

A Proton-Catalyzed Dimerization of a 2-Amino-1,3-diene which Ultimately Yields a 3-Aminobicyclo[4.2.0]octa-2,4-diene

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The 2-pyrrolidino-1,3-dienes (*E*)-**5** and (*Z*)-**5** are obtained by the reaction of lithium di(*tert*-butyl)cuprate with propyne iminium salt **3**. Quantitative *Z* → *E* isomerization of **5** takes place within 4 hours at 20 °C. In benzene solution, (*E*)-**5** slowly equilibrates with a [1,5]-H shift to form the 1-amino-1,3-diene derivative **6**. In concentrated chloroform solution, however, (*E*)-**5** is transformed into the 3-pyrrolidino-bicyclo[4.2.0]octa-2,4-diene **7** which is identified by X-ray crystal structure analysis. A mechanism for this transformation is proposed.

Key words: Aminoallenes, 2-Aminodienes, Electrocyclic Reaction, Iminium Salts, Organocuprates