1. The thermal rxn should be conjugatory to lead to bond formation. The W-H method states to examine the HOMO of the acyclic system:

\[ \psi_4 \quad \text{(HOMO)} \quad \Rightarrow \quad \Delta \quad \text{allowed} \]

The stereochemistry of the product for the thermal ring closure will be trans:

Under photochemical conditions the HOMO is the \( \psi_5 \) so now disrotatory motion is needed. And the stereochemistry of the product will be cis.
The thermal [1, 7] hydrogen shift can be analyzed in terms of a transition structure involving an H atom and a heptaatrienyl radical. The HOMO for the heptaatrienyl radical is $\Psi_4$, which has three nodes. This necessitates antarafacial movement of the H:

The thermal [1, 9] hydrogen shift analysis is similar, but here the nonotetraatrienyl radical is needed, and the HOMO is $\Psi_5$ (4 nodes). This will make the termini have an opposite phase relationship to that above and hence suprafacial motion will be required.

This problem is asking that MO correlation diagrams be constructed. Each of these is similar to the MO correlation diagram shown in Figure 1.62 for the Diels-Alder rxn. The key here is the four sigma-type orbitals that are used and that must be analyzed in terms of a transition structure with a plane of symmetry (only element obeyed throughout for a supra-supra interaction). The diagram for the $[\Pi_{2s} + \Pi_{6s}]$ is as follows:
The filled MO's do not correlate, thus forbidden thermally by the principles of orbital symmetry.
The MO correlation diagram for the \( \text{Br}_4S^6 \) is analogous (again, plane of symmetry is obeyed):

\[ \begin{array}{c}
\text{E} \\
\gamma_4 \\
\gamma_4 \\
\gamma_3 \\
\gamma_3 \\
\gamma_2 \\
\gamma_2 \\
\gamma_1 \\
\gamma_1 \\
\end{array} \quad \rightarrow \quad \begin{array}{c}
\text{A} \\
\text{A} \\
\text{S} \\
\text{S} \\
\text{S} \\
\text{S} \\
\text{S} \\
\text{S} \\
\end{array} \quad \begin{array}{c}
A = \sigma^* \\
S = \sigma^* \\
A = \pi^* \\
A = \pi^* \\
S = \pi_1 \\
S = \pi_1 \\
A = \sigma^* \\
S = \sigma \\
\end{array} \]

Like the previous example, the filled MO's do not correlate hence the \text{Br}_4S^6 is forbidden thermally by the principles of orbital symmetry.

4. (a) The antarctic-antarctic T.S. is shown below:
The problem is analyzed by using the \( \psi_2 \) of one allyl fragment (drawn at the back of the T.S.) and \( \psi_3 \) of the other fragment (drawn here at the front of the T.S):

\[
\begin{align*}
\begin{array}{c}
\text{anti-bonding} \\
\text{interaction}
\end{array}
\end{align*}
\]

(b) The diagram is very similar to Fig 11.62 (p.753), except an \( \pi^* \) is promoted from \( \psi_2 \) to \( \psi_3 \) in the diene. A tricky part of a problem like this is knowing the relative energies of the orbitals on each side of the diagram.
Since $\psi_3$ correlates with $\sigma^*$, this is a higher energy excited state for the Diels-Alder adduct that is desired when under hv conditions. It means an electronic state of the product where an $e^-$ is in a $\sigma^*$ orbital instead of a lower energy $\pi^*$ orbital. If a state correlation diagram was constructed, the ES-1 on each side would correlate with the ES-2 on the other with all having the same state symmetry. This would have the undesirable "avoided crossing.

The answer from the author is very thorough so it is reproduced here:

For the cation, only $\sigma$ is populated. In the disrotatory reaction a plane of symmetry is maintained, so a symmetric $\sigma$ orbital correlates with $\psi_1$ of the allyl cation and the reaction is allowed. For the conrotatory pathway, a $C_2$ rotation axis is maintained. Now the $\sigma$ orbital is symmetric, but $\psi_1$ of allyl is antisymmetric. Therefore the $\sigma$ orbital correlates with $\psi_2$ of allyl, so the reaction is thermally forbidden.

\[ \begin{array}{c}
\begin{array}{c}
\text{R} \\
\text{R}
\end{array}
\end{array} \bigg]^{+} & \text{dis} & \begin{array}{c}
\begin{array}{c}
\text{R} \\
\text{R} \\
\text{R}
\end{array}
\end{array} \bigg]^{+}
\end{array} \]

\[ \begin{array}{c}
\begin{array}{c}
\text{A} \\
\text{A}
\end{array}
\end{array} \bigg]^{+} \bigg]^{+}
\end{array} \]

\[ \begin{array}{c}
\begin{array}{c}
\text{S}
\end{array}
\end{array} \bigg]^{+} \bigg]^{+}
\end{array} \]

\[ \begin{array}{c}
\begin{array}{c}
\text{S}
\end{array}
\end{array} \bigg]^{+} \bigg]^{+}
\end{array} \]

\[ \begin{array}{c}
\begin{array}{c}
\text{S}
\end{array}
\end{array} \bigg]^{+} \bigg]^{+}
\end{array} \]

\[ \begin{array}{c}
\begin{array}{c}
\text{S}
\end{array}
\end{array} \bigg]^{+} \bigg]^{+}
\end{array} \]

\[ \begin{array}{c}
\begin{array}{c}
\text{S}
\end{array}
\end{array} \bigg]^{+} \bigg]^{+}
\end{array} \]

Symmetry with respect to $\sigma$ Symmetry with respect to $C_2$
In the anion, both $\sigma$ and $\rho$ of the cyclopropyl moiety are populated. Orbital symmetries are designated as above. Now the cyclopropyl anion correlates with the allyl anion by the conrotatory pathway.

\[
\begin{align*}
\begin{bmatrix}
\text{R} & \sigma & \text{R} \\
\end{bmatrix}^- & \xrightarrow{\text{dis}}
\begin{bmatrix}
\text{R} & \rho & \text{R} \\
\end{bmatrix}^-
\xrightarrow{\text{con}}
\begin{bmatrix}
\text{R} & \sigma & \text{R} \\
\end{bmatrix}^-
\end{align*}
\]

The state correlation diagrams are constructed from the molecular orbital correlation diagrams. For the cation, it is evident that the ground state (GS) of the cyclopropyl cation correlates with the ground state of the allyl cation for the disrotatory opening. (The state symmetry designations are the products of the MO symmetry designations for the molecular orbitals populated in each state.) However, the cyclopropyl cation correlates with the allyl cation for a photochemical reaction, because ES-1 of cyclopropyl correlates with ES-1 of allyl for that process.
The ground state of the cyclopropyl anion correlates with the ground state of the allyl anion by the conrotatory pathway. However, the first excited state of the cyclopropyl anion correlates with the first excited state of the allyl anion by the disrotatory pathway.
(a) If a cumulatively motion is used, the trans product is formed:

This is a [ππ] process so 0 (4n+2)π units and 1 (4n)π unit so the total is 1, which is odd, so allowed thermally. The transition structure should be Möbius aromatic:

(b) If a disrotatory motion is employed, the cis product is formed:

This is a [ππ] process so 1 (4n+2)π units and 2 (4n)π units so the total is odd, so allowed thermally. The transition structure is Hückel aromatic:
(c) If a super-super cycladdition is performed, this cis product shown below forms:

This is a $\{\pi(6S + \pi(5))\}$ process. The number of $(4n+2)$ units is one and the number of $(4n)$ units is zero, so the total is odd so allowed thermally.

The transition structure is Hückel aromatic.

Zero nodal zones

$\Rightarrow$ Hückel

has $10e^-$ (total)

thus an aromatic TS.