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V.I. Minkin on his 80th anniversary

## Atmospheric and High Pressure Ene Reaction of Norbornene with 4-Phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione

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**Abstract**—Thermodynamic and activation parameters (enthalpy, entropy, and volume) have been determined from the pressure and temperature dependences of the rate of the reaction of norbornene with 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione in toluene, which is accompanied by Wagner–Meerwein rearrangement. The enthalpy of the reaction in 1,2-dichloroethane has been determined by calorimetry. The obtained data correspond to a weakly polar transition state.

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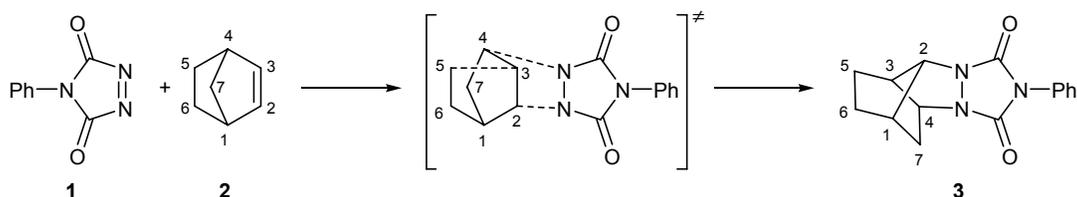
Enhanced electrophilicity of the N=N dyad in the molecule of 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione (**1**) and the reduced energy of dissociation of the N=N  $\pi$ -bond increase the reactivity of compound **1** in ene and Diels–Alder reactions by 5–6 orders of magnitude. Alkenes and cycloalkenes possessing an accessible allylic hydrogen atom readily react with compound **1** according to the ene reaction path with formation of stable substituted urazoles [1–4]. We have recently shown that the ene reaction of **1** with dicyclopentadiene involves the C=C bond of the cyclopentene fragment to give 1:1 adduct, while the norbornene C=C bond remains intact [5]. According to the Bredt rule, no double bond is formed at a bridging carbon atom in bicyclic structures because of the high strain energy. The same factor is responsible for the failure of conventional ene reaction of norbornene **2** with

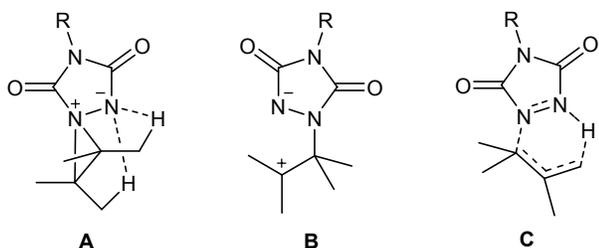
4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione (**1**). The reaction of **1** with **2** is accompanied by skeletal rearrangement of the norbornene fragment, yielding adduct **3** [6–8] (Scheme 1).

Analogous skeletal rearrangement was observed in the reactions of **1** with 2,3-benzonorbornadiene and 2,3-benzo-7-oxanorbornadiene [6–8]. Ene reactions are commonly assumed to proceed via three possible mechanisms [6–11]: aziridinium imide (**A**), dipolar (**B**), and concerted (**C**) (see below).

The concerted mechanism is possible in the additions of **1** to dienes and alkenes [1–4] but not in the reaction with norbornene. Therefore, in the present work we compared the rate, enthalpy, entropy, and volume of activation, as well as the enthalpy and volume of the reaction **1** + **2**  $\rightarrow$  **3** accompanied by the Wagner–Meerwein rearrangement with analogous data

Scheme 1.





obtained previously for some ene and [2+2+2]-cycloaddition reactions with compound **1** (Scheme 2).

The rate constants for the reaction **1** + **2** → **3** in toluene were determined by kinetic measurements,  $k_2$ ,  $l \text{ mol}^{-1} \text{ s}^{-1}$ :  $1.28 \times 10^{-4}$  (25°C),  $2.72 \times 10^{-4}$  (35°C),  $3.94 \times 10^{-4}$  (40°C),  $7.85 \times 10^{-4}$  (50°C),  $14.8 \times 10^{-4}$  (60°C); enthalpy of activation 55.3 kJ/mol; entropy of activation  $-134 \text{ J mol}^{-1} \text{ K}^{-1}$ ; Gibbs energy of activation 95.2 kJ/mol.

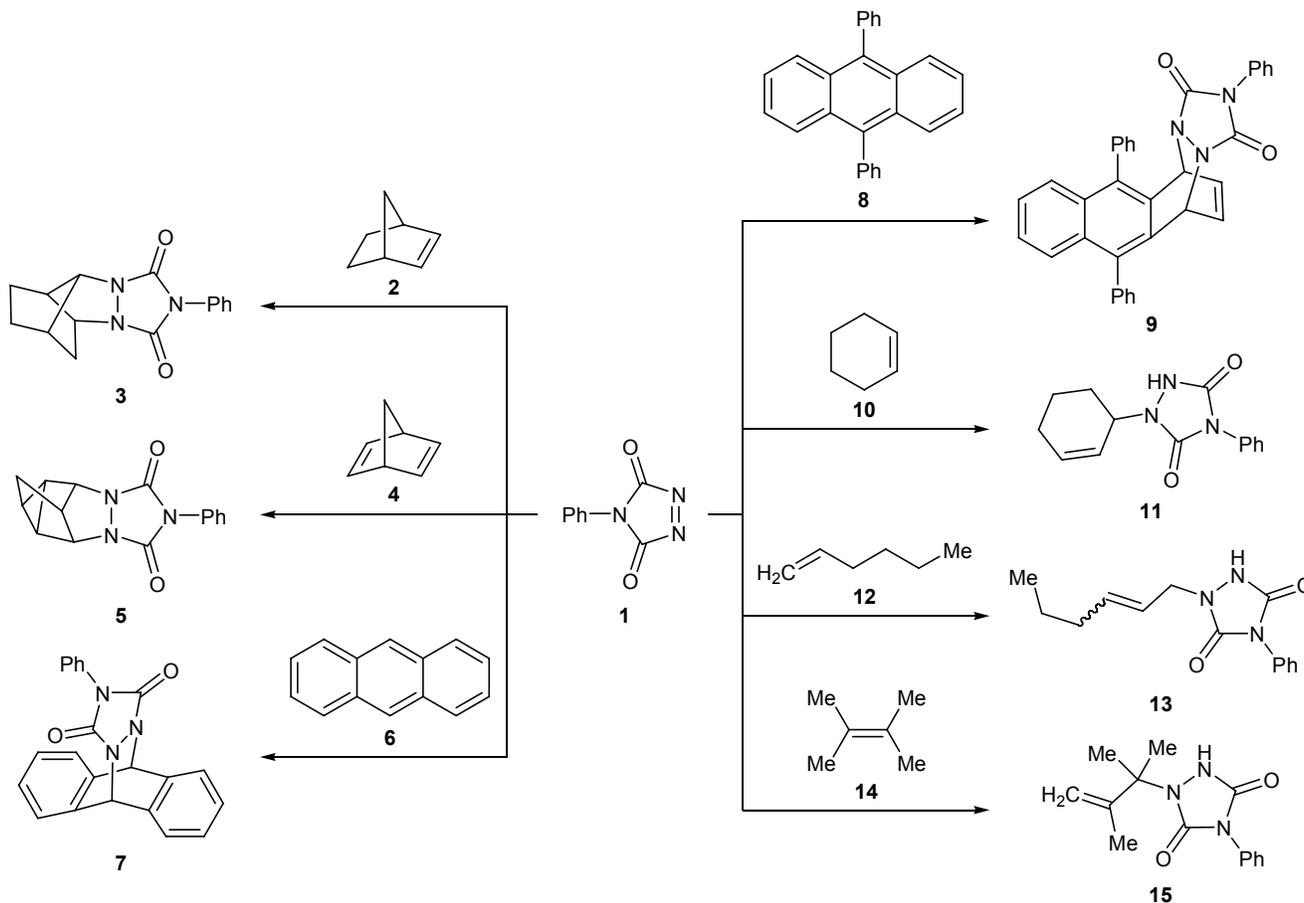
The volume of activation was calculated from the variation of the rate constant of the reaction **1** + **2** → **3** in toluene at 25°C on raising the pressure to 1000 bar:  $\ln(k_{P=1000}/k_{P=1}) = 0.9985$ ; the volume of activation

calculated from the experimental data is  $\Delta V_{\text{exp}}^\ddagger = -28.8 \text{ cm}^3/\text{mol}$ ; the volume of activation corrected for toluene compression is  $\Delta V_{\text{corr}}^\ddagger = -26.6 \pm 0.5 \text{ cm}^3/\text{mol}$ . The absolute value of the volume of activation also depends on the size of the reacting molecules; therefore, the volume of activation should be correlated with the volume of the same reaction. The latter was calculated using Eq. (1) [12] which describes the dependence of the specific volume of reactant solution ( $1/d_t$ ) in toluene on the concentration of the resulting adduct ( $c_3$ ) at  $25 \pm 0.002^\circ\text{C}$  (see figure):

$$1/d_t = 1/d_{t=0} + c_{3,t} \Delta V_t / 1000 d_{t=0}. \quad (1)$$

The enthalpy of the reaction **1** + **2** → **3** accompanied by skeletal rearrangement was compared with those of reactions involving no such rearrangement. The mean value of the enthalpy of this reaction in 1,2-dichloroethane, obtained from six measurements, was  $-170 \pm 4 \text{ kJ/mol}$ . The reaction **1** + **2** → **3** accompanied by skeletal rearrangement with formation of two C–N bonds is characterized by increased exo-

Scheme 2.



Rate constants, enthalpies, entropies, and volumes of activation, and enthalpies and volumes of the reactions of 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione (**1**) with norbornene (**1** + **2** → **3**), norbornadiene (**1** + **4** → **5**), anthracene (**1** + **6** → **7**), 9,10-diphenylanthracene (**1** + **8** → **9**), cyclohexene (**1** + **10** → **11**), hex-1-ene (**1** + **12** → **13**), and 2,3-dimethylbut-2-ene (**1** + **14** → **15**) in toluene at 25°C

Reaction	$k_2$ , l mol <sup>-1</sup> s <sup>-1</sup>	$\Delta H^\ddagger$ , kJ/mol	$-\Delta S^\ddagger$ , J mol <sup>-1</sup> K <sup>-1</sup>	$\Delta V^\ddagger/\Delta V$ , cm <sup>3</sup> /mol	$-\Delta H$ , kJ/mol
<b>1</b> + <b>2</b> → <b>3</b> <sup>a</sup>	$1.28 \times 10^{-4}$	55.3	134	26.6/24.6 = 1.08	170
<b>1</b> + <b>4</b> → <b>5</b> <sup>b</sup>	$3.95 \times 10^{-3}$	50.9	120	25.1/31.0 = 0.81	218
<b>1</b> + <b>6</b> → <b>7</b> <sup>b</sup>	0.33	43.1	109	–	96.7
<b>1</b> + <b>8</b> → <b>9</b> <sup>c</sup>	$2.72 \times 10^{-3}$	58.6	97	17.2/15.6 = 1.10	50.2
<b>1</b> + <b>10</b> → <b>11</b> <sup>d</sup>	$8.07 \times 10^{-3}$	53.3	106	29.1/25.0 = 1.16	156
<b>1</b> + <b>12</b> → <b>13</b> <sup>d</sup>	$2.35 \times 10^{-3}$	51.8	122	31.0/26.6 = 1.16	158
<b>1</b> + <b>14</b> → <b>15</b> <sup>d,e</sup>	55.6	20	144	–	150

<sup>a</sup> The reaction enthalpy was measured in 1,2-dichloroethane (our data).

<sup>b</sup> Data of [1].

<sup>c</sup> 1,4-Addition to diene **8** [13].

<sup>d</sup> Data of [2].

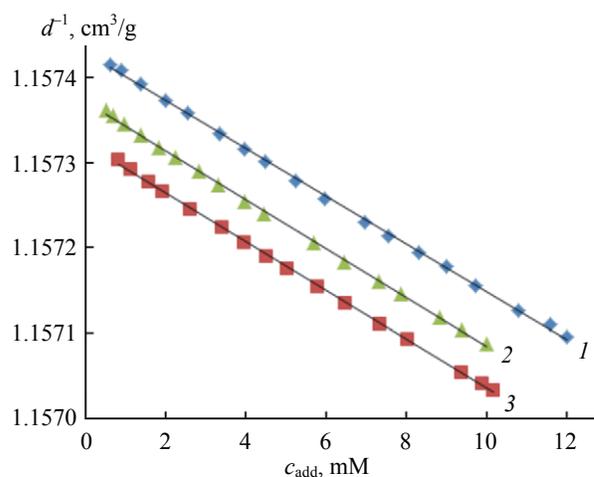
<sup>e</sup> In benzene.

thermic effect compared to conventional ene reactions. The energy and volume parameters of some ene reactions, Diels–Alder reactions, and homo reaction of norbornadiene with dienophile **1** are given in table.

Comparison of the parameters of the ene reaction **1** + **2** → **3** with those of typical ene reactions involving addition of the allylic hydrogen atom to nitrogen (**1** + **10** → **11**, **1** + **12** → **13**, **1** + **14** → **15**), as well as of the Diels–Alder reactions (**1** + **6** → **7**, **1** + **8** → **9**), allowed us to draw the following conclusions. If the rate-determining step of the reaction **1** + **2** → **3** is the formation of 1,4-dipolar ion **B**, increased electrostriction of the solvent due to solvation of such polar activated complex should be expected [14], in contrast to neutral compound **3**. On the other hand, close values of  $\Delta V^\ddagger/\Delta V$  for the reactions of **1** with norbornene ( $\Delta V^\ddagger/\Delta V = 1.08$ ), cyclohexene (1.16), and hex-1-ene (1.16; see table) suggest formation of similar low-polar activated complexes in these reactions.

The other activation parameters of the ene reactions also differ insignificantly. It is known [8] that solvent polarity weakly affects the rate of the reaction **1** + **2** → **3**. Furthermore, like ene and Diels–Alder reactions, its rate in polar acetonitrile is even lower than in benzene, toluene, and especially chloroform. The solvent effect on the rates of the reaction **1** + **2** → **3** and ene reaction of **1** with trimethylethylene [15] was almost the same ( $R = 0.96$ ). Analogous solvent effect was observed for the reactions with anthracene ( $R = 0.99$ ) and *trans,trans*-1,4-diphenylbuta-1,3-diene ( $R = 0.96$ ) [16]. The weak effect of the substituent in 4-aryl-3*H*-1,2,4-triazole-3,5(4*H*)-diones on the rate of their reactions

with norbornene **2** [8] is also inconsistent with the formation of 1,4-dipolar ion in the rate-determining step of the reaction **1** + **2** → **3**. All attempts to detect intermediate **B** with the use of inter- and intramolecular traps were unsuccessful [8]. These data allowed us to presume that all ene reactions considered here, including the reaction **1** + **2** → **3**, are more likely to involve a weakly polar transition state.



Plots of the specific volume of solution versus concentration of adduct **3** in the reaction of 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione (**1**) with norbornene (**2**) in toluene at 25 ± 0.002°C: (1)  $d^{-1} = -0.028010c_3 + 1.157429$ ,  $R^2 = 0.999317$ ,  $c_{0,1} = 0.02499$ ,  $c_{0,2} = 0.2495$  M,  $\Delta V_T = -24.20$  cm<sup>3</sup>/mol (because of superimposition, plot 1 is displaced upward by 0.00005 unit); (2)  $d^{-1} = -0.028803c_3 + 1.157372$ ,  $R^2 = 0.999342$ ,  $c_{0,1} = 0.02462$ ,  $c_{0,2} = 0.2451$  M,  $\Delta V_T = -24.89$  cm<sup>3</sup>/mol; (3)  $d^{-1} = -0.028627c_3 + 1.157322$ ,  $R^2 = 0.999223$ ,  $c_{0,1} = 0.02506$ ,  $c_{0,2} = 0.2438$  M,  $\Delta V_T = -24.74$  cm<sup>3</sup>/mol.

## EXPERIMENTAL

Commercial 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione (**1**; from Aldrich) was purified by sublimation at 100°C (10 Pa), mp 165–170°C (decomp.),  $\lambda_{\max}$ , nm ( $\epsilon$ ): 540 (248) in benzene, 527 (186) in 1,4-dioxane, 540 (245) in toluene. Commercial norbornene (**2**, bicyclo-[2.2.1]hept-2-ene; 99%, from Aldrich) was used without additional purification. The solvents were purified by standard methods [17]. The quantitative formation of adduct **3** in the reaction of **1** with **2** and its structure were proved previously [7, 8].

**Atmospheric pressure kinetic measurements.**

The rate of the second-order reaction **1** + **2** → **3** (first order in each reactant) was monitored by the absorbance of dienophile **1** ( $c_{0,1}$  = 0.003–0.005 M) in the region  $\lambda$  530–570 nm using a Hitachi U-2900 spectrophotometer. Neither norbornene ( $c_{0,2}$  = 0.2–0.45 M) nor adduct **3** absorbed in that region of the spectrum. The conversion was no less than 50%, and the correlation coefficients for the kinetic relations were higher than 0.9997.

**High pressure kinetic measurements.** The reactions were carried out in toluene at 25°C in a high-pressure setup using an HP-500 high-pressure pump and a PCI-500 high-pressure optical cell with sapphire windows (Syn Ltd., Japan) compatible with a Scinco spectrophotometer (Korea). Stock solutions of the initial reactants with the concentrations  $c_{0,1}$  = 0.0105 and  $c_{0,2}$  = 0.437 M were prepared. A working solution was prepared by mixing equal volumes (1 mL each) of the stock solutions. The high-pressure quartz cell path length was 0.4 cm. In all cases, the high-pressure kinetic dependences were characterized by correlation coefficients of higher than 0.9995. The experimental volume of activation under atmospheric pressure ( $-28.8 \pm 0.5$  cm<sup>3</sup>/mol) was calculated from  $\partial \ln k / \partial P = 1.16 \times 10^{-3}$ . The volume of activation corrected for variation of concentration due to compressibility of toluene ( $\beta_t = 80.1 \times 10^{-6}$  bar<sup>-1</sup> at 25°C [18]) was  $\Delta V_{\text{corr}}^\ddagger = -26.6 \pm 0.5$  cm<sup>3</sup>/mol.

**Calorimetric measurements.** The enthalpy of the reaction **1** + **2** → **3** was determined in 1,2-dichloroethane at 25°C using a TAM III precision dissolution calorimeter. The semi-automatic adiabatic calorimeter was equipped with a 25-mL glass vessel, gold stirrer, heater, and thermistor. The working volume (25 mL) was filled with a 1.75 M solution of norbornene. After temperature equilibration, the vessel was calibrated, and 60–80  $\mu$ L of a solution of **1** with a concentration of 0.15–0.18 M was injected using an electronically controlled microsyringe. The heat effect of each injection

was determined from the calorimetric curve by the Regnault–Pfaundler method. The heat effect of dilution due to addition of a solution of **1** (0.18 M) to pure 1,2-dichloroethane (25 mL) was negligible. The following enthalpies of the reaction **1** + **2** → **3** in 1,2-dichloroethane were obtained (six measurements):  $-174.6$ ,  $-165.9$ ,  $-166.7$ ,  $-173.7$ ,  $-167.5$ , and  $-175.0$  kJ/mol; mean value  $-170 \pm 4$  kJ/mol. The baseline was reached in  $\sim 60$  min, which corresponded to a conversion of no less than 98%.

**The density of the reaction mixture 1 + 2** in toluene was measured on an Anton Paar DSA 5000 M precision densimeter (Austria) at  $25 \pm 0.002$ °C. From the first two density measurements at initial reactant concentrations of  $c_{0,1}$  = 0.02499 and  $c_{0,2}$  = 0.2495 M we calculated the volumes of the reaction  $-24.20$  and  $-24.89$  cm<sup>3</sup>/mol. The next measurement ( $c_{0,1}$  = 0.02506,  $c_{0,2}$  = 0.2438 M) gave a value of  $-24.74$  cm<sup>3</sup>/mol (see figure). The current concentrations of the adduct ( $c_3$ ) were calculated from the kinetic equation for the same period of time as for the solution density ( $d$ ). This procedure for the calculation of the reaction volume does not require determination of partial molar volumes of all components.

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## REFERENCES

1. Kiselev, V.D., Shakirova, I.I., Kornilov, D.A., Kashaeva, H.A., Potapova, L.N., and Konovalov, A.I., *J. Phys. Org. Chem.*, 2013, vol. 26, p. 47.
2. Kiselev, V.D., Kornilov, D.A., Kashaeva, H.A., Potapova, L.N., and Konovalov, A.I., *J. Phys. Org. Chem.*, 2014, vol. 27, p. 401.
3. Kiselev, V.D., Kashaeva, E.A., Potapova, L.N., Kornilov, D.A., and Konovalov, A.I., *Russ. Chem. Bull., Int. Ed.*, 2014, vol. 63, p. 280.
4. Kiselev, V.D., Kashaeva, H.A., Potapova, L.N., Kornilov, D.A., and Konovalov, A.I., *Russ. J. Phys. Chem. A*, 2014, vol. 88, p. 890.
5. Kiselev, V.D., Kornilov, D.A., Lekomtseva, I.I., Reshetnikova, O.Yu., and Konovalov, A.I., *Russ. J. Org. Chem.*, 2015, vol. 51, p. 382.
6. Sasaki, T., Kanematsu, K., and Uchide, M., *Tetrahedron Lett.*, 1971, vol. 12, p. 4855.
7. Adam, W., De Lucchi, O., and Erden, I., *J. Am. Chem. Soc.*, 1980, vol. 102, p. 4806.
8. Adam, W. and Carballeira, N., *J. Am. Chem. Soc.*, 1984, vol. 106, p. 2874.
9. Seymour, C.A. and Greene, F.D., *J. Am. Chem. Soc.*, 1980, vol. 102, p. 6384.

10. Adam, W., De Lucchi, O., and Erden, I., *Angew. Chem.*, 1979, vol. 91, p. 512.
11. Thaler, W.A. and Franzus, B., *J. Org. Chem.*, 1964, vol. 29, p. 2226.
12. Kiselev, V.D., Kornilov, D.A., Kashaeva, E.A., Potapova, L.N., and Konovalov, A.I., *Russ. J. Org. Chem.*, 2014, vol. 50, p. 489.
13. Kiselev, V.D., Kornilov, D.A., Kashaeva, H.A., Potapova, L.N., Krivolapov, D.B., Litvinov, I.A., and Konovalov, A.I., *Russ. J. Phys. Chem. A*, 2014, vol. 88, p. 2073.
14. Kiselev, V.D., *Mendeleev Commun.*, 2008, vol. 18, p. 59.
15. Desimoni, G., Faita, G., Righetti, P.P., Sfulcini, A., and Tsyganov, D., *Tetrahedron*, 1994, vol. 50, p. 1821.
16. Konovalov, A.I., Breus, I.P., Sharagin, I.A., and Kiselev, V.D., *Zh. Org. Khim.*, 1979, vol. 15, p. 361.
17. Riddick, J.A., Bunger, W.B., and Sakano, T.K., *Organic Solvents: Physical Properties and Methods of Purification*, New York: Wiley, 1986, 4th ed.
18. Kiselev, V.D., Bolotov, A.V., Satonin, A.P., Shakirova, I.I., Kashaeva, E.A., and Konovalov, A.I., *J. Phys. Chem. B*, 2008, vol. 112, p. 6674.