2012.04.19

STeRéO Group Seminar
EXERCISE

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A Day in the Lab...

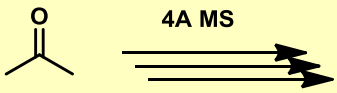
When we think about it, it is funny to realize all what can happen in a whole day... There is no exception in the lab! For me, that day was like one of those day when you are in the mood to investigate each and everything. Let me tell you what happened...

1. *It was not a long time ago in another galaxy but very recently in the course of our quest on optically active densely functionalized cyclobutanones. We had to study how solvents could affect the studied transformation. Arriving in front of our Brawn SPS friend I saw the usual choice of available solvents: THF, Et_2O, CH_2Cl_2, toluene and... Heineken of course!*
   But I suddenly wondered what kind of stabilizers were involved and how did they work?

2. *Then we wanted to add dioxane into the screened solvent array. Which conditions could fit a correct purification of that one? This kind of system is pretty practical in the sense that it shows color variations according to the failure/success of the purification process.*
   What are the colored intermediates involved?

3 *Later that day, being done with most of the reactions, I was running NMR in acetone-d_6 and decided to use some acetone for the transfer. I couldn't find the HPLC acetone we normally have standing around when I remembered that about 2 years ago I had made a bottle of acetone over Molecular Sieves (this is were all the alarm bells go off with the experienced chemist). I managed to find the bottle, however to my utter surprise I was unable to remove that solvent out of my flask on the rotary evaporator. On the high vacuum pump with a fair bit of heating most of it came off but by TLC there was a new UV active (and quite polar) compound. I had to re-column my product but it was still unpure! Before I proceeded to clean up my compound I decided to figure out what the source of the problem was and I quickly discovered that the acetone smelt funny. Initially, I thought it was contaminated with benzaldehyde but when more dilute it had a floral/perfume scent that reminded me of ketones/ester.*

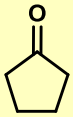
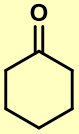
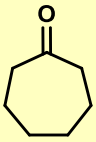
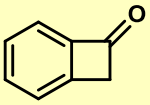
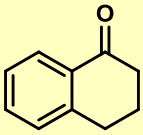
Try to guess what happened?! What was the 6-membered heterocyle mainly formed?



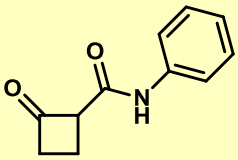
6-membered heterocycle

MW = $C_9H_{16}O_2$

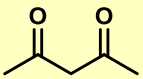
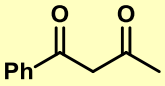
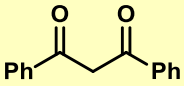
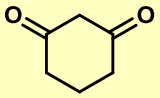
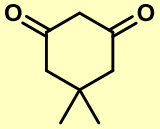
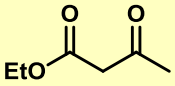
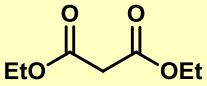
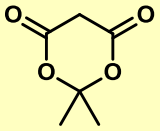
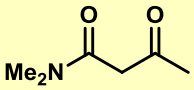
4 *Meanwhile the 400MHz is doing its job, I hope you will agree this is the good time to refresh our pKa memories of carbonyl compounds before getting the spectra.*

	pKa (DMSO)
	24.7
	25.1
	25.8
	26.4
	27.8
	

Extra question:

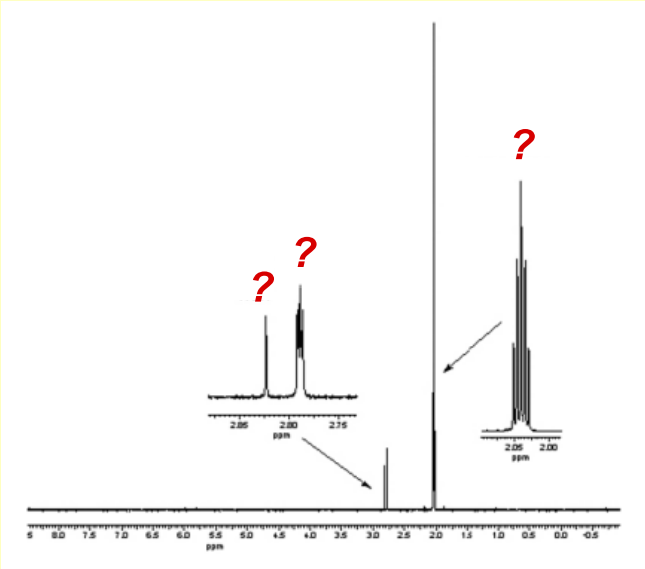


pKa (DMSO) = ?

	pKa (DMSO)
	7.3
	10.3
	11.2
	13.3
	13.4
	14.2
	16.4
	18.2
	

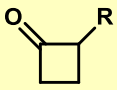
5 *You could now imagine that the adventure was not yet finished. Observing the obtained ^{1}H NMR spectra I noticed some undesired peaks. I ran the ^{1}H NMR of pure acetone-d_6 used and obtained that.*

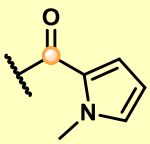
Who is who and why?

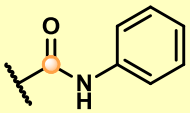


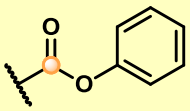
6 *Finally, it was time for ^{13}C NMR. Here are the collected data of some close cyclobutanones derivatives.*

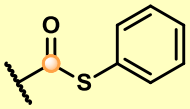
Guess who fits who and argue why?











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$\delta\ ^{13}C$ (ppm) ?

- **163.7**
- **165.2**
- **180.2**
- **189.5**

In conclusion, even if you're sad because you could not get one word of my story or solve the enigma, or if you are frustrated at thinking that I should have sent that exercise days ago, then the only advise I could give you is as follow: don't worry be happy because Momar will anyway soon invite everybody to have a drink and party his poster price!