Thermal Isomerisation of Substituted Semibullvalenes and Cyclooctatetraenes – A Kinetic Study

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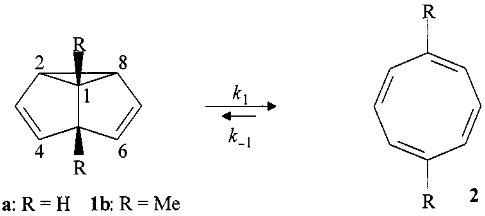
Whereas 1,5-dimethylsemibullvalene (**1b**) equilibrates with 1,5-dimethylcyclooctatetraene (**2b**), the semibullvalene-2,6-dicarbonitriles **13** rearrange irreversibly to afford mixtures of the isomeric cyclooctatetraene-1,5-dicarbonitriles **14** and **15**. Arrhenius and Eyring parameters of these thermal isomerisation reactions have been determined for the gas phase (**1b** ⇌ **2b**) and [D$_6$]benzene solutions (**1b** ⇌ **2b**, **13** → **14** + **15**). Furthermore, the activation parameters of the known rearrangement of octamethylcyclooctatetraene (**3**) to octamethylsemibullvalene (**4**) have been determined. – The data for these compounds, together with those for related compounds previously reported in the literature, show that substituents not only influence the relative stabilities of the semibullvalene and cyclooctatetraene systems but also the height of the energy barrier for their interconversion. Those substituents that lower the barrier toward the degenerate Cope rearrangement of semibullvalenes simultaneously accelerate their rearrangement to cyclooctatetraenes thus limiting the thermal stability of the former.

The 21 members of the (CH)$_8$ hydrocarbon family are interrelated through a complex multitude of thermal and/or photochemical transformations.[2–4] One of the most thoroughly studied is the interconversion of the parent hydrocarbons semibullvalene (**1a**) and cyclooctatetraene (**2a**). Martin, Urbanek, and Walsh demonstrated that these hydrocarbons equilibrate thermally in the gas phase at 270–360 °C and that the former is less stable than the latter by only 10 kJ mol^{-1}. A kinetic study in the temperature range of 200–240 °C afforded the activation parameters.[5] Equilibration of cyclooctatetraene in the temperature range of 400–700 °C followed by trapping of the mixture at −196 °C yielded semibullvalene (5%) besides bicyclo[4.2.0]-octa-2,4,7-diene and small amounts of a dihydropentalene.[6]

Less is known about the interconversion of *substituted* semibullvalenes and cyclooctatetraenes. As early as 1962, Criegee and co-workers observed the thermal rearrangement at 240 °C of octamethylcyclooctatetraene (**3**) to afford an isomer[7a] which was later recognized as octamethylsemibullvalene (**4**).[7b] Zimmerman and Iwamura found that 1,3,5,7-tetramethylcyclooctatetraene rearranged very slowly on heating at 250 °C to yield mainly 1,3,5,7-tetramethylsemibullvalene besides traces of an isomer, which was tentatively assigned the structure of 2,4,6,8-tetramethylsemibullvalene.[8] Subsequently, flash vacuum pyrolysis of 1,3- and 1,5-dimethylsemibullvalene (**1b**)[9] and of several 1,5-bridged semibullvalenes[10] was exploited by Paquette and co-workers as a preparative route to substituted cyclooctatetraenes. This technique was also adapted by Müllen and co-workers for the conversion of 1,5-dimethyl-3,7-diphenylsemibullvalene[11] and dimethyl 1,5-dimethylsemibullvalene-3,7-dicarboxylate[12] into substituted cyclooctatetraenes. Heating of 1,2,3,8-tetrakis(trifluoromethyl)cyclooctatetraene at 170–180 °C slowly yielded semibullvalene isomers that had the trifluoromethyl groups at the 3,4,5,6 and 2,3,4,5 positions. The former equilibrated with the precursor cyclooctatetraene and both were eventually converted into the 2,3,4,5-substituted semibullvalene on prolonged heating.[13] Substituted benzocyclooctatetraenes undergo thermal rearrangement to benzosemibullvalenes.[14] Theoretical aspects of the semibullvalene ⇌ cyclooctatetraene interconversion have been considered by Iwamura.[15]



1a: R = H **1b**: R = Me

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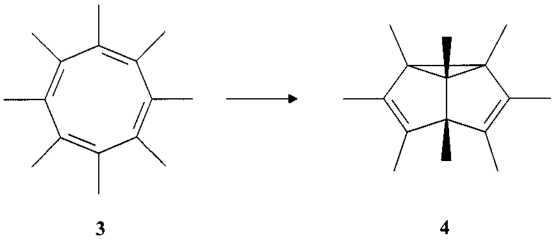

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While the semibullvalene → cyclooctatetraene rearrangement has been useful as a welcome access to substituted cyclooctatetraenes in some of these instances, the contrary is true in studies focussed on *thermally labile* semibullvalenes, e.g. the tetraester **5** which slowly rearranges to the cyclooctatetraenetetracarboxylate **6** at temperatures as low as 5 °C.[16] A kinetic study of this isomerisation was per-

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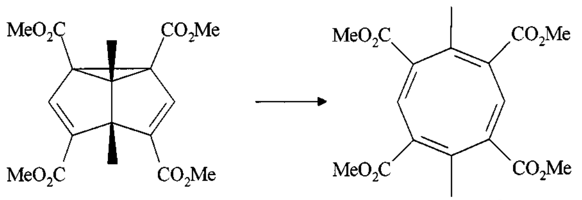
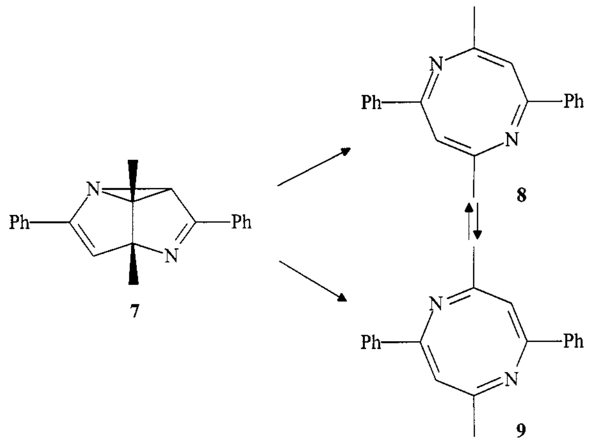
formed for carbon tetrachloride solutions in the temperature range 65−85°C.[17] Likewise, the 2,6-diazasemibullvalene **7** rearranged quantitatively into a thermally equilibrated mixture of the 1,5-diazocines **8** and **9** (2:3) within eight hours at 90°C. The 4-bromo and the 4,8-dibromo derivatives of **7** rearranged even faster yielding exclusively 1,5-diazocines corresponding to **9**.[11] The semibullvalene → cyclooctatetraene isomerisation clearly restricts the substitution pattern for semibullvalenes that are to be isolated under normal conditions. Instructive examples for this limitation may be found in the work of Gompper et al. who obtained 1,3,5,7-tetrazocines instead of the sought-for 2,4,6,8-tetraazasemibullvalenes.[18] On the basis of the knowledge accumulated so far, it appears that the rates of the degenerate Cope rearrangements roughly parallel those of the semibullvalene → cyclooctatetraene isomerisations. With a view of defining the factors that lower the energy barrier toward the latter process, we embarked on a kinetic study of the thermal isomerisation of substituted semibullvalenes, viz. **1b**, and the semibullvalene-2,6-dicarbonitriles **13a** and **b**. Furthermore, we measured the rates of the rearrangement of Criegee's octamethylcyclooctatetraene (**3**) to octamethylsemibullvalene (**4**) for the gas phase and solution.



5 **6**



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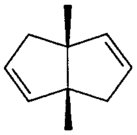
Methods and Results

The semibullvalenes **1b**,[19] **13a**,[20] **b**,[21] and **17**[22] used in this study were available from previous work. 1,5-Dimethylcyclooctatetraene (**2b**) has been synthesized from **1b** by flash vacuum pyrolysis.[9b] In view of the rapid, complex isomerisation and decomposition reactions in the gas phase at temperatures around 400°C and above, reported for dimethylcyclooctatetraenes,[23] one might suspect that these processes might more or less interfere with the planned kinetic study at lower temperatures. Therefore, the purity of the starting materials was of crucial importance and hence scrutinised by means of high-resolution capillary gas chromatography and high-field proton spectroscopy.

Recently, Askani's synthesis of 1,5-dimethylsemibullvalene (**1b**) was optimised and adapted to a larger scale.[24] Because this synthesis inevitably affords small amounts of 1,5-dimethylcyclooctatetraene (**2b**) as by-product, even at temperatures as low as 100−105°C, both isomers **1b** and **2b** were separated and purified by repeated preparative gas chromatography. The sample of **1b** that was eventually employed in the isomerisation experiments had a purity of better than 99%. Less than 0.1% of **2b** was present besides small amounts of the 1,5-dimethylbicyclo[3.3.0]octadienes **10** and **11**,[24] which served as internal standard.

The purified sample of **2b** was free of any trace of **1b** but still contained 1% of an isomer which appeared at shorter retention time in the gas chromatogram. The molecular mass of this compound was established by mass spectrometry. We tentatively assign the bicyclic structure **12** to this isomer. The assignment is supported by the observation that small amounts appear simultaneously with **2b** on thermal isomerisation of **1b**. The equilibration with bicyclo[4.2.0]octa-2,4,7-trienes is well known for the parent cyclooctatetraene (**2a**)[6][25] and a number of substituted cyclooctatetraenes.[7c,9b,10b,25a,26,27] In fact, prolonged treatment of **2b** with tetracyanoethylene in boiling ethyl acetate afforded the [4 + 2]cycloadduct of **12**, apparently by way of in situ trapping of **12**, which is formed by disrotatory ring closure of **2b**.[9b] In addition to the putative isomer **12**, traces (0.02−0.04%) of three compounds made their appearance shortly after the GC signal of **2b**. The high-field proton spectrum of **2b** exhibited two additional singlets close to the methyl signal of **2b**. They were little more intense than its carbon-13 satellites. Probably, these unknown impurities are isomeric dimethylcyclooctatetraenes, formation of which has been observed on flash vacuum pyrolysis of **2b**.[23] Only a poorly resolved 60-MHz proton spectrum has been reported for **2b**.[9b] Analysis of the high-field proton spectrum now yielded spectral parameters in accord with those of the parent cyclooctatetraene (**2a**)[28] and allowed the assignment of the carbon-13 signals with the help of a heteronuclear multiple quantum coherence spectrum.



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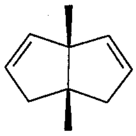

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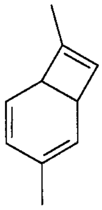

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The methyl groups at C-1 and C-5 of **2b** may be expected to stabilise the cyclooctatetraene system by hyperconjugation. On the other hand, steric interaction of the two methyl groups of **1b** increases the strain inherent in the semibullvalene skeleton.[29] Considering the small amount of semibullvalene (**1a**) in the equilibrium with the parent cyclooctatetraene (**2a**),[5] we were surprised to find that the methyl groups did *not* shift the balance completely towards **2b**. Thus, detection of **1b** was still possible in the thermal equilibrium with **2b**, which could be established by approach from both sides. Towards this end, the interconversion of **1b** and **2b** in [D$_6$]benzene or 3-methylpentane solution in the temperature range 160−220°C was monitored by high-resolution gas chromatography and 600-MHz proton spectra (Figure 1). Thermolysis of **1b** yielded **2b** almost exclusively. Only very small signals of unknown side products appeared slowly in the gas chromatograms and proton spectra. Even after complete equilibration, the proton signals of these unidentified compounds were still less intense than the carbon-13 satellites of the methyl signal of the main product **2b** and hence were neglected in the analysis. The temperature dependence of the equilibrium constant K = [**2b**]/[**1b**] in that range obeyed the linear relationship of Equation 1 displayed in Figure 2. The spread of the data points and the deviation from perfect linearity clearly reflect the difficulties in the determination of tiny amounts of **1b** present in the equilibrium with **2b**.

$$\ln K = (9.01 \pm 0.38)\ \mathrm{kJ\ mol^{-1}}/RT + (26.74 \pm 0.82)\ \mathrm{J\ mol^{-1}\ K^{-1}}/R \quad (1)$$

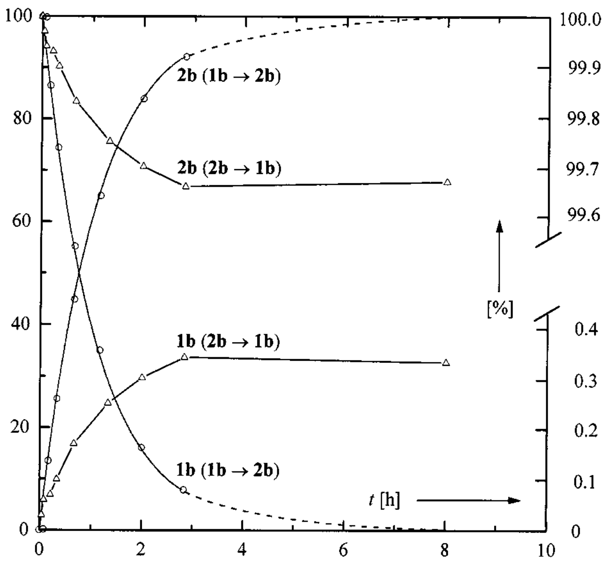


Figure 1. Diagram of conversion vs. time for the equilibration **1b** ⇌ **2b** at 190°C starting from semibullvalene **1b** (circles, left axis) and cyclooctatetraene **2b** (triangles, right axis, which has been expanded by a factor 100), and monitored by recording 600-MHz proton spectra

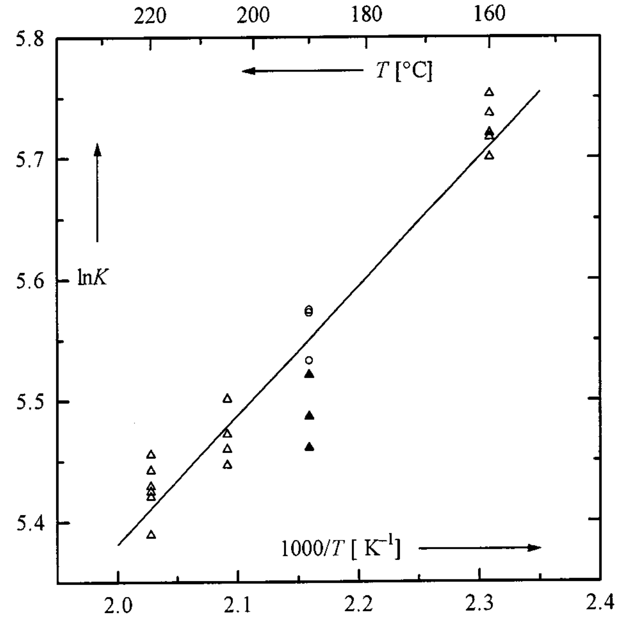
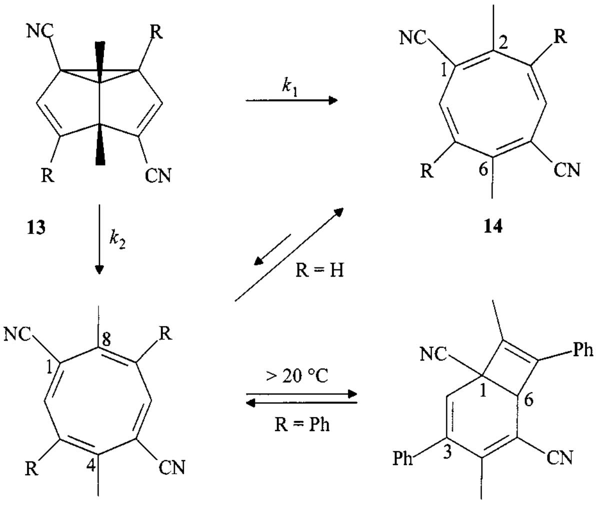


Figure 2. Diagram of ln$K$ vs. 1000/T for the equilibration **1b** ⇌ **2b**; the straight line corresponds to Equation 1, r = 0.9985; triangles: analysis by gas chromatography; circles: analysis by proton spectroscopy; hollow symbols: solutions in [D$_6$]benzene; filled triangles: solution in 3-methylpentane; the data were not used in the calculation of Equation 1

Kinetic studies of solutions in [D$_6$]benzene at 160 and 190°C showed a good fit to reversible first-order behaviour. Because of the one-sided position of the equilibrium **1b** ⇌ **2b**, the rate constant k_{-1} for the reverse reaction **2b** → **1b** constitutes only a fraction of less than half a percent of the sum ($k_1 + k_{-1}$) and is accordingly much smaller than the 95% confidence limit. Therefore, the Arrhenius and Eyring parameters were calculated from the temperature dependence of the sum ($k_1 + k_{-1}$) and taken for the forward reaction **1b** → **2b** (Table 1). The activation enthalpy of the reverse reaction, $\Delta H^{\ddagger}$ (**2b** → **1b**), was then assessed with the help of the enthalpy difference between **2b** and **1b** obtained from Equation 1.

Rates of the equilibration of **1b** with **2b** were also measured in the gas phase at seven different temperatures (179−230°C) by the technique described previously.[30] No loss of material was observed as shown by comparison with undecane employed as standard. Treatment of the data was performed by a simultaneous fit of all experimental values to a reversible first-order scheme with the help of a Marquardt routine.[31] This method proceeds without the calculation of individual rate constants and allows the estimate of significant error limits of the four variables involved, viz. the Arrhenius parameters for the forward and the reverse reaction. The results are included in Table 1.

A kinetic study of the isomerisation of octamethylcyclooctatetraene (**3**) to octamethylsemibullvalene (**4**) is complicated by the sensitivity of the latter towards molecular oxygen[7] and the tendency to undergo acid-catalysed isomerisation which leads to isomeric heptamethylmethylenebicyclo[3.3.0]octadienes.[7][32] Because of these rapid reactions, attempts to detect the reverse isomerisation, viz. **4** → **3**, met with failure. In the study of the rate of the isomerisation **3** → **4** in a mixture of hexane and triethylamine, the known endoperoxide of **4**[7] was formed as secondary product. Experiments in the gas phase yielded, besides **4**, products of the acid-catalysed isomerisation although the equipment had been carefully deactivated with triethylamine and hexamethyldisilazane. Even the presence of an excess of triethylamine did not completely suppress but only retarded the acid-catalysed isomerisation. Therefore, only the decrease of **3** relative to the standard tridecane could be monitored by gas chromatography. First-order rate constants and activation parameters are listed in Tables 6 and 1, respectively.



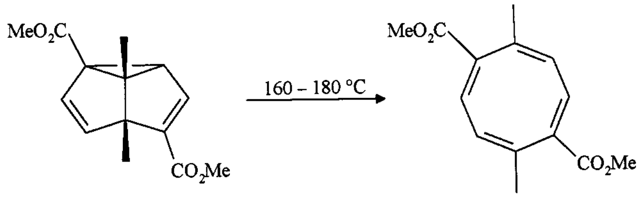
13 **14** **15** **16**

	R	Temp.	Ratio of isomers
13a – 15a	H	130 °C	**14a** : **15a** = 91 : 9
13b – 15b	Ph	50 – 70 °C	**14b** : (**15b** + **16**) = (59 ± 1) : (41 ± 1)

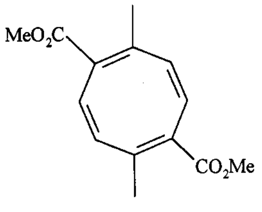
2,6-Dicyano-1,5-dimethylsemibullvalene (**13a**) was reported to rearrange irreversibly to the cyclooctatetraenedicarbonitrile **14a** with a rate constant $k = 3 \cdot 10^{-5}$ s^{-1} in [D$_6$]benzene solution at 130°C.[33] In the course of the reinvestigation and extension of the earlier work, simultaneous formation of a minor by-product of **14a** (10%) was uncovered by NMR-spectroscopic scrutiny. Besides the proton signals of **14a**, two multiplets of equal, low intensity emerged right away, which belonged to vinyl protons. The splitting pattern closely resembled those of the vinyl protons of the dimethyl cyclooctatetraenedicarboxylate **18** (see below) demonstrating the absence of large vicinal couplings. In the proton spectrum taken from a solution in [D]trichloromethane, a weak methyl pseudo triplet ($^4J = {}^5J =$ 1.6 Hz) emerged, which was obscured by the methyl signal of **14a** in the proton spectra of [D$_6$]benzene solutions. When a sharp-melting sample of **14a** was dissolved in cold [D$_6$]benzene, the proton signals of the minor thermolysis product appeared instantaneously. Attempts to separate the two compounds by HPLC met with failure, apparently because of rapid interconversion. Eventually, the carbon-13 spectra left no doubt of the structure of the bond-shift isomer **15a** for the minor thermolysis product.

The rate of the thermal rearrangement of **13a** was studied in the temperature range 130−160°C by proton spectroscopy of [D$_6$]benzene solutions. The disappearance of the methyl signal of **13a** relative to that of 1,3,5-tri-*tert*-butylbenzene, which was employed as internal standard, followed the first-order rate law over at least two half-lives. Rate constants and activation parameters are listed in Tables 5 and 1, respectively.

Recently, we found an unprecedented bifurcation of the semibullvalene-to-cyclooctatetraene isomerisation pathway for the thermally labile dicyanodiphenylsemibullvalene **13b**, which slowly rearranges at temperatures as low as room temperature.[27] On thermolysis of **13b** in strictly degassed [D$_6$]benzene solutions in the temperature range 50−70°C, three isomers **14b**, **15b**, and **16** arose in the constant ratio 60:22:18. While solutions of **14b** remained unchanged at temperatures below 100°C, the isomer **15b** equilibrated with the bicyclo[4.2.0]octatriene **16** in solution at room temperature. No interconversion of the bond-shift isomers **14b** and **15b** but slow, undefined decomposition of **15b** and **16** was observed at temperatures above 70°C. The rate of disappearance of **13b** was measured for [D$_6$]benzene solutions at four different temperatures in the range 50−70°C. First-order behaviour was observed during two half-lives. Rate constants ($k_1 + k_2$) and activation parameters are listed in Tables 5 and 1, respectively. Because the ratio k_1/k_2 = **14b**/(**15b** + **16**) = (59 ± 1):(41 ± 1) did not depend on the temperature within the limits of experimental error, most probably, one of the three scenarios prevails that have been detailed by Carpenter for the failure of the statistical models of kinetics.[34]



17 **18**



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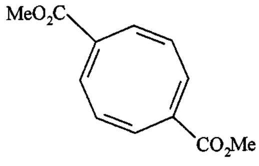

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A cursory study of the dimethyl 2,6-semibullvalenedicarboxylate **17** showed that its thermolysis did not proceed as cleanly as in the case of the other semibullvalenes, thus precluding a kinetic investigation. In [D$_6$]benzene solution, about a quarter of **17** disappeared on heating for one hour at 130 and subsequently 145°C, yielding many unidentified decomposition products. At higher temperatures, viz. 160 (1 h) and 180°C (1 h), the material balance remained nearly constant. A single product (**18**) emerged in 15 and 36% yield, respectively, while 28% of **17** survived one hour at both temperatures. The first-order rate constant for the thermal rearrangement of **17** at 180°C was roughly estimated at $2 \cdot 10^{-4}$ s^{-1}.

Table 1. Activation parameters and enthalpy differences for the thermal isomerisation of some semibullvalenes and cyclooctatetraenes; Arrhenius activation energies E_a and enthalpies are in kJ mol^{-1}, entropies of activation $\Delta S^{\neq}$ in J mol^{-1} K^{-1}

Isomerisation	Temp. [°C]	Conditions	E_a	log A	$\Delta H^{\neq}$	$\Delta S^{\neq}$	Ref.
1a → **2a**	200 – 240	gas phase (1 Torr)	166.61 ±0.79	13.81 ±0.08	161.97 ±0.36	–6.01 ±0.73	[5]
2a → **1a**	200 – 240	gas phase (1 Torr)	176.52 ±0.79	13.15 ±0.08	171.58 ±0.58	–11.79 ±1.17	[5]
1b → **2b**	179 – 230	gas phase	159.23 ±0.13	14.22 ±0.01	155.39 ±0.13	15.06 ±0.29	[a]
	160 – 190	C_6D_6	157.46 ±1.18	14.14 ±0.14	153.74 ±1.18	14.12 ±2.62	[a]
2b → **1b**	179 – 230	gas phase	170.83 ±8.03	13.29 ±0.85	166.90 ±8.03	–2.76 ±11.42	[a]
	160 – 190	C_6D_6			163		[a]
3 → **4**	108 – 160	gas phase	131.50 ±0.85	12.82 ±0.11	128.10 ±0.85	–10.39 ±2.08	[a]
	119 – 169	hexane/ Et_3N (3 : 1)	128.75 ±1.25	12.51 ±0.16	125.27 ±1.25	–16.49 ±3.01	[a]
5 → **6**	65 – 85	CCl_4	107	11.3			[17]
7 → **8** + **9**	69 – 82	[b]			115.5 ±8.8	6.7 ±20.9	[11b]
13a → **14a** + **15a**	130 – 160	C_6D_6	137.3 ±0.42	13.28 ±0.05	133.8 ±0.40	–1.8 ±0.97	[a]
13b → **14b** + **15b**	50 – 70	C_6D_6	106.9 ±3.27	12.89 ±0.52	104.2 ±3.26	–7.37 ±9.83	[a]

[a] This work. – [b] The solvent was not reported.

Regarding the results of the thermolyses of the semibullvalenedicarbonitriles **13a** and **b**, the structure of both bond-shift isomers **18** and **19** were considered for the thermolysis product of **17**. The parameters of the AMX_3 spectrum, observed for the ring protons and the *C*-methyl protons, left no doubt of the structure **18**. This assignment is supported by a comparison with the proton spectra of **20**[35] and several dimethyl cyclooctatetraene-1,4-dicarboxylates.[36] While, at room temperature, **20** undergoes fast degenerate exchange (on the 270-MHz NMR time scale) by dynamic bond shift, which can be "frozen" only at temperatures as low as −70 °C,[35] no bond-shift was observed for **18**. The apparently lower stability of **19** can be attributed to unfavourable steric interactions that are not present in **18**.

Discussion

Arrhenius and Eyring parameters for the thermal isomerisation of semibullvalenes and cyclooctatetraenes are listed in Table 1, which also contains data taken from the literature for comparison.

Reversibility of the rearrangements, as demonstrated by the presence of traces of the minor isomers in equilibrated mixtures, is observed only for the parent compounds **1a**, **2a**[4][5] and the dimethyl systems **1b**, **2b**. The semibullvalenedicarbonitriles **13** rearrange irreversibly to cyclooctatetraenes. By contrast, octamethylcyclooctatetraene (**3**) isomerises to octamethylsemibullvalene (**4**).[7] The reverse reaction could not be detected, even if it did occur to some extent, because the kinetic scheme is complicated by competing reactions of **4** that could not be suppressed completely.

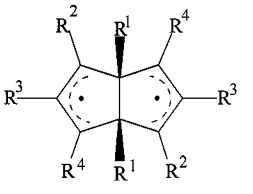
While **1a** and **b** are *less* stable by about 10 kJ mol^{-1} than their cyclooctatetraene isomers **2a** and **b**, the order of stability is reversed for Criegee's permethylated compounds **3** and **4**. Obviously, the interplay of subtle, variable electronic and steric effects of the methyl groups at the different positions governs the balance between the isomers. The enthalpies of formation of **1a** and **2a**, and their methyl-substituted derivatives were calculated with the MM2ERW force field.[37] Inspection of the results listed in Table 2 shows reasonable agreement between the calculated and the experimental data except that the calculated enthalpies of formation appear too high for the semibullvalenes **1a** and **b** by 4−8 kJ mol^{-1}.

Table 2. Enthalpies of formation [kJ mol^{-1}] of the parent semibullvalene (**1a**) and cyclooctatetraene (**2a**) and some methyl-substituted derivatives as calculated by the MM2ERW[37] force field, and experimental data

Semibullvalene		Cyclooctatetraene			ΔH^0_f(SB) – ΔH^0_f(COT)	
	ΔH^0_f		ΔH^0_f	exper.	$\Delta\Delta H^0_f$	exper.
1a	315.5	**2a**	298	295.9 ± 1.7[38]	17.5	9.9 ± 0.8[5]
1b	238.6	**2b**	224.1		14.5	9.0 ± 0.4[a]
4	55.7	**3**	66.1		–10.4	

[a] For [D_6]benzene solution; from Equation 1.

As pointed out above, the lack of kinetic stability is the limiting feature in the studies of a number of semibullvalenes. The data presented in Table 1 quantify the effect of substituents on this property and thus allow predictions concerning future work. All substituents investigated so far lower the barrier toward the rearrangement to cyclooctatetraenes. Introduction of methyl groups at the bridgehead carbon atoms C1 and C5 of the parent semibullvalene decreases the enthalpy of activation by 6.6 kJ mol^{-1}. The two nitrile groups at C2 and C6 of **13a** diminish the barrier further by no less than 20 kJ mol^{-1}. Formal attachment of two phenyl groups at C4 and C8 of **13a**, yielding **13b**, even results in a 30 kJ mol^{-1} reduction of the barrier toward the rearrangement. Thus, an increasing number of certain substituents leads to thermally labile semibullvalenes like **5** and **13b** whose handling at room temperature is a delicate matter.



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	R^1	R^2	R^3	R^4
21a	H	H	H	H
21b	Me	CN	H	H
21c	Me	CN	H	Ph
21d	Me	Me	Me	Me

Table 3. Enthalpies of formation [kJ mol^{-1}] of the parent semibullvalene (**1a**) and octamethylsemibullvalene (**4**) and the isomeric diradicals **21a**, **d** as calculated by the MMEVBH force field[40]

Semibullvalene ΔH^0_f(SB)		Diradical ΔH^0_f(**21**)		$\Delta\Delta H^0_f = \Delta H^0_f$(**21**) $- \Delta H^0_f$(SB)
1a	312.6	**21a**	374.8	62.2
4	54.2	**21d**	96.6	42.4

It is enlightening to compare the substituent effects on the thermal stability of semibullvalenes with those on the barriers toward the degenerate Cope rearrangement.[39] Though a quantitative comparison can be made only for a few systems, viz. **1b**, **13a**, and − approximately − **13b**, it appears safe to maintain that the two effects are related to each other in a qualitative way: *The faster the Cope rearrangement, the lower is the thermal stability of a semibullvalene.* This characteristic points to a certain degree of similarity between the mechanisms and, of course, transition states of both rearrangements. While the transition state of a degenerate Cope rearrangement almost certainly corresponds to a delocalised, bis-homoaromatic species of higher symmetry, the thermal semibullvalene $\leftrightharpoons$ cyclooctatetraene isomerisations have been postulated to proceed via intermediate diradicals **21**,[4,5,9a,16] which possess the same symmetry as the bis-homoaromatic transition state. The parent system **21a** has been estimated to reside in a depression on this side of the highest saddle point, approximately 90 kJ mol^{-1} above semibullvalene.[4][5] In fact, calculations of the enthalpies of formation of **21a** and its octamethyl homologue **21d** and the corresponding semibullvalenes **1a** and **4** with the MMEVBH force field, which is particularly suited for hydrocarbon radicals and diradicals,[40] place these diradicals only 62 and 42 kJ mol^{-1}, respectively, above the semibullvalenes from which they are generated (Table 3).[41] A comparison of these calculated values with the data of Tables 1 and 2 indicates that the diradicals **21** and the transition states that lead to cyclooctatetraenes differ considerably in energy. Nevertheless, substituents influence both structures in the same sense according to Hammond's postulate.[43]

Because the transition state of the Cope rearrangement and **21** share the same structural symmetry, the local minimum of the latter lies on the line that crosses perpendicularly the Cope reaction coordinate at the saddle point. Therefore, according to Thornton's theory of perpendicular effects,[44] any substituents that influence the energy of **21** will more or less affect the Cope transition state. This explains why the heights of the barriers toward the degenerate Cope rearrangement and the rearrangement to cyclooctatetraenes are roughly correlated. As a consequence, the conclusion appears inevitable that the holy grail of *stable* delocalised, bis-homoaromatic semibullvalenes, viz. single-minimum systems, cannot be achieved unless their rearrangement to cyclooctatetraenes is prohibited by either a short bridge across the C1−C5 bond, or simultaneous bracketing of the C2−C8 bond and the C4−C6 distance, or, perhaps, a bridge between C3 and C7. These conditions complicate synthetic efforts enormously. Hence it comes as no surprise that all such bridged or bracketed degenerate semibullvalenes synthesised so far[10,19b,24,45] lack a substituent pattern that confers bis-homoaromaticity.

Experimental Section

Results: Tables 1−5, Figures 1 and 2. − ^{1}H and ^{13}C NMR: Bruker AC 200, AC 250, WM 400, and DMX 600. − GC: Chrompack 436 equipped with integrator Shimadzu C-R6A; (50 m × 0.11 mm) WCOT fused-silica column coated with silicon oil CP-Sil 5 CB, film thickness 0.13 μm (Chrompack), 4.0 bar N_2, on column injection, column temp. 80 (40 min), 80−180 (10°C/min), 180°C (10 min): retention time t_R [min] = 19.1 (**11**), 19.2 (**10**), 21.0 (**1b**), 29.1 (**12** ?), 32.9 (**2b**). − GC-MS: Varian 3700 connected to mass spectrometer Finnigan MAT 8200 (70 eV); (30 m × 0.257 mm) WCOT fused-silica column coated with silicon oil SE30, film thickness 0.25 μm (DB1, J&W Scientific), 0.5 bar He, on column injection, column temp. 60 (25 min), 60−180 (10°C/min). − Preparative GC: Varian Aerograph 920, (3 m × 2 mm) glass column packed with Volaspher A2 (Merck) which was coated with silicon oil SE 30 (20%), column temp. 115°C, injector and detector temp. 180°C, 60 mL/min H_2, t_R [min] = 3.5 (**1b**), 9.5 (**2b**). − HPLC: Waters M-6000 A equipped with UV detector 440 (λ = 254 nm) and differential refractometer R401; (250 × 4.6) mm stainless steel column packed with silicagel LiChrosorb Si60, 5 μm (Merck); 0.5 mL/min petroleum ether (50−70°C) (PE)/ethyl acetate (EA) (95:5), t_R [min] = 26.7 (**15b**), 27.6 (**14b**), 33.3 (**16**); 1.0 mL/min PE/EA (90:10), t_R = 5.0 (**17**), 6.9 (**18**); 1.5 mL/min PE/EA (90:10), t_R = 4.4 (**14b**, **15b**), 4.8 (**16**), 6.8 (**13a**), 7.5 (**13b**), 8.4 (**14a**). − 3-Methylpentane (Baker) was pure by UV and GC. [D$_6$]benzene (> 99.9% deuteration, pure by GC, Acros Organics) was dried with lithium aluminium hydride. Cyclotetraene **3** was a gift from Professor R. Askani, Gießen.

1,5-Dimethyltricyclo[3.3.0.0^{2,8}]octa-3,6-diene (1b) was prepared according to the recently published procedure,[24] distilled at 40°C bath temp./10^{-2} Torr through a 20-cm Spaltrohr column (Fischer, D-53340 Meckenheim, Germany), and purified by repeated preparative GC. Colourless liquid [GC: 99.6% **1b**, 0.3% (**10** + **11**), < 0.1% **2b**; 600-MHz ^{1}H NMR: 98.3% **1b**, 1.3% **10**, 0.3% **11**, 0.04% **2b**].

1,5-Dimethyl-1,3,5,7-cyclooctatetraene (2b) was obtained as second fraction in the preparative GC of **1b**. Purification by repeated preparative GC afforded a yellow liquid [GC: 98.9% **2b**, 1.0% **12** (?), and traces (< 0.05%) at t_R (min) = 37.8, 38.6, 39.0; 600-MHz ^{1}H NMR: 97.5% **2b**, 2 unknown compounds, δ = 1.68 (s, 2%), 1.53 (s, 0.5%)]. − ^{1}H NMR (600 MHz, C_6D_6): δ = 1.61 (slightly broadened s, 2 Me); after decoupling of the methyl protons: δ = 5.52 (d, *J* = 3.7 Hz, 2-H, 6-H), 5.64 (d, *J* = 11.4 Hz, 4-H, 8-H), 5.71 (dd, *J* = 11.4, 3.7 Hz, 3-H, 7-H) [60-MHz ^{1}H-NMR spectrum ($CDCl_3$): ref.[9b]]. − ^{13}C NMR (151 MHz, C_6D_6): δ = 23.7 (2 Me), 127.0 (C-2, C-6), 130.9 (C-3, C-7), 134.2 (C-4, C-8), 140.1 (C-1, C-5); the assignment is based on a heteronuclear multiple quantum coherence spectrum.

2,6-Dimethyl-1,3,5,7-cyclooctatetraene-1,5-dicarbonitrile (14a): A solution of **13a** (182 mg, 1.0 mmol) in dry triethyleneglycol dimethyl ether (10 mL) was heated under N_2 for 4 h at 170−175°C while the conversion was monitored by HPLC. The solvent was distilled at 60°C bath temp./10^{-2} Torr. Sublimation of the solid residue at 130−135°C bath temp./10^{-2} Torr afforded a colourless product (0.14 g) which was recrystallised from ethyl acetate (3 mL) to yield colourless crystals (0.12 g, 47%), m.p. 152°C (ref.[33] 150−151°C). The brown residue of the sublimation was dissolved in CH_2Cl_2 (15 mL) and combined with the mother liquor. Filtration through a layer of silica gel (15 g, 32−63 μm), which was rinsed with CH_2Cl_2 (60 mL), and distillation of the solvent in vacuo yielded a pale yellow powder. Recrystallisation from ethyl acetate yielded a second crop (30 mg, 12%), m. p. 148−150°C. − ^{1}H NMR (400 MHz, C_6D_6): ref.[33a]; (400 MHz, $CDCl_3$): ref.[33b]. − ^{13}C NMR (100 MHz, $CDCl_3$): ref.[33a]

Equilibration of the Bond-Shift Isomers 14a and 15a: Samples of **14a** (m. p. 152°C) were dissolved in C_6D_6 or $CDCl_3$ at room temperature. The 600-MHz proton spectra showed the presence of **14a** and **15a** in a ratio of 91:9 and 93:7, respectively. − **15a**: ^{1}H NMR (600 MHz, C_6D_6): δ = 4.87 (dq, ^4J = 3.8, ^5J = 1.6 Hz, 3-H, 7-H), 5.74 (dq, ^4J = 3.7, ^5J = 1.7 Hz, 2-H, 6-H), the methyl signal is hidden under that of **14a**; (400 MHz, $CDCl_3$): δ = 1.97 (dd, ^4J = ^5J = 1.6 Hz, 2 Me), 6.63 (dq, ^4J = 3.7, ^5J = 1.6 Hz, 2-H, 6-H), the multiplet of 3-H and 7-H is hidden under a multiplet of **14a**. − ^{13}C NMR (151 MHz, C_6D_6): δ = 22.3 (2 Me), 117.5 (C-1, C-5), 138.4 (C-4, C-8), 128.2 (C-3, C-7), 144.7 (C-2, C-6), 118.8 (2 CN); the signals were assigned on the basis of a heteronuclear multiple quantum coherence spectrum.

Thermal Equilibration of 1b and 2b in the Gas Phase: The apparatus and the technique have been detailed previously.[30] The apparatus consisted of a 20-L Pyrex flask whose temperature was kept constant in an air thermostat to better than ±0.1°C. For monitoring the rates, samples were taken from the middle of the flask and subjected to GC analysis with a directly attached gas chromatograph Intersmat IGC 120 FB which was equipped with an integrator Hewlett-Packard 3390 A; (12.5 m × 0.20 mm) HP1 quartz column, film thickness 0.33 μm, injector temp. = detector temp. = 200, column temp. = 70°C, 1.8 bar He, retention time t_R [min]: 1.36 (**1b**), 2.26 (**2b**), 3.81 (standard undecane). − The apparatus was charged with a solution of **1b** in pentane [1% (vol/vol), 300 μL] containing undecane as standard (1%). The equilibration was monitored at 7 temp. between 179 and 230°C. The ratio of **1b** and **2b** in an equilibrated mixture at 270°C was $(7.7 \pm 0.4)\cdot 10^{-3}$. For the calculation of the Arrhenius parameters of the forward and the reverse reaction from the experimental data see text. The Eyring parameters were calculated from the Arrhenius parameters for the average temp. 204.5°C (Table 1).

Kinetic Experiments with Solutions: Thermal equilibration and kinetic experiments were performed by placing degassed, sealed NMR samples tubes or sealed melting-point capillary tubes containing solutions of **1b**, **2b**, **13a**, or **b** into a Lauda thermostat NS-S15/22/SP, filled with silicon oil whose temp. (± 0.1°C) was measured with calibrated thermometers (scale division 0.1°C). During the first two half-lives, 10−14 proton spectra were recorded. Alternatively, after each time interval, mixtures from 3−5 melting point capillary tubes were analysed by duplicate GC.

Thermal Equilibration of 1b and 2b in Solution: a) In a Schlenk tube, **1b** (40 mg, 0.3 mmol) was dissolved in dry C_6D_6 or 3-methylpentane (1.5 mL). The solution was degassed by freeze-pump-thaw cycles (3 ×) and eventually saturated with Ar. Under Ar, the solution (ca. 25 μL) was transferred into melting-point capillary tubes, which were sealed with a torch. The mass balance did not deteriorate as shown by comparison with the small amounts of **10** and **11** present which were taken as internal standard.

b) Degassed solutions of **1b** or **2b** (40 mg, 0.3 mmol) in dry C_6D_6 (0.6−0.7 mL) were sealed under vacuum (10^{-2} Torr) in NMR sample tubes and heated at 190.0°C. The solutions were analysed by 600-MHz proton spectra (65536 data points). The ratios of **1b**, **2b**, and **10** (= internal standard) were calculated from the integrations of the methyl signals which were fitted to a Lorentz function. If the ratio of **1b** and **2b** attained extreme values (> 9:1 or < 1:9), the ^{13}C satellites of the major component were employed. No loss of material was observed as shown by comparison with the internal standard **10**.

c) Degassed solutions of **1b** (13 mg, 0.1 mmol) and 1,3,5-tri-*tert*-butylbenzene (2.7 mg, 11 μmol) in dry C_6D_6 (ca. 0.5 mL) were sealed under vacuum (10^{-5} Torr) in NMR sample tubes. The conversion was monitored by recording 200- or 250-MHz proton spectra. The ratios of **1b**, **2b**, and the standard 1,3,5-tri-*tert*-butylbenzene were calculated from integrations of the methyl signals.

The sums of the rate constants of the equilibration ($k_1 + k_{-1}$) were calculated from the ratios [**2b**]/[**1b**] and the equilibrium constants $K = ([\mathbf{2b}]/[\mathbf{1b}])_{t=\infty}$ (Table 4), according to Equation 2 by the (nonlinear) least-squares procedure.[46] The activation parameters listed in Table 1 for the isomerisation were calculated from the Arrhenius (Equation 3) and Eyring equation (Equation 4) which are based on the 5 values for ($k_1 + k_{-1}$) listed in Table 5. $\Delta H^{\neq}$(**2b**→**1b**) was obtained from $\Delta H^{\neq}$(**1b**→**2b**) and the enthalpy difference between **1b** and **2b** (Equation 1).

$$(k_1 + k_{-1}) = 1/t \cdot \ln[(A_0K - B_0)/(AK - B)] \qquad (2)$$

A, A_0 and *B*, B_0 are the molar fractions of **2b** and **1b**, respectively.

$$\ln k_1 \approx \ln(k_1 + k_{-1}) = (32.56 \pm 0.31) - (18938 \pm 142)/T \qquad (3)$$

$$\ln(k_1/T) \approx \ln[(k_1 + k_{-1})/T] = (25.46 \pm 0.31) - (18490 \pm 142)/T \qquad (4)$$

Thermal Isomerisation of the 1,5-Dimethylsemibullvalene-2,6-dicarbonitriles 13a and b: Under Ar, 60−80 μmol of the semibullvalenes **13a** or **b** and 1,3,5-tri-*tert*-butylbenzene (5 mg, 20 μmol) were placed into NMR sample tubes which were attached to a vacuum line (10^{-5} Torr). Dry C_6D_6 was degassed by several freeze-pump-thaw cycles and allowed to condense in the NMR sample tubes (ca. 0.5 mL) which were cooled with liquid N_2, evacuated, and sealed with a torch. The conversions were monitored during the first two half-lives by recording 10−14 proton spectra (200 MHz). The sums of the rate constants ($k_1 + k_2$) were calculated by the (nonlinear) least-squares procedure according to Equation 5 where *SBV* and *ST* denote the integrals of the methyl signals of **13** and 1,3,5-tri-*tert*-butylbenzene, respectively. The activation parameters listed in Table 1 were calculated from the Arrhenius (Equations 6

Table 4. Conditions, methods of analysis, and results of the determination of the equilibrium constants K = [**2b**]/[**1b**] for the interconversion of dimethylsemibullvalene **1b** and dimethylcyclooctatetraene **2b**

Cpd.[a]		Temp. [°C]	Time[b] [h]	**2b** : **1b**	K_{calc}[c]
1b	C_6D_6	160.0	281	99.667 : 0.333[d]	305
				99.672 : 0.328	
				99.678 : 0.322	
				99.683 : 0.317	
				99.674 : 0.327	
	[e]	190.0	17.3	99.588 : 0.412[d]	(242)[f]
				99.602 : 0.398	
				99.577 : 0.423	
	C_6D_6	190.0	20.1	99.605 : 0.395[g]	259
2b	C_6D_6	190.0	20.1	99.612 : 0.388[g]	
				99.585 : 0.415[g]	
1b	C_6D_6	205.0	4.9	99.593 : 0.407[d]	241
				99.581 : 0.419	
				99.581 : 0.419	
				99.576 : 0.424	
				99.593 : 0.407	
				99.570 : 0.430	
	C_6D_6	220.0	1.5	99.561 : 0.439[d]	225
				99.545 : 0.455	
				99.563 : 0.437	
				99.559 : 0.442	
				99.569 : 0.431	
				99.574 : 0.426	

[a] Starting material. – [b] Period of time after which the ratios **2b**/**1b** were determined. – [c] Calculated from Equation 1. – [d] Ratio of peak areas in gas chromatograms recorded from solutions in sealed melting-point capillary tubes. – [e] Solvent: 3-methylpentane. – [f] Average from three independent equilibration experiments performed in a different solvent, viz. 3-methylpentane, which therefore were not considered in the calculation of Equation 1. – [g] Ratio of the methyl signals in 600-MHz proton spectra.

and 7) and Eyring equations (Equations 8 and 9) which are based on the data of Table 5.

$$(SBV/ST)_t = (SBV/ST)_{t=0}\exp[-(k_1 + k_2)t] \tag{5}$$

13a → **14a** + **15a** (6)

$$\ln(k_1 + k_2) = (30.58 \pm 0.12) - (16513 \pm 51)/T$$

13b → **14b** + **15b** (7)

$$\ln(k_1 + k_2) = (29.68 \pm 1.19) - (12867 \pm 394)/T$$

13a → **14a** + **15a** (8)

$$\ln[(k_1 + k_2)/T] = (23.55 \pm 0.12) - (16097 \pm 49)/T$$

13b → **14b** + **15b** (9)

$$\ln[(k_1 + k_2)/T] = (22.87 \pm 1.18) - (12535 \pm 392)/T$$

Thermal Isomerisation of Octamethylcyclooctatetraene (3) to Octamethylsemibullvalene (4): a) A solution of **3** [1% (vol/vol), 20 μL] in a mixture of hexane and triethylamine (3:1), containing tridecane (1%) as standard, was filled into melting-point capillary tubes, which were sealed with a torch and placed into openings of a brass block in the oven of a gas chromatograph whose temp. was kept constant to better than 0.1 °C. The conversion was monitored by recording gas chromatograms at 10 different times; gas chromatograph and column as described for the gas-phase equilibration of **1b** and **2b**, column temp. 100 °C, 2.2 bar He, t_R [min] = 3.98 (tridecane), 4.56 (**3**), 6.25 (**4**), 26.60 (endoperoxide of **4**).[7] First-order rate constants were calculated from the decrease of **3** relative to the standard (Table 6). The linear least-squares fit of the Arrhenius equation to the rate vs. temp. data afforded the parameters (r^2 = 0.999951, the errors refer to a 95% confidence interval), from which the Eyring parameters were calculated for the average temp. 144.52 °C (Table 1).

Table 5. Conditions, methods of analysis, and rate constants of the isomerisations in [D$_6$]benzene solution of some dimethylsemibullvalenes **1b**, **13a**, and **b** into dimethylcyclooctatetraenes

Cpd.	Temp. [°C]	Method of analysis	Time[a] [min]	Conv. [%]	[b]	$(k_1 + k_{-1})$ 10^6 [s^{-1}]
1b	160.0	NMR[c]	1860	78	13	14.29 ± 0.36
			1860	79	14	14.21 ± 0.21
	190.0	NMR[d]	170	92	8	248.9 ± 18.9
		(GC[e]	120	80	11	220.4 ± 18.1)
		NMR[c]	135	83	11	242.0 ± 2.32
			135	83	11	235.2 ± 1.35
						$(k_1 + k_2)$ 10^6 [s^{-1}]
13a	130.0	NMR[c]	670	71	13	31.1 ± 0.2
			670	70	13	31.0 ± 0.2
	150.0		105	74	12	213.1 ± 2
	160.0		60	85	11	532.2 ± 5
13b	50.0	NMR[c]	550	74	12	40.4 ± 1.5
			550	74	12	40.5 ± 1.5
	60.0		158	69	14	121.4 ± 3.2
	65.0		85	69	11	222.9 ± 5
	70.0		77	87	10	430.4 ± 8

[a] Period of time during which the ratios were monitored. – [b] Number of data points. – [c] 200- or 250-MHz proton spectra, 1,3,5-tri-*tert*-butylbenzene as internal standard. – [d] 600-MHz proton spectra. – [e] Solvent 3-methylpentane. The sum $(k_1 + k_{-1})$ was calculated (Equation 2) from ratios of peak areas recorded by gas chromatography from solutions in sealed melting point capillary tubes. The data were not used in the calculation of Equations 3 and 4.

Table 6. First-order rate constants of the thermal isomerisation of **3** to **4** in a solution of hexane/triethylamine (3:1) and in the gas phase

Temp. [°C]	$10^5\,k$ [s^{-1}]
isomerisation in solution	
119.35	2.3777
130.18	7.025
139.45	16.30
149.74	40.10
159.50	93.14
168.90	200.60
isomerisation in the gas phase	
108.40	0.6588
119.33	2.103
132.88	7.950
139.65	15.390
148.80	34.810
160.18	93.423

b) The apparatus employed for the gas-phase equilibration of **1b** and **2b** (see above)[30] was carefully deactivated with triethylamine and hexamethylsilazane. The 20-L flask was charged with triethylamine (2 mL) and a carefully degassed solution of **3** [1% (vol/vol), 500 µL] in pentane, containing tridecane (1%) as standard. The conversion was monitored by recording gas chromatograms at ca. 10 different times; gas chromatograph and column as described for the gas-phase equilibration of **1b** and **2b**, column temp. 90°C, 2.2 bar He, t_R [min] = 3.90 (tridecane), 4.46 (**3**), 6.05 (**4**), 8.80, 10.20, 14.18 (isomeric heptamethylmethylenebicyclo[3.3.0]octadienes).[7] The loss of material was up to 50% in the runs at the lower temperatures. The ratio of **3** vs. tridecane in the first gas chromatogram, recorded after ca. 100 s, was taken as 100%. First-order rate constants were calculated from the decrease of **3** relative to the standard (Table 6). The linear least-squares fit of the Arrhenius equation to the rate vs. temp. data afforded the parameters (r^2 = 0.999984, the errors refer to a 95% confidence limit), from which the Eyring parameters were calculated for the average temp. 134.87°C (Table 1).

Thermal Isomerisation of Dimethyl 1,5-Dimethylsemibullvalene-2,6-dicarboxylate (17), Dimethyl 4,8-Dimethylcycloocta-1,3,5,7-tetraene-1,5-dicarboxylate (18): As described for the experiments with **13a** and **b**, a solution of **17** and 1,3,5-tri-*tert*-butylbenzene in C_6D_6 was heated for 1 h at 130, 145, 160, and 180°C. After the first 2 h, about 25% of **17** had decomposed into a number of unknown products. At 160 and 180°C, the material balance did not deteriorate any further. Instead, 15 and 36%, respectively, of **18** was formed, while 28% of **17** remained unchanged. The first-order rate constant for the thermal isomerisation of **17** into **18** was estimated at $k = 2\cdot10^{-4}$ s^{-1} (180°C). − **18:** ^{1}H NMR (400 MHz, C_6D_6): δ = 1.88 (dd, ^4J = ^5J = 1.7 Hz, 2 Me), 3.31 (s, 2 OMe), 5.64 (dq, ^3J = 3.5, ^4J = 1.7 Hz, 3-H, 7-H), 7.18 (dq, ^3J = 3.5, ^5J = 1.7 Hz, 2-H, 6-H).

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