Advanced Organic Chemistry

- (1) List three methods for protecting an amino group. Indicate how to introduce these protecting groups and how to remove them. (10%)
- (2) Explain how the cis-2-methylcyclohexanol (A) is isomerized to trans-isomer (B) with aluminum isoproxide as shown below: (10%)

OH
$$(i-PrO)_3Al, i-PrOH$$

$$Me_2CO \text{ catalyst}$$

$$K_{equil.} = \frac{[B]}{[A]} = 6$$
(B)

(3) Using perspective representation, predict the sterweochemistry at C-5, C-8, C-9, C-10 and C-14 of the product (C) from the acid-catalyzed rearrangement. Rationalize the result. (10%)

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(4) Draw valid Lewis and any resonance structures for the following species. (10%)

(a)
$$CH_2N_2$$
 (b) N_3 (c) H_3CO —NO₂

(5) Draw a mechanism for each of the following reaction: (10%)

(a)
$$H O H (1) HBr, ether, -25 OC H Br Si(CH3)3 (2) BF3.(C2H5)2O, 0 OC C3H7 H$$

Advanced Orgamic Chemistry

(6) Give stereochemical formulas for each product A-C. (10%)

1-Methylcyclobutene
$$(1)$$
THF: BH₃ $A(C_5H_{10}O)$ \xrightarrow{TsCl} OH'

$$B(C_{12}H_{16}SO_3) \xrightarrow{OH} C(C_5H_{10}O)$$

- (7)A hydrocarbon (A) has the formula C_7H_{10} . On catalytic hydrogenation, A is converted to B (C_7H_{12}). On treatment with cold, dilute, ande basic KMnO₄, A is converted to C ($C_7H_{12}O_2$). When heated with KMnO₄ in basic solution, followed by acidification, either A or C produces the meso form of 1,3-cyclopentanedicarboxylic acid. Give structural formulas A-C. (10%)
- (8)(a) Give two methods for synthesizing phenyl propyl ketone from benzene and any other needed reagents. (b) Give two methods for transforming phenyl propyl ketone into butylbenzene. (10%)
- (9) Starting with benzene and succinic anhydride, and using any other needed reagents, outline a synthesis of 1-phenylnaphthalene. (10%)
- (10)(a) What products would you expect to be formed when each of the amines in the preceding problem reacts with benzenesulfonyl chloride and excess aqueous potassium hydroxide? (b) What would you observe in each reaction? (10%)