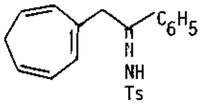
HETEROCYCLES, Vol 16, No 1, 1981

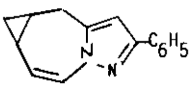
INTRAMOLECULAR 1,1-CYCLOADDITION REACTION OF ALLYLDIAZOMETHANES

Tsutomu Miyashi, Yoshinori Nishizawa, Yôsuke Fujii and Toshio Mukai
Department of Chemistry, Faculty of Science, Tohoku University, Sendai, 980 Japan

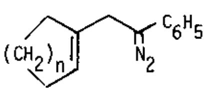
In general, diazoalkanes intermolecularly and diazoalkenes intramolecularly react with the C=C double bonds to afford 1,3-dipolar cycloaddition products in a concerted manner. In an intermolecular case, it is well known that a nitrene type 1,1-cycloadduct, aziridine, is a conjectured intermediate for the formation of a 1,3-dipolar cycloadduct. Among the large number of intramolecular cyclization reactions of diazoalkenes, those of allyldiazomethanes are apparently unknown. We report here a novel intramolecular reactivity of the terminal nitrogen of allyldiazomethane derivatives which undergo a formal nitrene type 1,1-cycloaddition to give 1,2-diazabicyclo[3.1.0]hex-2-enes instead of a usual 1,3-dipolar cycloaddition to give 2,3-diazabicyclo[3.1.0]hex-2-enes. Decomposition of the sodium salt of tosylhydrazone (1) afforded (2) in 66% yield. The formation of this unusual cyclization product (2) can be accounted for either by an initial intramolecular 1,3-dipolar addition or by an initial intramolecular 1,1-cycloaddition of the generated diazomethane to the C_3-C_4 double bond followed by rearrangements. The generality of an intramolecular 1,1-cycloaddition of allyldiazomethanes were confirmed by cyclizations of allyldiazomethanes (3), (4) and (5) which afforded aziridines (6), (7) and (8), respectively. The stereochemical course of a 1,1-cycloaddition reaction was also explored in cyclizations of allyldiazomethanes (9), (10) and (11). The exclusive formation of (12), (13) and (14) from (9), (10) and (11), respectively, provides the high stereospecific 1,1-cycloaddition reaction, supporting a concerted mechanism of an intramolecular 1,1-cycloaddition reaction of diazomethanes to the C=C double bond.



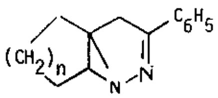
(1)



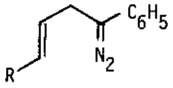
(2)



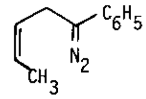
(3) n=1
(4) n=2
(5) n=3



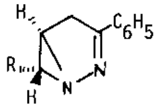
(6) n=1
(7) n=2
(8) n=3



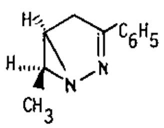
(9) $R=C_6H_5$
(10) $R=CH_3$



(11)



(12) $R=C_6H_5$
(13) $R=CH_3$



(14)