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Ab Initio Study of the Influence of Resonance Stabilization on the Intramolecular Ring Closure Reactions of Hydrocarbon Radicals

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Supporting Information

Figure S1 Comparison of activation energies at 298K for H-atom shift reactions in schemes 1-6 for different transition state ring sizes to those of analogous alkenyl radical reactions.

Figure S2 Transition state structures for the various ring closure reactions in schemes 1-3 for the endo-pathway, select reactions in schemes 4-6, and the reactions of alkenyl radicals. The reaction number is given in bold. Bond lengths are given in angstroms and bond angles in degrees.

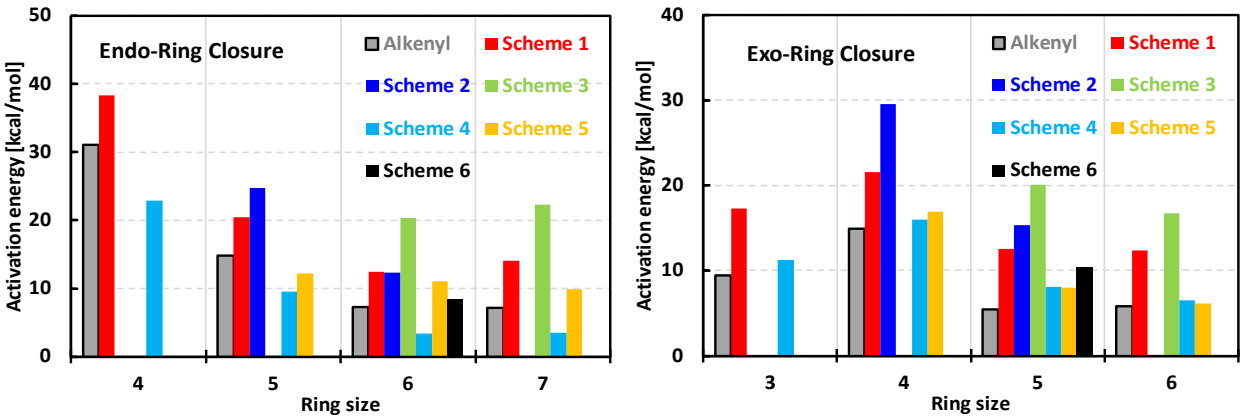
Figure S3 Transition state structures for the various ring closure reactions in schemes 1-3 for the exo-pathway, select reactions in schemes 4-6, and the reactions of alkenyl radicals. The reaction number is given in bold. Bond lengths are given in angstroms and bond angles in degrees.

Table S1 Calculated Rate Parameters, Rate Constants, and Heats of Reaction for the Endo- and Exo-Cycloaddition Reactions of Scheme 1.

Table S2 Calculated Rate Parameters, Rate Constants, and Heats of Reaction for the Endo- and Exo-Cycloaddition Reactions of Scheme 2.

Table S3 Calculated Rate Parameters, Rate Constants, and Heats of Reaction for the Endo- and Exo-Cycloaddition Reactions of Scheme 3.

Table S4 The energies for species and transition state in the C_6H_9 potential energy surface (PES) from estimation rate rules and CBS-QB3 calculations.



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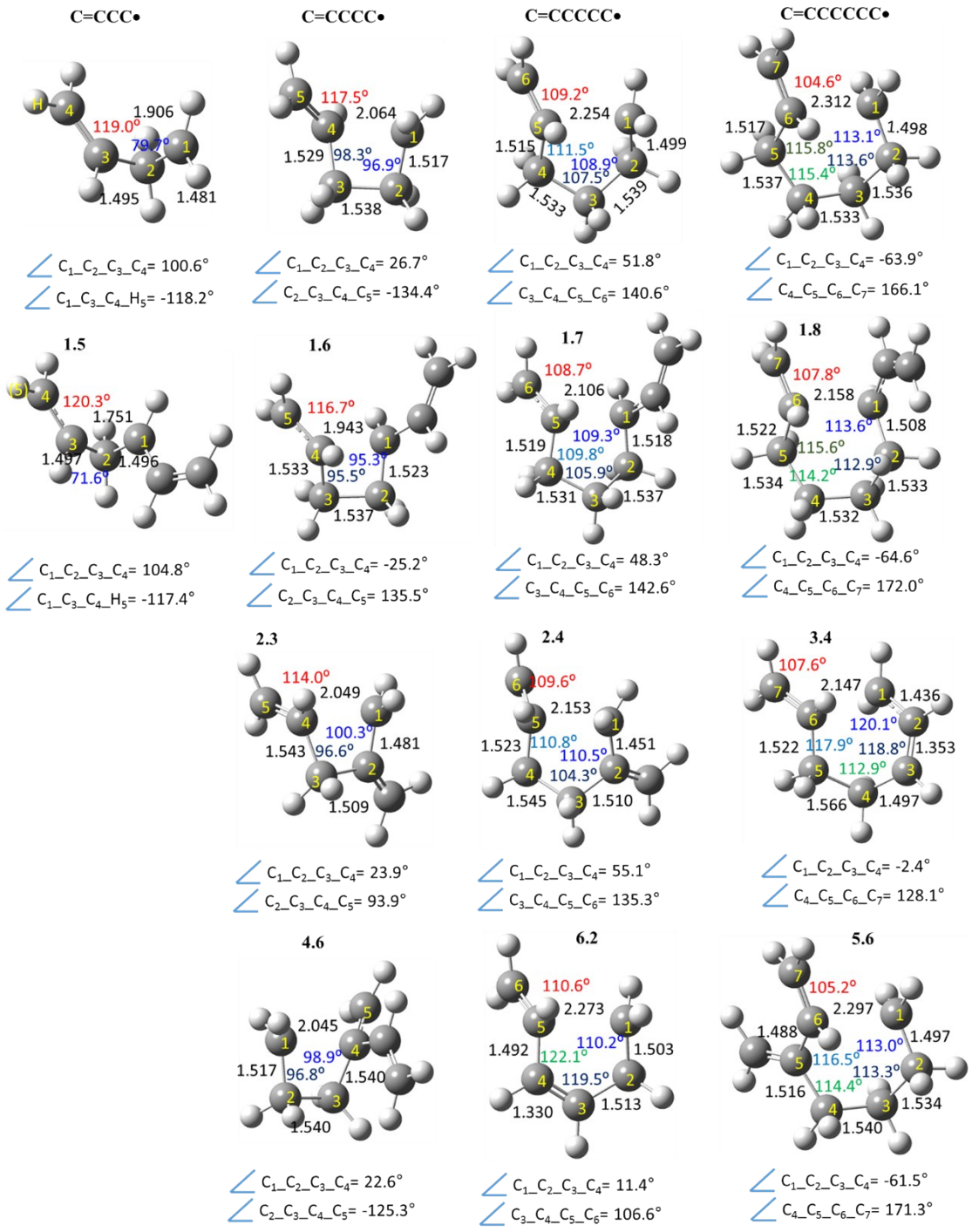

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Table S1 Calculated Rate Parameters, Rate Constants, and Heats of Reaction for the Endo- and Exo-Cycloaddition Reactions of Scheme 1.

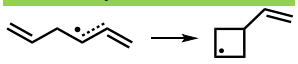
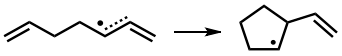
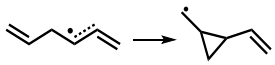
		300-2500 K			298 K			500-1500 K		
#	Reactants	Modified Arrhenius Parameters			Arrhenius Parameters		E_{strain}	Arrhenius Parameters		$\Delta_R H^{298}$
		A	*n*	E	A'	Ea		A''	E_a	[kcal/mol]
	1,4-Endo-Cycloaddition									
1	C=CCC·(C)C=C	2.31E+07	1.36	38.1	2.03E+11	38.9	27.2	8.96E+11	40.4	19.5
	1,5-Endo-Cycloaddition									
2	CC=CCCC·C=C	6.32E+06	1.14	18.5	1.33E+10	19.1	7.4	4.67E+10	20.4	-3.9
	1,4-Exo-Cyclization									
3	C=CCC(C)•C=C → trans product	1.96E+08	1.16	18.2	4.74E+11	18.9	6.3	1.70E+12	20.2	17.6
4	C=CCC(C)•C=C → cis product	5.52E+08	1.01	16.9	4.88E+11	17.5	4.9	1.48E+12	18.6	16.9
5	C=CCC•C=C → cis product	9.82E+08	1.00	18.1	8.01E+11	18.7	6.1	2.40E+12	19.8	15.8

Table S2 Calculated Rate Parameters, Rate Constants, and Heats of Reaction for the Endo- and Exo-Cycloaddition Reactions of Scheme 2.

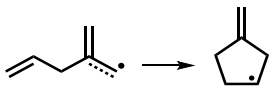
		300-2500 K			298 K			500-1500K		
#	Reactants	Modified Arrhenius Parameters			Arrhenius Parameters		E_{strain}	Arrhenius Parameters		$\Delta_R H^{298}$
		A	*n*	E	A'	E_a		A''	E_a'	[kcal/mol]
	1,5-Endo-Cycloaddition									
1	C=C(C•)CC(C)=C	6.00E+09	0.46	24.3	1.31E+11	24.5	13.1	2.16E+11	25.0	-4.5
2	C=C(C•)CC=CC	4.59E+08	0.80	22.7	9.94E+10	23.2	11.8	2.40E+11	24.1	-5.0

Table S3 Calculated Rate Parameters, Rate Constants, and Heats of Reaction for the Endo- and Exo-Cycloaddition Reactions of Scheme 3.

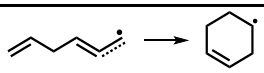
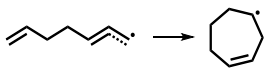
		300-2500 K			298 K			500-1500 K		
#	Reactants	Modified Arrhenius Parameters			Arrhenius Parameters		E_{strain}	Arrhenius Parameters		$\Delta_R H^{298}$
		A	*n*	E	A'	E_a		A''	E_a'	[kcal/mol]
	1,6-Endo-Cycloaddition									
1	CC=CCC=CC•	1.24E+07	1.14	19.4	2.63E+10	20.1	8.7	9.23E+10	21.4	-7.0
2	CC=CCC=CC•C	3.16E+08	0.70	19.3	3.43E+10	19.7	8.3	7.39E+10	20.4	-5.8
3	C=CCC=CC•C	1.29E+08	0.88	20.7	4.62E+10	21.2	9.8	1.21E+11	22.1	-6.7
4	CC=CCC(C)=CC•	2.55E+08	0.76	20.9	4.03E+10	21.3	9.9	9.23E+10	22.1	-7.1
5	C=C(C)CC=CC•	4.01E+08	0.72	19.2	5.12E+10	19.6	8.2	1.13E+11	20.4	-8.1
6	C=CCC=C(C)C•	2.37E+08	0.81	19.2	5.45E+10	19.7	8.3	1.33E+11	20.6	-9.1
	1,7-Endo-Cycloaddition									
7	CC=CCCC=CC•	2.24E+07	0.81	22.0	5.08E+09	22.4	11.0	1.38E+10	23.1	-2.8
8	C=CC(C)CC=CC•	5.14E+07	0.73	21.6	6.83E+09	22.0	10.6	1.52E+10	22.8	-3.8

Table S4 The energies for species and transition state in the C_6H_9 potential energy surface from estimation rate rules and CBS-QB3 calculations

species	$\Delta_f H^{298}$ (kcal/mol)			E (forward / reverse) (kcal/mol)		
	Calculated	Est.	Est. - Calculated	Calculated	Est.	Est. - Calculated
Stable species						
1	55.5	53.7	-1.8			
2	42.0	38.2	-3.8			
3	48.3	44.9	-3.4			
4	53.5	49.7	-3.8			
5	35.7	32.7	-3.0			
6	74.7	69.6	-5.1			
7	71.2	72.9	1.7			
8	72.3	67.4	-4.9			
9	74.9	69.9	-5.0			
10	75.1	72.7	-2.4			
Bimolecular products						
I	69.8	67.3	-2.5			
II	78.1	76.2	-1.9			
III	80.4	77.5	-2.9			
IV	80.5	78.2	-2.3			
V	80.9	77.6	-3.3			
VI	84.9	82.4	-2.5			
VII	94.5	91.7	-2.8			
VIII	100.0	97.7	-2.3			
IX	104.8	102.9	-1.9			
X	106.9	97.5	-9.4			
XI	112.1	109.2	-2.9			
XII	111.1	108.1	-3.0			
XIII	117.7	118.6	0.9			
Transition states						
1-2	86.7	83.0	-3.7	31.2 / 44.7	29.3 / 44.8	-1.9 / 0.1
1-3	75.9	74.1	-1.8	20.4 / 27.6	20.4 / 29.2	0.0 / 1.6
1-4	75.4	73.8	-1.6	21.9 / 21.9	20.1 / 24.1	-1.8 / 2.2
1-6	93.8	92.0	-1.8	38.3 / 19.1	38.3 / 22.4	0.0 / 3.3
1-7	72.8	73.0	0.2	17.3 / 1.6	19.3 / 0.1	2.0 / -1.5
1-VIII	102.3	100.2	-2.1	46.8 / 2.3	46.5 / 2.5	-0.3 / 0.2
1-VII	95.5	93.2	-2.3	40.0 / 1.0	39.5 / 1.5	-0.5 / 0.5
2-VII	94.5	91.7	-2.8	52.5 / 0.0	53.5 / 0.0	1.0 / 0.0
2-5	78.0	74.0	-4.0	36.0 / 42.3	35.8 / 41.3	-0.2 / -1.0
2-10	83.8	80.8	-3.0	41.8 / 8.7	42.6 / 8.1	0.8 / -0.6
3-IV	81.6	79.7	-1.9	33.3 / 1.1	34.8 / 1.5	1.5 / 0.4
3-III	81.4	79.0	-2.4	33.1 / 1.0	34.1 / 1.5	1.0 / 0.5
4-5	84.5	79.7	-4.8	31.0 / 48.8	30.0 / 47.0	-1.0 / -1.8
4-VI	87.5	85.4	-2.1	34.0 / 2.6	35.7 / 3.0	1.7 / 0.4
5-I	73.2	69.8	-3.4	37.5 / 3.4	37.1 / 2.5	-0.4 / -0.9
5-II	78.1	74.9	-3.2	42.4 / 0.0	42.2 / -1.3	-0.2 / -1.3
5-V	80.9	75.2	-5.7	45.2 / 0.0	42.5 / -2.4	-2.7 / -2.4
6-XII	112	108.6	-3.4	37.3 / 0.9	39.0 / 0.5	1.7 / -0.4
7-8	79.7	80.9	1.2	8.5 / 7.4	8.0 / 13.5	-0.5 / 6.1
7-XIII	120.8	120.1	-0.7	49.6 / 3.1	47.2 / 1.5	-2.4 / -1.6
8-9	102.3	98.8	-3.5	30.0 / 27.4	31.4 / 28.9	1.4 / 1.5
8-VIII	106.5	104.2	-2.3	34.2 / 6.5	36.8 / 6.5	2.6 / 0.0
9-XI	113.4	111.7	-1.7	38.5 / 1.3	41.8 / 2.5	3.3 / 1.2
9-IX	107.3	104.4	-2.9	32.4 / 2.5	34.5 / 1.5	2.1 / -1.0
9-XII	111.7	109.6	-2.1	36.8 / 0.6	39.7 / 1.5	2.9 / 0.9
10-X	110.6	100.6	-10	35.5 / 3.7	27.9 / 3.1	-7.6 / -0.6