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Synthesis and Structure of Systems Containing Pyramidalized and Strained Double Bond: An Investigation on the Cycloaddition Reactions of cis- and trans-3,8-dicarbomethoxy-3,8-dihydroheptalene

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Abstract: The cycloaddition reactions of cis-3,8-dicarbomethoxy-3,8-dihydroheptalene cis-2 and trans-3,8-dicarbomethoxy-3,8-dihydroheptalene trans-2 with various dienophiles such as dimethyl acetylenedicarboxylate (DMAD), p-benzoquinone, maleic anhydride, tetracyanoethylene, naphthoquinone gave monoaddition products 15-23. Further addition of benzyne and dimethyl acetylenedicarboxylate to 18 resulted in the formation of the compounds syn-25 and syn-26 having pyramidalized double bonds. The addition of benzyne to 21 and the addition of dimethyl acetylenedicarboxylate to 21, 22 and 23 gave the anti configuration products anti-26, 27 and 28, respectively. X-ray structures of syn-25, syn-26 and anti-26 show the pyramidalized angles to be 16.5° , 19.9° and 8.0° , respectively.

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