

Experiment 24

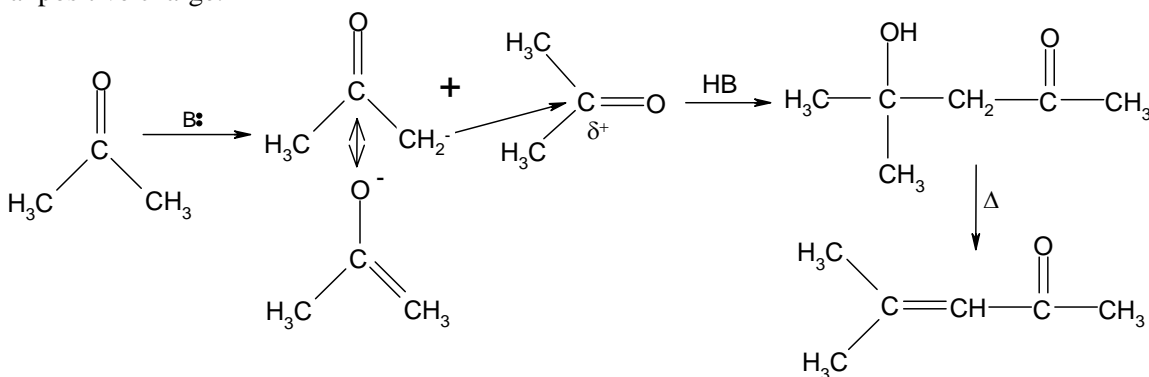
A DOUBLE ALDOL CONDENSATION

Text Topics and New Techniques

Aldol condensations, microwave oven assisted synthesis.

Discussion

The importance of reactions that form carbon to carbon bonds has been emphasized in previous experiments. Aldol reactions, Claisen condensations and several other similar reactions that take advantage of the acidity of hydrogens α to a carbonyl or carboxyl group are another indispensable class of reactions that form carbon to carbon bonds. Like the Grignard reactions and substitution reactions by cyanide and acetylide ions, these reactions are the result of a carbanion or carbanion like intermediate attack on a carbon with a partial positive charge.



The base catalyzed aldol condensation of acetone is illustrated above. The β -hydroxy ketone that results can be easily converted to the α,β unsaturated ketone by the application of heat. Normally elimination of water does not occur in base but the resulting conjugated system apparently lowers the activation energy sufficiently to make the elimination proceed. In fact, if the carbonyl group in the original aldehyde or ketone is conjugated to an aromatic ring, the aldol reaction does not stop at the β -hydroxy ketone but eliminates under the aldol reaction conditions to give the α,β unsaturated ketone. Because the aldol reactions form carbon-carbon bonds and result in products that contain at least two functional groups, the reactions are very versatile and a good method of building up a desired carbon skeleton.

Today's experiment uses a carbonyl conjugated to an aromatic ring thus elimination occurs unhindered subsequent to the aldol reaction. Additionally, the starting materials, 1,3-diphenylacetone and benzil, both contain two carbonyl groups so a double aldol condensation can take place. It should be noted that carbonyls with two different kinds of α hydrogens or attempted aldol reactions with two different carbonyl compounds can lead to complex mixtures of products (*why?*). For today's reaction, however, one

Fig. 24-1

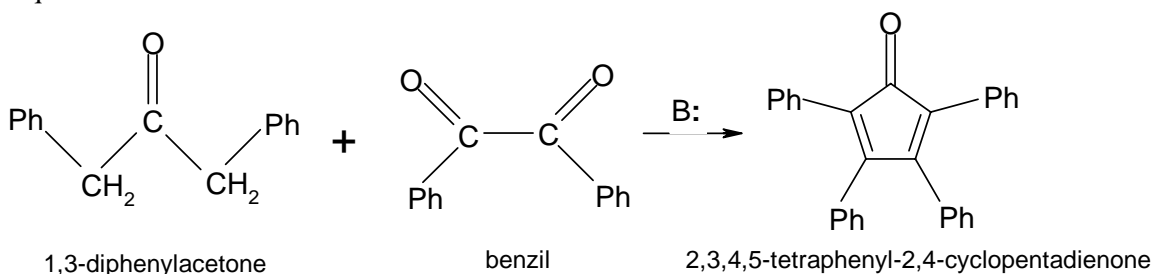


Rainer Ludwig Claisen (1851 - 1930) has glassware and several reactions including the Claisen condensation named after him.
http://en.wikipedia.org/wiki/Rainer_Ludwig_Claisen

of the reactants (benzil) does not contain α hydrogens and therefore cannot undergo an aldol reaction with itself. For this reaction, conditions need to be set up so that the conjugate base of 1,3-diphenylacetone reacts preferentially with benzil rather than with itself.

Techniques

Because 1,3-diphenylacetone is expensive (~\$1/g), the synthesis of 2,3,4,5-tetraphenyl-2,4-cyclopentadienone will be run with small amounts of starting material. Two methods for the synthesis are given below. The first is a traditional organic synthesis using reflux conditions for the base catalyzed aldol condensation. The second method uses a microwave oven to supply the energy and is considerably faster but unfortunately uses a rather odoriferous base. Ask your instructor which method you should use. If possible, work with a partner, do the experiment both ways and compare and evaluate the effectiveness of the two techniques.



When microwave radiation is absorbed by molecules, it results in activation of rotational energy levels of the molecule. This rotational energy can be converted into heat which in turn can increase the rate of chemical reactions. Microwave ovens usually use a band of energy centered at 2.45 GHz. This particular frequency is absorbed by water and is very effective at heating water. When food containing water is microwaved, the water throughout the food is activated and the entire sample is heated. With conventional heating, the heating must proceed from the outside inward and cooking is not as uniform as with the use of microwave ovens. Many chemicals including those in microwave safe plates do not absorb 2.45 GHz radiation and are not affected by it. For microwave sublimation to work for an organic compound, the compound, must absorb 2.45GHz radiation.

Procedure

Traditional procedure. Set up an apparatus that includes a 25 mL round bottom flask equipped with a reflux condenser. The apparatus should be mounted with the flask in a water bath on a heater or on a steam bath. Add 1.0×10^{-3} moles of benzil, 1.0×10^{-3} moles of 1,3-diphenylacetone and 10 mL of ethanol (preferably 100% but 95% should suffice) to the flask and swirl. Next add 1.0×10^{-3} moles of potassium hydroxide pellets to the flask and gently reflux for about 15 minutes. Allow the mixture to cool to room temperature and then cool in an ice bath. Collect the crystals using a Hirsch funnel with vacuum filtration. Wash the flask and the product with about 10 mL of ice water followed by 5 mL of ice-cooled methanol. After the product has dried, determine the yield, the percent yield, the melting range and the visible and near uv absorption spectrum in toluene. If desired, recrystallize from a minimum amount of triethylene glycol.

Microwave procedure. Add 5.0×10^{-4} moles of benzil and 5.0×10^{-4} moles of 1,3-diphenylacetone to a 13x100 mm test tube. Wash any solid clinging to the sides of the tube down with 1 mL of triethylene glycol. Stir the contents and microwave at 50% power for about 1 minute. Place the test tube in a working hood and add ten drops of 40% Triton B [$\text{C}_6\text{H}_5\text{CH}_2\text{N}^+(\text{CH}_3)_3\text{OH}^-$] in methanol to the tube and stir. Return the test tube to the microwave and radiate at 50% power for an additional minute. After the tube has cooled sufficiently to be handled, in a hood add 1 mL of methanol to the test tube and stir. Cool in an ice bath and

collect the solid using a Hirsch funnel with vacuum filtration. Wash the solid with a few milliliters of ice-cooled methanol. After the product has dried, determine the yield, the percent yield, the melting range and the visible and near uv absorption spectrum in toluene.

The uv-visible absorption spectrum of tetraphenylcyclopentadienone should exhibit an $n \rightarrow \pi^*$ absorption at 512 nm and an absorption in the near uv at about 343nm for a $\pi \rightarrow \pi^*$ transition. The latter should have an extinction coefficient that is about 3 times bigger than for the $n \rightarrow \pi^*$ transition.

References

Wilcox, C. F. and Wilcox, M. F. *Experimental Organic Chemistry: A Small Scale Approach*, Prentice-Hall, **1995**, p. 400.
Elder, J. W. *J. Chem. Educ.*, **1994**, *71*, pp. A142-4.
http://www.chem.ucla.edu/~bacher/UV-vis/uv_vis_tetracyclone.html.html (accessed 02/30/11)

Prelaboratory Preparation - *Experiment 24*

First, be sure to list all the goals of the experiment. Write a detailed step by step mechanism that shows how the starting materials could react to give the desired product. Prepare a table for insertion of useful and observed data such as molecular mass, mass, moles, melting points and percent yields and recoveries. Locate this type of reaction on the *Reaction-Map of Organic Chemistry in Appendix C* and include the reaction number in your report.

Observations

Report all relevant observations including masses, melting ranges and the absorption spectrum.

Conclusions

This section should include the following:

1. Were the goals of the experiment achieved? Explain your answer.
2. What was the identity of your product and did it agree with your prediction? Explain your answer.
3. How could the percent yield and recoveries have been improved? If the synthesis was performed using both methods, which method is preferred? Explain your answer.
4. Write a detailed step by step mechanism that shows how the starting materials could react to give the desired product.
5. Suggest a reason for the unusual observable property (color) of the product.