NAME (Print): _____

SIGNATURE: _____

Chemistry 320M/328M
Dr. Brent Iverson
3rd Midterm
November 15, 2012

Please print the first three letters of your last name in the three boxes

Please Note: This test may be a bit long, but there is a reason. I would like to give you a lot of little questions, so you can find ones you can answer and show me what you know, rather than just a few questions that may be testing the one thing you forgot. **I recommend you look the exam over and answer the questions you are sure of first**, then go back and try to figure out the rest. Also make sure to **look at the point totals** on the questions as a guide to help budget your time.

You must have your answers written in PERMANENT ink if you want a regrade!!!! This means no test written in pencil or ERASABLE INK will be regraded.

Please note: We routinely xerox a number of exams following initial grading to guard against receiving altered answers during the regrading process.

FINALLY, DUE TO SOME UNFORTUNATE RECENT INCIDENCTS YOU ARE NOT ALLOWED TO INTERACT WITH YOUR CELL PHONE IN ANY WAY. IF YOU TOUCH YOUR CELL PHONE DURING THE EXAM YOU WILL GET A "0" NO MATTER WHAT YOU ARE DOING WITH THE PHONE. PUT IT AWAY AND LEAVE IT THERE!!!

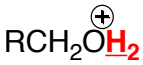
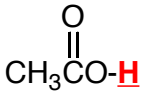
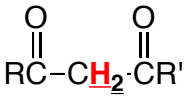
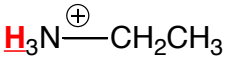
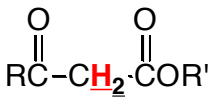
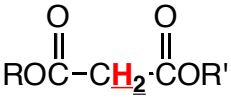
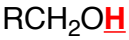
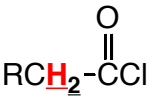
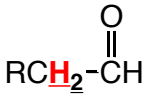
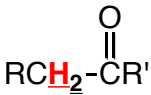
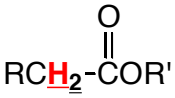
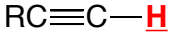
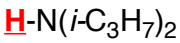
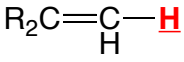
Honor Code

The core values of the University of Texas at Austin are learning, discovery, freedom, leadership, individual opportunity, and responsibility. Each member of the University is expected to uphold these values through integrity, honesty, trust, fairness, and respect toward peers and community.

_____

(Your signature)

Page	Points	
1		(25)
2		(13)
3		(14)
4		(18)
5		(20)
6		(26)
7		(24)
8		(16)
9		(19)
10		(20)
11		(15)
12		(17)
13		(8)
14		(8)
Total		(243)

Compound		pK_a
Hydrochloric acid		-7
Protonated alcohol		-2
Hydronium ion		-1.7
Acetic acid		4.8
Ammonium ion		9.2
β-Dicarbonyls		10
Ethyl ammonium ion		10.8
β-Ketoesters		11
β-Diesters		13
Water		15.7
Alcohols		15-19
Acid chlorides		16
Aldehydes		18-20
Ketones		18-20
Esters		23-25
Terminal alkynes		25
LDA		40
Terminal alkenes		44
Alkanes		51

PERIODIC TABLE OF THE ELEMENTS

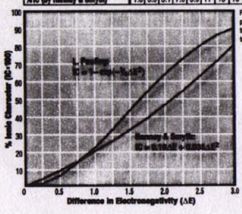
▼ Elementary Subatomic Particles

	Electron	Proton	Neutron	Photon	Neutrino
Symbol	e	P	n	γ	ν
Rest mass (kg)	9.1093897(54) x 10^{-31}	1.6726231(10) x 10^{-27}	1.6749286(10) x 10^{-27}	0	≈ 0
Molar mass (kg/mol)	5.4857990(13) x 10^{-7}	1.0072764(10(12) x 10^{-3}	1.0086649(4(14) x 10^{-3}	0	≈ 0
Particle-electron mass ratio	1	1836.152701(37)	1838.683662(40)	0	≈ 0
Particle-proton mass ratio	5.44617013(11) x 10^{-4}	1	1.001378404(9)	0	≈ 0
Particle-neutron mass ratio	5.438673x10^{-4}	0.998624	1	0	≈ 0
Specific charge (C/kg)	−1.7588196(53) x 10^{+11}	9.5788309(29) x 10^{+7}	0	0	0
Radius (m)	< 1 x 10^{-18}	8 x 10^{-16}	8 x 10^{-16}	0	≈ 0
Spin quantum number	1/2	1/2	1/2	1	1/2
Compton wavelength (m)	2.4263105(22) x 10^{-12}	1.321410(12(12) x 10^{-15}	1.3195910(12) x 10^{-15}	–	–
Magnetic moment (μ/T); μ	928.47701(31) x 10^{-26}	1.41060761(47) x 10^{-26}	0.9662370(40) x 10^{-26}	0	0
In Bohr magnetons; μ/μ_B	1.0011596521(10)	1.521032202(15) x 10^{-3}	1.0416736(25) x 10^{-3}	0	0
In nuclear magnetons; μ/μ_N	1838.282000(37)	2.792847356(63)	1.91304275(45)	0	0

Elementary particles are the fundamental constituents of energy and matter. The positron (e^+) is a positive-energy particle which has the same mass as an ordinary electron. The antineutrino ($\bar{\nu}$) has similar properties as that of a neutrino (ν) except its spin is directed along the direction of motion, whereas the neutrino's spin is always opposite to the direction of motion. Negative beta decay is the transformation of a neutron into a proton, a beta particle (negative electron) and a antineutrino ($n \rightarrow p + e^- + \bar{\nu}$). Positive beta decay involves the transformation of a proton into a neutron, a positron and a neutrino ($p \rightarrow n + \beta^+ + \nu$). The magnetic moment ($\mu$) of a particle can also be expressed as a dimensionless quantity by dividing it with either the Bohr magneton (μ_B = 9.2740154(31) x 10^{-24} J/T) or the nuclear magneton (μ_N = 5.0507699(17) x 10^{-27} J/T).

▼ % Ionic Character of a Single Chemical Bond

Difference in Electronegativity	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	2.9	3.0	3.1	3.2
%IC (by L. Pauling)	0.2	1.0	2.2	3.9	6.1	8.6	12	15	18	22	26	30	34	39	43	47	51	56	59	63	67	70	73	76	79	82	84	86	88	89	91	92
%IC (by Hannay & Smyth)	1.6	3.3	5.1	7.0	8.9	11	13	15	17	20	22	24	27	29	32	35	37	40	43	46	49	52	55	59	62	65	68	72	76	80	83	87



Percent ionic character describes the nature of a bond. Bonds possessing 50% or greater ionic character are commonly termed ionic; bonds with less than 50% ionic character are termed covalent. Pauling's equation was modified by Hannay & Smyth in order to achieve better agreement between experimental and calculated values. Transition from ionic to covalent binding is usually accompanied by a reduction in electrical conductance, melting point and boiling point.

1 IA																		18 VIII 0
1.00794 −259.34 −252.87 0.0899 2.20 13.598 $1s^1$	1 H Hydrogen	2 IIA										13 IIIB IIIA	14 IVB IVA	15 VB VA	16 VIB VIA	17 VIIB VIIA	4.0026022 −272.2 (26 atm) −268.93 0.1785 – 24.587 $1s^2$	2 He Helium
6.941 180.5 1342 0.534 0.98 5.392 [He]$2s^1$	3 Li Lithium	9.012182 1287 2471 1.8477 1.57 9.322 [He]$2s^2$ Beryllium										10.811 2075 – 2.31 8.296 [He]$2s^2 2p^1$	12.011 4492* 3825* 2.25 2.55 11.260 [He]$2s^2 2p^2$	14.00674 −210.00 −195.79 1.25046 3.04 14.534 [He]$2s^2 2p^3$	15.9994 −218.79 −182.95 1.429 3.44 13.618 [He]$2s^2 2p^4$	18.9984032 −219.62 −188.12 1.69 3.98 17.422 [He]$2s^2 2p^5$	20.1797 −248.59 −246.08 0.0002 – 21.564 [He]$2s^2 2p^6$	10 Ne Neon
22.989768 97.72 883 0.97 0.83 5.139 [Ne]$3s^1$	11 Na Sodium	24.3050 650 1090 1.74 1.31 7.646 [Ne]$3s^2$ Magnesium										26.981539 660.32 2519 2.702 1.61 5.986 [Ne]$3s^2 3p^1$ Aluminum	28.0855 1414 3265 2.33 1.90 8.151 [Ne]$3s^2 3p^2$ Silicon	30.973762 44.15 277 1.82 2.19 10.486 [Ne]$3s^2 3p^3$ Phosphorus	32.066 115.21 444.60 2.07 2.58 10.360 [Ne]$3s^2 3p^4$ Sulfur	35.4527 −101.5 −34.04 3.214 3.16 12.967 [Ne]$3s^2 3p^5$ Chlorine	39.948 −189.35 −185.85 1.784 – 15.759 [Ne]$3s^2 3p^6$ Argon
39.0983 63.38 759 0.86 0.82 4.341 [Ar]$4s^1$	19 K Potassium	40.078 842 1484 1.54 1.00 6.113 [Ar]$4s^2$ Calcium	44.955910 1541 2830 2.989 1.36 6.54 [Ar]$3d^1 4s^2$ Scandium	47.88 1668 3287 4.5 1.54 6.82 [Ar]$3d^2 4s^2$ Titanium	50.9415 1910 3407 5.96 1.63 6.74 [Ar]$3d^3 4s^2$ Vanadium	51.9961 1907 2671 7.20 1.66 6.766 [Ar]$3d^5 4s^1$ Chromium	54.93805 1246 2061 7.47 1.55 7.435 [Ar]$3d^5 4s^2$ Manganese	55.847 1538 2861 7.86 1.83 7.870 [Ar]$3d^6 4s^2$ Iron	58.93320 1495 2927 8.92 1.88 7.86 [Ar]$3d^7 4s^2$ Cobalt	58.6934 1455 2913 8.90 1.91 7.635 [Ar]$3d^8 4s^2$ Nickel	63.546 1084.62 2562 8.94 1.90 7.726 [Ar]$3d^{10} 4s^1$ Copper	65.39 419.53 907 7.14 (20°C) 1.65 9.394 [Ar]$3d^{10} 4s^2$ Zinc	69.723 29.76 2204 5.095 1.81 5.999 [Ar]$3d^{10} 4s^2 p^1$ Gallium	72.61 938.25 2833 5.35 2.01 7.899 [Ar]$3d^{10} 4s^2 p^2$ Germanium	74.92159 817* 614* 5.727 (85°C) 2.18 9.81 [Ar]$3d^{10} 4s^2 p^3$ Arsenic	78.96 221 685 4.81 2.55 9.752 [Ar]$3d^{10} 4s^2 p^4$ Selenium	79.904 −7.2 58.8 3.119 2.96 11.814 [Ar]$3d^{10} 4s^2 p^5$ Bromine	83.80 −157.36 −153.22 3.74 – 13.999 [Ar]$3d^{10} 4s^2 p^6$ Krypton
85.4678 38.31 688 1.532 0.82 4.177 [Kr]$5s^1$	37 Rb Rubidium	87.62 777 1382 2.6 0.95 5.806 [Kr]$5s^2$ Strontium	88.90585 1526 3336 4.469 1.22 6.38 [Kr]$4d^1 5s^2$ Yttrium	91.224 1855 4409 6.49 1.33 6.84 [Kr]$4d^2 5s^2$ Zirconium	92.90638 2477 4744 8.57 1.6 6.9 [Kr]$4d^4 5s^1$ Niobium	95.94 2623 4639 10.2 2.16 7.099 [Kr]$4d^5 5s^1$ Molybdenum	(97.9072) 2157 4265 11.5 1.9 7.28 Tc [Kr]$4d^5 5s^2$ Technetium	101.07 2334 4150 12.3 2.2 7.37 [Kr]$4d^7 5s^1$ Ruthenium	102.90550 1964 3695 12.4 2.28 7.46 [Kr]$4d^8 5s^1$ Rhodium	106.42 1554.9 2963 12.02 2.20 8.34 [Kr]$4d^{10}$ Palladium	107.8682 961.78 2162 10.5 1.93 7.576 [Kr]$4d^{10} 5s^1$ Silver	112.411 321.07 767 8.642 1.69 8.993 [Kr]$4d^{10} 5s^2$ Cadmium	114.818 156.60 2072 7.30 1.78 5.786 [Kr]$4d^{10} 5s^2 p^1$ Indium	118.710 231.93 2833 7.28 1.96 7.344 [Kr]$4d^{10} 5s^2 p^2$ Tin	121.757 630.63 1587 6.684 (99°C) 2.05 8.641 [Kr]$4d^{10} 5s^2 p^3$ Antimony	127.60 449.51 988 6.25 2.1 9.009 [Kr]$4d^{10} 5s^2 p^4$ Tellurium	126.90447 113.7 184.4 4.93 2.66 10.451 [Kr]$4d^{10} 5s^2 p^5$ Iodine	131.29 −111.75 −108.04 5.89 – 12.130 [Kr]$4d^{10} 5s^2 p^6$ Xenon
132.90543 28.44 671 1.879 0.79 3.894 [Xe]$6s^1$	55 Cs Cesium	137.327 727 1897 3.594 0.89 5.212 [Xe]$6s^2$ Barium	138.9055 920 3455 6.146 1.10 5.577 [Xe]$5d^1 6s^2$ Lanthanum	178.49 2233 4603 13.31 1.3 7.0 [Xe]$4f^{14} 5d^2 6s^2$ Hafnium	180.9479 3017 5458 16.6 1.5 7.89 [Xe]$4f^{14} 5d^3 6s^2$ Tantalum	183.84 3422 5555 19.35 2.36 7.98 [Xe]$4f^{14} 5d^4 6s^2$ Tungsten	186.207 3180 5596 20.5 1.9 7.88 [Xe]$4f^{14} 5d^5 6s^2$ Rhenium	190.23 3033 5012 22.61 2.2 8.7 [Xe]$4f^{14} 5d^6 6s^2$ Osmium	192.22 2446 4428 22.65 2.20 9.1 [Xe]$4f^{14} 5d^7 6s^2$ Iridium	195.08 1768.4 3825 21.45 2.28 9.0 [Xe]$4f^{14} 5d^9 6s^1$ Platinum	196.96654 1064.18 2856 19.31 2.54 9.225 [Xe]$4f^{14} 5d^{10} 6s^1$ Gold	200.59 −38.83 356.72 13.546 2.00 10.437 [Xe]$4f^{14} 5d^{10} 6s^2$ Mercury	204.3833 304 1473 11.85 2.04 6.108 [Xe]$4f^{14} 5d^{10} 6s^2 p^1$ Thallium	207.2 327.46 1749 11.34 2.33 7.416 [Xe]$4f^{14} 5d^{10} 6s^2 p^2$ Lead	208.98037 271.40 1564 9.78 2.02 7.289 [Xe]$4f^{14} 5d^{10} 6s^2 p^3$ Bismuth	(208.9824) 254 962 9.196 2.0 8.42 [Xe]$4f^{14} 5d^{10} 6s^2 p^4$ Polonium	(209.9871) 302 – – 2.2 – 10.748 [Xe]$4f^{14} 5d^{10} 6s^2 p^5$ Astatine	(222.0176) −71 −61.7 9.73 – – 10.748 [Xe]$4f^{14} 5d^{10} 6s^2 p^6$ Radon
(223.0197) 27 677 – 0.7 – [Rn]$7s^1$	87 Fr Francium	(226.0254) <1140 5.8 0.9 5.279 [Rn]$7s^2$ Radium	89 ** Ac Actinium	(261.11) – – – – – [Rn]$5f^{14} 6d^2 7s^2$ Unnilquadium	104 Unq Unnilpentium	(262.114) – – – – – [Rn]$5f^{14} 6d^3 7s^2$	105 Unp Unnilhexium	(263.118) – – – – – [Rn]$5f^{14} 6d^4 7s^2$	106 Unh Unnilseptium	(262.12) – – – – – [Rn]$5f^{14} 6d^5 7s^2$	107 Uns Unniloctium	(265) – – – – – [Rn]$5f^{14} 6d^6 7s^2$	108 Uno Unnilennium	(266) – – – – – [Rn]$5f^{14} 6d^7 7s^2$	109 Une Unnilunium	(272) – – – – – [Rn]$5f^{14} 6d^8 7s^2$	110 Uun Ununnium	

*indicates approximate values and/or inconsistent literature data.

3 IIIA IIIB	4 IVA IVB	5 VA VB	6 VIA VIB	7 VIIA VIIB	8 VIIIA VIII	9 VIIIA VIII	10 VIIIA VIII	11 IB IB	12 IIB IIB
140.115 798 3424 6.710 1.12 5.466 [Xe]$4f^1 5d^1 6s^2$ Cerium	58 Ce	140.90765 931 3510 6.773 1.13 5.42 [Xe]$4f^3 6s^2$ Praseodymium	59 Pr	144.24 1016 3068 7.00 1.14 5.489 [Xe]$4f^4 6s^2$ Neodymium	60 Nd	(144.9127) 1042 3000 7.264 1.13 5.554 Pm [Xe]$4f^5 6s^2$ Promethium	61	150.36 1072 1700 7.536 1.17 5.631 [Xe]$4f^6 6s^2$ Samarium	62 Sm	151.965 822 1596 5.244 1.2 5.666 [Xe]$4f^7 6s^2$ Europium	63 Eu	157.25 1314 3264 7.901 1.20 5.141 [Xe]$4f^7 5d^1 6s^2$ Gadolinium	64 Gd	158.92534 1359 3221 8.230 1.2 5.842 [Xe]$4f^9 6s^2$ Terbium	65 Tb	162.50 1411 2561 8.551 1.22 5.927 [Xe]$4f^{10} 6s^2$ Dysprosium	66 Dy	164.93032 1472 2694 8.80 1.23 6.018 [Xe]$4f^{11} 6s^2$ Holmium	67 Ho	167.26 1529 2862 9.066 1.24 6.101 [Xe]$4f^{12} 6s^2$ Erbium	68 Er	168.93421 1545 1946 9.321 1.25 6.184(b) [Xe]$4f^{13} 6s^2$ Thulium	69 Tm	173.04 824 1194 6.966 – 6.25304 [Xe]$4f^{14} 6s^2$ Ytterbium	70 Yb	174.967 1663 3393 9.84 1.27 5.42589 [Xe]$4f^{14} 5d^1 6s^2$ Lutetium	71 Lu
232.0381 1750 4788 11.72 1.3 6.08 [Ra]$6d^2 7s^2$ Thorium	90 Th	231.03588 1572 – 15.37 1.5 5.89 [Rn]$5f^2 6d^1 7s^2$ Protactinium	91 Pa	238.0289 1135 4131 19.05±0.02 1.38 6.05 [Rn]$5f^3 6d^1 7s^2$ Uranium	92 U	(237.0482) 644 3909 26.45 1.36 6.19 Np [Rn]$5f^4 6d^1 7s^2$ Neptunium	93	(244.0642) 640 3228 19.816 1.28 5.8 Pu [Rn]$5f^6 7s^2$ Plutonium	94	(243.0614) 1176 2607 13.67 1.3 5.993 Am [Rn]$5f^7 7s^2$ Americium	95	(247.0703) 1345 – 13.51 1.3 6.02 Cm [Rn]$5f^7 6d^1 7s^2$ Curium	96	(247.0703) 1050 – 14.78 1.3 6.23 Bk [Rn]$5f^9 7s^2$ Berkelium	97	(251.0796) 900 – – 1.3 6.30 Cf [Rn]$5f^{10} 7s^2$ Californium	98	(252.083) 860 – – 1.3 6.42 Es [Rn]$5f^{11} 7s^2$ Einsteinium	99	(257.0951) 1527 – – 1.3 6.50 Fm [Rn]$5f^{12} 7s^2$ Fermium	100	(258.10) 827 – – 2.3 1.3 6.58 Md [Rn]$5f^{13} 7s^2$ Mendelevium	101	(259.1009) 827 – – 2.3 1.3 6.65 No [Rn]$5f^{14} 7s^2$ Nobelium	102	(262.11) 1627 – – 2.3 1.3 6.10 Lr [Rn]$5f^{14} 6d^1 7s^2$ Lawrencium	103

The data for this reference guide were obtained from the latest scientific and governmental sources (IUPAC, CODATA, National Bureau of Standards, etc.). Italicized values and/or inconsistent data are marked with an asterisk (*).

1. Ratio of the average mass per atom of the element to 1/12 of the mass of an atom of ^{12}C. Round brackets indicate atomic weight of the most stable or best known isotope. 2. Number of protons in the nucleus of each atom of an element. 3. Number of charges an atom would have in a molecule (or an ionic compound) if electrons were transferred completely. 4. Names and symbols of elements 104-110 are those recommended by the International Union of Pure and Applied Chemistry (IUPAC)—alternative names have been proposed by other groups. 5. Distribution of electrons among the various atomic orbitals. 6. Two other group classifications systems still in use today rely on an A/B coding scheme to categorize periodic properties. Because of the potential for confusion between these two systems (i.e., IIIA in one scheme is equal to IIIB in the other), IUPAC recommends the use of an unambiguous 1-18 group classification system. 7. Melting point: temperature at which solid and liquid phases coexist in equilibrium. Boiling point: temperature at which the vapor pressure of a liquid is equal to the external atmospheric pressure. Unless otherwise stated values are at 1 atm; TP = sublimation point at 1 atm; TP = triple point. 8. Mass of the substance divided by its volume (g/cm³ at 20°C for gases: g/L at 0°C, 1 atm). 9. Relative measure of the attraction of an atom in a chemical bond for the shared electrons. 10. Minimum energy to remove an electron from an isolated atom in its ground state (1eV = 96.487 kJ/mol).

PAPERTECH

Editors: T. K. Varga, M.A.Sc. & C. Bello, M.A.Sc.

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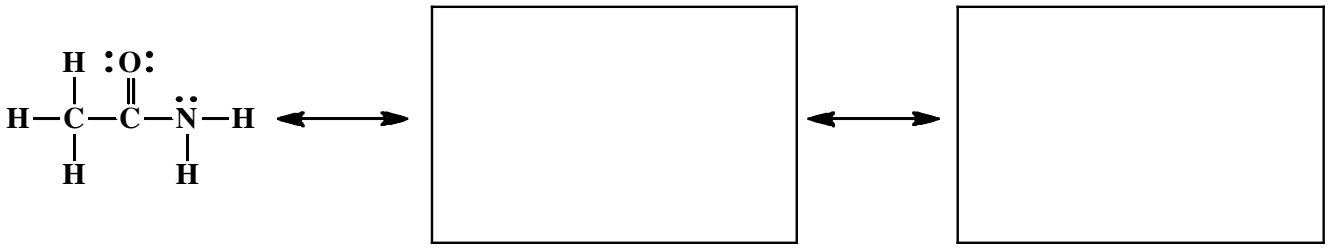
Signature_____ Pg 1 _____(25)

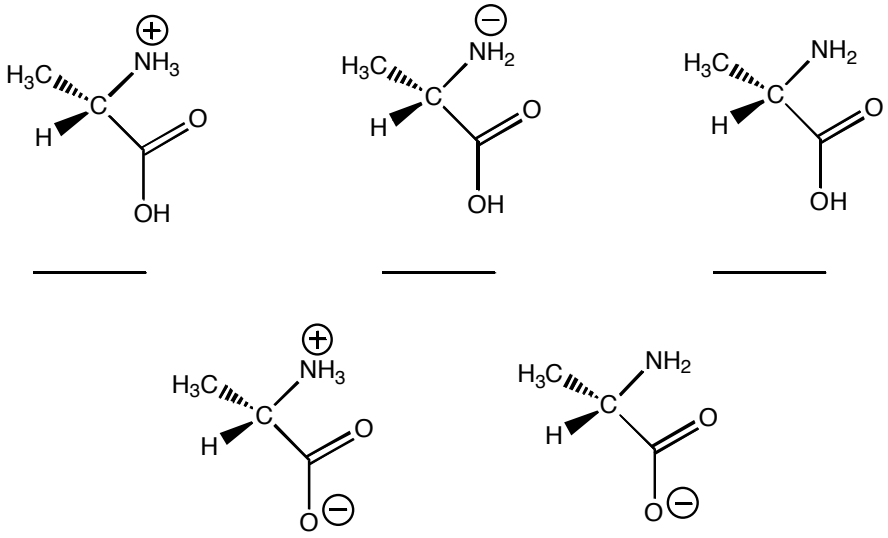
1. (5 pts) What is the most important question in organic chemistry?

2. (10 pts) Amides are best represented as the hybrid of three contributing structures. Draw the second and third important contributing structures in the spaces provided, including all lone pairs and formal charges. For the two structures on the left in each problem, use arrows to indicate the movement of electrons to give the structures you drew. There is no need to draw any circles around any of these contributing strucures. You might want to read these directions again to make sure you know what we want



3. (10 pts) Put a 7 under the species that will be present at pH 7.0, put a 2 under the species that will be present at 2.0, and put a 12 under the species that will be present at pH 12.0. **Put an "X" under the two species that cannot predominate at any pH.**

The pKa of a carboxylic acid (RCO_2H) is generally in the 4-5 range. The pKa of ammonium ions ($RNH_3^{\oplus}$) is in the 9-10 range.



_____ _____ _____

_____ _____

4. (13 pts) Consider the following statements that refer to **S_N1, S_N2, E1, E2** or a **radical chain reaction** mechanism. To which mechanism(s), if any, does each statement apply?

Mechanisms

A. Involves a carbocation intermediate _____

B. When reaction occurs at a chiral center on a pure sample of a single enantiomer, a single enantiomer product with inversion of configuration is created. _____

C. When reaction occurs at a chiral center on a pure sample of a single enantiomer, a mixture of product enantiomers will be created _____

D. Involves an antiperiplanar transition state geometry _____

E. The order of reactivity is methyl halides > 1° haloalkanes > 2° haloalkanes and not 3° haloalkanes _____

F. For alkane starting materials, the order of reactivity is 3° hydrogens > 2° hydrogens > 1° hydrogens _____

G. The reaction mechanism(s) that will occur when KOtBu reacts with a 1° haloalkane _____

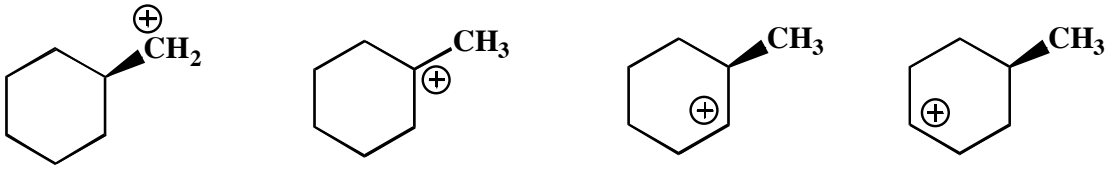
H. The reaction mechanism(s) that will occur when Br_2 and light are used _____

I. The reaction mechanism(s) that will occur when HBr and peroxides with light are used _____

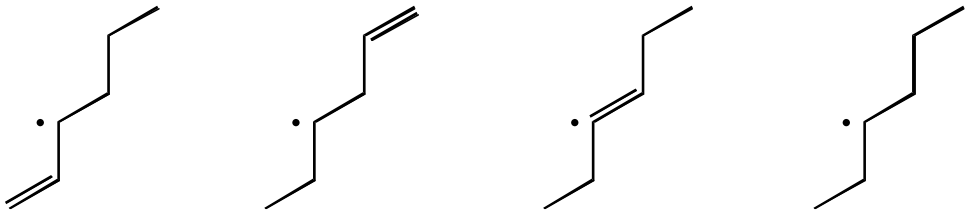
J. The reaction mechanism(s) that will occur when NBS and light are used _____

K. The reaction mechanism that occurs when the anion of a terminal alkyne reacts with a 1° haloalkane. _____

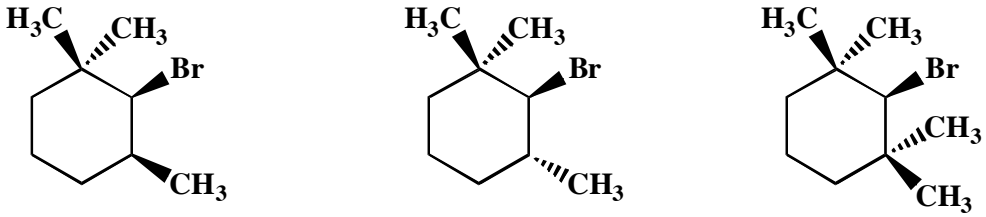
5. (4 pts) For the following series of cations, **circle the most stable cation.**



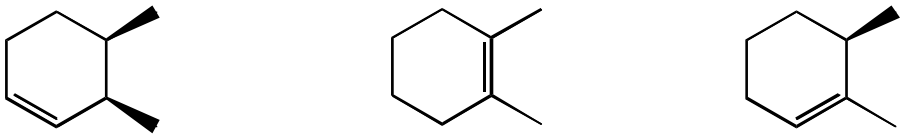
6. (4 pts) For the following series of radicals, **circle the most stable radical.**



7. (3 pts) Circle the molecule that will react the fastest with strong base through an E2 mechanism.



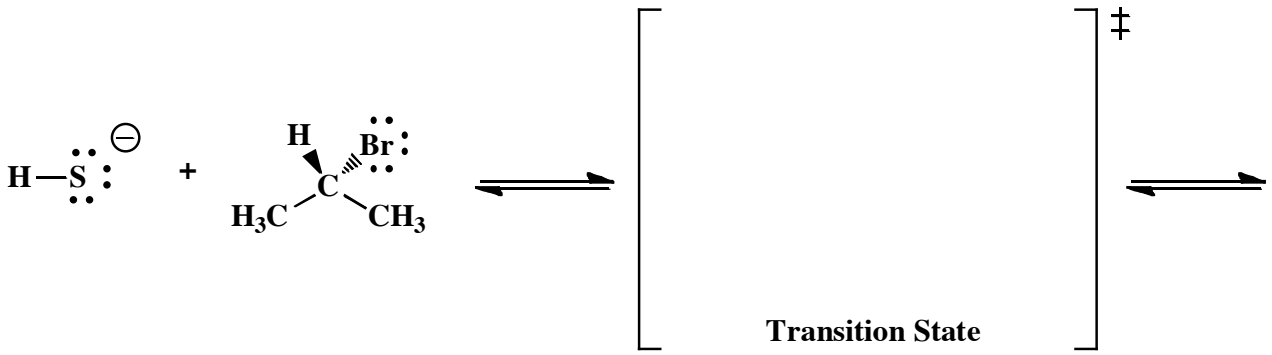
8. (3 pts) For the following constitutional isomers, rank them from 1-3 according to overall alkene stability, with a 1 under the LEAST STABLE ALKENE and a 3 under the MOST STABLE ALKENE.



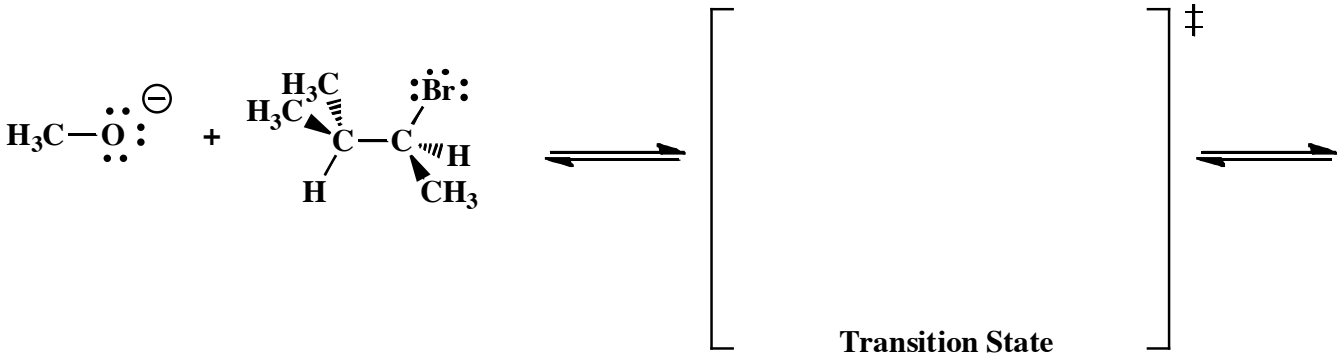
_____ _____ _____

9. (13 pts total) For each set of reagents below, draw the **key transition state** that occurs during the indicated reaction. We do not want the entire mechanism or products, just the first key transition state. **Use dotted lines (ıılıılıılıı) to indicate bonds that are in the process of being broken or made. Write any formal charges that you think are important. On the starting structures, draw all appropriate arrows to indicate the flow of electrons.**

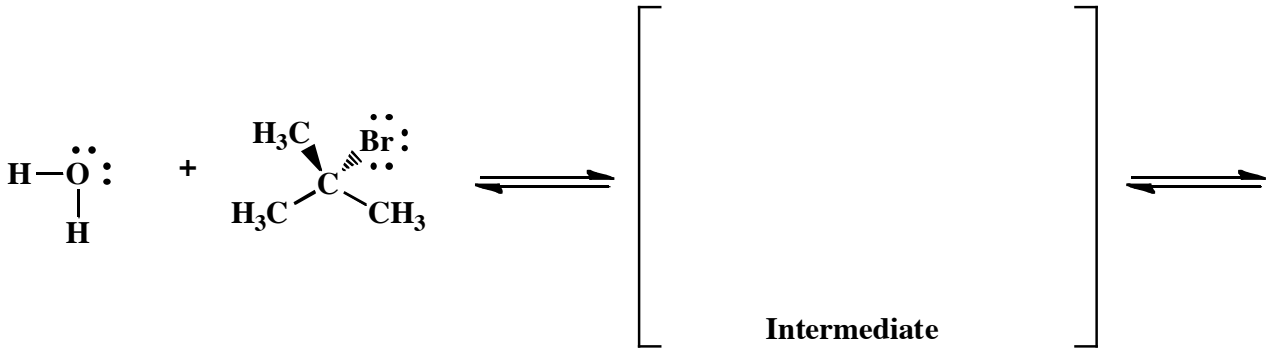
A.



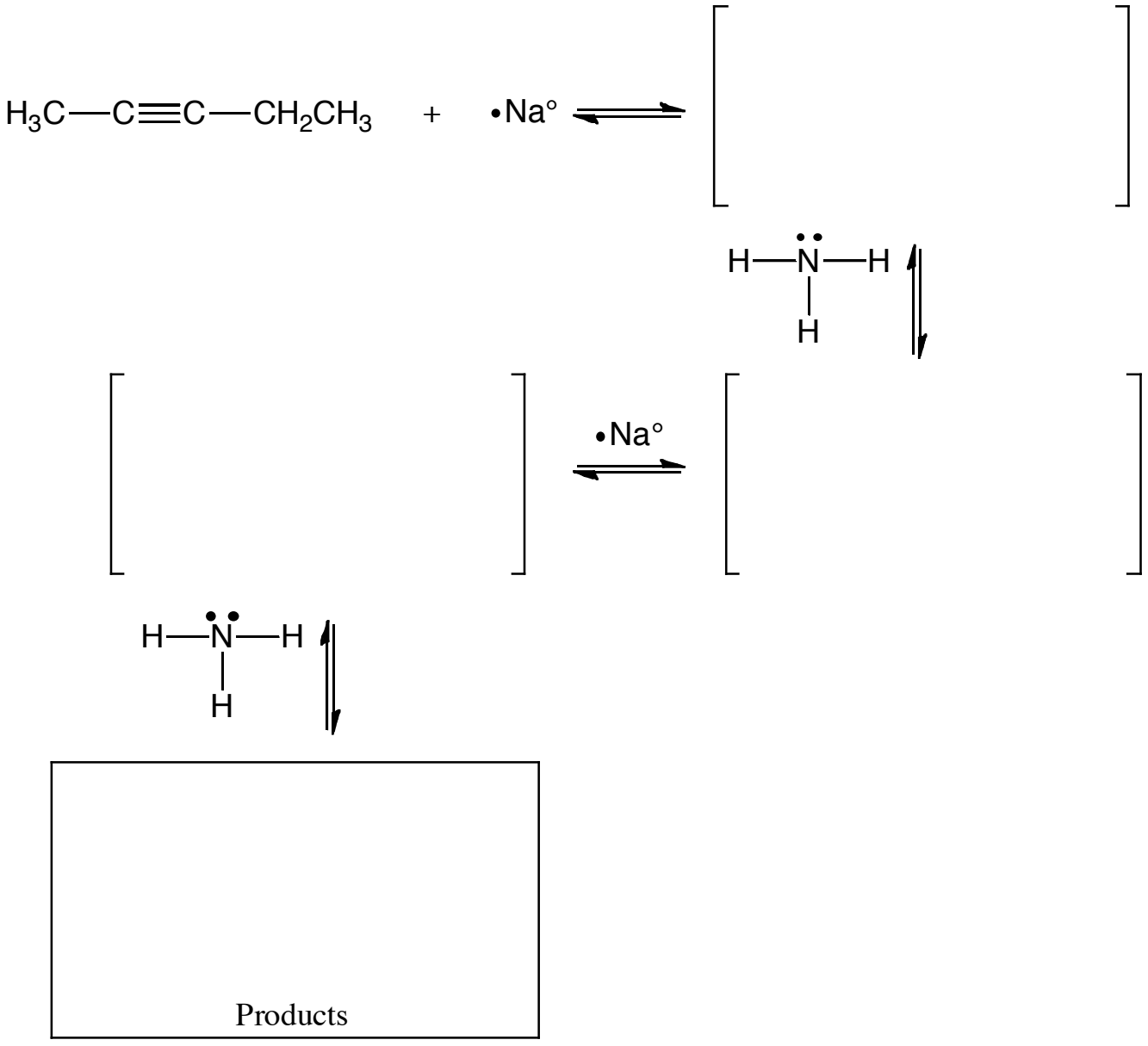
B.



10. (5 pts total) For the set of reagents below, draw the **first key intermediate** that occurs during the indicated reaction. We do not want the entire mechanism or products, just the first key intermediate. **Write any formal charges that you think are important. On the starting structures, draw all appropriate arrows to indicate the flow of electrons.**

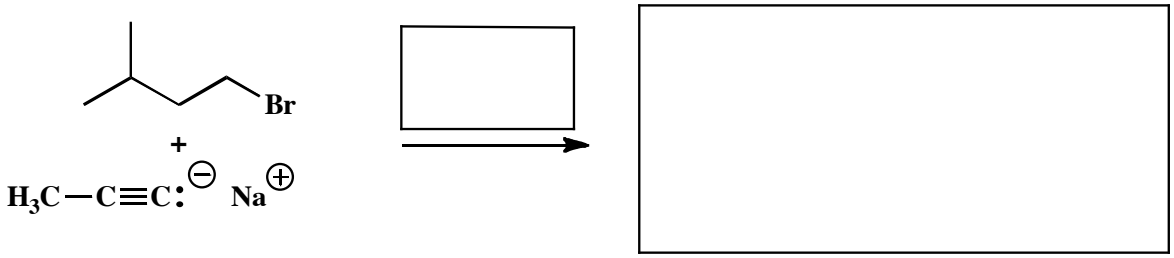


11. (20 pts total) Complete the following mechanism for reaction of the alkyne with sodium metal in ammonia. Use appropriate arrows to show movement of electron density, and show all non-bonding electrons as dots and show any formal charges. **If any of the species are really a racemic mixture of enantiomers, you only need to draw one stereoisomer and write "racemic"**

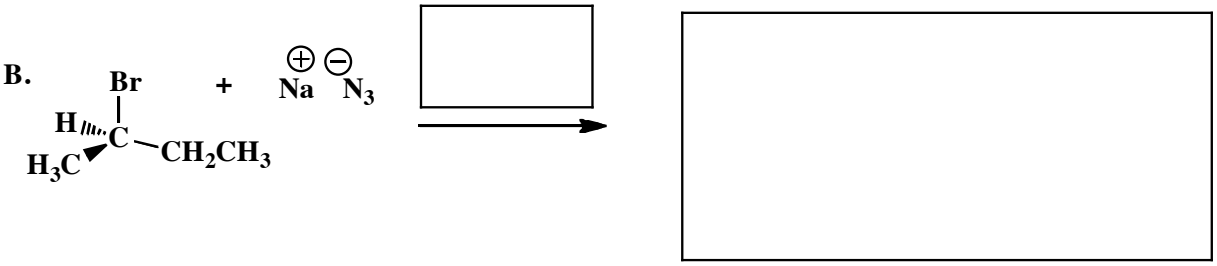


12. (5 or 6 pts each) The following reactions all involve chemistry of haloalkanes. **Fill in the box above the arrow with the mechanism that will be followed (S_N2, E2, etc.). Then draw only the predominant product or products** and please remember that **you must draw the correct stereoisomers**. For S_N1/E1 reactions you must draw all significant products (including all stereoisomers).

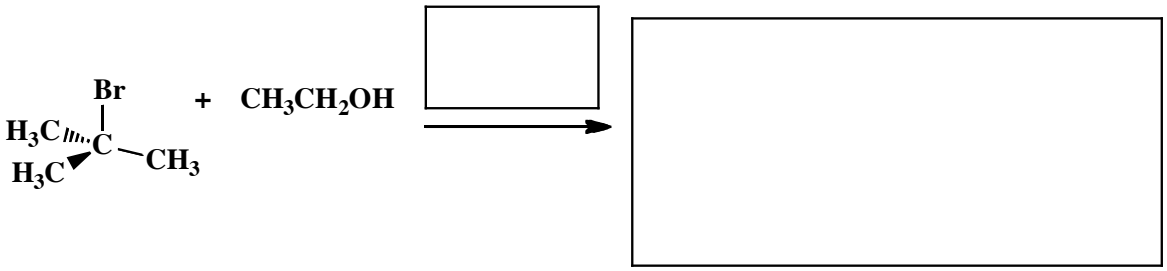
A.



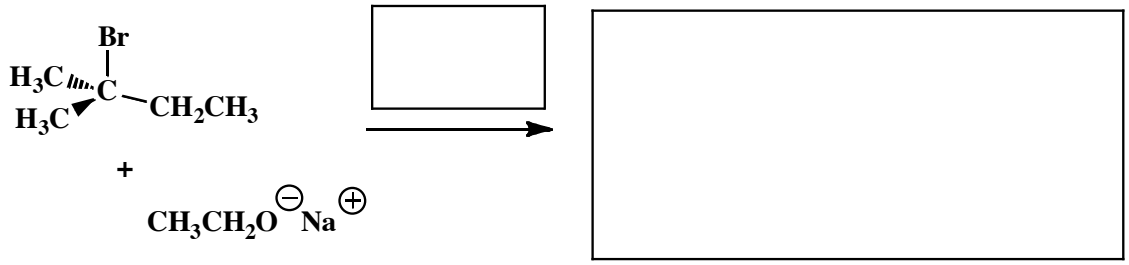
B.



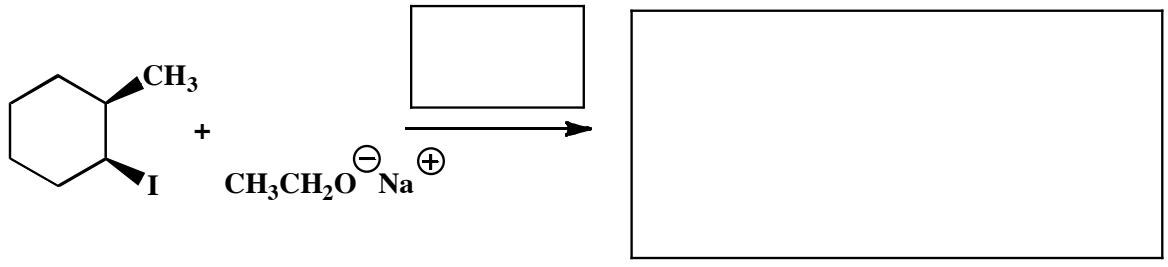
C.



D.

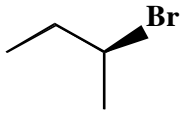


E.



12. (5,7 or 9 pts each) The following reactions all involve chemistry of haloalkanes. **Fill in the box above the arrow with the mechanism that will be followed (S_N2, E2, etc.)**. **Then draw only the predominant product or products** and please remember that **you must draw the correct stereoisomers**. For S_N1/E1 reactions you must draw all significant products (including all stereoisomers).

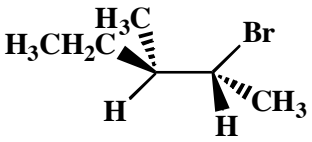
F.



+

CH_3OH

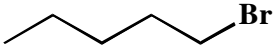
G.



+

$CH_3CH_2O^{\ominus}Na^{\oplus}$

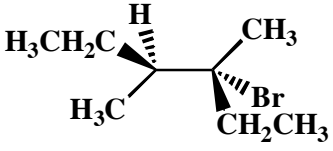
H.



+

$(CH_3)_3CO^{\ominus}K^{\oplus}$

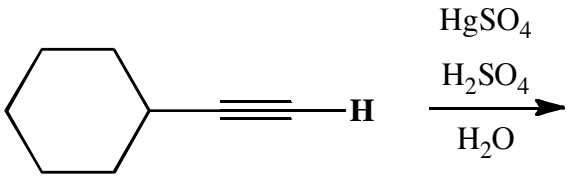
I.

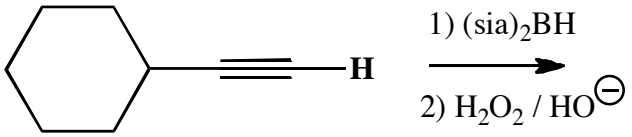


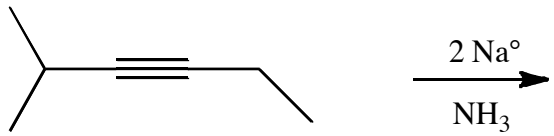
+

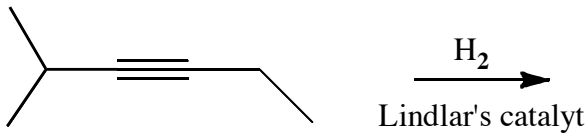
$CH_3CH_2O^{\ominus}Na^{\oplus}$

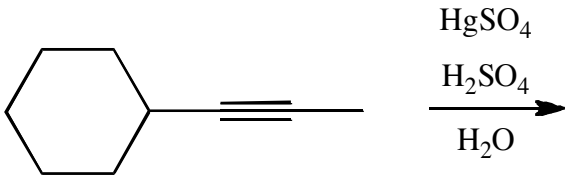
13. (3 or 4 pts each) For the following, complete the reactions with the predominant product or products. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate. Assume no rearrangements take place.



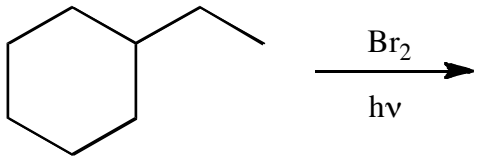


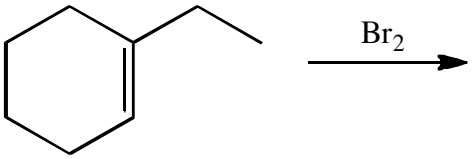


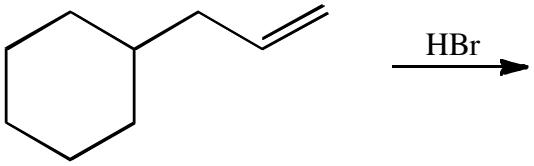


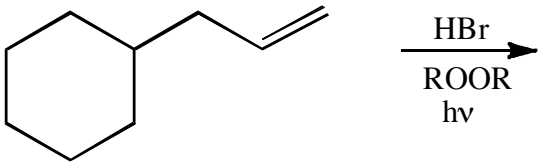


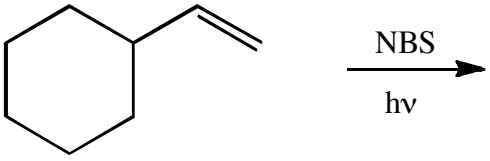
14. (3 or 5 pts each) For the following reactions, all of which involve reagents containing bromine atoms, complete the reactions with the predominant product or products. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate. Assume no rearrangements take place.



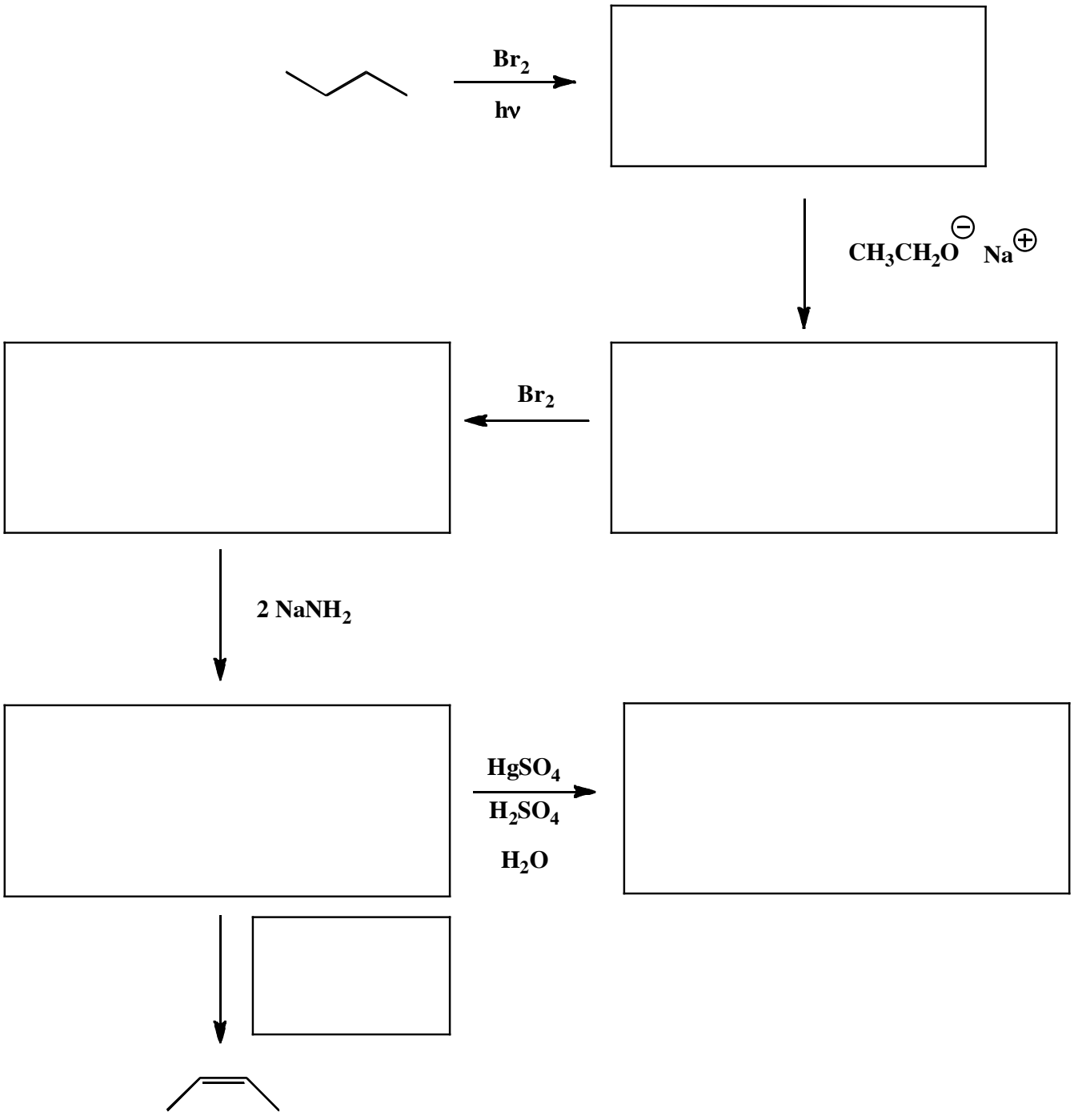




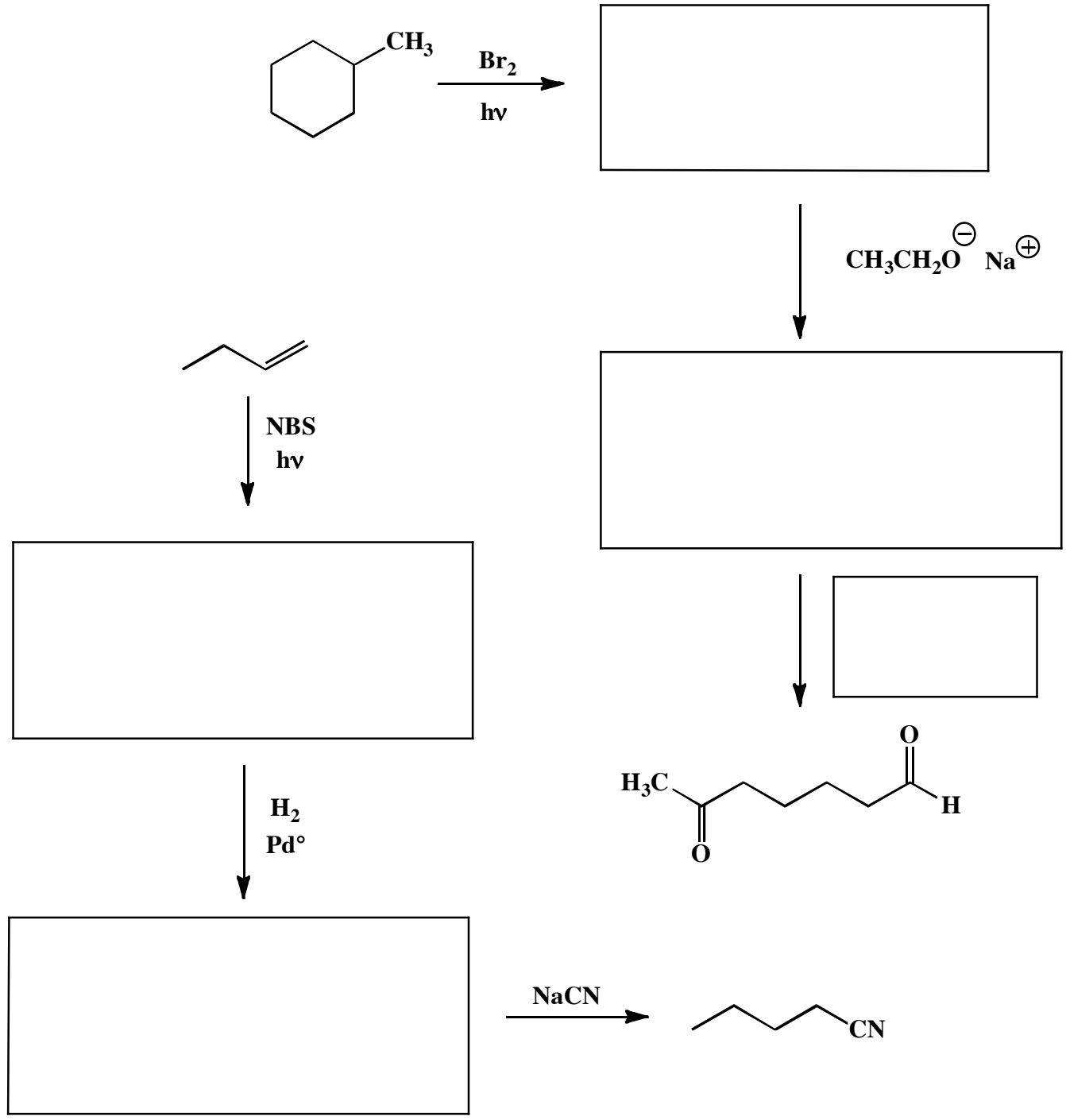




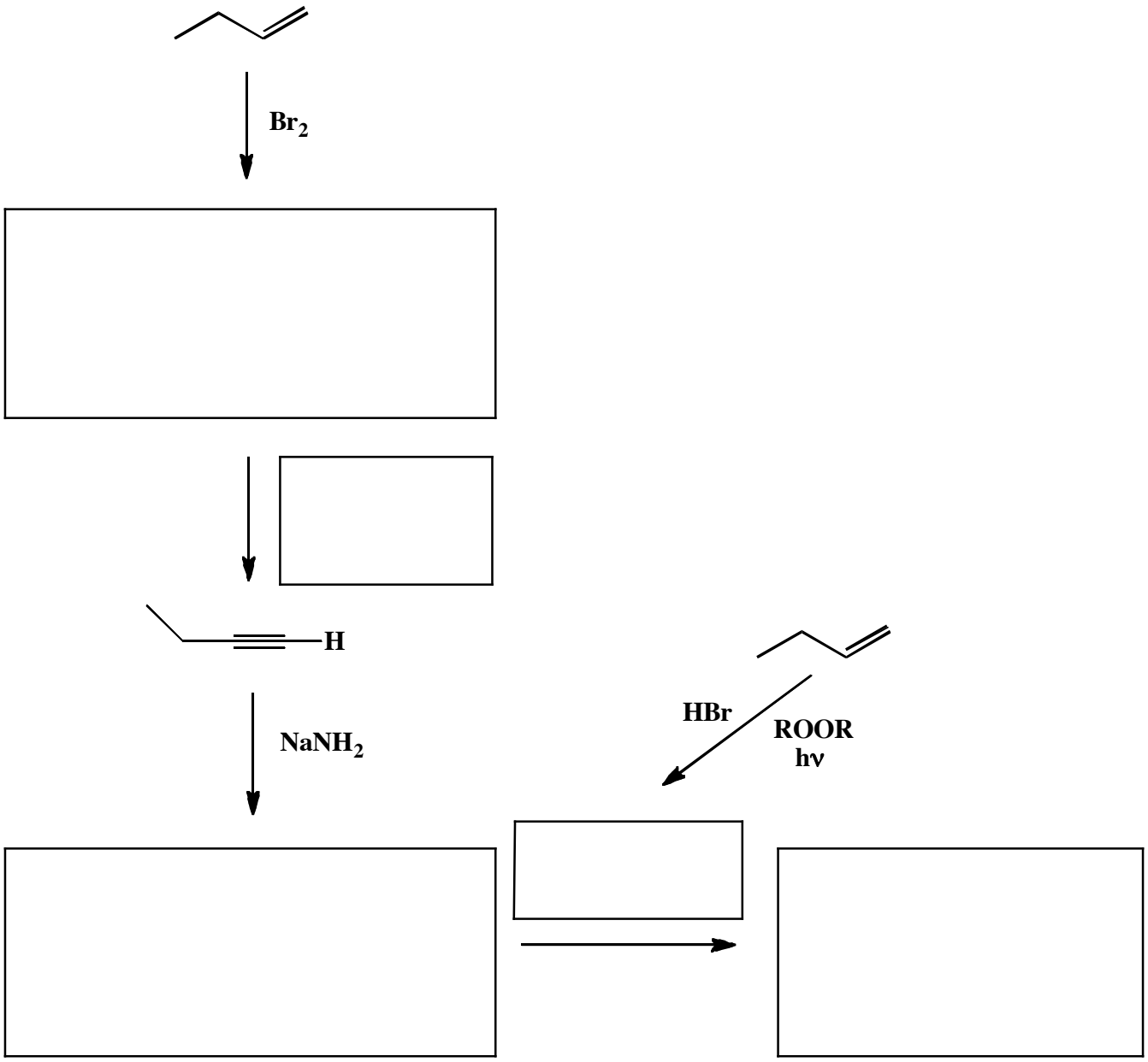
15. (3 or 5 pts each) For the following reactions, fill in the box with the predominant products or reagents necessary to complete the following syntheses. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate. Assume no rearrangements take place.



16. (3 or 5 pts each) For the following reactions, fill in the box with the predominant products or reagents necessary to complete the following syntheses. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate. Assume no rearrangements take place.



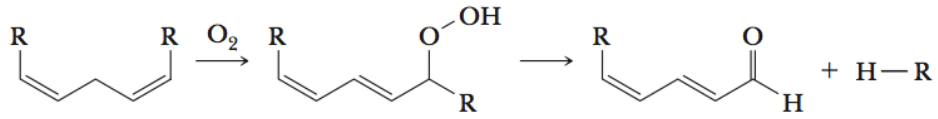
17. (3 or 5 pts each) For the following reactions, fill in the box with the predominant products or reagents necessary to complete the following syntheses. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate. Assume no rearrangements take place.



18. Here is an "apply what you know" problem in the format of an MCAT style passage. Circle the correct answers.

Antioxidants

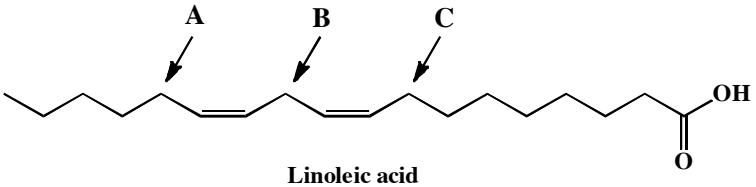
Many plants contain polyunsaturated fatty acid esters in their leaves or seeds, as do the foods derived from these plants. Such structures are prone to autoxidation that gives hydroperoxides leading to lower molecular weight oxidized products, such as volatile aldehydes, ketones, and hydrocarbons. These products are indicative of the rotting of the food, and result in the unpleasant "rancid" odors familiar to anyone who has smelled old cooking oil.



Part of a polyunsaturated fatty acid

More volatile species with rancid odors

1. Linoleic acid is shown below. This common fatty acid is particularly susceptible to autoxidation because the hydrogens at certain position(s) on the chain are very reactive in a radical process. Which ones?



Linoleic acid

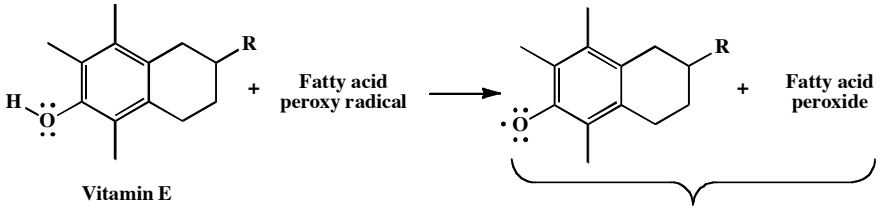
A. A hydrogen on the carbon labeled as "A" will be the most likely to be abstracted to create a radical.
B. A hydrogen on the carbon labeled as "B" will be the most likely to be abstracted to create a radical.
C. A hydrogen on the carbon labeled as "C" will be the most likely to be abstracted to create a radical.
D. Hydrogens on both carbons labeled as "A" and "C" will be tied for the most likely to be abstracted to create a radical.

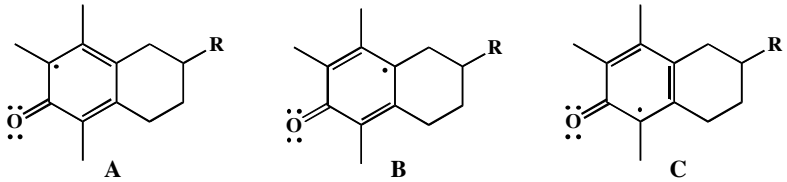
2. Your answer to part 1 above is due to the fact that:

A. The radical created on the carbon labeled as "A" will be doubly allylic, and therefore highly stabilized by resonance delocalization (a pi-way).
B. The radical created on the carbon labeled as "B" will be doubly allylic, and therefore highly stabilized by resonance delocalization (a pi-way).
C. The radical created on the carbon labeled as "C" will be doubly allylic, and therefore highly stabilized by resonance delocalization (a pi-way).
D. The radicals created on the two carbons labeled as "A" and "C" will be equally doubly allylic, and therefore equally highly stabilized by resonance delocalization (a pi-way).

18. (cont.).

Nature protects against autoxidation by a variety of agents, one of the most important of which is α-tocopherol (vitamin E). This compound is a phenol, which is defined as an OH group on a benzene ring as shown in the diagram. The characteristic of phenols that makes them protective agents against autoxidation is their O-H bond, which is even better at forming radicals than the C-H bond from which hydrogen is abstracted by O_2 in the polyunsaturated fatty acid. This means that vitamin E reacts quickly with the peroxy radical formed during fatty acid autoxidation to give a highly stabilized radical, that ultimately results in termination of the radical chain process.



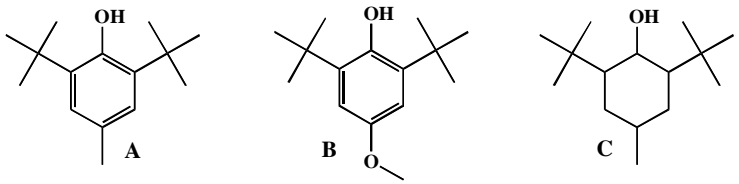


3. The radical formed from vitamin E is highly stable because of resonance delocalization of the radical. Which of the following statements best describes why this radical is so stable.

A. The structure labeled as "A" is a significant resonance contributor of the radical.
B. The structure labeled as "B" is a significant resonance contributor of the radical.
C. The structure labeled as "C" is a significant resonance contributor of the radical.
D. All three structures, "A" ,"B", and "C", are significant resonance contributors of the radical.

Vitamin E is often referred to as a natural preservative because it prevents autoxidation and therefore food spoilage. Processing of foods can remove the natural vitamin E, so artificial preservatives are added to these foods in order to retard their spoilage.

4. Based on your answer to 3 above, consider the following structures. Select the statement that best describes which of the structures could serve as a preservative in place of vitamin E?



A. The structure labeled as "A" could be a preservative.
B. The structure labeled as "B" could be a preservative.
C. The structure labeled as "C" could be a preservative.
D. Both structures "A" and "B" could be preservatives.