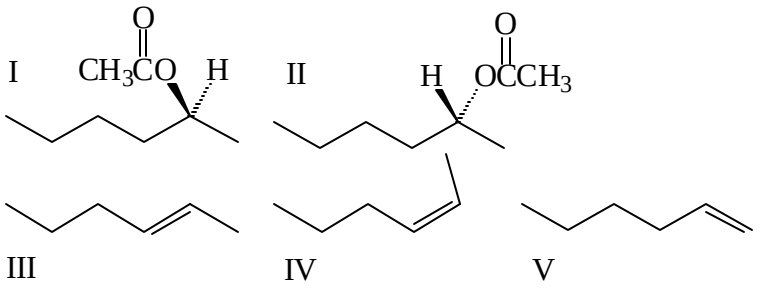
(A) I&II, (B) III&IV, (C) I, (D) II

11. Which of the following mechanism types is(are)*impossible* in this reaction:
$CH_3I + KOH \rightarrow CH_3OH + KI$

(I) S_N1, (II) S_N2, (III) E1, (IV) E2

(A) I&II, (B) III&IV, (C) I, (D) II

12. What would be the major product(s) that would form from reaction of (S)-2-bromohexane with acetate ion at room temperature if the reaction exhibits second order kinetics?



(A) I, (B) II, (C) III, (D) IV, (E) V, (F) I&II; racemic mixture, (G) I&II; unequal amounts,
(H) III, IV&V; III > IV > V, (I) III, IV&V; V > III > IV

13. Rank the following substrates in order of decreasing reactivity in an S_N2 reaction (most reactive first, least reactive last).

(I) $(CH_3)_3C\text{-}Br$, (II) CH_3Br, (III) CH_3CH_2Cl, (IV) CH_3CH_2Br

(A) I > II > III > IV, (B) IV > I > II > III, (C) IV > III > II > I,
(D) I > IV > II > I, (E) II > IV > III > I

14. Rank the following substrates in order of decreasing reactivity in an S_N1 reaction (most reactive first, least reactive last). [Note: C_6H_5 represents the phenyl group, *ie* a benzene ring.]

(I) CH_3Br, (II) $C_6H_5(CH_3)_2CBr$, (III) $(CH_3)_3CBr$, (IV) $(C_2H_5)_2CHBr$, (V) C_2H_5Br

(A) I > II > III > IV > V, (B) I > V > IV > III > II, (C) II > III > IV > V > I
(D) II > III > IV > I > V, (E) None of the previous answers is correct.

15. In which of the solvents listed below would the following S_N2 reaction be fastest?

$CH_3(CH_2)_3Br + NaN_3 \rightarrow CH_3(CH_2)_3N_3 + NaBr$

(A) hexane, (B) methanol, CH_3OH, (C) diethyl ether, $(C_2H_5)_2O$, (D) acetonitrile, $CH_3C{\equiv}N$

16. If a reaction proceeds through an E2 mechanism and the concentrations of both the substrate and base are doubled, the reaction rate will

(A) remain the same. (B) double. (C) triple. (D) quadruple.
(E) None of the previous answers is correct.

17. If a reaction proceeds through an S_N1 mechanism and the concentrations of both the substrate and base are doubled, the reaction rate will

(A) remain the same. (B) double. (C) triple. (D) quadruple.
(E) None of the previous answers is correct

18. For the following reaction carried out in aqueous ethanol, select the more reactive nucleophile in each pair: $CH_3Br + Nu: \rightarrow CH_3\text{-}Nu + Br^-$

<u>Nucleophiles</u>
First pair: I^- and Cl^-. Second pair: HS^- and H_2S.

(A) I^- & HS^-, (B) Cl^- & H_2S, (C) I^- & H_2S, (D) Cl^- & HS^-

19. Rank the following groups in order of decreasing ability to function as leaving groups (best leaving group first).

(I) $TosO^-$, (II) HO^-, (III) Cl^-

(A) I > II > III, (B) II > I > III, (C) III > I > II, (D) III > II > I, (E) I > III > II

20. $(CH_3)_3C\text{-}Br$ + $H\text{-}C{\equiv}C^{-}Na^{+}$))))))))> major product(s)

(A) $(CH_3)_3C\text{-}C{\equiv}C\text{-}H$ + NaBr, (B) $(CH_3)_2C{=}CH_2$ + $H\text{-}C{\equiv}C\text{-}H$ + NaBr,
(C) $(CH_3)_3C^{-}Na^{+}$ + $H\text{-}C{\equiv}C\text{-}Br$, (D) There would be no reaction.
(E) None of the above answers.

21. The structure of the transition state for the reaction of hydroxide ion with methyl iodide is best represented by

(A) $\overset{\ominus}{HO}$ - - - - - - - - - - - - CH_3—I (B) $\overset{\delta-}{HO}$ - - - - - - - CH_3 - - - - - - - - $\overset{\delta-}{I}$

(C) HO—CH_3 - - - - - - - - - - - - $\overset{\ominus}{I}$ (D) $\overset{\ominus}{HO}$ - - - - - - - $\overset{\oplus}{CH_3}$ - - - - - - - - $\overset{\ominus}{I}$

22. If a reaction between potassium iodide and 2-bromopropane is carried out under conditions where the S_N1 and S_N2 mechanisms are in competition, and the concentration of potassium iodide is doubled, what will be the result?

(A) There will be no change in how the reaction takes place.
(B) More product will be formed via the S_N1 mechanism.
(C) More product will be formed via the S_N2 mechanism.
(D) Bogus question. 2-Bromopropane cannot react by the S_N1 mechanism.
(E) Bogus question. 2-Bromopropane cannot react by the S_N2 mechanism.

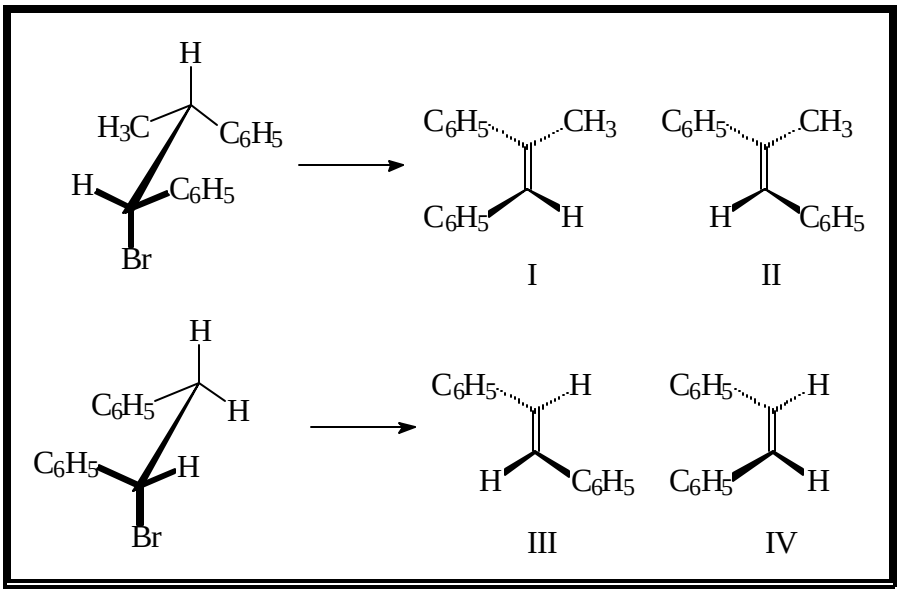
The following two questions consist of a statement followed by the connecting word **because** followed by a reason: <statement> **because** <reason>. In each question choose the correct description of the statement and the reason from the list below:

(A) The statement and the reason are both factually true, <u>and</u> the reason is the correct explanation of the statement.
(B) The statement and the reason are both factually true, but the reason is <u>not</u> the correct explanation of the statement.
(C) The statement is true and the reason is false.
(D) The statement is false and the reason is true.
(E) Both the statement and reason are false.

23. Reaction of a bulky base such as $(CH_3)_3CO^- K^+$ with secondary alkyl halides gives predominantly E2 elimination rather than S_N2 substitution **because** the transition state for S_N2 reaction is more sterically hindered than that for E2 reaction.

24. S_N2 reactions of the type $RBr + NaOH \rightarrow ROH + Na^+ Br^-$ generally go slower in a solvent like dimethyl sulfoxide (DMSO) than in a solvent like ethanol **because** dimethyl sulfoxide can solvate cations well but cannot solvate anions very well.

25. Consider the two E2 eliminations shown in the figure to the right. From the list of answers below, select the answer which best describes how much of each of the listed compounds, I-IV, would form.



(A) I-IV would form in approximately equal amounts.
(B) I-IV would form, but there would be more II than I and more III than IV.
(C) I would form but not II. III and IV would form, with more III than IV.
(D) I would form but not II. III and IV would form, with more IV than III.
(E) II would form but not I. III and IV would form, with more III than IV.
(F) II would form but not I. III and IV would form, with more IV than III.
(G) I and II would form, with more I than II. III would form but not IV.
(H)I and II would form, with more II than I. III would form but not IV.
(I) I and II would form, with more I than II. IV would form but not III.
(J)I and II would form, with more II than I. IV would form but not III.

☹ Help! Anybody got an acetylsalicyclic acid tablet?

26. Which of the following nuclei does *not* have a magnetic moment, and is, therefore, not NMR active?

(A) ^{1}H, (B) ^{12}C, (C) ^{13}C, (D) ^{19}F

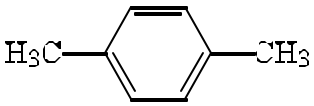
27. In an NMR spectrum, signals arising from hydrogens and carbons that are near an electronegative element are moved

(A) upfield. (B) downfield. (C) to the outfield. (D) to the infield. (E) to "The Field of Dreams."

28. The NMR signal from a proton that has three proton neighbors, equivalent to each other but different from itself, will be split into a

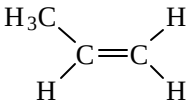
(A) doublet. (B) triplet. (C) quartet. (D) quintet. (E) sextet.

29. How many signals would the compound to the right give in a ^{13}C NMR spectrum?



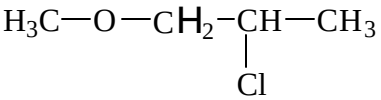
(A) 1, (B) 2, (C) 3, (D) 4, (E) 5

30. How many signals would the compound to the right give in a proton NMR spectrum?



(A) 2, (B) 3, (C) 4, (D) 5, (E) 6

31. Into what type of multiplet would the bold hydrogens in the compound to the right be split in a proton NMR?



(A) doublet, (B) triplet, (C) quartet, (D) quintet, (E) sextet

For questions 32-34 consider the following compound: $H_3C—O—CH_2—O—CH_3$

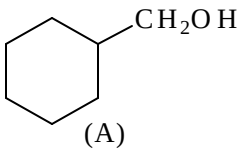
32. How many signals will appear in the proton NMR of this compound?

(A) 1, (B) 2, (C) 3, (D) 4, (E) 5, (F) 8

33. Which protons would appear furthest downfield?

(A) CH_3 on left, (B) CH_2, (C) CH_3 on right.

In questions 34-36 match the broadband decoupled carbon-13 NMR data given in the question with one of the structures shown below:



(A)

(B) $CH_3CH_2CH{=}CHCH_2CH_3$

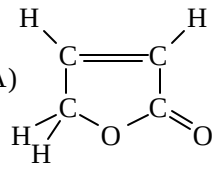
(C) $H_2C{=}CHC(=O)OCH_2CH(CH_3)CH_3$

34. Signals at the following δ values (ppm downfield from TMS): 68.2, 40.5, 29.9, 26.1, 26.9.

35. Signals at the following δ values (ppm downfield from TMS): 132, 27, 16.

36. Signals at the following δ values (ppm downfield from TMS): 19.1, 28.0, 70.5, 129.0, 129.8, 165.8.

In questions 37-40 match the proton NMR data given in the question with one of the structures shown below:

(A) 

(B) $CH_3CH_2\underset{\underset{O}{\|}}{C}CH_3$

(C) $CH_3OCH_2CH_2C{\equiv}N$

(D) $CH_3CH_2\underset{\underset{Br}{|}}{C}H\overset{\overset{O}{\|}}{C}OH$

37. Signals at the following δ values (ppm downfield from TMS): 1.08(triplet), 2.07(quintet), 4.23(triplet), 10.97(singlet).

38. Signals at the following δ values (ppm downfield from TMS): 1.05(triplet), 2.13(singlet), 2.47(quartet).

39. Signals at the following δ values (ppm downfield from TMS): 2.62(triplet), 3.40(singlet), 3.62(triplet).

40. Signals at the following δ values (ppm downfield from TMS): 4.92(a doublet, each peak of which is split into doublets), 6.15(a doublet, each peak of which is split into a triplet), 7.63(a doublet, each peak of which is split into a triplet).

41. Molecules give rise to infrared spectra owing to

(A) electronic transitions. (B) molecular vibrations. (C) molecular rotations.
(D) molecular translations. (E) spin "flipping."

42. The "fingerprint" region of the IR spectrum is

(A) most useful for determining which functional groups are present in the compound.
(B) most useful for determining the molecular weight of the compound.
(C) most useful for demonstrating whether two chemical samples are merely similar in structure or are, very likely, the same compound.
(D) what you get if you touch the faces of the salt plates that hold the sample in the IR spectrometer with your fingers.

43. The spectroscopy most useful for determination of molecular weight is

(A) NMR. (B) MS. (C) IR.

44. The type of spectroscopy that fragments molecules to determine their structure is

(A) NMR. (B) MS. (C) IR.

45. Molecules give rise to NMR spectra owing to

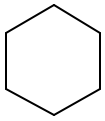
(A) electronic transitions. (B) molecular vibrations. (C) molecular rotations.
(D) molecular translations. (E) spin "flipping."

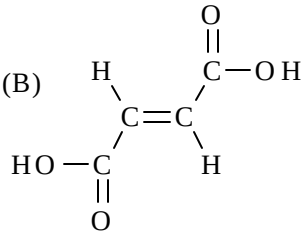
46. The region of the infrared spectrum between 4,000 cm^{-1} and 1,300 cm^{-1} is

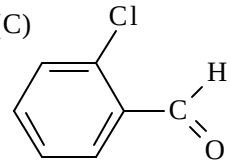
(A) the "fingerprint" region.
(B) the most useful region for identifying organic functional groups.
(C) the long-wavelength end of the spectrum.

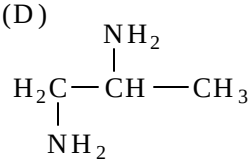
In questions 47-55 you will find an IR spectrum of a compound. Match the spectrum with one of the compounds (A-I) shown below.

[Hint: The compounds have not been selected randomly. Each compound has a structural feature, or group of features, that make it unique in the group. Look for absorptions in the IR spectra that correspond to these identifying features.]

(A) 

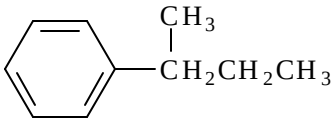
(B) 

(C) 

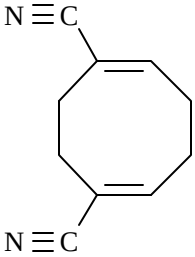
(D) 

(E) $H_3C-\underset{\underset{O}{\|}}{C}-CH_2CH_3$

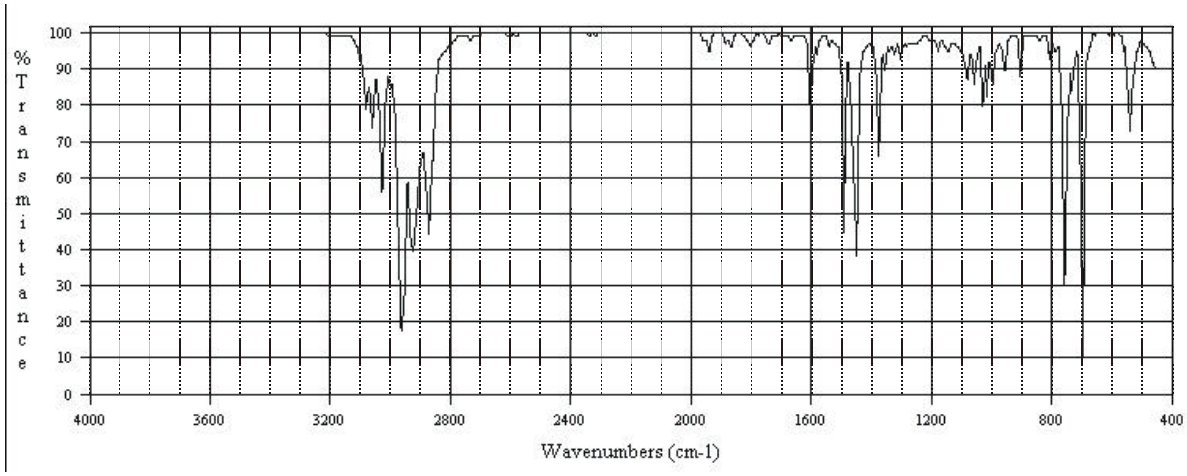
(F) $CH_3CH_2CH_2OH$

(G) 

(H) $CH_3(CH_2)_3C\equiv CH$

(I) 

Raise the shields, Mr. Spock.
We appear to be under attack
by some strange looking vessels.

47. 

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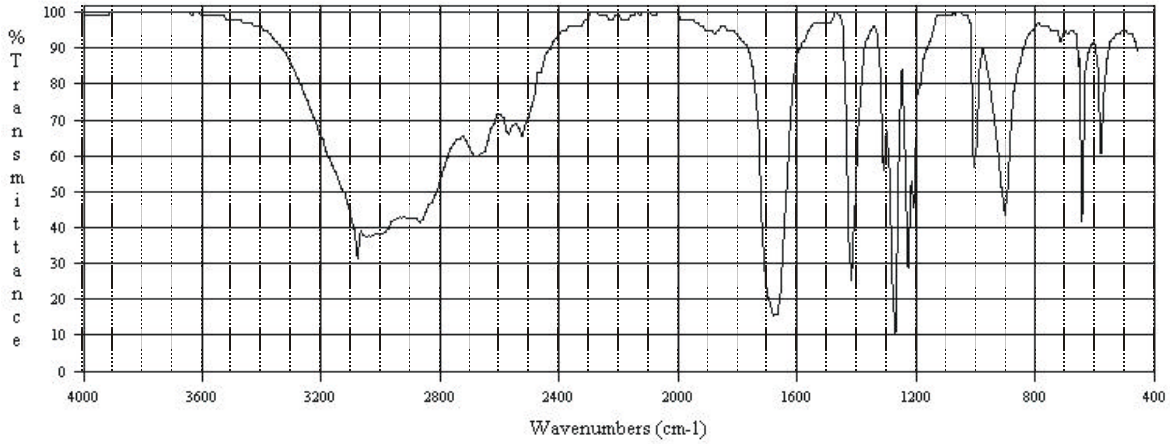
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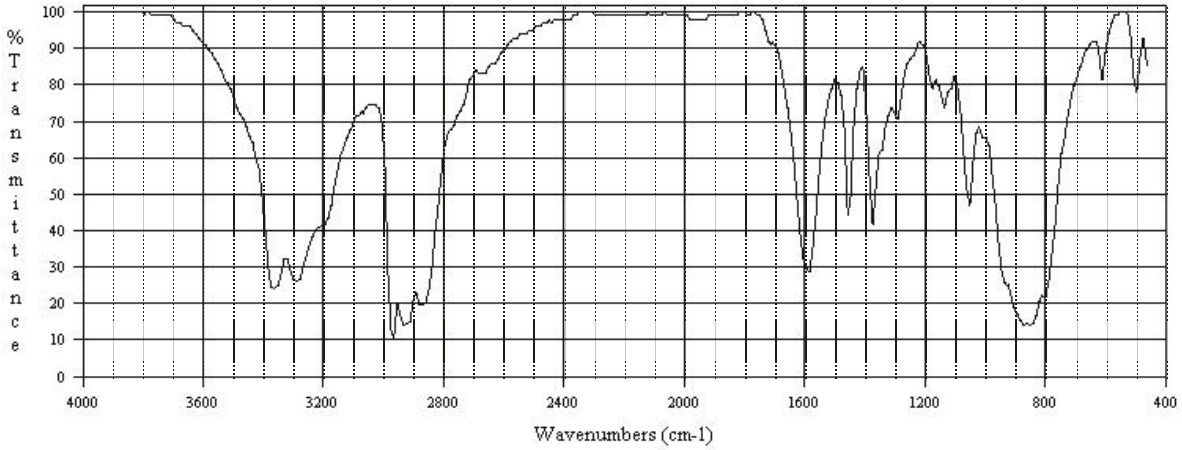
Wavenumbers (cm-1)

49.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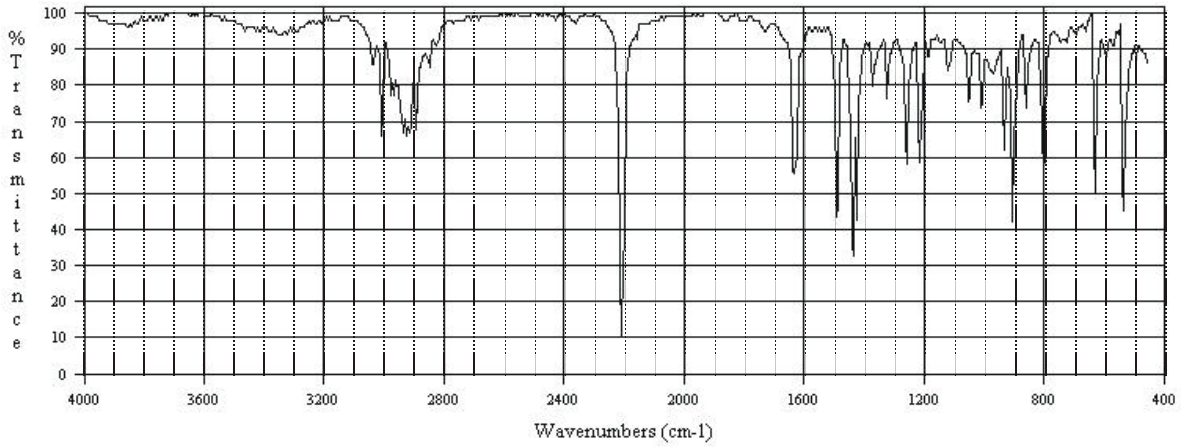
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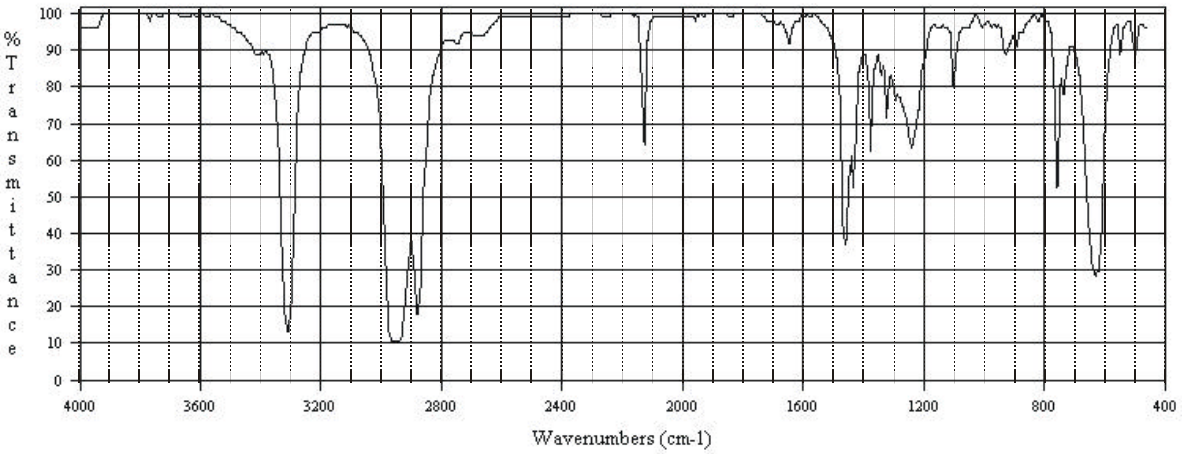
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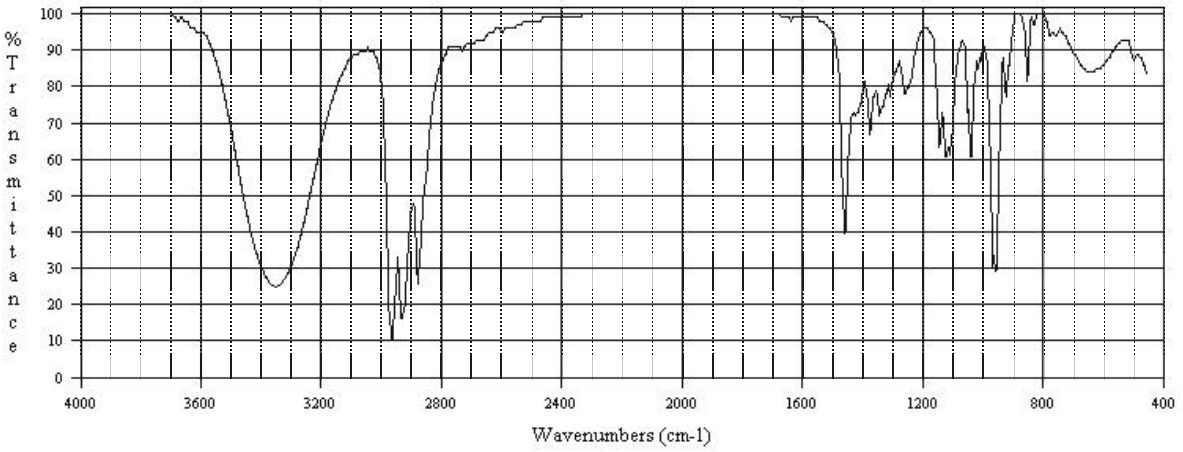
Wavenumbers (cm-1)

52.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Wavenumbers (cm-1)

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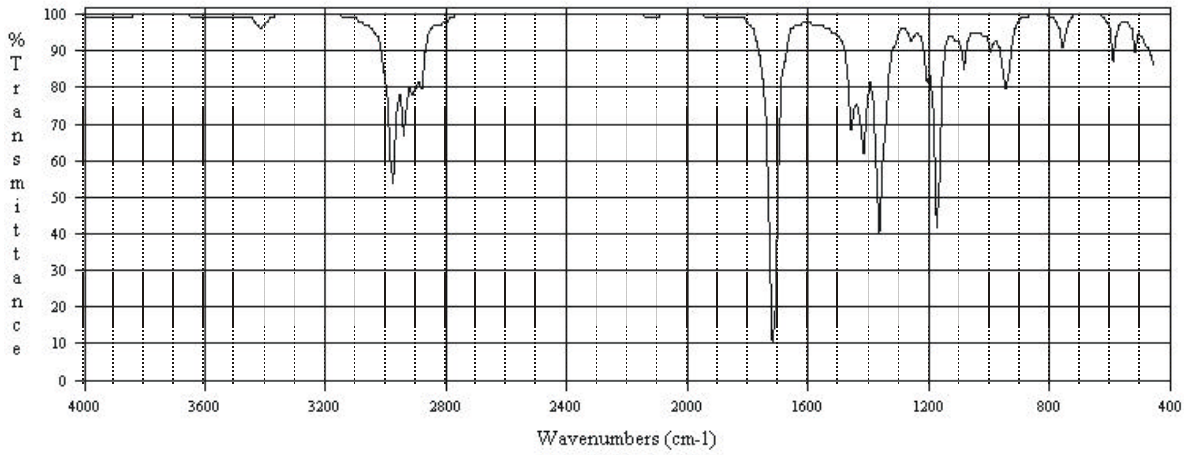
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Wavenumbers (cm-1)

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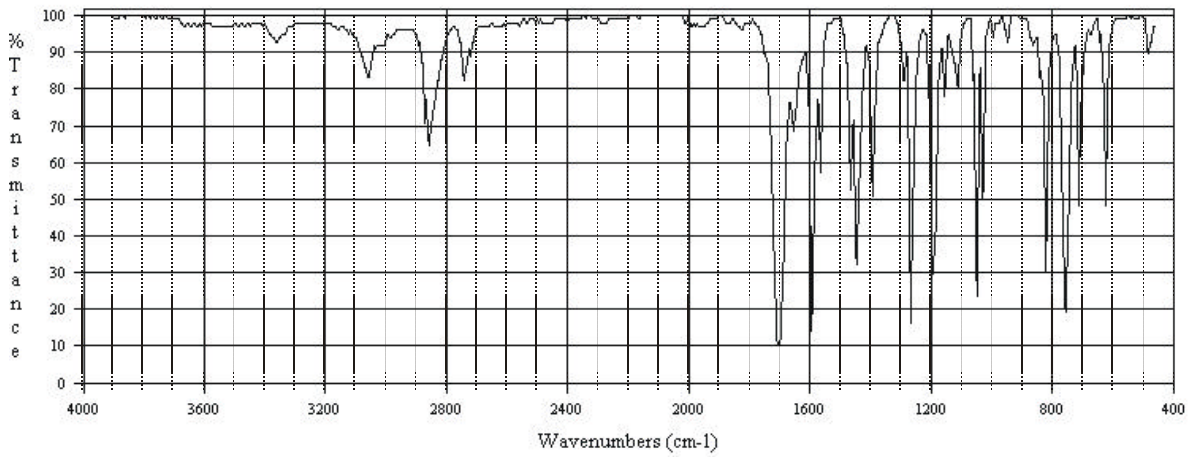
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Wavenumbers (cm-1)

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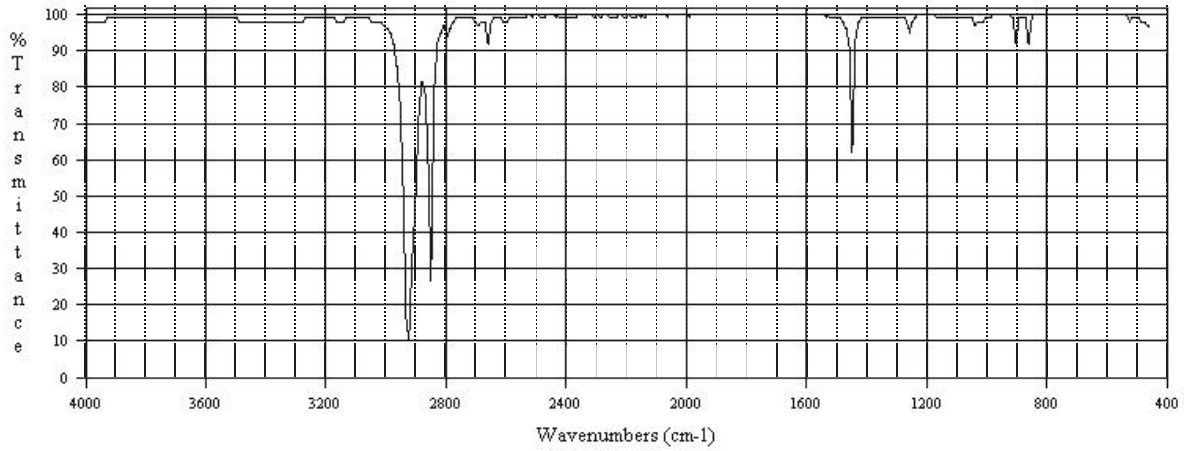
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Wavenumbers (cm-1)