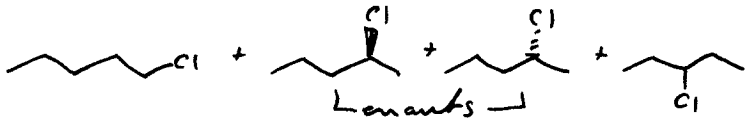
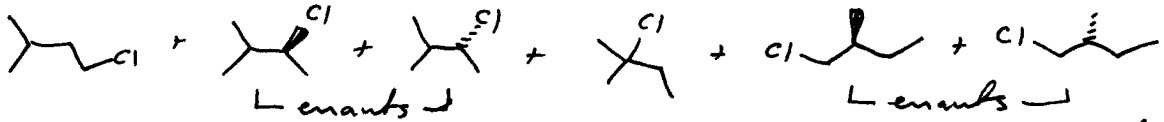
Chem 21 HW set 13

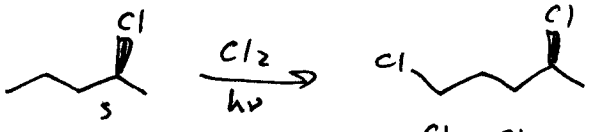
1. (a)



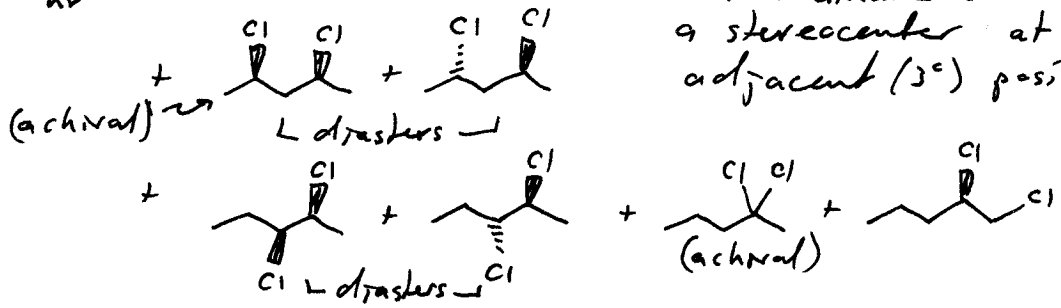
(b)



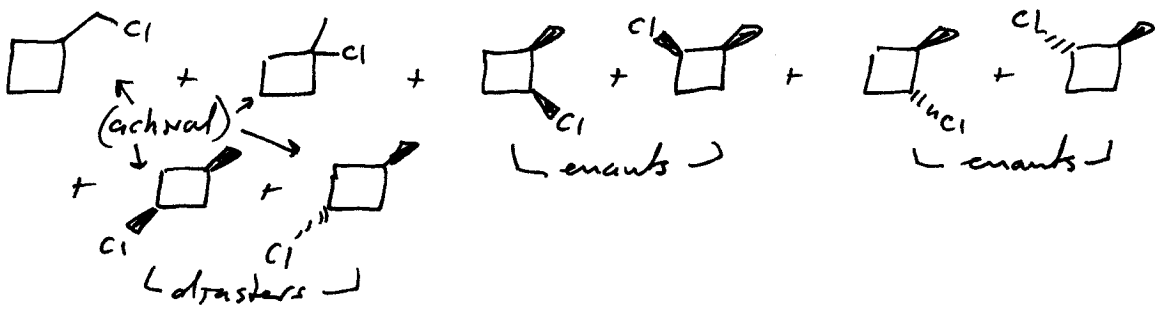
(c)



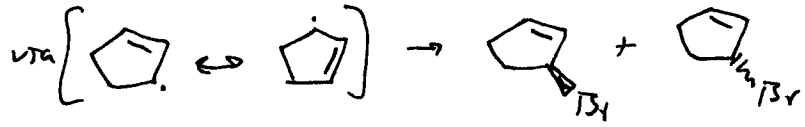
note that rxn at one of the two equiv CH_3 s of the alkane creates a stereocenter at the adjacent (3^c) position



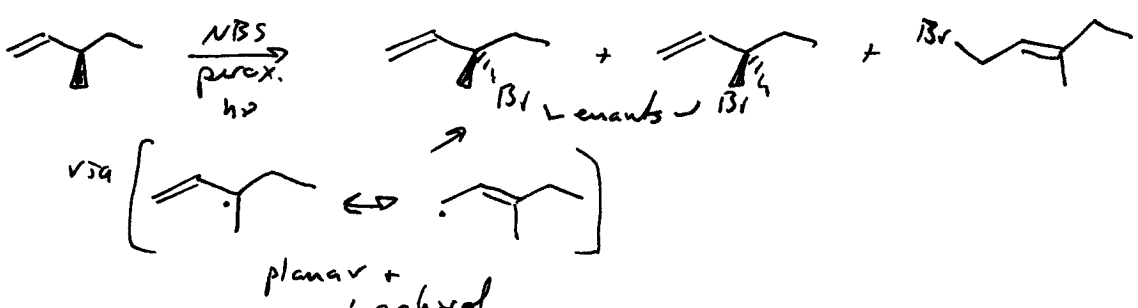
(d)



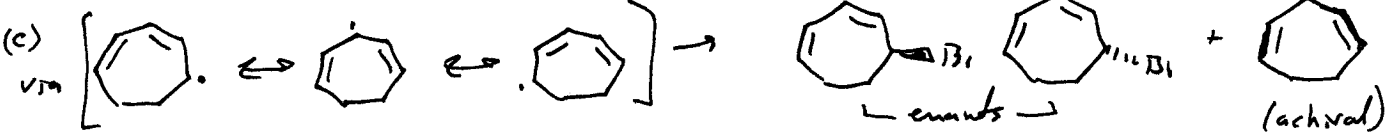
2. (a)



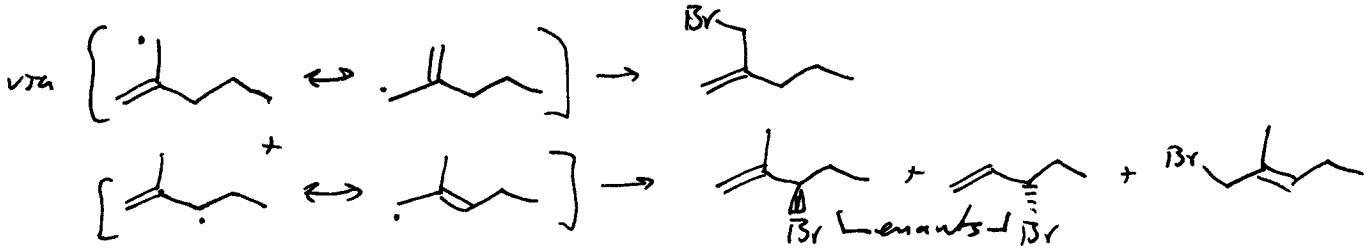
(b)

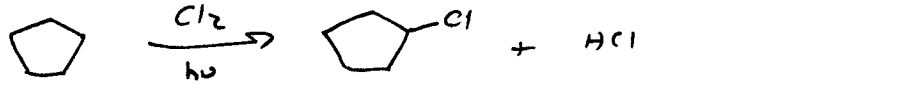


(c)

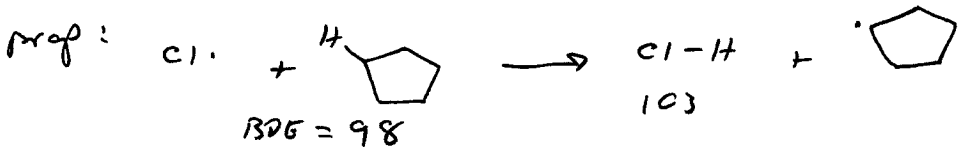


(d)

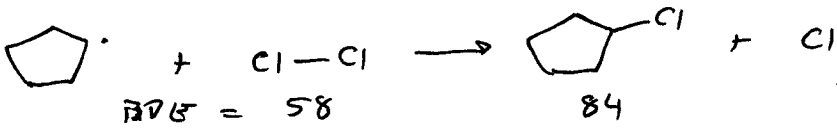


3. (a) 

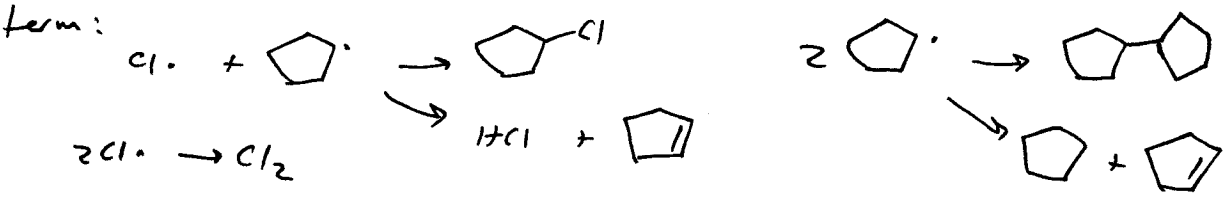
init: $Cl_2 \xrightarrow{h\nu} 2\ Cl\cdot$

prop: 

$\Rightarrow \Delta H^\circ = -5$ kcal/mol



$\Rightarrow \Delta H^\circ = -26$ kcal/mol

term: 

(b) ΔH° calc above

overall $\Delta H^\circ = -31$ kcal/mol

(c)

	ΔH° (kcal/mol) prop-1	prop-2	overall rxn	
F	−38	−72	−110 !!!	goes boom (unless one is very careful)
Cl	−5	−26	−31	
Br	+10	−24	−14	
I	+27	−19	+8	uphill – + since $\Delta S^\circ \approx 0$, ΔG° is also positive ∴ "equilib" favors reactants

4. (a) $\frac{k_1}{k_2} = \frac{A_1 e^{-E_a(1)/RT}}{A_2 e^{-E_a(2)/RT}}$ we're comparing similar rxns, so $A_1 \approx A_2$

$\frac{k_1}{k_2} = e^{\left(-E_a(1) - -E_a(2)\right)/RT}$

$RT \ln\left(\frac{k_1}{k_2}\right) = E_a(2) - E_a(1) = \Delta E_a$

$R = 1.987$ cal/mol K, $T = 298$ K, $\frac{k_1}{k_2} = 5 \Rightarrow \Delta E_a = 0.95$ kcal/mol

(b) $\frac{k_1}{k_2} = 2000 \Rightarrow \Delta E_a = 4.5$ kcal/mol

4. (c) $\Delta E_a = 0.95$ kcal/mol

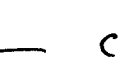
$T = 473K \Rightarrow k_1/k_2 = 2.7$ – abstraction by Cl· is less selective at 200°C

$T = 195K \Rightarrow k_1/k_2 = 11.6$ – " " " more selective at −78°C

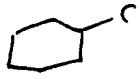
This is the case in general – at high T, molecules have enough thermal energy to rapidly cross over barriers with little regard for small differences in E_a's. At low T, the little guys are just barely able to crawl over the barriers – very few will be able to cross over the higher barrier.

5. On problems like these it's especially important to follow the instructions so you get off on the right foot –

(a) $tBuO-Cl \xrightarrow{h\nu} \boxed{tBu-O\cdot} + \cdot Cl$

init { $Cl\cdot$ +  → $Cl-H$ (trace) + 

2-step init sequence creates the two "chain-carrying" radicals

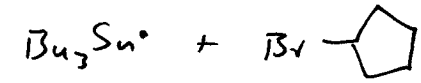
prop {  + $Cl-OtBu$ →  + $\cdot OtBu$

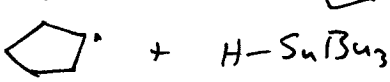
$HBuO\cdot$ +  → $HBuOH$ + 

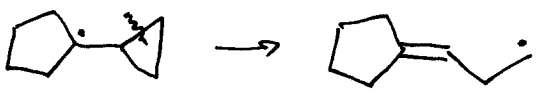
note that these (MUST!) add to the overall rxn.

↑ reactants ↑ products

(b) $RO-OR \xrightarrow{h\nu} 2\,RO\cdot$ $RO\cdot + H-SnBu_3 \rightarrow ROH$ (trace) + $\boxed{\cdot SnBu_3}$

prop. { $Bu_3Sn\cdot$ +  → Bu_3Sn-Br + 

 + $H-SnBu_3$ →  + $\cdot SnBu_3$

(c) same as above, but 

then the 1° radical abstracts H from Bu_3Sn-H – this rxn has a 3-step propagation sequence.