GTQ on Aldol Reactions. (40 points, reactivity, synthesis, disconnection)

(a) When a mixture of two different aldehydes is treated with base, four aldol products are possible. Write down the structures of these four aldol reaction products for the reaction between propanal and butanal and **describe in words** how they are formed. (10 points)

propanal dimerization	butanal dimerization
OH H	OH O
propanal carbanion and butanal	butanal carbanion and propanal
OH OH	OH O

(b) A "mixed aldol reaction" does not always produce the complex mixture of products indicated in (a). A "mixed aldol reaction" often can be a practical synthetic alternative. For example, the reaction of furfural with propanal yields the one product shown in rather high yield (72%). Explain this outcome. What other products are possible and why are their formations inhibited? (10 points)

Only one aldehyde is enolizable. The possibility for conjugation facilitates the double bond formation.

(c) The "mixed aldol reaction" between a ketone and a non-enolizable aldehyde is usually clean and leads to one product. This is so because the carbonyl activity of the aldehyde far exceeds that of the ketone. To make sure that the ketone does not react several times (at the same or at different -positions) one uses an excess of the ketone. Draw the structures of the products formed from cyclohexanone and benzaldehyde.

(10 points)

NaOH,
$$H_2O$$

$$25 \, ^{\circ}C, 4 \text{ hours}$$
NaOH, H_2O

$$25 \, ^{\circ}C, 10 \text{ days}$$

(d) Write the structures of the diketones that would give each of the following cyclic , -unsaturated ketones upon treatment with KOH in ethanol. (10 points)