

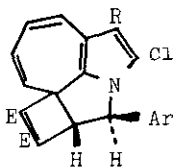
CYCLOADDITIONS OF STYRYL-SUBSTITUTED AZA-ANALOGUES OF AZULENE WITH
DIMETHYL ACETYLENEDICARBOXYLATE. FORMATION AND THERMAL REACTIONS OF
THE 7H-6a-AZACYCLOBUTA[j]CYCLOPENTA[1,2,3-cd]AZULENE RING SYSTEM

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Cycloaddition reactions of nitrogen-heterocycles with acetylenic esters are a versatile synthetic method of heterocycles otherwise difficult to obtain and have been extended recently to the aza-azulene and aza-pentalene ring systems by us. This paper concerns the cycloaddition reactions of 8-styryl-substituted aza-analogues of azulene with dimethyl acetylenedicarboxylate (DMAD).

The reaction of 8-E-styryl-1-aza-azulene (1) with DMAD proceeded stereospecifically to give trans-7H-6a-azacyclobuta[j]cyclopenta[1,2,3-cd]azulene (3), which was found to rearrange thermally to 3-E-styryl-3H-2a-azacyclopent[cd]azulene (4) and 7,8-dihydro-1-azabenz[h]azulene (5) or to isomerize to 3H-2a-azacyclopenta[ef]heptalene (6) by contact with silica gel. During the reaction, the compound (5) is oxidized to give 10-oxo-7,10-1-azabenz[h]azulene (7) or forms 6a,7,8,9-tetrahydro-6a,9-etheno-1-azabenz[h]azulene (8) with DMAD. The formation of (3) could be accounted for in terms of a symmetry-allowed $[\pi_s^2 + \pi_a^2 + \pi_a^6]$ cycloaddition. The mechanisms leading to (4), (5), and (6) are also discussed. 4-E-Styryl-1,3-diaza-azulene (2) similarly reacts to produce 3-E-styryl-3H-1,2a-diazacyclopent[cd]azulene (9) and 3H-1,2a-diazacyclopenta[ef]heptalene (10).



(3)