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Cyclic and Acyclic NN Bonds in Reactions with Some Alkenes and Dienes

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Abstract

© 2017 Wiley Periodicals, Inc., A Wiley Company. The kinetics of the Diels-Alder (DA) reactions of 4-phenyl-1,2,4-triazoline-3,5-dione **1**, trans-diethyl azodicarboxylate **2**, and tetracyanoethene **3** with 1,3-cyclohexadiene **4**, cycloheptatriene **5**, 1,3-cycloheptadiene **6**, cyclooctatetraene **7**, and 1,3-cyclooctadiene **8** in a range of temperatures and pressures has been studied. Values of the enthalpy, entropy, and volume of activation, as well as the enthalpy and volume of reaction have been obtained. Observed reaction rates of **5**+**1** and **7**+**1** have been compared with the known rate of norcaradiene **17** formation in the equilibrium **5**⇌**17**, and that of bicyclo[4,2,0]octa-2,4,7-triene **20** in the equilibrium **7**⇌**20**. The kinetic data show that the rate of formation of **17** from **5** is much greater than the loss rate of dienophile **1** in reaction of **5**+**1**. In contrast, the formation rate of tautomer **20** is less than the loss rate of dienophile **1** in reaction of **7**+**1**. This reflects that the consecutive reaction of **5** → **17** (+**1**) → **15** is possible whereas the consecutive reaction of **7** → **20** (+**1**) → **22** does not occur as the only way.

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