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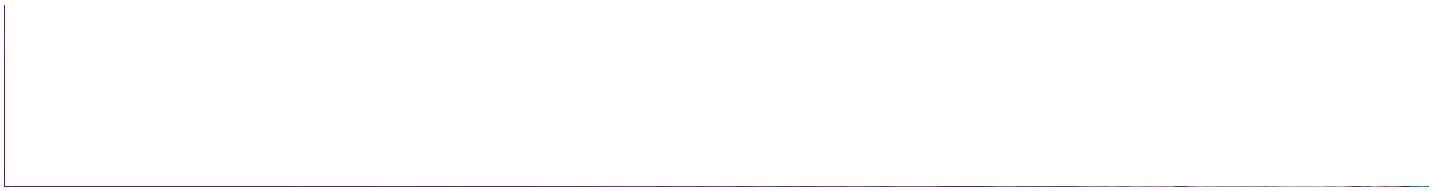

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LABORATORY EXPERIMENT | August 18, 2024

Energy Transfer Photocatalytic *(E)* *(Z)* Isomerization of 2-Nitrocinnamaldehyde using an Inexpensive, 3-D Printed Photoreactor Monitored by ^{1}H NMR Spectroscopy and Computational Modeling I!I Clicktocopyarticlelink

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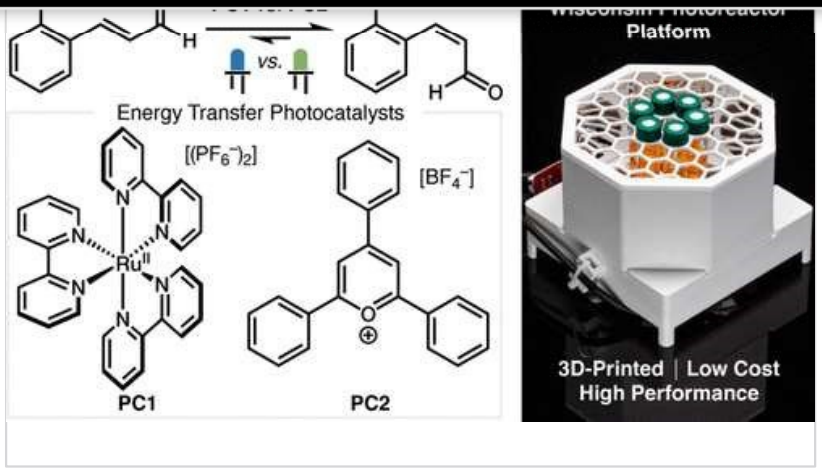

Synthesis of (Z)-alkenes is challenging because the (E) stereoisomers are usually more stable. Energy transfer photocatalysis has emerged as an efficient strategy for (E) - (Z) alkene isomerization. We report the development of an advanced undergraduate laboratory experiment that introduces students to contemporary organic photocatalysis methods and theory within the context of the energy transfer photocatalyzed (E) - (Z) isomerization of 2-nitrocinnamaldehyde. Students assess the ability of the photocatalysts [Ru(bpy)3][PF_6h and [TPP][BF_4] to promote substrate isomerization, monitor and analyze reactions by ^{1}H NMR spectroscopy, and probe the isomerization mechanism via computational chemistry. This work uses the Wisconsin Photoreactor Platform, a source of affordable, readily fabricated, and reliable photoreactors.

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Subjects©

Energy Transfer Isomerization Molecular Structure Photocatalysts Students

Keywords©

Upper-Division Undergraduate Laboratory Instruction Organic Chemistry Photocatalysis Energy Transfer Hands-On Learning/Manipulatives Problem Solving/Decision Making Catalysis Computational Chemistry NMR Spectroscopy

Introduction

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example, Gilmour and co-workers reported the selective conversion of trisubstituted (f)-alkenes to (Z)-alkenes via visible light-mediated energy transfer catalysis by (-)-riboflavin, a naturally occurring photocatalyst. .(Z).

A range of photochemical organic transformations have been reported in this journal. For example, Volpe and Podlesny detailed an exercise involving the photoreductive coupling of benzophenone under both batch and continuous flow conditions using UV irradiation, .(3.).and Miao et al. outlined the synthesis of the fluorophore 4-(1-methyl-1 H-pyrrol-2-yl)methylbenzoate via visible light-induced C-C coupling of 4-iodobenzoate and N-methylpyrrole..(4). Among other examples, (5-11) Chen described an experiment probing outcomes of the visible light-mediated [2 + 2] homodimerization of *trans-anethole* catalyzed by the coordination complexes Ru(bpy)/+ and Ru(bpm)/+_ .(12). These experiments utilize inexpensive, *ad hoc* photoreaction setups. However, small differences in light source identity and reaction vessel dimensions and orientation can dramatically affect photoreaction time and outcome. .(13). Thus, reliable reproduction of literature results typically requires precise replication of reported photoreaction setups. Commercially available photoreactors standardize reaction parameters, thereby enhancing reproducibility while minimizing reaction set up time, but these devices are expensive. Recently, Nicewicz et al. detailed a series of experiments probing structure-activity relationships among pyrylium photoredox catalysts utilizing a commercially available photoreactor. .(14). Excellent reproducibility was achieved; however, the high cost of the photoreactor (~$2000) potentially limits adoption in the instructional laboratory.

Lampkin et al. recently detailed the development of the Wisconsin Photoreactor Platform (WPP), an affordable source of versatile and reliable photoreactors. .(15). WPP devices are composed of commercial electronic components in a modular 3O-printed enclosure; high-power pseudomonochromatic LEDs are used as the photon source. Photoreactors can be fabricated in less than a day and cost < $150. Open-source design files as well as part sourcing and fabrication guides are provided on the project GitHub .(16). and in the Supporting Information of this paper. For those without access to the necessary fabrication tools, on-demand 3O-printing and circuit board manufacturing services are widely available. The WPP provides good results for a wide range of photoreactions driven by wavelengths across the UV-visible spectrum at a variety of reaction scales. .(15). Single and parallel reactions are readily conducted using WPP reactors (Figure 1).

Figure 1

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Figure 1. Overview of 3D-printed Wisconsin Photoreactor Platform (WPP) with 2-, 4-, 8-, and 24-ml reactor modules.

The project described herein introduces students to practical and theoretical aspects of contemporary organic photochemistry within the context of the (£) - *(Z)* isomerization of an alkene. Students assess the ability of the ruthenium(!!) bipyridyl complex [Ru(bpy)3][PF_6h **(PC1)** and the organic heterocycle 2,4,6-triphenylpyrylium tetrafluoroborate [TPP][BF_4] **(PC2)** to promote the photocatalytic isomerization of (£)-2-nitrocinnamaldehyde to the (Z)-diastereomer under visible light irradiation at 450 and 530 nm in acetone solution (Scheme 1). This project employs WPP reactors equipped with analog control boards, 450 or 530 nm LEDs, 2 ml reaction modules, and light-blocking covers. Photoreactions are conducted in parallel using the "multiple reaction" configuration of the WPP at full light intensity. The reaction mixture is sampled at various time points to determine the extent of(£) - *(Z)* conversion, and the %yield of (Z)-2-nitrocinnamaldehyde generated under each reaction condition is calculated via ^{1}H NMR data. The mechanism of the isomerization process is explored by generation of a potential energy surface (PES) via computational chemistry. The exercise has been successfully completed by >70 students since its initial implementation in 2021, and each round of screening is completed within a 3-4-h laboratory session. To our knowledge, this is the first example of an energy transfer photocatalysis project in the undergraduate curriculum.

Scheme 1

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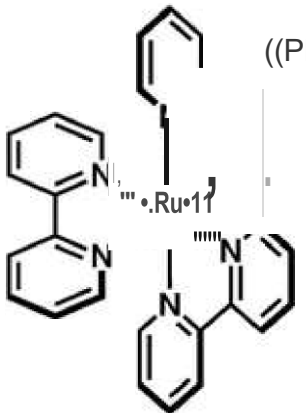
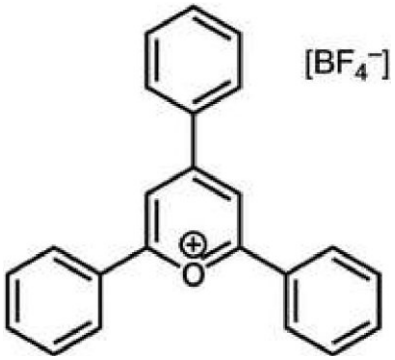


PC1
[Ru(bpy)s)l(PF6h]

Er::::: 49 cal/mol
Amax 452 nm
e :r::::I 14¦600 M"1,cm-1



PC2
[17PPUBFJ

& -= 53 kcal/mol
.:\maxQ::405 nm
e 23,200 M·1cm-1

Scheme 1. (a) Photocatalytic Isomerization of (E)-2-Nitrocinnamaldehyde to (Z)-2-Nitrocinnamaldehyde and (b) Photocatalysts [Ru(bpy)3][PF_6h **(PC1)** and [TPP][BF_4] **(PC2)** and Selected Photophysical Parameters

The learning objectives of the project are (a) to introduce theoretical concepts related to energy transfer photocatalysis (l01);(b) to practice the manipulation and monitoring of multiple photocatalytic reactions (l02); (c) to present NMR data via stacked spectra and scatterplots and use these data to calculate %conversion of starting material to product and %yield of a product (l03); and (d) to develop arguments based on experimental and theoretical data to support claims regarding the effectiveness of the reaction conditions in terms of current mechanistic models and relevant photophysical properties of the catalysts (l04)..(17).

Experimental Outline

To a 2 ml screw-cap vial equipped with a micro stir bar are added stock solutions of (E)-2-nitrocinnamaldehyde (1.2 ml 0.1 M solution in acetone, 120 µmol) and **PC1 or PC2** (0.081 ml 0.03 M solution in acetone, 2.4 µmol, 0.02 equiv., 2 mol %) via micropipette. The reaction mixture is diluted to 1 _S ml with ar.etone (0_219 mL 0_08 M) and 1 - -S-trimethvlbenzene is added as an

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Appropriate personal protective equipment, such as disposable gloves, goggles, closed shoes, and a lab coat should always be worn, and the procedures should be performed in a fume hood or similarly ventilated workspace. Caution should be used when handling chemicals. Solid and liquid waste should be disposed into sealed, appropriately labeled containers. [Ru(bpy)3][PF_6h **(PC1)** and [TPP][BF_4] **(PC2)** are skin irritants and harmful via ingestion. (E)-2-Nitrocinnamaldehyde is potentially toxic and a skin and eye irritant; safety data are not available for (Z)-2-nitrocinnamaldehyde, but this compound should be handled similarly to the *(E)* isomer. Acetone and 1,3,5-trimethylbenzene (mesitylene) are flammable and irritants to skin and mucus membranes. Deuterated chloroform is a skin irritant and potential carcinogen. Detailed safety and toxicity information for each compound is available in the corresponding SOS. Light blocking covers should be used while photoreactors are in operation, and reactors should be turned off while aliquots are obtained.

Educational Context

The project described herein is a component of the single-semester, upper-level organic chemistry laboratory course (CHEM 346) at the University of Wisconsin-Madison. .(18).Students enrolled in this course have completed a two-semester organic chemistry lecture sequence and a separate, introductory organic chemistry laboratory course described previously..(19). CHEM 346 is offered in the fall semester for 1 or 2 credits; both options include instruction in practical techniques such as manipulation of air-sensitive reagents, .(20). cyclic voltammetry, .(21).column chromatography, *in situ* sampling of reactions, and use of an NMR spectrometer via a series of multisession group projects. Students also develop skills in scientific writing, citation of literature, and oral presentation, along with instruction in the use of ChemDraw and SciFinder software. Most students enroll in the 2-credit option, which includes a semi-independent research project during the final ~6 weeks of the course, the results of which are presented during a poster session.

Introducing the Topic

Given that C=C bond isomerization reactions and organic photochemistry are not typical components of sophomore organic chemistry courses, .(22).the introduction of this topic begins in the classroom with a short review of conformational isomerism. Attention is drawn to the interconversion of exemplar molecules to highlight the fact that the height of the energy barrier to interconversion( ) determines whether or not the relative abundance of each conformer in a given sample is dictated by the energy difference between the conformers (G) For example

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(typically in the UV range) excites an electron in the TI bond to a TI* orbital, effectively breaking the TI component of the C=C bond and enabling rotation about the CJ bond to generate a twisted structure. The TI - TI* photoexcitation process causes population of the singlet (S_1) or triplet (T_1) electronic state, each of which corresponds to a diradical species. On relaxation to the singlet ground state (S_0), rotation about the C-C CJ bond leads to reformation of the TI bond and generates either the *(E)*- or (Z)-stereoisomer (Figure 2). The resultant ratio of diastereomers is thus no longer based upon the energy barrier between the two but rather the extent to which each isomer can be excited from the ground state to the S_1 or T_1 state using a chosen wavelength of light.

Figure 2

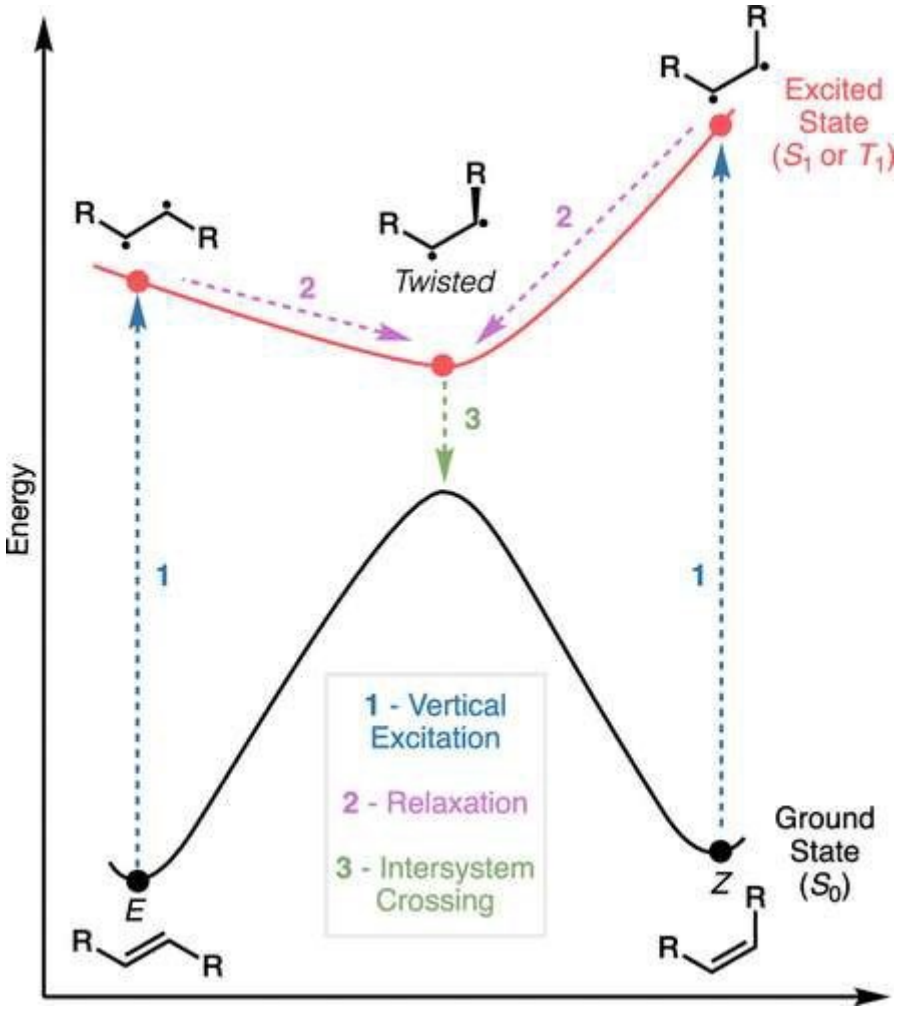

Figure 2. Simplified potential energy surface showing photoexcitation of an alkene and subsequent

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radiation rather than visible light, a requirement that limits selectivity, utility, and scope. Many organic species absorb UV light; thus, careful reaction design must be employed to achieve selective photoexcitation of specific substrates while avoiding unproductive side reactions driven by unwanted excitation of other species in the reaction mixture. In contrast, modern photochemical methods utilize photocatalysts that absorb visible light to facilitate photoredox and energy transfer reactions of organic substrates. Most organic species do not absorb visible light; therefore, photocatalysts excited via absorption of visible light can drive selective reactions of organic molecules. Such processes require organic substrates that have appropriate ground state redox potentials or triplet excited state energies (Er) to allow electron transfer or energy transfer interactions with the photoexcited catalyst. By decoupling the role of light absorber and reactant, contemporary photocatalytic reactions can achieve enhanced selectivity, scope, and utility relative to classical photochemical methods.

Energy transfer in photocatalytic systems generally involves transfer of an electron from a high-energy orbital from the excited state of the photocatalyst (typically the triplet state, T_1) to the ground state of the substrate (typically the singlet state, S_0), which simultaneously transfers an unexcited electron to the photocatalyst. This formal double electron transfer process generates a substrate in an excited state (typically T_1) and returns the photocatalyst to the ground state (S_0) (Figure 3). The excited substrate may undergo further reaction or engage in relaxation and intersystem crossing processes. For this energy transfer process to be rapid, the energy of the excited triplet state of the photocatalyst ($E_{T(Pc)}$) must generally be higher than that of a possible excited triplet state of the organic substrate ($E_{T(Sub)}$)-

Figure 3

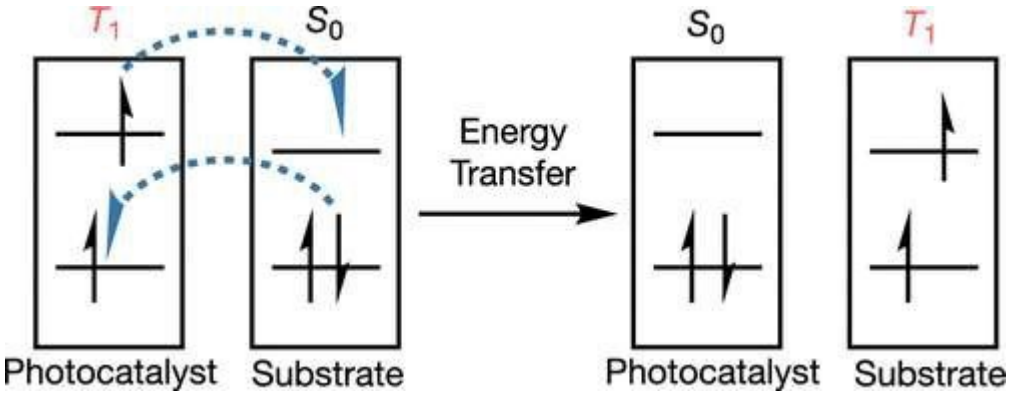

Figure 3. Simplified view of energy transfer from a photoexcited catalyst (T_1) to ground state substrate (S) resulting in an excited substrate (T) and regeneration of the ground state

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care must be taken to select a photocatalyst and (f'J/(Z) alkene pair with appropriate ETvalues (Figure 4).

Figure 4

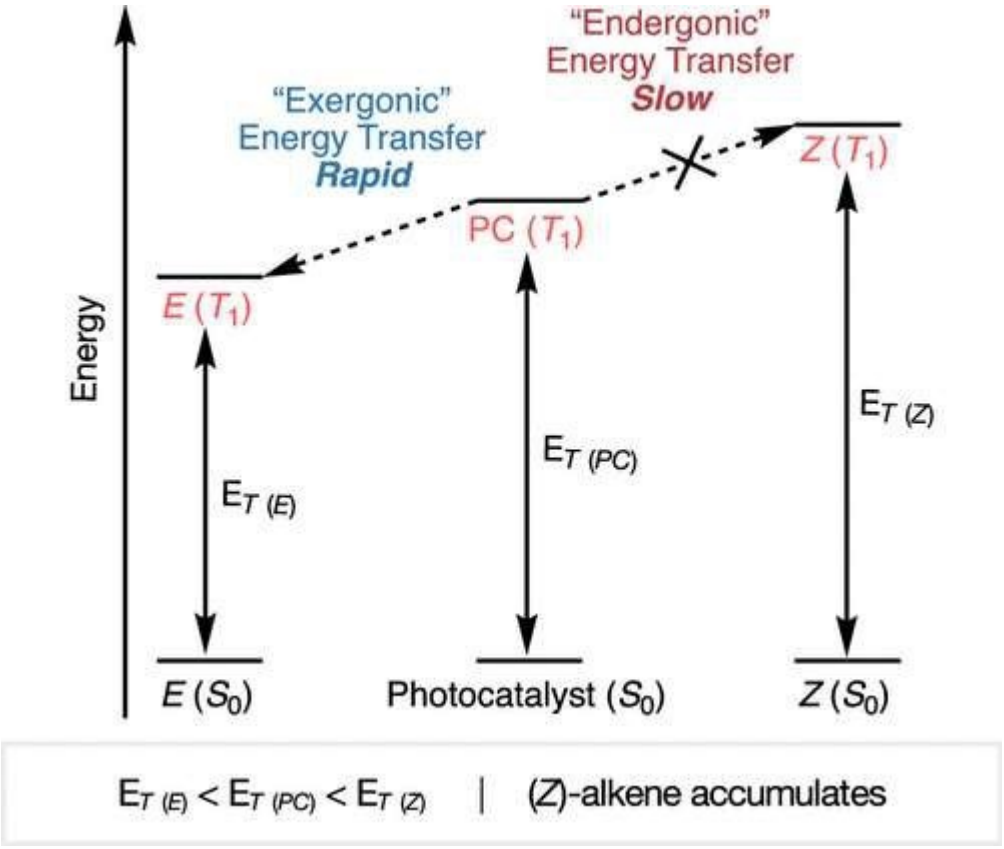

Figure 4. Mechanistic scenario wherein an (f'J-alkene exhibiting a triplet energy (ET) lower than that of a photocatalyst engages in rapid energy transfer ("exergonic") while the isomeric (Z)-alkene, with ET higher than that of the same photocatalyst, reacts slowly ("endergonic" energy transfer).

Results and Discussion

Student pairs were assigned reaction conditions based upon the screening parameters, i.e., one of the two photocatalysts **(PC1 or PC2)** and one of the two wavelengths of radiation (450 or 530 nm). Each pair performed separate reactions under the assigned conditions. All reaction conditions were evaluated at least in duplicate and most in quadruplicate. Students were provided with experimental UV-vis spectra for both photocatalysts which upon normalization allowed comparison of their

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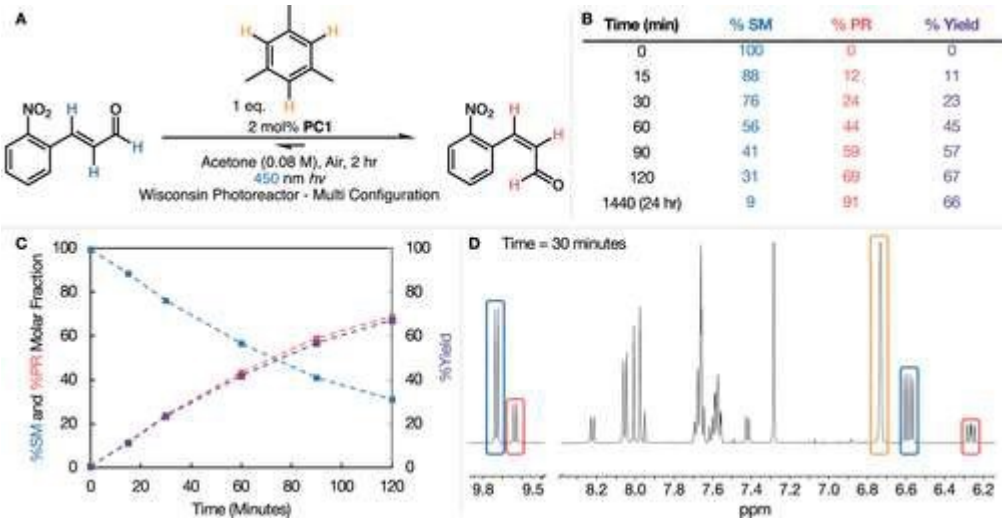
of product at each time point. This information is useful for the study of reaction kinetics and understanding how changes in experimental conditions impact the progress of a reaction. In this module, we opted to use ^{1}H NMR spectroscopic data generated from a 400 MHz instrument as a simple means to gauge the extent of *(E)* - (Z) isomerization. Each reaction mixture was sampled (50 µL) after stirring under irradiation for 15, 30, 60, 90, and 120 min in the WPP in the presence of 1 equiv of 1,3,5-trimethylbenzene as an internal standard. All samples were processed via an automated NMR platform, and the data were provided to students via a local server. The MestReNova software package was used to process raw NMR data. Prior to engaging with their experimental data, students were provided with NMR data obtained from the photocatalytic *(E)* - (Z) isomerization of (E)-cinnamaldehyde and coached in the processes of manipulation of multiple spectra and generation of tables and scatterplots in a spreadsheet via a detailed written guide (see Supporting Information). The goal of the practice material is to build competence such that students can perform these tasks independently (or with minimal instructor input) upon the experimental data obtained from their photoisomerization reaction mixtures. A representative data table, a scatterplot depicting SM:PR ratio and %yield over time, and an ^{1}H NMR spectrum for the *(E)* - (Z) isomerization driven by **PC1** illuminated by 450 nm light are shown in Scheme 2. Chromatographic methods of reaction monitoring such as TLC, GC, or LC may be feasible but were not explored during development of the project.

Scheme 2



Scheme 2. (a) Reaction Scheme Showing Conversion of (E)-2-Nitrocinnamaldehyde to (Z)-2-Nitrocinnamaldehyde Using **PC1** and a 100% Intensity 450 nm WPP Reactor in the Multireaction Configuration; (b) Tab e Reporting Starting Materia (SM) and Product (PR) Mo ar Fractions and%

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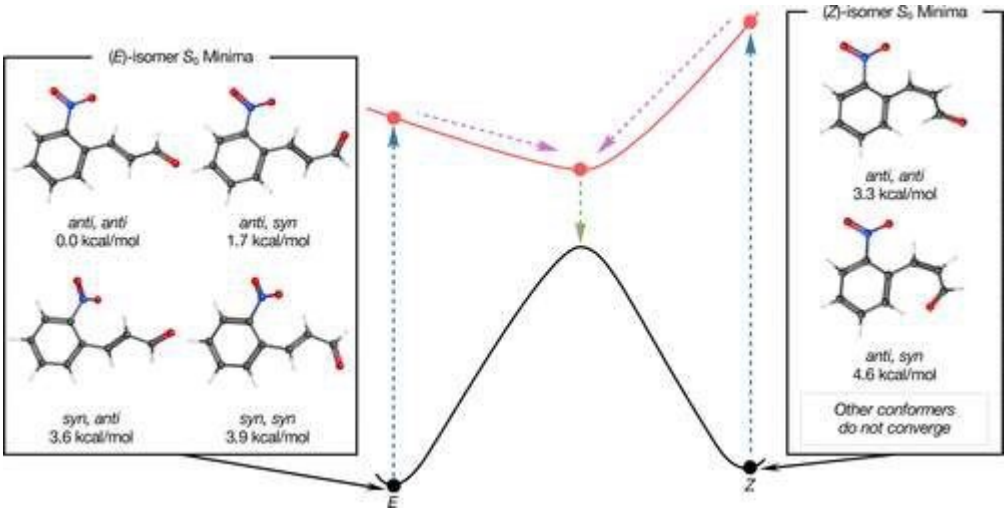
chemistry into the undergraduate laboratory curriculum has been described previously. (25,26) The guide takes the form of a series of focused exercises, starting with identification of the possible conformers of the *(E)*- and (Z)-diastereomers of the substrate. Students are prompted to draw the *(anti, ant,), (anti, syn), (syn, ant,),* and *(syn, syn)* conformers of each of the *(E)*- and (Z)-alkenes in the ground state (S_0), obtain the energies of the optimized geometries via computational chemistry, and rank the energies of each conformer. Identification of the lowest energy S_0 conformers of the(£)- and (Z)-alkenes provides a logical starting point for the PES. The *(anti, ant,)* conformers of both diastereomers are the lowest in energy, with the (£)-conformer lower in energy than the corresponding (Z)-species by ~3.3 kcal/mol (see Scheme 3).

Scheme 3



Scheme 3. Partially Completed PES Diagram Showing Structures and Energies (kcal/mol) of Possible Ground-State Conformers of *(E)*- and (Z)-2-Nitrocinnamaldehyde

Students next determine the triplet vertical excitation energies (Er) required to generate the T_1 excited state species from the S_0 minimum of each diastereomer. The Ervalue describes the difference in energy between the lowest energy S_0 conformer and the corresponding conformer in the T_1 electronic state and allows the student to generate the T_1 excited PES. Based on the Franck-Condon principle, photoexcitation of each alkene is approximated as a direct vertical excitation from the ground state. The Ervalues obtained from B3LYP/6-31G(d) calculations for the *(E)-anti, anti* and *(Z)-anti, anti* species are 62.5 and 64.4 kcal/mol, respectively. The vertical Ervalues are *qualitatively* accurate, and general trends may be extrapolated from these data; however, *quantitative* agreement with experimental Ervalues of photocatalysts is not expected from these values.

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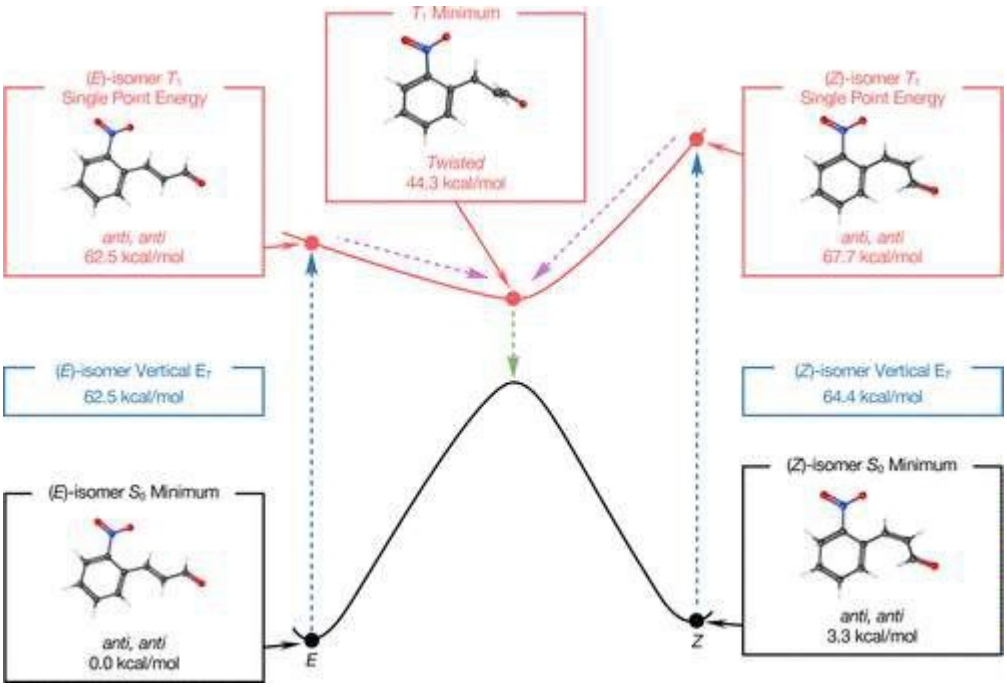
Scheme 4



Scheme 4. Complete PES Diagram Using Energy Values for *So* and T_1 Species

The electronic structure of the C=C bond in the S_0 and T_1 electronic states is explored via Natural Bond Order (NBO) calculations .(27). on the optimized geometries of the relevant species. Students observe that the molecular orbitals and electron occupancy of the TI orbitals in the S_0 diastereomers are those of a conventional TI-bond, in that the TI orbital is spread over two C atoms and contains two electrons. In contrast, a TI bond does not exist between the two relevant C atoms in the twisted geometry of the T_1 minimum; rather, a singly occupied p-orbital is localized on each C atom, indicating the T_1 species is a diradical (Figure 5).

Figure 5

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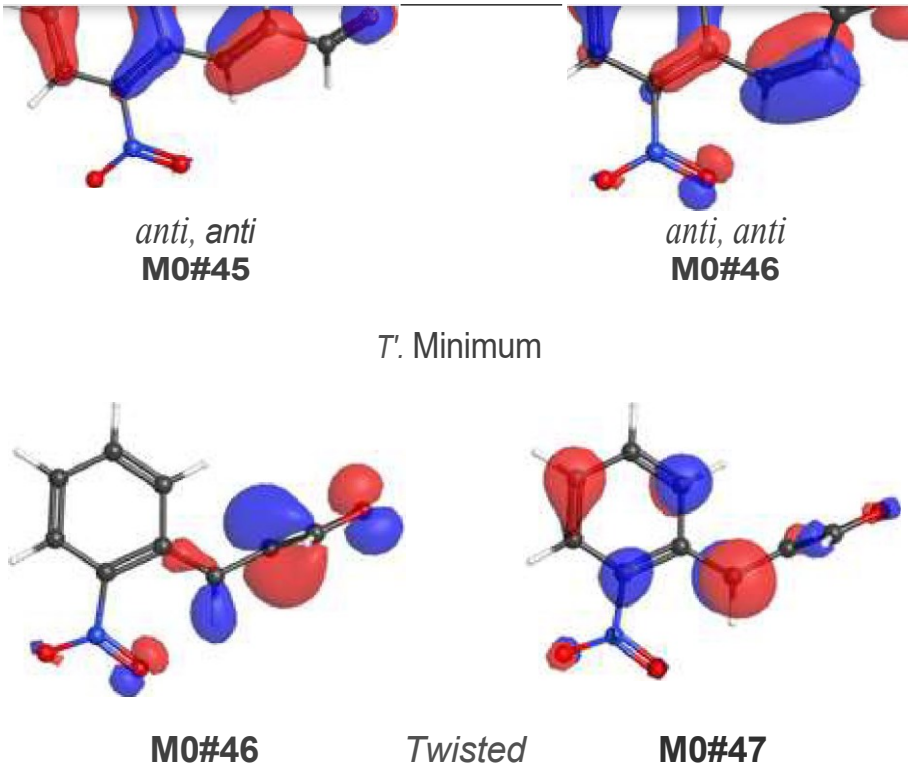

Figure 5. Molecular orbitals showing a localized alkene n bond in the singlet S_0 states of the (f'J and *(Z)* diastereomers, and molecular orbitals showing two singly occupied p-orbitals in the twisted T_1 states.

Assessment

Conceptual learning objectives LO1, LO3, and LO4 were assessed indirectly (not for credit) via classroom sessions in which the computational and experimental ^{1}H NMR data were discussed, and directly (for credit) via a written report. Students used the classroom discussion as a basis for numerical and written analysis of the experimental outcomes for each reaction condition and, based on this analysis, they selected the optimal combination of photocatalyst and wavelength. Students used the scatterplots, SM:PR ratios, and %yields obtained from experimental NMR data to explain whether **PC1 or PC2** was most effective for the conversion of (f'J-2-nitrocinnamaldehyde to the *(Z)*-diastereomer at each wavelength employed. Most students correctly identified the combination of **PC1** and 450 nm radiation as the most effective reaction condition for generation of (Z)-2-nitrocinnamaldehyde in high yield within the 2 h sampling window. It is noteworthy that (Z)-2-nitrocinnamaldehyde is obtained in highest yield following 24 h irradiation at 530 nm (Table 1); this

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		2 h Reaction			24 h R
Reaction	**Photocatalyst**	**Wavelength (nm)**	**(E):(Z) ratio**	**% Yield (Z)-isomer**	**(E):(**
1	PC1	450	31:69	67	9:91
2	PC2	450	67:33	32	43:47
3	PC1	530	67:33	32	7:93
4	PC2	530	96:4	4	96:4

The NMR data also show that **PC1** is a more effective photocatalyst than **PC2** at both 450 and 530 nm. Using the UV-vis spectra, students noted that **PC1** has a broader absorption window than **PC2** and thus can promote the reaction at both wavelengths, whereas **PC2** can only promote the reaction at 450 nm. Furthermore, **PC2** has a higher triplet T_1 energy than **PC1** and thus is less selective for the(£) *(Z)* isomerization because the reverse *(Z)* *(£)* isomerization reaction is more accessible.

Issues of synthetic accessibility, cost of catalyst vs reaction rate, and (Z)-selectivity for each photocatalyst were also addressed. For example, as part of the report, students searched the chemical literature for synthetic routes to **PC1** and **PC2** and compared the routes in terms of number of steps, %yield, and $/mmol of material. **PC2** is less expensive than **PC1,** but the experimental data show that **PC2** is not a viable photocatalyst at 530 nm and has poorer selectivity for the (Z)-alkene than **PC1** at 450 nm.

Students were also required to propose simple follow-up experiments to probe the impact of the stereoelectronic properties of the alkene and/or identity of the photocatalyst on the efficacy of the isomerization. For example, many students suggested the use of 3- and 4-nitrocinnamaldehyde to gauge the role of steric interactions of the $N0_2$ group on the process; others proposed altering the identity of the substituent group on the ring (and varying its position), and/or the nature of the carbonyl group. Although these are not necessarily highly insightful proposals, the goal of the prompt was to provide students with practice in thinking about the logical next steps in a research project, a useful experience as they embark on a semi-independent project later in the course.

Items related to L02 were indirectly assessed in the laboratory via instructor and TA observation of

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practices (SEPs) with disciplinary core ideas (DCIs) of chemistry and cross-cutting concepts (CCCs) that focus on specific aspects of phenomena. Collectively, these items have been used to construct "three-dimensional" (3D) performance expectations that have guided the generation, assessment, and refinement of lecture and instructional laboratory environments. Researchers and instructors have used the 3-Dimensional Learning Assessment Protocol (3D-LAP) (29) to quantify the extent to which an assessment has the potential to engage students in 3D learning. Essentially, 3D learning can be prompted by providing students with a phenomenon (*e.g.,* the stereoselectivity of a reaction), and asking them to explain that phenomenon by connecting ideas related to structure and energy (*e.g.,* steric interactions lower the energy of one transition state relative to another, leading to the major product). We recently applied the 3D-LAP to the postlab and exam-based assessments within a high-enrollment sophomore level organic chemistry laboratory course.. (19).

We wished to gauge the extent to which the goals of LO4 contained potential for 3D learning. 3D-LAP analysis shows that 26% of the credit available (35 points out of 135 total) is assigned to tasks that have the potential to engage students in 3D learning. These tasks require students to construct models and/or data-supported arguments to explain an aspect of the *(E)* *(Z)* isomerization being explored. An additional 44% of the total credit (60 points out of 135 total) is assigned to tasks that have the potential to engage students in SEPS only (*e.g.,* analyzing and interpreting data). While these tasks do not necessarily require the use of structure and energy ideas to explain a phenomenon and thus are not 3D, several of these questions scaffold the analysis of experimental data necessary to determine the outcome of the photoreaction prior to explaining how and why that outcome occurred. There is no widely agreed "ideal" %3D and %SEP for effective assessments; however the values for the items in this work are comparable to those reported recently.. (19).

Conclusion

The operationally simple laboratory exercise described above serves to introduce energy transfer photocatalysis and C=C bond isomerization reactions to upper-level undergraduates. Key to the process is a versatile yet inexpensive photoreactor utilizing open-source parts and fabricated by 3D printing. Potential energy surfaces associated with the ground and excited electronic states of the *(E)*- and (Z)-diastereomers are generated via computational chemistry and used to provide mechanistic understanding of the isomerization. Analysis of the postlab questions via 3D-LAP shows that ~25% of the assessment is related to 3D learning and a further ~40% is related to SEPs.

Data Availability

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- Student guides, lab manual chapters, and assessments questions (PDF)

Energy Transfer Photocatalytic (E) -▸ (Z) Isomerization of 2-Nitrocinnamaldehyde using an Inexpensive, 3-D Printed Photoreactor Monitored by ^{1}H NMR Spectroscopy and Computational Modeling

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- **635939 E -Anti Anti - C1**
- **635940 E -Anti Syn - C1**
- **635941 E - Syn Anti - C1**
- **635942 E - Syn Syn - C1**
- **635943 E -Anti Anti - C1 - T1 SPE**
- **635945 E -Anti Anti - C1 - NBO**
- **635946 Z -Anti Anti - C1**
- **635947 Z -Anti Syn - C1**
- **635948 Z -Anti Anti - C1 - NBO**
- **635949 Twisted - T1**
- **635950 Twisted -T1 - NBO**

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