Two-Carbon Ring Enlargement of Five-, Six-, and Seven-Membered 1-Aza-2-vinylcycloalk-2-enes with Dimethyl Acetylenedicarboxylate and Subsequent Thermal Isomerization Reactions*

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2-Aminodienes, in which the enamine function is incorporated in a five-, six-, or seven-membered ring, react with dimethyl acetylenedicarboxylate in a sequence of [2+2] cycloaddition and electrocyclic ring-opening to form the two-carbon ring expanded unsaturated heterocycles, *i.e.*, 3,4-dicarboxylate substituted 6,7-dihydro-1*H*-azepines **3**, **8** and **21**, 1,6,7,8-tetrahydroazocines **22**, and 6,7,8,9-tetrahydro-1*H*-azonines **13**. Similarly, 2-[(2-thienyl)ethynyl]-4,5,6,7-tetrahydro-1*H*-azepine **9** is converted into 2-[(2-thienyl)ethynyl]-6,7,8,9-1*H*-azonine-3,4-dicarboxylate **10** which was characterized by X-ray structure determination. The eight- and nine-membered azaheterocycles **22** and **13**, which have not been isolated, undergo thermal isomerization at elevated temperatures. Thus, ring contraction by a 6π-electrocyclic reaction takes place for *N*-methyl substituted azonine **13**, while the *N*-allyl moiety of azocines **22** engages in an intramolecular Diels-Alder reaction or a 1,7-electrocyclization reaction.

Key words: Enamines, 2-Aminodienes, Medium-Sized Aza Heterocycles, Ring Enlargement, Ring Contraction