



Kelly Jo Boarman

Class: Junior

Major: Chemistry

As a Howard Hughes Undergraduate Research Scholar working under the direction of Dr. Jin Liu, I was able to synthesize more than 30 model compounds as we attempted to gain a better understanding of the photochemical properties of visual pigments. Our work suggests that the electron-withdrawing effect caused by the fluorine substituents weakens the carbon-carbon double bond nearest to the substituted phenyl ring and allows for isomerization to take place. While I enjoyed and spent many hours working in the lab, I was also able to complete all my required courses in three years and will be pursuing my degree in pharmacy by the time this article is published.

ABSTRACT

Synthesis and Photochemistry of Cisoid 1,4-diphenyl-1,3-butadienes

This study looks at the synthesis and the photochemistry of cisoid 1,4-diphenyl-1,3-butadienes. These structures are very similar in character to a variety of pigments found in plants and animals. Therefore, a better understanding of the mechanisms of the photochemistry of butadienes could lead to a more in-depth understanding of the mechanisms of photochemical reactions that occur in living organisms. Herein, the results from the photoirradiation of two specific cisoid 1,4-diphenyl-1,3-butadienes, cisoid 1-pentafluorophenyl-4-phenyl-1,3-butadiene and 1-*p*-methoxyphenyl-4-phenyl-1,3-butadiene, are reported.

FACULTY MENTOR



Jin Liu, a bioorganic chemist, joined Murray State University's Department of Chemistry in the fall of 2000. Liu has ardently supported the use of research as a pedagogical tool. She has provided more than 15 undergraduates with opportunities to engage in research in her laboratory since coming to Murray State. Her collaboration with HHMI Undergraduate Research Scholar Kelly J. Boarman resulted in a publication in *Chemical Communications* entitled, "Regiospecific Topochemical Reactions Controlled by Trifluoromethyl Directing Groups."

Synthesis and Photochemistry of Cisoid 1,4-diphenyl-1,3-butadienes

My research has been focused on the synthesis and photochemistry of cisoid 1,4-diphenyl-1,3-butadienes. A cisoid 1,4-diphenyl-1,3-butadiene is nothing more than a large conjugated system, meaning that it contains alternating carbon-carbon double bonds. A better understanding of the mechanisms of the photochemistry of cisoid 1,4-diphenyl-1,3-butadienes, could lead to a greater understanding of the isomerization of various carotenoids and retinoids, the process in which the compound changes from one conformation or shape to another conformation or shape.

Photochemistry, the study of the chemistry of the effects of light on chemical systems, plays a key role in many biological systems, including the “bleaching reaction” of rhodopsin, a pigment found in rod cells in the eyes. In the bleaching reaction, rhodopsin dissociates into its two components: retinaldehyde and opsin. This dissociation occurs as a result of light striking the rod cells containing the protein. In response to the absorbed light, the 11-*cis*-retinene is converted to its all-*trans*-isomer. This change in conformation causes a change in ionic permeability of the rod cells, where the rhodopsin is found. This change in permeability ultimately results in the production of nerve impulses. This particular reaction is just one of the many photochemical reactions that occur in living organisms. The results from our research will certainly serve as a useful tool for scientists seeking to gain a greater understanding of various biological photochemical reactions.

Method and Results

Cisoid 1-pentafluorophenyl-4-phenyl-1,3-butadiene (Figure 1) was prepared using the approach shown in Scheme 1 (Liu, Liu, and Simmons, 1997). Aldol condensation of racemic norcamphor with benzaldehyde produced an enone. The enone was then coupled with pentafluorobenzaldehyde to produce the desired cisoid 1-pentafluorophenyl-4-phenyl-1,3-butadiene.

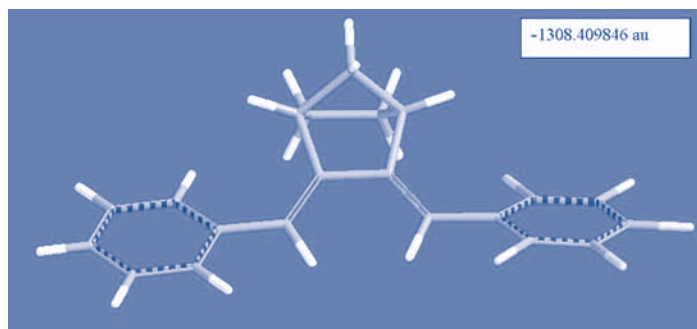
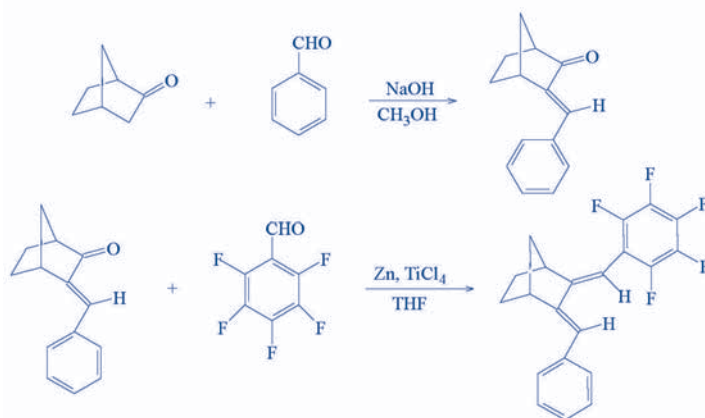


Figure 1. Ground state energy of cisoid 1-pentafluorophenyl-4-phenyl-1,3-butadiene calculated by Density Function Theory-B3LYP/6-31G.



Scheme 1. Preparation of cisoid 1-pentafluorophenyl-4-phenyl-1,3-butadiene.

Using the same approach, cisoid 1-*p*-methoxyphenyl-4-phenyl-1,3-butadiene (Figure 2) was prepared by treating racemic norcamphor with benzaldehyde to produce an enone, as shown in Scheme 2 (Liu et al., 1997). The enone was further treated with 4-methoxybenzaldehyde to produce 1-*p*-methoxyphenyl-4-phenyl-1,3-butadiene.

The cisoid, or conjugated, products from each synthesis contained two stereoisomers. Stereoisomers are two very similar shapes of the same compound. The isomers, or two similar shapes, were

separated from each other upon completion of the synthesis using silica gel column chromatography. The structures of the products were then characterized using ^1H NMR and ^{13}C NMR spectroscopy.

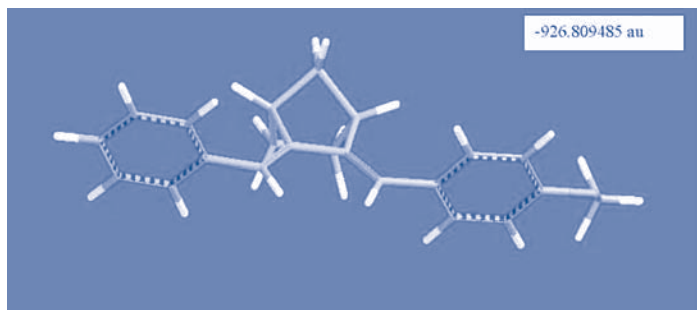
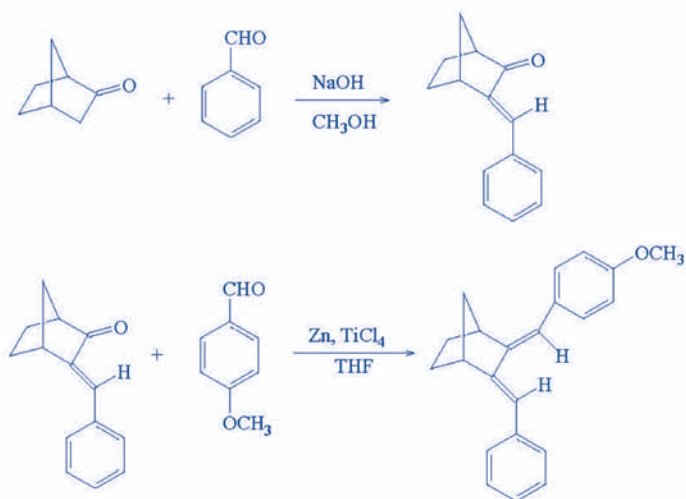


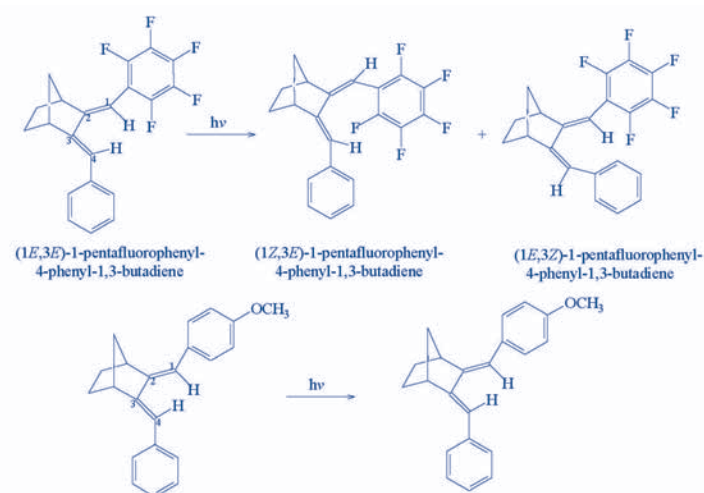
Figure 2. Ground state energy of cisoid 1-*p*-methoxyphenyl-4-phenyl-1,3-butadiene calculated by Density Function Theory-B3LYP/6-31G.



Scheme 2. Preparation of cisoid 1-*p*-methoxyphenyl-4-phenyl-1,3-butadiene.

E/Z photoisomerization of cisoid 1,4-diphenyl-1,3-butadienes was studied using direct excitation (Scheme 3). E/Z photoisomerization is the process through which the compound changes from one shape, denoted in the science of chemistry as the E isomer, to another shape which is called the Z isomer. Photoisomerization was monitored using ^1H -NMR spectroscopy. We used the NMR instrument to watch for a change in the spectra, which allows us to know that the compound is changing from one shape to another shape. After reaching equilibrium, the percentages of the three isomers were determined (Table 1). The ratio of (1Z,3E)/(1E,3Z)

of 1-pentafluorophenyl-4-phenyl-1,3-butadiene at equilibrium was 26:1. However, no photoisomerization activity was observed for (1E,3E)-1-*p*-methoxyphenyl-4-phenyl-1,3-butadiene, and the starting material was recovered (Liu, Suits, and Boorman, 2003).



Scheme 3. Photoisomerization of (1E,3E)-1-pentafluorophenyl-4-phenyl-1,3-butadiene and (1E,3E)-1-*p*-methoxyphenyl-4-phenyl-1,3-butadiene by direct irradiation.

TABLE 1		
	1-pentafluorophenyl-4-phenyl-1,3-butadiene	1- <i>p</i> -methoxyphenyl-4-phenyl-1,3-butadiene
(1E,3E) (%)	26.6	99
(1Z,3E) (%)	70.8	0
(1E,3Z) (%)	2.7	0
(1Z,3E)/(1E,3Z) ratio	26:1	—

Table 1. The percentages of the three isomers of 1-pentafluorophenyl-4-phenyl-1,3-butadiene and 1-*p*-methoxyphenyl-4-phenyl-1,3-butadiene in the photostationary mixtures, and the (1Z,3E)/(1E,3Z) ratios at the photostationary states.

Discussion

Our results reveal that isomerization of cisoid 1-pentafluorophenyl-4-phenyl-1,3-butadiene occurs selectively at the carbon-carbon double bond nearest to the fluorinated phenyl ring. However, no isomerization was observed for 1-*p*-methoxyphenyl-4-phenyl-1,3-butadiene. We determined that the isomerization occurring on the fluorinated butadiene was related to the electron-withdrawing effect induced by the fluorine substituents. The fluorine substituents are believed to weaken the carbon-carbon double bond, allowing for isomerization. Conversely, the methoxy substituent on the other butadiene provided strength to the carbon-carbon double bond. This additional strength prevented the isomerization from occurring (Liu et al., 2003).

We are currently investigating the photoisomerization of 1,4-diphenyl-1,3-butadienes in which the locked cisoid system does not exist. We are interested in determining if the same pattern of results will be revealed when the locked cisoid structure is not present. Synthesis and photoirradiation of 1-*p*-methoxyphenyl-4-phenyl-1,3-butadiene (Figure 3) has already been performed. The (*E,E*)-isomer was found to be photostable upon direct irradiation, and the starting material was recovered. These results are consistent with those found for the cisoid 1-*p*-methoxyphenyl-4-phenyl-1,3-butadiene.

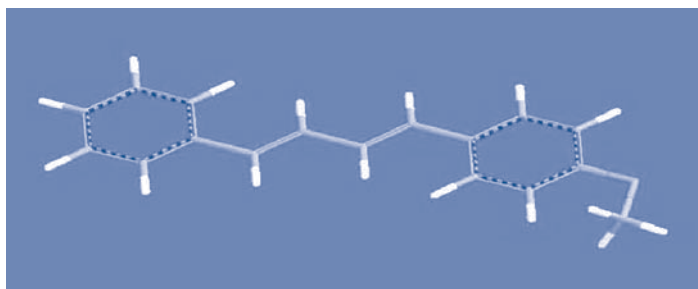


Figure 3. 1-*p*-methoxyphenyl-4-phenyl-1,3-butadiene

Acknowledgements

This work was supported by grants from the Howard Hughes Medical Institute. My experiences in the organic chemistry research lab have enabled me to learn research techniques that are not generally taught in the classroom. A large portion of the research process must be learned by hands-on experience. I am privileged to have been given the opportunity to participate in a program that provides undergraduates with this level of hands-on experience. I have also been given the opportunity to use laboratory equipment that few students have a chance to use. My experiences in the research lab have undoubtedly given me an advantage over many of my classmates, who have not had the opportunity to work in a research setting.

Working with my research advisor on a daily basis has played a key role in developing my understanding of the various scientific techniques used in the laboratory. It was critical that someone was available to answer questions and provide assistance whenever it was needed. A special “Thank You” must go to my advisor, Dr. Jin Liu, for her assistance, without which this project could not have been completed.

References

- Liu, Jin, Suits, Eric L., and Boarman, Kelly J. (2003). Regioselectivity of *E/Z* Photoisomerization of Fluorinated Cisoid (1*E*,3*E*)-1,4-Diphenylbutadienes via Direct Irradiation. *Tetrahedron Letters*, 44, 8103-8107.
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