The Effects of Substituents on the Degenerate Cope Rearrangement of Semibullvalenes and Barbaralanes[1]

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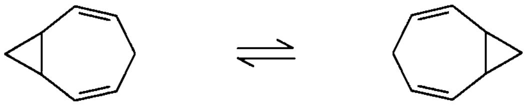
Received March 25, 1998

Keywords: Automerization / Carbocycles / Fluxionality / Hydrocarbons / NMR spectroscopy / Pericyclic reactions / Polycycles / Rearrangements / Strained molecules /Substituent effects / Valence isomerisation

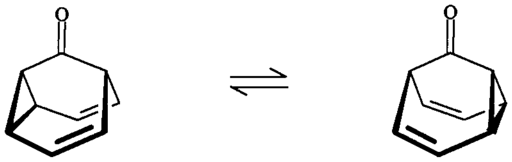
The activation parameters [ΔG^{+} (200 K), ΔH^{+}, and ΔS^{+}] for the degenerate Cope rearrangements of barbaralane (**1a**) and several semibullvalenes (**3a**, **7a**, **8a**), and for those of a number of their 3,7- and 2,6-disubstituted derivatives, have been determined by variable-temperature carbon-13 NMR spectroscopy at 126 and 151 MHz. the disubstituted compounds studied include the barbaralanes **1c**, **d**, **e**, **h**, **j**, **k**, and **2e**, **h**, **j**, and the semibullvalenes **3d**, **e**, **h**, **4e**, **h**, **i**, **l**, **m**, and **5h**−**8h**. Careful attention has been given to the measurement of temperatures. The data for these compounds, together with those for related compounds previously reported in the literature, show that conjugating subsituents (e. g. aryl, CN, CO_2R) in the 2,6 positions lower the barriers of the degenerate Cope rearrangement, whereas substituents that are electron-withdrawing through the inductive effect (e. g. Cl, CF_3, SO_2Ar) retard the reaction. Substituents in the 3,7 positons have little effect or are rate-retarding. The presence of 1,5-tri- and -tetramethylene bridges in semibullvalenes accelerates the rearrangements, the effect being larger in the case of the former.

Introduction

There are a number of molecular systems that, in the absence of precise knowledge of energies, can be considered as having either ground states with double minimum potentials or ones with unique structures of higher symmetry. These include[2] the annulenes[3], certain intramolecularly hydrogen-bonded systems (e. g. the hydrogen maleate ion)[4], carbocations[5], and radical cations and anions[6], as well as many that involve conformational interchange rather than valence tautomerism. A particularly interesting class, conceived some 30 years ago by von E. Doering[7], consists of molecules that can undergo *degenerate* Cope rearrangements. His first examples of such Cope rearrangements were found with 3,4-homotropilidene and barbaralone.[7] In all above systems, the question arises as to whether it is possible to move from a structure having a double minimum to one of higher symmetry by introduction of suitable, symmetrically positioned substituents or heteroatoms. The degenerate Cope rearrangements in barbaralanes **1** and **2** and the related semibullvalenes **3** and **4** provide a convenient opportunity to study substituent effects in neutral molecules. A fascinating aspect of this problem is that if a compound with a symmetric ground state could be obtained it could be regarded as a perfectly delocalized derivative of bishomobenzene.[8]



3,4-homotropilidene[7]

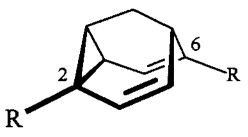


barbaralone[7]

The effects of substituents on the Cope rearrangement in barbaralanes and semibullvalenes have been the subject of several theoretical studies using semiempirical methods. Hoffmann and Stohrer[9], employing extended Hückel calculations, predicted that acceptor substituents (e. g. CN) at the 2,4,6,8 positions should enhance the rate of rearrangement while donor groups (e. g. F) in those positions should have the opposite effect. The effects of these substituents in the 1 and 5 positions are reversed. Dewar[10][11] reached similar conclusions on the basis of MINDO/2 calculations.

Subsequent studies using geometry optimization and including some configuration interaction in MNDO[12] and AM1[13] calculations further confirmed the above trends and even lead to the predictions that semibullvalene 2,4,6,8-tetracarbonitriles as well as the 2,6- and 2,4-dicarbonitriles should have bishomobenzene ground state structures. Other features that are predicted computationally to favour the homoaromatic ground state are symmetrical replacement of carbon atoms of the allylic moieties by nitrogen[11] and small ring annelation across positions 1 and 5,[12][14][15] and also across positions 2 and 8, 4 and 6.[14][15]

A number of experimental values for the barriers of the degenerate Cope rearrangement have been reported for the parent barbaralane[16][17][18] and semibullvalene,[19][20] substituted barbaralanes[17][21][22][23][24][25][26][27][28][29][30][31] and semibullvalenes,[32][33][34][35][36][37][38][39][40] as well as for heterobarbaralanes[41][42] and heterosemibullvalenes.[40][43] In this paper we present data for additional systems which provide us with some quantitative answers concerning the effects of the nature and positions of substituents on the free enthalpies of activation of the rearrangements. The total data now available allows us to assess the directions that offer the best chances of realizing a true, fully delocalized bishomobenzene.



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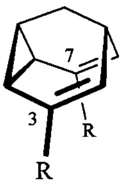

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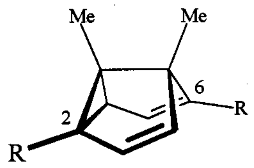

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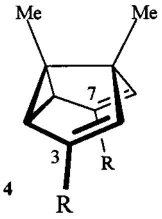

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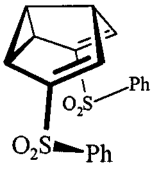
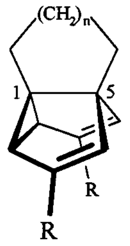


6h



7: n = 1
8: n = 2

	R
1a, 3a, 5a, 7a, 8a	H
2b	Me
1c	CF_3
1d – 4d	CN
1e – 4e	CO_2Me
1f, 4f	Cl
2g, 3g	Br
1h – 8h	Ph-SO_2
4i	4-*t*Bu-C_6H_4-SO_2
1j, 2j, 4j	Ph
1k	4-*t*Bu-C_6H_4
4l	4-Me-C_6H_4
4m	3-OMe-C_6H_4
1n	4-OMe-C_6H_4

	R
1o	4-pyridyl
1p	4-pyridyl•HCl
1q	4-pyridyl-*N*-oxide
1r	2-furyl

Methods

Scope and Limitations

In order to assess the rate enhancing effects of substituents on the degenerate Cope rearrangement we have confined our attention to barbaralanes and semibullvalenes symmetrically substituted in the 2,6 or 3,7 positions, principally by π-acceptor groups, which semiempirical MO calculations indicate to be the most effective for lowering the Cope barrier. We have also included some other substituents and some examples of 1,5-bridged semibullvalenes **7** and **8**.

The rate studies have all been performed by line-shape analysis of variable-temperature carbon-13 spectra obtained at 126 and 151 MHz. This method has the advantage, that the differences in chemical shifts (Δν) for the exchange-related carbon nuclei (2,8 and 4,6) under slow-exchange conditions are of the order of 10^4 Hz, so that in many cases meaningful rate data can be obtained over a wide temperature range. A disadvantage of the large values of Δν is that it is not feasible to collect data at or near the coalescence temperatures where the accuracy of line-shape analysis is highest. Accordingly, rates must be obtained from measurements of line widths at half hight (*W*) in the fast- and slow-exchange temperature ranges for which eq. 1 and eq. 2, respectively, apply.

$$k = \frac{\pi(\Delta\nu)^2}{2\,W_{ex}} \qquad \text{fast exchange (1)}$$

$$k = \pi\, W_{ex} \qquad \text{slow exchange (2)}$$

Since the contribution of exchange (W_{ex}) to the total line width of a signal must be separated from other contributions (T_2, field inhomogeneity, etc.) there is a lower limit on the $\Delta G^{\neq}$ of the process which can be determined by this method. Assuming that the frequency difference in the limit of slow exchange Δν is about $1.5 \cdot 10^4$ Hz and, because of instrumental problems and/or limitations in solubility in suitable solvents, the lowest accessible temperature is ca. 100 K we estimate this limit to be $\Delta G^{\neq}_{100} \approx 8.3$ kJ mol^{-1} corresponding to $k \approx 10^8$ s^{-1} at that temperature. All the compounds studied here involve slower Cope rearrangements.

An alternative way for the determination of rates of exchange might be offered by EXSY experiments in the region of slow exchange.[44] This method is not feasable for the present purpose, however, because this region is reached, in most cases, only at very low temperatures where the required long-time measurements meet considerable experimental difficulties.

Estimation of Carbon-13 Chemical Shifts for Non-Exchanging Valence Tautomers

We first note that an error ΔΔν in the value of Δν and an error ΔW_{ex} in the value of W_{ex} translate only into small errors $\Delta\Delta G^{\neq}$ in the free enthalpy of activation $\Delta G^{\ddagger}$ because of the logarithmic relationship of eq. 3 derived from eq. 1 and the Eyring equation. For example, experimental errors of 10% result, according to eq. 4 and 5 which are derived from eq. 3 with $\Delta f(x) = f(x + \Delta x) - f(x)$, in errors $\Delta\Delta G^{\ddagger}$

of −0.32 and 0.16 kJ mol^{-1}, respectively, at a temperature of 200 K.

$$\Delta G^{\neq} = RT\left[\ln\frac{k_BT}{h} - \ln\frac{\pi(\Delta\nu)^2}{2W_{ex}}\right] \tag{3}$$

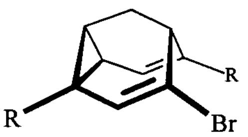
k_B = Bolzmann's constant, h = Planck's constant

$$(\Delta\Delta G^{\neq})_{T,W_{ex}} = -2RT\ln\left(1 + \frac{\Delta\Delta\nu}{\Delta\nu}\right) \tag{4}$$

$$(\Delta\Delta G^{\neq})_{T,\Delta\nu} = RT\ln\left(1 + \frac{\Delta W_{ex}}{W_{ex}}\right) \tag{5}$$

For most compounds studied here, Δν can be directly measured at low temperatures and the assumption that its value is the same at temperatures corresponding to fast exchange will certainly not introduce significant errors since the temperature dependence of ^{13}C-chemical shifts rarely exceeds 0.02 ppm K^{-1}.[45]

For certain 2,6-substituted 1,5-dimethylsemibullvalenes (**3d** and **e**) and the 1,5 annelated semibullvalenes (**7a**, **8a**), slow-exchange spectra could not be obtained, even at 151 MHz, and the calculation of rate constants for their Cope rearrangements therefore necessitates the use of estimated values of Δν. We previously used chemical shift data for 4-bromo derivatives of 2,6-substituted semibullvalenes[34] and barbaralanes[25a][26], which exist only as single valence tautomers, and assumed that the values of Δν were the same for the parent compounds. With the availability of higher-field spectrometers, however, we have been able to reach the low-temperature limit for several compounds for which the 4-bromo derivatives are also available, viz. **9d**[25a], **9j**[26] and **10a**[33b], **10d**[34], **11i**, and have thus been able to test this assumption. The appropriate data are presented in Table 1. We see, in fact, that the values predicted by the 4-bromo models vary appreciably from one system to another and that a generally applicable correction for the presence of the bromine atom is not feasible. Because of this and because in any case some of the required 4-bromo derivatives are unavailable, we have used an alternative approach for the estimation of Δν.



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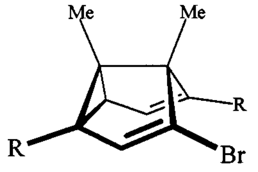

10

	R
10a	H
9d, 11d	CN
11i	4-*t*Bu-C_6H_4-SO_2
9j	Ph

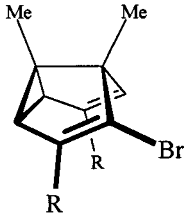

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Table 1. Comparison of $\Delta\delta_{6,2} = \delta_6 - \delta_2$ for barbaralanes **1** and 1,5-dimethylsemibullvalenes **3** and **4** with those for their 4-bromo derivatives **9**−**11**, respectively

Cpd.	R	*T* [K]	$\Delta\delta_{6,2}$	Difference	Ref.
1d	CN	128	91.4		this work
9d	CN	183	88.5	2.9	[25a]
1k	4-*t*Bu-C_6H_4	105	100.1		this work
9j	Ph	243	96.2	3.9	[26]
3a	H	108	87.3		[20]
10a	H	146	94.7	−7.4	[20]
		150	94.6	−7.3	[33b]
4d	CN	130	99.8		[43]
11d	CN	163	106.4	−6.6	[33b]
4i	4-*t*Bu-C_6H_4-SO_2	123	97.0		this work
11i	4-*t*Bu-C_6H_4-SO_2	144	100.4	−3.4	this work

All barbaralanes and semibullvalenes that possess the same substitution pattern of their allylic parts and could be investigated in the limit of slow exchange are presented in Table 2. We note that for the 3,7-substituted series (**2**, **4**), in cases where the comparison can be made, the differences between $\Delta\delta_{6,2}$ (= $\Delta\delta_{4,2}$) for the barbaralane and the semibullvalene are very similar, being equal to that observed for the parent hydrocarbons. In the one case where we can make the comparison between the 3,7 and 2,6-substituted series [(**2h**−**4i**) vs. (**1h**−**3h**)], there is rather close agreement. Accordingly, we have assumed that this is also true for the dinitriles and diesters and have estimated the values of Δδ for **3d** and **e** by subtracting the differences found for the appropriate pairs of 3,7 derivatives (**2d**, **4d**: 15.7 ppm; **2e**, **4e**: 15.4 ppm) from the values of Δδ of the corresponding 2,6-substituted barbaralanes **1d** and **1e**, respectively. The errors associated with this assumption are almost certainly less than from other sources (see below).

Table 2. Differences Δδ [ppm] in chemical shifts for exchange-related carbon atoms of barbaralanes (B) and semibullvalenes (S) from low-temperature (slow-exchange limit) carbon-13 spectra or estimated as described in the text (*in italics*); $\Delta\delta_{x,y} = \delta_x - \delta_y$

R	Cpd.	$\Delta\delta_{6,2}$B	Cpd.	$\Delta\delta_{6,2}$S	$\Delta\delta_{6,2}$B − $\Delta\delta_{6,2}$S
H	**1a**	103.1[17]	**3a**	87.3[20]	15.8
CN	**2d**	115.5[17]	**4d**	99.8[43]	15.7
CO_2Me	**2e**	111.3	**4e**	95.9	15.4
$PhSO_2$	**2h**	110.2	**4i**	97.0[a]	13.2
Ph	**2j**	97.8	**4j**	82.2[43]	15.6

R	Cpd.	$\Delta\delta_{6,2}$B	$\Delta\delta_{4,8}$B	Cpd.	$\Delta\delta_{6,2}$S	$\Delta\delta_{4,8}$S	$\Delta\delta_{6,2}$B −$\Delta\delta_{6,2}$S	$\Delta\delta_{4,8}$B −$\Delta\delta_{4,8}$S
CN	**1d**	91.4	97.5	**3d**	*75.7*	*83.7*		
CO_2Me	**1e**	96.0	103.1	**3e**	*80.6*	*87.7*		
$PhSO_2$	**1h**	92.0	107.3	**3h**	80.1 (*78.8*)	96.1 (*94.1*)	11.9	10.8

[a] The *tert*-butyl groups at the *para* position of the phenyl rings of **4i** improve the solubility at low temperatures. Their influence on $\Delta\delta_{6,2}$ was neglected.

Estimation of Line Widths in the Absence of Exchange

The observed line widths (W_{obs}) of resonances of nuclei undergoing exchange at rates comparable with the NMR time scale also contain contributions from other sources, e. g. spin spin relaxation (T_2), magnetic field inhomogeneity, and incomplete spin decoupling, which must be subtracted to give W_{ex} used in eqs. 1 and 2. The errors introduced in estimating these contributions are, of course, most serious as the fast- and slow-exchange limits are approached. For this reason we have tried to confine the data to temperature regions for which the corrections $W_{ref} = W_{obs} - W_{ex}$ are less than 10% of W_{obs}.

The way in which we have estimated the line width in the absence of exchange, i. e. W_{ref} in Tables 8−12, varies from one structure to another and is given explicitly in the Experimental Section for each of the compounds studied. Here we point out some of the general considerations regarding these estimates. At high temperatures (> 250 K), the only significant contributions to the line width in the absence of exchange are the inhomogeneity of the applied field and, in the case of proton-bearing carbon nuclei, a small residual broadening (0.5−1 Hz) due to incomplete proton decoupling. In this temperature range, any estimate of resolution (e. g. a solvent line in the proton spectrum) serves to provide an estimate of the almost negligible correction to W_{obs} of exchanging quaternary carbon nuclei, provided the decoupling channel is carefully tuned at each temperature. At lower temperatures, spin spin relaxation (T_2) becomes significant and eventually the dominant source of line broadening and must be estimated in other ways. In case of poor signal-to-noise ratios or very broad signals, FIDs, that were recorded at 151 MHz spectrometer frequency, were multiplied with small line broadening factors, which never exceeded 3 Hz. Because they affected both W_{obs} and W_{ref} very similarly, the errors introduced in this way were smaller than the deviation between repeated calculations of the exchange broadening W_{ex} from the same FID.

In the 3,7-substituted barbaralanes **2**, a careful study of the parent hydrocarbon **1a** reveals that the correction to W_{obs} for C-2,4,6,8 is closely approximated by W for C-9. We have compared (Table 3) the line widths for the nuclei C-9 and C-3,7, which are unaffected by exchange, as a function of temperature and proton decoupling frequency. It can be seen that, at their optimal decoupling frequencies, W for C-9 and C-3,7 are almost equal and, indeed they are when the decoupler frequency is set to its normal value in the "middle" of the proton spectrum. We have therefore used W for C-9 as the correction to W_{obs} of C-2,8 and C-4,6 in this series. That T_2 for C-9 is not approximately twice as short as that for C-3,7 is somewhat surprising and must be due to the longer carbon hydrogen bonds in the methylene group, and/or to the correlated reorientation of the C−H bond vectors.

In the case of the 2,6-substituted barbaralanes **1**, W of C-9 again provides a correction for that of C-4,8 but not of course for that of the quaternary carbons C-2 and C-6. Semibullvalenes pose a more difficult problem. In the 2,6-substituted series **3** and **5** there is no carbon atom that is unaffected by exchange on which to base estimates of line widths in the absence of exchange. In the 3,7-substituted semibullvalenes **4** (R ≠ H) and **6h**−**8h**, the exchange-invariant carbon atoms, i. e. C-3,7, are quaternary and hence their line widths are not appropriate estimates of those of C-2,4,6,8 in the absence of exchange. With the 1,5-substituted (**3a**) or 1,5-annelated derivatives (**7a**, **8a**) that have no other substituents, the line width of the C-3,7 resonance can be used. Line width data for carbon atoms of phenyl groups prove useful for some systems (**1h**, **j**, **k**, **3h**, **4h**, **i**, **l**, **5h**−**8h**).

Table 3. Comparison of the line widths [Hz] of C-9 and C-3,7 of barbaralane **1a** and the solvent chlorodifluoromethane (central line of the triplet) as a function of the proton decoupler frequency (expressed as δ* [ppm] at 600.13 MHz) and temperature

T [K]	δδ* = δδ of 3,7-H = 6.20			δδ* = middle of proton spectrum = 4.50			δδ* = δδ of 9-H = 1.90		
	C9	C3,7	$CHClF_2$	C9	C3,7	$CHClF_2$	C9	C3,7	$CHClF_2$
303	1.42	1.25	1.83	0.90	1.12	2.00	0.97	1.92	6.63
270	1.35	1.14	1.70	0.92	1.13	1.79	0.92	1.59	7.03
250	1.83	1.23	1.69	1.15	1.46	1.85	1.08	1.90	6.08
210	1.97	1.62	2.40	1.67	1.62	2.64	1.71	2.08	8.42
190	3.17	2.30	3.27	2.40	2.26	3.45	2.35	2.74	8.68
175	3.28	2.63	3.60	2.83	2.65	3.78	2.87	2.90	10.03
160	3.70	3.72	4.08	3.60	3.75	4.61	3.38	3.82	10.90

The Activation Parameters

Accurate determinations of the parameters of the Arrhenius and Eyring equations from the types of experiments used here present considerable difficulty. Ideally, they require measurements at 10−20 temperatures, divided between the fast- and slow-exchange rate regimes, with high signal-to-noise ratio and with careful tuning of both proton and carbon-13 channels between measurements. Usually a compromise between the optimum time for the total experiment and the availability of the spectrometer, as well as its overall long-term stability at low temperatures, necessitates use of less than optimal signal-to-noise and experiments at fewer than the optimal number of temperatures to be performed. In addition to these problems, other sources of errors, both random and systematic, may affect the accuracy of the determination of the activation parameters. Some of these are implicit in the preceding section. Furthermore, measurements of line widths are performed by fitting to a Lorentzian line shape which may not always be strictly valid. In addition, it is always necessary to assume that the frequency difference in the absence of exchange, Δν, is invariant with temperature although it is sometimes possible to test this assumption over a small range of temperatures in the slow-exchange region.[17]

As an inspection of the Eyring diagrams shows (Figures 1−4), errors in the temperature are most serious at low temperatures where calibration is difficult, because, so far, precise NMR shift thermometers were limited to temperatures above 175 K.[46][47] In most experiments, we employed a recently developed high-precision carbon-13 shift thermometer (temperature range 100−300 K)[48] and thus are able to estimate the temperature error at 1 K.

A considerable number of variable-temperature NMR experiments have been duplicated in two different laboratories on spectrometers of different frequencies as well as

Figure 1. Eyring diagrams for the degenerate Cope rearrangement of the hydrocarbons barbaralane (**1a**), 1,5-dimethylsemibullvalene (**3a**), 1,5-trimethylenesemibullvalene (**7a**) and 1,5-tetramethylenesemibullvalene (**8a**)

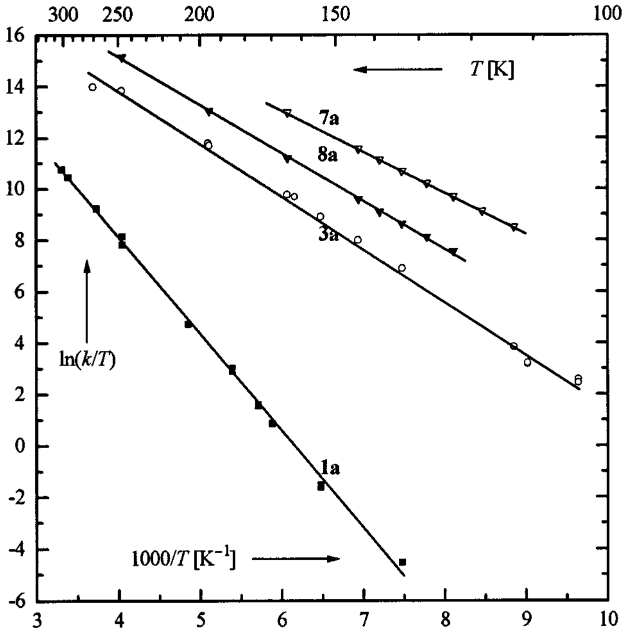


Figure 2. Eyring diagrams for the degenerate Cope rearrangement of disubstituted barbaralanes, viz. 2,6-bis(trifluoromethyl)barbaralane (**1c**), 2,6-barbaralanedicarbonitrile (**1d**), dimethyl 2,6-barbaralanedicarboxylate (**1e**), 2,6-bis(4-*tert*-butylphenyl)barbaralane (**1k**), dimethyl 3,7-barbaralanedicarboxylate (**2e**) and 3,7-diphenylbarbaralane (**2j**)

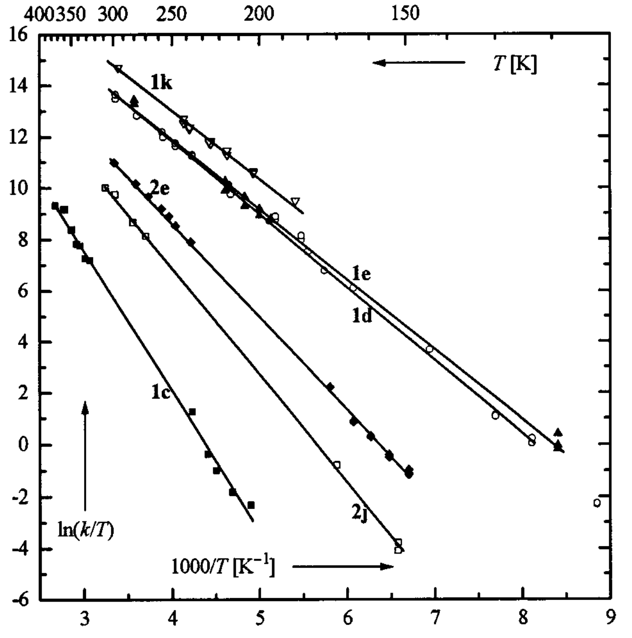


Figure 3. Eyring diagrams for the degenerate Cope rearrangement of disubstituted 1,5-dimethylsemibullvalenes, viz. dimethyl 1,5-dimethyl-2,6-semibullvalenedicarboxylate (**3e**), 1,5-dimethyl-2,6-semibullvalenedicarbonitrile (**3d**), 1,5-dimethyl-2,6-bis(phenylsulfonyl)semibullvalene (**3h**), 1,5-dimethyl-3,7-bis(4-*tert*-butylphenylsulfonyl)semibullvalene (**4i**), and 3,7-bis(3-methoxyphenyl)-1,5-dimethylsemibullvalene (**4m**)

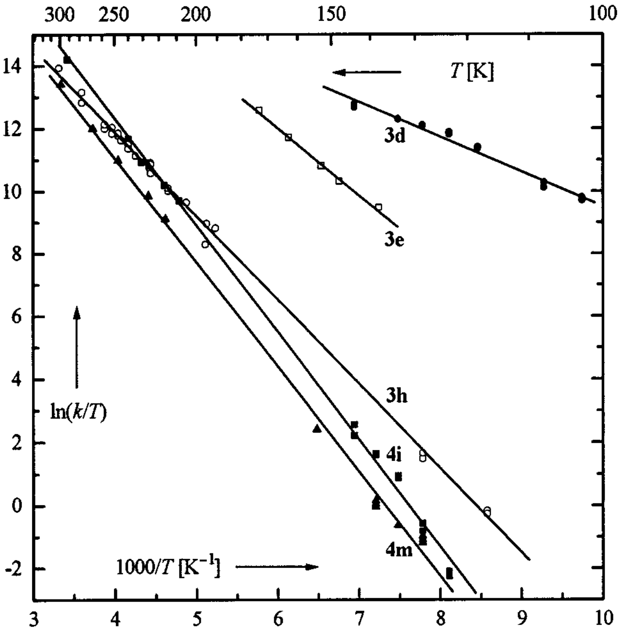
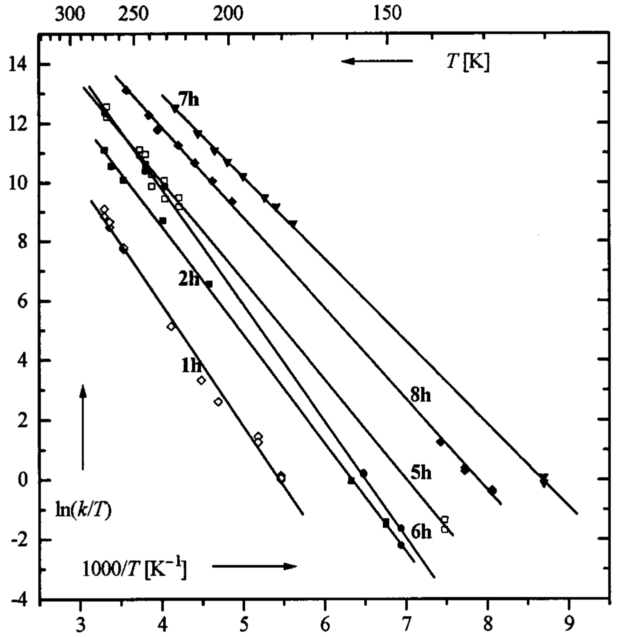


Figure 4. Eyring diagrams for the degenerate Cope rearrangement of the bis(phenylsulfonyl)barbaralanes **1h, 2h** and the bis(phenylsulfonyl)semibullvalenes **5h**−**8h**



on the same instrument (**1a**, **k**, **2e**, **3a** at 151 MHz). While satisfactory agreement between the two sets of data was observed in most cases, only those obtained at the highest field are listed in Tables 8−12 and employed in the calculations of the activation parameters.

By tradition, Arrhenius and Eyring parameters are calculated from rate vs. temperature data by the *linear* least-squares method according to the equations $\ln k = a - b/T$ and $\ln(k/T) = a - b/T$, respectively. Since a relatively large set of k data from a broad temperature range was available for several compounds, we calculated the Eyring parameters by a *nonlinear* least-squares fit according to $k = aT\exp(b/T)$ for the barbaralanes **1a**, **d** and the semibullvalenes **3a** and **h**. The results are included in Tables 4 and 5 and demonstrate that both methods yield the same values for $\Delta G^{\neq}$ at 200 K (within ca. 0.5 kJmol^{-1}). The enthalpies and entropies of activation, that were calculated with both the *linear* and the *nonlinear* least-squares method, differed by up to 2.5 kJ mol^{-1} and 10 J mol^{-1}K^{-1}, however, as shown for **3h**. For the sake of consistency with previous work and

Table 4. Parameter of the Eyring equation for the degenerate Cope rearrangement of barbaralanes **1** and **2**; data that are based only on line widths obtained in the fast-exchange regime are given in square brackets; enthalpies ($\Delta H^{\neq}$) and free enthalpies of activation at 200 K ($\Delta G^{\neq}_{200}$) are in kJ mol^{-1} K^{-1}, entropies of activation ($\Delta S^{\neq}$) in J mol^{-1} K^{-1}, and temperatures in Kelvin; the errors are statistical errors of regression analyses; the errors given in brackets [%] result from the analysis of kinetic errors devised by Benson[49] which was was performed according to the formulae given by Heinzer and Oth[50]

Cpd.	R	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta G^{\neq}_{200}$	T	[a]	Ref.
1a	H	31.71 ± 0.37 (1.5)	−3.34 ± 2.02 (24.4)	32.38 (0.59)	134 – 302	C/E	this work
		30.74 ± 0.21	−6.46 ± 0.65	32.04		[b]	this work
		30.54 ± 0.33 (1.6)	−2.47 ± 1.55 (70.9)	31.03	146 – 305	F/S	[17]
		30.71 ± 0.21 (1.8)	−3.64 ± 1.05 (99.7)	31.44	146 – 305	F/S	[17]
				32.1	184 – 204	[c]	[16]
				[31.9]	174 – 307	D[d]	[18a]
		30.63	−3.05	31.24		S	[18b]
1c	CF_3	45.10 ± 0.77 (1.4)	1.02 ± 2.88 (50.4)	44.89 (0.55)	204 – 373	C/E, D, T	this work
1d	CN	23.87 ± 0.17 (1.7)	−3.45 ± 0.97 (39.3)	24.56 (0.63)	113 – 257	C/E	this work
		24.02 ± 0.53	−4.03 ± 1.78	24.83		[b]	this work
				[24.3]	209 – 249	D[e]	[25a]
1e	CO_2Me	22.45 ± 0.38 (1.6)	−9.14 ± 2.18 (26.4)	24.28 (0.63)	119 – 280	C/D	this work
1f	Cl			36.4	178 – 298	D[e]	[28]
1h	$PhSO_2$	33.80 ± 0.75 (1.7)	−13.21 ± 3.30 (36.7)	36.44 (0.57)	183 – 303	A	this work
1j	Ph	[19.54 ± 0.62 (1.9)	−13.81 ± 2.97 (24.4)	22.30 (0.65)]	175 – 302	C/E[e]	this work
				[21.6]	169 – 233	D[e]	[26]
1k	4-*t*Bu-C_6H_4	[21.63 ± 0.47 (1.9)	−3.17 ± 2.05 (9.2)	22.27 (0.65)]	185 – 295	C/E[d]	this work
1n	4-MeO-C_6H_4			[21.1]	192 – 271	D[e]	[29]
1o	4-pyridyl			[20.1]	146 – 238	D[e]	[29]
1p	4-pyridyl•HCl			[<17.2]	163 – 294	M[e]	[29]
1q	4-pyridyl-*N*-oxide			[17.2]		D[e]	[29]
1r	2-furyl			[17.2]		[e]	[30]
2b	Me	39.41 ± 0.50 (1.5)	−1.72 ± 2.22 (78.8)	39.55	172 – 307	F/S	[17]
				[37]	206	[d]	[23]
2d	CN	29.50 ± 0.38 (1.8)	−12.43 ± 2.34 (29.5)	31.99	148 – 306	B/D	[17]
2e	CO_2Me	30.46 ± 0.18 (1.6)	−3.65 ± 1.03 (31.1)	31.19 (0.59)	149 – 299	C/D/E	this work
2g	Br	33.72 ± 0.71 (1.5)	−16.15 ± 3.31 (16.9)	36.95	159 – 306	F/S	[17]
2h	$PhSO_2$	30.18 ± 0.26 (1.5)	−5.98 ± 1.41 (30.0)	31.38 (0.59)	148 – 303	A/C	this work
2j	Ph	34.69 ± 0.32 (1.5)	−1.30 ± 1.60 (126)	34.95 (0.58)	152 – 308	C/D	this work
				34.5	206 – 240	[c]	[23]

[a] Solvents (ratios of solvent mixtures are given in the Tables in the Experimental Section): A = [D$_6$]acetone, B = dichlorodifluoromethane, C = chlorodifluoromethane, D = [D$_2$]dichloromethane, E = [D$_6$]dimethyl ether, F = [D$_8$]tetrahydrofuran, M = [D$_4$]methanol, S = carbon disulfide, T = [D$_8$]toluene. − [b] Nonlinear least-squares regression analysis according to $k = aT\exp(b/T)$. − [c] From proton spectra. − [d] Line widths in the limit of slow exchange were not used in the calculation. − [e] The limit of slow exchange has not been reached.

because the nonlinear method requires larger data sets of particularly high quality, which are not always available, we preferred the linear least-squares method.

Results

The Eyring diagrams of nine barbaralanes and twelve semibullvalenes of the total of 25 compounds that we have studied are displayed in Figures 1−4. Figure 1 comprises the plots for the hydrocarbons that lack substituents at their allylic parts. The lines for disubstituted barbaralanes and 1,5-dimethylsemibullvalenes are plotted in Figures 2 and 3, respectively, while the results from six phenylsulfonyl compounds are compiled in Figure 4. In all cases, straight lines were obtained without any suggestion of a curvature. A cursory inspection shows that most lines approximately converge on about the same point at the vertical axis thus indicating similar entropies of activation. Furthermore, the statistical errors in the activation parameters may be anticipated being small.

The enthalpies and entropies of activation for degenerate Cope rearrangements of the barbaralanes and semibullvalenes of the present work were computed by a linear least-squares treatment of the rate vs. temperature data, compiled in the Experimental Section (Tables 8−12), and are listed

Table 5. Parameter of the Eyring equation for the degenerate Cope rearrangement of semibullvalenes **3−8**; data that are based only on line widths obtained in the fast-exchange regime are given in brackets; enthalpies ($\Delta H^{\neq}$) and free enthalpies of activation at 200 K ($\Delta G^{\neq}_{200}$) are in kJ mol^{-1} K^{-1}, entropies of activation ($\Delta S^{\neq}$) in J mol^{-1} K^{-1}, and temperatures in Kelvin; the errors are statistical errors of regression analyses; the errors given in brackets [%] result from the analysis of kinetic errors devised by Benson,[49] which was performed according to the formulae given by Heinzer and Oth[50]

Cpd.	R	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta G^{\neq}_{200}$	T	[a]	Ref.
3a	H	17.03 ±0.30 (1.6)	−14.09 ±2.15 (1.7)	19.85 (0.68)	104 – 271	C/E	this work
		16.34 ±0.09	−16.52 ±0.35	19.64		[b]	this work
		[18.54 ±0.54 (2.3)	−6.82 ±3.35 (48)	19.90]	132 – 211	B/D	[20]
		19.20 ±7.5 (2.9)	−6.15 ±5.56 (78)	20.43	108 – 168	B/R	[20]
3d	CN	[9.19 ±0.39 (4.8)	−26.24 ±3.26 (12.8)	14.44 (0.80)]	103 – 144	C/E[c]	this work
				[13[d]]	115		[34]
3e	CO_2Me	[17.70 ±0.75 (5.1)	8.62 ±4.90 (73.3)	15.97 (0.76)]	138 – 173	C/D[c]	this work
3g	Br	31.38 ±0.50 (1.9)	1.26 ±2.59 (162)	31.13	156 – 251	D/V	[20]
3h	$PhSO_2$	22.33 ±0.28 (1.6)	−9.57 ±1.57 (132)	24.24 (0.63)	117 – 301	A/C, C/E	this work
		24.84 ±0.38	0.75 ±1.18	24.83		[b]	this work
4d	CN	23.4 ±0.8	−5.0 ±13	24.4	128 – 197	C/D	[43]
4e	CO_2Me	21.00 ±0.49 (1.8)	−14.86 ±2.66 (16.8)	23.98 (0.64)	108 – 247	C/E	this work
4f	Cl	20.9 ±0.9	−2.6 ±1.9	21.4	118 – 198	E/F	[40]
4h	$PhSO_2$	[25.03 ±1.18 (3.2)	1.08 ±5.16 (945)	24.81 (0.63)]	205 – 247	C/D[c]	this work
4i	4-*t*Bu-$C_6H_4SO_2$	28.25 ±0.39 (1.5)	17.53 ±2.51 (8.8)	24.74 (0.63)	123 – 292	C/E	this work
4j	Ph	25.5 ±0.8	−0.8 ±1.3	25.7	133 – 197	E	[43]
4l	4-Me-C_6H_4	28.66 ±0.81 (1.5)	6.90 ±4.39 (19.6)	27.28 (0.61)	128 – 301	C/D	this work
4m	3-MeO-C_6H_4	27.76 ±0.46 (1.5)	5.81 ±2.88 (30.5)	26.60 (0.62)	129 – 253	C/D/E	this work
5a	H	20.1 ±0.8	−22.6 ±13	24.6	106 – 170	B[e]	[19]
		21.92 ±0.38 (2.1)	−13.56 ±2.30 (37)	24.63	141 – 211	B/D[c]	[20]
5h	$PhSO_2$	27.66 ±0.46 (1.5)	−3.68 ±2.08 (88.6)	28.40 (0.78)	134 – 300	C/E	this work
6h	$PhSO_2$	32.61 ±0.57 (1.5)	14.08 ±3.20 (12.5)	29.80 (0.73)	144 – 302	C/E	this work
7a	H	[13.43 ±0.03 (3.7)	−8.25 ±0.20 (41.4)	15.08 (0.60)]	113 – 165	C/E[c]	this work
7h	$PhSO_2$	22.97 ±0.14 (1.9)	2.11 ±0.82 (61.5)	22.55 (0.60)	115 – 240	C/D	this work
8a	H	[15.56 ±0.16 (2.0)	−9.46 ±1.06 (17.1)	17.45 (0.65)]	123 – 247	C/E[c]	this work
8h	$PhSO_2$	25.40 ±0.18 (1.7)	2.51 ±1.11 (10.5)	24.90 (0.63)	116 – 248	A/C	this work

[a] Solvents (ratios of solvent mixtures are given in the Tables in the Experimental Section): Table 4, R = bromotrifluoromethane, V = vinyl chloride. − [b] Nonlinear least-squares regression analysis according to $k = aT\exp(b/T)$. − [c] The limit of slow exchange has not been reached. − [d] $\Delta G^{\neq}$ at 115 K.− [e] From proton spectra.

in Tables 4 and 5, respectively, which also include the results of early studies by von E. Doering,[16] Anet,[19] and Kessler[23] and their co-workers, and more recent investigations by Günther,[17][20] Müllen,[40][43] and Schröder[18][28][29][30] and their groups. Eyring parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ that are based only on rate data of the fast-exchange regime are given in square brackets. In a single case, viz. **1k** (Table 8), the quality of the spectrum from the slow-exchange region (ca. 100 K) allowed only the determination of the shift difference of the exchange-related carbon atoms but not of the corresponding line widths. The Tables 4 and 5 also contain the statistical errors of the least-squares regression analyses and the percentage errors from the error propagation treatment of kinetic data that has been devised by Benson[49] and detailed for activation parameters by Heinzer and Oth.[50]

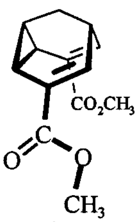
We note that, for the 11 barbaralanes and 15 semibullvalenes for which rate data was obtained in the fast- and slow-rate regions, the average $\Delta S^{\neq}$ value is ca. -4 ± 8 J mol^{-1} K^{-1}. The translational and rotational partition functions for ground and transition states of the Cope rearrangements of semibullvalene and barbaralane themselves should be very similar since orientation of solvent molecules is expected to be unimportant. This is presumably also true for derivatives with atomic, linear, or methyl substituents. It may not be true for compounds with substituents that need to adopt different conformations in the ground and transition states. In contrast to $\Delta H^{\neq}$ and $\Delta S^{\neq}$, the free enthalpy of activation, $\Delta G^{\neq}$, can be determined rather accurately since in most cases this involves an interpolation of the rate vs. temperature data. We will therefore base our evaluation of substituent effects on this quantity but we will draw attention to those special cases where conformational aspects may cause a problem. $\Delta G^{\neq}$ was calculated for the arbitrarily chosen intermediate temperature of 200 K that we have introduced previously for the purpose of comparison.[26] This temperature offers the advantage, that a short extrapolation is necessary only for a small number of the compounds studied, viz. **1c**, **3e**, **d** and **7a**.

The degenerate Cope rearrangement of *substituted* semibullvalenes and barbaralanes may be complicated by conformational ambiguities unless the substituents exhibit local symmetry $C_{\infty v}$, like halogen atoms or the cyano group, or C_{3v} associated with very low barriers like methyl and trifluoromethyl groups. In the 2,6-substituted series **1** and **3**, the conformation at the cyclopropane ring (C2) of substituents that have lower local symmetry differs from that at the double bond (C6), that is, the corresponding torsional angles involving the bonds to the substituents are different. This has been shown for the solid state by a number of X-ray diffraction analyses (**1h**, **1j**,[51] **3h**, **5h**[52]) and most probably is true for the molecules in solutions. If those conformations are maintained during the Cope rearrangement, such substituents would eventually end up with a different, less favorable torsion angle. Rotation would be required to restore the initial conformations. In reality, both processes are, of course, correlated. As long as these changes of torsional angles are small and rotational potentials flat, the conformational contributions to the activation parameters are small. This holds for phenyl and phenylsulfonyl groups at the 2,6 positions as in **1h**, **1j**, **3h** and **5h**, respectively, where the changes of the torsional angles may be estimated from X-ray data[51][52] to be less than 60° (**1h**: 51, 53°; **1j**: 34°; **5h**: 58°). Furthermore, flat torsional potentials of phenyl rings have been demonstrated for 2-phenyl- and 2,6-diphenylhomotropilidene,[53] phenylcyclopropane,[54] and α-methylstyrene[55], which may be taken as references for comparison.

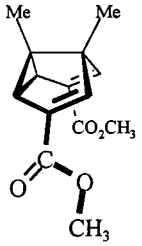
In the series of 3,7-substituted barbaralanes **2** and semibullvalenes **4**, **6h**−**8h**, the substituents are attached at carbon atoms that are *not* exchanged by the Cope rearrangement. Conformational effects are expected to be small for phenyl groups (**2j**, **4j**, **4l**, **4m**) whose planes certainly lie close to the plane of the double bonds. According to X-ray diffraction analyses, phenylsulfonyl groups adopt different conformations at the two sides (C3 and C7) of each semibullvalene **4h**−**8h**[52] but similar conformations at C3 and C7 of barbaralane **2h**.[56] As shown by carbon-13 spectra recorded for solutions in the temperature range of slow exchange, both sides of **4h**−**8h** are still equivalent on the NMR time scale at those temperatures. This attests to low barriers for the rotations around the S−C3 and S−C7 bonds. In addition, twisting around these bonds, which is required for degeneracy of the valence isomerisations (vide supra), is small as may be estimated from X-ray data (**2h**: 47, 60°[56]; **4h**: 11, 58°; **6h**: 0, 34°; **7h**: 11, 67°; **8h**: 6, 60°[52]). Therefore, we conclude that conformational effects by phenylsulfonyl groups raise the barrier for the degenerate exchange of **2h** and **4h**−**8h** very little if at all.

A different situation is presented by the dimethyl 3,7-barbaralane- and 3,7-semibullvalenedicarboxylates **2e**[56] and **4e**[57] whose ester groups and double bonds are virtually coplanar and adopt the *s-trans* conformation at both sides according to X-ray diffraction analyses. Different pathways may be envisaged for the degenerate exchange. No matter which of the two possible *symmetrical* conformations is preferred in solution, Cope rearrangement of the skeleton converts it into the less stable symmetrical conformation which subsequently relaxes by 180° rotations at both sides, for example (*s-trans*)$_2$-**4e** → (*s-cis*)$_2$-**4e**′ → (*s-trans*, *s-cis*)-**4e**′ → (*s-trans*)$_2$-**4e**′. The second pathway involves both *unsymmetrical* conformations (*s-cis*, *s-trans*)-**4e** and (*s-trans*, *s-cis*)-**4e**′ whose interconversion by Cope rearrangement is degenerate in every respect. The latter pathway is lower in energy by the energy difference between the *s-cis* and *s-trans* conformations and hence followed irrespective of the predominating conformation in solution. If this is a symmetrical one, the degenerate valence isomerisations of **2e** and **4e** resemble that of homotropilidene, which involves a conformational change and a Cope rearrangement.[7][58]

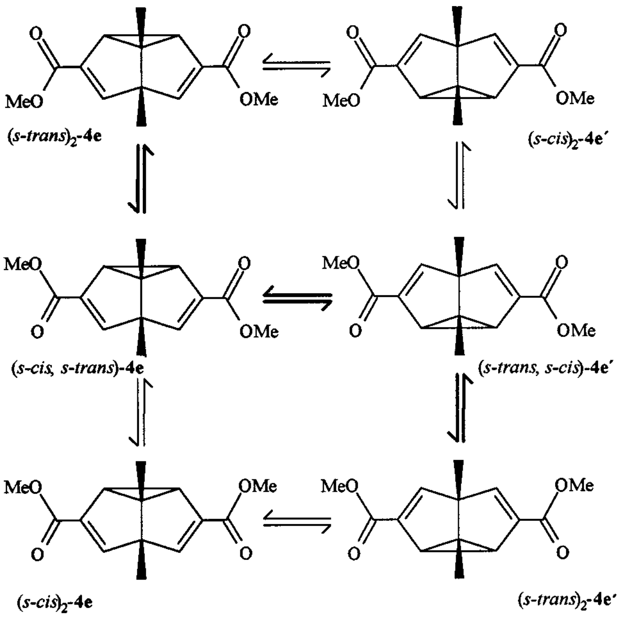
Unfortunately, the *s-cis*/*s-trans* conformational preference of enoates is not straightforward. So far, mostly *acyclic* enoates have been studied experimentally[59] and by ab initio calculations,[60][61] which give an estimated rotational barrier of 31 kJ mol^{-1}, relative to the (slightly more stable)



2e



4e



s-cis conformation, for methyl acrylate[60]. This value falls within the range of activation enthalpies for *s-cis* ⇌ s-*trans* interconversions of enoates determined experimentally (21–33.5 kJ mol^{-1}).[62] Methyl carboxylates derived from bicyclo[3.3.0]oct-2-ene and -octa-2,6-diene,[63] and bicyclo[3.3.1]nona-2,6-diene[51][56] prefer either the *s-cis*[51] or the *s-trans* conformation[56][63] as shown by X-ray diffraction analyses. Likewise, the ester groups at C4 and C6 of tetramethyl 2,4,6,8-barbaralanetetracarboxylate exist in the *s-cis* conformation,[27] while those of tetramethyl 1,5-dimethyl-2,4,6,8-semibullvalenetetracarboxylate adopt the *s-cis* conformation at one side but the *s-trans* conformation at the other.[64] These results demonstrate that the energetic similarity of acyclic *s-cis* and *s-trans* enoates[59][60][61] holds also for cyclic systems. Therefore, the energy difference between the *s-cis* and *s-trans* conformations adds probably little to the height of the barrier toward the valence isomerization of **2e** and **4e**.

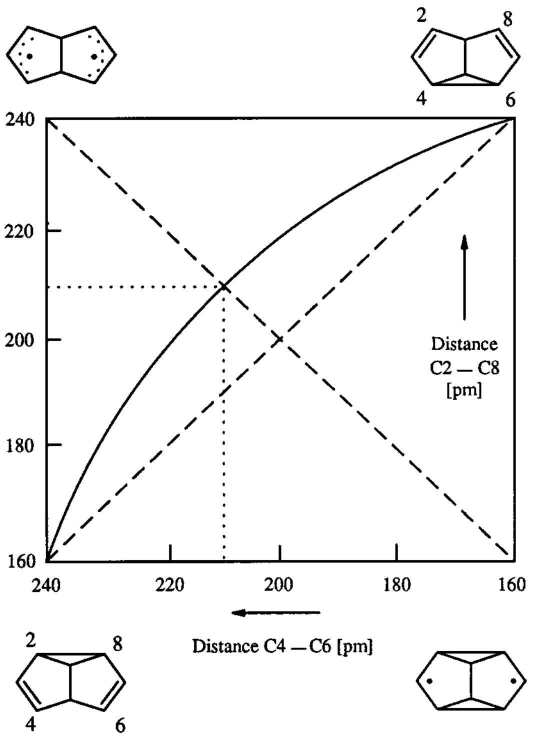
Some information concerning the predominating conformations of the ester groups can be obtained from carbon-13 spectra of **4e** recorded in the slow-exchange regime (108 and 113 K). Each of the pairs of the terminal atoms of the allylic system, viz. the cyclopropane carbon atoms C2 and C8 and the vinyl carbons C4 and C6, give rise to *two* signals (ratio 3:2) which are separated by 0.39 and 1.54 ppm, respectively. The higher intensity is observed for the downfield signal in case of the C4, C6 absorptions. The ratio is reversed for the C2, C8 absorptions. Obviously, the observed shift differences are caused by different conformations of the ester groups, which are interconverting slowly on the NMR time scale. Consequently, we interpret the low-temperature spectra in terms of the simultaneous presence of the unsymmetrical conformation (*s-cis*, *s-trans*-**4e**) and one of the symmetrical ones, either (*s-cis*)$_2$-**4e** or (*s-trans*)$_2$-**4e** in the ratio 4:1. Because the contributions to the exchange broadening W_{ex} of the Cope rearrangement and the rotation of the ester groups could not be separated on the basis of the available spectroscopic evidence, rate data for the slow-exchange limit were calculated only from the line widths of the two methyl signals.

Discussion

Any interpretation of substituent effects must be based on the relative weighting of transition state vs. reactant and product stabilisation, which depend on the respective geometric and electronic structures.

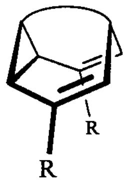
The precise timing of changes of any two bonds gives rise to a situation which may be expressed diagrammatically in terms of More O′Ferrall-Jencks energy surfaces. Since some twenty years, they provide a useful pictorial description of substituent effects on the transition states of Cope and Claisen rearrangements.[65][66][67][68][69] The structural coordinates for the degenerate Cope rearrangement of barbaralanes and semibullvalenes, are those for C2,8 bond breaking and for C4,6 bond making. They can be approximated by the distances C2–C8 and C4–C6 (Figure 5). By definition, the transition states of *degenerate* Cope rearrangements lie along the diagonal connecting the bis(allylic) and the diyl structures.[70] The precise position of the transition state for the parent semibullvalene (**5a**) on this diagonal may be inferred from recent quantum chemical calculations. On moving to the transition state structure, the C2–C8 and C4···C6 distances [159.4 and 241.0 pm in the (6,6)CASSCF/6-31G* geometry] are extended and contracted, respectively, to an interallylic distance of 211.7 pm (CASPT2N/6-31G* geometry). The CASSCF wave function of C_{2v} semibullvalene is dominated by a configuration that corresponds to the orbital occupancy of a fully delocalized aromatic species, but the second of the two most important configurations confers some diradical character to the bishomoaromatic systems.[15] This modest diradical character has its geometrical equivalent in the size of the interallylic distance, which is significantly longer than the average of the C2–C8 and C4···C6 distances in **5a**, and corresponds to the view that relief of strain is the major driving force for the degenerate Cope rearrangement of bridged homotropilidenes. Considering Dewar′s statement that the transition state becomes increasingly like a pair of allyl radicals as the length of that bridge is decreased,[10] we conclude that the transition state for the parent barbaralane **1a** lies between that of semibullvalene and the center of the More O′Ferrall-Jencks diagram.

Figure 5. More O'Ferrall-Jencks diagram for the Cope rearrangement of semibullvalene (**5a**)

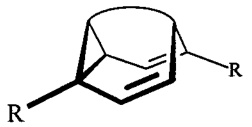


Substituents may modify the transition-state structure according to Thornton's "perpendicular effects". These substituent effects change the transition state geometry by perturbations of the vibrational potentials for the normal coordinate motions that are perpendicular to the reaction coordinate motion.[72] For the substituted degenerate barbaralanes and semibullvalenes, this variation reflects the delicate balance of the effects on the *three* limiting structures, viz. the bis(allylic) and 3,7-diyl structures at the corners of the More O'Ferrall-Jencks diagram and the homoaromatic structure in its center.

Regarding the ground state, we estimate the magnitude of substituent effects on the basis of two approximations. First we neglect subtle differences between barbaralanes and semibullvalenes and assume that substituents influence both systems in the same way. Second, we note that the two substitution pattern studied here differ, in the first place, by the position of *only one* of the two substituents. In the 2,6 series (**1**, **3**) this is attached to the cyclopropane ring, while in the 3,7 series (**2**, **4**, **6**−**8**) both substituents occupy a vinylic position. Thus, we approximate the difference of the substituent effects on both series by the enthalpy change of the isodesmic reaction eq. 6,[73] which, for phenyl and nitrile groups, can be calculated from thermochemical data to be surprisingly small [$\Delta\Delta H^0{}_f$(CN) = 0.4; $\Delta\Delta H^0{}_f$(Ph) = 1.8 kJ mol^{-1}].[74] Hence differences between the 2,6 and 3,7 series appear to be mainly due to substituent effects on the transition states.



2, 4, 6 – 8



1, 3

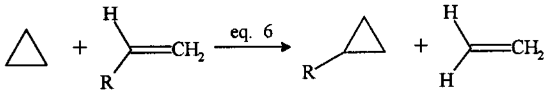


Table 6. Effect of substituents R on the degenerate Cope rearrangement of barbaralanes and semibullvalenes. $\Delta\Delta G^{\neq}$ [kJ mol^{-1}] is defined as ΔG^{+}(R)$-\Delta G^{+}$ (R = H) for 200 K; the values of the parent compounds used are ΔG^{+}(**1a**) = 32.38 and ΔG^{+}(**3a**) = 19.85. $\Delta\Delta H^{\neq}$ [kJ mol^{-1}] is the difference of the enthalpies of activation calculated by semiempirical methods for dicyanosemibullvalenes and the parent semibullvalene (**5a**)[12][13]

	Barbaralanes		Semibullvalenes		
$R_{2,6}$	Cpd.	$\Delta\Delta G^{\neq}{}_{200}$	Cpd.	$\Delta\Delta G^{\neq}{}_{200}$	$\Delta\Delta H^{\neq}$
CF_3	**1c**	12.5			
CN	**1d**	−7.8	**3d**	−5.4	−24.7,[a] −19.2[b]
CO_2Me	**1e**	−8.1	**3e**	−3.9	
Cl	**1f**	4.0			
Br			**3g**	11.2, 10.7[c]	
$PhSO_2$	**1h**	4.1	**3h**	4.4	
			5h	3.8	
Ph	**1j**	−10.1			
4-*t*Bu-C_6H_4	**1k**	−10.1			
4-MeO-C_6H_4	**1n**	−11.3			
4-pyridyl	**1o**	−12.3			
4-pyridyl·HCl	**1p**	<−15.2			
4-pyridyl-*N*-oxide	**1q**	−15.2			
2-furyl	**1r**	−15.2			
$R_{3,7}$					
Me	**2b**	8.5[d]			
CN	**2d**	1.0[d]	**4d**	4.6	17.2,[a] 4.6[b]
CO_2Me	**2e**	−1.2	**4e**	4.1	
Cl			**4f**	1.6	
Br	**2g**	5.9[d]			
$PhSO_2$	**2h**	−1.0	**4h**	5.0	
			6h	5.2	
			7h	7.5	
			8h	7.5	
4-*t*Bu-C_6H_4-SO_2			**4i**	4.9	
Ph	**2j**	2.6	**4j**	5.9	
4-Me-C_6H_4			**4l**	7.4	
3-OMe-C_6H_4			**4m**	6.8	

[a] MNDO calculation with 2×2 CI for homoconjugated structures.[12] – [b] AM1 calculation.[13] – [c] Calculated with the two slightly different data sets for **3a** given by Günther et al.[20] – [d] Calculated with the data for **1a** reported by Günther et al.[17]

Inspection of Table 6, which summarizes the effects of substituents on the free enthalpies $\Delta\Delta G^{\neq} = \Delta G^{\neq}(R) - \Delta G^{\neq}(H)$ at 200 K of the degenerate Cope rearrangement for a number of semibullvalenes and barbaralanes, permits several observations and conclusions.

First, we consider substituents at the termini of the allylic moities (R_2 and R_6). (i) Only electron-withdrawing groups that are classified as π acceptors lower the barrier in accord with Hoffmann′s predictions[9] and semiempirical calculations of 2,6-dicyanosemibullvalene.[12][13] The trifluoromethyl group, which Dewar suspected would lower the barrier,[10] in fact *raises* it considerably. Halogen substituents and the phenylsulfonyl group exert the same influence but to a lesser extent. (ii) The lowering of the barrier by π acceptor groups is more pronounced in barbaralanes than in semibullvalenes. (iii) The data in Table 6 confirm our previous finding that aryl groups at C2 and C6 are even more efficient than π acceptor groups.[26] (iv) Since both, the former and the latter interact by stabilizing both allyl radicals[75] and delocalized systems, it is difficult to estimate the extent of the operation of the perpendicular effect.[72]

π Acceptor groups, phenylsulfonyl groups, and phenyl rings at C3 and C7 change the Cope barriers of barbaralane very little but raise that of semibullvalene. The latter result was found for cyano groups by MNDO[12] and AM1 calculations.[13] These substituents interact similarly with the ground and transition state of barbaralane but destabilize the transition state for the Cope rearrangement of semibullvalene, given that their influence on the ground states is predicted to be the same for both systems (see above).

Table 7. Effect $\Delta\Delta G^{\neq}$ [kJ mol^{-1}] of substituents at C1 and C5 (R_1, R_5) of semibullvalenes on the degenerate Cope rearrangement; $\Delta\Delta G^{\neq}$ is defined as $\Delta G^{\neq}(R_1, R_5) - \Delta G^{\neq}(R_1 = R_5 = H)$ for 200 K

Cpd.	$R_{2,6}$ or $R_{3,7}$	R_1	R_5	$\Delta\Delta G^{\neq}_{200}$	Parent ($R_{1,5}$ = H)
3a	H	Me	Me	–4.8	**5a**
3h	$PhSO_2$			–4.2	**5h**
4h	$PhSO_2$			–5.0	**6h**
7a	H	$-(CH_2)_3-$		–9.6	**5a**
7h	$PhSO_2$			–7.3	**6h**
8a	H	$-(CH_2)_4-$		–7.2	**5a**
8h	$PhSO_2$			–4.9	**6h**

As has been observed by Günther et al.,[20] methyl substitution at the bridgeheads C1 and C5 of semibullvalene decreases the barrier toward the Cope rearrangement. This result is confirmed by the data for the phenylsulfonylsemibullvalenes **3h**−**6h** listed in Table 7. 1,5-Annulation of semibullvalene is even more effective. The tetramethylene bridge as in **8** and, in particular, the trimethylene bridge as in **7** lower the barrier more than any of the substituents on the allylic moiety that have been investigated so far! Obviously, this is caused by the relief of strain on the way to the Cope transition state. Extrapolation of the experimental result, viz. further shortening of the 1,5 bridge, would eventually lead to semibullvalenes that cope with the imposed strain by avoiding closure of the C2−C8 bond; in other words, by existing as delocalized, bishomoaromatic molecules. This hypothetical approach to homoaromatic semibullvalenes is suggested by chemical intuition and has been put on a more quantitative basis by semiempirical[12] and recent ab initio calculations.[14][15]

In addition to increase of strain in the σ skeleton of the localized semibullvalene structures, stabilizing electronic effects of π acceptors and aryl groups on the delocalized structures favor the existence of homoaromatic semibullvalenes. The magnitude of these effects may be deduced from the results presented in Tables 4−6. Clearly, four groups from these categories, attached to the termini of the two allylic moieties, do lower the Cope barrier beyond the limit of dynamic carbon-13 spectroscopy. Repulsion of the substituents on the cyclopropane ring (C2 and C8) of the localized form that are eclipsing will contribute to diminishing the barrier. We note that the effects of phenyl and cyano groups may be not only additive but cooperative, i. e. in terms of a donor-acceptor stabilisation of the delocalized system.

The syntheses of several promising candidates for neutral homoaromaticity in semibullvalenes and barbaralanes have been reported. Grohmann′s semibullvalene tetraesters[64][76][77] and William′s semibullvalene bisanhydride[78] are *not*, however, delocalized according to all experimental criteria. The same is true for 2,6-dicyano-4,8-diphenylbarbaralane[79] and 2,4,6,8-tetraphenylbarbaralane[80] as shown for the solid state by X-ray crystallography and by Saunder′s isotopic perturbation method for solutions.[81] No experimental decision has been reached so far in the case of 2,6-dicyano-1,5-dimethyl-4,8-diphenylsemibullvalene whose pronounced absorption of visible light suggests the as yet smallest energy difference between a localized and a delocalized semibullvalene structure[82] Clearly, this substitution pattern of a semibullvalene combined with a trimethylene bridge connecting C1 and C5 provides the safest, albeit perhaps not the most convenient recipe for a homoaromatic semibullvalene.

We are indebted to Professor *J. Sauer*, Regensburg, for samples of **4e**, **l**, and **m**. Professor *G. Schröder*, Karlsruhe, was so kind to bring data of **1n**−**r**, which were obtained by his group, to our attention. We thank Dr. *W. Ott*, *Merck*, Darmstadt, for providing the rate constants of the Cope rearrangement of **2j** and Dr. *K. Peters*, *Max-Planck-Institut für Festkörperforschung*, Stuttgart, for the calculation of torsional angles from X-ray data. M. H. is particulary grateful to Ms. *E. Ruckdeschel* and Dr. *D. Scheutzow* for technical advice. 4-*tert*-Butylthiophenol was a gift by the *Hoechst AG*, Frankfurt am Main. Chlorodifluoromethane was donated by *Solvay*, Hannover.

Experimental Section

Variable-Temperature NMR Experiments

Instrumentation: Bruker DMX 600 (Würzburg), operating at 150.90 MHz for carbon-13, equipped with a temperature control assembly B-VT-2000 (display and control unit BTO-2000-E) and a probe head heater BMT 05. − Bruker AM 500 (125.76 MHz), AM 360 (90.59 MHz, PSU) and AC 200 (50.32 MHz, Würzburg) equipped with a variable-temperature unit B-VT-1000. − Chemical shifts from carbon-13 spectra recorded at various temperatures are reported in ref.[83]. 91-MHz and 126-MHz carbon-13 spectra are reported in ref.[84] for **1e**, **h**, **2h**, **j**, **3e**, **h**, **4h**, and **7h**.

Table 8. Experimental line widths W_obs [Hz], line widths of reference signals W_ref and calculated exchange broadenings $W_\text{ex} = W_\text{obs} - W_\text{ref}$ and rate constants k [s^{-1}] for the degenerate Cope rearrangements of barbaralanes (**1**, **2**); the solvents employed and shift differences $\Delta\nu$ [Hz] in the slow-exchange limit, which were obtained from spectra recorded at the lowest temperatures listed, are also given; abbreviations used for solvents: A = [D$_6$]acetone, B = dichlorodifluoromethane, C = chlorodifluoromethane, D = [D$_2$]dichloromethane, E = [D$_6$]dimethyl ether, T = [D$_8$]toluene

1c	W_obs	W_ex	W_ref	$10^{-5}\,k$
T	C4,8		[a]	C4,8
	50 MHz, T, $\Delta\nu_{4,8} = 5466$			
373	13.4	11.3	2.1	41.4
361	15.7	13.7	2.0	34.3
359	15.8	13.9	1.9	33.8
350	33.9	30.9	3.0	15.1
343	57.1	55.2	1.9	8.51
338	61.5	59.7	1.8	7.87
332	103.4	99.5	3.9	4.71
326	110.3	109.5	0.8	4.29
	W_obs	W_ex	W_ref	$10^{-2}\,k$
	C4		C9	C4
	151 MHz, C / E = 3 : 1			
236.5	264	263	1.04	8.26
204.1	7.58	6.26	1.32	0.194
	151 MHz, D			
226.7	52.3	50.0	2.3	1.57
221.6	28.5	25.9	2.6	0.814
213.4	14.4	10.7	3.7	0.338

1e	W_obs			W_ex			W_ref	$10^{-5}\,k$		
T	C2,6	C4,8		C2,6	C4,8		CHClF$_2$	C2,6	C4,8	
	126 MHz, C / D = 3:1, $\Delta\nu_{6,2} = 12067$, $\Delta\nu_{4,8} = 12970$									
280	2.9	2.9		1.4	1.4		1.5	1634	1887	
217	55.7	44.6		54.1	43.0		1.6	42.2	61.5	
207	108	87.0		104	82.8		4.2	21.9	31.9	
200	156	140		154	138		2.0	14.9	19.1	
195	181			179			1.6	12.8		
	W_obs			W_ex				$10^{-2}\,k$		
	C2	C6	C8	C2	C6	C8		C2	C6	C8
119	38.3	43.1	63.0	31.3	36.1	56.0	7.0	0.97	1.13	1.76

1j	W_obs	W_ex	W_ref	W_obs	W_ex	W_ref	$10^{-5}\,k$	
T	C2,6		*i*-C	C4,8		*m*-C	C2,6	C4,8
	151 MHz, C / E = 3:1, $\Delta\nu_{6,2} = 15105$, $\Delta\nu_{4,8} = 13943$[b]							
302.2[c]	4.3	0.7	3.6	4.5	0.9	3.6	5510	3549
250.5[c]	8.0	4.5	3.5	7.9	4.2	3.7	796	727
247.4	8.5	4.2	4.3	8.7	4.3	4.4	853	710
216.4	20.5	16.2	4.3	21.6	17.0	4.6	221	180
211.2	40.1	35.7	4.4	26.6	21.9	4.7	100	139
206.0	50.7	46.8	3.9	49.7	45.5	4.2	76.5	67.1
200.9	44.7	40.2	4.5	48.5	43.6	4.9	89.1	70.0
195.7	60.6	55.4	5.2	57.3	51.5	5.8	64.6	59.3
189.4[c]	102	97.4	4.6	98.5	93.6	4.9	36.8	32.6
185.4[c]	176	171	5.1	157	152	5.3	20.9	20.1
175.0[c]	476	470	6.0	402	396	5.6	6.49	

1k	W_obs	W_ex	W_ref	W_obs	W_ex	W_ref	$10^{-5}\,k$	
T	C2,6		*t*Bu	C4,8		*m*-C	C2,6	C4,8
	151 MHz, C / E = 3:1, $\Delta\nu_{6,2} = 15105$, $\Delta\nu_{4,8} = 13943$ (at ~ 100 K)							
295	2.51	0.51	2.00	2.55	0.43	2.12	7027	7102
242	8.07	5.29	2.78	7.01	3.86	3.15	677.5	791.1
238[d]	10.45	6.98	3.47	9.31	5.52	3.79	513.5	553.2
226[d]	20.85	16.34	4.51	15.46	10.17	4.57	219.3	300.3
225	13.20	10.14	3.06	14.81	11.24	3.57	353.4	271.7
216	13.10	10.6	3.04	22.49	18.90	3.59	338.1	161.6
203[d]	46.8	42.9	3.85	44.0	39.0	4.97	83.5	78.3
185			2.43	130	126	3.60		24.2

2h	W_obs			W_ex			W_ref	$10^{-5}\,k$		
T	C2,4,6,8	C1,5		C2,4,6,8	C1,5		C9	C2,4,6,8	C1,5	
	126 MHz, A / C = 2:1, $\Delta\nu_{4,2} = 13858$, $\Delta\nu_{5,1} = 1635$									
303	15.8			15.2			0.6	198		
295	27.5			26.9			0.6	112		
283	45.0			44.3			0.7	68.1		
249		3.6			2.8		0.8		15.0	
218		28.7			27.5		1.2		1.53	
	W_obs			W_ex				$10^{-2}\,k$		
	C2,8	C4,6	C1	C2,8	C4,6	C1		C2,8	C4,6	C1
158	52.6		51.7	48.5		47.6	4.1		1.52	1.49
148	16.5	16.6	15.7	11.2	11.3	10.4	5.3	0.352	0.355	0.327

Table 8 *(Continued)*

2j	W_obs		W_ex		W_ref	$10^{-5}\,k$	
T	C2,4,6,8		C2,4,6,8	C1,5	C9	C2,4,6,8	C1,5
	126 MHz, A / C = 2:1, $\Delta\nu_{4,2} = 12299$						
308	35.5		34.9		0.6	68.1	
298	47.7		47.1		0.6	50.4	
281	150		149		0.8	15.9	
270	263		262		0.7	9.07	
	W_obs		W_ex			$10^{-2}\,k$	
	C2,8	C4,6	C2,8	C4,6		C2,8	C4,6
170	26.0	25.7	24.3	24.0	1.7	0.76	0.75
152	4.6	4.9	0.8	1.1	3.8	0.03	0.04

[a] Line width of C4,8 of 2,6-bis(trifluoromethyl)bicyclo[3.3.1]nona-3,7-diene, which was added to the sample. – [b] Shift differences of the 4-*tert*-butyl derivative **1k**. – [c] In [D$_2$]dichloromethane/[D$_6$]dimethyl ether (1:3). – [d] These data were obtained in a separate experiment.

Source of Compounds: The barbaralanes **1a**[85], **c**[51], **d**[25b], **e**, **h**[51], **j**[26], **2e**, **h**, **j**,[56] and semibullvalenes **3a**, **7a**, **8a**[85], **3d**[34], **e**[63], **3h**–**8h**,[52] were available from previous work. The 3,7-substituted 1,5-dimethylsemibullvalenes **4e**, **l** and **m** were kindly provided by Professor *J. Sauer*, Regensburg[57][86]. The syntheses of barbaralane **1k** and semibullvalene **4i**, which bear a *tert*-butyl group in the *para* position of their phenyl rings for improved solubility, follow the published routes for **1j**[26] and **4h**[52], respectively, and are described at the end of this Section.

Sample Preparation: The selection of suitable solvents was crucial because very low temperatures were required for rate studies in the slow-exchange limit. Sufficient solubilities were achieved in CHClF$_2$ mixed with deuterated solvents ([D$_6$]acetone, CD$_2$Cl$_2$ or [D$_6$]dimethyl ether) in a ratio that would provide a deuterium lock signal down to the lowest temperatures. [D$_8$]Toluene was used for experiments at higher temperatures. The solvents employed are given in Tables 8–12. – Samples were prepared from 20–100 mg of the barbaralanes or semibullvalenes in high-precision 5-mm tubes (Varian 507 PP) which were attached to a vacuum line (10^{-2} Torr) connected to the sources of CHClF$_2$ and [D$_6$]dimethyl ether, which were kept in steel cylinders. Solutions in CD$_2$Cl$_2$ and [D$_6$]-acetone were degassed by standard freeze-thaw techniques prior to the addition of CHClF$_2$. Solutions in neat solvents (**1c**, **h**) were degassed in the same way. Eventually, the tubes were evacuated at −196°C/10^{-2} Torr and sealed with a torch. The samples were allowed to thaw *very slowly*, which prevented breakage due to rapid expansion.

Carbon-13 Spectra: Because the limit of slow exchange is reached only at very low temperatures, if at all, for a number of compounds, the cooling rate of the samples became a critical factor. Very rapid cooling resulted in the precipitation of the dissolved compounds. – The sample tubes were allowed to equilibrate thermally for 15 min. At each temperature, changes of the frequencies of proton and carbon-13 channels and the impedance of the receiver circuit were carefully compensated before recording WALTZ-16-decoupled carbon-13 spectra without spinning (Bruker DMX 600 and AM 500). – Each temperature was calibrated with the help of NMR shift thermometers; DMX 600: carbon-13 shift thermometer for the range of 100–300 K, based on the temperature dependence of shifts of the rapidly equilibrating valence tautomers 1-ethyl-5-methyl-2,6-semibullvalenedicarbonitrile and 5-ethyl-1-methyl-2,6-semibullvalenedicarbonitrile[48]. AM 500: Methanol proton shift thermometer[46] (175–300 K). In a single experiment (**1c**, Table 8), broadband decoupled 50.3-MHz carbon-13 spectra were recorded at temperatures above 310 K with a Bruker AC200 and calibrated with the ethylene glycol proton shift thermometer.[87a] − Zero filling to 4 times the number of measured data points was performed resulting in a digital resolution ≤ 0.034 Hz/point. When signals were broad (W_{obs} > 50 Hz) or spectra had a poor signal-to-noise ratio, the FIDs, that were recorded with the Bruker DMX 600, were multiplied with exponential functions having small line-broadening factors of maximal 3.0 Hz. The influence of various line-broadening factors on W_{ex} was tested for **1a** at 302 and 247 K. Line-broadening factors of 0, 3, and 5 Hz gave W_{ex} = 28.0 ± 0.1, 28.4 ± 0.1, and 28.6 ± 0.2 Hz for the former, 461 ± 6, 466 ± 12, and 465 ± 13 Hz for the latter temperature, respectively. Particular attention was paid to the phase and the baseline corrections because small deviations from the optimum resulted in considerable errors in the line widths. − The Lorentzian lineshape least-squares fitting routine, which is part of the Bruker software package, was used for the determination of the line widths. Computed lineshapes were adjusted to strongly expanded experimental signals by inspection. When six values of the line widths obtained in this way agreed within 5%, their average was calculated and is reported as W_{obs} and W_{ref} in Tables 8−12.

Table 9. Experimental line widths W_{obs} [Hz], line widths of reference signals W_{ref} and calculated exchange broadenings W_{ex} = W_{obs} − W_{ref} and rate constants k [s^{-1}] for the degenerate Cope rearrangements of semibullvalenes (**3**, **5h**, **7a**, **8a**); the solvents employed and shift differences Δν [Hz] in the slow-exchange limit, which were obtained from spectra recorded at the lowest temperatures listed, are also given; solvents: see Table 8

3a	W_{obs}		W_{ex}		W_{ref}	$10^{-5}\,k$	
T	C2,4,6,8		C2,4,6,8		C3,7	C2,4,6,8	
	151 MHz, C / E = 7:1, $\Delta\nu_{4,2}$ = 13248						
271.2[a]	5.2		0.9		4.3	3206	
247.4	4.9		1.1		3.8	2580	
196.0[a]	13.8		10.8		3.0	255	
195.7	15.1		11.7		3.4	235	
164.7	100		96.6		3.4	28.5	
162.4[a]	109		106		3.4	26.0	
154.3[a]	251		247		3.5	11.2	
144.0[a]	663		658		4.7	4.19	
133.7	2131		2127		4.4	1.30	
	W_{obs}		W_{ex}			$10^{-2}\,k$	
	C2,6	C4,8	C2,6	C4,8		C2,6	C4,8
113.0	1655		1648		6.8	51.8	
110.9	854	871	847	864	7.1	26.8	27.1
103.7	442	388	432	378	9.8	13.6	11.9

3d	W_{obs}		W_{ex}		W_{ref}	$10^{-5}\,k$	
T	C2,6	C4,8	C2,6	C4,8	C3,7	C2,6	C4,8
	151 MHz, C / E = 7:1, $\Delta\nu_{6,2}$ = 11423, $\Delta\nu_{4,8}$ = 12630[b]						
144	7.2	8.7	4.0	5.5	3.2	510	456
134	10.2	11.7	7.0	8.5	3.2	292	295
129	13.2	15.3	8.9	11.0	4.3	230	228
123	22.7	24.4	12.3	14.0	10.4	167	179
118	37.9	43.2	19.2	24.5	18.7	107	102
108	106	109	76.8	79.6	29.2	26.7	31.5
103	153	166	121	134	31.7	16.9	18.7

3e	W_{obs}	W_{ex}	W_{ref}	$10^{-5}\,k$
T	C2,6	C2,6	$CHClF_2$	C2,6
	126 MHz, C / D = 4:1, $\Delta\nu_{6,2}$ = 10131[c]			
173	4.1	3.2	0.9	504
163	8.9	8.0	0.9	202
153	21.7	20.9	0.8	77.1
148	36.6	35.7	0.9	45.2
138	87.0	86.0	1.0	18.7

5h	W_{obs}		W_{ex}		W_{ref}		$10^{-5}\,k$	
T	C2,6	C4,8	C2,6	C4,8	*i*-C	*m*-C	C2,6	C4,8
	151 MHz, C / E = 3:1, $\Delta\nu_{6,2}$ = 12570, $\Delta\nu_{4,8}$ = 14517							
300.1	5.90	8.43	2.92	5.51	2.98	2.92	850	601
268.1	19.2	29.1	13.9	22.0	5.32	7.10	179	151
262.9	29.0	27.7	23.1	22.1	5.88	5.55	107	150
257.7	54.8	49.9	49.8	44.3	4.98	5.64	49.8	74.7
247.4	84.5	64.1	79.8	57.0	4.70	7.05	31.1	58.1
237.1	114	112	109	106	5.30	6.51	22.8	31.2
	W_{obs}		W_{ex}				$10^{-2}\,k$	
	C2	C4	C2	C4			C2	C4
133.6	14.8	17.8	7.8	10.8	7.0	7.0	0.245	0.339

7a	W_{obs}	W_{ex}	W_{ref}	$10^{-5}\,k$
T	C2,4,6,8	C2,4,6,8	C3,7	C2,4,6,8
	151 MHz, C / E = 7:1, Δν = 13301[d]			
164.7	6.5	3.4	3.1	708
144.0	21.9	18.8	3.1	150
138.8	33.5	30.2	3.3	94.8
133.7	53.3	50.1	3.2	58.2
128.5	95.4	91.1	4.3	34.4
123.3	163	146	16.3	19.6
118.2	276	258	18.2	10.6
113.0	476	456	20.3	5.49

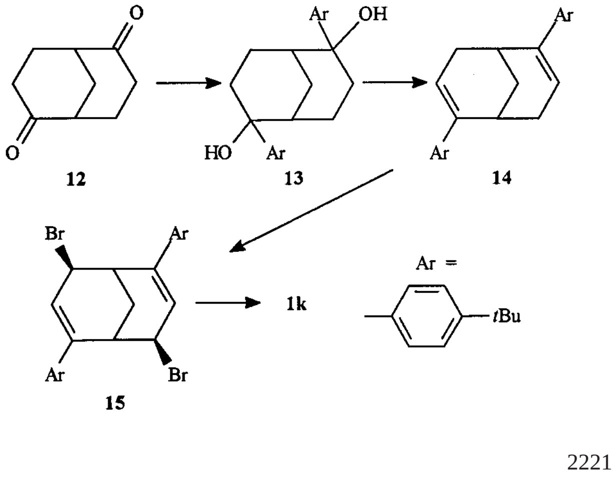
Table 9 *(Continued)*

8a	W_{obs}	W_{ex}	W_{ref}	$10^{-5}\,k$
T	C2,4,6,8	C2,4,6,8	C3,7	C2,4,6,8
	151 MHz, C / E = 3:1, Δν = 13301[d]			
247	1.5	0.3	1.2	9310
196	5.2	3.1	2.1	896
165	30.0	23.5	6.5	119
144	148	135	12.9	20.7
139	241	229	12.4	12.2
134	392	379	12.9	7.38
129	670	656	13.8	4.26
123	1219	1203	16.3	2.32

[a] These data were obtained in a separate experiment. − [b] $\Delta\nu_{6,2}$ and $\Delta\nu_{4,8}$ were estimated from the barbaralane **1d** [Δδ(**3d**) = Δδ(**1d**) − 15.7 ppm, see Table 2]. − [c] $\Delta\nu_{6,2}$ was estimated from the barbaralane **1e** [Δδ(**3e**) = Δδ(**1e**) − 15.4 ppm, see Table 2]. − [d] Shift difference of C-2 and C-4 in the low-temperature spectrum (ca. 100 K) of 1-ethyl-5-methylsemibullvalene[83], which is the major isomer of the pair of valence tautomers.

Rate Constants and Eyring Parameters: Rate constants k were calculated from line widths with the help of eq. 1 and 2 as appropriate (Tables 8−12). The Eyring parameters listed in Tables 4 and 5 were obtained by least-squares fits of ln(k/T) vs. $1/T$ data (Figures 1−4). The errors given in Tables 4 and 5 are statistical errors that result from the regression analysis of the Eyring plots. In addition, the error treatment for kinetic parameters given by Benson[49] was used for the Eyring parameters. It is based on the errors in k and T at the highest and lowest temperature employed for the measurements.[50] The error in k was estimated as 5% owing to the error in line width and Δν. The error in T was estimated to be ±1 K. The percental errors determined in this way are given in brackets in Tables 4 and 5.

Synthesis of Barbaralane **1k**[88]



2,6-Bis(4-tert-butylphenyl)bicyclo[3.3.1]nonane-2,6-diol (**13**): To a stirred solution of 4-*tert*-butylbromobenzene (20.8 ml, 120 mmol) in diethyl ether (150 ml), kept under N_2 at −60°C, a solution of butyllithium in hexane (1.286 M, 80 ml, 103 mmol) was added within 45 min. After 1 h at −78°C, the yellow solution was allowed to warm, while a solution of **12** (5.0 g, 33 mmol)[89] in a mixture of diethyl ether (225 ml) and tetrahydrofuran (150 ml) was added within 1 h. The solution was heated under reflux for 15 h. After cooling at 0°C, sat. aq. NH_4Cl (25 ml) was added slowly. The organic layer was extracted with a mixture of sat. aq. NH_4Cl and water (1:1, 2 × 125 ml) and water (125 ml). The aq. layers were extracted with diethyl ether (2 × 50 ml). Drying of the combined organic layers with $MgSO_4$ and distillation of the solvent i. vac. yielded a colorless, waxy solid, which was recrystallized twice from CH_2Cl_2 at 0°C to afford colorless crystals (9.71 g, 70%, m. p. 252−254°C). − IR (KBr) [cm^{-1}]: ν = 3550 (OH). − MS: *m/z* (%): 402 (3) [$M^+ - H_2O$], 384 (40) [$M^+ - 2H_2O$], 287 (3) [$M^+ - t\mathrm{BuC_6H_4}$], 241 (14), 240 (11), 214 (31), 199 (14), 169 (18), 161 (100) [$t\mathrm{BuC_6H_4CO^+}$], 133 (13) [$t\mathrm{BuC_6H_4^+}$], 57 (67).

Table 10. Experimental line widths W_{obs} [Hz], line widths of reference signals W_{ref} and calculated exchange broadenings $W_{\mathrm{ex}} = W_{\mathrm{obs}} - W_{\mathrm{ref}}$ and rate constants k [s^{-1}] for the degenerate Cope rearrangements of semibullvalenes (**4**, **6h**, **7h**); the solvents employed and shift differences $\Delta\nu$ [Hz] in the slow-exchange limit, which were obtained from spectra recorded at the lowest temperatures listed, are also given; solvents: see Table 8

4e	W_{obs}		W_{ex}		W_{ref}		$10^{-5}\,k$	
T	C2,4,6,8		C2,4,6,8		$CHClF_2$		C2,4,6,8	
	151 MHz, C / E = 7:1, $\Delta\nu_{4,2}$ = 14471[a]							
247.4	8.7		7.0		1.7		473	
221.6	44.7		43.0		1.7		76.9	
216.4	68.0		66.0		2.0		50.1	
211.2	83.2		81.4		1.8		40.6	
206.0	131		129		1.9		25.7	
	W_{obs}		W_{ex}				$10^{-2}\,k$	
	C1	C5	C1	C5			C1	C5
113.0	46.2	46.8	20.3	20.9	25.9		0.64	0.66
107.8	49.3	48.6	11.1	10.4	38.2		0.35	0.33
4h	W_{obs}		W_{ex}		W_{ref}		$10^{-5}\,k$	
T	C2,4,6,8		C2,4,6,8		*p*-C		C2,4,6,8	
	126 MHz, C / D = 3:1, $\Delta\nu_{4,2}$ = 12200[b]							
270	3.5		2.6		0.9		899	
247	8.8		8.4		0.4		278	
237	13.0		12.5		0.5		187	
232	19.5		18.7		0.8		125	
219	34.2		33.4		0.8		70.0	
211	89.5		88.6		0.9		26.4	
205	116		115		1.0		20.3	
4i	W_{obs}		W_{ex}		W_{ref}		$10^{-5}\,k$	
T	C2,4,6,8		C2,4,6,8		*o*-C		C2,4,6,8	
	151 MHz, C / E = 8:1, $\Delta\nu_{4,2}$ = 14637							
292	2.99		0.79		2.20		4260	
240	14.6		12.0		2.62		280	
231	29.5		26.1		3.42		129	
226	33.6		30.2		3.36		111	
217	61.1		57.7		3.42		58.3	
209	102		97.8		3.66		34.4	
	W_{obs}		W_{ex}				$10^{-2}\,k$	
	C2,8	C4,6	C2,8	C4,6			C2,8	C4,6
144	428	611	414	589	13.4		13.0	18.5
139	240	232	225	217	15.2		7.06	6.82
134	121	128	101	108	19.7		3.17	3.39
129	42.7	47.8	17.9	23.0	24.8		0.562	0.722
123	37.0	37.6	4.1	4.7	32.9		0.129	0.148
4l	W_{obs}		W_{ex}		W_{ref}		$10^{-5}\,k$	
T	C2,4	1,5Me	C2,4	1,5Me	*o*-C	*p*-C	C2,4	1,5Me
	151 MHz C / D = 7:1, $\Delta\nu_{4,2}$ = 12348, $\Delta\nu_{\mathrm{Me}}$ = 273							
301.2	2.8		0.9		1.9		2677	
257.7	14.7		12.7		2.0		190	
252.6	17.9		16.7		1.2		144	
247.4	24.0		22.7		1.3		106	
242.2	30.1		28.9		1.2		83.3	
237.1	40.0		37.8		2.2		63.7	
226.7	78.7		76.5		2.2		31.5	
185.4		5.4		3.3		2.1		0.355
169.9		18.3		16.7		1.6		0.070
154.3		153		151		2.1		0.008
	W_{obs}		W_{ex}				$10^{-2}\,k$	
	1Me		1Me				1Me	
144.0	71.6		67.9			3.7	2.13	
133.7	21.1		15.0			6.1	0.50	
128.5	20.0		12.7			7.3	0.40	
6h	W_{obs}		W_{ex}		W_{ref}		$10^{-2}\,k$	
T	C2,4	C1,5	C2,4	C1,5	*p*-C		C2,4	C1,5
	151 MHz, C / E = 6:1, $\Delta\nu_{4,2}$ = 15149, $\Delta\nu_{5,1}$ = 665							
302.2	6.5		5.2		1.3		699	
262.9	43.1		41.8		1.3		86.0	
247.4	77.1		75.5		1.6		47.7	
195.7		24.3		21.2	3.1			0.63
	W_{obs}		W_{ex}				$10^{-2}\,k$	
	C2,8	C4,6	C2,8	C4,6			C2,8	C4,6
154.3	68.1	65.4	61.2	58.5	6.9		1.92	1.84
144.0	14.3	18.2	5.0	8.9	9.3		0.16	0.28
7h	W_{obs}		W_{ex}		W_{ref}		$10^{-5}\,k$	
T	C2,4,6,8		C2,4,6,8		*p*-C		C2,4,6,8	
	126 MHz, C / D = 3:1, $\Delta\nu$ = 12312							
240	4.3		3.6		0.7		660	
225	10.0		9.2		0.8		260	
215	18.1		17.1		1.0		140	
208	28.3		25.9		2.4		92	
200	45.7		44.3		1.4		54	
190	95.8		94.0		1.8		25	
185	137		135		2.0		18	
178	251		249		2.2		9.6	
	W_{obs}		W_{ex}				$10^{-2}\,k$	
	C2,8	C4,6	C2,8	C4,6			C2,8	C4,6
115	37.0	44.0	32.0	39.0	5.0		1.01	1.23

[a] $\Delta\nu_{4,2}$ is the difference between the average shifts of the low-field (C4, C6) and the high-field pair (C2, C8) of signals (see text). − [b] Calculated from the shift difference in the 151-MHz carbon-13 spectrum of the 4-*tert*-butyl derivative **4i** for the slow-exchange limit.

2,6-Bis(4-tert-butylphenyl)bicyclo[3.3.1]nona-2,6-diene (**14**): Diol **13** (8.00 g, 19 mmol) was added to a mixture of acetic acid (16 ml) and conc. H_2SO_4 (4 ml). The mixture was shaken for 5 min to afford a suspension which was diluted with water (120 ml) and extracted with petroleum ether (b. p. 30−50°C, 2 × 175 ml). The organic layer was extracted with sat. aq. $NaHCO_3$ (2 × 80 ml) and water (80 ml), and dried with $MgSO_4$. Distillation of the solvent i. vac. and drying of the residue (10^{-2} Torr) yielded colorless crystals (7.19 g, 99%, m. p. 125−127°C). Recrystallization from methanol gave colorless crystals m. p. 127−128°C. − IR (KBr) [cm^{-1}]: ν = 1630 (C=C). − MS: *m/z* (%): 384 (25) [M^+], 343 (16) [$M^+ - C_3H_5$], 271 (5), 183 (6), 177 (17), 163 (10), 149 (9), 91 (6), 57 (100).

4,8-Dibromo-2,6-bis(4-tert-butylphenyl)bicyclo[3.3.1]nona-2,6-diene (**15**): A solution of **14** (4.0 g, 10.4 mmol) in cyclohexane (400 ml) was heated under reflux and *N*-bromosuccinimide (4.44 g, 25 mmol) and azodiisobutyronitrile (0.1 g) were added. The conversion was monitored by reversed-phase HPLC with acetonitrile. After 2 h, the cooled solution was extracted with aq. NaOH (0.5 M, 2 × 300 ml), sat. aq. $NaHCO_3$ (300 ml), and water (300 ml), and dried with $MgSO_4$. Distillation of the solvent i. vac. yielded a yellow crude product (5.18 g, m. p. 172−175°C) consisting of **15** (92%), **14** (1%) and a monobromo compound (4%, RP-HPLC). Recrystallization from ethyl acetate afforded yellow crystals (4.58 g, 89%, m. p. 177−178°C). − MS: *m/z* (%): 542 (< 1) [M^+], 463

Table 11. Experimental line widths W_{obs} [Hz], line widths of reference signals W_{ref} and calculated exchange broadenings $W_{\mathrm{ex}} = W_{\mathrm{obs}} - W_{\mathrm{ref}}$ and rate constants k [s^{-1}] for the degenerate Cope rearrangements of barbaralanes (**1**, **2e**); the solvents employed and shift differences $\Delta\nu$ [Hz] in the slow-exchange limit, which were obtained from spectra recorded at the lowest temperatures listed, are also given; solvents: see Table 8

1a	W_{obs}		W_{ex}		W_{obs}		W_{ex}		W_{ref}		$10^{-5}\,k$			
T	C2,4,6,8				C1,5				C3,7		C2,4,6,8		C1,5	
	151 MHz, C / E = 3:1, $\Delta\nu_{4,2}$ = 15783, $\Delta\nu_{5,1}$ = 1795.7													
302.2	28.7		27.8						1.1		141			
295[a, b]	39.6		38.7						0.9		101			
268.1	147		146						1.1		26.8			
247.0	469		465						3.4		8.41			
206.0					223		219		3.6				0.229	
	W_{obs}		W_{ex}		W_{obs}		W_{ex}				$10^{-2}\,k$			
	C2,8	C4,6	C2,8	C4,6	C1	C5	C1	C5			C2,8	C4,6	C1	C5
185.4	1047	1183	1045	1181					2.3		32.8	37.1		
175[a, b]	257	251	254	248					3.0		7.99	7.79		
169.9	129	131	126	128					2.7		3.96	4.02		
154.3	13.4	13.5	9.7	9.8	14.2	14.0	10.5	10.3	3.7		0.305	0.308	0.330	0.324
133.7[b]	5.8		0.45						5.3		0.014			
1d	W_{obs}		W_{ex}			W_{obs}	W_{ex}		W_{ref}		$10^{-5}\,k$			
T	C2,6	C4,8	C2,6	C4,8		C1,5			C9		C2,6	C4,8	C1,5	
	151 MHz, C / E = 3:1, $\Delta\nu_{6,2}$ = 13795, $\Delta\nu_{4,8}$ = 14707, $\Delta\nu_{5,1}$ = 665													
256.7	9.4	10.4	7.4	8.4					2.0		404	404		
247.4	14.4	15.8	11.1	12.5					3.3		272	306		
214.3	86.6	97.3	81.5	92.2					5.1		36.8	36.7		
195.7		291		286					5.1			11.9		
180.2		1042		1037		7.5	2.1		5.4			3.28	3.31	
174.1						10.1	4.5		5.6				1.54	
164.7						17.5	9.7		7.8				0.7336	
144.0						135	127		8.3				0.056	
	W_{obs}		W_{ex}			W_{obs}	W_{ex}				$10^{-2}\,k$			
	C2	C4	C2	C4		C1					C2	C4	C1	
130.1	134	132	126	124		128	120		7.6		3.96	3.90	3.75	
123.3	51.8	60.4	40.3	48.9		60.6	49.1		11.5		1.27	1.54	1.54	
113.0		20.2		3.7		20.1	3.6		16.5			0.116	0.113	
1h	W_{obs}		W_{ex}		W_{obs}		W_{ex}		W_{ref}		$10^{-5}\,k$			
T	C2,6				C4,8	C1,5	C4,8	C1,5	*i*-C	C9	C2,6	C4,8		C1,5
	91 MHz, A, $\Delta\nu_{6,2}$ = 8331.5, $\Delta\nu_{4,8}$ = 9717.1, $\Delta\nu_{5,1}$ = 371.3													
303	40.0		39.7		70.7		69.3		0.3	1.4	27.5	21.4		
297	76.5		76.1		86.7		85.3		0.4	1.4	14.3	17.4		
283	170		170		218		216.5		0.4	1.5	6.41	6.85		
243						8.7		5.2		3.5				0.416
223						38.5		34.6		3.9				0.063
213						77.5		74.4		3.1				0.029
	W_{obs}		W_{ex}		W_{obs}		W_{ex}				$10^{-2}\,k$			
	C2	C6	C2	C6	C4		C4				C2	C6	C4	
193	270	225	263	218					7.4		8.24	6.84		
183	64.5	72.5	58.5	66.5	66.6		61.3		6.0	5.3	1.84	2.09	1.93	
2e	W_{obs}		W_{ex}						W_{ref}		$10^{-5}\,k$			
T	C2,4,6,8								C9		C2,4,6,8			
	151 MHz, C / D / E = 1:2:7, $\Delta\nu\Delta\nu_{4,2}$ = 16804, $\Delta\nu\Delta\nu_{5,1}$ = 1464.2													
299.1	26.4		25.4						1.0		175			
278.4	63.0		62.0						1.0		71.5			
267.8[b]	107		105						2.0		42.2			
257.7	178		177						1.3		25.1			
252.1[b]	247		244						2.9		18.2			
247.4	356		355						1.1		12.5			
237.1	695		693						1.6		6.4			
	W_{obs}		W_{ex}		W_{obs}		W_{ex}				$10^{-2}\,k$			
	C2,8	C4,6	C2,8	C4,6	C1	C5	C1	C5			C2,8	C4,6	C1	C5
172.3[b]	506	499	502	495					4.3		15.8	15.6		
164.7	134	128	130	124	129	126	125	122	4.1		4.08	3.91	3.92	3.85
159.5	74.6	72.5	68.9	66.8	76.2	75.6	70.5	69.9	5.7		2.16	2.10	2.21	2.20
154.3	45.2	37.6	32.4	30.1	40.7	40.9	33.1	33.3	7.5		1.02	1.05	1.05	1.04
149.2	25.2	28.4	14.9	18.1	25.3	26.0	15.0	15.7	10.3		0.47	0.57	0.47	0.49

[a] The temperature was calibrated with a methanol shift thermometer[87b]. – [b] These data were obtained in separate experiments.

(9) and 461 (8) [$M^+ - Br$], 383 (17), 382 (50) [$M^+ - 2\,Br$], 367 (27), 325 (25), 269 (11), 191 (15), 176 (32), 162 (15), 148 (17), 57 (100).

2,6-Bis(4-tert-butylphenyl)tricyclo[3.3.1.0^{2,8}]nona-3,6-diene (**1k**): A stirred suspension of **15** (1.0 g, 1.84 mmol) and freshly prepared zinc/copper couple (2.3 g) in diethyl ether (300 ml) under N_2, was heated under reflux while the conversion was monitored by RP-HPLC with acetonitrile. After 2 h, the mixture was filtered through a 6-cm layer of Celite. The filtrate was extracted with water (2 × 75 ml) and dried with K_2CO_3. The solvent was distilled and the

Table 12. Experimental line widths W_{obs} [Hz], line widths of reference signals W_{ref} and calculated exchange broadenings $W_{ex} = W_{obs} - W_{ref}$ and rate constants k [s^{-1}] for the degenerate Cope rearrangements of semibullvalenes (**3h**, **4m**, **8h**); the solvents employed and shift differences $\Delta\nu$ [Hz] in the slow-exchange limit, which were obtained from spectra recorded at the lowest temperatures listed, are also given; solvents: see Table 8

3h *T*	W_{obs} C2,6	W_{ex} C2,6	W_{ref} *i*-C	W_{obs} C4,8	W_{ex} C4,8	W_{ref} *p*-C	10^{-5} *k* C2,6	10^{-5} *k* C4,8
	126 MHz, A / C =1:4, $\Delta\nu_{6,2}$ = 10073, $\Delta\nu_{4,8}$ = 12085							
278	2.9	1.1	1.8	3.0	2.2	0.8	1450	1040
258	4.4	3.8	0.6	5.4	4.8	0.6	419	478
245	6.6	5.8	0.8	9.0	8.3	0.7	275	276
240	7.2	6.7	0.5	11.8	11.1	0.7	238	207
235	10.4	9.9	0.5	14.8	14.0	0.8	161	164
225	14.2	13.4	0.8	26.8	25.8	1.0	119	88.9
205				76.8	72.4	4.4		31.7
195				152	151	1.4		15.2
191				178	176	1.6		13.0
	151 MHz, C / E = 3:1, $\Delta\nu_{6,2}$ = 12102, $\Delta\nu_{4,8}$ = 14532							
301.2	2.05	0.68	1.3	1.93	0.63	1.3	3383	5265
252.1	8.80	5.4	3.4	13.0	9.5	3.5	426	349
247.4	8.1	7.1	1.0	10.8	9.50	1.3	324	349
225.4	23.1	18.6	4.5	38.4	33.4	5.0	124	99.3
214.9	51.5	47.8	3.7	67.4	62.5	3.9	48.1	53.1
195.7				423	421	1.9		7.88

T	W_{obs} C2	W_{ex} C2		W_{obs} C4	W_{obs} C8	W_{ex} C4	W_{ex} C8		10^{-2} *k* C2	10^{-2} *k* C4	10^{-2} *k* C8
128.5	217	181	36.3	232		215		17.0	5.69	6.75	
116.6				49.4	46.4	31.1	28.1	18.3		0.98	0.88

4m *T*	W_{obs} C2,4,6,8	W_{ex} C2,4,6,8	W_{ref} *m*-C	W_{obs} C-Me	W_{ex} C-Me	W_{ref} OMe	10^{-5} *k* C2,4,6,8	10^{-5} *k* C-Me
	151 MHz, C / D / E = 1:1:1, $\Delta\nu_{4,2}$ = 12525, $\Delta\nu_{Me}$ = 267							
299.1	3.15	1.24	1.91				1987	
268.1	7.66	5.68	1.98				434	
247.4	18.9	16.7	2.21				147	
226.7	59.8	57.2	2.60				43.1	
216.4	129	126	3.49				19.6	
154.3				74.5	65.1	9.43		0.017

T	W_{obs} C2,8	W_{obs} C4,6	W_{ex} C2,8	W_{ex} C4,6		W_{obs} 5-Me	W_{obs} 1-Me	W_{ex} 5-Me	W_{ex} 1-Me		10^{-2} *k* C2,8	10^{-2} *k* C4,6	10^{-2} *k* 5-Me	10^{-2} *k* 1-Me
138.8	59.0	64.3	45.7	51.0	13.3		62.5		42.6	19.9	1.44	1.60		1.33
133.7	54.2		22.7		31.5						0.71			
128.5	78.9		12.4		66.5	60.6	62.1	13.8	15.3	46.8	0.39		0.43	0.48

8h *T*	W_{obs} C2,4,6,8	W_{ex} C2,4,6,8	W_{ref} *m*-C	10^{-5} *k* C2,4,6,8
	151 MHz, A / C = 1:5, $\Delta\nu_{4,2}$ = 14548			
280.0	5.9	2.4	3.5	1385
260.2	9.4	5.9	3.5	563
253.1	13.6	10.0	3.6	332
237.9	21.5	17.9	3.6	186
226.9	37.9	34.2	3.7	97.2
216.2	70.3	66.4	3.9	50.1
205.5	144.0	140.0	4.0	23.7

T	W_{obs} C2,8	W_{obs} C4,6	W_{ex} C2,8	W_{ex} C4,6	W_{ref} *p*-C	10^{-2} *k* C2,8	10^{-2} *k* C4,6
134.7	167	169	150	152	16.8	47.1	47.8
129.5	70.4	77.1	54.9	61.6	15.5	17.2	19.4
124.1	41.8	43.5	26.1	27.8	15.7	8.20	8.73

yellow residue (0.7 g, 99%) was dried at 10^{-2} Torr. Flash chromatography on silica gel with petroleum ether (b. p. 40−65°C) and elution with CH_2Cl_2 afforded yellow crystals (0.37 g, 67%, m. p. 110 − 112°C). − MS: *m/z* (%): 382 (2) [M^+], 191 (44), 189 (44), 188 (29), 163 (28), 148 (15), 147 (96), 117 (10), 105 (12), 91 (15), 85 (10), 71 (26), 69 (10), 57 (100).

Synthesis of the Semibullvalenes **4i** *and* **11i**[88]

3,7-Bis(4-tert-butylphenylthio)-1,5-dimethylbicyclo[3.3.0]-octadienes **17** *and* **18**: Titanium(IV) chloride (34.5 ml, 315 mmol) was added under N_2 to a stirred, cooled (0−10°C) solution of **16**[90] (24.9 g, 160 mmol) in tetrahydrofuran (400 ml). The orange-red suspension was stirred vigorously and kept at 20−25°C while a solution of 4-*tert*-butylthiophenol[91] (54.9 g, 330 mmol) and triethylamine (90 ml, 646 mmol) in tetrahydrofuran (110 ml) was added dropwise within 6 h. Stirring was continued for 15 h. The mixture was cooled to 0°C and $Na_2CO_3 \cdot 10\ H_2O$ (40 g, 140 mmol) was added. After stirring for 4 d, the suspension was filtered through a 6-cm layer of Celite. The solid material was washed with cyclohexane (4 × 100 ml). The combined organic layers were extracted with sat. aq. K_2CO_3 (4 × 300 ml), sat. aq. KH_2PO_4 (2 × 300 ml), and water (2 × 300 ml). After drying with K_2CO_3, the solvent was distilled i. vac. to afford a brown, viscous residue (73.9 g, quant.) consisting of **17** and **18** (1:1, HPLC, NMR). Flash chromatography on silica gel with petroleum ether/ethyl acetate (99:1) yielded a colorless, viscous oil.

3,7-Bis(4-tert-butylphenylsulfonyl)-1,5-dimethylbicyclo[3.3.0]octadienes **19** *and* **20**: A stirred solution of the crude

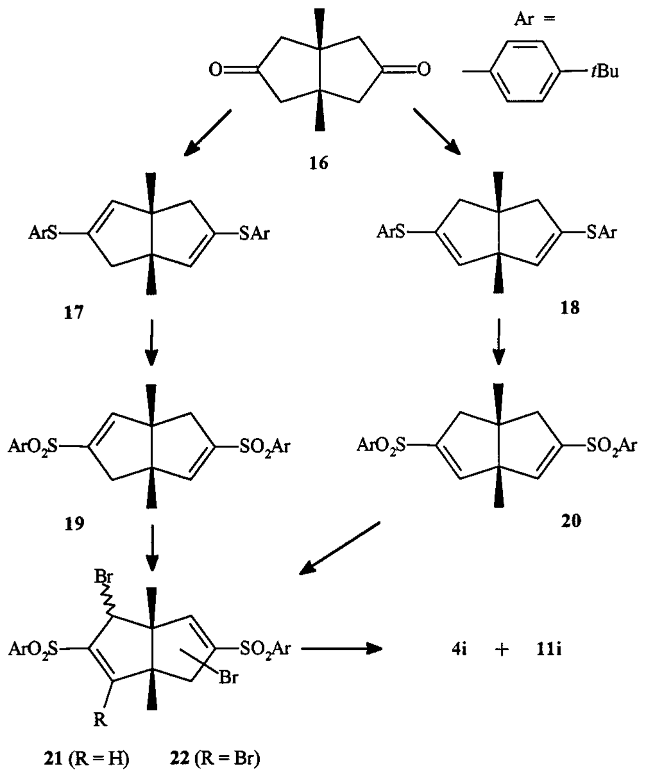


Table 13. Chemical shifts (δ values) and coupling constants (absolute values [Hz]) in proton spectra recorded from [D]trichloromethane solutions

Cpd.	1-H 5-H	3-H 7-H	4-H$_n$ 8-H$_n$	4-H$_x$ 8-H$_x$	9-H	Ar-H	t-Bu	OH
1k	2.92dt	6.12d	4.21dd		1.35t	7.3 – 7.5	1.27	
13[a]	2.19m	2.25m 2.05m	1.71m	2.32m	1.19t	7.0 – 7.6	1.32	1.87
14	3.12m	5.98dd	2.48dm	2.11dd	1.98t	7.3 – 7.4	1.33	
15	3.61m	6.14d	4.71dm		2.54t	7.3 – 7.5	1.35	
	$^2J_{4n,4x}$ $^2J_{8n,8x}$	$^3J_{1,9}$ $^3J_{5,9}$	$^3J_{1,8x}$ $^3J_{4x,5}$	$^3J_{1,8n}$ $^3J_{4n,5}$	$^3J_{3,4n}$	$^3J_{3,4x}$		
1k	2.45	6.6		8.30				
14	18.1	2.93		5.80	2.26	4.93		
15		2.61	4.91					
	2-H 8-H	4-H 6-H	4-H 8-H	2-H 6-H	Me-H	Ar-H	t-Bu	
4i	4.63				1.11	7.5 – 7.7	1.33	
11i	3.25dd 3.54d	5.79 (6-H)			1.13 1.24	7.5 – 7.8	1.33	
17[a]			2.40	5.49	1.07	7.3 – 7.7	1.35	
18	5.41				1.12 1.09	7.3 – 7.7	1.32	
19[a]			2.64	6.33	1.12	7.4 – 7.9	1.38	
20	6.42	2.39 2.46			1.11 0.98	7.4 – 7.9	1.36	
	$^2J_{AB}$	$^4J_{AX}$	$^4J_{BX}$	$^4J_{6,8}$	$^3J_{2,8}$			
11i				1.02	5.75			
18	16.5	0.97	0.97					
20	16.3	1.62	1.62					

[a] The coupling constants were not determined.

Table 14. Chemical shifts (δ values) in carbon-13 NMR spetra; hemical shifts of carbon atoms that are equivalent by virtue of rapid degenerate Cope rearrangement (**4i**) are given only once; similar chemical shifts of carbon atoms (*in italics*) that bear the same number of protons may be exchanged

	C-1 C-5	C-2 C-6	C-3 C-7	C-4 C-8	C-9	C-Ar i-C	 o-C, m-C	 p-C	tBu C	 CH_3
1k	29.6	87.8	121.9	79.5	19.3	140.7	125.6, 126.7	149.2	34.4	31.5
13	38.2	75.2	33.8	24.4	28.0	144.5	125.1, 125.7	149.7	34.4	31.3
14	29.9	138.4	121.9	34.4	29.2	139.7	125.2, 125.4	149.5	34.4	31.4
15	38.4	135.0	123.3	50.8	20.2	139.0	125.5, 125.8	151.8	34.6	31.2
					Me					
4i	61.9	92.1	*136.4*		14.8	*137.0*	126.4, 127.6	157.3	35.2	31.0
11i	57.4 67.4	52.7 136.3	*135.7* *135.2*	139.3 51.1	14.8 14.4	*135.7*	126.3, 127.7 126.6, 127.9	157.6	35.3	31.0
17	56.9	135.0	135.4	46.8	21.2	140.1	125.9, 126.1	150.1	34.5	31.2
18	51.5 49.4	135.6 49.2	135.3	49.2 135.6	21.6 21.5	140.1	125.9, 126.1	150.1	34.5	31.2
19	58.0	148.6	135.8	41.3	20.1	141.5	126.3, 127.6	157.6	35.3	31.1
20	64.0 53.6	143.0 44.0	135.8	44.0 143.0	21.6 18.2	144.1	126.3, 127.6	157.7	35.3	31.0

Table 15. Molecular formulae, masses, and elemental analyses

Cpd.		Molecular Mass	Elemental Analysis	C	H	S
1k	$C_{29}H_{34}$	382.6	Calcd. Found	91.04 90.90	8.96 8.91	
4i	$C_{30}H_{36}O_4S_2$	524.7	Calcd. Found	68.67 68.39	6.91 6.85	12.22 12.01
11i	$C_{30}H_{35}BrO_4S_2$	603.6	Calcd. Found	59.69 59.55	5.84 5.73	10.62 10.44
13	$C_{29}H_{40}O_2$	420.6	Calcd. Found	82.81 82.63	9.58 9.82	
14	$C_{29}H_{36}$	384.6	Calcd. Found	90.57 90.29	9.43 9.28	
15	$C_{29}H_{34}Br_2$	542.4	Calcd. Found	64.22 64.33	6.32 6.16	
19	$C_{30}H_{38}O_4S_2$	526.8	Calcd. Found	68.41 68.23	7.27 7.15	12.17 12.19
20			Found	68.23	7.15	12.19

mixture of **17** and **18** (46.3 g, 100 mmol) in acetic acid (750 ml) was heated at 50−55°C and sodium perborate tetrahydrate (140 g, 910 mmol) was added in small portions. The mixture was stirred for 4 h at this temperature. Water (500 ml) was added and the white suspension was cooled to 20−25°C. The precipitate was isolated by filtration, washed with water and dried i. vac. to yield a colorless powder (**19**/**20**, 1:1, 50.6 g, 96%). Repeated recrystallizations from ethanol yielded colorless crystals (**19**/**20**, 3:1) which were treated with hot CCl_4 to afford pure **19**, m. p. 287°C.

Brominated 3,7-Bis(4-tert-butylphenylsulfonyl)-1,5-dimethylbicyclo[3.3.0]octadienes **21** *and* **22**: *N*-Bromosuccinimide (4.28 g, 24 mmol) and azodiisobutyronitrile (0.1 g) were added to a solution of the crude mixture of **19** and **20** (1:1, 5.25 g, 10 mmol) in CH_2Cl_2 (100 ml) contained in a closed Schlenk tube. The mixture was placed just above a 250-W daylight lamp (Phillips ML) and irradiated for 12 h. The conversion was monitored by RP-HPLC with acetonitrile/water (90:10). The suspension was extracted with aq. NaOH (0.5 M, 100 ml), sat. aq. $NaHCO_3$ (100 ml), and sat. aq. NaCl (100 ml). The combined aq. layers were extracted with CH_2Cl_2 (4 × 20 ml). Drying of the combined organic layers were dried with $MgSO_4$ and distillation of the solvent i. vac. yielded a brown solid (mixture of **21** and **22**, 4.24 g), which was used for the next step without purification.

3,7-Bis(4-tert-butylphenylsulfonyl)-1,5-dimethyltricyclo[3.3.0.$0^{2,8}$*]octa-2,6-diene* (**4i**) *and 2-Bromo-3,7-bis(4-tert-butylphenylsulfonyl)-1,5-dimethyltricyclo[3.3.0.*$0^{2,8}$]octa-*2,6-diene* (**11i**): The crude mixture of **21** and **22** (2.1 g) was dissolved in tetrahydrofuran (480 ml). Freshly prepared zinc/copper couple (2.1 g) was added and the suspension was heated under reflux for 2.5 h. The conversion was monitored by HPLC with petroleum ether/ethyl acetate (80:20). The solid material was removed by filtration through a 6-cm layer of Celite. Distillation of the solvent i. vac. afforded a solid (mixture of **4i** and **11i).** Separation by flash chromatography on silica gel with petroleum ether/ethyl acetate (82:18) yielded colorless crystals of **4i** (1st fraction, 0.26 g, m. p. 188−190°C). Recrystallization from ethyl acetate afforded colorless needles, m.p. 190−191°C. − MS: *m/z* (%): 524 (10) $[M^+]$, 403 (14), 327 (28) $[M^+ - tBuC_6H_4SO_2]$, 182 (12), 181 (100) $[tBuC_6H_4SO^+]$, 166 (27), 146 (15), 145 (14), 133 (15), 131 (24), 130 (48), 129 (45), 128 (17), 118 (13), 117 (18), 115 (28).

Bromosemibullvalene **11i** was obtained as pale yellow crystals (2nd fraction, 0.33 g, m.p. 103−105°C). − MS: *m/z* (%): 604 (9) and 602 (7) $[M^+]$, 523 (5) $[M^+ - Br]$, 210 (17), 209 (11), 208 (19), 182 (12), 181 (100) $[tBuC_6H_4SO^+]$, 166 (28), 145 (11), 133 (10), 129 (19), 128 (21), 117 (12).

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