***Student Name* (first, last):**

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Student Number:

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CHEMISTRY 3371
THIRD MIDTERM EXAMINATION

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1. (15 points) Check the correct statements only and make no other marks:

( ) The α hydrogen is less acidic in acetaldehyde than in methyl acetate.
( ) The Hell-Volhard-Zelinsky α-bromination of carboxylic acids is done with bromine and red phosphorus.
( ) Halogenation of an aldehyde or a ketone in acidic solution usually results in the replacement of one hydrogen with a halogen.
( ) Aldol reaction of acetaldehyde in aqueous base produces 3-hydroxybutanal.
( ) Aldol condensation cannot be catalyzed by acid.
( ) Claisen condensation of ethyl acetate in the presence of EtONa followed by acidic workup affords ethyl acetoacetate, CH_3COCH_2COOEt.
( ) Methanethiol adds to acrylonitrile (CH_2=CHCN) under basic conditions to produce 3-(methylthio)propanenitrile.
( ) α,β-Unsaturated carbonyl compounds undergo carbonyl addition with organolithium reagents and conjugate addition with lithium organocuprates.
( ) *p*-Nitroaniline is more basic than aniline.
( ) Cyclohexylamine is less basic than aniline.
( ) The benzenediazonium cation reacts with potassium iodide to yield iodobenzene.
( ) Diazotization of an aromatic amine with nitrous acid followed by reaction with aniline will produce an azo compound.
( ) Curtius rearrangement of an acyl azide $RCON_3$ yields an alkyl isocyanate R-N=C=O in which the stereochemistry on R has been preserved.
( ) Sodium borohydride is a good reagent for reducing nitrobenzene to aniline.
( ) Under Pd catalysis, chlorobenzene can be converted to *N*,*N*-dimethylaniline by reaction with dimethylamine and base.

2. (20 pts) Write a plausible mechanism for the haloform reaction of tert.-butyl methyl ketone with excess Br_2 and NaOH in a water/dioxane mixture (include all steps and intermediates and use curved arrows to indicate electron movement in each step).

3. (30 pts) Propose a reaction sequence for the synthesis of 1,3,5-tribromobenzene from benzene and inorganic reagents. Show all steps and all reagents (no mechanisms, no curved arrows, no solvents).

4. (20 pts) Write the structures of the principal organic product in the following reactions. You do not need to show solvents, mechanisms, or curved arrows.

(a) $PhCH_2COOEt$ + EtO-CO-OEt; 1. heat with 1 equiv. of EtONa, 2. H_3O^+ ➜

(b) $(CH_3)_3CCH_2CONH_2 + Br_2 + NaOH/H_2O$ ➜

5. (15 points) Explain the principle of phase-transfer catalysis in 50 words or fewer and illustrate it on a reaction of octyl bromide with potassium cyanide.