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Ene Reaction of β -Pinene with 4-Phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione: Effects of Temperature, High Pressure, and Solvent Nature

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Abstract—The effects of temperature, solvent nature, and high hydrostatic pressure on the rate of the ene reaction of 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione with β -pinene have been studied. The reaction gives only one product and is accompanied by a large heat effect. Comparison of the activation and reaction volumes indicates cyclic structure of the transition state. The reaction rate changes by a factor of 200 in the series of nine examined solvents, but this variation is not determined by solvent polarity.

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Among alkenes and cycloalkenes studied in ene reactions with 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione (**1**), the highest activity was observed for 2,3-dimethylbut-2-ene ($k_2 = 200 \text{ L mol}^{-1} \text{ s}^{-1}$ in toluene at 20°C) [1]. Compound **1** showed enhanced reactivity in [4+2]- and [2+2]-cycloadditions and ene reactions in comparison to other dienophiles, including tetracyanoethylene which is the strongest π -acceptor dienophile [1–7]. Triazole **1** reacted at a moderate rate with 9,10-diphenylanthracene in which the reaction centers (C^9 and C^{10}) are completely shielded due to almost orthogonal orientation of the phenyl rings with respect to the plane of the tricyclic fragment [8]. This Diels–Alder reaction proceeds fairly readily, but it involves accessible 1,4-positions [8] rather than 9,10 as presumed previously [9].

β -Pinene **2** reacts with triazole **1** to give adduct **3** as the only product [10]. However, there are no data on

quantitative parameters of this ene reaction. In the present work we have determined rate constants of the reaction **1** + **2** \rightarrow **3** (Scheme 1) in nine solvents at 20, 30, and 40°C and reaction enthalpy, estimated pressure effect on the reaction rate, calculated the activation and reaction volumes, and compared the obtained data with the corresponding parameters of some other ene reactions with compound **1** (Table 1).

The reaction rate in polar solvents such as DMF and acetonitrile was significantly lower than in weakly polar media. The entropy of activation of the reaction **1** + **2** \rightarrow **3** was close to the entropy of activation of other ene reactions, as well as of [4+2]-cycloaddition, but considerably lower than of [2+2]-cycloaddition reactions (Table 2, Scheme 2).

The ene reaction of **1** with **7** involving C=C bond migration to the bridgehead carbon atom of **7** is forbidden by Bredt's rule due to high strain energy;

Scheme 1.

