

Formal Halo-Meyer–Schuster Rearrangement of Propargylic Acetates through a Novel Intermediate and an Unexampled Mechanistic Pathway



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Invited for the cover of this issue are Santu Sadhukhan and Beeraiah Baire at the Indian Institute of Technology Madras. Read the full text of the article at [10.1002/chem.201901856](https://doi.org/10.1002/chem.201901856).

What is the most significant result of this study?

The reported study uncovers a novel reactivity of propargylic acetates under metal-free conditions, and shows a new class of α,α -dihalo- β -acetoxyketone intermediates as well as mechanistic pathway. The key player here is the water, which acts as a Lewis base in contrast to traditional nucleophilicity.

What aspects of this project do you find most exciting?

Developing a new transformation to access highly useful building blocks is always an exciting and challenging task. We feel that the mechanism of the discovered domino transformation and the competitive yet selective reactivity of water are most exciting to the synthetic community.

What prompted you to investigate this topic/problem?

Our motivation for the development of the current work comes from the aim to develop new reactions by exploring the unconventional reactivity of propargylic derivatives and unravelling their mechanistic details. Our desire to explore water as a greener reagent for organic synthesis also stimulated us.

What other topics are you working on at the moment?

Apart from current reported work, our research group is mainly involved in the exploration of unexampled reactivity of alkynes and propargylic derivatives such as propargylic alcohols, acetates, and ynones. The motivation here was to discover and develop greener, practically accessible new synthetic methodologies. One such example from our groups is the umpolung functionalization (nucleophilic) of propargylic alcohols via a conceptually novel Z-enoate assisted Meyer–Schuster rearrangement. We are also actively involved in the total synthesis of complex, bioactive natural products and drug molecules. As the current work is new and can potentially be utilized in organic synthesis, a group of students is continuously working on various aspects of these novel intermediates α,α -dihalo- α' -acetoxyketones and α,α -dihalo- β -acetoxyketones.

Is your current research mainly curiosity driven (fundamental) or rather applied?

Our current research is focused both on the development of fundamental chemistry as well as on applications towards medicinal chemistry, materials, and pharmaceuticals.

