

Department of Chemistry
SUNY/Oneonta

Chem 221 - Organic Chemistry I

Examination #4 - ANSWERS - December 11, 2000

Answer to question #32 corrected 12/13/00, 8:30pm.

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 1.85185... points each.

You have 90 minutes. Good luck!

1. Select all of the reaction mechanisms below that involve carbocations.

I - S_N1, II - S_N2, III - E1, IV - E2

(a) I only, (b) II only, (c) III only, (d) IV only, (e) I&II, (f) III&IV, (g) I&III,
(h) II&IV, (i) I-IV

2. Select all of the reaction mechanisms below that occur in one step.

I - S_N1, II - S_N2, III - E1, IV - E2

(a) I only, (b) II only, (c) III only, (d) IV only, (e) I&II, (f) III&IV, (g) I&III,
(h) II&IV, (i) I-IV

3. Select all of the reaction mechanisms below that require that the nucleophile attack the substrate at the back side of the carbon bonded to the leaving group.

I - S_N1, II - S_N2, III - E1, IV - E2

(a) I only, (b) II only, (c) III only, (d) IV only, (e) I&II, (f) III&IV, (g) I&III,
(h) II&IV, (i) I-IV

4. Select all of the reaction mechanisms below that will proceed more rapidly if a better leaving group is employed.

I - S_N1, II - S_N2, III - E1, IV - E2

(a) I only, (b) II only, (c) III only, (d) IV only, (e) I&II, (f) III&IV, (g) I&III,
(h) II&IV, (i) I-IV

5. Select all of the reaction mechanisms below that will proceed more slowly as the substrate is changed from primary to secondary to tertiary.

I - S_N1, II - S_N2, III - E1, IV - E2

(a) I only, (b) II only, (c) III only, (d) IV only, (e) I&II, (f) III&IV, (g) I&III,
(h) II&IV, (i) I-IV

6. Select all of the reaction mechanisms below that proceed much more quickly when the leaving group and a β -hydrogen are anti-periplanar to each other.

I - S_N1 , II - S_N2 , III - E1, IV - E2

(a) I only, (b) II only, (c) III only, (d) IV only, (e) I&II, (f) III&IV, (g) I&III, (h) II&IV, (i) I-IV

7. Select all of the reaction mechanisms below that will double in rate if the concentration of nucleophile/base is doubled.

I - S_N1 , II - S_N2 , III - E1, IV - E2

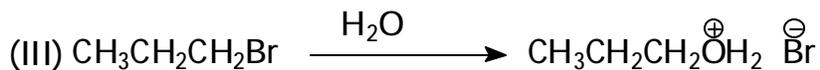
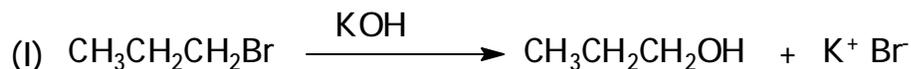
(a) I only, (b) II only, (c) III only, (d) IV only, (e) I&II, (f) III&IV, (g) I&III, (h) II&IV, (i) I-IV

8. Select all of the reaction mechanisms below that will double in rate if the concentration of substrate is doubled.

I - S_N1 , II - S_N2 , III - E1, IV - E2

(a) I only, (b) II only, (c) III only, (d) IV only, (e) I&II, (f) III&IV, (g) I&III, (h) II&IV, (i) I-IV

9. Rank the following reactions in order of decreasing rate (fastest first).



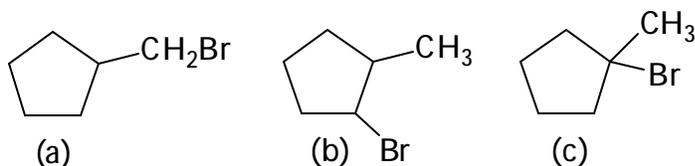
(a) I>II>III, (b) III>II>I, (c) II>I>III, (d) II>III>I, (e) I>III>II, (f) III>I>II

10. The reactions shown in question #9 proceed via an _____ mechanism.

(a) S_N1 , (b) S_N2 , (c) E1, (d) E2

For questions 11 through 14 choose a compound from the following list that best fits each

description.



11. Which compound would undergo S_N2 reaction with cyanide ion most rapidly? (a)
12. Which compound would undergo E1 elimination in t-butyl alcohol most rapidly? (c)
13. Which compound would be most likely to undergo rearrangement in a substitution reaction? (b)
14. Which compound might be expected to *not* exhibit a deuterium isotope effect in an elimination reaction with a weak base. (c)
15. Rank the following leaving groups in order of decreasing leaving group ability (best leaving group first).

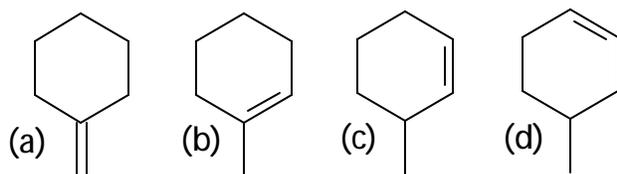
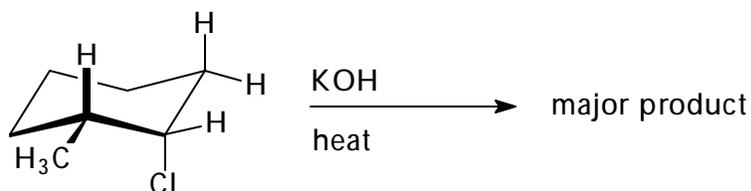
I: HO^- , II: Cl^- , III: Br^- , IV: I^-

- (a) $\text{I} > \text{II} > \text{III} > \text{IV}$, (b) $\text{IV} > \text{III} > \text{II} > \text{I}$, (c) $\text{II} > \text{IV} > \text{I} > \text{III}$, (d) $\text{IV} > \text{I} > \text{III} > \text{II}$,
(e) None of the above answers is correct.

16. Fill in the blanks by selecting the correct answer below.
The Markovnikov rule relates to the orientation (regioselectivity) of addition reactions of an alkene with electrophiles (H-X , for example). The ① rule relates to the orientation (regioselectivity) of elimination reactions of alkyl halides; this rule states that the ② highly substituted alkene will form preferentially. The ③ rule has less predictive power in the sense that mixtures containing substantial amounts of all possible isomeric products are frequently formed in situations where it would be employed.

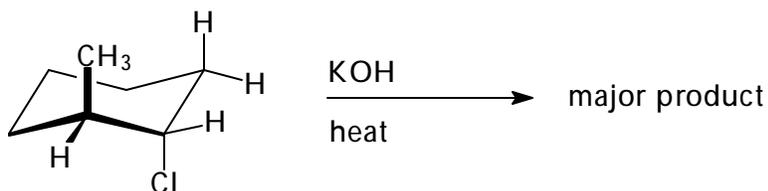
	❶	❷	❸
(a)	Hammond	more	Hammond
(b)	Zaitsev	more	Markovnikov
(c)	Zaitsev	less	Zaitsev
(d)	Zaitsev	more	Zaitsev
(e)	Hammond	less	Markovnikov
(f)	Hammond	more	Markovnikov

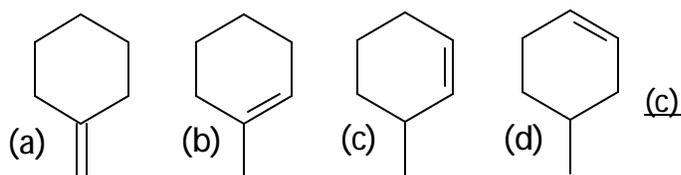
17. Predict the major elimination product in the following reaction.



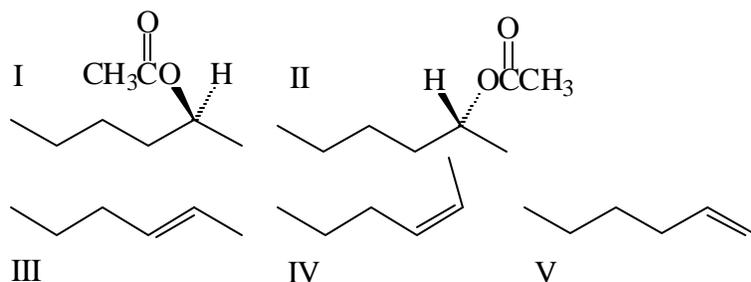
(b)

18. Predict the major elimination product in the following reaction.





19. 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

20. 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.

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



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

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, and the reason is the correct explanation of the statement.
- (B) The statement and the reason are both factually true, but the reason is not 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.

22. Reaction of a bulky base such as $(\text{CH}_3)_3\text{CO}^- \text{K}^+$ with secondary alkyl halides gives predominantly E2 elimination rather than $\text{S}_{\text{N}}2$ substitution because the transition state for the $\text{S}_{\text{N}}2$ reaction is more sterically hindered than that for E2 reaction.
(A)
23. $\text{S}_{\text{N}}2$ reactions of the type $\text{RBr} + \text{Na}^+ \text{OH}^- \rightarrow \text{ROH} + \text{Na}^+ \text{Br}^-$ 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.
(D)
24. For a nucleus to exhibit the nuclear magnetic resonance phenomenon it must be magnetic. Magnetic nuclei include:
(I) all nuclei with even masses and even atomic numbers.
(II) all nuclei with odd-numbered masses.
(III) all nuclei with even-numbered masses and odd atomic numbers.
(a) I only, (b) II only, (c) III only, (d) I&II, (e) II&III, (f) I&III
25. A basic equation relating to NMR is: $H_{\text{effective}} = H_{\text{applied}} - H_{\text{local}}$, where $H_{\text{effective}}$ is the magnetic field experienced by a nucleus, H_{applied} is the magnetic field produced by the spectrometer magnet, and H_{local} is the magnetic field produced by electrons located near the nucleus in question.

It is the case in NMR spectroscopy that all nuclei of a given type (all protons or all carbon-13 nuclei, for example) will absorb at the same value of

(a) $H_{\text{effective}}$, (b) H_{applied} , (c) H_{local} , (d) Bogus question. Nuclei of a given type do not all absorb at the same value of any of these quantities.

Questions 26-29 pertain to the charting of NMR spectra. Select one of the terms below to fill in the blanks in the questions. Each term may be used only once.

(a) TMS, (b) benzene, (c) high-field or upfield, (d) parts-per-million change in the applied magnetic field (δ), (e) low-field or downfield, (f) chemical shift, (g) specific absorption, (h) wavenumbers

26. When looking at an NMR chart the right side of the chart is the _____ side.

(c)

27. The exact place on the chart at which a nucleus absorbs is called its _____.

(e)

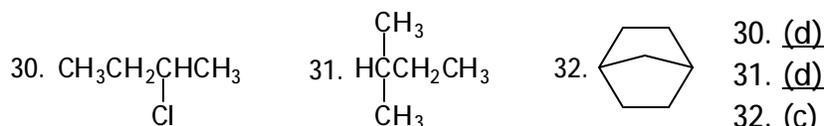
28. The calibration standard for ^1H and ^{13}C NMR is _____.

(a)

29. NMR charts are calibrated using a scale that is divided into _____.

(d)

In questions 30-32, select the answer that corresponds to the number of signals the compound would give in an ordinary (broadband-decoupled) carbon-13 NMR spectrum.



(a) 1, (b) 2, (c) 3, (d) 4, (e) 5, (f) 6, (g) 7

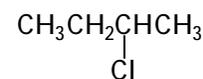
33. How many signals would the compound in question #30 generate in a carbon-13 DEPT-90 NMR spectrum?

(a) 1, (b) 2, (c) 3, (d) 4, (e) none

34. How many negative signals would the compound in question #30 generate in a carbon-13 DEPT-120 NMR spectrum?

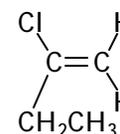
(a) 1, (b) 2, (c) 3, (d) 4, (e) none

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



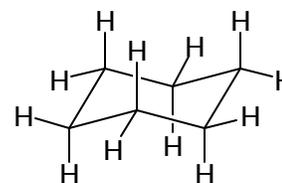
(a) 1, (b) 2, (c) 3, (d) 4, (e) 5, (f) 6, (g) 7, (h) 8, (i) 9, (j) 10

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



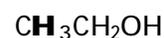
(a) 1, (b) 2, (c) 3, (d) 4, (e) 5, (f) 6, (g) 7, (h) 8, (i) 9, (j) 10

37. How many signals would the compound to the right give rise to in a proton NMR spectrum at room temperature?



(a) 1, (b) 2, (c) 3, (d) 4, (e) 5, (f) 6, (g) 7, (h) 8, (i) 10, (j) 12

38. The NMR signal from the emphasized hydrogens in the compound to the right would be split into a



(a) singlet (no splitting). (b) doublet. (c) triplet. (d) quartet. (e) quintet. (f) sextet.

39. The NMR signal, at room temperature, from the emphasized hydrogen in the compound to the right would be split into a

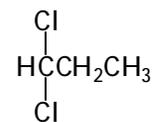


(a) singlet (no splitting). (b) doublet. (c) triplet. (d) quartet. (e) quintet. (f) sextet.

40. If a set of equivalent protons produces a signal that is a quartet in the NMR spectrum of a compound one can conclude that ___ nearby protons are causing the splitting.

(a) 1, (b) 2, (c) 3, (d) 4, (e) 5, (f) 6.

41. The proton NMR of the compound to the right would exhibit three signals, the intensities (integrated areas) of which would be _____ when going from downfield to upfield in the spectrum.



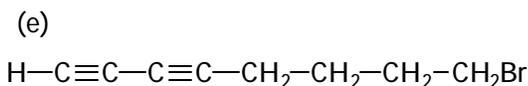
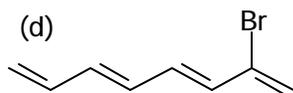
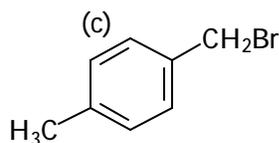
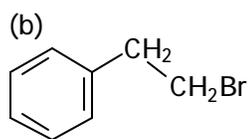
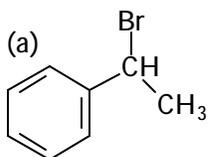
(a) 1:2:3, (b) 3:2:1, (c) 1:1:1, (d) 2:1:3, (e) 2:3:1

42. Both ^1H and ^{13}C NMR spectra *can* display four general features: (I) number of signals, (II) position of signals in the spectrum, (III) signal size (area), and (IV) spin-spin splitting. However two of these features are much less important in ^{13}C NMR, and indeed ^{13}C NMR spectra are often obtained in such a way that these two features do not show up. Which features are these?

(a) I&II, (b) II&III, (c) III&IV, (d) I&III, (e) I&IV, (f) II&IV

43. The molecular formula is $\text{C}_8\text{H}_9\text{Br}$. Select the structure below that best fits the following proton NMR data.

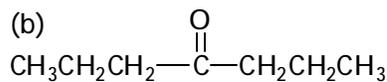
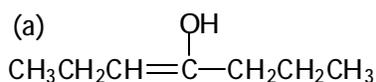
- doublet at $\delta = 2.0\text{ppm}$, area = 3,
- quartet at $\delta = 5.0\text{ppm}$, area = 1,
- signal(s) at $\delta \approx 7.3\text{ppm}$, area = 5.



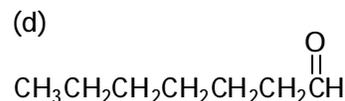
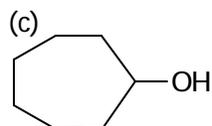
(a)

44. The molecular formula is $\text{C}_7\text{H}_{14}\text{O}$. Select the structure below that best fits the following proton NMR data.

- triplet at $\delta = 0.9\text{ppm}$, area = 3,
- sextet at $\delta = 1.6\text{ppm}$, area = 2,



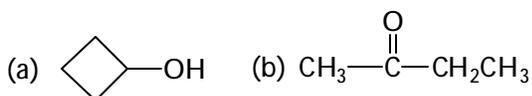
3. triplet at $\delta = 2.4\text{ppm}$, area = 2.



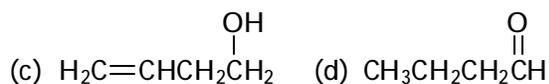
(b)

45. The molecular formula is C_4H_8O . Select the structure below that best fits the following proton NMR data.

1. quartet at $\delta = 2.4\text{ppm}$, area = 2,
2. singlet at $\delta = 2.1\text{ppm}$, area = 3,
3. triplet at $\delta = 1.0\text{ppm}$, area = 3.



(b)



46. Which of the following does not involve the interaction of molecules with electromagnetic energy?

- (a) mass spectroscopy, (b) infrared spectroscopy, (c) ultraviolet spectroscopy,
(d) nuclear magnetic resonance spectroscopy

47. The amount of energy in infrared radiation corresponds to

- (a) the amount of energy needed to promote one electron from a bonding to an antibonding molecular orbital.
(b) the amount of energy needed to “flip” the spin of a ^{13}C or ^1H nucleus.
(c) the amount of energy needed to strip a molecule of one electron to generate a cation radical.
(d) the amount of energy needed to increase certain molecular motions, like bond vibrations, in molecules.

48. Examining the infrared spectrum of a compound allows us to

- (a) determine the types of functional groups present in the compound.
(b) determine the carbon-hydrogen framework of the compound.
(c) determine the molecular weight of the compound.
(d) determine the molecular formula of the compound.

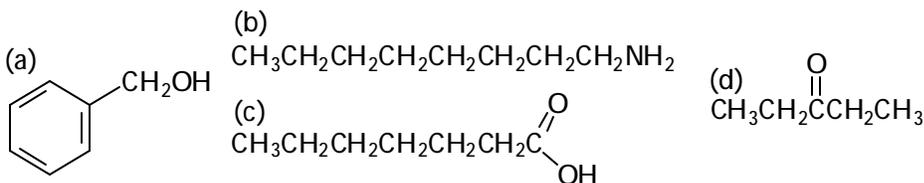
49. Select the answer which correctly matches the various bond types with the region of the infrared spectrum in which their absorptions occur.

	C-C, C-O, C-N, and C-X single bond stretching vibrations	C=O, C=N, and C=C stretching vibrations	N-H, C-H, and O-H stretching vibrations	C≡C and C≡N stretching vibrations
(a)	4000-2500 cm ⁻¹	2500-2000 cm ⁻¹	2000-1500 cm ⁻¹	< 1500 cm ⁻¹
(b)	2500-2000 cm ⁻¹	2000-1500 cm ⁻¹	< 1500 cm ⁻¹	4000-2500 cm ⁻¹
(c)	< 1500 cm ⁻¹	2000-1500 cm ⁻¹	4000-2500 cm ⁻¹	2500-2000 cm ⁻¹
(d)	4000-2500 cm ⁻¹	2500-2000 cm ⁻¹	< 1500 cm ⁻¹	2000-1500 cm ⁻¹
(e)	2500-2000 cm ⁻¹	4000-2500 cm ⁻¹	2000-1500 cm ⁻¹	< 1500 cm ⁻¹
(f)	2000-1500 cm ⁻¹	< 1500 cm ⁻¹	2500-2000 cm ⁻¹	4000-2500 cm ⁻¹

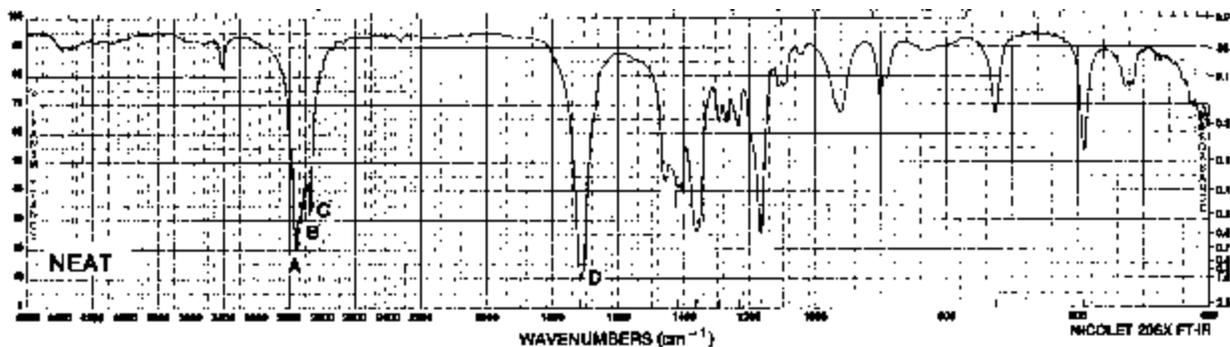
50. Currently, IR spectra are usually presented as _____, as ordinate, vs. _____, as abscissa. The abscissa is directly proportional to the _____ of the infrared radiation.

- (a) absorbance ... wavelength ... energy
 (b) % transmittance ... wave number ... frequency
 (c) % transmittance ... wavelength ... frequency
 (d) absorbance ... wave number ... wavelength
 (e) None of the above answers is correct.

In questions 51-54 match one of the compounds below with its infrared spectrum. The lettered absorptions in the spectra may be the most helpful in trying to identify the compound. In any event, to prevent eye strain, the locations of these absorptions, in cm⁻¹, are listed below the spectrum.

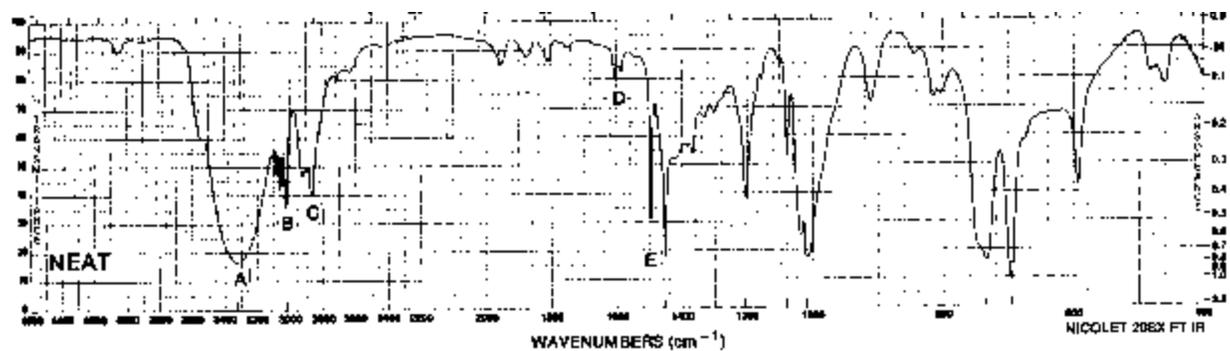


51. (d)



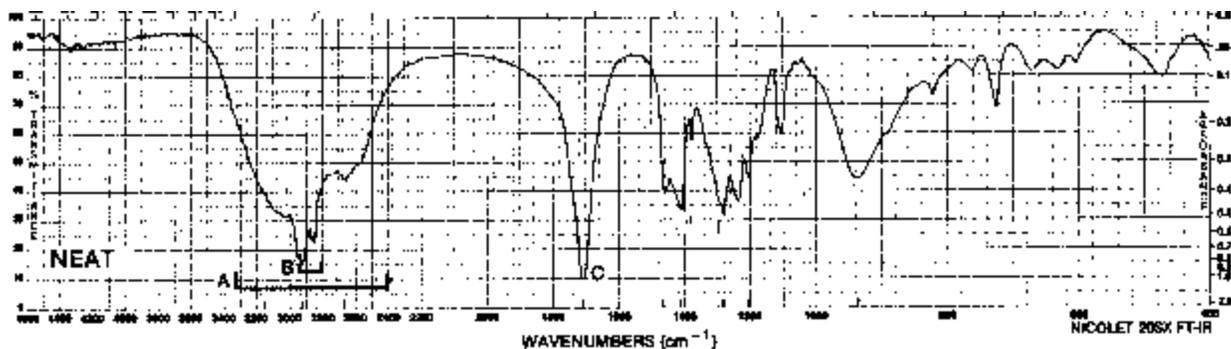
Absorption locations: A = 2964, B = 2935, C = 2870, D = 1717

52. (a)



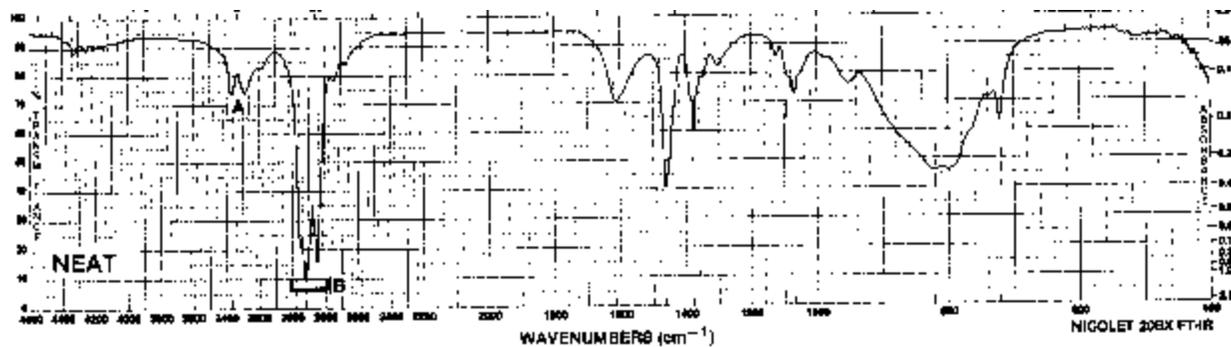
Absorption locations: A = 3331, B = several absorptions between 3100 and 3000, including one at 3030, C = 2980 and 2840, D = 1600 and 1580, E = 1497 and 1454.

53. (c)



A = Broad absorption centered around 2900, B = 2950 and 2932, C = 1711.

54. (b)



A = 3372, 3290, and ~3200, B = 2925 and 2850.