Chemistry 130 CL Quiz 3 (Amides) Fáll 1998 (10-26-98)

Please fill out the information as best as you can. Please indicate your TA or the section that you are attending.

You have 10 minutes to complete the quiz.

Name: Kev

UCLA ID:

Section/TA: Zhe Thach Joe

Alf

1. Draw the product and name the functional group present in the product. (10 pts.)

2. Why are there 2 sets of methyls in the ¹³C and ¹H for N,N-dimethylbenzamide in the presence of H⁺?

"trans" to the

"cis" to the phenyl

There are two sets of methyls because protonation of the carbonyl leads to greater double bond character between the carbonyl carbon and the amide nitrogen (hindered rotation) thereby leading to a formation of nonsymmetrical methyls. The methyls are different because one is "cis" to the phenyl and the other is "trans" to the phenyl.

3. Given the chemical shifts for the carbonyls in the ¹³C spectra, explain why the other carbonyl groups are downfield of the aldehyde and how does this reflect on the reactivities of those carbonyls. (15 pts.)

Note: There was a mistake on this problem - it should have said 'upfield' instead of 'downfield'. In any case, I was very generous with the points and if a reasonable trend was written, I awarded points. Sorry for the mistake. J.W.

The trend for the upfield shifts in the carbonyls corresponds well with reactivity (except for the acyl chloride). Aldehydes are more reactive than esters, are more reactive than amides, are more reactive than carbamates. The carbonyls are more upfield than the aldehyde carbonyl because the neighboring atoms donate electron density into the carbonyl carbon. This gives the carbonyl carbon more electron density relative to the aldehyde and therefore are less reactive than the aldehyde. The exception is the acyl chloride: the donation of electrons into the carbonyl carbon causing the upfield shift of the carbonyl is not enough to lower the reactivity of the carbonyl carbon.