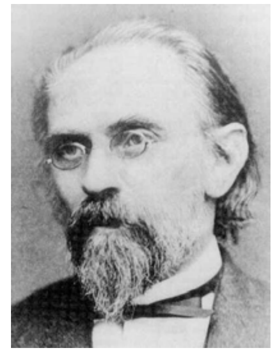
Experiment 23

Fig. 23-1



Emil Erlenmeyer (1825 - 1909). While known by many because of the flask named after him, Emil Erlenmeyer did ground breaking work in organic chemistry including research on enols.
http://en.wikipedia.org/wiki/Emil_Erlenmeyer

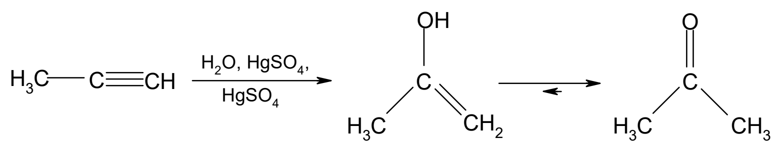
TAUTOMERISM OF 2,4-PENTANEDIONE

Text Topics

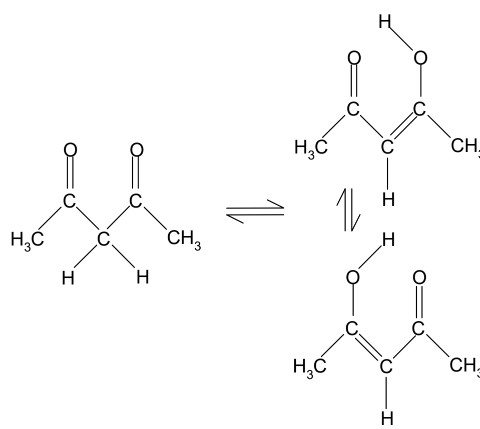
Keto-enol equilibria.

Discussion

The addition of water with an acid catalyst (and mecuric ion for a terminal alkyne) across one of the π bonds of an alkyne might be expected to yield an enol product. However, as you know, most enols exist in equilibrium with isomeric carbonyl compounds and the addition of water to the alkyne yields a ketone. The enol-keto transformation is accomplished by the transfer of a proton from the oxygen to a carbon. This process is called tautomerization. For most tautomers, the equilibrium lies far to the carbonyl side. The infrared spectrum of acetone does not exhibit any noticeable evidence of an O-H or a C=C stretch as the amount of enol present is about $1.4x10^{-4}$%.



One of the interesting and intriguing features of chemistry is that there are usually exceptions to every generalization. For a small number of carbonyl compounds including β-dicarbonyl compounds, measurable amounts of both the keto and enol forms are present at equilibrium. There are at least two contributing reasons for the relative increase in enol stability. The energy of the enol compared to the keto form is more favorable for β dicarbonyl compounds than for simple carbonyls because of the presence of conjugation and intramolecular hydrogen bonding. In this experiment, you will use ^{1}H-nmr to investigate the equlbrium for 2,4-pentanedione (acetylacetone) and its enol.



Procedure

You should run the ^{1}H-nmr spectrum of the pure liquid (10% in $CDCl_3$ gives about the same results). The analysis of the spectrum and the determination of the equilibrium constant will be left up to you. Notice that the enolic hydrogen resonates at very low field and may be missed unless the scan range is adjusted. However, it is not necessary to use the enolic hydrogen for your analysis. In fact, for the pure 2,4-pentanedione, you will be able to determine the enol to keto ratio two ways (the ratio of the integrals of the methyl hydrogens and also the ratio of double the enol sp^2 hydrogen to the keto CH_2.)

You should also run the ^{1}H-nmr spectrum of a solution of 2,4-pentanedione in D_2O. Add enough D_2O to an nmr tube to make the liquid level about 5 cm high. Then add a few drops of 2,4-pentanedione so that there is about a 0.5cm layer of 2,4-pentanedione on top of the D_2O. There are now two approaches that can be used for the study of this system. For a simple equilibrium determination, mix the nmr tube contents and allow the tube to sit for about an hour and then run the nmr. For a more interesting and thorough study of the system, make sure the nmr is ready before addition of the 2,4-pentanedione to the D_2O. Add the 2,4-pentanedione and then mix and run the nmr as quickly as possible starting a timer when you run the spectrum. Then run additional spectra every 15 minutes until the spectrum no longer changes. This should take about an hour. Determine the equilibrium constant for this solvent from the final nmr and also determine the enol to keto ratio as a function of time. Also report the changes in the enol sp^2 H and the keto CH_2 and account for these changes.

Additional options include the determination of the ir and the gas chromatogram of the pure liquid.

References

Cook, G.; Feltman, P. M. *J. Chem. Ed.*, **2007**, *84*, 1827-1829.
Koudriavtsev, A., B.; Linert, W. *J. Chem. Ed.*, **2009**, *86*, 1234-1237.
Sandusky, O. *J. Chem. Ed.*, **2014**, *91*, 739-742. (added after this expt. was written)
Smith, K. T.; Young, S. C.; DeBlasio, J. W.; Hamann, C. S. *J. Chem. Ed.*, **2016**, *93*, 790-794 and references therein (added after this expt. was written).

Prelaboratory Preparation - *Experiment 23*

First, be sure to list the goals of the experiment. Write a mechanism for the acid catalyzed conversion of the 2,4-pentadione to its enol. Look up the ^{1}H-nmr spectrum of 2,4-pentadione on the NIMC site. Try to figure out a way to determine the value for the equilibrium constant from the integration results that you will have on your ^{1}H-nmr spectrum (2 ways for the pure liquid and one way in D_2O). Predict how the change of medium will shift the position of equilibrium and how the spectrum will change with time in D_2O.

Observations

Report all relevant observations including the H-nmr spectra with the integrations (as a function of time if performed).

Conclusions

This section should include the following:

1. Were the goals of the experiment achieved? Explain your answer.
2. What were the equilibrium constants for the pure sample and in the D_2O solutions? Was the direction of the shift consistent with your expectations? How confident are you in the results?
3. Explain why the equilibrium constants are different in the two different media.
4. Explain why the spectrum changes with time in D_2O. Is it possible to estimate a rate constant for the process from your results?
5. Literature values for the % enol are 80% for the pure liquid and 15% in water. Were your results within experimental error of these values? Explain your answer.
6. How general are the methods used in this experiment? For example, could the % enol in acetone or ethyl acetoacetate be determined using the same ^{1}H-nmr approach?