

## Peter A. Wade

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(b. 1946), B.S. 1968, Lowell Technological Institute; Ph.D. 1973, Purdue University; Postdoctoral Fellow, 1974, Rijksuniversiteit, Groningen, The Netherlands (with H. Hogeveen); IBM Postdoctoral Fellow 1975-1976, Harvard University (with R. B. Woodward).

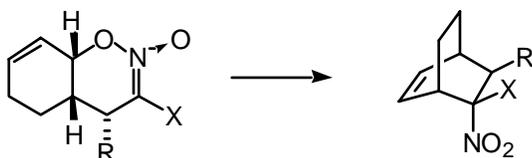
### Current Research

Work in my research group focuses on three main areas:

1) exploration of a newly discovered [3,3]-sigmatropic rearrangement in which *O*-allyl nitronic esters are thermally converted to  $\gamma,\delta$ -unsaturated nitro compounds; 2) development and exploitation of a carbon-based hemiacetal mimic; and 3) exploration of cycloaddition reactions involving nitroethylene derivatives and novel nitrile oxides.

### Sigmatropic Rearrangement of *O*-Allyl Nitronic Esters

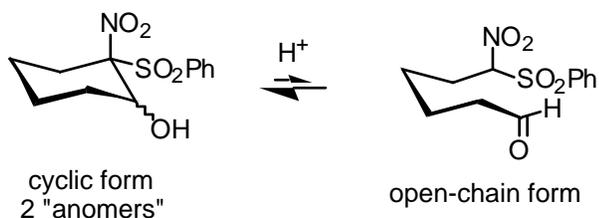
The Claisen rearrangement, in all of its many variations, has proven an extremely versatile reaction for the construction of desired target molecules. One major feature of the Claisen rearrangement (and related sigmatropic rearrangements) is the high degree of stereocontrol: synthetic chemists can confidently predict what stereoisomer will arise in a given reaction. We are investigating a new sigmatropic rearrangement with features similar to the Claisen rearrangement. This new rearrangement involves thermal conversion of *O*-allyl nitronic esters to  $\gamma,\delta$ -unsaturated nitro compounds, in some cases at room temperature. Single diastereomers are obtained as products.



A number of diverse features of the *O*-allyl nitronic ester rearrangement are under study. The nature of substituents at the nitronic C-atom, the degree of substitution at the migration terminus, and the amount of strain that can be introduced are all being determined. The potential to extend the rearrangement to *O*-benzyl nitronic esters is under study. Simple methods for synthesizing chiral *O*-allyl nitronic esters are also under investigation, permitting the extension of the rearrangement to enantioselective synthesis.

### A Carbon-Based Hemiacetal Mimic

Simple monosaccharides typically exist as a complex mixture of cyclic hemiacetal forms (anomers) that interconvert through an open-chain aldehyde form. We have observed that  $\beta$ -hydroxy-  $\alpha$ -nitrosulfones (cyclic forms) also undergo interconversion through an open-chain aldehyde form.



The necessary conditions for isomer interconversion are under study. Mildly acidic conditions give rise to interconversion of the cyclic forms ("anomers") reminiscent of the behavior in naturally occurring monosaccharides. Construction of unnatural sugars possessing  $\beta$ -hydroxy-  $\alpha$ -nitrosulfone functionality is being attempted. It is hoped that the anomeric behavior of the resulting sugars can be systematically controlled by modifying the sulfone functionality. Competition between closure of an aldehyde to give the hemiacetal or the  $\beta$ -hydroxy-  $\alpha$ -nitrosulfone will be studied.

### Cycloaddition Reactions

Nitroethylene derivatives substituted at the  $\alpha$ -position with a second electron-attracting group (W-group) are highly reactive in Diels-Alder reactions and can function as either the dienophile (predominantly) or the diene (occasionally). We have developed methods that allow use of these nitroethylene derivatives in situ for synthesis. The products ( $\alpha$ -nitrosulfones,  $\alpha$ -nitro ketones, and  $\alpha$ -nitro esters) undergo  $S_{RN}1$  replacement of the nitro or sulfone groups. We are also examining reactions of the first sulfoximine nitrile oxide, a chiral dipolarophile useful for asymmetric synthesis.



### Recent Publications

Peter A. Wade\*, James K. Murray, Jr., Sharmila Shah-Patel, Bruce A. Palfey, Patrick J. Carroll, "Tandem Nitroaldol-Dehydration Reactions Employing the Dianion of Phenylsulfonylnitromethane," *J. Org. Chem.* **2000**, 65, 7723.

Peter A. Wade\*, Hung T. Le, Nayan V. Amin, "Preparation, Properties, and Chemical Reactivity of  $\alpha$ -Nitrosulfoximines, Chiral Analogs of  $\alpha$ -Nitrosulfones," *J. Org. Chem.* **2002**, 67, 2859.

Peter A. Wade\*, James K. Murray, Jr, Sharmila Shah-Patel, Patrick J. Carroll, "Generation and In Situ Diels-Alder Reactions of Activated Nitroethylene Derivatives," *Tetrahedron Lett.* **2002**, 43, 2585.

Peter A. Wade\*, James K. Murray, Jr, Sharmila Shah-Patel, Hung T. Le, "Competing Diels-Alder Reactions of Activated Nitroethylene Derivatives and [3,3]-Sigmatropic Rearrangements of the Cycloadducts," *Chem. Commun.* **2002**, 1090.

Peter A. Wade\*, Susan A. Rutkowsky, Daniel B. King, "A Simple Combinatorial Experiment Based on Fischer Esterification", *J. Chem. Educ.*, **2005**. 82, 0000 [In Press].