

On the $\pi^2S + \pi^2S$ pathways toward $[n]$ -prismanes

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Abstract. Empirical force field calculations indicate that 1c, 2c and 3c rather than 1a, 2a and 3a are more favourable precursors for photocycloadditions to give [5]-, [6]- and [7]-prismane respectively.

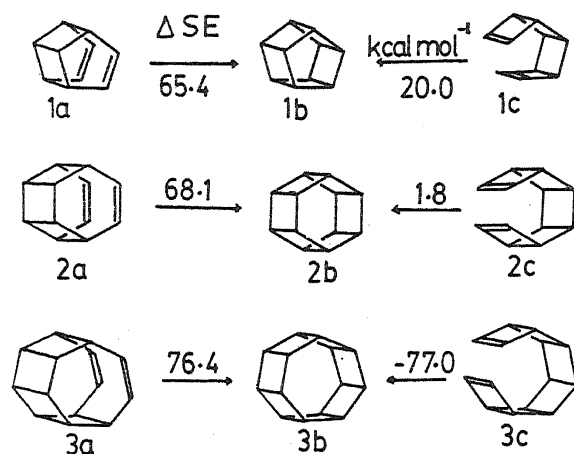
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There is considerable experimental and theoretical interest in the higher members of the $[n]$ -prismanes (Reddy and Jemmis 1986; Eaton *et al* 1981; Mehta and Padma 1987; Yang and Horner 1986; Mehta *et al* 1987; Allinger and Eaton 1983). The last step in many of the planned synthesis is a photochemical $\pi^2S + \pi^2S$ cycloaddition (scheme 1. 1a \rightarrow 1b, 2a \rightarrow 2b, 3a \rightarrow 3b). Unfortunately these are not successful (Mehta and Padma 1987; Eaton *et al* 1986; Mehta *et al* 1987). In this communication we analyse the problems with these reactions and suggest alternative precursors which have never been considered before.

There are several factors working against these reactions. The major hurdle is the construction of three cyclobutane rings in one step. If an average of 20 kcal/mol of strain is assumed for each cyclobutane the strain energy increase would be 60 kcal/mole on this count alone. Besides there are considerable destabilizing changes in the CCC angles in the products of these reactions. 2a, for example, has comfortable angles around the sp^2 carbon but the angles cannot change much during the formation of 2b though the carbons become tetra-coordinate. These are reflected in the large strain energy differences (ΔSE) calculated for them using empirical force field calculations (Allinger 1977, Allinger and Yuh 1980).

The two unfavourable factors can be avoided by a small change in the precursors. Consider 1c, 2c and 3c where the double bonds are parallel to the C_n axis of the target prismanes. Only one four-membered ring will be added as a consequence of the 2+2 addition now. The change of angle at the trigonal carbons is not very large, but the carbon centre has become 'tetrahedral' so that the initial small angle is better accommodated. In addition to these the two ethylene units in 1c, 2c and 3c should be close together. The all-cis-fused four-membered rings bring them close.

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Empirical force field calculations (scheme 1) show that ΔSE s for cycloaddition of 1a, 2a and 3a are larger than 50 kcal/mol, an empirical limit arrived at previously beyond which the reactions may not take place (Osawa *et al* 1977; Mehta *et al* 1987). According to the same criterion 1c, 2c and 3c should react easily. There is only an increase of 20 kcal/mol of strain in going from 1c to 1b, well within the limits of ΔSE mentioned above. The ethylenes are close to each other (adjacent C-C distances are 2.9 Å each). The reaction 2c \rightarrow 2b should be a facile one. With 3c, the prismane becomes the less strained species. Should it be possible to make 3c, conversion to 3b should not pose any problems. Though the precursors 1c, 2c and 3c may be more difficult to prepare because of the all cis-fused rings, attempts in this direction should be rewarding.

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