ABSTRACT

Carbon-carbon bond cleavage reactions are useful transformations due to their ability to directly provide synthetic intermediates that are otherwise difficult to prepare. Furthermore, ring fragmentations are particularly useful because the two, newly-formed functional groups are tethered to one another at a specific distance and these can be used in subsequent synthetic transformations. Recently, the Brewer research group has discovered that γ -siloxy- β -hydroxy- α diazoacetates fragment efficiently to give synthetically useful compounds that contain an aldehyde tethered to an ynoate. However, a fragmentation substrate that contained two protected cis alcohols failed to fragment. It was hypothesized that this was due to steric hindrance between the alcohols, which prevented the molecule from adopting the necessary conformation to achieve proper stereoelectronic alignment of the diazo ester and the departing alcohol group that is necessary for fragmentation. This study is aimed at testing this hypothesis. To do this we prepared a similar γ -siloxy- β -hydroxy- α -diazoacetate fragmentation substrate in which the two protected alcohols are *trans*, which accommodates the correct syn periplanar alignment without steric hindrance. The substrate was obtained via a 6-step pathway from readily available cyclohexane-1,4-diol and was subsequently fragmented by treatment with catalytic SnCl₄ to produce promising results at a 40% yield. Future work includes the optimizing of the ring fragmentation reaction by investigation of the effects of temperature and coordinating solvents. Once the ring fragmentation is optimized the product of this reaction will be used in the synthesis of the mesembrine and chi alkaloids.