Chemistry 547 (Reich)

Second Hour Exam

Nov. 21, 2013

1 _____/24

2 _____/28

3 _____/24

4 _____/24

Total _____ /100

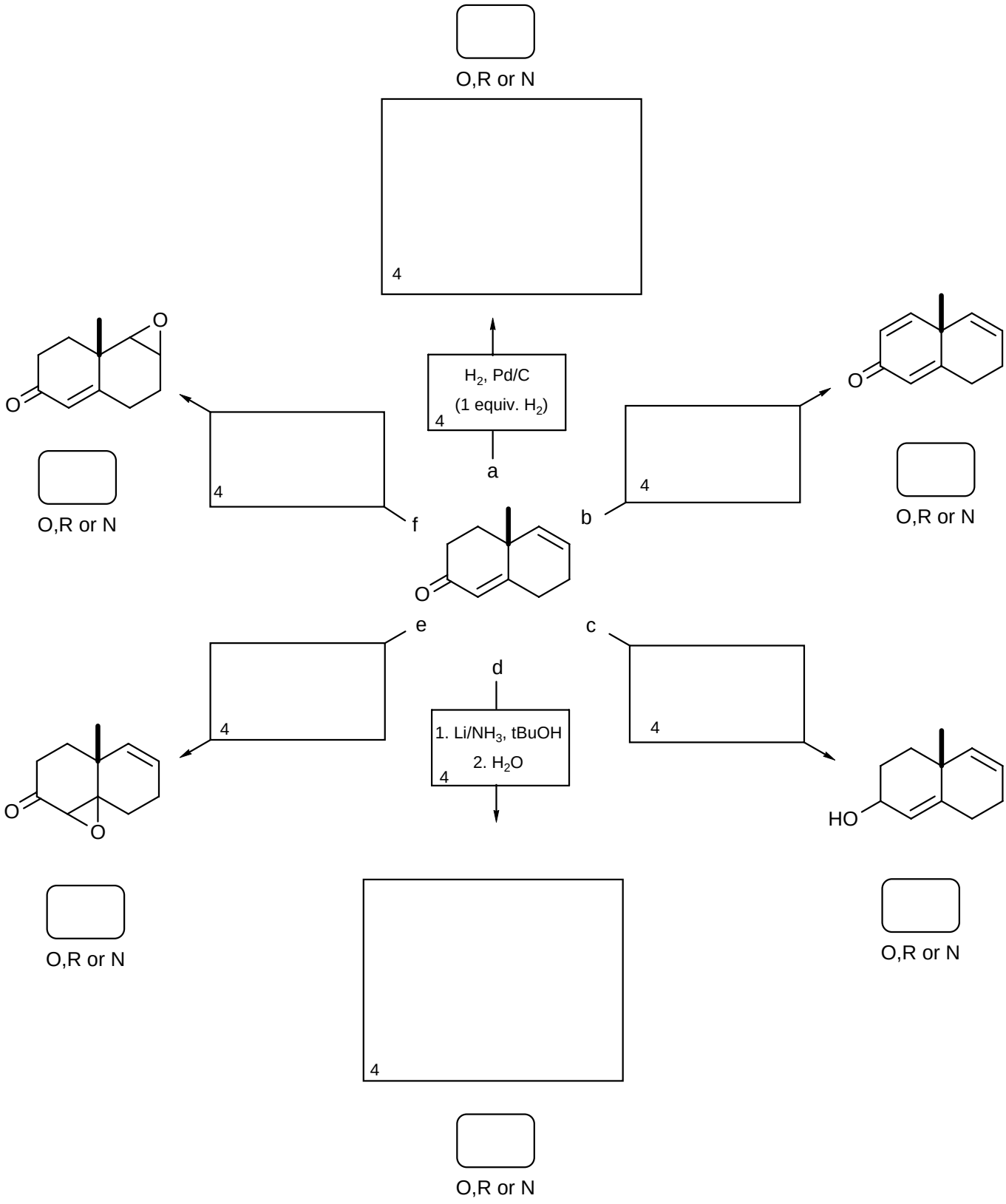
Name _____

If you place answers anywhere else except in the spaces provided,
clearly indicate this on the answer sheets.

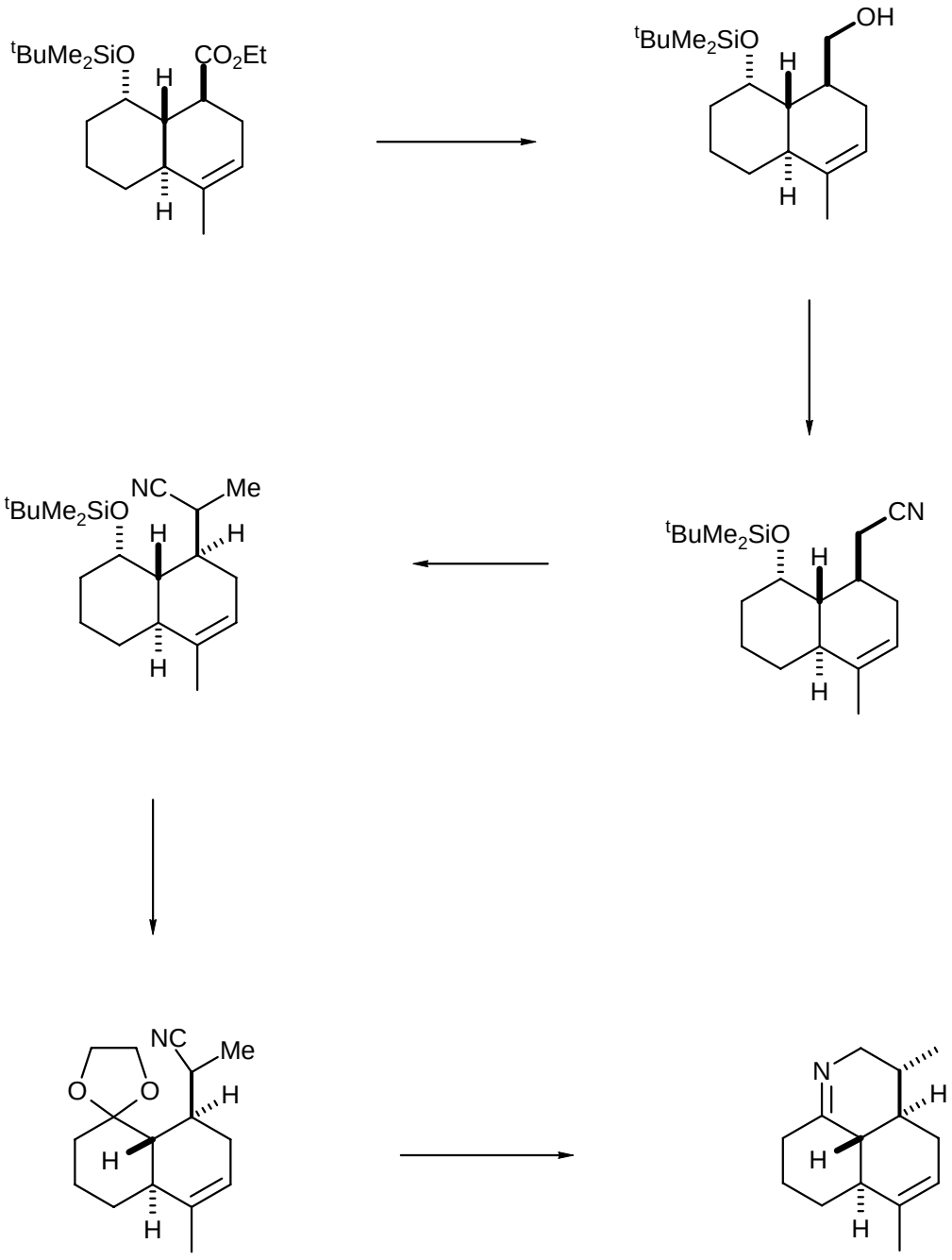
NOTE: Do not use acronyms for reagents or solvents, unless you define them first.

For the synthetic transformations which involve more than one step, you should show the product of the reaction after each step, but you do not need to write mechanisms.

1. (24) Show how the synthetic transformations below can be performed. In the boxes provided give the reagents needed, or the expected product, and indicate whether the reaction is an oxidation[O], reduction [R] or neither [N]

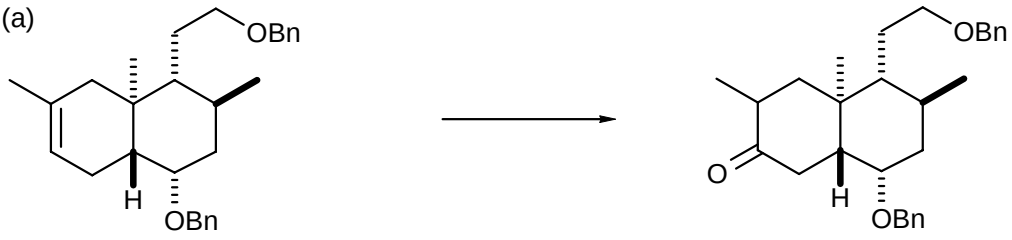


2. (28) The sequence of transformations below was taken from the total synthesis of Neosymbioimine (the structures have been simplified to avoid clutter). Provide the missing reagents. Do not do more than two steps without showing intermediate structures.



3. (24) These examples were taken from natural product syntheses. Provide suitable reagents. More than one step may be needed. Make sure you consider stereochemistry. Do not do more than two steps without showing intermediate structures.

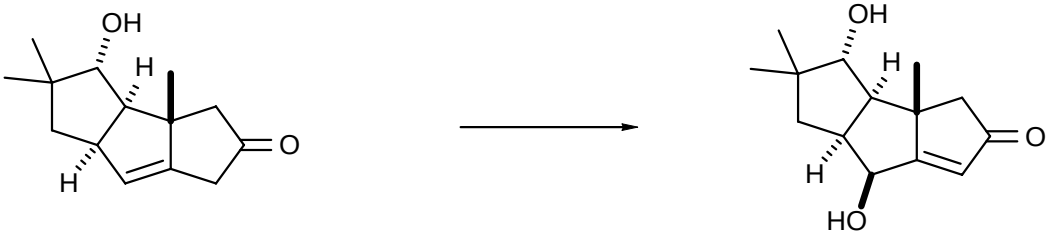
(a)



Bn = CH_2-Ph

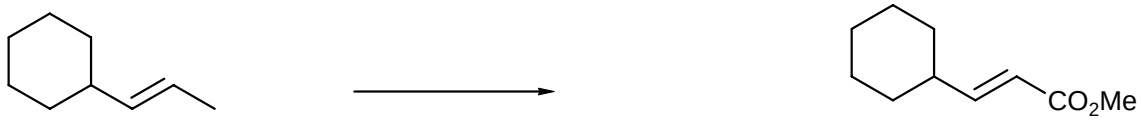
From a synthesis of Kempene-2

(b)

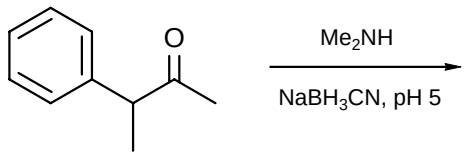


From a synthesis of Coriolin

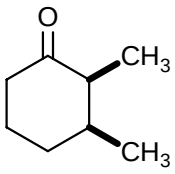
(c)



4 (a) (8) Predict the major product of the reaction below. **Show stereochemistry** and provide a rationale for the stereochemical result. You do not need to write a complete mechanisms.

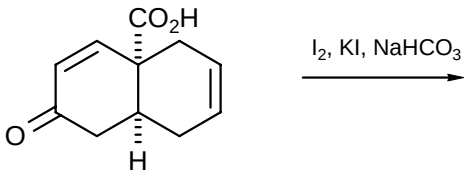


(b) (8) Draw good representations of the two chair forms of A. Indicate which will be more stable, and by approximately how much (kcal/mol).



A

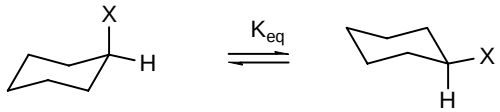
(c) (8) Predict the product of the following reaction. Show stereochemistry, and draw a stable conformation of the product.



DATA-5.0 Typical A-Values

H. J. Reich

A Value = $-\Delta G°_x = RT \ln(K)$ (R = 1.987 cal/deg, 8.314 J/deg)



X	"A" Value	X	"A" Value	X	"A" Value
D	0.008[1]			HgBr	0.0
F	0.15 (0.36)[9]	NC	0.21 (0.19)[9]	HgCl	-0.3
Cl	0.43 (0.51)[9]	N=C=O	0.51	HgOAc	0.0[2]
Br	0.38 (0.49)[9]	N=C=S	0.28 (0.21)[9]		
I	0.43 (0.49)[9]	N=C=NR	1.1	Me	1.70
O-H*	0.87 (1.0)[9]	NH_2*	1.2-1.7 (1.23)[9]	CF_3	2.1
O-Me	0.60 (0.75)[9]	NHMe*	1.0	Et	1.75
O-CD_3	0.56	NMe_2	2.1	$CH=CH_2$	1.35 (1.68)[8]
O-Et	0.9	NH_3^+	1.9	C≡C-H	0.41 (0.52)[9]
O-Ac	0.6 (0.79)[9]	N_3	0.62[9]	C≡N	0.17 (0.21)[9]
O-C(=O)CF_3	0.68 (0.58)[9]	NO_2	1.1 (1.13)[9]	CH_2CMe_3	2.0
O-CHO	0.27 (0.62)[9]	PH_2	1.6[4]	CH_2OTs	1.75
O-Ts	0.50 (0.48)[9]	PMe_2	1.5[4]	iPr	2.15
O-Ms	0.56[2]	PCl_2	1.9[4]	c-Hexyl	2.15
O-NO_2	0.59	$P(OMe)_2$	1.5[4]	t-Bu	>4.5
O-$SiMe_3$	0.74[9]	PMe_3^+	>3.0[4]	Ph	3.0
S-H	1.9 (1.22)[9]	P(S)Me_2	>3.0[4]	CO_2H*	1.35
S-C≡N	1.23	P(O)Ph_2	2.6[5]	CO_2^-*	1.92
S-Me	0.7 (1.1)[2]			CO_2Me	1.27
S-Ph	0.8	$SiCl_3$	0.61	CO_2iPr	1.20
S^-	1.3	$SiMe_3$	2.5[6]	C(=O)H	0.8
S(O)Ph	1.9	$GeMe_3$	2.1[7]	C(=O)Cl	1.25
S(O)Me	1.2	$GePh_3$	2.9[7]	C(=O)Me	1.17
$S(O)_2Ph$	2.5	$SnMe_3$	1.1[7]		
$S(O)_2Me$	2.5	$SnPh_3$	1.4[7]		
Se-Ph	1.1[3]	$PbMe_3$	0.7[7]		
Te-Ph	0.9				

* Solvent dependent. General: Hirsch, *Topics in Stereochemistry*, **1967**, *3*, 199; Jensen. F. R., Bushweller, C. H., *Adv. Alicyclic Chem* **1971**, *3*, 139. 1. *Tetrahedron Lett.* **1989**, *30*, 1059. Eliel, Wilen *Stereochemistry of Organic Compounds*, Wiley, 1993, p. 696. 2. By NMR: Jensen *J. Am. Chem. Soc.* **1969**, *91*, 344. 3. *Tetrahedron Lett.* **1985**, *26*, 1205. 4. *J. Am. Chem. Soc.* **1976**, *98*, 18; *J. Org. Chem.* **1976**, *41*,1690. 5. *J. Org. Chem.* **1986**, *51*, 1357. 6. *J. Org. Chem.* **1982**, *47*, 5153. 7. *J. Org. Chem.* **1982**, *47*, 1901. 8. Eliel *J. Org. Chem.* **1981**, *46*, 1959. 9. Direct observation of ^{13}C signals of axial and equatorial conformers: Schneider, Hoppen *J. Org. Chem.* **1978**, *43*, 3866.

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