

## **[2 $\pi$ +2 $\pi$ ]-Cycloaddition of Biadamantylidene to 4-Phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione. Effects of Temperature, High Pressure, and Solvent**

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**Abstract**—The effects of temperature, solvent nature, and high hydrostatic pressure on the rate of the reaction of biadamantylidene with 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione have been estimated. Significant shielding of the C=C double bond in biadamantylidene is responsible for the high entropy and volume of activation. Quantitative yield of the reaction in the temperature range 25–45°C is related to its exothermicity. The rate of the [2 $\pi$ +2 $\pi$ ]-cycloaddition unexpectedly weakly depends on the solvent polarity, which makes it radically different from the [2 $\pi$ +2 $\pi$ ]-reaction with tetracyanoethylene.

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A large number of studies have been performed on [2+2]-cycloadditions with various pairs of substituted ethylenes, where one component exhibits pronounced electron donor properties (vinyl ethers, tetramethoxyethylene, cyclopropyl-substituted ethylenes) and the other is an electron acceptor (di-, tri-, and tetracyanoethylenes) [1–5]. In most publications, an appreciable effect of molecular asymmetry of the donor and acceptor reagents on the reaction rate was noted. Reactions of vinyl ethers with tetracyanoethylene were found to accelerate in polar medium [1, 5, 6]. The stereospecificity of the addition was conserved by about 90%. The reduced stereospecificity in [2+2]-cycloadditions gave grounds to presume that thermal reactions forbidden by the Woodward–Hoffmann orbital symmetry conservation rules involve intermediate formation of zwitterionic species. Huisgen [1] concluded that the rate of zwitterion transformation into cyclobutane derivative is approximately 5 times higher than the rate of its decomposition into initial tetracyanoethylene and vinyl ether. For the reaction of tetracyanoethylene with anethole the rate constant ratio  $k(\text{acetonitrile})/k(\text{cyclohexane})$  is 29000, for the reaction with ethoxyisobutene, 10800, and for the reaction with butyl vinyl ether, 2600. The ratio  $k(\text{MeCN})/k(\text{CCl}_4)$  for

the reaction of tetracyanoethylene with 3,4-dihydro-2*H*-pyran is 17000 [6]. The observed differences in the rates of [2+2]-cycloadditions with tetracyanoethylene in polar and nonpolar solvents is consistent with the greater stabilization of polar transition state by 5–6 kcal/mol relative to low-polar initial molecules [1, 6].

In the dienophile series 1,1-dicyanoethylene (electron affinity  $E_a = 1.53$  eV), tricyanoethylene ( $E_a = 2.10$  eV), and tetracyanoethylene ( $E_a = 2.88$  eV) [7, 8], the rate of the Diels–Alder reactions with dienes increases in parallel with the electron affinities of dienophiles [8, 9], whereas [2+2]-cycloadditions of the same dienophiles with vinyl ether display the opposite variation of the reaction rate [1]. A strong effect of the alkene asymmetry on the reaction rate was also observed in [2+2]-cycloadditions of tetracyanoethylene to cyclopropyl-substituted ethylene. 1,1-Dicyclopropylethylene turned out to be more reactive by almost 6 orders of magnitude than *cis*- and *trans*-1,2-dicyclopropylethylenes [3, 4]. The strong influence of solvent on the rate of reactions involving tetracyanoethylene may be rationalized by significant change of solvation and reactivity of tetracyanoethylene. The rate of the nonpolar Diels–Alder reaction of 9,10-dimethyl-