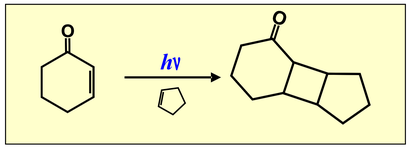
Towards the Synthesis of Specifically Deuterated Cyclohexenones

Dexter C. Davis, David E. Lewis, and Stephen Drucker

Department of Chemistry, University of Wisconsin-Eau Claire, Eau Claire, WI 54702

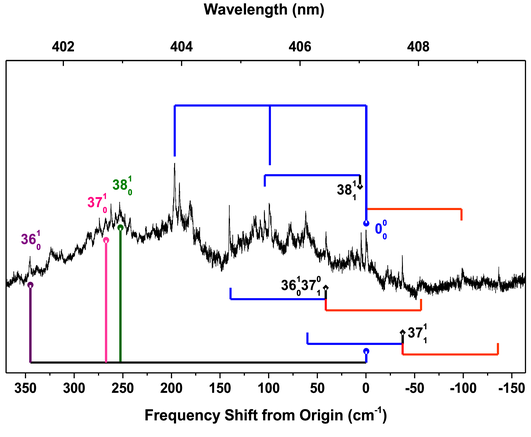
Photochemistry and Triplet Intermediates



$S_0 \xrightarrow{h\nu} S_1 \rightsquigarrow T_{1,2} \rightarrow$ products

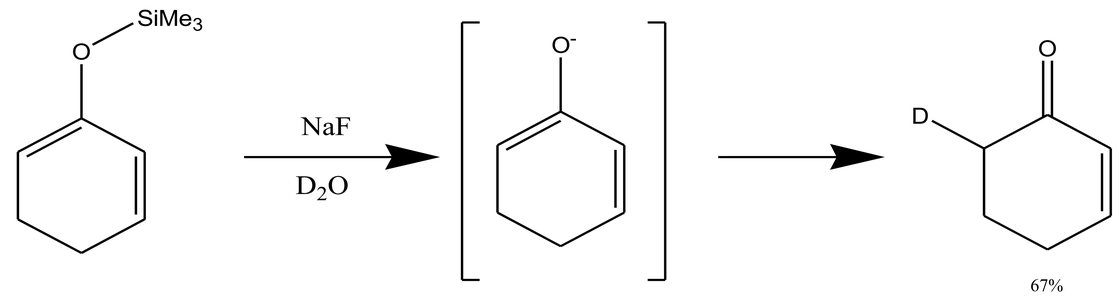
Triplet excited states often play a central role in molecular photochemistry. An example is the photocycloaddition reaction shown above. The lowest-energy triplet states, $T_1(\pi,\pi^*)$ and $T_2(n,\pi^*)$, are populated in a solution-phase environment, via rapid nonradiative relaxation (intersystem crossing) from the initially photoexcited $S_1(n,\pi^*)$ state.

A primary goal of our research is to acquire benchmark structural and dynamical information on the triplet states. This information can be used to test the accuracy of computational predictions of photochemistry. We have used Cavity Ringdown absorption spectroscopy to record the $T_2(n,\pi^*)\leftarrow S_0$ band system of 2-cyclohexen-1-one (2CH) in the gas phase.

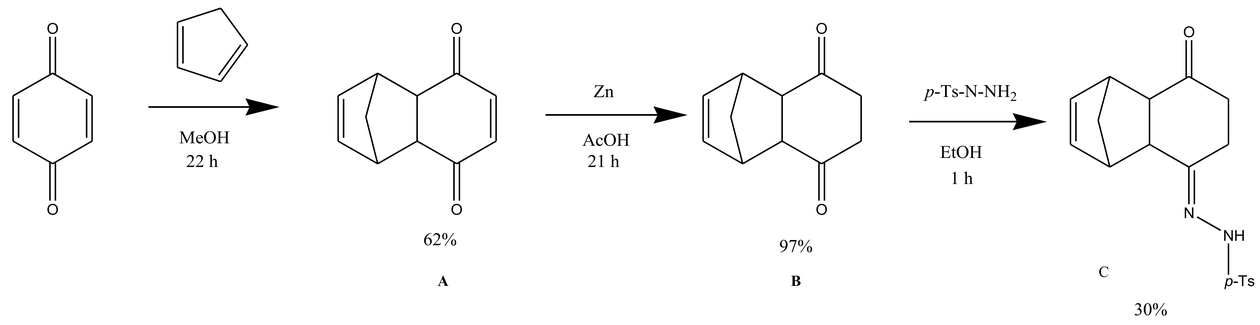


Tentative vibronic assignments are shown above. By synthesizing specifically deuterated derivatives of 2CH, more specific vibronic assignments can be made in the crowded regions by observing shifts in the corresponding frequencies due to the change in nucleur mass at the end of the bond.

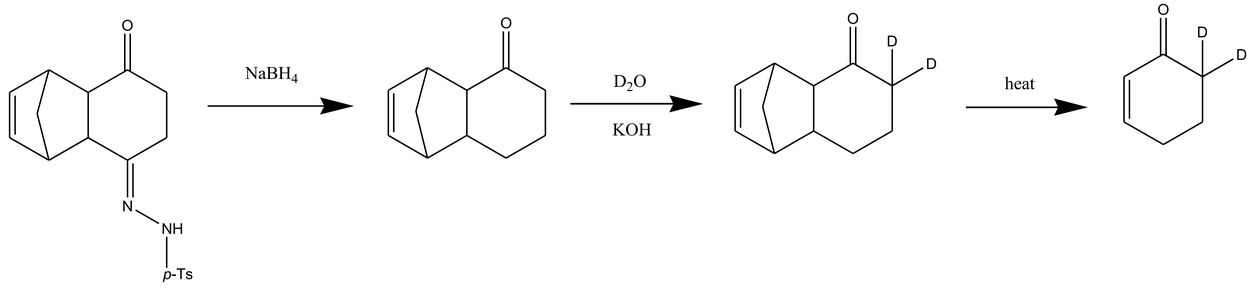
Synthetic Pathways



This synthetic pathway towards a monodeuterated derivative of 2CH uses sodium fluoride to cleave the oxygen-silicon bond of 2-trimethylsiloxy-cyclohexa-1,3-diene, producing an enolate anion. By performing the reaction using deuterium oxide as a solvent, the enolate anion quickly undergoes proton transfer to produce the monodeuterated 2CH derivative as a brown oil at very high purity with 60-70% yields.



This synthetic pathway towards a dideuterated derivative of 2CH begins with a concerted Diels Alder reaction between *para*-benzoquinone and cyclohexadiene to yield the diketone **A** as yellow crystals with 62% yield. A reduction of the diketone was then carried out using zinc dust in acetic acid, giving the diketone **B** as a brown oil in very high yields. One of the carbonyls was then substituted with a tosyl hydrazone group using *p*-toluenesulfonhydrazide, giving **C** as a white solid with 30% yeild.



The continuation of this pathway would involve a sodium borohydride reduction of the tosyl hydrazone **C** into a ketone, which can then be deuterated using deuterium oxide and potassium hydroxide. The resulting deuterated ketone could then be heated to split off a dideuterated derivative of 2CH. So far, the sodium borohydride reaction has failed to yield the expected ketone. Options involving reducing the diketone **B** directly into an alcohol which can then be reoxidized are being explored.

Acknowledgments

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