

Comparing Density Functional Theory with Experimental Results of



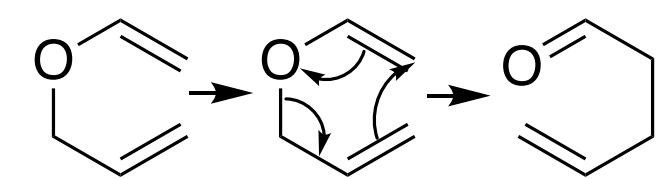
Claisen Rearrangements

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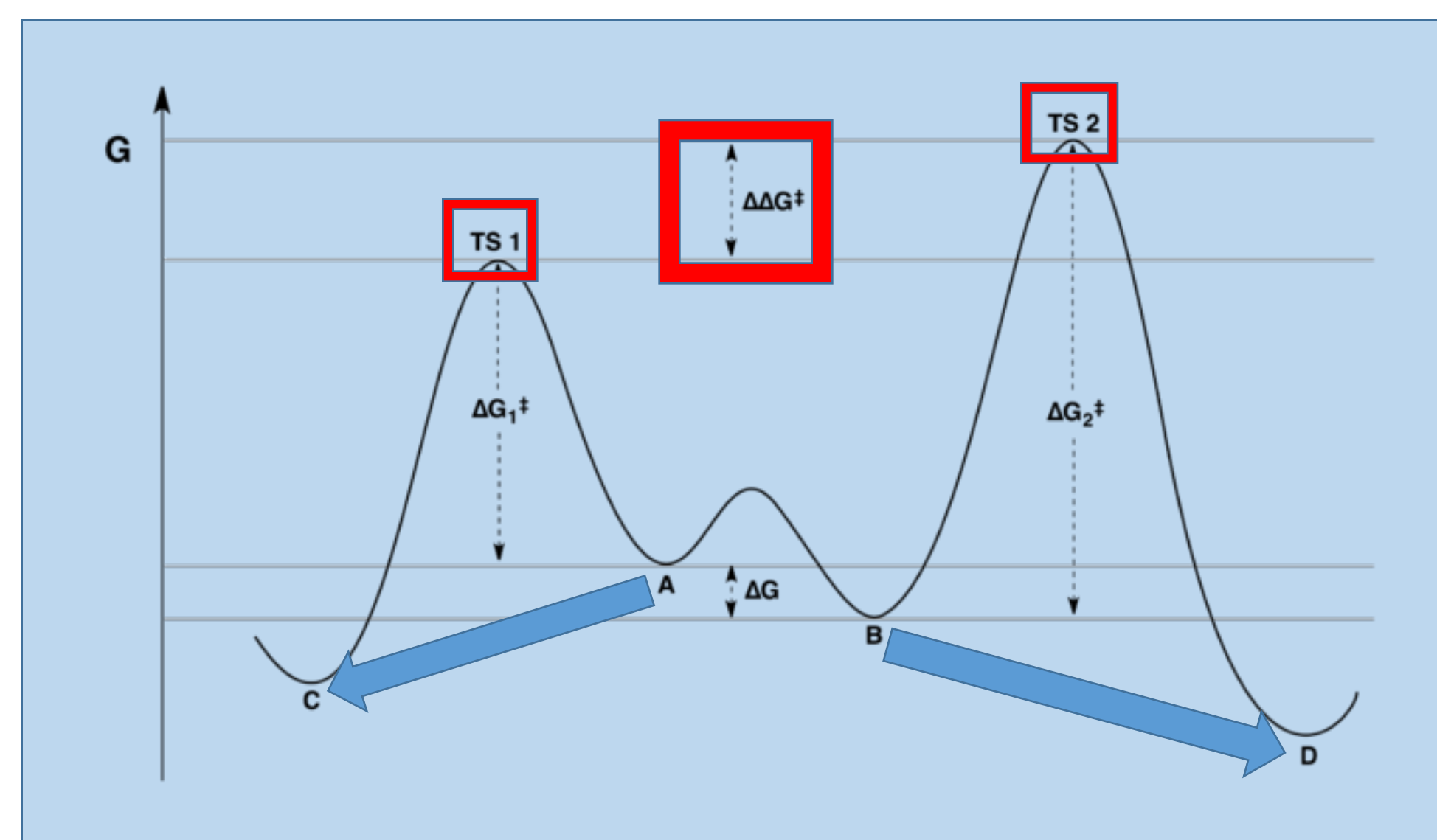
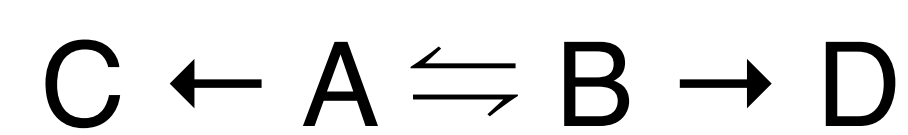


General Information About Claisen Rearrangements

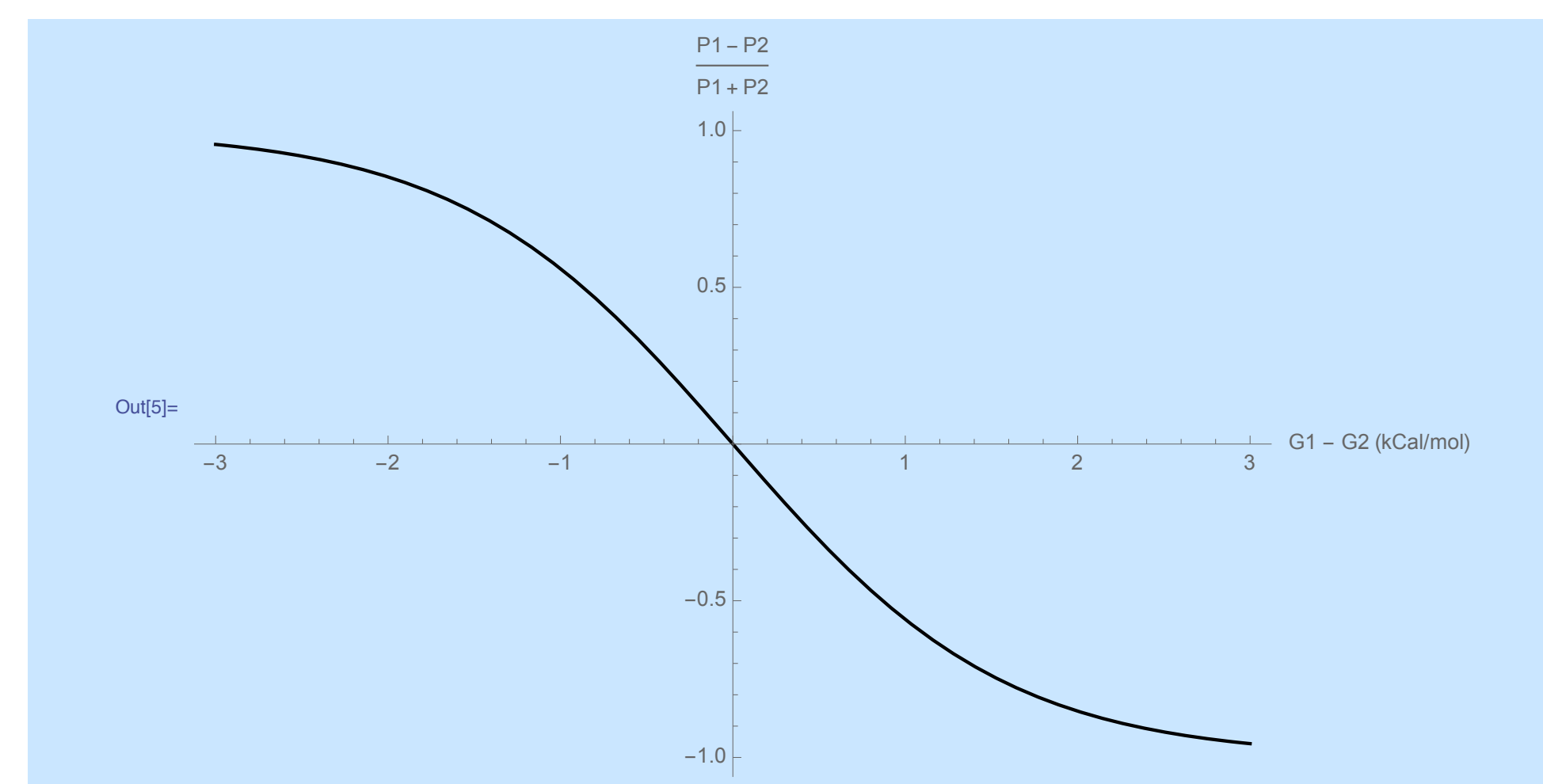
- The reaction is a pericyclic reaction.
- 398 K is the temperature at which the experiment was conducted.
- Very versatile and powerful reaction for synthesis.



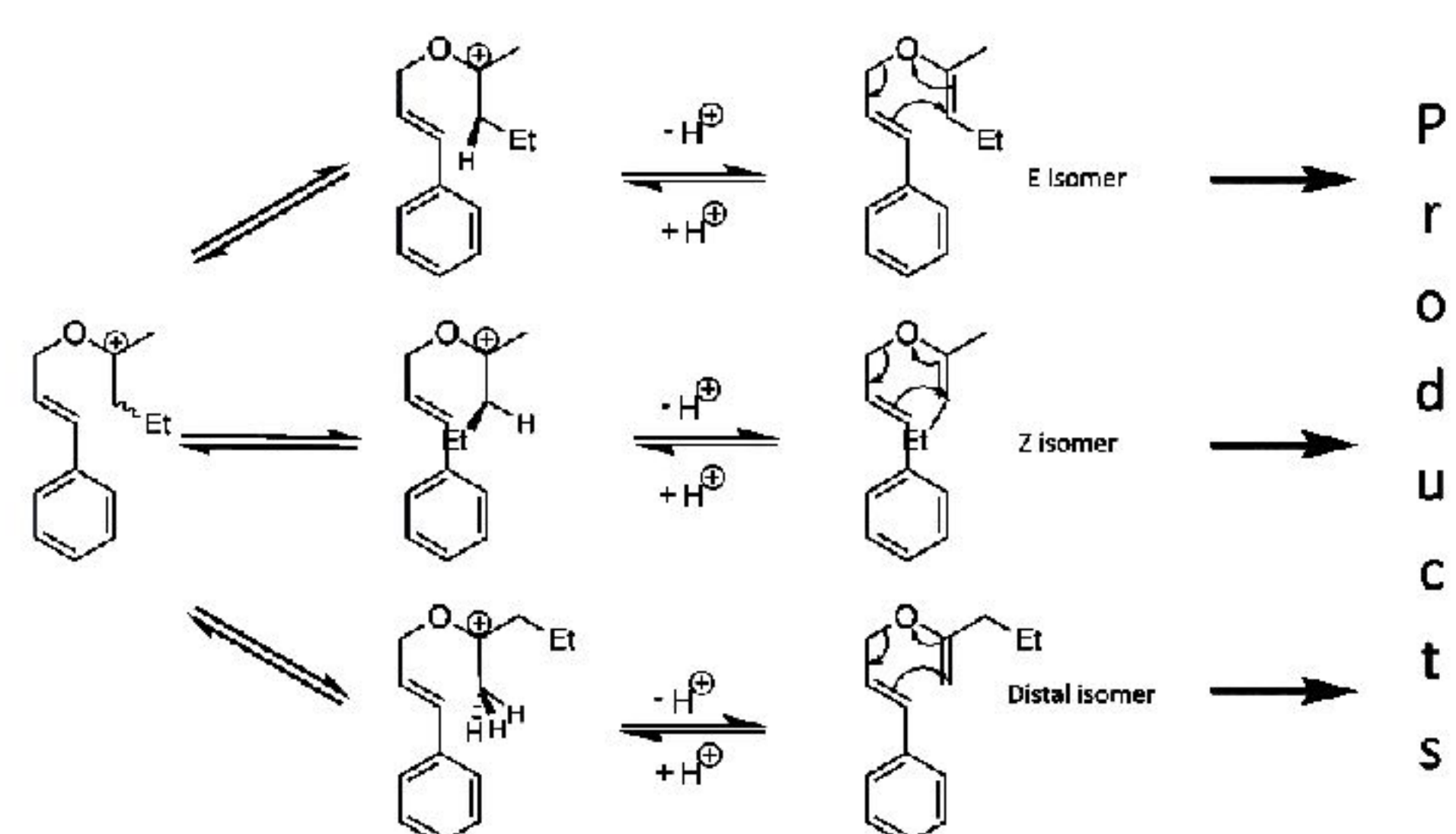
Curtin-Hammett Principle



$$[P_a]/[P_b] = \text{Exp}[-(G^\ddagger_a - G^\ddagger_b)/RT]$$



Transition States



Phenyl Substituent Results

Case 1

Isomer	B3LYP	B3LYP GD3BJ	Experiment
Syn	56%	60%	53.5%
Anti	41%	39%	44.8%
Distal	3%	0%	1.7%

Case 3

Isomer	B3LYP	B3LYP GD3BJ	Experiment
Proximal	100%	100%	69%
Distal	0%	0%	31%

Case 5

Isomer	B3LYP	B3LYP GD3BJ	Experiment
Syn	13%	23%	36.85%
Anti	12%	45%	30.15%
Distal	75%	32%	33%

Case 9

Isomer	B3LYP	B3LYP GD3BJ	Experiment
Syn	40%	43%	86%
Anti	56%	57%	86%
Distal	4%	1%	14%

Case 11

Isomer	B3LYP	B3LYP GD3BJ	Experiment
Syn	42%	47%	83%
Anti	56%	53%	83%
Distal	2%	0%	17%

Case 7

Isomer	B3LYP	B3LYP GD3BJ	Experiment
Syn	75%	76%	80%
Anti	25%	24%	20%

Case 13

Isomer	B3LYP	B3LYP GD3BJ	Experiment
Syn	87%	84%	86%
Anti	13%	16%	14%

Case 2

Isomer	B3LYP	B3LYP GD3BJ	Experiment
Syn	82%	96%	78.8%
Anti	14%	4%	17.4%
Distal	5%	0%	3.8%

Case 4

Isomer	B3LYP	B3LYP GD3BJ	Experiment
Syn	50%	52%	51%
Anti	47%	48%	42%
Distal	3%	1%	7%

Case 6

Isomer	B3LYP	B3LYP GD3BJ	Experiment
Syn	0%	5%	0%
Anti	0%	2%	0%
Distal	100%	93%	100%

Case 10

Isomer	B3LYP	B3LYP GD3BJ	Experiment
Syn	51%	44%	48%
Anti	47%	56%	48%
Distal	2%	0%	4%

Case 12

Isomer	B3LYP	B3LYP GD3BJ	Experiment
Syn	56%	76%	88%
Anti	40%	24%	88%
Distal	4%	0%	12%

Case 8

Isomer	B3LYP	B3LYP GD3BJ	Experiment
Syn	94%	95%	91%
Anti	6%	5%	9%

Case 14

Isomer	B3LYP	B3LYP GD3BJ	Experiment
Syn	96%	98%	93%
Anti	4%	2%	7%

n-Propyl Substituent Results

Case 15

Isomer	B3LYP	Experiment
Syn	28%	82%
Anti	67%	82%
Distal	5%	18%

Case 17

Isomer	B3LYP	Experiment
Syn	39%	80%
Anti	56%	80%
Distal	5%	20%

Case 19

Isomer	B3LYP	Experiment
Syn	55%	58%
Anti	42%	58%
Distal	3%	42%

Case 16

Isomer	B3LYP	Experiment
Syn	32%	40.47%
Anti	60%	30.53%
Distal	8%	29%

Case 18

Isomer	B3LYP	Experiment
Syn	38%	58%
Anti	57%	58%
Distal	5%	42%

Case 20

Isomer	B3LYP	Experiment
Syn	60%	62%
Anti	36%	62%
Distal	5%	38%

Results Summary

- Remarkably good agreement between theory and experiment in many of the phenyl substituent results.
- B3LYP did not agree with experiment for cases 3 & 5.
- Not as good agreement between theory and experiment in the n-propyl substituent results.

Computational Details

- All stationary points were verified by calculating second derivatives at the stationary points. In particular, all transition states had exactly one imaginary frequency. Transition states were connected to particular reactants and products via Intrinsic Reaction Coordinate calculations.

Future Work

- Use another method, RPA, on the phenyl substituent cases.
- Further explore the cases that did not agree well.

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