Unlike most acyclic enones which are observed to give mechanistically simplistic photochemistry, we have examined several sterically congested acyclic enones exhibiting unique photorearrangement reactions. Insights into the mechanistic pathways of this novel photorearrangement will be given.

During the course of the investigation, a highly strained 10-oxapentacyclo[5,3,1,05.7,0,8,9,02.11]undecene derivative was synthesized under high-intensity laser-jet conditions. The structure of this unusual species as well as other photoproducts will be presented.

The semibullvalenes have been recognized as the system most closely approaching neutral homoaromaticity. Theoretical calculations indicate the homoaromatic 1c to be the ground state. However X-ray structure determinations at 293K, 243K, 163K, 148K and 123K show an equal mixture of 1a & 1b at the lower temperatures. The existence of both 1a & 1b is confirmed by solution NMR. The solid state NMR is not able to distinguish 1a ⇔ 1b from 1c. The result leave open the possibility that 1c exists in the gas phase.

In continuation of our research program [1] we have determined the crystal and molecular structures of six tri-O-isopropylidene derivatives of openchain alditols. Contrary to the "so-called" Hassel-Ottar effect, our investigations show that the avoidance of 1,3-parallel interactions between O and C atoms (designated as O/O and C/O, respectively) is NOT the dominating factor in determining the conformations of higher alditols in the solid state [2]. Acetylated alditols in particular are able to adopt "unexpected" conformations [3]. A systematic search in the CAMBRIDGE FILE for the occurrence of such O/O and C/O interactions in the conformations of acyclic carbohydrate derivatives and the six new structure determinations confirm these results. Several examples will be discussed to illustrate that it is difficult to predict "preferred" conformations of alditols.