Why can the Diels–Alder reaction of 9,10-diphenylanthracene with 4-phenyl-1,2,4-triazoline-3,5-dione pass by an abnormal way?

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9,10-Diphenylanthracene reacts with dienophile by 1,4-positions rather than 9,10-ones of trivial anthracenes, that has been justified with estimation of kinetic and thermodynamic parameters of the process.

4-Phenyl-1,2,4-triazoline-3,5-dione exhibits the highest reactivity in the Diels–Alder reaction with dienes, as compared with other dienophiles.1–3 For fifteen dienes, the rate constants and enthalpies of reactions with 4-phenyl-1,2,4-triazoline-3,5-dione, tetracyanoethylene and maleic anhydride were compared.4 From these data, it follows that the activity of 4-phenyl-1,2,4-triazoline-3,5-dione is higher than that of maleic anhydride by five or six orders of magnitude.

We studied the reaction rate of a very inactive diene, 9,10-diphenylanthracene 1a, with the most active dienophile, 4-phenyl-1,2,4-triazoline-3,5-dione 2, in a toluene solution at 5–45 °C and 1–2126 bar (Scheme 1). The enthalpy, entropy, activation volume, reaction volume and the structure of adduct 3a were determined.

The overlapping of the 1,8-hydrogen atoms of the anthracene moiety and 2,6-hydrogen atoms of the phenyl group in 9-phenylanthracene 1d leads to a dihedral angle of about 60° between these fragments.5 For 9,10-diphenylanthracene 1a, the almost orthogonal planes of phenyl groups to the anthracene plane were observed.6 The rate constant of the Diels–Alder reaction with the C=C bonds can be estimated7 from the equation

\[
\log k_2 = -28.81 + 316.3/(IP - EA) - 0.699R_{C(1)-C(4)}/(IP - EA) - 0.054AA, \Delta H, r = 0.972
\]

(1)

Here the value of \(k_2\) is in \(dm^3\ mol^{-1} \ s^{-1}\), the ionization potential (IP) and electron affinity (EA) are in eV, \(R_{C(1)-C(4)}\) is in pm, the enthalpy of reaction, \(\Delta H\), is in kJ mol\(^{-1}\), and \(r\) is the correlation coefficient.

The rate of reaction of 9-phenylanthracene 1d with maleic anhydride in toluene at 25 °C (3.6×10\(^{-7}\) dm\(^3\) mol\(^{-1}\) s\(^{-1}\)) is 2.5 orders of magnitude lower than that predicted from equation (1).7 From these data, it follows that the difference in the heats of hydrogenation of 9,10- and 1,4-anthracene atoms is –65±8 kJ mol\(^{-1}\), the investment of energy required for the flattening of diene 1a is more than 20 kJ mol\(^{-1}\), the direction of cycloaddition can be changed to less active but sterically accessible 1,4-atoms of anthracene.

The \(^1\)H NMR spectrum (Figure 1) of adduct 3a (400 MHz, CDCl\(_3\), 25 °C, \(\delta:\) 5.92 [t, \(C(1)H, C(12)H\)], 6.87 [t, \(C(18)H, C(19)H\)], atom numbering as in Figure 2) is very different from the spectra of adducts 3b–h. The presence of two protons at the saturated carbon atoms C(1) and C(12) and the ethylene fragment \(=C(18)H, =C(19)H\), atom numbering as in Figure 2) is consistent with the formation of 1,4-adduct 3a, which is not observed in the spectrum of adduct 3f (Figure 1). Additionally, X-ray analysis (Figure 2) confirms the formation of the exo-configuration of adduct 3a – 3,10,15-triphenyl-13,15,17-triazapentacyclo[10.5.2.02,11.04.9.013,17]nonadeca-2,4(9),5,7,10,18-hexaene-14,16-dione. The formation of endo-isomer may inhibit 9,10-phenyl substituents.

Note that the \(^1\)H NMR spectrum of 3a is identical to that reported elsewhere,12 but the possible formation of such adduct was not considered.
We studied the rate of the reaction 1a + 2 → 3a in toluene at atmospheric pressure in a temperature range of 15–50°C and in a pressure range of 1–2126 bar at 25°C. The dependence of ln k2 on P is described by the relation

\[
\ln \left( \frac{k_2}{k_{2,\text{corr}}} \right) = -0.004 + 7.84 \times 10^{-4} P - 9.10 \times 10^{-6} P^2.
\]

The experimental activation volume \( \Delta V_{\text{act}} \) is \(-19.4 \pm 1.2 \text{ cm}^3 \text{ mol}^{-1}\). Taking into account the change of the concentration of reactants under pressure, \((n-1) \beta P RT\), the corrected value of \( \Delta V_{\text{corr}} \) is \(-17.2 \pm 1.2 \text{ cm}^3 \text{ mol}^{-1}\).

Table 1 compares the values of enthalpy, entropy, activation volume and the volume of reaction for 9,10-reaction centre with the parameters for reactions on 9,10-reaction centre of substituted anthracenes with maleic anhydride (MA). Note that the absolute values of the entropy of activation and the reaction volume on the 1,4-atoms of anthracene are much smaller than those for the reactions on 9,10-atoms.

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References


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\[*\] In kinetic measurements, the concentration of diene 1a, 60–100 mmol dm\(^{-3}\), was much higher than that of dienophile 2, 4–8 mmol dm\(^{-3}\). The reaction rate was followed by the change of the absorption of 2 at 540 nm (ε 245 mol dm\(^{-3}\) cm\(^{-1}\) in toluene), where 1a and 3a are transparent.

Table 1 Enthalpy (\(\Delta H^*\)), entropy (\(\Delta S^*\)), activation volume (\(\Delta V_{\text{act}}\)) and the volume of reactions (\(\Delta V\)) in toluene at 25°C.

<table>
<thead>
<tr>
<th>Reaction (reaction centre)</th>
<th>(\Delta H^*/\text{kJ mol}^{-1})</th>
<th>(-\Delta S^*/\text{J mol}^{-1} \text{K}^{-1})</th>
<th>(\Delta V_{\text{act}}/\text{cm}^3 \text{ mol}^{-1})</th>
<th>(\Delta V/\text{cm}^3 \text{ mol}^{-1})</th>
<th>(\Delta V^*/\text{cm}^3 \text{ mol}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>9,10-Diphenylnaphthalene + 2 (1,4)</td>
<td>58.8</td>
<td>97</td>
<td>-17.2</td>
<td>-15.5</td>
<td>1.11</td>
</tr>
<tr>
<td>9,10-Dimethylanthracene + MA (9,10)</td>
<td>40.2</td>
<td>150</td>
<td>-21.7</td>
<td>-18.9</td>
<td>1.15</td>
</tr>
<tr>
<td>9-Phenylanthracene + MA (9,10)</td>
<td>68.0</td>
<td>140</td>
<td>-23.2</td>
<td>-27.3</td>
<td>0.85</td>
</tr>
<tr>
<td>2-Methyl-1,3-butadiene + MA</td>
<td>59.0</td>
<td>149</td>
<td>-34.8</td>
<td>-34.5</td>
<td>1.0</td>
</tr>
</tbody>
</table>

\(\text{This work.}^{b}\) From ref. 4. \(\text{At } 60^\circ\text{C.}^{\text{c}}\) From ref. 13. \(\text{At } 35^\circ\text{C.}^{\text{d}}\)