Oxonium ions for the synthesis of strained alkynes and allenes

M. Fresia, J. W. Burton
Department of Chemistry, University of Oxford
12 Mansfield Road, Oxford, OX1 3TA, United Kingdom
marvin.fresia@chem.ox.ac.uk

The history of strained alkynes and alkenes begins with benzyne, which was first proposed as a reactive intermediate in 1927 by Bachman and Clarke from the reaction of sodium with chlorobenzene.[1] More recently, Smith and Burton have reported the use of dibenzofuranyl oxonium ions as bench-stable salts that generate arynes under very mild conditions (K_3PO_4, MeCN, rt).[2] This prompted us to investigate oxonium ion precursors **1** for the synthesis of other strained alkynes and allenes.

Besides cyclohexyne (**2**, X = CH_2) and 1,2-cyclohexadiene (**3**, X = CH_2), perhaps the most interesting and potentially the most synthetically useful functionalised strained alkynes/allenes are the cyclohexynones **2** (X = C=O) and corresponding α,β,β,γ-unsaturated cyclohexanones **3** (X = C=O), as well as their five-membered ring analogues. The synthetic approach to these should be straightforward and allow the study of these unusual strained alkynes, of which little has been reported.[3]

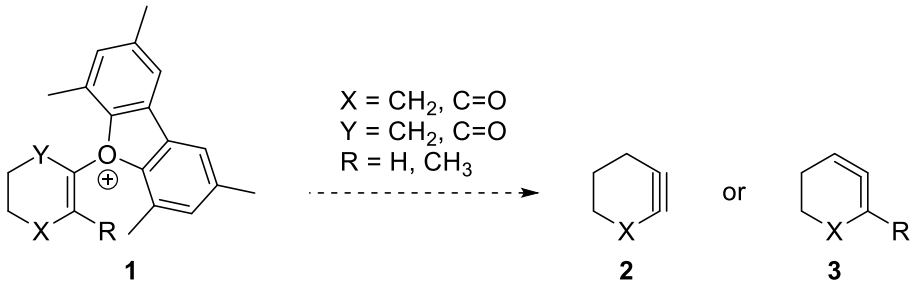

Figure 1. Oxonium ions **1** as precursor for strained alkynes **2** and allenes **3**.

1 W. E. Bachmann, H. T. Clarke, *J. Am. Chem. Soc.*, **1927**, *49*, 2089.
2 O. Smith, M.J. Hindson, A. Sreenithya, V. Tataru, R. S. Paton, J. W. Burton, M. D. Smith, *Nat. Synth.*, **2023**, *3*, 58.
3 H. Ohmori, H. Maeda, C. Ueda, M. Masui, *J. Chem. Soc., Chem. Commun.*, **1998**, 874.