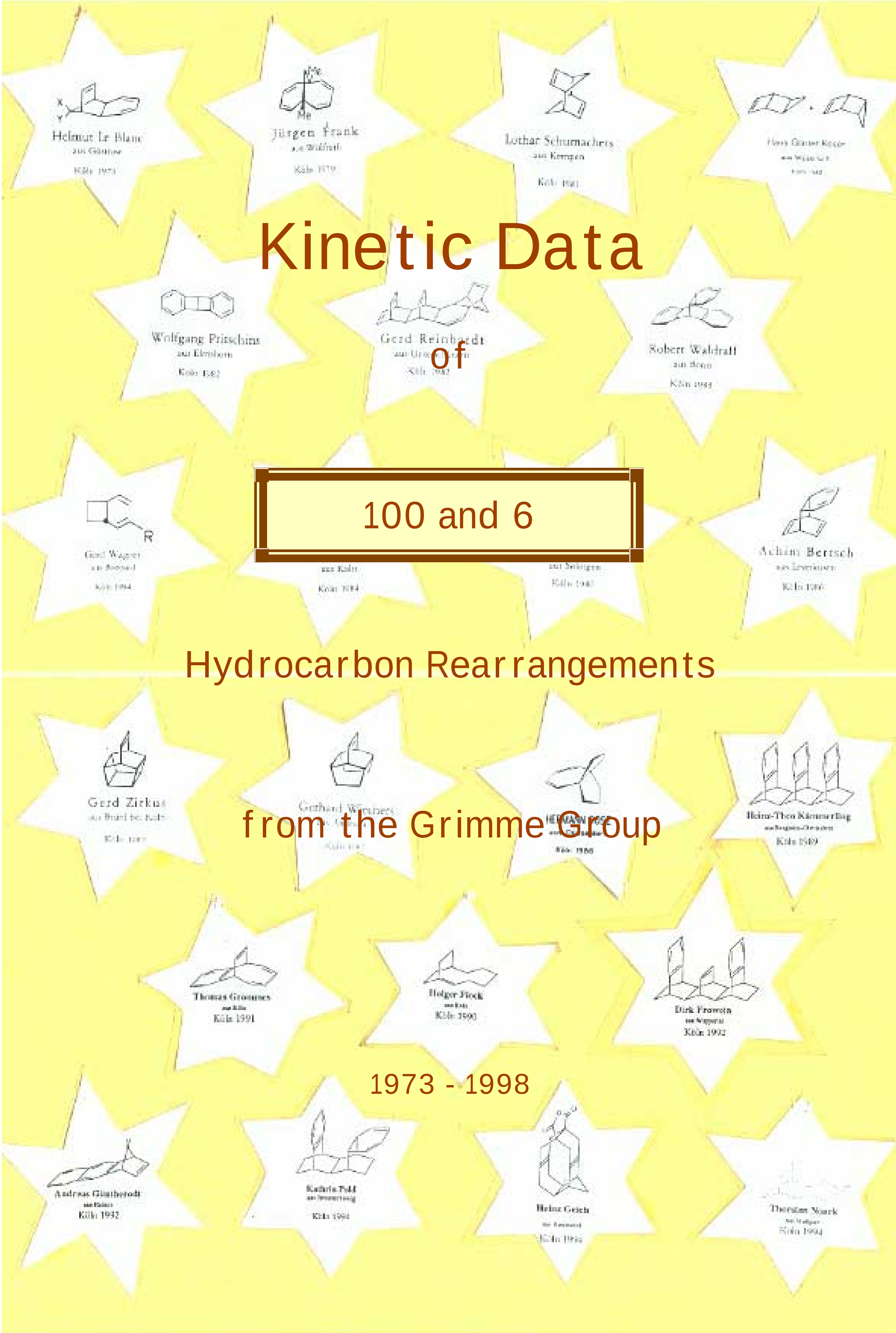

Kinetic Data

of

100 and 6

Hydrocarbon Rearrangements

from the Grimme Group

1973 - 1998

Foreword

If chemistry is defined as the making and breaking of bonds, molecular rearrangements represent its archetype. Without the interaction of reagents or solvent, only by the influx of energy, bonds cleave and form in either a concerted or stepwise manner. Theory has become ever more successful in the understanding of the influence of structure, orientation and heat flow in these reactions. The least predictable parameter remains their kinetics but with a growing accumulation of experimental data theory may become successful also in this field.

In the course of a quarter century I was happy to teach the charm of this purest form of chemistry to many students, several of whom decided to do their dissertation in my group. These coworkers have created in their theses an abundance of synthetic and kinetic work of which only about one third has been published. It is the aim of this collection to make this lode available to the interested chemical community.

The kinetic data are listed here according to reaction types, which are classified in the usual terms of concerted reactions. This in no way implies that all are proven to occur via synchronous bond reorganizations. In a time when the extend of concert is being actively discussed this question is difficult to answer. Where possible, the reactions are further classified as permutations of a paradigm, e. g. (4 + 2)-cycloreversions of norbornenes, bicyclo[2.2.2]octenes or bicyclo[2.2.2]octadienes. Combined with the calculated heat of reaction the kinetic data of these sets of permutations might be used in a mechanistic analysis along the lines of the Broenstedt catalysis law.

Full details of the original kinetic data together with the synthesis and the spectral properties of the compounds studied here are documented in the dissertations cited. These may be obtained by interlibrary loan from the Universitäts- und Stadtbibliothek , Universitätsstraße 33, D-50931 Koeln, FAX +49 (0)221 470 5166; http:// www.ub.uni-koeln.de

Cologne, January 6, 2001 Wolfram Grimme

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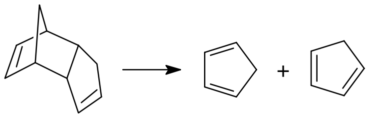
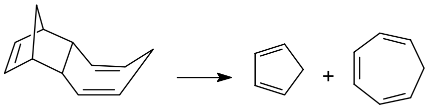
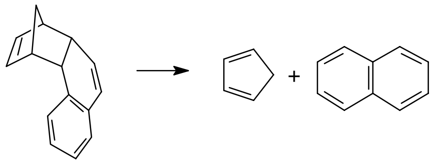
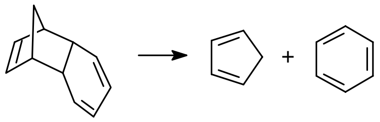
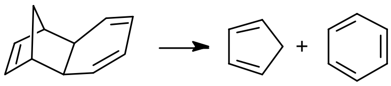
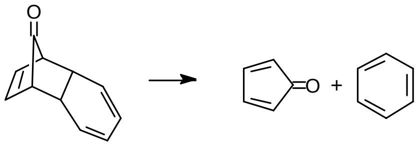
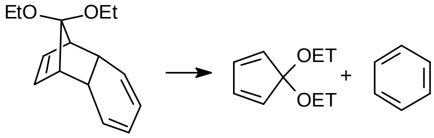
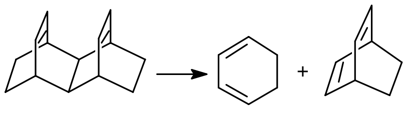
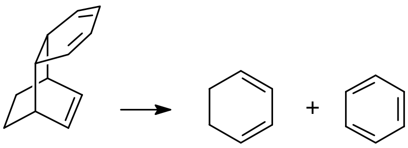
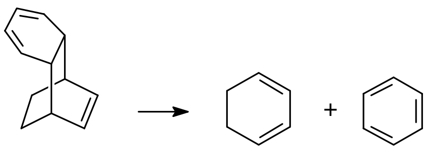
	15
	16
	17
	18
	19
	20
	21
	22
	23
	24

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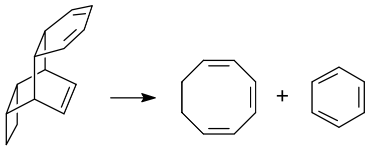
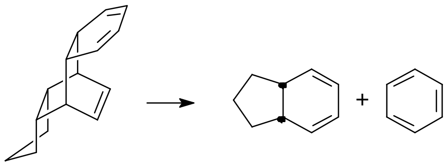
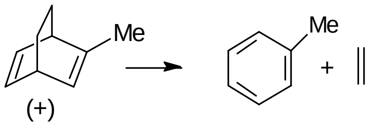
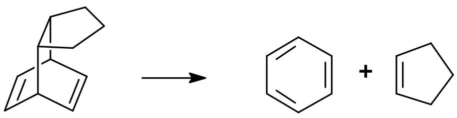
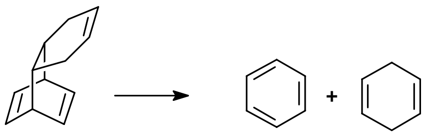
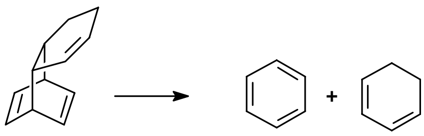
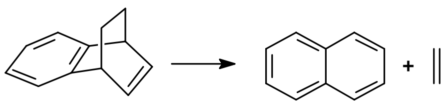
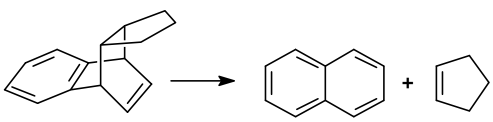
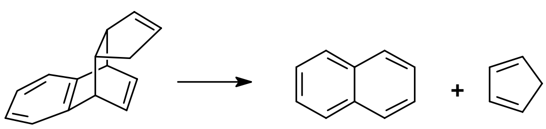
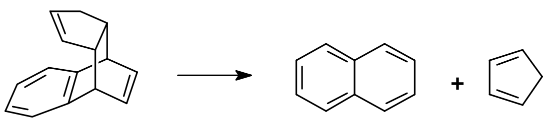
	25
	26
	27
	28
	29
	30
	31
	32
	33
	34

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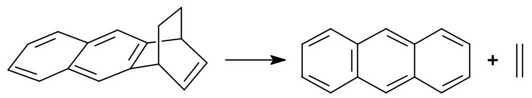
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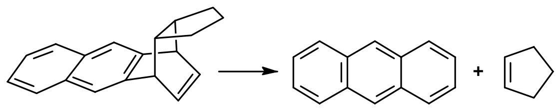
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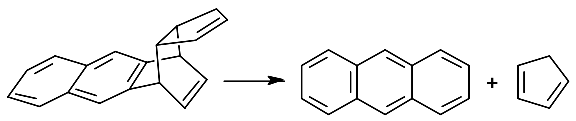
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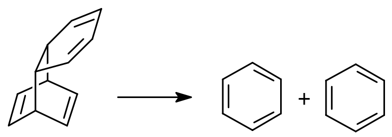
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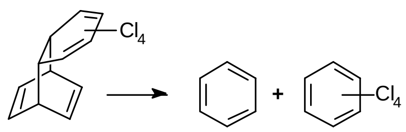

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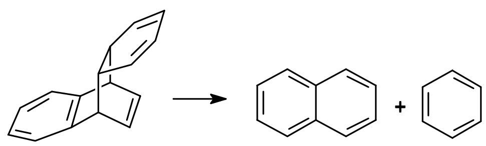
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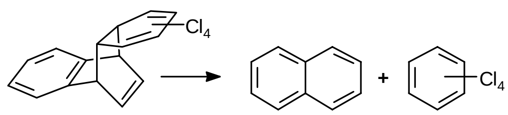

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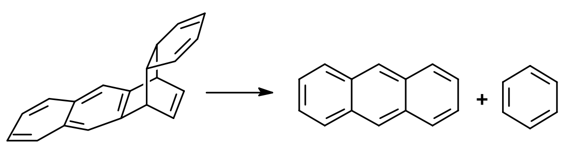
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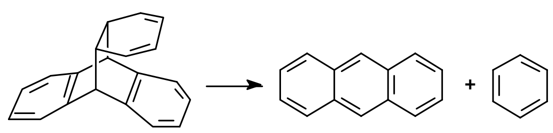
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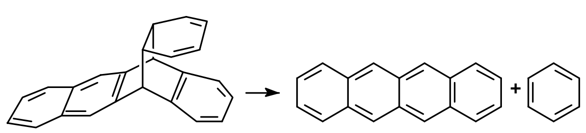
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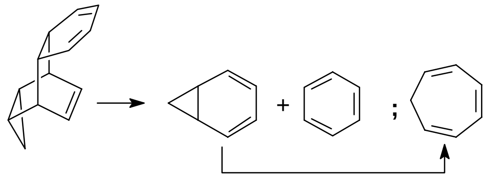
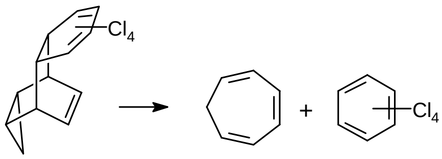
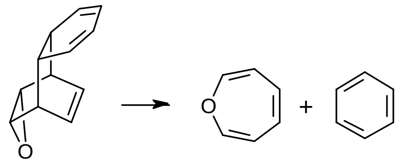
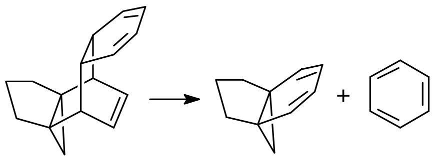
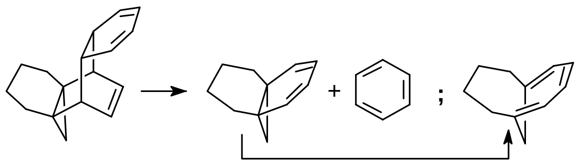
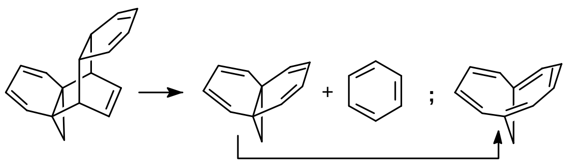
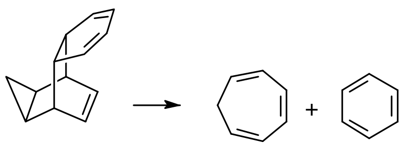
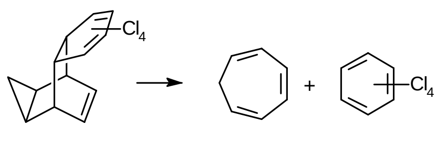
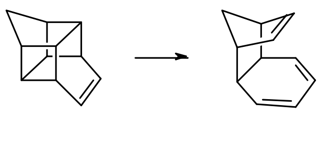
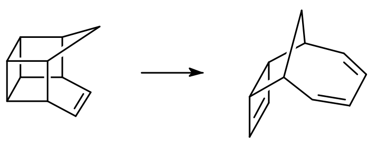
	45
	46
	47
	48
	59
	50
	51
	52
	53
	54

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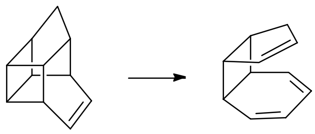
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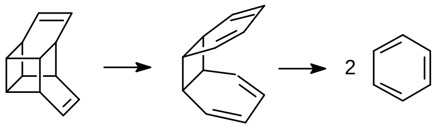

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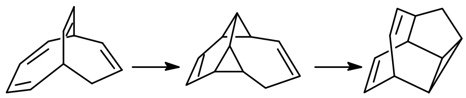
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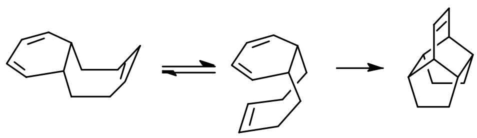
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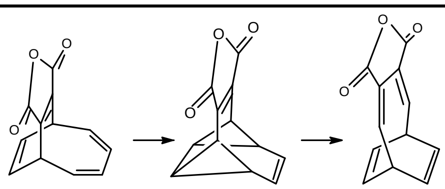

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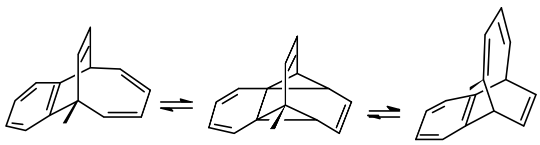
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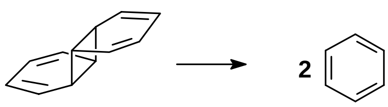

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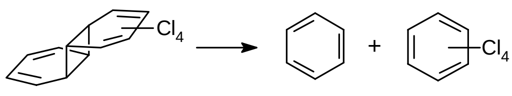

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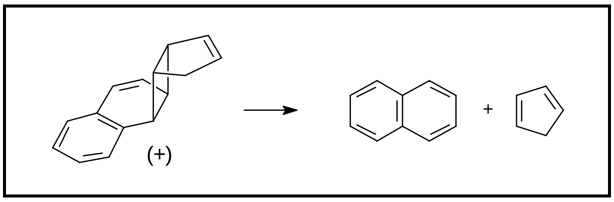

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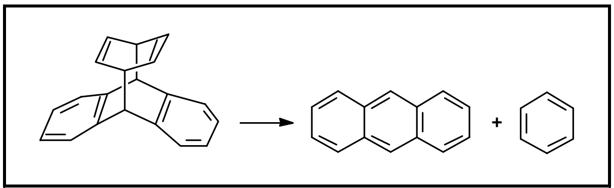

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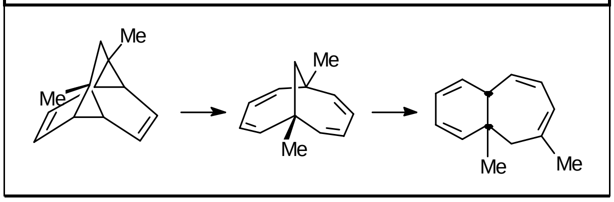

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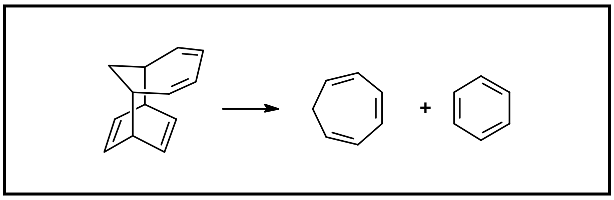

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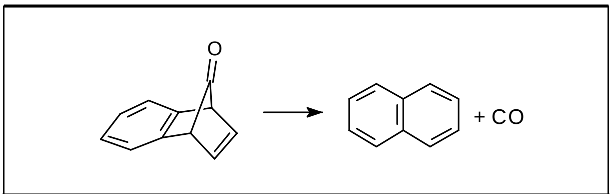

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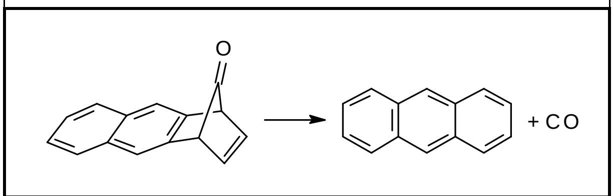

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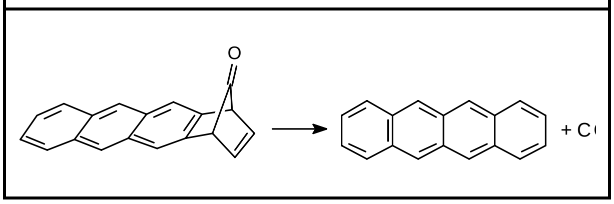

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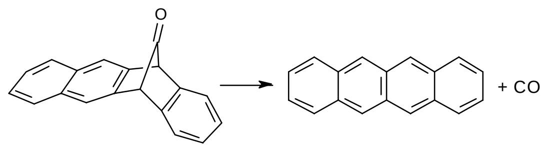

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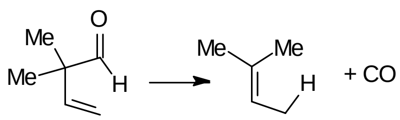

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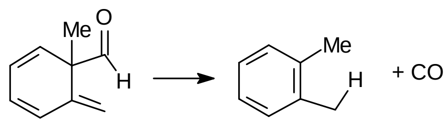

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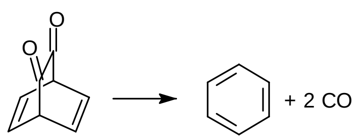
Extrusion of 2 CO via diradical



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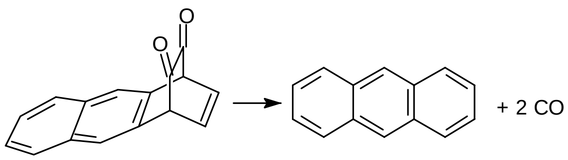

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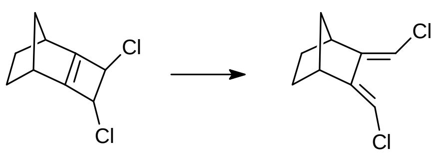

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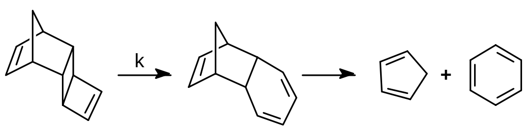

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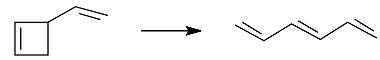
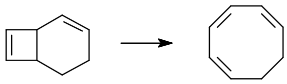
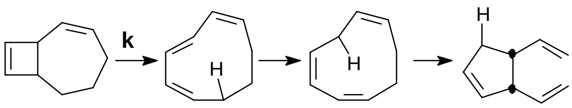
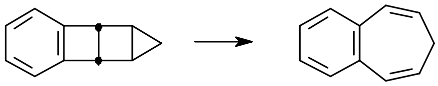
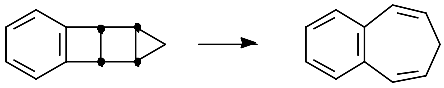
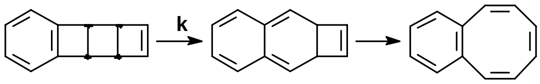
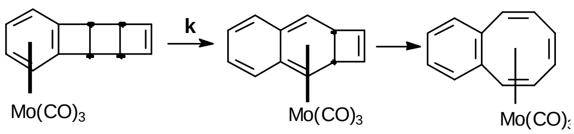
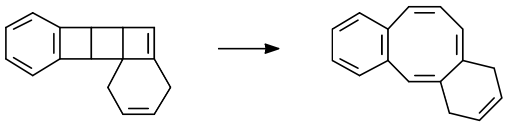
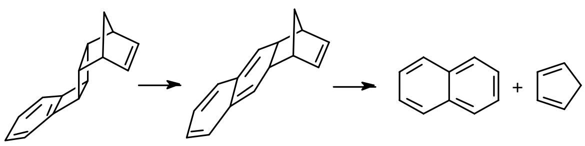
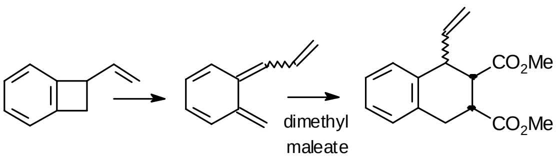
	77
	78
	79
	80
	81
	82
	83
	84
	85
	86

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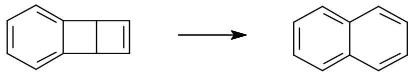
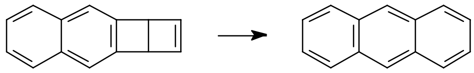
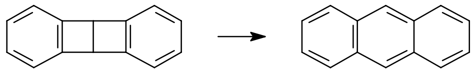
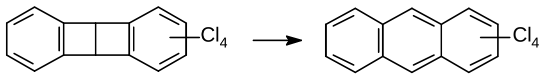
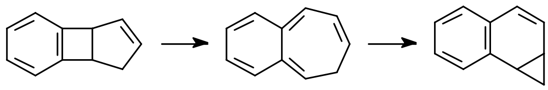
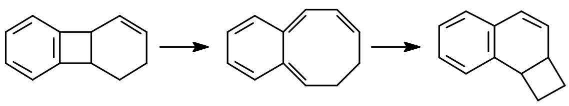
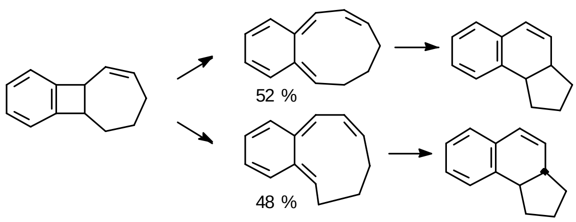
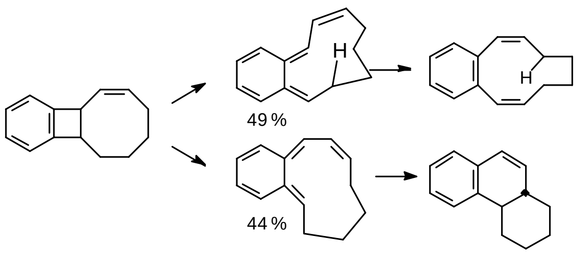
	87
	88
	89
	90
	91
	92
	93
	94

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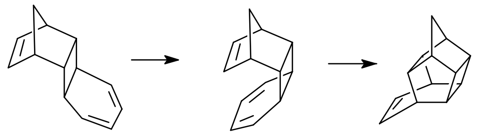

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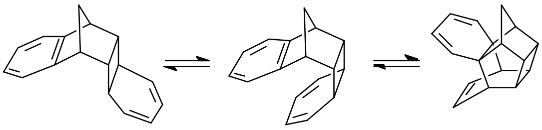

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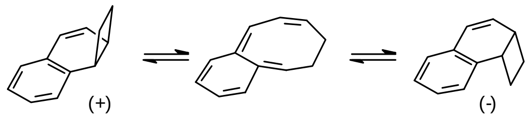

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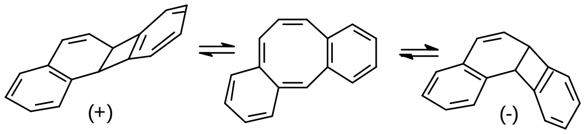

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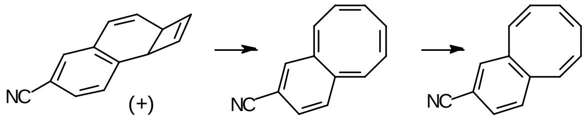
6e-Electrocyclic reaction



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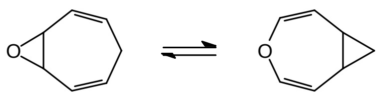
3,3-Sigmatropic rearrangement



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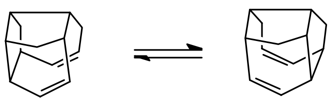

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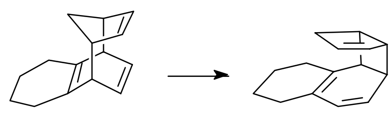
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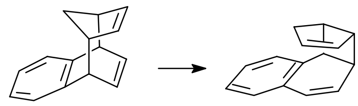
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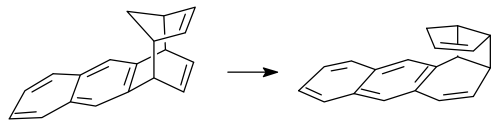
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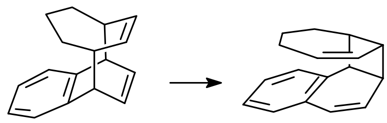
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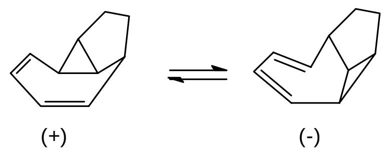
1,5-Sigmatropic rearrangement



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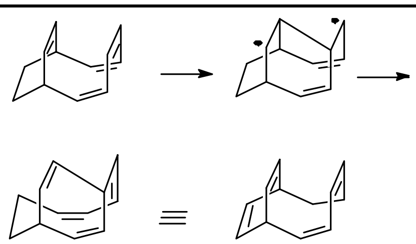
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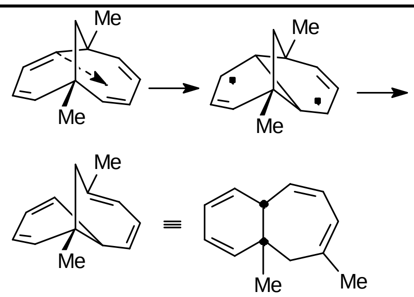

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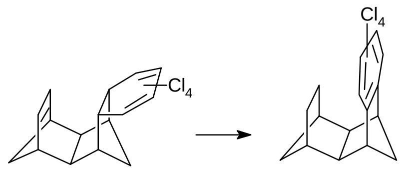
6e-Dyotropic hydrogen transfer



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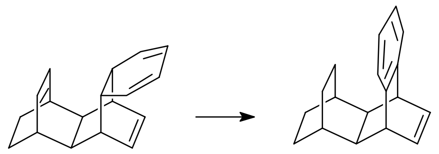

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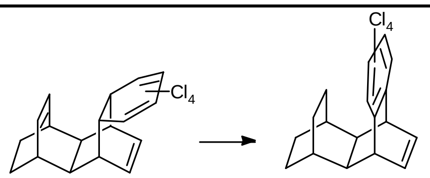

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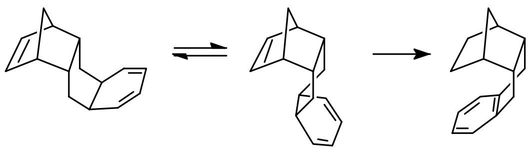

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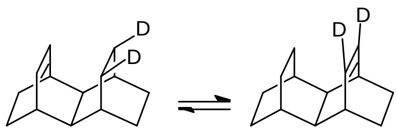

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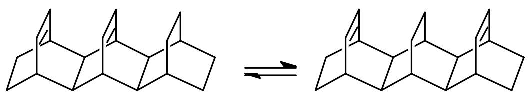

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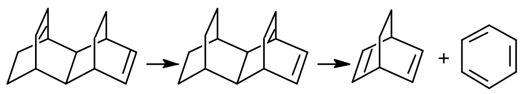

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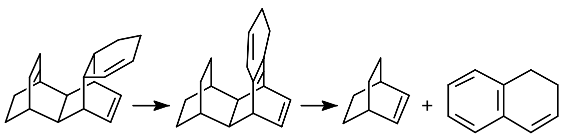

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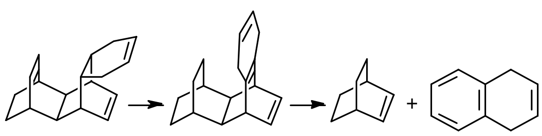

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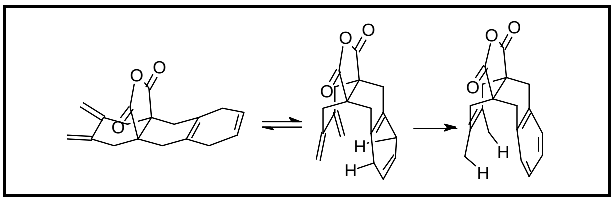

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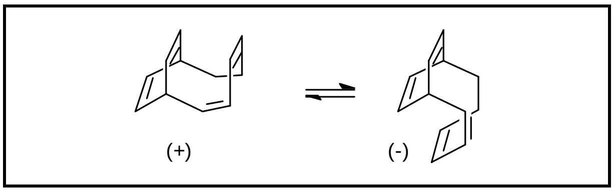
Ring inversion



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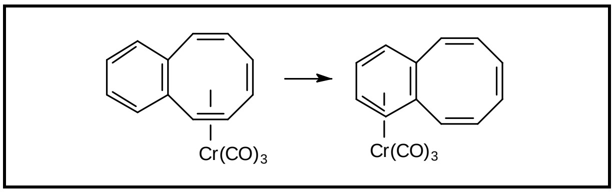
6e-Haptotropic rearrangement



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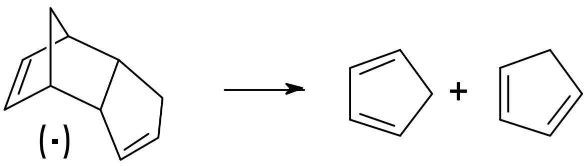
$C_{10}H_{12}$

endo-Tricyclo[5.2.1.0^{2,6}]deca-3,8-diene

(4+2)-Cycloreversion



(-)

t/min	90	135	180	225	270	315	355	385
% conversion	35.1	48.1	57.7	64.4	70.7	76.6	80.9	83.7

k = (7.71 + 0.1) 10^{-5} s^{-1} at 160°C

$\Delta G^{\#}$ = 33.71kcal mol^{-1}

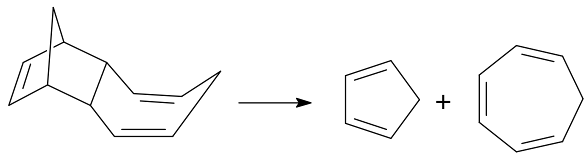
Method: in iso-octane, ampules in thermostat, polarimetry at 365 nm

Literature: Susanne Krauthäuser, dissertation, University of Cologne 1996.

$C_{12}H_{14}$

endo-Tricyclo[6.2.1.0^{2,5}]dodeca-3,6,10-triene

(4+2)-Cycloreversion



T/ °C	138.4	148.47	158.55	168.22	177.94	187.51	198.23
k/10^{-4} s^{-1}	0.153	0.433	1.177	3.048	7.241	16.849	40.549

log k = (14.33 ± 0.13) - (36.03 ± 0.20)/2.303 RT;   R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 30.24 kcal mol^{-1}, $\Delta H^{\#}$ = 35.16 kcal mol^{-1}, $\Delta S^{\#}$ = 4.3 cal mol^{-1} K^{-1}

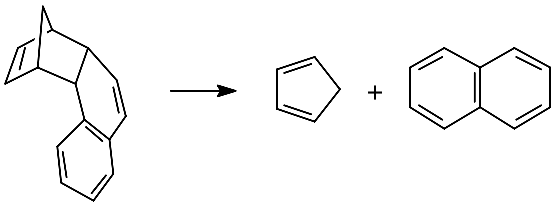
Method: in the gas phase, 1 Torr, flask (20 l) in thermostat, tetralin as internal standard, glpc analysis.

Literature: Lothar Schumachers, dissertation, University of Cologne 1981.

$C_{15}H_{14}$

endo-3,4-Benzotricyclo[6.2.1.0^{2,7}]undeca-3,5,9-triene

(4+2)-Cycloreversion



T/ °C	80.3	82.1	84.05	86.0	88.05	89.75	92.05
$k/10^{-4}\ s^{-1}$	1.090	1.388	1.666	2.231	2.647	3.041	3.956

$\log k = 13.20 \pm 0.54 - (27.75 \pm 0.88)/2.303\ RT$; $R = 1.98\ 10^{-3}$ kcal mol^{-1} K^{-1}

$\Delta G^{\#} = 27.22$ kcal mol^{-1}, $\Delta H^{\#} = 27.04$ kcal mol^{-1}, $\Delta S^{\#} = -0.5$ cal mol^{-1} K^{-1}

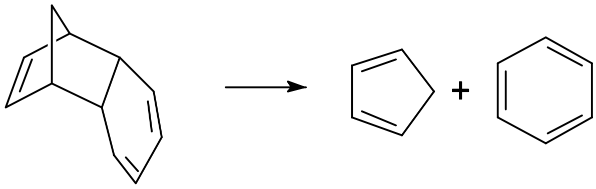
Method: in *n*-dodecane, double-walled cell (l = 5 cm), continuous monitoring of increase of E at 311 nm.

Literature: Robert Waldraff, dissertation, University of Cologne 1983.

$C_{11}H_{12}$

endo-Tricyclo[6.2.1.0^{2,7}]undeca-3,5,9-triene

(4+2)-Cycloreversion



T/ °C	40.2	42.2	44.2	47.2	49.2
$k/10^{-5}\ s^{-1}$	4.12	5.43	7.22	10.39	13.64

$\log k = 14.11 \pm 0.25 - (26.53 \pm 0.36)/2.303\ RT$; $R = 1.98\ 10^{-3}$ kcal mol^{-1} K^{-1}

$\Delta G^{\#} = 24.65$ kcal mol^{-1}, $\Delta H^{\#} = 25.90$ kcal mol^{-1}, $\Delta S^{\#} = 3.9$ cal mol^{-1} K^{-1}

Method: in CCl_4, $C_2H_2Br_4$ as internal standard, sealed nmr-tube in thermostat, ^{1}H-nmr analysis.

$\Delta H_{rx} = -11.1$ kcal mol^{-1}

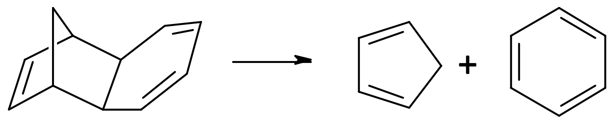
Method: Differential calorimetry in squalane solution from 17 - 137°C

Literature: Ulrich Heinze, Diplomarbeit, University of Cologne 1975.

$C_{11}H_{12}$

exo-Tricyclo[6.2.1.0^{2,7}]undeca-3,5,9-triene

(4+2)-Cycloreversion



T/ °C	27.3	29.2	32.2	34.2	36.2
$k/10^{-5}\ s^{-1}$	4.61	5.59	8.74	11.80	14.38

log k = 13.53 ± 0.70 - (24.58 ± 0.98)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 23.56 kcal mol^{-1}, $\Delta H^{\#}$ = 23.98 kcal mol^{-1}, $\Delta S^{\#}$ = 1.3 cal mol^{-1} K^{-1}

Method: in CCl_4, $C_2H_2Br_4$ as internal standard, sealed nmr-tube in thermostat, ^{1}H-nmr analysis.

ΔH_{rx} = -10.4 kcal mol^{-1}

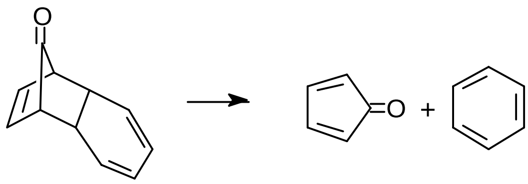
Method: Differential calorimetry in squalane solution from 17 - 137°C

Literature: Ulrich Heinze, Diplomarbeit, University of Cologne 1975.

$C_{11}H_{10}O$

endo-Tricyclo[6.2.1.0^{2,7}]undeca-3,5,9-trien-11-one

(4+2)-Cycloreversion



T/ °C	30.75	31.6	32.15	32.8	34.55	35.4
k/10^{-4} s^{-1}	2.47	2.76	2.86	3.19	3.90	4.40

log k = 12.93 ± 0.48 - (23.01 ± 1.51)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 22.83 kcal mol^{-1}, $\Delta H^{\#}$ = 22.40 kcal mol^{-1}, $\Delta S^{\#}$ = -1.4 cal mol^{-1} K^{-1}

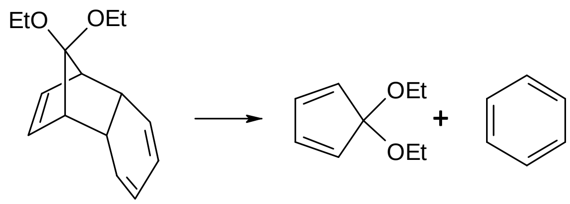
Method: in *n*-dodecane, double-walled cell (l = 5 cm), continuous monitoring of decrease of E at 278 nm.

Literature: Helmut LeBlanc, dissertation, University of Cologne 1979.

$C_{15}H_{20}O_2$

11,11,-Diethoxytricyclo[6.2.1.0^{2,7}]undeca-3,5,9-triene

(4+2)-Cycloreversion



T/ °C	95.3	98.1	99.6	101.1
k/10^{-5} s^{-1}	2.01	2.74	3.44	4.04

log k = 15.14 ± 0.89 - (33.46 ± 1.51)/2.303   R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 29.63 kcal mol^{-1}, $\Delta H^{\#}$ = 32.72 kcal mol^{-1}, $\Delta S^{\#}$ = 8.3 cal mol^{-1} K^{-1}

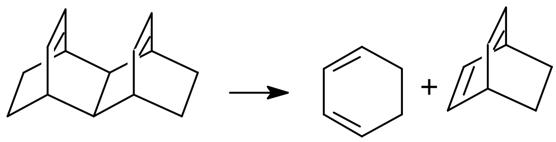
Method: in terachloroethane-d$_2$, sealed nmr-tube, butyl formiate as internal standard, ^{1}H-nmr analysis.

Literature: Helmut LeBlanc, dissertation, University of Cologne 1979.

$C_{14}H_{18}$

syn-Tetracyclo[6.2.2.2.^{3,6}0^{2,7}]tetradeca-4,9-diene

(4+2)-Cycloreversion



T/ °C	319.96	330.33	339.61	349.20	359.16
k/10^{-5} s^{-1}	1.310	2.812	5.671	11.411	21.817

$\log k = 14.96 \pm 0.16 - (53.85 \pm 0.46)/2.303\ RT$; $R = 1.98\ 10^{-3}$ kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 48.65 kcal mol^{-1}, $\Delta H^{\#}$ = 52.64 kcal mol^{-1}, $\Delta S^{\#}$ = 6.5 cal mol^{-1} K^{-1}

($\Delta S^{\#}$ is corrected by – R ln2 due to the s_2 symmetry of the educt)

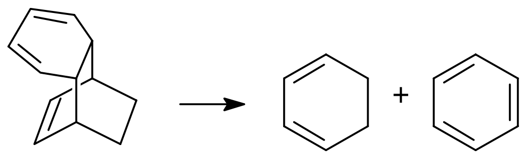
Method: in the gas phase, flask (100 l) in thermostat, glpc analysis.

Literature: Dirk Frowein, dissertation, University of Cologne 1992.

$C_{12}H_{14}$

endo-Tricyclo[6.2.2.0^{2,7}]dodeca-3,5,9-triene

(4+2)-Cycloreversion



T/ °C	179.34	189.51	199.33	209.45	219.47	229.89	240.31	249.93
$k/10^{-4}\ s^{-1}$	0.672	1.719	4.149	9.778	22.18	49.99	109.9	219.0

log k = 14.46 ± 0.11 - (38.57 ± 0.24)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 35.29 kcal mol^{-1}, $\Delta H^{\#}$ = 37.60 kcal mol^{-1}, $\Delta S^{\#}$ = 4.6 cal mol^{-1} K^{-1}

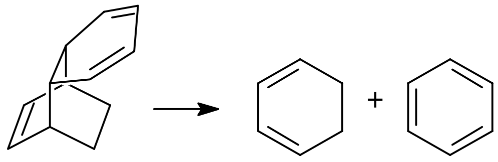
Method: in the gas phase, flask (100 l) in thermostat, glpc analysis.

Literature: Achim Bertsch, dissertation, University of Cologne 1986.

$C_{12}H_{14}$

exo-Tricyclo[6.2.2.0^{2,7}]dodeca-3,5,9-triene

(4+2)-Cycloreversion



T/ °C	159.51	169.47	179.97	189.33	199.18	209.72	219.56
k/10^{-4} s^{-1}	0.765	1.932	5.081	11.43	26.00	60.24	127.7

log k = 14.13 ± 0.11 - (35.99 ± 0.24)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 33.84 kcal mol^{-1}, $\Delta H^{\#}$ = 35.02 kcal mol^{-1}, $\Delta S^{\#}$ = 3.3 cal mol^{-1} K^{-1}

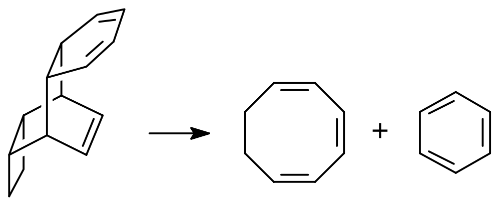
Method: in the gas phase, flask (100 l) in thermostat, glpc analysis

Literature: Achim Bertsch, dissertation, University of Cologne 1986.

$C_{14}H_{16}$

anti-Tetracyclo[6.4.2.0.^{2,7}0^{9,12}]tetradeca-3,5,13-triene

(4+2)-Cycloreversion



t/min	30	100	160	230	301	370	410	540	610	670
% conversion	3.6	10.9	18.2	25.6	30.6	37.2	42.2	51.2	56.4	60.5

k = (2.32 ± 0.044) 10^{-5} s^{-1} at T = 131 °C

$\Delta G^{\#}$ = 32.35 kcal mol^{-1}

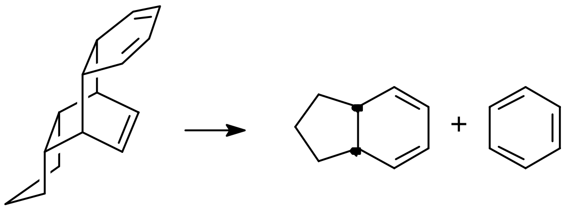
Method: in tetrachloroethane-d_2, sealed nmr-tube in thermostat, ^{1}H-nmr analysis.

Literature: Hermann Rose, dissertation, University of Cologne 1988;
A. Bertsch, W. Grimme, G. Reinhardt, H. Rose, P. M. Warner, *J. Am. Chem. Soc.* **1988**, *110*, 5112

$C_{15}H_{18}$

anti-Tetracyclo[6.5.2.0.^{2,7}0^{9,13}]pentadeca-3,5,14-triene

(4+2)-Cycloreversion



t/min	60	120	180	240	300
% conversion	35.0	59.3	75.0	82.8	90.4

k = (1.30 ± 0.04) 10^{-4} s^{-1} at T = 164.5 °C

$\Delta G^{\#}$ = 33.61 kcal mol^{-1}

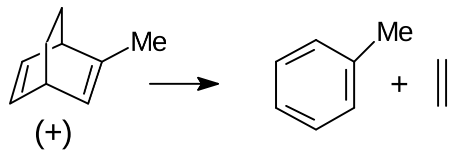
Method: in tetrachloroethane-d_2, sealed nmr-tube in thermostat, ^{1}H-nmr analysis.

Literature: Hermann Rose, dissertation, University of Cologne 1988;
A. Bertsch, W. Grimme, G. Reinhardt, H. Rose, P.M. Warner, *J. Am. Chem. Soc.* **1988**, *110*, 5112.

C_9H_{12}

2-Methylbicyclo[2.2.2]octa-2,5-diene

(4+2)-Cycloreversion



T/ °C	104.90	109.90	114.90	119.95	125.15
k/10^{-5} s^{-1}	1.955	3.514	5.895	10.39	17.45

log k = 13.99 ± 0.17 - (32.34 ± 0.30)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 30.42 kcal mol^{-1}, $\Delta H^{\#}$ = 31.57 kcal mol^{-1}, $\Delta S^{\#}$ = 3.0 cal mol^{-1} K^{-1}

Method: in *n*-hexane, sealed ampules in thermostat, polarimetry at 365 nm

T/ °C	116.10	126.60	137.90	148.30	158.30	163.30	168.90	174.40
k/10^{-4} s^{-1}	0.5002	1.4967	4.6268	12.273	29.894	48.722	75.426	115,77

log k = 13.90 ± 0.03 - (32.43 ± 0.05)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

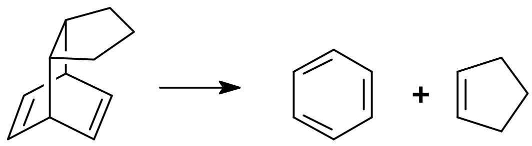
Method: in the gas phase (2 Torr), benzene as internal standard, flask (20 l) in thermostat, glpc analysis.

Literature: Susanne Krauthäuser, Diplomarbeit, University of Cologne 1992.

$C_{11}H_{14}$

Tricyclo[5.2.2.0^{2,6}]undeca-8,10-diene

(4+2)-Cycloreversion



T/ °C	113.1	115.1	119.05	122.56	126.03	128.55	132.32	135.53
$k/10^{-5}$ s^{-1}	6.028	7.367	10.99	16.22	23.25	30.23	42.27	58.45

$\log k = 13.86 \pm 0.25 - (31.96 \pm 0.45)/2.303\ RT$; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 30.25 kcal mol^{-1}, $\Delta H^{\#}$ = 31.17 kcal mol^{-1}, $\Delta S^{\#}$ = 2.3 cal mol^{-1} K^{-1}

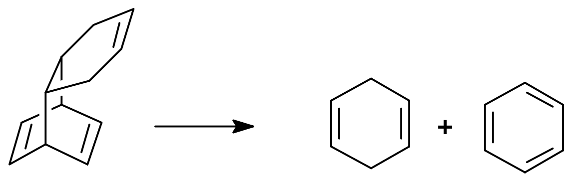
Method: in isooctane, ampules in thermostat, glpc analysis

Literature: Robert Waldraff, dissertation, University of Cologne 1986.

$C_{12}H_{14}$

Tricyclo[6.2.2.0^{2,7}]dodeca-4,9,11-triene

(4+2)-Cycloreversion



t/min	30	60	90	120	210
% conversion	27.67	49.03	54.75	62.88	85.73

k = (1.49 ± 0.09) 10^{-4} s^{-1} at T = 101.2 °C

$\Delta G^{\#}$ = 28.53 kcal mol^{-1}

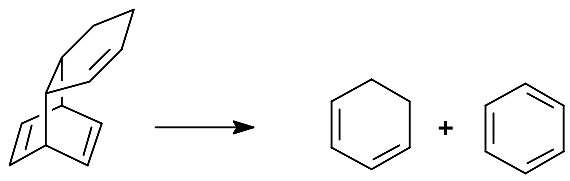
Method: in CCl_4, sealed nmr-tube in thermostat, ^{1}H-nmr analysis.

Literature: Gerd Reinhardt, dissertation, University of Cologne 1982.

$C_{12}H_{14}$

Tricyclo[6.2.2.0^{2,7}]dodeca-3,9,11-triene

(4+2)-Cycloreversion



T/ °C	76.83	82.48	86.62	92.69
k/10^{-4} s^{-1}	1.100	1.960	3.160	5.830

og k = 12.85 ± 0.30 - (26.93 ± 0.50)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 26.97 kcal mol^{-1}, $\Delta H^{\#}$ = 26.22 kcal mol^{-1} , $\Delta S^{\#}$ = -2.1 cal mol^{-1} K^{-1}

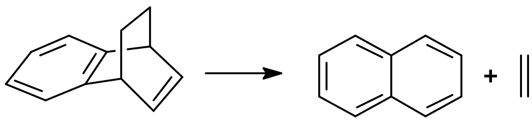
Method: in *n*-dodecane, double-walled cell (l = 5 cm), continuous monitoring of increase of E at 284 nm.

Literature: Gerd Wagner, Diplomarbeit, University of Cologne 1981.

$C_{12}H_{12}$

Benzobicyclo[2.2.2]octa-2,5-diene

(4+2)-Cycloreversion



t/h	7.15	10.33	15.75	22.21	25.47	32.09	35.86	39.99
% conversion	7.7	10.6	15.4	22.4	27.1	32.2	36.4	41.3

k = (1.40 ± 0.11) 10^{-5} s^{-1} at T = 150 °C

$\Delta G^{\#}$ = 34.34 kcal mol^{-1}

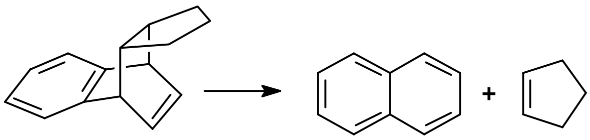
Method: in tetrachloroethane-d_2, sealed nmr-tube in thermostat, ^{1}H-nmr analysis.

Literature: Andreas Kirst, dissertation, University of Cologne 1995.

$C_{15}H_{16}$

8,9-Benzotricyclo[5.2.2.0^{2,6}]undeca-8,10-diene

(4+2)-Cycloreversion



t/min	0	54	95	125	157	188	222	252	312
% conversion	9.1	33.3	49	60.3	65.7	71.2	76.7	82.1	86.0

k = (1.03 + 0.06) 10^{-4} s^{-1} at T = 187 °C

$\Delta G^{\#}$ = 35.60 kcal mol^{-1}

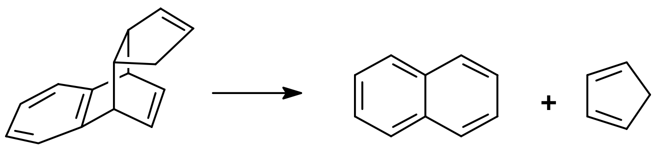
Method: in tetrachloroethane-d_2, sealed nmr-tube in thermostat, ^{1}H-nmr analysis.

Literature: Andreas Kirst, dissertation, University of Cologne 1995.

$C_{15}H_{14}$

10,11-Benzotricyclo[5.2.2.0^{2,6}]undeca-3,8,10-triene

(4+2)-Cycloreversion



T/ °C	101.2	104.2	106.2	109.2	113.2	115.2
$k/10^{-5}$ s^{-1}	1.657	2.258	3.100	4.068	6.404	7.924

log k = 14.13 ± 0.45 - (32.39 ± 0.79)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 30.24 kcal mol^{-1}, $\Delta G^{\#}$ = 31.64 kcal mol^{-1}, $\Delta S^{\#}$ = 3.6 cal mol^{-1} K^{-1}

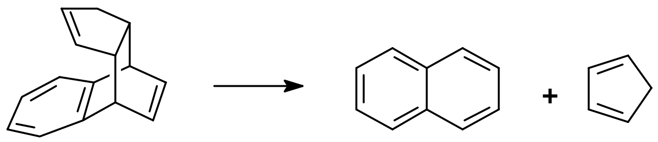
Method: in isooctane, ampules in thermostat, glpc analysis.

Literature: Robert Waldraff, dissertation, University of Cologne 1986.

$C_{15}H_{16}$

8,9-Benzotricyclo[5.2.2.0^{2,6}]undeca-3,8,10-triene

(4+2)-Cycloreversion



t/min	1	30	60	90	120	180	240
% conversion	2.9	17.9	22.9	35.3	48.8	60.8	73.2

k = (8.96 ± 0.37) 10^{-5} s^{-1} at T = 132 °C

$\Delta G^{\#}$ = 31.35 kcal mol^{-1}

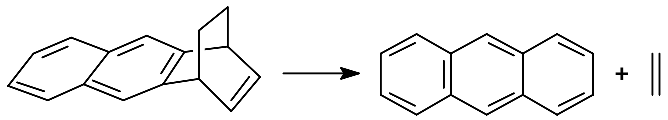
Method: in tetrachloromethane, sealed nmr-tube in thermostat, ^{1}H-nmr analysis.

Literature: Gerd Reinhardt, dissertation, University of Cologne 1982.

$C_{16}H_{14}$

Naphtho[b]bicyclo[2.2.2]octa-2,5--diene

(4+2)-Cycloreversion



t/min	82	135	215	313	391	495	556	640	742
% conversion	9.7	12.6	19.4	26.1	31.4	39.3	44.1	51.1	59.7

k = (1.92 + 0.06) 10^{-5} s^{-1} at T = 194 °C

$\Delta G^{\#}$ = 37.71 kcal mol^{-1}

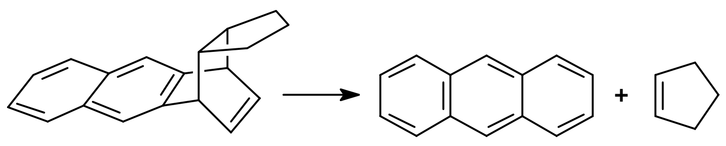
Method: in tetrachloroethane-d_2, sealed nmr tube in thermostat, ^{1}H-nmr analysis.

Literature: Andreas Kirst, dissertation, University of Cologne 1995.

$C_{19}H_{18}$

8,9-Naphtho[b]tricyclo[5.2.2.0^{2,6}]undeca-8,10-diene

(4+2)-Cycloreversion



t/min	61	184	287	400	525	646	737	881	1087
% conversion	4.7	14.1	20.9	26.9	30.3	39.8	40.2	50.6	58.9

k = (1.31 + 0.06) 10^{-5} s^{-1} at T = 193 °C

$\Delta G^{\#}$ = 37.98 kcal mol^{-1}

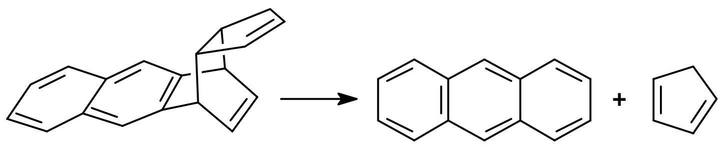
Method: in tetrachloroethane-d_2, sealed nmr-tube in thermostat, ^{1}H-nmr analysis.

Literature: Andreas Kirst, dissertation, University of Cologne 1995.

$C_{19}H_{16}$

8,9-Naphtho[b]tricyclo[5.2.2.0^{2,6}]undeca-3,8,10-triene

(4+2)-Cycloreversion



T/ °C	129.72	133.20	137.55	142.47	143.78	146.67
$k/10^{-5}\ s^{-1}$	3.77	5.74	7.93	14.5	17.9	22.4

log k = 14.70 ± 0.65 - (35.26 ± 1.22)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 31.93 kcal mol^{-1}, $\Delta H^{\#}$ = 34.45 kcal mol^{-1} , $\Delta S^{\#}$ = 6.1 cal mol^{-1} K^{-1}

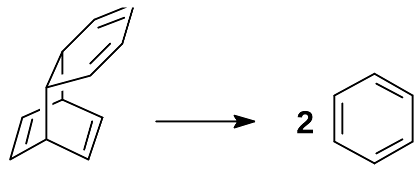
Method: in isooctane, *n*-dodecane as internal standard, ampules in thermostat, glpc analysis.

Literature: Robert Waldraff, dissertation, University of Cologne 1983.

$C_{12}H_{12}$

Tricyclo[6.2.2.0^{2,7}]dodeca-3,5,9,11-tetraene

(4+2)-Cycloreversion



T/ °C	20.1	25.1	30.1	35.0	40.0	45.0	50.0	55.0
k/10^{1} s^{-1}	1.088	1.844	2.835	4.513	6.930	10.32	15.60	21.85

log k = 13.32 ± 0.22 - (16.47 ± 0.23)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 15.75 kcal mol^{-1}, $\Delta H^{\#}$ = 15.85 kcal mol^{-1}, $\Delta S^{\#}$ = 0.3 cal mol^{-1} K^{-1}

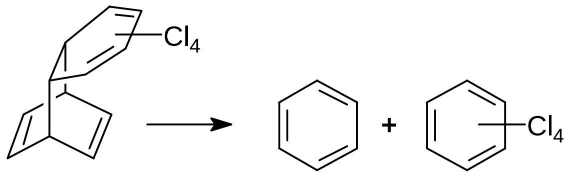
Method: in isooctane, generation by flash photolysis, continuous monitoring of decrease of E at 280 nm.

Literature: A. Bertsch, W. Grimme, G. Reinhardt, *Angew. Chem.* **1985**, *98*, 361.

$C_{12}H_8Cl_4$

3,4,5,6-Tetrachlorotricyclo[6.2.2.0^{2,7}]dodeca-3,5,9,11-tetraene

(4+2)-Cycloreversion



t/min	0	5	10	15	20.5	30	40	50	60
% conversion	36	40.5	44.1	47.7	51.5	56.7	61.8	64.9	69.7

k = (1.75 ± 0.15) 10^{-4} s^{-1} at T = – 60 °C

$\Delta G^{\#}$ = 15.94 kcal mol^{-1}

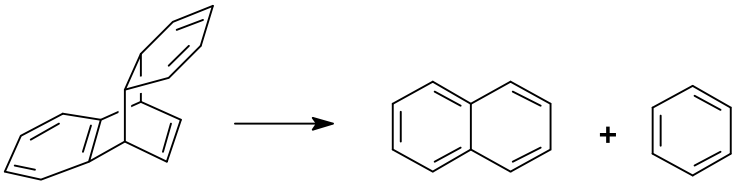
Method: in acetone-d_6, nmr-tube, ^{1}H-nmr analysis.

Literature: Andreas Kirst, dissertation, University of Cologne 1995.

$C_{16} H_{14}$

9,10-Benzotricyclo[6.2.2.0^{2,7}]dodeca-3,5,9,11-tetraene

(4+2)-Cycloreversion



T/ °C	2.75	4.10	6.10	8.15	10.00	12.00	14.1
k/10^{-4} s^{-1}	3.59	4.18	5.13	6.87	8.44	10.24	15.60

log k = 12.10 ± 0.75 - (19.65 ± 0.92)/2.303 RT;   R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 20.51 kcal mol^{-1}, $\Delta H^{\#}$ = 19.09 kcal mol^{-1} , $\Delta S^{\#}$ = -5.0 cal mol^{-1} K^{-1}

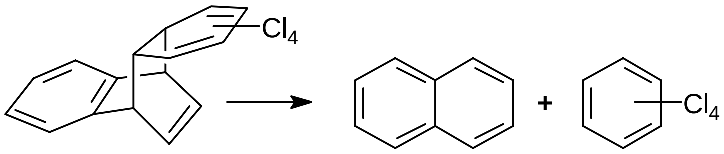
Method: in isooctane, double-walled cell (l = 5 cm), continuous monitoring of increase of E at 320 nm.

Literature: W. Grimme, H. G. Köser, *Angew. Chem. Int. Ed. Engl.* **1980**, *19,* 307.

$C_{16}H_{10}Cl_4$

3,4,5,6-Tetrachloro-9,10-benzotricyclo[6.2.2.0^{2,7}]dodeca-3,5,9,11-tetraene

(4+2)-Cycloreversion



t/min	10	20	30	40	50	60	70	80	90
% conversion	16.0	27.5	37.4	46.8	53.2	59.2	64.1	68.5	72.3

k = (2.80 ± 0.43) 10^{-4} s^{-1} at T = - 9 °C

$\Delta G^{\#}$ = 19.62 kcal mol^{-1}

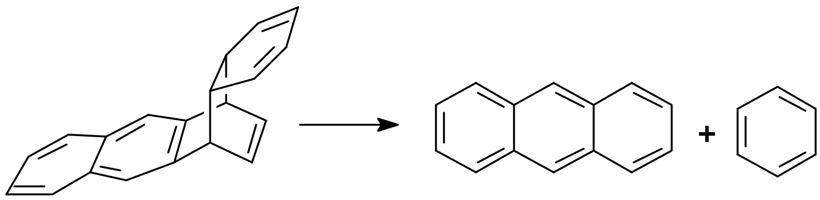
Method: in chloroform-d_1, nmr-tube, ^{1}H-nmr analysis.

Literature: Andreas Kirst, dissertation, University of Cologne 1995.

$C_{20}H_{16}$

9,10-Naphthotricyclo[6.2.2.0^{2,7}]dodeca-3,5,9,11-tetraene

(4+2)-Cycloreversion



T/ °C	20.0	25.0	30.0	35.0	40.0	45.0
k/10^{-4} s^{-1}	1.13	2.10	3.79	6.75	12.75	22.38

log k = 12.56 ± 0.37 - (22.14 ± 0.55)/2.303 RT;   R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 22.48 kcal mol^{-1}, $\Delta G^{\#}$ = 21.53 kcal mol^{-1} , $\Delta S^{\#}$ = -3.1 cal mol^{-1} K^{-1}

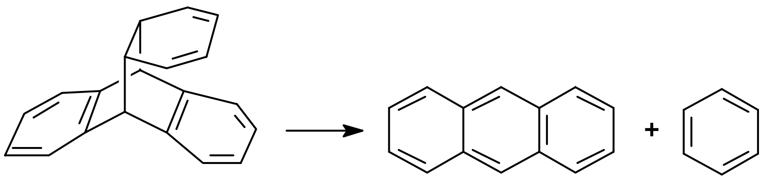
Method: in *n*-dodecane, double-walled cell (l = 5 cm), continuous monitoring of increase of E at 376 nm.

Literature: G. Reinhardt, dissertation, University of Cologne 1982;
A. Bertsch, W. Grimme, G. Reinhardt, *Angew. Chem.* **1986**, *98*, 361.

$C_{20}H_{16}$

9,10,11,12-Dibenzotricyclo[6.2.2.0^{2,7}]dodeca-3,5,9,11-tetraene

(4+2)-Cycloreversion



T/ °C	56.0	58.0	61.0	64.9	69.0	72.8	75.95	80.0
$k/10^{-4}\ s^{-1}$	0.89	1.10	1.55	2.83	4.75	7.72	11.12	17.82

log k = 15.46 ± 0.48 - (29.42 ± 0.75)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 25.35 kcal mol^{-1}, $\Delta H^{\#}$ = 28.74 kcal mol^{-1}, $\Delta S^{\#}$ = 9.9 cal mol^{-1} K^{-1}

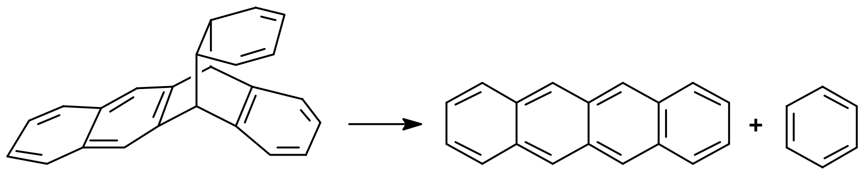
Method: in *n*-dodecane, double-walled cell (l = 5 cm), continuous monitoring of increase of E at 376 nm.

Literature: Gerd Reinhardt, dissertation, University of Cologne 1986:
A. Bertsch, W. Grimme, G. Reinhardt, *Angew. Chem.* **1986**, *98*, 361.

$C_{24}H_{18}$

9,10-Benzo-11,12-naphthotricyclo[6.2.2.0^{2,7}]dodeca-3,5,9,11-tetraene

(4+2)-Cycloreversion



T/ °C	80	85	90	95
$k/10^{-4}\ s^{-1}$	5.10	9.40	17.5	31.0

log k = 15.01 ± 0.48 - (31.20 ± 0.50)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 27.67 kcal mol^{-1}, $\Delta H^{\#}$ = 30.49 kcal mol^{-1}, $\Delta S^{\#}$ = 7.8 cal mol^{-1} K^{-1}

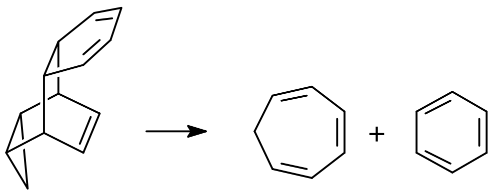
Method: in *n*-dodecane, double-walled cell (l = 5 cm), continuous monitoring of increase of E at 482 nm.

Literature: Gerd Reinhardt, dissertation, University of Cologne 1986;
A. Bertsch, W. Grimme, G. Reinhardt, *Angew. Chem.* **1986**, *98*, 361.

$C_{13}H_{14}$

anti-Tetracyclo[6.3.2.0.^{2,7}0^{9,11}]trideca-3,5,12-triene

(4+2)-Cycloreversion



t/min	60	120	180	240	300	360	420	480	560
% conversion	11.5	23.2	33.1	41.8	48.5	55.8	61.1	65.2	71.5

k = (3.744 ± 0.034) 10^{-5} s^{-1} at T = 77.5 °C

$\Delta G^{\#}$ = 27.64 kcal mol^{-1}

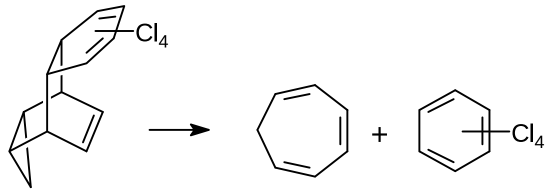
Method: in tetrachloromethane, sealed nmr-tube in thermostat, ^{1}H-nmr analysis.

Literature: Achim Bertsch, dissertation, University of Cologne 1986;
A. Bertsch, W. Grimme, G. Reinhardt, H. Rose, P. M. Warner, *J. Am. Chem. Soc.* **1988**, *110*, 5112.

$C_{13}H_{10}Cl_4$

3,4,5,6-Tetrachloro-*endo*-tetracyclo[6.3.2.0^{2,7}.0^{9,11}]trideca-3,5,12-triene

(4+2)-Cycloreversion



T/ °C	74.35	79.31	84.69	89.52
k/10^{-4} s^{-1}	1.27	2.35	4.03	6.53

log k = 13.00 ± 0.50 - (26.85 ± 0.81)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

ΔG$^{\#}$ = 26.64 kcal mol^{-1}, ΔH$^{\#}$ = 26.15 kcal mol^{-1}, ΔS$^{\#}$ = -1.4. cal mol^{-1} K^{-1}

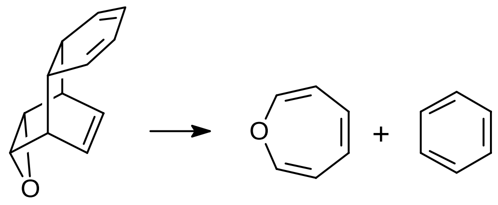
Method: in *n*-dodecane, double-walled cell (l = 5 cm), continuous monitoring of decrease of E at 316 nm.

Literature: Gerd Reinhardt, dissertation, University of Cologne1982.

$C_{12}H_{12}O$

anti-endo-10-Oxatetracyclo[6.3.2.0^{2,7}.0^{9,11}]trideca-3,5,12-triene

(4+2)-Cycloreversion



T/ °C	74.07	77.80	81.24	83.50	86.90	90.35	93.66
k/10^{-4} s^{-1}	0.677	1.013	1.566	2.006	2.810	4.479	5.926

log k = 13.75 ± 0.31 - (28.48 ± 0.50)/2.303 RT;   R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 27.04 kcal mol^{-1}, $\Delta G^{\#}$ = 27.77 kcal mol^{-1} , $\Delta S^{\#}$ = 2.0 cal mol^{-1} K^{-1}

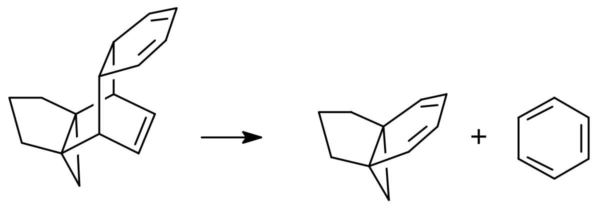
Method: in *n*-dodecane, double-walled cell (l = 5 cm), continuous monitoring of increase of E at 350 nm.

Literature: Gerd Wagner, Diplomarbeit, University of Cologne 1981.

$C_{16}H_{16}$

Pentacyclo[6.5.2.1^{9,13}.0^{2,7}.0^{9,13}]hexadeca-3,5,14-triene

(4+2)-Cycloreversion



T/ °C	85.0	90.05	95.0
k/10^{-4} s^{-1}	0.88	1.54	2.69

log k = 13.81 ± 0.23 - (29.28 ± 0.37)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 27.73 kcal mol^{-1}, $\Delta H^{\#}$ = 28.56 kcal mol^{-1} , $\Delta S^{\#}$ = 2.3 cal mol^{-1} K^{-1}

Method: in *n*-dodecane, double-walled cell (l = 5 cm), continuous monitoring of decrease of E at 314 nm.

ΔH_{rx} = -8.4 ± 1.0 kcal mol^{-1}

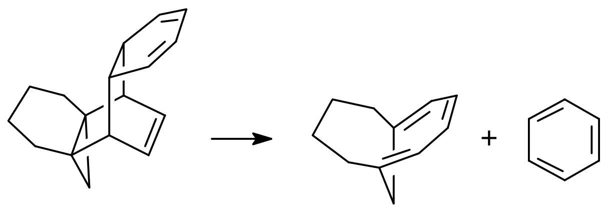
Method: Differential scanning calorimetry in squalane solution from 27 - 187°C

Literature: Gerd Reinhardt, dissertation, University of Cologne 1982.
A. Bertsch, W. Grimme, G. Reinhardt, H. Rose, P. M. Warner, *J. Am. Chem. Soc*. **1988**, *110*, 5112

$C_{17}H_{18}$

Pentacyclo[6.6.2.1^{9,14}.0^{2,7}.0^{9,14}]heptadeca-3,5,15-triene

(4+2)-Cycloreversion



T/ °C	84.96	88.97	89.24	94.07
$k/10^{-4}\ s^{-1}$	0.72	1.21	1.28	1.98

log k = 13.49 ±1.43 - (28.87 ± 2.37)/2.303 RT;   R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 27.85 kcal mol^{-1}, $\Delta H^{\#}$ = 28.15 kcal mol^{-1}, $\Delta S^{\#}$ = 0.8 cal mol^{-1} K^{-1}

Method: in *n*-dodecane, double-walled cell (l = 5 cm), continuous monitoring of decrease of E at 281 nm.

ΔH_{rx} = -12.6 ± 1.0 kcal mol^{-1}

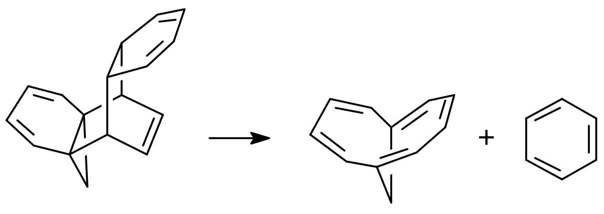
Method: Differential scanning calorimetry in squalane solution from 27 - 187°C

Literature: Gerd Reinhardt, dissertation, University of Cologne 1982.

$C_{17}H_{16}$

Pentacyclo[6.6.2.1^{2,7}.0^{2,7}.0^{9,14}]heptadeca-3,5,10,12,15-pentaene

(4+2)-Cycloreversion



T/ °C	75.90	79.55	85.10	89.95	95.10
$k/10^{-4}$ s^{-1}	0.48	0.79	1.52	2.58	4.14

log k = 13.67 ± 0.53 - (28.70 ± 0.86)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 27.39 kcal mol^{-1}, $\Delta G^{\#}$ = 27.99 kcal mol^{-1}, $\Delta S^{\#}$ = 1.7 cal mol^{-1} K^{-1}

Method: in *n*-dodecane, double-walled cell (l = 5 cm), continuous monitoring of increase of E at 375 nm.

ΔH_{rx} = -18.7 ± 1.0 kcal mol^{-1}

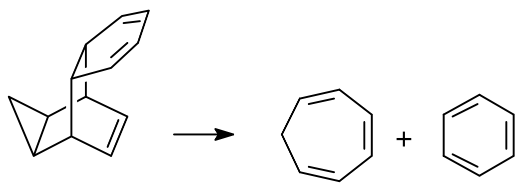
Method: Differential scanning calorimetry in squalane solution from 27 - 187°C

Literature: Gerd Reinhardt, dissertation, University of Cologne 1982.

$C_{13}H_{14}$

syn-Tetracyclo[6.3.2.0.^{2,7}0^{9,11}]trideca-3,5,12-triene

(4+2)-Cycloreversion



t/min	60	120	180	300	420	480	600	720	840	960
% conversion	4.1	7.4	11.0	16.8	22.5	25.6	31.0	35.7	39.6	44.2

k = (1.008 ± 0.018) 10^{-5} s^{-1} at T = 164.5 °C

$\Delta G^{\#}$ = 35.83 kcal mol^{-1}

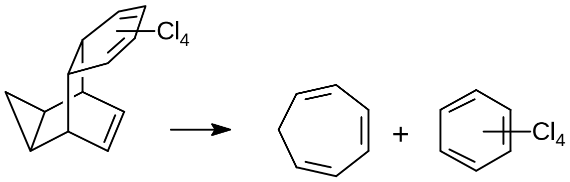
Method: in tetrachloroethane-d_2, sealed nmr-tube in thermostat, ^{1}H-nmr analysis.

Literature: Achim Bertsch, dissertation, University of Cologne 1986;
A. Bertsch, W. Grimme, G. Reinhardt, H. Rose, P. M. Warner, *J. Am. Chem. Soc*. **1988**, *110*, 5112.

$C_{13}H_{10}Cl_4$

3,4,5,6-Tetrachloro-*exo*-tetracyclo[6.3.2.0^{2,7}.0^{9,11}]trideca-3,5,12-triene

(4+2)-Cycloreversion



t/h	0	0.5	2.5	3.5	4.5	6	7
% conversion	11.9	15.1	32.8	39.4	42.8	48.1	52.8

k = (2.50 ± 0.15) 10^{-5} s^{-1} at T = 164.6 °C

$\Delta G^{\#}$ = 35.05 kcal mol^{-1}

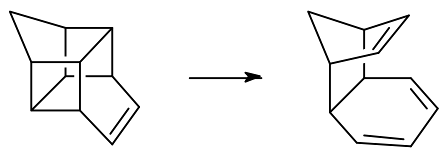
Method: in tetrachloroethane-d_2, sealed nmr-tube in thermostat, ^{1}H-nmr analysis.

Literature: Gerd Reinhardt, dissertation, University of Cologne 1982.

$C_{11}H_{12}$

Pentacyclo[5.4.0.0^{2,6}.0^{3,9}.0^{4,8}]undec-10-ene

(4+2)-Cycloreversion



T/ °C	81.3	82.35	83.3	84.3	85.15
$k/10^{-4}\ s^{-1}$	0.990	1.105	1.214	1.339	1.477

log k = 11.98 ± 0.25 - (25.94 ± 0.41)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 27.39 kcal mol^{-1}, $\Delta H^{\#}$ = 25.23 kcal mol^{-1}, $\Delta S^{\#}$ = -6.0 cal mol^{-1} K^{-1}

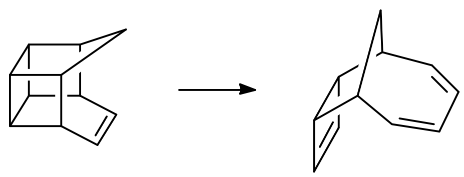
Method: in *n*-dodecane, double-walled cell (d = 5 cm), continuous monitoring of increase of E at 264 nm (cyclopentadiene).

Literature: Wolfgang Mauer, dissertation, University of Cologne 1978;
W. Grimme, W. Mauer, Ch. Sarter, *Angew. Chem. Int. Ed. Engl.* **1985,** 24, 331.

$C_{11}H_{12}$

Pentacyclo[5.4.0.0^{2,6}.0^{3,11}.0^{5,8}]undec-9-ene

(4+2)-Cycloreversion



T/ °C	150.1	154.0	159.8	164.25
$k/10^{-5}\ s^{-1}$	1.318	1.917	2.864	4.259

$\log k = 10.50 \pm 0.64 - (29.77 \pm 1.26)/2.303\ RT$; $R = 1.98\ 10^{-3}$ kcal mol^{-1} K^{-1}

$\Delta G^{\#} = 34.60$ kcal mol^{-1}, $\Delta H^{\#} = 28.92$ kcal mol^{-1}, $\Delta S^{\#} = -13.2$ cal mol^{-1} K^{-1}

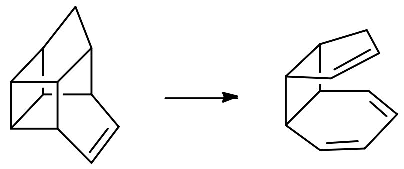
Method: in *n*-heptane, ampules in thermostat, glpc analysis.

Literature: Wolfgang Mauer, Diplomarbeit, University of Cologne 1975; Christian Sarter, Diplomarbeit, University of Cologne 1984; W. Grimme, W. Mauer, Ch. Sarter, *Angew. Chem. Int. Ed. Engl.* **1985,** *24*, 331.

$C_{11}H_{12}$

Pentacyclo[7.2.0.0^{2,6}.0^{3,11}.0^{5,10}]undec-7-ene

(4+2)-Cycloreversion



T/ °C	185.35	187.20	188.15	190.10
$k/10^{-4}\ s^{-1}$	0.830	0.973	1.08	1.25

$\log k = 13.44 \pm 0.76 - (36.8 \pm 1.6)/2.303\ RT; R = 1.98\ 10^{-3}$ kcal mol^{-1} K^{-1}

$\Delta G^{\#} = 35.83$ kcal mol^{-1}, $\Delta H^{\#} = 35.89$ kcal mol^{-1}, $\Delta S^{\#} = 0.1$ cal mol^{-1} K^{-1}

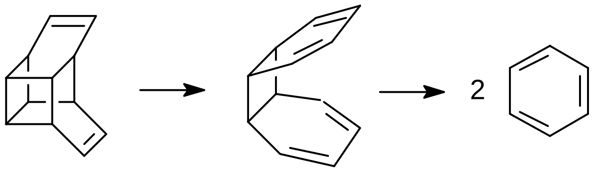
Method: in *n*-dodecane, ampules in thermostat, tetralin as internal standard, glpc analysis.

Literature: Wolfgang Mauer, Diplomarbeit, University of Cologne 1975;
W. Grimme, W. Mauer, Ch. Sarter, *Angew. Chem. Int. Ed. Engl.* **1985,** *24*, 331.

$C_{12}H_{12}$

Pentacyclo[6.4.0.0.^{2,5}0.^{3,12}0^{4,9}]dodeca-6,10-diene

(4+2) Cycloreversion



T/ °C	159	161.15	163	166.8	169	170.8	175	177.1	179.3
$k/10^{-4}$ s^{-1}	2.141	2.712	3.517	4.917	6.255	6.635	10.078	12.002	14.881

log k = 14.64 ± 0.43 - (36.17 ± 0.87)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 32.78 kcal mol^{-1}, $\Delta H^{\#}$ = 35.29 kcal mol^{-1}, $\Delta S^{\#}$ = 5.7 cal mol^{-1} K^{-1}

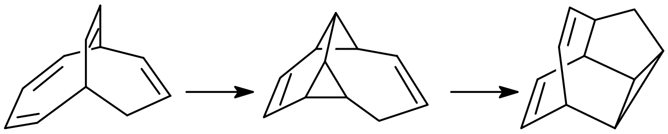
Method: in *n*-dodecane, *n*-decane as internal standard, ampules in thermostat, glpc analysis.

Literature: Hans Günter Köser, Diplomarbeit, University of Cologne 1978.

$C_{11}H_{12}$

Bicyclo[4.3.2]undecadeca-2,4,7,10-tetraene

(4+2)-Cycloaddition



T/ °C	77.24	79.59	84.42	89.38	94.21
$k/10^{-5}s^{-1}$	9.13	10.94	19.45	35.99	59.24

$\log k = 13.96 \pm 0.51 - (28.95 \pm 0.84)/2.303\ RT$; $R = 1.98\ 10^{-3}$ kcal mol^{-1} K^{-1}

$\Delta G^{\#} = 27.16$ kcal mol^{-1}, $\Delta H^{\#} = 28.24$ kcal mol^{-1}, $\Delta S^{\#} = 3.0$ cal mol^{-1} K^{-1}

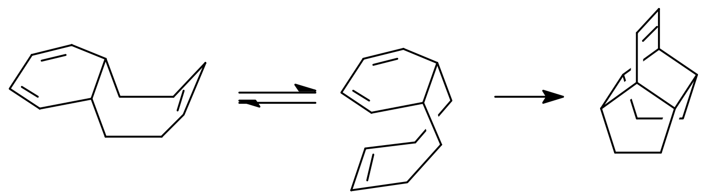
Method: in *n*-dodecane, double-walled cell (l = 5 cm), continuous monitoring of decrease of E at 293 nm.

Literature: Gerhard Wiechers, dissertation, University of Cologne 1987;
W. Grimme and G. Wiechers, *Tetrahedron Lett.*, **1987**, *28*, 6035.

$C_{12}H_{16}$

Bicyclo[6.4.0]dodecadeca-4,9,11-triene

(4+2)-Cycloaddition



T/ °C	50.34	55.17	59.86	64.97	70.21	75.04
$k/10^{-5}\ s^{-1}$	7.11	10.61	16.89	28.53	47.67	77.02

log k = 10.57 ± 0.33 - (21.84 ± 0.50)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 25.34 kcal mol^{-1}, $\Delta G^{\#}$ = 21.17 kcal mol^{-1}, $\Delta S^{\#}$ = -12.4 cal mol^{-1} K^{-1}

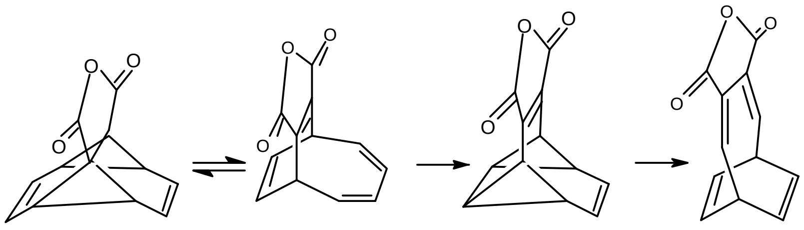
Method: in *n*-dodecane, double-walled cell (l = 5 cm), continuous monitoring of decrease of E at 285 nm.

Literature: Gerhard Wiechers, dissertation, University of Cologne 1987;
W. Grimme and G. Wiechers, *Tetrahedron Lett.*, **1987**, *28*, 6035.

$C_{12}H_8O_3$

Bicyclo[4.2.2]deca-2,4,7,9-tetraene-7,8-dicarboxylic anhydride

(4+2)-Cycloaddition



T/ °C	17.03	20.05	23.10	25.05
$k/10^{-5}\ s^{-1}$	3.40	6.10	8.06	10.7

$$\log k = 13.9 \pm 0.5 - (24.5 \pm 2.7)/2.303\ RT; \quad R = 1.98\ 10^{-3}\ \text{kcal mol}^{-1}\ \text{K}^{-1}$$

$\Delta G^{\#}$ = 23.0 kcal mol^{-1}, $\Delta H^{\#}$ = 23.9 kcal mol^{-1}, $\Delta S^{\#}$ = 3.1 cal mol^{-1} K^{-1}

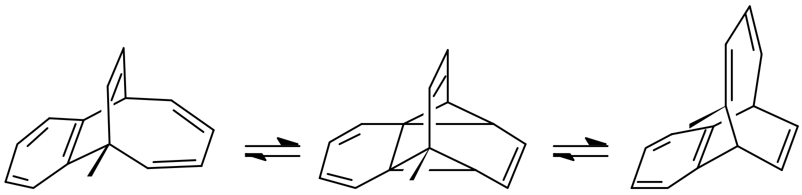
Method: in chloroform-d_1, sealed nmr-tube in thermostat, ^{1}H-nmr analysis

Literature: Hans-Jochem Riebel, dissertation, University of Cologne 1968;
W. Grimme, H. J. Riebel, E. Vogel, *Angew. Chem.* **1968,** *80*, 803.

$C_{15}H_{14}$

1-Methyl-7,*8*-benzobicyclo[4.2.2]deca-2,4,7,9-tetraene

reversible (4+2)-cycloaddition



T/ °C	231.13	240.27	251.63	260.39	271.23	280.77	290.73
$k_f + k_b/10^{-5}\ s^{-1}$	0.929	1.935	4.674	8.855	19.88	37.91	74.01

$\log (k_f + k_b) = 12.97 \pm 0.04 - (41.55 \pm 0.01)/2.303\ RT$; $R = 1.98\ 10^{-3}$ kcal mol^{-1} K^{-1}

$k_f / k_b = 13$ at 271 °C

$\Delta G^{\#}_f = 41.84$ kcal mol^{-1}, $\Delta H^{\#}_f = 40.47$ kcal mol^{-1} , $\Delta S^{\#}_f = -2.3$ cal mol^{-1} K^{-1}

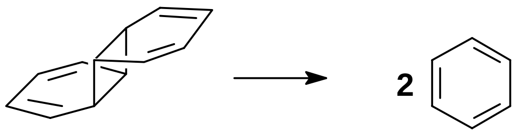
Method: in the gas phase, flask (100 l) in thermostat, glpc analysis.analysis

Literature: Thomas Grommes, dissertation, University of Cologne, 1991.
W. Grimme, Th. Grommes, W. R. Roth, R. Breuckmann, *Angew. Chem. Int. Engl*. **1992**, *104*, 867.

$C_{12}H_{12}$

Tricyclo[6.4.0.0^{2,7}]dodeca-3,5,9,11-tetraene

(2+2)-Cyloreversion



T/ °C	50.40	54.00	58.60	62.30	66.30	70.05	74.15
k/10^{-4} s^{-1}	1.375	2.048	3.378	5.290	8.023	12.26	18.51

log k = 12.76 ± 0.32 - (24.53 ± 0.88)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 24.66 kcal mol^{-1}, $\Delta H^{\#}$ = 23.87 kcal mol^{-1}, $\Delta S^{\#}$ = -2.4 cal mol^{-1} K^{-1}

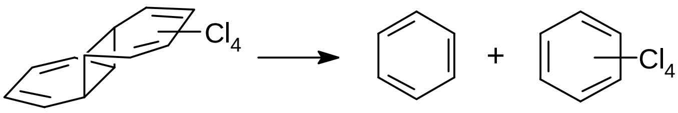
Method: in *n*-dodecane, continuous monitoring of decrease of E at 310 nm.

Literature: Ulrich Heinze, planned dissertation, University of Cologne 1986.

$C_{12}H_8Cl_4$

anti-3,4,5,6-Tetrachlorotricyclo[6.4.0.0^{2,7}]dodeca-3,5,9,11-tetraene

(2+2)-Cycloreversion



T/ °C	80.3	82.1	84.05	86.0	88.05	89.75	92.05
k/10^{-4} s^{-1}	1.090	1.388	1.666	2.231	2.647	3.041	3.956

log k = 13.20 ± 0.54 - (27.75 ± 0.88)/2.303 RT;   R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

ΔG$^{\#}$ = 27.21 kcal mol^{-1}, ΔH$^{\#}$ = 27.04 kcal mol^{-1}, ΔS$^{\#}$ = -0.5 cal mol^{-1} K^{-1}

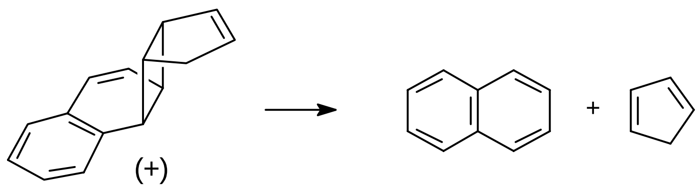
Method: in *n*-dodecane, double-walled cell (l = 5 cm), continuous monitoring of increase of E at 311 nm.

Literature: Gerd Zirkus, Dilomarbeit, University of Cologne 1983.

$C_{15}H_{14}$

8,9-Benzobicyclo[5.4.0.0^{2,6}]undeca-3,8,10-triene

(2+2)-Cyloreversion



T/ °C	118.95	121.9	127.1	129.9	131.9	134.6	136.85
k/10^{-5} s^{-1}	1.84	2.82	5.00	6.40	7.70	9.80	12.20

log k = 13.70 ± 0.55 - (33.03 ± 1.02)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 31.60 kcal mol^{-1}, $\Delta H^{\#}$ = 32.24 kcal mol^{-1}, $\Delta S^{\#}$ = 1.5 cal mol^{-1} K^{-1}

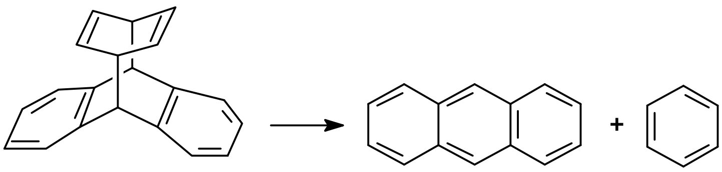
Method: in 95% ethanol, sealed ampules in thermostat, polarimetry at 365 nm.

Literature: Thomas Grommes, Diplomarbeit, University of Cologne 1987.

$C_{20}H_{16}$

3,4,11,12-Dibenzotricyclo[4.2.2.2^{2,5}]dodeca-3,7,9,11-tetraene

(4+4-Cycloreversion



T/ °C	75.60	78.15	80.95	83.30	85.50	87.45	89.30	90.60
k/10^{-5} s^{-1}	4.40	6.30	9.10	11.70	15.70	19.00	24.20	27.50

log k = 14.84 ± 0.48 - (30.62 ± 0.81)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

ΔG$^{\#}$ = 27.42 kcal mol^{-1}, ΔG$^{\#}$ = 29.91 kcal mol^{-1}, ΔS$^{\#}$ = 7.0 cal mol^{-1} K^{-1}

Method: in isooctane, ampules in thermostat, glpc analysis.

Literature: Hans Günter Köser, dissertation, University of Cologne 1986.
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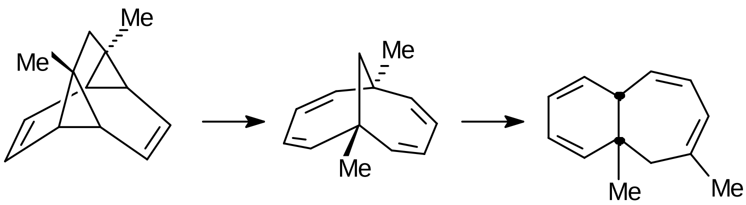
C$_{13}$H$_{16}$

1,6-Dimethyltetracyclo[4.4.1.0.^{2,10}0^{5,7}]undeca-3,8-diene

(4+4)-Cycloreversion followed by 5,5-sigmatropic migration



T/ °C	65	70	75
k/10^{-4}s^{-1}	1.783	3.130	5.424

log k = 13.08 ± 0.31 - (26.04 ± 0.69)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 25.68 kcal mol^{-1}, $\Delta H^{\#}$ = 25.36 kcal mol^{-1}, $\Delta S^{\#}$ = -1.0 cal mol^{-1} K^{-1}

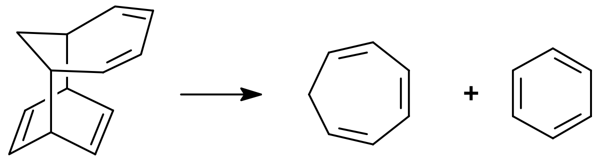
Method: in *n*-dodecane, double-walled cell (l = 5 cm), continuous monitoring of increase of E at 295 nm.

Literature: Ralf Busch, Diplomarbeit, University of Cologne 1981.

$C_{13}H_{14}$

Tricyclo[5.2.2.1^{2,7}]trideca-2,4,9,11-tetraene

(6+4)-Cyloreversion



T/ °C	80.0	82.0	83.9	84.8	85.95	88.0	89.0	95.0
$k/10^{-5}\ s^{-1}$	7.700	9.400	12.50	13.50	15.50	20.00	22.90	42.30

log k = 14.12 ± 0.64 - (29.46 ± 1.05)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 27.41 kcal mol^{-1}, $\Delta H^{\#}$ = 28.75 kcal mol^{-1}, $\Delta S^{\#}$ = 3.7 cal mol^{-1} K^{-1}

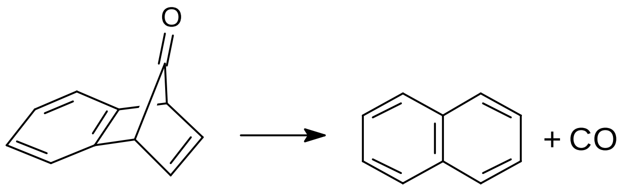
Method: in isooctane, ampules in thermostat, glpc analysis.

Literature: Lothar Schumachers, dissertation, University of Cologne 1986.

$C_{11}H_8O$

2,3-Benzobicyclo[2.2.1]hepta-2,5-dien-7-one

(4+2)-Cheletropic extrusion of CO



T/ °C	-32	-29	-23	-19	-16
$k/10^{-4}\ s^{-1}$	0.457	1.054	2.286	3.754	5.700

log k = 12.45 ± 1.25 - (18.45 ± 1.43)/2.303 RT;   R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 18.75 kcal mol^{-1}, $\Delta H^{\#}$ = 17.86 kcal mol^{-1}, $\Delta S^{\#}$ = -3.2 cal mol^{-1} K^{-1}

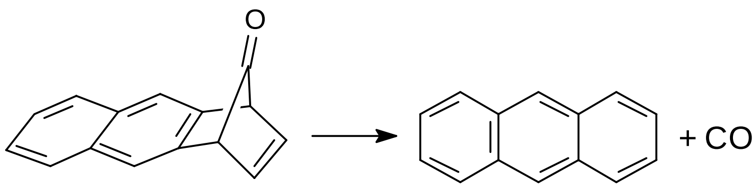
Method: in chloroform-d_1, sealed nmr-tube, ^{1}H-nmr analysis.

Literature: Andreas Güntherodt, Diplomarbeit, University of Cologne 1989.

$C_{15}H_{10}O$

2,3-Naphtho[b]bicyclo[2.2.1]hepta-2,5-dien-7-one

(4+2)-Cheletropic extrusion of CO



T/ °C	-9.0	-4.0	-1.0	4.0	8.0
$k/10^{-4}\ s^{-1}$	0.655	1.778	2.500	4.208	8.845

$\log k = 13.55 \pm 1.22 - (21.40 \pm 1.52)/2.303\ RT$; $R = 1.98\ 10^{-3}$ kcal mol^{-1} K^{-1}

$\Delta G^{\#} = 20.4$ kcal mol^{-1}, $\Delta H^{\#} = 20.9$ kcal mol^{-1}, $\Delta S^{\#} = 1.6$ cal mol^{-1} K^{-1}

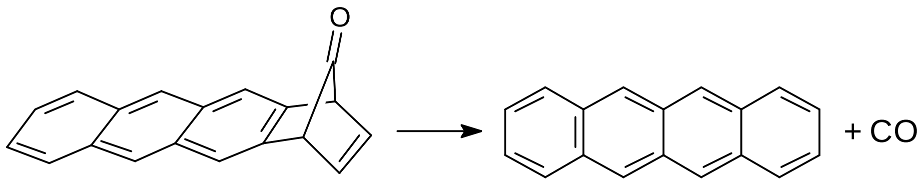
Method: in chloroform-d_1, sealed nmr-tube, ^{1}H-nmr analysis.

Literature: Andreas Güntherodt, dissertation, University of Cologne 1993.

$C_{19}H_{12}O$

2,3-Anthra[b]bicyclo[2.2.1]hepta-2,5-dien-7-one

(4+2)-Cheletropic extrusion of CO



T/ °C	3.45	6.00	8.41	10.48	12.27	14.48	16.41	18.21
$k/10^{-3}\ s^{-1}$	0.627	0.821	1.048	1.511	1.763	2.283	3.237	4.121

$\log k = 12.98 \pm 0.57 - (20.52 \pm 0.74)/2.303\ RT$; $R = 1.98\ 10^{-3}$ kcal mol^{-1} K^{-1}

$\Delta G^{\#} = 20.25$ kcal mol^{-1}, $\Delta H^{\#} = 19.96$ kcal mol^{-1}, $\Delta S^{\#} = -1.0$ cal mol^{-1} K^{-1}

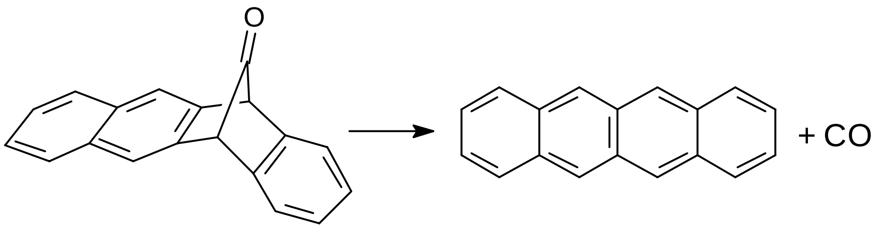
Method: in chloroform-d_1, sealed nmr-tube, ^{1}H-nmr analysis.

Literature: Andreas Güntherodt, dissertation, University of Cologne 1993.

$C_{19}H_{12}O$

5,12-Dihydro-5,12-oxomethanonaphthacene

(4+2)-Cheletropic extrusion of CO



T/ °C	52.0	54.1	56.8	59.0	61.5	63.7	66.1	68.8	71.5
$k/10^{-4}$ s^{-1}	0.877	1.007	1.321	1.710	2.072	2.630	3.532	5.327	6.644

log k = 11.85 ± 0.56 - (23.73 ± 0.86)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 25.25 kcal mol^{-1}, $\Delta H^{\#}$ = 23.07 kcal mol^{-1}, $\Delta S^{\#}$ = -6.5 cal mol^{-1} K^{-1}

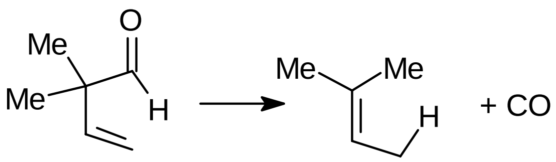
Method: in *n*-decane, double-walled cell (l = 5 cm), continuous monitoring of increase of E at 472 nm.

Literature: Michael W. Härter, Diplomarbeit, University of Cologne 1992.

$C_6H_{10}O$

2,2-Dimethylbut-3-enal

(4+2)-Cheletropic retro-ene-extrusion of CO



T/ °C	251.8	262.05	271.2	281.25	291.05	300.25	311.25	320.75	331.3
$k/10^{-4}\ s^{-1}$	0.161	0.244	0.654	1.318	2.512	4.628	9.004	15.711	29.36

$\log k = 12.38 \pm 0.07 - (41.25 \pm 0.17)/2.303\ RT$; $R = 1.98\ 10^{-3}$ kcal mol^{-1} K^{-1}

$\Delta G^{\#} = 43.03$ kcal mol^{-1}, $\Delta H^{\#} = 40.13$ kcal mol^{-1}, $\Delta S^{\#} = -5.1$ cal mol^{-1} K^{-1}

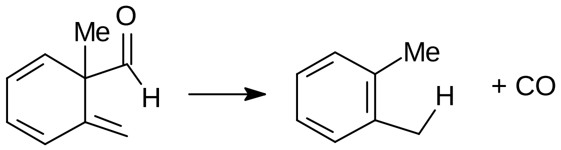
Method: in the gas phase, 4 Torr, flask (100 l) in thermostat, *n*-heptane as internal standard, glpc analysis.

Literature: Michael W. Härter, dissertation, University of Cologne 1995; W. Grimme, M. W. Härter, Ch. A. Sklorz, *J. Chem. Soc., Perkin Trans 2*, **1999**, 1959.

$C_9H_{10}O$

1-Methyl-6-methylenecyclohexa-2,4-diene-1-carbaldehyde

(4+2)-Cheletropic retro-ene-extrusion of CO



T/ °C	64.56	67.14	69.63	72.14	74.44	76.84	79.24	81.65	83.25
$k/10^{-3}$ s^{-1}	0.400	0.527	0.647	0.840	1.041	1.400	1.706	2.007	2.201

log k = 11.2 ± 0.33 - (22.41 ± 0.52)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 24.57 kcal mol^{-1}, $\Delta H^{\#}$ = 21.72 kcal mol^{-1}, $\Delta S^{\#}$ = -9.5 cal mol^{-1} K^{-1}

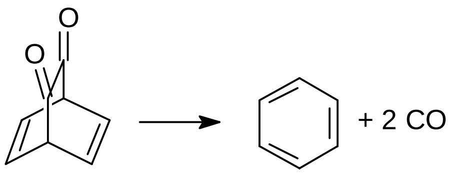
Method: in *n*-dodecane, double-walled cell (l = 5 cm), continuous monitoring of decrease of E at 305 nm.

Literature: Michael W. Härter, dissertation, University of Cologne 1995; W. Grimme, M. W. Härter, Ch. A. Sklorz, *J. Chem. Soc., Perkin Trans 2*, **1999**, 1959.

$C_8H_6O_2$

Bicyclo[2.2.2]octa-5,7-diene-2,3-dione

Extrusion of 2 CO via diradical



T/ °C	187.95	198.16	202.89	208.02	213.30	218.78	223.70	229.04	233.56	239.19
$k/10^{-4}\ s^{-1}$	0.103	0.269	0.412	0.654	1.015	1.614	2.444	3.729	5.270	8.231

$\log k = 14.01 \pm 0.04 - (40.07 \pm 0.08) / 2.303\ RT$; $R = 1.98\ 10^{-3}\ kcal\ mol^{-1}\ K^{-1}$

$\Delta G^{\#} = 37.83\ kcal\ mol^{-1}$, $\Delta H^{\#} = 39.11\ kcal\ mol^{-1}$, $\Delta S^{\#} = 2.6\ cal\ mol^{-1}\ K^{-1}$

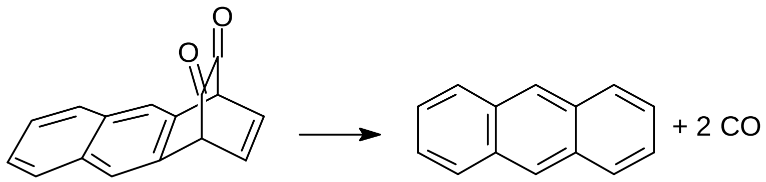
Method: in the gas phase, 1 Torr, flask (100 l) in thermostat, glpc analysis. A minor product C_7H_5O (ca. 5%) is formed with $\log k = 14.65 \pm 0.4 - (44.25 \pm 0.9) / 2.303\ RT$.

Literature: Andreas Kirst, dissertation, University of Cologne 1995.

$C_{16}H_{10}O_2$

5,6-Naphtobicyclo[2.2.2]octa-5,7-diene-2,3-dione

Extrusion of 2 CO via diradical



t/min	0	21	71	121	181	251	449	526	736	856	1202
% conversion	30.5	33.8	35.2	39.1	40.6	44.5	50.5	55.5	62.7	65.1	72.9

k = (1.26 + 0.04) 10^{-5} s^{-1} at 177 °C

$\Delta G^{\#}$ = 36.68 kcal mol^{-1}

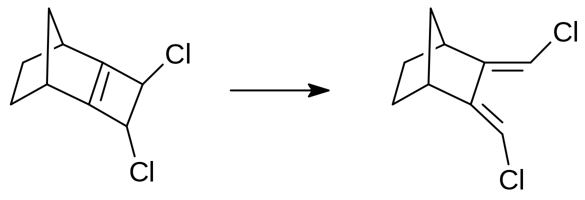
Method: in tetrachloroethane-d_2 , sealed nmr-tube, ^{1}H-nmr analysis.

Literature: Andreas Kirst, dissertation, University of Cologne 1995.

$C_9H_{10}Cl_2$

trans-3,4-Dichloro-tricyclo[4.2.1.0^{2,5}]non-2(5)-ene

4e-Electrocyclic reaction



T/ °C	30.62	35.86	40.41	45.65
$k/10^{-4}\ s^{-1}$	1.752	3.758	6.714	11.391

$$\log k = 13.56 \pm 0.84 - (24.05 \pm 1.19)/2.303\ RT; \qquad R = 1.98\ 10^{-3}\ kcal\ mol^{-1}\ K^{-1}$$

$\Delta G^{\#}$ = 22.98 kcal mol^{-1}, $\Delta H^{\#}$ = 23.43 kcal mol^{-1}, $\Delta S^{\#}$ = 1.4 cal mol^{-1} K^{-1}

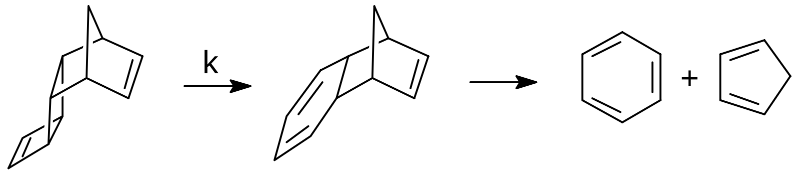
Method: in *n*-dodecane, double-walled cell (l = 5 cm), continuous monitoring of increase of E at 281 nm.

Literature: Ralf Busch, dissertation, University of Cologne 1984.

$C_{11}H_{12}$

Tetracyclo[6.2.1.0^{2,7}.0^{3,6}]undeca-4,9-diene

4e-Electrocyclic reaction



T/ °C	110.3	112.5	114.6	117.5	119.9	124.6	130.0
$k/10^{-5}\ s^{-1}$	4.052	5.102	6.422	8.426	11.03	18.25	30.23

log k = 13.61 ± 0.32 - (31.60 ± 0.60)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 30.35 kcal mol^{-1}, $\Delta H^{\#}$ = 30.82 kcal mol^{-1}, $\Delta S^{\#}$ = 1.2 cal mol^{-1} K^{-1}

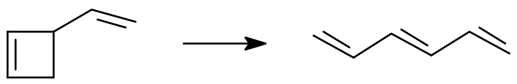
Method: in isooctane, ampules in thermostat, glpc analysis.

Literature: Hans Günther Köser, dissertation, University of Cologne 1986.

C_6H_8

3-Vinylcyclobutene

4e-Electrocyclic reaction



T/ °C	76.95	79.15	80.4	82.6	83.8	84.7	85.65	86.3
$k/10^{-4}$ s^{-1}	1.81	2.41	2.70	3.57	4.01	4.46	5.21	5.46

log k = 14.66 ± 0.33 - (29.49 ± 0.54)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 26.58 kcal mol^{-1}, $\Delta H^{\#}$ = 28.79 kcal mol^{-1}, $\Delta S^{\#}$ = 6.2 cal mol^{-1} K^{-1}

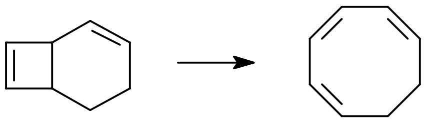
Method: in *n*-dodecane, double-walled cell (l = 5 cm), continuous monitoring of increase of E at 268 nm.

Literature: Ulrich Pinski, dissertation, University of Cologne 1979.

C_8H_{10}

Bicyclo[4.2.0]octa-2,7-diene

4e-Electrocyclic reaction



T/ °C	160.72	163.0	166.95	169.1	171.05	175.3
$k/10^{-5}\ s^{-1}$	5.20	6.68	9.57	11.09	13.64	19.31

log k = 13.07 ± 0.37 - (34.44 ± 0.74)/2.303 RT;   R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 34.22 kcal mol^{-1}, $\Delta H^{\#}$ = 33.57 kcal mol^{-1}, $\Delta S^{\#}$ = -1.5 cal mol^{-1} K^{-1}

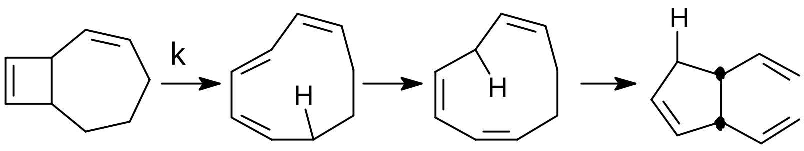
Method: in *n*-dodecane, ampules in thermostat, glpc analysis.

Literature: Ulrich Pinski, dissertation, University of Cologne 1979.

C_9H_{12}

Bicyclo[5.2.0]nona-2,8-diene

4e-Electrocyclic reaction



T/ °C	152.85	155.9	159.05	161.9	164.3
$k/10^{-5}\ s^{-1}$	4.25	5.71	7.60	9.24	12.43

log k = 12.87 ± 0.74 - (33.61 ± 1.45)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 33.77 kcal mol^{-1}, $\Delta H^{\#}$ = 32.76 kcal mol^{-1}, $\Delta S^{\#}$ = -2.4 cal mol^{-1} K^{-1}

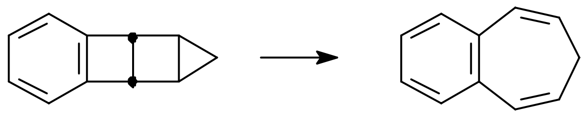
Method: in *n*-dodecane, ampules in thermostat, glpc analysis.

Literature: Ulrich Pinski, dissertation, University of Cologne 1979.

$C_{11}H_{10}$

anti-Benzotricyclo[3.2.0.0^{2,4}]hept-6-ene

4e-Electrocyclic reaction



T/ °C	44.96	49.79	54.65	59.20	64.45	69.14
k/10^{-4} s^{-1}	1.249	2.125	3.538	5.606	9.751	15.920

log k = 11.68 ± 0.13 - (22.69 ± 0.20)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 24.44 kcal mol^{-1}, $\Delta H^{\#}$ = 22.04 kcal mol^{-1}, $\Delta S^{\#}$ = -7.3 cal mol^{-1} K^{-1}

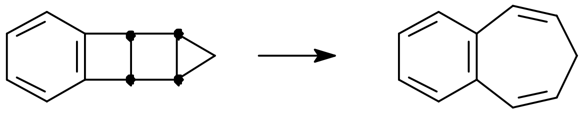
Method: in *n*-dodecane, double-walled cell (l = 5 cm), continuous monitoring of increase of E at 310 nm.

Literature: Ralf Busch, dissertation, University of Cologne 1984;
W. R. Roth, F.-G. Klärner, W. Grimme, H. G. Köser, R. Busch, B. Musculus, R Breuckmann, B. P.Scholz, H.-W. Lennartz, *Chem. Ber.* **1983**, *116*, 2717.

$C_{11}H_{10}$

syn-Benzotricyclo[3.2.0.0^{2,4}]hept-6-ene

4e-Electrocyclic reaction



T/ °C	99.02	109.24	119.01	129.03	139.50	149.47
$k/10^{-4}$ s^{-1}	0.571	1.690	4.640	12.20	32.40	80.4

log k = 13.72 ± 0.18 - (30.61 ± 0.30)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 29.15 kcal mol^{-1}, $\Delta H^{\#}$ = 29.82 kcal mol^{-1}, $\Delta S^{\#}$ = 1.7 cal mol^{-1} K^{-1}

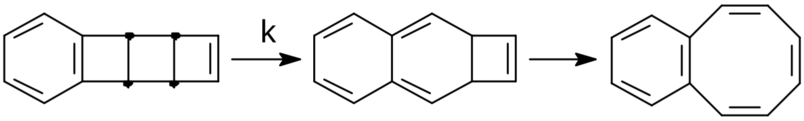
Method: in the gas phase, flask (100 l) in thermostat, glpc analysis.

Literature: Ralf Busch, dissertation, University of Cologne 1984:
W. R. Roth, F.-G. Klärner, W. Grimme, H. G. Köser, R. Busch, B.. Musculus, R. Breuckmann, B. P. Scholz, H.-W. Lennartz, *Chem. Ber*. **1983**, *116*, 2717.

$C_{12}H_{10}$

syn-Benzotricyclo[4.2.0.0^{2,5}]octa-3,7-diene

4e-Electrocyclic reaction



T/ °C	84.42	89.66	94.07
k/10^{-4} s^{-1}	1.383	2.385	3.743

log k = 12.59 ± 0.13 - (26.93 ± 0.70)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 27.41 kcal mol^{-1}, $\Delta H^{\#}$ = 26.21 kcal mol^{-1} , $\Delta S^{\#}$ = -3.3 cal mol^{-1} K^{-1}

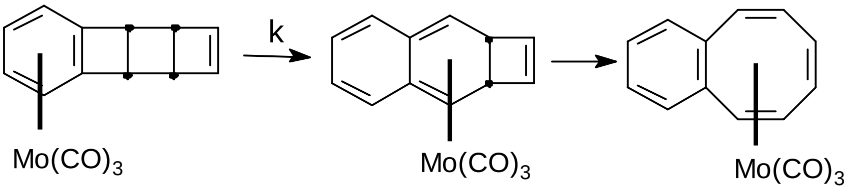
Method: in *n*-dodecane, double-walled cell (l = 5 cm), continuous monitoring of increase of E at 314 nm.

Literature: Ralf Busch, dissertation, University of Cologne 1984.

$C_{12}H_{10}Mo\ (CO)_3$

syn-Benzotricyclo[4.2.0.0^{2,5}]octa-3,7-diene-tricarbonyl molybdenum

4e-Electrocyclic reaction with haptotropy



t/h	1.58	2.67	3.67	4.67	5.67	6.67	7.67
% conversion	31	37	44	49	56	62	67

k = (3.51 + 0.05) 10^{-5} s^{-1} at T = 67.4 °C

$\Delta G^{\#}$ = 26.87 kcal mol^{-1}

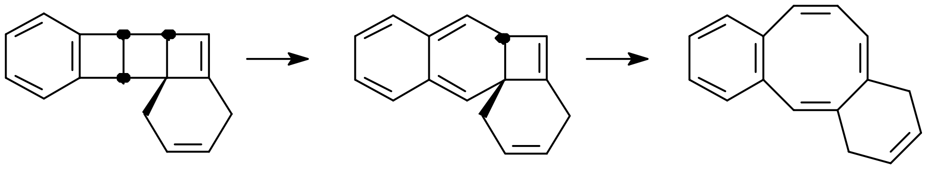
Method: in cyclohexane-d_{12}, sealed nmr-tube in thermostat, ^{1}H-nmr analysis.

Literature: Thomas Schmidt, dissertation, University of Cologne 1986.

$C_{16}H_{14}$

3,4-Benzotetracyclo[6.4.0.0^{1,6}.0^{2,5}]dodeca-3,7,10-triene

4e-Electrocyclic reaction



T/ °C	79.59	86.62	94.07
k/10^{-4} s^{-1}	2.980	6.464	13.26

log k = 12.92 ± 0.43 - (26.54 ± 0.71)/2.303 RT;   R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 26.46 kcal mol^{-1}, $\Delta G^{\#}$ = 25.83 kcal mol^{-1}, $\Delta S^{\#}$ = -1.8 cal mol^{-1} K^{-1}

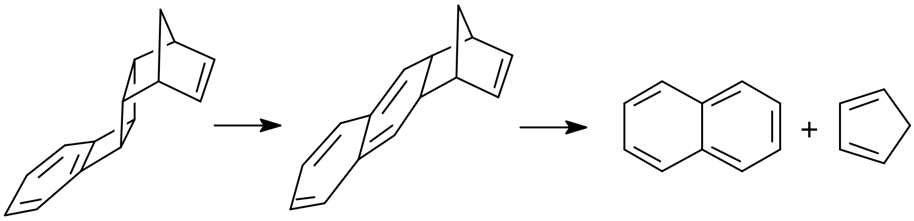
Method: in *n*-dodecane, double-walled cell (l = 5 cm), continuous monitoring of increase of E at 314 nm.

Literature: Ralf Busch, dissertation, University of Cologne 1984.

$C_{15}H_{14}$

4,5-Benzotetracyclo[6.2.1.0.^{2,7}0^{3,6}]undeca-4,9-diene

4e-Electrocyclic reaction



T/ °C	84.9	88.0	89.6	93.15
k/10^{-4} s^{-1}	1.415	2.092	2.500	3.471

log k = 13.44 ± 0.96 - (28.31± 1.58)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 27.38 kcal mol^{-1}, $\Delta H^{\#}$ = 27.59 kcal mol^{-1}, $\Delta S^{\#}$ = 0.6 cal mol^{-1} K^{-1}

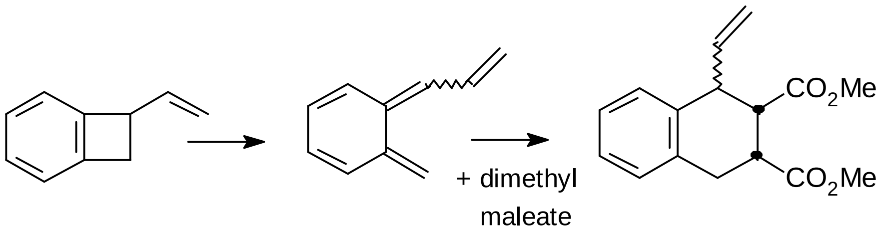
Method: in *n*-dodecane, double-walled cell (l = 5 cm), continuous monitoring of increase of E at 315 nm.

Literature: Peter Höner, Examensarbeit zur Ersten Staatsprüfung, Prüfungsamt Köln 1980; W. Grimme, P. Höner, H.-T. Kämmerling, R. Waldraff, J. Wirz, *Angew. Chem.* **1989**, *101*, 1390.

$C_{10}H_9$

7-Vinylbenzocyclobutene

4e-Electrocyclic reaction



T/ °C	102.0	106.0	108.0	110.0	114.0	116.0	120.0
$k/10^{-5}$ s^{-1}	2.31	3.51	4.78	5.72	8.37	11.08	15.82

log k = 13.74 ± 0.42 - (31.54 ± 0.74)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 30.07 kcal mol^{-1}, $\Delta H^{\#}$ = 30.78 kcal mol^{-1}, $\Delta S^{\#}$ = 1.8 cal mol^{-1} K^{-1}

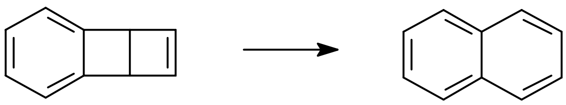
Method: in dimethyl maleate, *cis*-decalin as internal standard, ampules in thermostat, glpc analysis.

Literature: Ulrich Pinski, dissertation, University of Cologne 1979.

$C_{10}H_8$

Benzobicyclo[2.2.0]hexa-2,5-diene

4e-Electrocyclic reaction



T/ °C	55.8	57.65	58.40	59.5	61.40
$k/10^{-4}\ s^{-1}$	3.24	3.94	4.25	4.83	5.94

log k = 12.28 ± 0.42 - (23.74 ± 0.64)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 24.56 kcal mol^{-1}, $\Delta H^{\#}$ = 23.02 kcal mol^{-1}, $\Delta S^{\#}$ = -4.5 cal mol^{-1} K^{-1}

Method: in *n*-dodecane, double-walled cell (l = 5 cm), continuous monitoring of increase of E at 310 nm.

ΔH_{rx} = -59.4 ± 1.9 kcal mol^{-1}

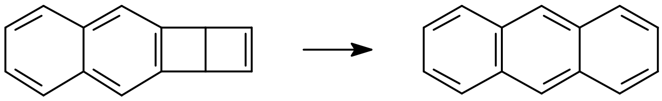
Method: Differential calorimetry in squalane solution from 17 - 137°C

Literature: W. Grimme, U. Heinze, *Chem. Ber.* **1978**, *111*, 2563.

$C_{14}H_{10}$

Naphthobicyclo[2.2.0]hexa-2,5-diene

4e-Electrocyclic reaction



T/ °C	50.0	55.0	60.0	65.0	70.0	75.0	80.0
$k/10^{-4}\ s^{-1}$	1.735	3.081	5.169	9.392	16.60	26.74	41.86

log k = 12.73 ± 0.19 - (24.38 ± 0.30)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 24.56 kcal mol^{-1}, $\Delta H^{\#}$ = 23.71 kcal mol^{-1} , $\Delta S^{\#}$ = -2.5 cal mol^{-1} K^{-1}

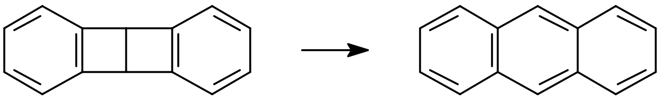
Method: in *n*-dodecane, double-walled cell (l = 5 cm), continuous monitoring of increase of E at 382 nm.

Literature: Wolfgang Pritschins, dissertation, University of Cologne 1982;
W. Pritschins, W. Grimme, *Tetrahedron Lett.* **1982**, *23*, 1151.

$C_{14}H_{10}$

Dibenzobicyclo[2.2.0]hexa-2,5-diene

4e-Electrocyclic reaction



T/ °C	25.10	29.93	34.90	40.00	44.69	49.52
k/10^{-4} s^{-1}	1.698	3.319	5.998	11.00	18.16	34.07

log k = 13.16 ± 0.23 - (23.10 ± 0.33)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 21.98 kcal mol^{-1}, $\Delta H^{\#}$ = 22.49 kcal mol^{-1} , $\Delta S^{\#}$ = -0.4 cal mol^{-1} K^{-1}

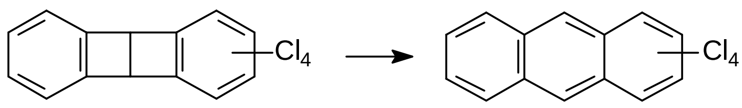
Method: in *n*-dodecane, double-walled cell (l = 5 cm), continuous monitoring of increase of E at 382 nm.

Literature: Wolfgang Pritschins, dissertation, University of Cologne 1982;
W. Pritschins,, W. Grimme, *Tetrahedron Lett*. **1982**, *23*, 1151.

$C_{14}H_6Cl_4$

Benzo-tetrachlorobenzo-bicyclo[2.2.0]hexa-2,5-diene

4e-Electrocyclic reaction



T/ °C	36.72	38.75	40.75	42.75	44.75	46.75	48.75
$k/10^{-4}\ s^{-1}$	5.26	6.95	8.83	11.05	14.98	18.36	23.45

$\log k = 14.07 \pm 0.26 - (24.59 \pm 0.37)/2.303\ RT$; $R = 1.98\ 10^{-3}$ kcal mol^{-1} K^{-1}

$\Delta G^{\#} = 22.78$ kcal mol^{-1}, $\Delta H^{\#} = 23.96$ kcal mol^{-1} , $\Delta S^{\#} = 3.7$ cal mol^{-1} K^{-1}

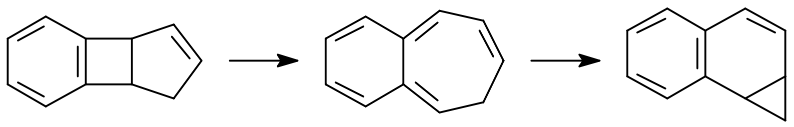
Method: in *n*-dodecane, double-walled cell (l = 5 cm), continuous monitoring of increase of E at 297 nm.

Literature: Wolfgang Pritschins, Diplomarbeit, University of Cologne 1982;
W. Pritschins,, W. Grimme, *Tetrahedron Lett*. **1979**, *20*, 4545.

$C_{11}H_{10}$

6,7-Benzobicyclo[3.2.0]hepta-2,6-diene

4e-Electrocyclic reaction



T/ °C	176.2	178.05	180.3	182.7	184.8	186.2	188.65	190.85
$k/10^{-5}\ s^{-1}$	1.35	1.69	2.01	2.63	3.35	3.45	4.36	5.60

log k = 14.21 ± 0.55 - (39.22 ± 1.16)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 36.65 kcal mol^{-1}, $\Delta H^{\#}$ = 38.31 kcal mol^{-1} , $\Delta S^{\#}$ = 3.6 cal mol^{-1} K^{-1}

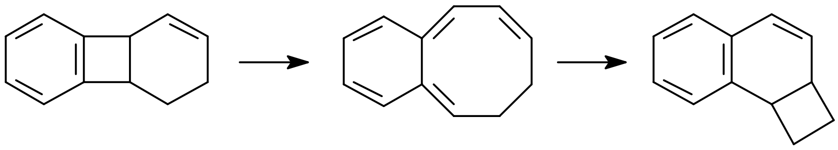
Method: in *n*-dodecane, tetralin as internal standard, ampules in thermostat, glpc analysis.

Literature: Ulrich Pinski, dissertation, University of Cologne 1979.

$C_{12}H_{12}$

7,8-Benzobicyclo[4.2.0]octa-2,7-diene

4e-Electrocyclic reaction



T/ °C	178.0	183.5	185.0	188.35	190.9	193.7
$k/10^{-5}\ s^{-1}$	3.59	5.74	6.75	8.96	10.79	13.78

log k = 12.92 ± 0.25 - (35.84 ± 0.52)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 35.96 kcal mol^{-1}, $\Delta H^{\#}$ = 34.93 kcal mol^{-1} , $\Delta S^{\#}$ = -2.3 cal mol^{-1} K^{-1}

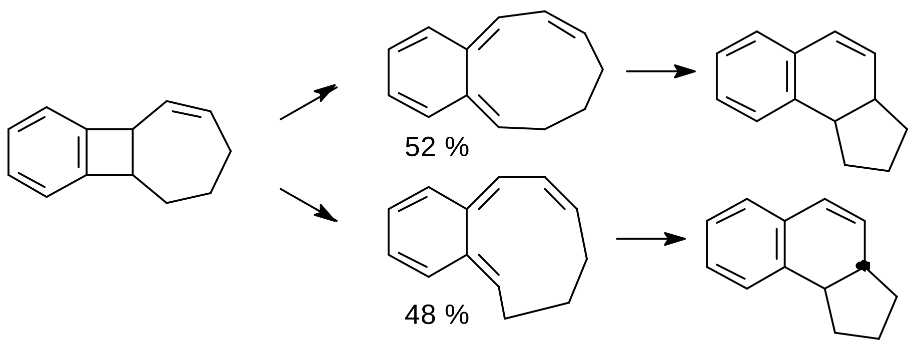
Method: in *n*-dodecane, tetralin as internal standard, ampules in thermostat, glpc analysis.

Literature: Ulrich Pinski, dissertation, University of Cologne 1979.

$C_{13}H_{14}$

8,9-Benzobicyco[5.2.0]deca-2,8-diene

4e-Electrocyclic reaction



T/ °C	173.0	176.2	178.1	180.0	182.35	183.0	186.0	188.2
$k/10^{-5}\ s^{-1}$	2.87	3.83	4.71	5.50	6.40	6.73	8.95	11.49

log k = 13.15 ± 0.50 - (36.12 ± 1.03)/2.303 RT; $R = 1.98\ 10^{-3}$ kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 35.76 kcal mol^{-1}, $\Delta H^{\#}$ = 35.22 kcal mol^{-1} , $\Delta S^{\#}$ = -1.2 cal mol^{-1} K^{-1}

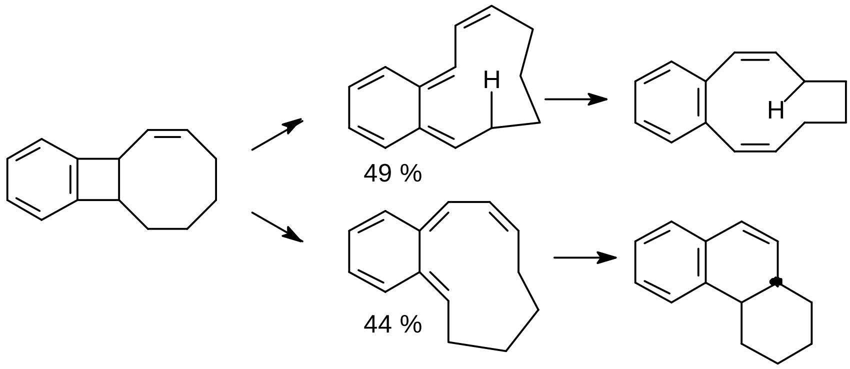
Method: in *n*-dodecane, ampules in thermostat, glpc analysis.

Literature: Ulrich Pinski, dissertation, University of Cologne 1979.

$C_{14}H_{16}$

9-Benzobicyco[6.2.0]deca-2,9-diene

4e-Electrocyclic reaction



T/ °C	147	150	154	155.45	158	164	167	170
$k/10^{-5}\ s^{-1}$	3.50	4.77	6.92	7.87	10.10	17.33	22.78	29.69

log k = 13.37 ± 0.06 - (34.27 ± 0.11)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 33.45 kcal mol^{-1}, $\Delta H^{\#}$ = 33.42 kcal mol^{-1}, $\Delta S^{\#}$ = -0.1 cal mol^{-1} K^{-1}

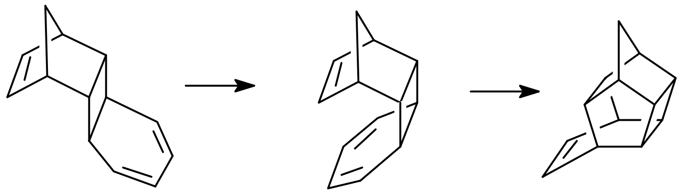
Method: in *n*-dodecane, ampules in thermostat, glpc analysis.

Literature: Ulrich Pinski, dissertation, University of Cologne 1979.

$C_{13}H_{14}$

Tetracyclo[8.2.1.0^{2,9}.0^{3,8}]trideca-4,6,11-triene

6e-Electrocyclic ring inversion followed by (4+2)-cycloaddition



T/ °C	180	190
k/10^{-5} s^{-1}	1.20	3.04

log k = 13.78 - (38.78)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 37.1 kcal mol^{-1}, $\Delta H^{\#}$ = 37.9 kcal mol^{-1}, $\Delta S^{\#}$ = 1.6 cal mol^{-1} K^{-1}

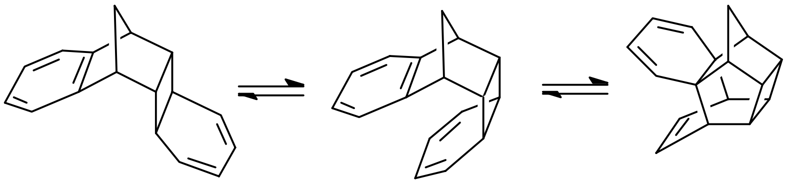
Method: in *o*-xylene, ampules in thermostat, glpc analysis.

Literature: Harold Pliskat, dissertation, University of Cologne 1996.

$C_{17}H_{16}$

11,12-Benzotetracyclo[8.2.1.0^{2,9}.0^{3,8}]trideca-4,6,11-triene

6e-Electrocyclic ring inversion followed by reversible (4+2)-cycloaddition



t/h	0	1	2	3	4	5	6	7	9.15	55
% conversion	4.69	17.00	25.45	33.73	41.00	47.22	51.79	56.62	62.11	77.88

$(k_f + k_b) = (4.74 \pm 0.07)\ 10^{-5}\ s^{-1}$, $k_f / k_b = 3.52$ at T = 200 °C, $k_f = 3.69\ 10^{-5}\ s^{-1}$

$\Delta G^{\#}_f = 37.59$ kcal mol^{-1}

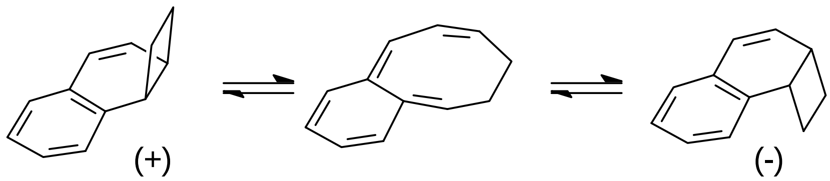
Method: in *o*-xylene, ampules in thermostat, glpc analysis.

Literature: Harold Pliskat, dissertation, University of Cologne 1996.

$C_{12}H_{12}$

2,3-Benzobicyclo[4.2.0]octa-2,4-diene

6e-Electrocyclic reaction



T/ °C	169.6	174.7	179.6	185.2	190.1	194.8
$k/10^{-5}$ s^{-1}	0.404	0.627	1.021	1.616	2.645	3.992

$\log k = 13.14 \pm 0.27 - (37.58 \pm 0.57)/2.303\ RT$; $R = 1.98\ 10^{-3}$ kcal mol^{-1} K^{-1}

$\Delta G^{\#} = 37.24$ kcal mol^{-1}, $\Delta H^{\#} = 36.69$ kcal mol^{-1}, $\Delta S^{\#} = -1.2$ cal mol^{-1} K^{-1}

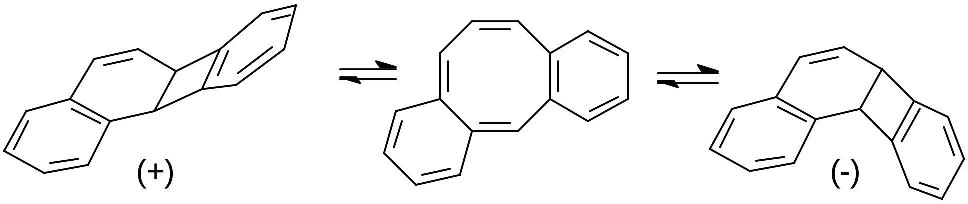
Method: in isooctane, sealed ampules in thermostat, polarimetry at 365 nm.

Literature: Thomas Grommes, dissertation, University of Cologne 1991.

$C_{16}H_{12}$

2,3;7,8-Dibenzobicyclo[4.2.0]octa-2,4,7-triene

6e-Electrocyclic reaction



t/min	60	95	120	145	180	210	270	330
% conversion	17.7	29.6	37.3	44.1	53.1	58.8	68.7	76.1

k = (7.67 ± 0.04) 10^{-5} s^{-1} at T = 100.6 °C

$\Delta G^{\#}$ = 28.98 kcal mol^{-1}

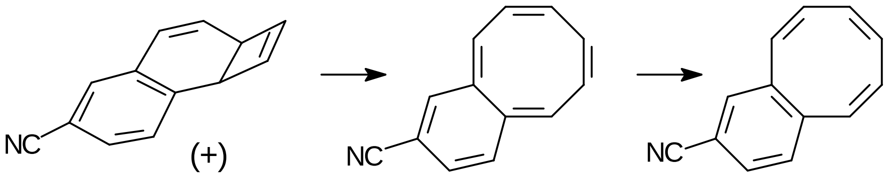
Method: in benzene, ampules in thermostat, polarimetry at 365 nm.

Literature: Thomas Schmidt, dissertation, University of Cologne 1986;
W. Grimme, J. Lex and T. Schmidt, *Angew. Chem.* **1987**, 99**,** 1277.

$C_{13}H_9N$

2,3-(2´-Cyanobenzo)bicyclo[4.2.0]octa-2,4,7-triene

6e-Electrocyclic reaction



t/min	30	60	120	180	270	450	540	630
% conversion	5.7	8.3	18.4	27.3	41.0	59.7	66.2	72.3

k = (3.47 ± 0.05) 10^{-5} s^{-1} at T = 110.3 °C

$\Delta G^{\#}$ = 30.35 kcal mol^{-1}

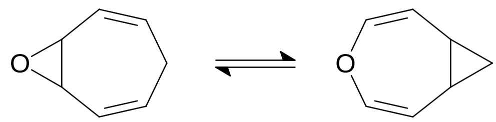
Method: in acetonitrile, ampules in thermostat, polarimetry at 365 nm.

Literature: Thomas Schmidt, dissertation, University of Cologne 1986;
W. Grimme, J. Lex and T. Schmidt, *Angew. Chem.* **1987**, *99*, 1277

C_7H_8O

8-Oxabicyclo[5.1.0]octa-2,5-diene

3,3-Sigmatropic rearrangement



$(k_f + k_b) = 400 \pm 25\ s^{-1}$; $k_f / k_b = 0.43 \pm 0.02$ at T = 80 °C

$\Delta G^{\#}_{f} = 17.37$ kcal mol^{-1},

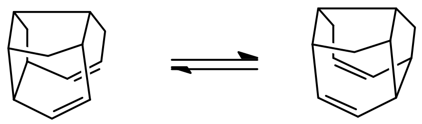
Method: from integral and coalescence of ^{1}H-NMR signals.

Literature: Helmut Klein, dissertation, University of Cologne 1976; H. Klein, W. Kursawa, W. Grimme, *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 580.

$C_{13}H_{16}$

Tetracyclo[7.3.1.0.^{2,8}0.^{4,12}]trideca-5,10-diene

Racemisation via *3,3-sigmatropic rearrangement*



(+) (–)

T/ °C	39.4	43.2	47.9	52.4	57.1
$k/10^{-5}\ s^{-1}$	2.16	3.44	7.56	13.33	25.35

log k = 15.55 ± 0.52 - (28.9 ± 0.76)/2.303 RT R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 24.89 kcal mol^{-1}

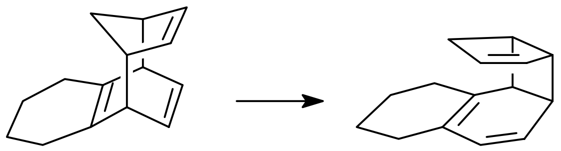
Method: in *n*-dodecane, double-walled cell (l = 10 cm), continuous monitoring of decrease of α at 365 nm

Literature: Susanne Krauthäuser, dissertation, University of Cologne 1996; W. Grimme, S. Krauthäuser, *Tetrahedron* **1997**, *53*, 9903.

$C_{15}H_{18}$

Tetracyclo[6.4.2.1^{9,12}.0^{2,7}]pentadeca-2(7),10,13-triene

3.3-Sigmatropic rearrangement



T/ °C	70.05	76.60	79.70	85.40	89.25
k/10^{-4} s^{-1}	0.97	2.20	3.12	5.92	8.96

log k = 14.18 ± 0.17 - (28.56 ± 0.27)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 26.60 kcal mol^{-1}, $\Delta H^{\#}$ = 28.20 kcal mol^{-1}, $\Delta S^{\#}$ = 4.0 cal mol^{-1} K^{-1}

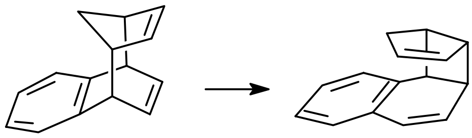
Method: in *n*-dodecane, double-walled cell (l = 5 cm), continuous monitoring of increase of E at 313.5 nm.

Literature: Gerd Reinhardt, dissertation, University of Cologne 1982.

$C_{15}H_{14}$

7,8-Benzotricyclo[4.2.2.1^{2,5}]undeca-3,7,9-triene

3.3-Sigmatropic rearrangement



T/ °C	81.2	83.2	85.3	87.5	89.3	91.3	92.6	94.5
$k/10^{-4}\ s^{-1}$	0.94	1.12	1.45	1.75	2.31	2.78	3.45	4.19

log k = 14.14 ± 0.38 - (29.49 ± 0.62)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 27.40 kcal mol^{-1}, $\Delta H^{\#}$ = 28.78 kcal mol^{-1}, $\Delta S^{\#}$ = 3.8 cal mol^{-1} K^{-1}

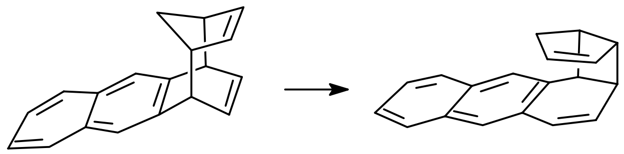
Method: in *n*-dodecane, double-walled cell (l = 5 cm), continuous monitoring of increase of E at 303 nm.

Literature: Gerd Reinhardt, dissertation, University of Cologne 1982.

$C_{19}H_{16}$

7,8-Naphthotricyclo[4.2.2.1^{2,5}]undeca-3,7,9-triene

3.3-Sigmatropic rearrangement



T/ °C	84.1	86.2	88.1	90.7	91.9	93.8
$k/10^{-4}$ s^{-1}	1.20	1.60	2.05	2.66	2.94	3.57

log k = 13.78 ± 0.67 - (28.91 ± 1.11)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 27.41 kcal mol^{-1}, $\Delta H^{\#}$ = 28.78 kcal mol^{-1}, $\Delta S^{\#}$ = 2.1 cal mol^{-1} K^{-1}

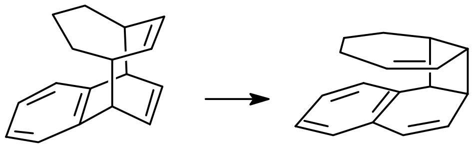
Method: in *n*-dodecane, double-walled cell (l = 5 cm), continuous monitoring of increase of E at 355 nm.

Literature: Gerd Reinhardt, dissertation, University of Cologne 1982.

$C_{17}H_{18}$

8,9-Benzotricyclo[5.2.2.2^{2,6}]trideca-8,10,12-triene

3,3-Sigmatropic rearrangement



t/min	30	60	90	120
% conversion	19.9	46.6	55.8	61.1

k = (1.31 ± 0.25) 10^{-4} s^{-1} at T = 101.2 °C

$\Delta G^{\#}$ = 28.63 kcal mol^{-1}

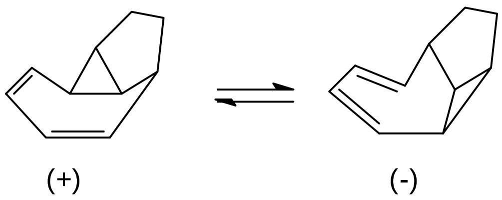
Method: in tetrachloromethane, sealed nmr-tube in thermostat, ^{1}H-nmr analysis.

Literature: Gerd Reinhardt, dissertation, University of Cologne 1982.

$C_{10}H_{12}$

Tricyclo[5.3.0.0^{2,10}]deca-3,5-diene

Racemisation via 1,5-sigmatropic rearrangement



T/ °C	178.95	183.75	188.0	193.05
k/10^{-5} s^{-1}	0.87	1.38	2.06	3.21

log k = (13.7 ± 0.2) - (38.8 ± 0.4)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 37.29 kcal mol^{-1}, $\Delta H^{\#}$ = 37.9 kcal mol^{-1}, $\Delta S^{\#}$ = 1.3 cal mol^{-1} K^{-1}

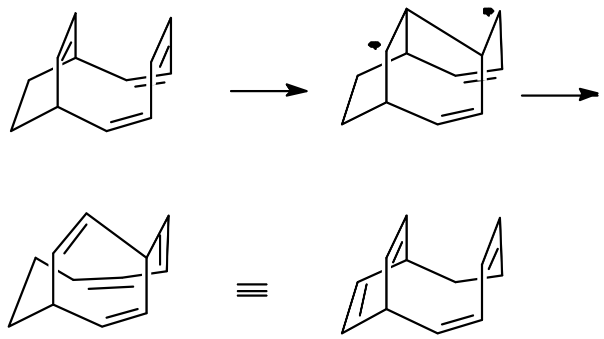
Method: in *n*-dodecane, ampules in thermostat, polarimetry at 407 nm.

Literature: Klaus Heger, dissertation, University of Cologne 1978; K. Heger, W. Grimme, *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 53.

$C_{12}H_{14}$

Bicyclo[6.2.2]dodeca-2,4,6,9-tetraene

1,5-Sigmatropic rearrangement



T/ °C	70.5	75.35	80.0	85.2	90.2	95.2
$k/10^{-4}\ s^{-1}$	0.785	1.263	2.165	3.684	6.336	9.384

log k = 12.31 ± 0.29 - (25.82 ± 0.47)/2.303 RT; $R = 1.98\ 10^{-3}$ kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 26.71 kcal mol^{-1}, $\Delta H^{\#}$ = 25.13 kcal mol^{-1}, $\Delta S^{\#}$ = -4.5 cal mol^{-1} K^{-1}

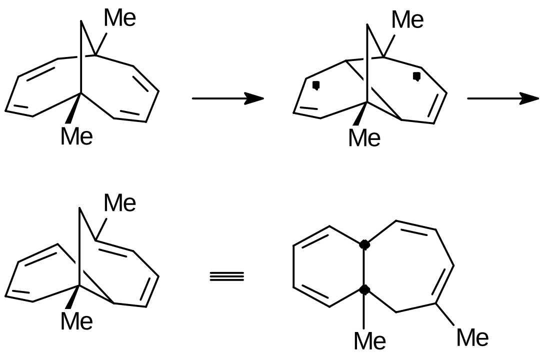
Method: in *n*-dodecane, double-walled cell (l = 5 cm), continuous monitoring of decrease of E at 298 nm.

Literature: Achim Bertsch, dissertation, University of Cologne 1986;
W. Grimme, A. Bertsch, H. Flock, T. Noack and S. Krauthäuser, *Synlett.* **1998**, 1175.

$C_{13}H_{16}$

1,6-Dimethylbicyclo[4.4.1]undeca-2,4,7,9-tetraene

1,5-Sigmatropic rearrangement



t/min	60	150	250	335	435	985	1385	1565
% conversion	13	20	27	33	39	60	70	74

k = (1.31 + 0.06) 10^{-5} s^{-1} at T = 26 °C

$\Delta G^{\#}$ = 24.11 kcal mol^{-1}

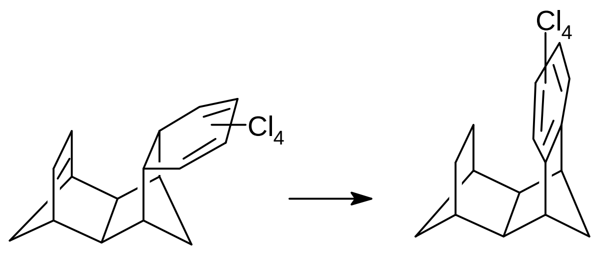
Method: in chloroform-d_1, sealed nmr-tube in thermostat, ^{1}H-nmr analysis.

Literature: Jürgen Frank, dissertation, University of Cologne 1979;
J. Frank, W. Grimme, J. Lex, *Angew Chem*. **1978**, *90*, 1002; *Angew. Chem. Int. Ed. Engl*. **1978**, *17*, 943.

$C_{16}H_{12}Cl_4$

3,4,5,6-Tetrachloro-pentacyclo[6.6.1.1.^{10,13}0.^{2,7}0$^{9.14}$]hexadeca-3,5,11-triene

6e-Dyotropic hydrogen transfer



T/ °C	40	42	44	46	48	50	52
$k/10^{-4}$ s^{-1}	5.176	6.097	7.399	9.011	10.95	13.21	15.70

log k = 9.99 ± 0.15 - (19.04 ± 0.23)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 26.71 kcal mol^{-1}, $\Delta H^{\#}$ = 18.41 kcal mol^{-1}, $\Delta S^{\#}$ = -14.9 cal mol^{-1} K^{-1}

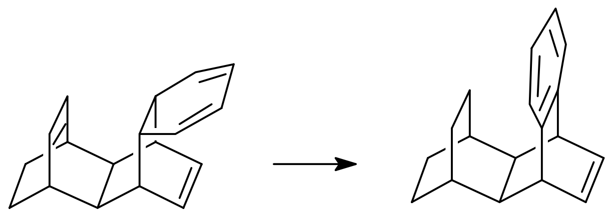
Method: in isooctane, double-walled cell (l = 5 cm), continuous monitoring of decrease of E at 315 nm.

Literature: Kathrin Pohl, dissertation, University of Cologne 1994.

$C_{18}H_{20}$

Pentacyclo[6.6.2.2.^{10,13}0.^{2,7}0$^{9.14}$]octadeca-3,5,11,15-tetraene

6e-Dyotropic hydrogen transfer



T/ °C	48	50	52	54	56	58	60
$k/10^{-4}\ s^{-1}$	4.644	5.449	6.501	7.958	9.398	11.12	13.48

log k = 9.56 ± 0.17 - (18.96 ± 0.25)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 23.86 kcal mol^{-1}, $\Delta H^{\#}$ = 18.31 kcal mol^{-} , $\Delta S^{\#}$ = -16.9 cal mol^{-1} K^{-1}

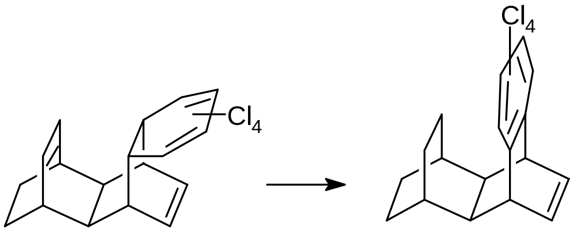
Method: in isooctane, double-walled cell (l = 5 cm), continuous monitoring of decrease of E at 283 nm.

Literature: Kathrin Pohl, dissertation, University of Cologne 1994;
W. Grimme, K. Pohl, J. Wortmann, D. Frowein, *Liebigs Ann*. **1996**, 1905.

$C_{18}H_{16}Cl_4$

3,4,5,6-Tetrachloro-pentacyclo[6.6.2.2.^{10,13}0.^{2,7}0$^{9.14}$]octadeca-3,5,11,15-tetraene

6e-Dyotropic hydrogen transfer



T/ °C	54	56	58	60	62	64	66	68
$k/10^{-4}\ s^{-1}$	3.72	4.28	5.36	6.89	7.86	9.84	11.69	13.72

$\log k = 10.78 \pm 0.33 - (21.29 \pm 0.50)/2.303\ RT$; $R = 1.98\ 10^{-3}$ kcal mol^{-1} K^{-1}

$\Delta G^{\#} = 24.44$ kcal mol^{-1}, $\Delta H^{\#} = 20.63$ kcal mol^{-1}, $\Delta S^{\#} = -11.4$ cal mol^{-1} K^{-1}

Method: in isooctane, double-walled cell (l = 5 cm), continuous monitoring of decrease of E at 315 nm.

$\Delta H_{rx} = -28.3 \pm 0.5$ kcal mol^{-1}

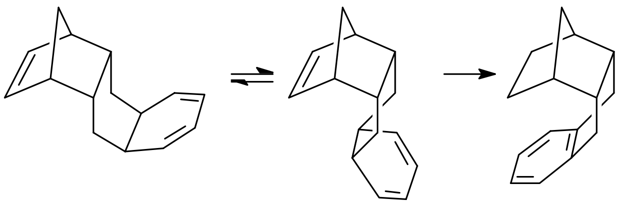
Method: Differential scanning calorimetry in squalane solution from 89 - 119°C

Literature: Kathrin Pohl, dissertation, University of Cologne 1994;
W. Grimme, K. Pohl, J. Wortmann, D. Frowein, *Liebigs Ann*. **1996**, 1905.

$C_{15}H_{18}$

Tetracyclo[10.2.1.0.^{2,11}0^{4,9}]pentadeca-5,7,13-triene

6e-Dyotropic hydrogen transfer



T/ °C	75	80	85	90
$k/10^{-5}\ s^{-1}$	1.51	2.28	3.76	6.00

$\log k = 9.77 \pm 0.82 - (23.25 \pm 1.03)/2.303\ RT$; $R = 1.98\ 10^{-3}$ kcal mol^{-1} K^{-1}

$\Delta G^{\#} = 28.29$ kcal mol^{-1}, $\Delta H^{\#} = 22.55$ kcal mol^{-1}, $\Delta S^{\#} = -16.1$ cal mol^{-1} K^{-1}

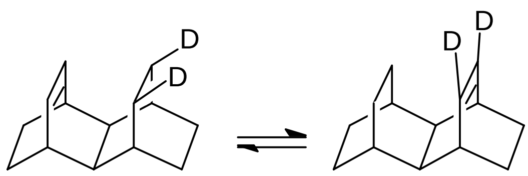
Method: in CCl_4/CD_3NO_2 4:1, sealed nmr-tube in thermostat, ^{1}H-nmr analysis..

Literature: Harold Pliskat, dissertation, University of Cologne 1996.

$C_{14}H_{18}D_2$

9,10-Dideuteriotetracyclo[6.2.2.2.^{3,6}0^{2,7}]tetradec-4-ene

6e-Dyotropic hydrogen transfer



t/h	0	6	13	20	35	54	74	100	200
% conversion	2.1	6.5	9.0	11.5	15.4	18.9	23.7	28.0	41.0

$(k_f + k_b) = (2.90 \pm 0.08)\ 10^{-6}\ s^{-1}$, $k_f / k_b = 0.695$ at T = 205 °C

$\Delta G^{\#}_f = 41.25\ kcal\ mol^{-1}$

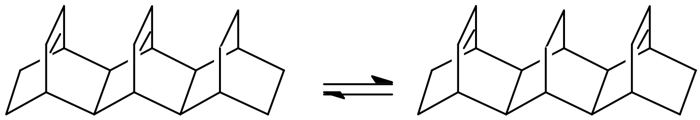
Method: in *o*-xylene-d_{10}, sealed nmr-tube in thermostat, ^{1}H-nmr analysis.

Literature: Kathrin Pohl, dissertation, University of Cologne 1994;.
W. Grimme, K. Pohl, J. Wortmann, D. Frowein, *Liebigs Ann*. **1996**, 1905.

$C_{20}H_{26}$

syn-Hexacyclo[6.6.2.2.^{3,6}2^{10,13}0.^{2,7}0^{9,14}]eicosa-4,15-diene

6e-Dyotropic hydrogen transfer



T/ °C	244.93	254.96	264.68	275.25	285.51	294.94	305.26
k_f /10^{-4} s^{-1}	0.5729	1.1103	2.1444	4.1164	7.7152	14.0346	23.0339
k_b /10^{-4} s^{-1}	0.9490	1.890	3.7439	7.3162	13.9543	25.7085	42.5344
k_f / k_b	0.6037	0.5875	0.5728	0.5627	0.5529	0.5459	0.5410

$\log k_f = 11.31 \pm 0.13 - (36.88 \pm 0.32)/2.303\ RT$; $R = 1.98\ 10^{-3}$ kcal mol^{-1} K^{-1}

$\log k_b = 11.69 \pm 0.14 - (37.96 \pm 0.36)/2.303\ RT$; $R = 1.98\ 10^{-3}$ kcal mol^{-1} K^{-1}

$\log (k_f / k_b) = -(3.11 \pm 0.13)/2.303\ R + (1086 \pm 69)/2.303\ RT$; R= 1.98 cal mol^{-1} K^{-1}

$\Delta G^{\#}_f = 41.26$ kcal mol^{-1}, $\Delta H^{\#}_f = 35.79$ kcal mol^{-1}, $\Delta S^{\#} = -10.0$ cal mol^{-1} K^{-1}

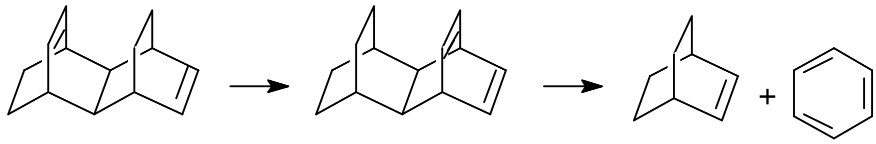
Method: in the gas phase, flask (100 l) in thermostat, glpc analysis.

Literature: Kathrin Pohl, dissertation, University of Cologne 1994;
W. Grimme, K. Pohl, J. Wortmann, D. Frowein, *Liebigs Ann*. **1996**, 1905

$C_{14}H_{18}$

as-Tetracyclo[6.2.2.2.^{3,6}0^{2,7}]tetradeca-4,9-diene

6e-Dyotropic hydrogen transfer



T/ °C	251.33	262.65	271.33	281.60
$k/10^{-5}\ s^{-1}$	1.714	3.745	6.795	13.216

log k = 11.51 ± 0.07 - (39.08 ± 0.16)/2.303 RT; R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 43.02 kcal mol^{-1}, $\Delta H^{\#}$ = 38.01 kcal mol^{-} , $\Delta S^{\#}$ = -9.0 cal mol^{-1} K^{-1}

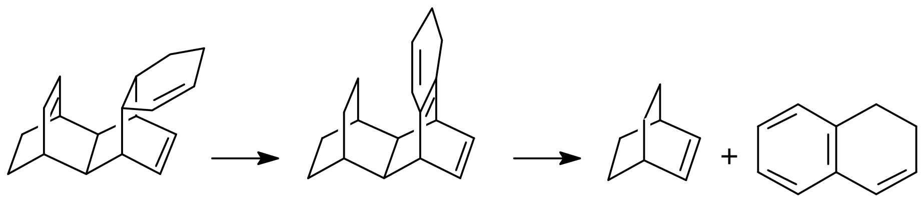
Method: in the gas phase, flask (100 l) in thermostat, glpc analysis.

Literature: Ulrich Burkert, Diplomarbeit, University of Cologne 1995.

$C_{18}H_{22}$

Pentacyclo[6.6.2.2.^{3,6}0.^{2,7}0^{9,14}]octadeca-4,10,15-triene

6e-Dyotropic hydrogen transfer



t/min	230	1240	1577	2557	2937	3830	4240
% conversion	5.21	29.09	29.67	47.40	51.09	60.65	65.60

$k = (4.13 \pm 0.1)\ 10^{-6}\ s^{-1}$ at t = T = 144 °C

$\Delta G^{\#} = 34.85$ kcal mol^{-1}

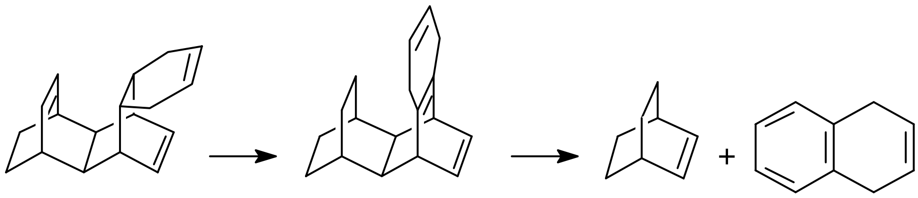
Method: in xylene-d_{10}, sealed nmr-tube in thermostat, ^{1}H-nmr analysis.

Literature: Björn Ewig, dissertation, University of Cologne 1998.

$C_{18}H_{22}$

Pentacyclo[6.6.2.2.^{3,6}0.^{2,7}0^{9,14}]octadeca-4,11,15-triene

6e-Dyotropic hydrogen transfer



t/min	2435	5105	7980	10620	13140	17100	21240	25380
% conversion	9.17	21.59	32.18	41.21	50.68	60.65	69.78	75.45

k = (9.49 ± 0.19) 10^{-7} s^{-1} at = T =144 °C

$\Delta G^{\#}$ = 36.06 kcal mol^{-1}

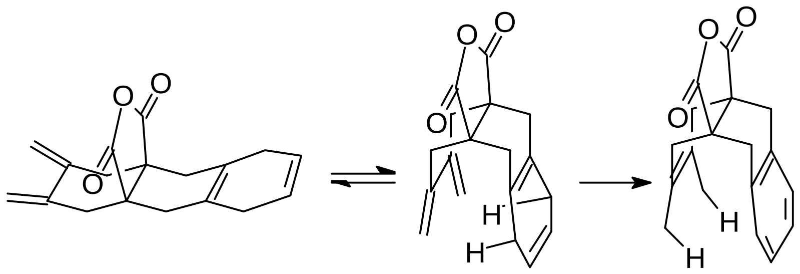
Method: in xylene-d_{10}, sealed nmr-tube in thermostat, ^{1}H-nmr analysis.

Literature: Björn Ewig, dissertation, University of Cologne 1998.

$C_{18}H_{18}O_3$

2,3-Bis(methylene)-1,2,3,4,4a,5,8,9,9a,10-decahydroanthracene-4a,9a-dicarboxylic anhydride

10e-Dyotropic hydrogen transfer



T/ °C	160	165	170	174.8	180	185
$k/10^{-5}s^{-1}$	1.82	2.12	3.32	5.11	7.60	12.62

log k = 11,04 ± 1.05 - (31.43 ± 2.14)/2.303 RT;   R = 1.98 10^{-3} kcal mol^{-1} K^{-1}

$\Delta G^{\#}$ = 35.36 kcal mol^{-1}, $\Delta H^{\#}$ = 30.55 kcal mol^{-1}, $\Delta S^{\#}$ = -10.8 cal mol^{-1} K^{-1}

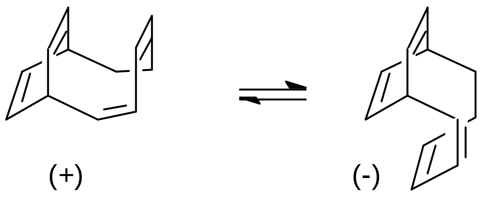
Method: in isooctane, sealed ampules in thermostat, monitoring of increase of E at 295 nm.

Literature: Heinz Geich, Diplomarbeit, University of Cologne 1991;
H. Geich, W. Grimme, K. Proske, *J. Am. Chem. Soc.* **1992**, *114*, 1492.

$C_{12}H_{14}$

Bicyclo[6.2.2]dodeca-2,4,6,9-tetraene

Racemization via *ring inversion*



T/ °C	-6.4	-2.5	1.1	6.4	10.8
$k/10^{-4}\ s^{-1}$	0.871	1.670	2.863	5.274	8.090

$\log k = 11.85 \pm 0.82 - (19.36 \pm 1.03)/2.303\ RT$; $R = 1.98\ 10^{-3}$ kcal mol^{-1} K^{-1}

$\Delta G^{\#} = 20.50$ kcal mol^{-1}, $\Delta H^{\#} = 18.81$ kcal mol^{-1}, $\Delta S^{\#} = -6.1$ cal mol^{-1} K^{-1}

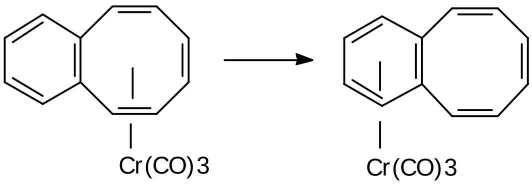
Method: in *n*-hexane, double-walled cell (l = 10 cm), continuous monitoring of decrease of α at 365 nm; $\alpha_0/\alpha = \exp(2kt)$.

Literature: Susanne Krauthäuser, dissertation, University of Cologne 1996; W. Grimme, A. Bertsch, H. Flock, T. Noack, S. Krauthäuser, *Synlett*. **1998**, 1175.

$C_{12}H_{10}Cr(CO)_3$

Benzocyclooctatetraene-5,6,7,8,9,10 -η_6-tricarbonyl-chromium

6e-Haptotropic reaction



t/min	30	90	150	210	370
% conversion	5.7	52.1	73.7	86.7	92.1

k = (1.65 ± 0.5) 10^{-4} s^{-1} at T = 125.6 °C

$\Delta G^{\#}$ = 30.36 kcal mol^{-1}

Method: in cyclohexane-d_{12}, sealed nmr-tube in thermostat, ^{1}H-nmr analysis.

Literature: Thomas Schmidt, dissertation, University of Cologne 1986.

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