An One-Pot Synthesis of Semibullvalenes and Its Mechanism

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Keywords: Cycloadditions / Kinetics / Linear free-energy relationships / Semibullvalenes / 1,2,4,5-Tetrazines

1,2,4,5-Tetrazines **7** readily react with 3,3′-bicyclopropenyl **8** in a cycloaddition–cycloelimination sequence to give 3,4-diazanorcaradienes **9** with *endo* configuration of the methyl group at C-7. On gentle heating in inert solvents, these 3,4-diazanorcaradienes **9** are cleanly transformed into semibullvalenes **11**. This reaction sequence can also be performed as a one-pot method. Kinetic investigations and comparisons with two model systems are in agreement with the proposed reaction mechanism.

Introduction

In 1940 Cope reported the first examples of thermally induced rearrangements of 1,5-hexadienes,[1−4] today termed [3,3]-sigmatropic rearrangements in Woodward−Hoffmann nomenclature.[5] Of special interest are the so-called *degenerate* Cope rearrangements,[6] as observed in homotropilidenes,[7,8] bullvalenes,[6,9] barbaralanes,[10,11] and semibullvalenes.[12−14]

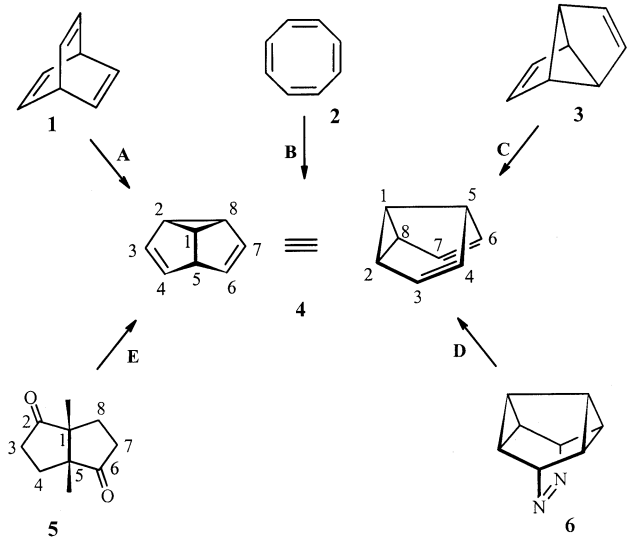
In this contribution, we give a full account of our investigations involving the synthesis of symmetrically substituted semibullvalenes by means of a simple cycloaddition−cycloelimination sequence utilizing 1,2,4,5-tetrazines and bifunctional cyclopropene derivatives.[15−18]

Results and Discussion

Scheme 1 summarizes some principal pathways to the semibullvalene skeleton. In all cases the C_8 unit is present in the precursors that are transformed into semibullvalene (**4**).

Zimmerman and his group were the first to isolate the parent compound **4** and demonstrate the extremely rapid *degenerate* Cope rearrangement. Thus, photolysis of 1−2% solutions of barrelene (**1**) in isopentane containing 3−8% of acetone as a sensitizer afforded 25−40% of an isomeric hydrocarbon, tricyclo[3.3.0.0^{2,8}]octa-3,6-diene [semibullvalene (**4**)] (path A).[19−21]

Cyclooctatetraene (COT, **2**) has been found to be a suitable precursor for **4**. The phototransformation of COT into semibullvalene can be achieved in solution in the presence of acetone at −60 °C[22] or in the gas phase at 70 °C;[23] under the latter conditions **4** is produced in almost quantitative yield, with traces of **2** and benzene as impurities (path B).



Scheme 1. Synthetic pathways to the semibullvalene skeleton

Paths C and D utilize thermal reactions for formation of semibullvalene. Tricyclo[3.3.0.0^{2,8}]octa-3,7-diene (**3**) − obtained from the saturated tricyclo[3.3.0.0^{2,8}]octane in a photochlorination−elimination sequence − is transformed into **4** at slightly elevated temperatures ($\tau_{1/2} \approx 1$ h).[24−26] 9,10-Diazasnoutene (**6**), a very unstable azo compound, affords semibullvalene (**4**) after denitrogenation.[27−30]

In Quast's laboratories, *cis*-1,5-dimethylbicyclo[3.3.0]octane-2,6-dione (**5**) was found to be the derivative capable of greatest structural variation, especially for the introduction of substituents at positions 2, 3, 4, 6, 7, and 8 in semibullvalene (**4**).[12,31]

1,2,4,5-Tetrazines are valuable electron-deficient 4π components in Diels−Alder reactions with inverse electron demand, making a large variety of interesting compounds

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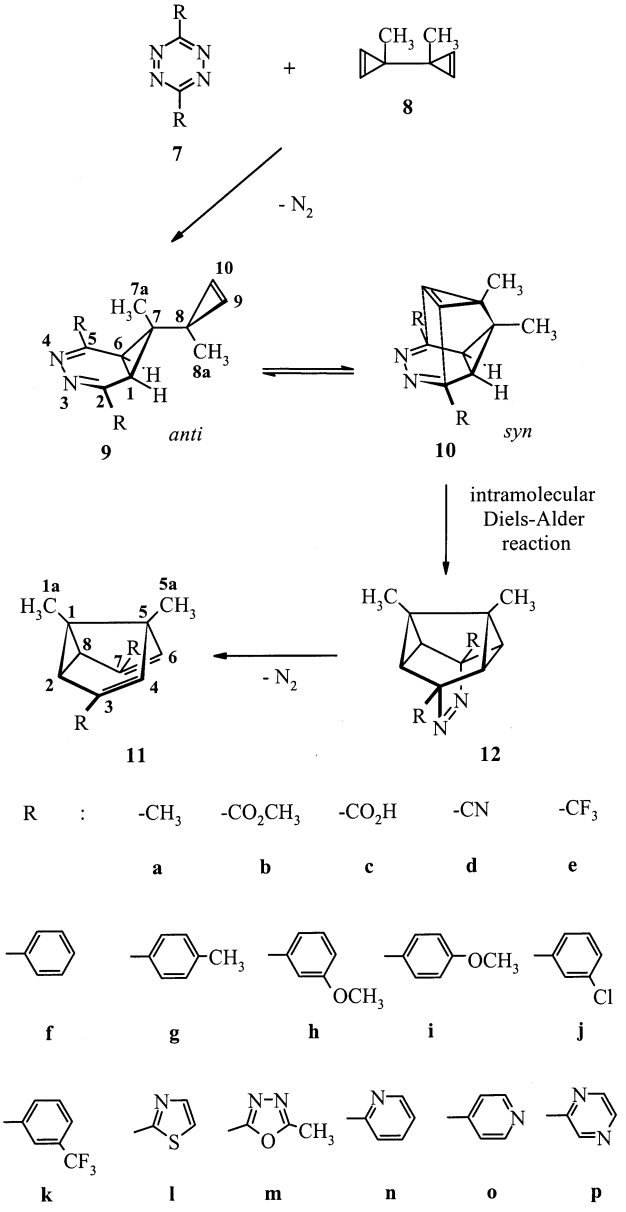
available.[32] We have quite recently reported a cycloaddition−cycloelimination sequence utilizing, for instance, 1,2,4,5-tetrazines and 2 equiv. of cyclopropenes as dienophiles. After photochemically induced denitrogenation, this afforded homotropilidenes in great variety.[8] Consequently, use of the bifunctional 3,3′-bicyclopropenyls as dienophiles would be expected to give semibullvalenes, which in principle represent bridged homotropilidenes.

Indeed, when the bicyclopropenyl **8**[15,33] was added to a solution of highly reactive tetrazinediester **7b**[32] in dichloromethane the reaction mixture decolourized within a few minutes with accompanying loss of nitrogen, and a 70% yield of the colourless crystalline semibullvalene **11b** could be isolated (Scheme 2). The diester compound **11b** was transformed into the dicyano compound **11d** by conventional pathways ($CO_2CH_3 \rightarrow CO_2H \rightarrow COCl \rightarrow CONH_2 \rightarrow CN$). 3,6-Bis(trifluoromethyl)-1,2,4,5-tetrazine (**7e**) showed reactivity equal to that of the diester compound **7b** in [4+2] cycloaddition reactions with inverse electron demand,[32] and could be treated with **8** to give **11e** in 83% yield as a colourless, distillable oil (60 °C/0.01 Torr). The same reaction sequence starting from **7a** and **8** provided 1,3,5,7-tetramethylsemibullvalene (**11a**) in 39% yield as a colourless liquid.



Scheme 2. One-pot synthesis of semibullvalene derivatives **11a**−**11p**

Proof of the structures of semibullvalenes **11a**, **11b**, **11d**, and **11e** was based on ^1H and ^{13}C NMR spectral analysis as well as on X-ray crystal structure analyses performed on two crystalline representatives (**11b**, **11d**).[16] The extremely rapid *degenerate* Cope rearrangement causes equivalency of positions 1 and 5 and also of 2, 4, 6, and 8, as demonstrated by singlets for 1a/5a-CH_3 and for 2/4/6/8-H in the ^1H NMR spectra; a similar rapid exchange of signals was also observed in the ^{13}C NMR spectra (Table 1). X-ray analysis shows normal bond lengths and distances for **11b** (i.e., C2−C8 = 160.2 pm; C4−C6 = 228.4 pm) but the 3,7-dicyanosemibullvalene **11d** has an extended cyclopropane bond C2−C8 (171.2 pm) and a shortened C4−C6 distance (219.3 pm).[16] The one-pot pathway presented above can also be applied to the synthesis of a number of 3,7-diaryl- and 3,7-bis(heteroaryl)semibullvalenes **11f**−**11p** (Scheme 2), with yields varying from 16−93% (see Exp. Sect.). As these tetrazines **7f**−**7p** are less reactive than **7b** and **7e**, higher reaction temperatures and longer reaction times were necessary. The NMR data obtained for the semibullvalenes **11f**−**11p** were in the same chemical shift ranges as typical for **11a**−**11e**, with no unexpected deviations being found in the ^1H or ^{13}C NMR spectra (Table 1).

Scheme 2 offers a tentative mechanistic explanation for the overall reactions **7** + **8** → **11**. Certainly, the first step is the formation of a diazanorcaradiene species resulting from a [4+2] cycloaddition between one cyclopropene unit in **8** and the 1,2,4,5-tetrazines **7**.[34] If the tetrazine were to approach **8** from the sterically less hindered side, the diazanorcaradiene stereoisomer **9** would be expected to be formed, with the methyl group 7-CH_3 in a *syn* orientation and the second cyclopropene unit *anti* to the cyclic heterodiene system. Hence, no further intramolecular [4+2] cycloaddition to the diazadiene system of **9** would be possible; *anti-syn* isomerization through 7*H*-3,4-diazepine intermediates, such as **9** ⇄ **10**, are well known in the literature and have been intensively studied by D NMR methods.[35,36] Diazanorcaradienes with strongly electron-withdrawing substituents R in positions 2 and 5 (**9b** and **9e**) display rather low $\Delta G^{\neq}$ values for this stereoisomerization process (ca. 13−14 [kcal·mol^{-1}]),[35] whereas 2,5-diaryldiazanorcaradienes **9f**−**9p** isomerize considerably more slowly ($\Delta G^{\neq} \approx 20-23$ [kcal·mol^{-1}]).[36,37] Intramolecular [4+2] cycloadditions of type **10** → **12** are entropically favoured and are therefore quite fast; the same fast process is observed for nitrogen extrusion from the polycyclic azo compound **12**,[27−29,38] the last nonisolable intermediate en route to the semibullvalene derivatives **11**.

From these arguments we expected to have a high probability of isolating diazanorcaradienes **9** as early intermediates in the reaction sequence for the 2,5-diaryldiazanorca-

Table 1. ^{1}H and ^{13}C NMR chemical shifts [δ values; $CDCl_3$/TMS; 60, 90, or 250 MHz] of semibullvalenes **11a−11p**

11	^{1}H NMR chemical shifts [ppm]		^{13}C NMR chemical shifts [ppm]			
	δ(1a-CH_3, 5a-CH_3)	δ(2,4,6,8-H)	δ(1a-C, 5a-C)	δ(1-C, 5-C)	δ(2,4,6,8-C)	δ(3,7-C)
a	0.98 (s)	3.74 (s)	15.8	59.0	90.9	128.4
b	1.13 (s)	4.79 (s)	14.9	60.6	93.7	127.2
c[a]	1.12 (s)	4.74 (s)	–	–	–	–
d	1.13 (s)	4.67 (s)	14.5	61.6	97.8	105.8
e	1.10 (s)	4.48 (s)	14.7	60.2	90.4	122.0
f[a]	1.07 (s)	4.43 (s)	15.8	58.5	88.7	133.3
g	1.18 (s)	4.38 (s)	15.9	58.4	88.4	133.0
h	1.20 (s)	4.36 (s)	15.8	58.5	88.9	133.3
i[b]	1.24 (s)	4.34 (s)	15.9	58.6	88.3	132.5
j	1.20 (s)	4.43 (s)	15.7	59.0	89.2	132.3
k	1.20 (s)	4.40 (s)	15.6	59.1	89.4	132.4
l	1.25 (s)	4.79 (s)	15.4	59.9	90.2	128.2
m	1.24 (s)	4.87 (s)	15.0	60.7	91.5	118.7
n	1.25 (s)	4.82 (s)	15.6	59.3	89.9	134.0
o	1.25 (s)	4.59 (s)	15.5	59.3	90.0	131.8
p	1.28 (s)	4.91 (s)	15.6	60.2	90.8	132.1

[a] In CD_3OD. [b] In CD_2Cl_2.

Table 2. ^{1}H and ^{13}C NMR chemical shifts [δ values; $CDCl_3$/TMS; 60, 90, or 250 MHz] of diazanorcaradienes **9f−9k**

9	^{1}H NMR chemical shifts [ppm]			^{13}C NMR chemical shifts [ppm]						
	δ (7a-CH_3)	δ(8a-CH_3)	δ(1,6-H)	δ(7a-C)	δ(8a-C)	δ(7-C)	δ(8-C)	δ(1,6-C)	δ(9,10-C)	δ(2,5-C)
f	0.76 (s)	1.55 (s)	2.29 (s)	11.0	24.7	25.3	26.8	31.0	118.3	157.4
g	0.73 (s)	1.57 (s)	2.30 (s)	11.0	24.8	25.4	26.9	30.7	118.4	156.9
h	0.73 (s)	1.52 (s)	2.23 (s)	11.1	24.8	25.3	26.9	31.0	118.4	159.7
i	0.53 (s)	1.35 (s)	2.05 (s)	11.0	24.8	25.7	26.9	30.4	118.4	156.0
j	0.66 (s)	1.53 (s)	2.14 (s)	11.0	24.7	25.5	26.9	31.1	118.4	156.8
k	0.77 (s)	1.60 (s)	2.40 (s)	11.2	24.6	25.7	26.9	31.1	118.4	157.0

radienes **9f−9p**, which show the weakest tendency towards the *anti-syn* isomerization **9** ⇄ **10**. Indeed, when 1,2,4,5-tetrazines **7f−7k** and bicyclopropenyl **8** were subjected to reaction for short periods at ca. 60 °C we were able to isolate crystals with the typical yellow colour and UV spectra of 2,5-diaryl-3,4-diazanorcaradienes ($\lambda_{max} \approx 350$ nm).[34] The ^{1}H and ^{13}C NMR spectra, as collected in Table 2, were in accordance with the proposed structure **9** with the methyl group 7a-CH_3 *syn* to the diazacyclohexadiene unit, causing the highfield singlets between δ = 0.53−0.77 in the ^{1}H NMR spectra and corresponding signals at high field (δ = 11) in the ^{13}C NMR spectra.

Unfortunately, no correct elemental analyses could be obtained for these compounds, because the yellow crystals included traces of solvent and were already slowly decomposing at room temperature. By monitoring these reactions by NMR and UV spectroscopy in solution, we were able to prove a clean transformation **9** → **11**, with no further intermediates being observed by NMR. The UV spectra permitted a kinetic study for the disappearance of **9** in over 80−95% of the reaction (rate constants and values for $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are collected in Table 3). Electron-withdrawing substituents R at positions 2 and 5 in diazanorcaradienes **9** slightly increased the rate, while donors decreased the rate constants; a ρ value of 0.93 (60 °C) is characteristic for a relatively small substituent effect on the rate. The $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values were consistent with those found for other *anti* ⇄ *syn* isomerizations in diazanorcaradienes.[35−37] These re-

Table 3. Transformation of 3,4-diazanorcaradienes **9** into semibullvalenes **11** in dioxane at 60 °C; values for $10^5 \cdot k$ [s^{-1}], $\Delta H^{\neq}$ [kcal·mol^{-1}], and $\Delta S^{\neq}$ [cal·K^{-1}·mol^{-1}]

9	R	$10^5 \cdot k$ [s^{-1}]	$\Delta H^{\neq}$ [a] [kcal·mol^{-1}]	$\Delta S^{\neq}$ [a] [cal·K^{-1}·mol^{-1}]
j	3-ClC_6H_4	44.5	24.6	−0.2
k	3-$CF_3C_6H_4$	42.5	25.4	1.9
f	C_6H_5	21.0	25.4	0.7
h	3-$CH_3OC_6H_4$	12.2	25.9	1.3
g	4-$CH_3C_6H_4$	11.1	25.3	−0.9
i	4-$CH_3OC_6H_4$	3.27	26.7	0.9

[a] $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values obtained from *k* values (θ = 39−85 °C) for the transformation **9** → **11**.

sults corroborated the mechanistic pathway presented in Scheme 2, the stereoisomerization **9** → **10** representing the first rate-determining step toward semibullvalene formation.

Our results encouraged us to extend the synthetic approach of Scheme 2 to the bifunctional cyclopropene **13**,[39] which would thus have made dihydrobullvalenes accessible. Unfortunately, all attempts to synthesize **13** analogously to the bicyclopropenyl **8** (double addition of dibromocarbene to 2,5-dimethyl-1,5-hexadiene, subsequent reduction to the symmetrical dibromide and elimination of 2 equiv. of HBr) failed. Only complex mixtures were obtained, containing **13** according to ^{1}H NMR analysis, but undergoing sudden exothermic polymerization for unknown reasons.

Success was achieved in obtaining **14**.[39] Compound **14** is a reasonably stable dienophile, which readily combined with 1,2,4,5-tetrazines **7** in refluxing dichloromethane, yielding mixtures of the stereoisomeric diazanorcaradienes **15** and **16**. These stereoisomeric mixtures could be separated by column chromatography and handled in pure form at sufficiently low temperature. Above 30 °C in $CHCl_3$ slow *anti-syn* isomerization was again observed, readily yielding mixtures of **15/16** in a 36:64 ratio, slightly dependent on the nature of the substituents R in the 2,5-positions of the diazanorcaradiene skeleton (Table 4).

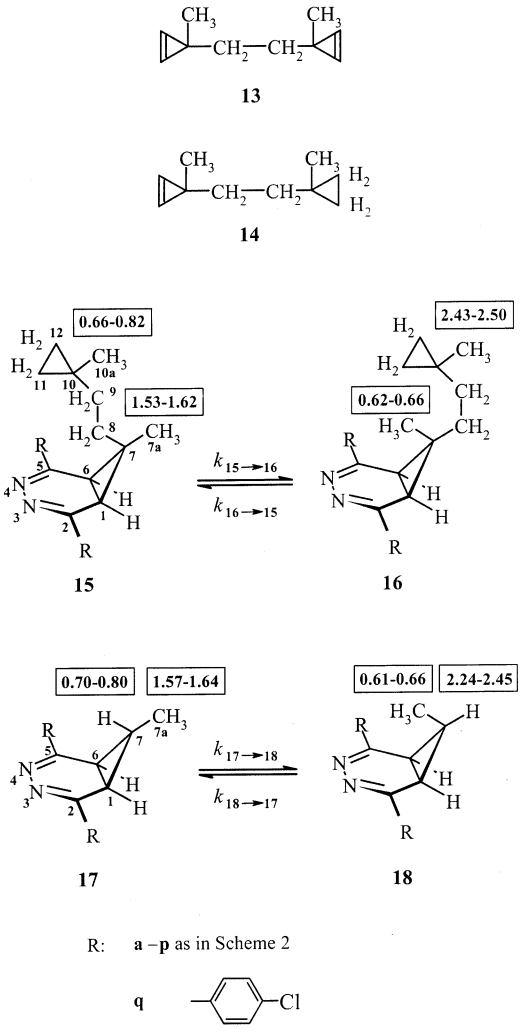
Table 4. *anti-syn* isomerization **15** ⇄ **16** in $CHCl_3$ at 58.3 °C; values for $10^5 \cdot k_{15\rightarrow16}$ [s^{-1}], $10^5 \cdot k_{16\rightarrow15}$ [s^{-1}], and equilibrium mixture **15/16** [%]

15/16	R	**15/16**	$10^5 \cdot k_{15\rightarrow16}$ [s^{-1}]	$10^5 \cdot k_{16\rightarrow15}$ [s^{-1}]
j	3-ClC_6H_4	38:62	106.3 [a]	65.1[b]
f	C_6H_5	38:62	48.6	29.1
i	4-$CH_3OC_6H_4$	32:68	7.67	3.56

[a] $\Delta H^{\neq}$ = 24.7 [kcal·mol^{-1}] and $\Delta S^{\neq}$ = 2.3 [cal·K^{-1}·mol^{-1}] obtained from *k* values (θ = 35−58 °C) for the transformation **15** → **16**. [b] $\Delta H^{\neq}$ = 24.7 [kcal·mol^{-1}]; $\Delta S^{\neq}$ = 1.23 [cal·K^{-1}·mol^{-1}] obtained from *k* values (θ = 35−58 °C) for the transformation **16** → **15**.

Their ^{1}H NMR spectra clearly distinguished between the two stereoisomers **15** and **16** (Scheme 3). The typical high-field singlet between δ = 0.62 and 0.66 definitely established the *syn* position of 7-CH_3 in **16**, while the isomeric diazanorcaradienes **15** showed a singlet at much lower field (δ = 1.53−1.62) for the methyl group in an *anti* orientation. This observation also supports the structure assignment of diazanorcaradienes **9** formed in the first **7** + **8** cycloaddition step (Scheme 2, Table 2).

Having the pure isomers **15** and **16** in hand allowed us to study the stereoisomerization process of **15** ⇄ **16** and its equilibrium. Table 4 summarizes $k_{15\rightarrow16}$ and $k_{16\rightarrow15}$ as well as the activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for **15/16j**. Interestingly the *k* values show the same substituent dependence as found for the transformation **9** → **11** (Scheme 2, Table 3). In addition, the activation parameters in Tables 3 and 4 correspond to those found in the literature.[35−37]



Scheme 3. *anti-syn* isomerizations **15** ⇄ **16** and **17** ⇄ **18**; selected ^{1}H NMR spectroscopic data in boxes (δ values in ppm)

Additional support for the derived mechanistic pathway presented in Scheme 2 is based on a further model system: 1,2,4,5-tetrazines and 3-methylcyclopropene readily react at −78 °C with almost exclusive formation of *anti*-7-methyl-3,4-diazanorcaradienes **17**. Again, this results from the approach of tetrazines **7** to 3-methylcyclopropene from the sterically less hindered side. Under very mild conditions, even at room temperature, the *anti* isomers **17** slowly isomerize to give the equilibrium mixture **17/18** ≈ 52:48.

As the *syn* isomers **18** are slightly less soluble in ethyl acetate, we could successfully enrich this stereoisomer in the **17/18** isomer mixtures by fractional crystallization from this solvent. Subsequently, we were able to study the equilibria and the rate constants $k_{17\rightarrow18}$ and $k_{18\rightarrow17}$, as well as $\Delta H^{\neq}$ and $\Delta S^{\neq}$ in one case (**17g** → **18g**). Table 5 lists all relevant kinetic data, indicating the same small substituent effect of R in the 2,5-positions of **17/18** on the rate constants as found in Tables 3 and 4. The $\Delta H^{\neq}$ and $\Delta S^{\neq}$ activation parameters so far determined also parallel each other in Tables 3 to 5. The suggested mechanistic picture as shown in Scheme 2 therefore seems to be valid.

Table 5. *anti-syn* isomerization **17** ⇄ **18** in benzene at 31.8 °C; values for $10^5 \cdot k_{17\rightarrow18}$ [s^{-1}], $10^5 \cdot k_{18\rightarrow17}$ [s^{-1}], and equilibrium mixture **17/18** [%]

17/18	R	17/18	$10^5 \cdot k_{17\rightarrow18}$ [s^{-1}]	$10^5 \cdot k_{18\rightarrow17}$ [s^{-1}]
j	3-ClC_6H_4	51:49	33.3	36.1
q	4-ClC_6H_4	52:48	18.1	19.6
f	C_6H_5	52:48	14.6	15.9
g	4-$CH_3C_6H_4$[a]	52:48	7.00 [a]	7.60
i	4-$CH_3OC_6H_4$	52:48	3.30	3.50

[a] $\Delta H^{\neq} = 23.2$ [kcal·mol^{-1}]; $\Delta S^{\neq} = -1.5$ [cal·K^{-1}·mol^{-1}] obtained from k values (θ = 20−50 °C) for the transformation **17g** → **18g**.

Conclusion

1,2,4,5-Tetrazines **7** and the bifunctional cyclopropene **8** as dienophile readily react together to afford semibullvalenes **11** in a one-pot method, as demonstrated with 14 examples. The reaction can be understood as a sequence of cycloaddition−cycloelimination−valence isomerization steps **7** + **8** → **9** → **10** → **12** → **11**. The mechanistic proposal (Scheme 2) is in accordance with preparative, stereochemical, and kinetic data in two model systems **15/16** and **17/18** (Scheme 3, Tables 2 to 5).

Experimental Section

General Remarks: IR spectra were recorded with a Beckman Acculab 1 machine and UV/Vis spectra with a Karl Zeiss Specord M500 UV spectrophotometer. UV/Vis kinetic measurements were performed using a Zeiss PMQ II spectrometer with a Colora thermostat. NMR spectra were obtained with a Varian T-60, a Bruker WH 90, and a Bruker AC 250 (60, 90, and 250 MHz for ^{1}H and 22.63 and 63 MHz for ^{13}C); δ values are reported in ppm downfield from tetramethylsilane; s, d, dd, dt, and m indicate singlet, doublet, doublet of doublets, doublet of triplets, and multiplet. The degree of substitution of the C atoms was determined by DEPT-135 and DEPT-90 methods and is indicated as quat. C, =CH, $-CH_2-$, $-CH_3$. Mass spectra were measured at an ionizing voltage of 70 eV by electron impact or field desorption with a Varian MAT311A instrument. In addition, high resolution mass spectrometry MS (HR) was used for identification. Melting points were determined either with a Büchi melting point apparatus (< 280 °C) or with a copper block (> 280 °C) and are uncorrected. Elemental analyses were performed in the microanalytical laboratory of the University of Regensburg with Heraeus Mikro U/E and CHN-Rapid instruments. As compounds **9** are thermally transformed into **11**, no correct elemental analyses were obtained, as was also the case for some oily semibullvalenes **11**. For analytical thin layer chromatography, precoated plastic sheets (POLYGRAM SIL G/UV254, Macherey & Nagel) were used. Silica gel 60 (particle size 0.040−0.063 nm, Merck) was used for flash column chromatography (FC). Reactions were carried out under nitrogen. Solvents for reactions were dried according to standard procedures. The synthesis of tetrazines **7a**, **7b**, and **7e**−**7q**[34] were performed according to published procedures. The petroleum ether (PE) used had a boiling range of 40−60 °C.

UV/Vis Kinetic Measurements: Separate solutions of pure (> 99% by HPLC analysis) 2,5-diaryldiazanorcaradienes **9f**−**9k** were prepared in degassed dry 1,4-dioxane at 20.0 °C. Solutions usually containing $0.67-0.96\times10^{-3}$ mol·L^{-1} of **9f**−**9k** were pipetted into quartz cuvettes for UV measurements and heated to the desired reaction temperature (θ = 39−85 °C; Δθ = ±0.1 °C). The reaction progress was followed by monitoring the π→π* transition of the diazanorcaradiene **9** at the absorption maximum near λ = 350 nm, usually covering 10−90% of the reaction. All kinetic runs were duplicated at least once, *k* values differed by less than ±4%. Further experimental details for kinetic runs can be found in the literature.[39]

HPLC Kinetic Measurements: Isomeric mixtures of diazanorcaradienes **15f/16f**, **15i/16i**, and **15j/16j** were separated by FC (vide infra) to give pure isomers **15f**, **15i**, **15j**, **16f**, **16i**, and **16j**. Separate solutions of pure (> 99% by HPLC analysis) isomers **15f**, **15i**, **15j**, **16f**, **16i**, and **16j** were prepared in dry $CHCl_3$ (UVASOL) at 20.0 °C. Standard solutions usually containing $0.24-0.29\times10^{-2}$ mol·L^{-1} of **15**−**16** were pipetted into HPLC vials, sealed, and heated to the desired reaction temperature (θ = 35−58 °C; Δθ = ±0.1 °C). Samples were taken at appropriate time intervals and cooled to −78 °C (dry ice/acetone bath) to stop the isomerization reaction. The isomeric ratio **15/16** was determined by reversed-phase HPLC (silica column Si-100; CH_2Cl_2/THF). The isomerization reaction was monitored by integration of the relevant signal peaks corresponding to the starting compound and the isomerization product, relative to the values obtained for the standard solution (pure isomer). All kinetic runs were duplicated at least once, *k* values differed by less than ±4%. Further experimental details for kinetic runs can be found in the literature.[39] Separate solutions of pure (> 99% by HPLC analysis) 2,5-diaryldiazanorcaradienes **17f**, **17g**, **17i**, **17j**, and **17q** were prepared in dry benzene at 20.0 °C, pipetted into HPLC vials, sealed, and heated to the desired reaction temperature (θ = 20−50 °C; Δθ = ±0.1 °C). Samples (5 μL) were taken at appropriate time intervals, diluted with 50 μL of CH_2Cl_2 (BAKER) and injected into reversed-phase HPLC systems (APS column Bischoff; CH_2Cl_2/CH_3CN) run with various solvent-gradient programs. The isomerization reaction was monitored by integration of the relevant signal peaks corresponding to the *anti* isomer **17** and the *syn* isomer **18**, relative to the values obtained for the standard solution (pure *anti* isomer **17**). All kinetic runs were duplicated at least once, *k* values differed by less than ±4%. Further experimental details for kinetic runs can be found in the literature.[40]

Activation Parameters $\Delta H^{\neq}$ (±0.3 kcal·mol^{-1}) and $\Delta S^{\neq}$ (±1 cal·K^{-1}·mol^{-1}) were determined graphically by values for *k* ($k_{9\rightarrow11}$, $k_{15\rightarrow16}$, $k_{16\rightarrow15}$, and $k_{17\rightarrow18}$) at different temperatures by using linear least-squares computer simulation (Tables 3 to 5).

Synthesis of Dienophiles 13 and 14:[16,39] 2,5-Dimethyl-1,5-hexadiene (8.47 g, 77.0 mmol) was subjected to treatment with dibromocarbene (generated under phase-transfer conditions) analogously to the method given in ref.[16] by vigorously stirring at room temperature for 2 d. After evaporation of volatile solvent under reduced pressure, extraction with PE and purification of the crude product by FC (PE), 1,1′-(2,2,2′,2′-tetrabromo-1,1′-dimethyl)ethane-1,2-diylbis(cyclopropane) (22.7 g, 50.0 mmol, 65%) was obtained as a pale yellow oil and used without further purification. IR (KBr): $\tilde{\nu}$ = 3070, 2980, 2930, 1450, 1430, 1385, 1165, 1075, 1040, 1025, 690 cm^{-1}. ^{1}H NMR (60 MHz, $CDCl_3$): δ = 1.50 (br.

s, 6 H), 1.60 (br. s, 4 H), 1.65−2.25 (m, 4 H). ^{13}C NMR (22.63 MHz, $CDCl_3$): δ = 22.4 (−CH_3, 2 C), 29.2 (quat. C, 2 C), 34.9 (−CH_2−, 2 C), 35.4 (−CH_2−, 2C), 38.6 (quat. C, 2 C). $C_{10}H_{14}Br_4$ (453.8): calcd. C 26.46, H 3.11; found C 26.49, H 3.10. A stirred mixture of the tetrabromo compound (22.7 g, 50.0 mmol) and zinc (26.3 g, 400 mmol) in acetic acid (260 mL) was heated at 80 °C for 3 h. After evaporation of the solvent under reduced pressure and extraction (3 × 100 mL of CCl_4), the organic phase was concentrated under reduced pressure to give a yellow oil, which was then subjected to Vigreux column distillation to give two fractions, A and B. Fraction A (35 °C/0.01 Torr) afforded monobromo compound (2.60 g, 12.0 mmol, 24%), fraction B (70−73 °C/0.01 Torr) afforded dibromo compound (8.70 g, 29.4 mmol, 59%). Both fractions were used without further purification.

3,3′-(3,3′-Dimethyl)ethane-1,2-diylbis(cyclopropene) (13): The dibromo compound (6.00 g, 20.0 mmol) was added dropwise to a stirred mixture of potassium *tert*-butoxide (5.00 g, 44.0 mmol) in DMSO (20 mL) maintained at 100 °C under vacuo over a period of 2 h. The generated cyclopropene **13** (1.30 g, 9.70 mmol, 48%) was condensed into a trap maintained at −60 °C. Because of the instability (exothermic polymerization) of cyclopropene **13**, only ^{1}H NMR analysis could be performed, and use in further reactions was not possible. ^{1}H NMR (60 MHz, CCl_4): δ = 1.03 (s, 6 H, −C*H*$_3$), 1.15 (s, 4 H, −CH_2−), 7.16 (s, 4 H, cyclopropenyl-H).

3-Methyl-3-[2-(1-methylcycloprop-1-yl)ethyl]cyclopropene (14): The monobromo compound (8.50 g, 3.91 mmol) was added dropwise to a stirred mixture of potassium *tert*-butoxide (5.00 g, 44.0 mmol) in DMSO (20 mL) maintained at 100 °C under vacuo over a period of 2 h. The generated cyclopropene **14** (2.30 g, 1.69 mmol, 43%) was condensed into a trap maintained at −60 °C. ^{1}H NMR (60 MHz, CCl_4): δ = 0.01 (s, 4 H, cyclopropyl-H), 0.83 (s, 3 H, −C*H*$_3$), 1.00 (s, 3 H, −C*H*$_3$),1.52 (m, 4 H, −CH_2−), 7.03 (s, 2 H, cyclopropenyl-H).

General Procedure (1) for the Synthesis of 3,4-Diazanorcaradienes 9f−9k and the Semibullvalenes 11a−11p: The tetrazine **7** was dissolved in an inert solvent (vide infra). The dienophile 3,3′-bicyclopropenyl **8**, synthesized by an optimized procedure reported by Bickelhaupt and de Wolf,[16,33] was added and the reaction mixture was stirred until the characteristic red colour of the tetrazine disappeared (reaction times: see below). The solution was concentrated to dryness, and the crude material was purified by flash column chromatography (FC) and recrystallization to afford the product.

General Procedure (2) for the Synthesis of 3,4-Diazanorcaradienes 15f/16f, 15i/16i, and 15j/16j: The tetrazine **7** was dissolved in an inert solvent (vide infra). The dienophile 3-methyl-3-[2-(1-methylcyclopropyl)ethyl]cyclopropene (**14**), synthesized by an optimized procedure reported by Schuster,[39] was added and the reaction mixture was stirred until the characteristic red colour of the tetrazine disappeared (reaction times: see below). The solution was concentrated to dryness, and the crude material was purified by flash column chromatography (FC) and recrystallization to afford the product.

General Procedure (3) for the Synthesis of 3,4-Diazanorcaradienes 17f/18f, 17g/18g, 17i/18i, 17j/18j, and 17q/18q: A stirred suspension of tetrazine **7** in an inert solvent (vide infra) was cooled to −78 °C under Ar. A ca. 20-fold excess of the dienophile (3-methylcyclopropene), generated in situ by an optimized literature procedure reported by Closs and Krantz,[41] was passed through the cooled suspension. The reaction mixture was allowed to warm to room temperature and stirring was continued until the red colour of the tetrazine had disappeared. After completion of the reaction, the solvent was evaporated and the crude product was purified as described below.

Synthesis of Diazanorcaradienes 9f−9k

7-Methyl-7-(1-methylcycloprop-2-enyl)-2,5-diphenyl-3,4-diazabicyclo[4.1.0]hepta-2,4-diene (9f): This compound was obtained by General Procedure (1). Compounds **7f** (1.00 g, 4.20 mmol) and **8** (600 mg, 5.42 mmol) in $CHCl_3$ (20 mL), after stirring at 60 °C for 5 h and purification by recrystallization (*n*-pentane) at −40 °C, yielded **9f** (1.00 g, 3.21 mmol, 75%) as yellow crystals, m.p. 129 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 3100, 1960, 1635, 1540, 1500, 1445, 1390, 1060, 770, 711, 687, 635, 620 cm^{-1}. ^{1}H NMR (60 MHz, $CDCl_3$): δ = 0.76 (s, 3 H, 7a-CH_3), 1.55 (s, 3 H, 8a-CH_3), 2.29 (s, 2 H, 1-H, 6-H), 7.36 (m, 8 H, cyclopropenyl-H and Ar-H), 7.92 (m, 4 H, Ar-H). ^{13}C NMR (22.63 MHz, $CDCl_3$): δ = 11.0 (−CH_3, 1 C, 7a-CH_3), 24.7 (−CH_3, 1 C, 8a-CH_3), 25.3 (quat. C, 1 C, C-7), 26.8 (quat. C, 1 C, C-8), 31.0 (=CH, 2 C, C-1, C-6), 118.3 (=CH, 2 C, C-9, C-10), 127.7 (=CH, 4 C, Ar-C), 128.4 (=CH, 4 C, Ar-C), 130.4 (=CH, 2 C, Ar-C), 137.4 (quat. C, 2 C, Ar-C), 157.4 (quat. C, 2 C, C-2, C-5). MS (FD): *m*/*z* = 312 [M$^+$]. UV/Vis (1,4-dioxane): λ_{max} (ε)= 325 (15100), 259 (10500).

7-Methyl-7-(1-methylcycloprop-2-enyl)-2,5-di-*p*-tolyl-3,4-diazabicyclo[4.1.0]hepta-2,4-diene (9g): This compound was obtained by General Procedure (1). Compounds **7g** (780 mg, 2.97 mmol) and **8** (500 mg, 4.52 mmol) in $CHCl_3$ (10 mL), after stirring at 60 °C for 7 h and purification by recrystallization ($CHCl_3$/*n*-pentane = 1:10), yielded **9g** (600 mg, 1.76 mmol, 59%) as yellow crystals, m.p. 138 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 3100, 3070, 2950, 2920, 1600, 1525, 1400, 1380, 1175, 1090, 1010, 810, 625, 570 cm^{-1}. ^{1}H NMR (60 MHz, $CDCl_3$): δ = 0.73 (s, 3 H, 7a-CH_3), 1.57 (s, 3 H, 8a-CH_3), 2.30 (s, 2 H, 1-H, 6-H), 2.50 (s, 6 H, Ar-C*H*$_3$), 7.19 (m, 4 H, Ar-H), 7.43 (s, 2 H, cyclopropenyl-H), 7.90 (m, 4 H, Ar-H). ^{13}C NMR (22.63 MHz, $CDCl_3$): δ = 11.0 (−CH_3, 1 C, 7a-CH_3), 21.5 (−CH_3, 2 C, Ar-*C*H$_3$), 24.8 (−CH_3, 1 C, 8a-CH_3), 25.4 (quat. C, 1 C, C-7), 26.9 (quat. C, 1 C, C-8), 30.7 (=CH, 2 C, C-1, C-6), 118.4 (=CH, 2 C, C-9, C-10), 127.6 (=CH, 4 C, Ar-C), 129.1 (=CH, 4 C, Ar-C), 134.9 (quat. C, 2 C, Ar-C) 140.9 (quat. C, 2 C, Ar-C), 156.9 (quat. C, 2 C, C-2, C-5). MS (FD): *m*/*z* = 340 [M$^+$]. UV/Vis (1,4-dioxane): λ_{max} (ε) = 330 (19100), 258 (11200).

2,5-Bis(3-methoxyphenyl)-7-methyl-7-(1-methylcycloprop-2-enyl)-3,4-diazabicyclo[4.1.0]hepta-2,4-diene (9h): This compound was obtained by General Procedure (1). Compounds **7h** (1.10 g, 3.70 mmol) and **8** (2.00 g, 18.1 mmol) in CCl_4 (20 mL), after stirring at 60 °C for 4 h and purification by FC (acetone/PE = 1:5) followed by recrystallization (Et_2O) at −40 °C, yielded **9h** (550 mg, 1.47 mmol, 40%) as yellow crystals, m.p. 99 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 3080, 2960, 2830, 1600, 1585, 1505, 1465, 1430, 1382, 1270, 1215, 1180, 1050, 790, 645 cm^{-1}. ^{1}H NMR (60 MHz, $CDCl_3$): δ = 0.73 (s, 3 H, 7a-CH_3), 1.52 (s, 3 H, 8a-CH_3), 2.23 (s, 2 H, 1-H, 6-H), 3.76 (s, 6 H, −OC*H*$_3$), 6.93−7.42 (m, 10 H, cyclopropenyl-H and Ar-H). ^{13}C NMR (22.63 MHz, $CDCl_3$): δ = 11.1 (−CH_3, 1 C, 7a-CH_3), 24.8 (−CH_3, 1 C, 8a-CH_3), 25.3 (quat. C, 1 C, C-7), 26.9 (quat. C, 1 C, C-8), 31.0 (=CH, 2 C, C-1, C-6), 55.42 (−CH_3, 2 C, -O*C*H$_3$), 111.6 (=CH, 2 C, Ar-C), 117.8 (=CH, 2 C, Ar-C), 118.4 (=CH, 2 C, C-9, C-10), 120.7 (=CH, 2 C, Ar-C), 129.4 (=CH, 2 C, Ar-C), 138.8 (quat. C, 2 C, Ar-C), 157.5 (quat. C, 2 C, C-2, C-5), 159.7 (quat. C, 2 C, Ar-C). MS (FD): *m*/*z* = 372 [M$^+$]. UV/Vis (1,4-dioxane): λ_{max} (ε) = 332 (18200), 267 (7900).

2,5-Bis(4-methoxyphenyl)-7-methyl-7-(1-methylcycloprop-2-enyl)-3,4-diazabicyclo[4.1.0]hepta-2,4-diene (9i): This compound was obtained by General Procedure (1). Compounds **7i** (1.00 g,

3.31 mmol) and **8** (700 mg, 6.59 mmol) in $CHCl_3$ (20 mL), after stirring at 65 °C for 9 h and purification by recrystallization (EtOAc), yielded **9i** (1.00 g, 2.69 mmol, 79%) as yellow crystals, m.p. 153 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 3080, 2960, 2930, 1600, 1505, 1460, 1385, 1275, 1230, 1040, 800, 685, 645 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): δ = 0.53 (s, 3 H, 7a-CH_3), 1.35 (s, 3 H, 8a-CH_3), 2.05 (s, 2 H, 1-H, 6-H), 3.57 (s, 6 H, -OCH_3), 6.54 (m, 4 H, Ar-H), 7.03 (s, 2 H, cyclopropenyl-H), 7.60 (m, 4 H, Ar-C). ^{13}C NMR (22.63 MHz, $CDCl_3$): δ = 11.0 (−CH_3, 1 C, 7a-CH_3), 24.8 (−CH_3, 1 C, 8a-CH_3), 25.7 (quat. C, 1 C, C-7), 26.9 (quat. C, 1 C, C-8), 30.4 (=CH, 2 C, C-1, C-6), 55.3 (−CH_3, 2 C, −OCH_3), 113.9 (=CH, 4 C, Ar-C), 118.1 (=CH, 2 C, C-9, C-10), 129.2 (=CH, 4 C, Ar-C), 130.3 (quat. C, 2 C, Ar-C), 156.0 (quat. C, 2 C, C-2, C-5), 161.7 (quat. C, 2 C, Ar-C). MS (EI, 70 eV): *m/z* = 372 [M^+]. MS (HR): calcd. 344.17762 [$M^+ - N_2$]; found 344.17729 [$M^+ - N_2$]. UV/Vis (1,4-dioxane): λ_{max} (ε) = 342 (21900), 275 (7900), 222 (14100).

2,5-Bis(3-chlorophenyl)-7-methyl-7-(1-methylcycloprop-2-enyl)-3,4-diazabicyclo[4.1.0]hepta-2,4-diene (9j): This compound was obtained by General Procedure (1). Compounds **7j** (900 mg, 2.98 mmol) and **2** (800 mg, 7.53 mmol) in $CHCl_3$ (20 mL), after stirring at 60 °C for 5 h and purification by recrystallization ($CHCl_3$/PE) at −78 °C, yielded **9j** (450 mg, 1.20 mmol, 40%) as yellow crystals, m.p. 97 °C. IR (KBr): $\tilde{\nu}$ = 3060, 2960, 2940, 1595, 1570, 1500, 1425, 1375, 1245, 1100, 1080, 780, 730, 700, 675, 620 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): δ = 0.66 (s, 3 H, 7a-CH_3), 1.53 (s, 3 H, 8a-CH_3), 2.14 (s, 2 H, 1-H, 6-H), 7.19−8.00 (m, 10 H, cyclopropenyl-H and Ar-H). ^{13}C NMR (22.63 MHz, $CDCl_3$): δ = 11.0 (−CH_3, 1 C, 7a-CH_3), 24.7 (−CH_3, 1 C, 8a-CH_3), 25.5 (quat. C, 1 C, C-7), 26.9 (quat. C, 1 C, C-8), 31.1 (=CH, 2 C, C-1, C-6), 118.1 (=CH, 2 C, C-9, C-10), 125.8 (=CH, 2 C, Ar-C), 127.8 (=CH, 2 C, Ar-C), 129.7 (=CH, 2 C, Ar-C), 130.8 (=CH, 2 C, Ar-C), 134.6 (quat. C, 2 C, Ar-C), 138.9 (quat. C, 2 C, Ar-C), 156.8 (quat. C, 2 C, C-2, C-5). MS (FD): *m/z* = 380 [M^+]. UV/Vis (1,4-dioxane): λ_{max} (ε) = 328 (12000), 259 (11750).

7-Methyl-7-(1-methylcycloprop-2-enyl)-2,5-bis[3-(trifluoromethyl)-phenyl]-3,4-diazabicyclo[4.1.0]hepta-2,4-diene (9k): This compound was obtained by General Procedure (1). Compounds **7k** (1.00 g, 2.70 mmol) and **8** (700 mg, 6.60 mmol) in $CHCl_3$ (10 mL), after stirring at 50 °C for 1 h and purification by recrystallization (*n*-pentane) at −40 °C, yielded **9k** (350 mg, 0.79 mmol, 30%) as yellow crystals, m.p. 70 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 2960, 1330, 1240, 1165, 1128, 1072, 800, 700, 620 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): δ = 0.77 (s, 3 H, 7a-CH_3), 1.60 (s, 3 H, 8a-CH_3), 2.40 (s, 2 H, 1-H, 6-H), 7.50−8.40 (m, 10 H, cyclopropenyl-H and Ar-H). ^{13}C NMR (22.63 MHz, $CDCl_3$): δ = 11.2 (−CH_3, 1 C, 7a-CH_3), 24.6 (−CH_3, 1 C, 8a-CH_3), 25.7 (quat. C, 1 C, C-7), 26.9 (quat. C, 1 C, C-8), 31.1 (=CH, 2 C, C-1, C-6), 118.4 (=CH, 2 C, C-9, C-10), 124.0 (quat. C, 2 C, -CF_3), 124.3 (quat. C, 2 C, Ar-C), 124.8 (=CH, 2 C, Ar-C), 127.4 (=CH, 2 C, Ar-C), 127.6 (=CH, 2 C, Ar-C), 129.2 (=CH, 2 C, Ar-C), 137.9 (quat. C, 2 C, Ar-C), 157.0 (quat. C, 2 C, C-2, C-5). MS (FD): *m/z* = 448 [M^+]. UV/Vis (1,4-dioxane): λ_{max} (ε) = 324 (12900), 255 (12600).

Synthesis of Diazanorcaradienes 15f/16f, 15i/16i, and 15j/16j

2,5-Bis(3-methoxyphenyl)-7-methyl-7-[2-(1-methylcyclopropyl)-ethyl]-3,4-diazabicyclo[4.1.0]hepta-2,4-diene (15i and 16i): These compounds were prepared according to General Procedure (2). Compounds **7i** (700 mg, 2.37 mmol) and **14** (1.00 g, 7.35 mmol), after stirring in CH_2Cl_2 (30 mL) under reflux for 5 days and separation by FC (CH_2Cl_2/EtOA*c* = 3:1) followed by recrystallization ($CHCl_3$/PE) at −30 °C, yielded **15i** (200 mg, 0.50 mmol, 21%) and **16i** (500 mg, 1.20 mmol, 50%) as yellow crystals. Analytical data of **15i**: m.p. 181−182 °C. IR (KBr): $\tilde{\nu}$ = 2960, 2920, 1600, 1510, 1390, 1250, 1180, 1040, 1020, 840 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = −0.10−0.02 (m, 4 H, 11-H, 12-H), 0.73 (s, 3 H, 10a-CH_3), 0.91−1.09 (m, 4 H, 8-H, 9-H), 1.58 (s, 3 H, 7a-CH_3), 2.44 (s, 2 H, 1-H, 6-H), 3.87 (s, 6 H, -OCH_3), 7.02−8.03 (m, 8 H, Ar-H). MS (EI, 70 eV): *m/z* = 403 (25), 402 (84) [M^+], 306 (24), 293 (64), 201 (31), 200 (100), 132 (36). UV/Vis (1,4-dioxane): λ_{max} (ε) = 343 (26900), 270 (8900), 225 (14800). MS (HR): calcd. 402.23073; found 402.23165. Analytical data of **16i**: m.p. 178−180 °C. IR (KBr): $\tilde{\nu}$ = 2960, 2920, 1600, 1510, 1390, 1250, 1180, 1040, 1020, 845 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.36 (m, 4 H, 11-H, 12-H), 0.62 (s, 3 H, 7a-CH_3), 1.13 (s, 3 H, 10a-CH_3), 1.62−1.92 (m, 4 H, 8-H, 9-H), 2.43 (s, 2 H, 1-H, 6-H), 3.87 (s, 6 H, -OCH_3), 7.04−8.01 (m, 8 H, Ar-H). MS (EI, 70 eV): *m/z* = 403 (34), 402 (100) [M^+], 306 (24), 293 (75), 201 (30), 200 (100), 132 (42). UV/Vis (1,4-dioxane): λ_{max} (ε) = 343 (26900), 270 (8900), 225 (14800). MS (HR): calcd. 402.23073; found 402.23165.

2,5-Bis(3-chlorophenyl)-7-methyl-7-[2-(1-methylcyclopropyl)ethyl]-3,4-diazabicyclo[4.1.0]hepta-2,4-diene (15j and 16j): These compounds were prepared according to General Procedure (2). Compounds **7j** (790 mg, 2.60 mmol) and **14** (1.00 g, 7.35 mmol), after stirring in CH_2Cl_2 (20 mL) under reflux for 12 h and separation by FC (CH_2Cl_2/EtOAc/PE = 10:1:8) followed by recrystallization ($CHCl_3$/PE) at −30 °C, yielded **15j** (250 mg, 0.63 mmol, 24%) and **16j** (400 mg, 0.976 mmol, 38%) as yellow crystals. Analytical data of **15i**: m.p. 176−177 °C. IR (KBr): $\tilde{\nu}$ = 3070, 2960, 2930, 1570, 1535, 1500, 1430, 1380, 1245, 790, 780, 680 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = −0.06−0.05 (m, 4 H, 11-H, 12-H), 0.74 (s, 3 H, 10a-CH_3), 0.93−1.09 (m, 4 H, 8-H, 9-H), 1.62 (s, 3 H, 7a-CH_3), 2.50 (s, 2 H, 1-H, 6-H), 7.38−8.07 (m, 8 H, Ar-H). MS (EI, 70 eV): *m/z* = 412 (34), 410 (47) [M^+], 341 (40), 303 (66), 301 (100), 206 (34), 205 (31), 204 (100), 136 (51). UV/Vis (1,4-dioxane): λ_{max} (ε) = 330 (15100), 263 (12300). MS (HR): calcd. 410.13165; found 410.13206. Analytical data of **16j**: m.p. 179−180 °C. IR (KBr): $\tilde{\nu}$ = 3080, 2950, 1575, 1540, 1500, 1430, 1385, 1250, 790, 780, 670 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.38 (m, 4 H, 11-H, 12-H), 0.64 (s, 3 H, 7a-CH_3), 1.14 (s, 3 H, 10a-CH_3), 1.69 (m, 4 H, 8-H, 9-H), 2.48 (s, 2 H, 1-H, 6-H), 7.42−8.05 (m, 8 H, Ar-H). MS (EI, 70 eV): *m/z* = 412 (35), 410 (49) [M^+], 341 (35), 303 (64), 301 (100), 206 (38), 205 (35), 204 (100), 136 (45). UV/Vis (1,4-dioxane): λ_{max} (ε) = 330 (15100), 263 (12300). MS (HR): calcd. 410.13165; found 410.13142.

7-Methyl-7-[2-(1-methylcyclopropyl)ethyl]-2,5-diphenyl-3,4-diazabicyclo[4.1.0]hepta-2,4-diene (15f and 16f): These compounds were prepared according to General Procedure (2). Compounds **7f** (1.00 g, 4.30 mmol) and **14** (1.00 g, 7.35 mmol), after stirring in CH_2Cl_2 (20 mL) under reflux for 12 h and separation by FC (CH_2Cl_2/EtOAc/PE = 3:1:3) followed by recrystallization ($CHCl_3$/PE) at −30 °C, yielded **15f** (380 mg, 1.10 mmol, 26%) and **16f** (530 mg, 1.55 mmol, 37%) as yellow crystals. Analytical data of **15f**: m.p. 117−119 °C. IR (KBr): $\tilde{\nu}$ = 3060, 2960, 2930, 1540, 1505, 1445, 1400, 770, 710, 690 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = −0.05−0.05 (m, 4 H, 11-H, 12-H), 0.66 (s, 3 H, 10a-CH_3), 0.93 (s, 4 H, 8-H, 9-H), 1.53 (s, 3 H, 7a-CH_3), 2.46 (s, 2 H, 1-H, 6-H), 7.32−8.34 (m, 10 H, Ar-H). ^{13}C NMR (22.63 MHz, $CDCl_3$): δ = 13.0 (−CH_2−, 2 C, 11-CH_2, 12-CH_2), 15.2 (quat. C, 1 C, C-7), 18.8 (quat. C, 1 C, C-10), 22.2 (−CH_3, 1 C, 10a-CH_3), 23.4 (−CH_3, 1 C, 7a-CH_3), 26.2 (−CH_2−, 1 C, 8-CH_2), 32.1 (=CH, 2 C, C-1, C-6), 36.2 (−CH_2−, 1 C, 9-CH_2), 126.6−137.1 (quat. C, =CH, 12 C, Ar-C), 157.1 (quat. C, 2 C, C-2, C-5). MS (EI, 70 eV): *m/z* = 342 (32) [M^+], 273 (17), 245 (17), 239 (18), 233 (85), 170 (100), 100

(31). UV/Vis (1,4-dioxane): λ_{max} (ε) = 329 (16600), 260 (12000). MS (HR): calcd. 342.20960; found 342.20964. Analytical data of **16f**: m.p. 84−85 °C. IR (KBr): ṽ = 3070, 2930, 1540, 1500, 1440, 1390, 1020, 770, 710, 690 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.34 (m, 4 H, 11-H, 12-H), 0.66 (s, 3 H, 7a-CH_3), 1.11 (s, 3 H, 10a-CH_3), 1.76 (m, 4 H, 8-H, 9-H), 2.49 (s, 2 H, 1-H, 6-H), 7.30−8.33 (m, 10 H, Ar-H). ^{13}C NMR (22.63 MHz, $CDCl_3$): δ = 12.2 (−CH_3, 1 C, 7a-CH_3), 13.3 (−CH_2−, 2 C, 11-CH_2, 12-CH_2), 15.4 (quat. C, 1 C, C-7), 18.1 (quat. C, 1 C, C-10), 22.7 (−CH_3, 1 C, 10a-CH_3), 32.1 (=CH, 2 C, C-1, C-6), 36.9 (−CH_2−, 1 C, 8-CH_2), 37.9 (−CH_2−, 1 C, 9-CH_2), 127.0−137.1 (quat. C, =CH, 12 C, Ar-C), 157.1 (quat. C, 2 C, C-2, C-5). − MS (EI, 70 eV): *m*/*z* = 342 (53) [M$^+$], 233 (100), 170 (100), 100 (58). UV/Vis (1,4-dioxane): λ_{max} (ε) = 329 (16600), 260 (11750). MS (HR): calcd. 342.20964; found 342.20960.

Synthesis of Diazanorcaradienes 17f/18f, 17g/18g, 17i/18i, 17j/18j, and 17q/18q

7-Methyl-2,5-diphenyl-3,4-diazabicyclo[4.1.0]hepta-2,4-diene (17f and 18f):[37] These compounds were prepared according to General Procedure (3). Compounds **7f** (1.30 g, 5.55 mmol) and 3-methylcyclopropene, after stirring in CH_2Cl_2 (80 mL) at −78 °C for 4 h and purification by FC (CH_2Cl_2 → CH_2Cl_2/EtOAc = 1:1) followed by recrystallization (CH_2Cl_2/EtOAc), yielded a mixture of **17f/18f** (1.41 g, 5.40 mmol, 98%) as yellow crystals. ^{1}H NMR (250 MHz, $CDCl_3$): **17f**: δ = 0.73 (m, 1 H, ^3J = 6.0, ^3J = 4.3 Hz, 7-H$_{syn}$), 1.60 (d, ^3J = 6.0 Hz, 3 H, 7a-CH_{3anti}), 2.47 (d, ^3J = 4.3 Hz, 2 H, 1-H, 6-H), 7.41−8.34 (m, 10 H, Ar-H). **18f**: δ = 0.65 (d, ^3J = 6.0 Hz, 3 H, 7a-CH_{3syn}), 2.34 (m, 1 H, ^3J = 6.0, ^3J = 9.0 Hz, 7-H$_{anti}$), 2.75 (d, ^3J = 9.0 Hz, 2 H, 1-H, 6-H), 7.41−8.34 (m, 10 H, Ar-H). UV/Vis (CH_3CN): λ_{max} (ε) = 315 (17800).

2,5-Bis(4-chlorophenyl)-7-methyl-3,4-diazabicyclo[4.1.0]hepta-2,4-diene (17g and 18g): These compounds were prepared according to General Procedure (3). Compound **7g** (2.00 g, 6.60 mmol) and 3-methylcyclopropene, after stirring in CH_2Cl_2 (80 mL) at −78 °C for 4 h and purification by FC (CH_2Cl_2 → CH_2Cl_2/EtOAc = 1:1) followed by recrystallization (CH_2Cl_2/EtOAc), yielded a mixture of **17g/18g** (1.95 g, 5.90 mmol, 89%) as yellow crystals. IR (KBr): ṽ = 3050, 2920, 2860, 1590, 1530, 1490, 1400, 1380, 1090, 1000, 840, 830 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): **17f**: δ = 0.72 (m, 1 H, ^3J = 6.1, ^3J = 4.4 Hz, 7-H$_{syn}$), 1.59 (d, ^3J = 6.1 Hz, 3 H, 7a-CH_{3anti}), 2.43 (d, ^3J = 4.4 Hz, 2 H, 1-H, 6-H), 7.42−8.05 (m, 8 H, Ar-H). **18f**: δ = 0.61 (d, ^3J = 6.1 Hz, 3 H, 7a-CH_{3syn}), 2.33 (m, 1 H, ^3J = 6.1, ^3J = 9.0 Hz, 7-H$_{anti}$), 2.71 (d, ^3J = 9.0 Hz, 2 H, 1-H, 6-H), 7.42−8.05 (m, 8 H, Ar-H). UV/Vis (CH_3CN): λ_{max} (ε) = 321 (17800). $C_{18}H_{14}Cl_2N_2$ (329.2): calcd. C 65.67, H 4.28, N 8.51; found C 65.69, H 4.09, N 8.59.

2,5-Bis(4-methoxyphenyl)-7-methyl-3,4-diazabicyclo[4.1.0]hepta-2,4-diene (17i and 18i): These compounds were prepared according to General Procedure (3). Compound **7i** (2.40 g, 8.14 mmol) and 3-methylcyclopropene, after stirring in CH_2Cl_2 (80 mL) at −78 °C for 4 h and purification by FC (CH_2Cl_2 → CH_2Cl_2/EtOAc = 1:1) followed by recrystallization (CH_2Cl_2/EtOAc), yielded a mixture of **17i/18i** (2.58 g, 8.06 mmol, 99%) as yellow crystals. IR (KBr): ṽ = 3050, 3000, 2960, 2840, 1600, 1530, 1510, 1390, 1300, 1240, 1170, 1030, 830 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): **17i**: δ = 0.71 (m, 1 H, ^3J = 6.1, ^3J = 4.4 Hz, 7-H$_{syn}$), 1.58 (d, ^3J = 6.1 Hz, 3 H, 7a-CH_{3anti}), 2.42 (d, ^3J = 4.4 Hz, 2 H, 1-H, 6-H), 3.88 (s, 6 H, OCH_3), 6.97−8.09 (m, 8 H, Ar-H). **18i**: δ = 0.62 (d, ^3J = 6.1 Hz, 3 H, 7a-CH_{3syn}), 2.24 (m, 1 H, ^3J = 6.1, ^3J = 9.0 Hz, 7-H$_{anti}$), 2.70 (d, ^3J = 9.0 Hz, 2 H, 1-H, 6-H), 3.88 (s, 6 H, OCH_3), 6.97−8.09 (m, 8 H, Ar-H). UV/Vis (CH_3CN): λ_{max} (ε) = 335 (29500). $C_{20}H_{20}N_2O_2$ (320.4): calcd. C 74.98, H 6.29, N 8.74; found C 75.06, H 6.34, N 8.80.

2,5-Bis(3-chlorophenyl)-7-methyl-3,4-diazabicyclo[4.1.0]hepta-2,4-diene (17j and 18j): These compounds were prepared according to General Procedure (3). Compound **7j** (2.00 g, 6.60 mmol) and 3-methylcyclopropene, after stirring in CH_2Cl_2 (80 mL) at −78 °C for 4 h and purification by FC (CH_2Cl_2 → CH_2Cl_2/EtOAc = 1:1), yielded a mixture of **17j/18j** (1.79 g, 5.29 mmol, 80%) as yellow crystals. IR (KBr): ṽ = 3050, 2960, 1590, 1570, 1530, 1490, 1400, 1380, 1240, 1070, 780, 770 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): **17j**: δ = 0.73 (m, 1 H, ^3J = 6.1, ^3J = 4.4 Hz, 7-H$_{syn}$), 1.61 (d, ^3J = 6.1 Hz, 3 H, 7a-CH_{3anti}), 2.44 (d, ^3J = 4.4 Hz, 2 H, 1-H, 6-H), 7.38−8.07 (m, 8 H, Ar-H). **18j**: δ = 0.62 (d, ^3J = 6.1 Hz, 3 H, 7a-CH_{3syn}), 2.39 (m, 1 H, ^3J = 6.1, ^3J = 9.0 Hz, 7-H$_{anti}$), 2.73 (d, ^3J = 9.0 Hz, 2 H, 1-H, 6-H), 7.38−8.07 (m, 8 H, Ar-H). UV/Vis (CH_3CN): λ_{max} (ε) = 320 (17800). $C_{18}H_{14}Cl_2N_2$ (329.2): calcd. C 65.67, H 4.28, N 8.51; found C 65.69, H 4.09, N 8.59.

7-Methyl-2,5-di-*p*-tolyl-3,4-diazabicyclo[4.1.0]hepta-2,4-diene (17q and 18q): These compounds were prepared according to General Procedure (3). Compound **7q** (3.00 g, 11.4 mmol) and 3-methylcyclopropene, after stirring in CH_2Cl_2 (80 mL) at −78 °C for 4 h and purification by FC (CH_2Cl_2 → CH_2Cl_2/EtOAc = 1:1) followed by recrystallization (CH_2Cl_2/EtOAc), yielded a mixture of **17q/18q** (3.02 g, 10.5 mmol, 92%) as yellow crystals. IR (KBr): ṽ = 3030, 2960, 2940, 1605, 1530, 1400, 1385, 1180, 1110, 1070, 1010, 830, 780 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): **17q**: δ = 0.70 (m, 1 H, ^3J = 6.1, ^3J = 4.4 Hz, 7-H$_{syn}$), 1.57 (d, ^3J = 6.1 Hz, 3 H, 7a-CH_{3anti}), 2.42 (broad s, 8 H, ^3J = 4.4 Hz, 1-H, 6-H, Ar-CH_3), 7.27−8.01 (m, 8 H, Ar-H). ^{13}C NMR (22.63 MHz, $CDCl_3$): δ = 16.5 (=CH, 1 C, 7-CH), 17.1 (−CH_3, 1 C, 7a-CH_3), 21.4 (−CH_3, 2 C, Ar-CH_3), 26.4 (=CH, 2 C, C-1, C-6), 127.5 (=CH, 4 C, Ar-CH), 129.1 (=CH, 4 C, Ar-CH), 133.8 (quat. C, 2 C, Ar-C), 141.0 (quat. C, 2 C, Ar-C), 158.2 (quat. C, 2 C, C-2, C-5). **18q**: δ = 0.62 (d, ^3J = 6.1 Hz, 3 H, 7a-CH_{3syn}), 2.26 (m, 1 H, ^3J = 6.1, ^3J = 9.0 Hz, 7-H$_{anti}$), 2.42 (broad s, 6 H, Ar-CH_3), 2.71 (d, ^3J = 9.0 Hz, 2 H, 1-H, 6-H), 7.27−8.01 (m, 8 H, Ar-H). ^{13}C NMR (22.63 MHz, $CDCl_3$): δ = 8.1 (−CH_3, =CH, 2 C, 7a-CH_3, 7-CH), 21.4 (−CH_3, 2 C, Ar-CH_3), 23.7 (=CH, 2 C, C-1, C-6), 127.5 (=CH, 4 C, Ar-CH), 129.1 (=CH, 4 C, Ar-CH), 134.6 (quat. C, 2 C, Ar-C), 141.0 (quat. C, 2 C, Ar-C), 156.4 (quat. C, 2 C, C-2, C-5). UV/Vis (CH_3CN): λ_{max} (ε) = 317 (20400). $C_{20}H_{20}N_2$ (288.4): calcd. C 83.30, H 6.99, N 9.71; found C 83.17, H 6.91, N 9.74.

Synthesis of Semibullvalenes 11a−11p

1,3,5,7-Tetramethylsemibullvalene (11a): This compound was obtained by General Procedure (1). Compounds **7a** (510 mg, 4.64 mmol) and **8** (660 mg, 6.25 mmol) in $CDCl_3$ (10 mL), after stirring at room temperature for 1 d and purification by bulb tube distillation (40 °C/0.01 Torr), yielded **11a** (290 mg, 1.81 mmol, 39%) as a yellow oil. IR (KBr): ṽ = 3030, 2960, 2930, 2870, 1615 cm^{-1}. ^{1}H NMR (90 MHz, $CDCl_3$): δ = 0.98 (s, 6 H, 1a-CH_3, 5a-CH_3), 1.63 (s, 6 H, 3-CH_3, 7-CH_3), 3.74 (s, 4 H, 2-H, 4-H, 6-H, 8-H). ^{13} C NMR (22.63 MHz, $CDCl_3$): δ = 15.8 (−CH_3, 2 C, 1a-CH_3, 5a-CH_3), 16.3 (−CH_3, 2 C, 3-CH_3, 7-CH_3), 59.0 (quat. C, 2 C, C-1, C-5), 90.9 (=CH, 4 C, C-2, C-4, C-6, C-8), 128.4 (quat. C, 2 C, C-3, C-7). MS (EI, 70 eV): *m*/*z* (%) = 160 (63) [M$^+$]. MS (HR): calcd. 160.12519; found 160.12521. UV/Vis (1,4-dioxane): λ_{max} (ε) = 240 (2500, sh).

Dimethyl 1,5-Dimethylsemibullvalene-3,7-dicarboxylate (11b): This compound was obtained by General Procedure (1). Compounds **7b** (1.74 g, 8.80 mmol) and **8** (1.11 g, 10.3 mmol) in CH_2Cl_2 (20 mL), after stirring at room temperature for 1 h and purification by

recrystallization (methanol/*n*-hexane), yielded **11b** (1.54 g, 6.2 mmol, 70%) as yellow crystals, m.p. 99 °C. IR (KBr): $\tilde{\nu}$ = 2960, 1715, 1585, 1445, 1250, 1080 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.13 (s, 6 H, 1a-CH_3, 5a-CH_3), 3.67 (s, 6 H, -OCH_3), 4.79 (s, 4 H, 2-H, 4-H, 6-H, 8-H). ^{13}C NMR (22.63 MHz, $CDCl_3$): δ = 14.9 (−CH_3, 2 C, 1a-CH_3, 5a-CH_3), 51.4 (−CH_3, 2 C, -OCH_3), 60.6 (quat. C, 2 C, C-1, C-5), 93.7 (=CH, 4 C, C-2, C-4, C-6, C-8), 127.2 (quat. C, 2 C, C-3, C-7), 164.7 (quat. C, 2 C, ester-C). MS (EI, 70 eV): *m*/*z* (%) = 248 (38) [M^+]. UV/Vis (1,4-dioxane): λ_{max} (ε) = 263 (5700), 220 (10800). $C_{14}H_{16}O_4$ (248.3): calcd. C 67.73, H 6.50; found C 67.18, H 6.50.

1,5-Dimethylsemibullvalene-3,7-dicarboxylic Acid (11c): Basic hydrolysis of the carboxylic ester **11b** (1.14 g, 4.60 mmol) with KOH (890 mg, 15.5 mmol) in aqueous methanol (15 mL, H_2O/methanol = 1:2; stirring under reflux for 1 d) and crystallization in conc. HCl yielded **11c** (890 mg, 4.05 mmol, 88%) as colourless crystals, m.p. 243 °C. IR (KBr): $\tilde{\nu}$ = 3300−2400 (O−H), 1680, 1585, 1435, 1270 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): δ = 1.12 (s, 6 H, 1a-CH_3, 5a-CH_3), 4.74 (s, 4 H, 2-H, 4-H, 6-H, 8-H), 4.78 (s, 2 H, −CO_2H). UV/Vis (1,4-dioxane): λ_{max} (ε) = 257 (4840), 220 (8800). The dicarboxylic acid **11c** was transformed into **11d** without further purification.

1,5-Dimethylsemibullvalene-3,7-dicarbonitrile (11d): The dicarboxylic acid **11c** (880 mg, 4.00 mmol) was dissolved in $SOCl_2$ (11.6 g, 98.0 mmol) and stirred under reflux for 3 h. After the excess of $SOCl_2$ had been removed at reduced pressure, the desired diacyl halide was obtained. A slow stream of ammonia gas was passed into a solution of the diacyl halide in dry benzene (20 mL) to give the amido compound (800 mg, 3.67 mmol, 92%) as a colourless crystalline solid, m.p. 250 °C (decomp.). Trifluoroacetic anhydride (1.20 mL, 8.00 mmol) was added dropwise to a solution of the amido compound (670 mg, 3.07 mmol) in 1,4-dioxane (5 mL) and dry pyridine (1.30 mL, 16.1 mmol). After the mixture had been stirred for 1 d at room temperature, the crude material was isolated. FC (benzene) and recrystallisation (EtOAc) yielded **11d** (120 mg, 0.66 mmol, 21%) as colourless crystals, m.p. 197 °C. IR (KBr): $\tilde{\nu}$ = 3055, 2965, 2930, 2200, 1455, 1310, 883, 870, 685, 670, 650 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): δ = 1.13 (s, 6 H, 1a-CH_3, 5a-CH_3), 4.67 (s, 4 H, 2-H, 4-H, 6-H, 8-H). ^{13}C NMR (22.63 MHz, $CDCl_3$): δ = 14.5 (−CH_3, 2 C, 1a-CH_3, 5a-CH_3), 61.6 (quat. C, 2 C, C-1, C-5), 97.8 (=CH, 4 C, C-2, C-4, C-6, C-8), 105.8 (quat. C, 2 C, C-3, C-7), 115.5 (quat. C, 2 C, -CN). MS (EI, 70 eV): *m*/*z* (%) = 182 (94) [M^+]. MS (HR): calcd. 182.08439; found 182.08427. UV/Vis (1,4-dioxane): λ_{max} (ε): 252 (6460), 213 (11500).

1,5-Dimethyl-3,7-bis(trifluoromethyl)semibullvalene (11e): This compound was obtained by General Procedure (1). Compounds **7e** (915 mg, 4.20 mmol) and **8** (450 mg, 4.24 mmol) in CCl_4 (15 mL), after stirring at room temperature for 30 min and purification by bulb tube distillation (60 °C/0.01 Torr), yielded **11e** (935 mg, 3.49 mmol, 83%) as a colourless oil. IR (KBr): $\tilde{\nu}$ = 3050, 2970, 2940, 2880, 1620, 1450, 1390, 1350, 1310, 1270, 1190, 1150, 1110, 1050, 1020, 900, 860, 840, 720, 700, 660 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): δ = 1.10 (s, 6 H, 1a-CH_3, 5a-CH_3), 4.48 (s, 4 H, 2-H, 4-H, 6-H, 8-H). ^{13}C NMR (22.63 MHz, $CDCl_3$): δ = 14.7 (−CH_3, 2 C, 1a-CH_3, 5a-CH_3), 60.2 (quat. C, 2 C, C-1, C-5), 90.4 (=CH, 4 C, C-2, C-4, C-6, C-8), 122.0 (quat. C, 2 C, C-3, C-7), 123.8 (quat. C, 2 C, −CF_3). MS (EI, 70 eV): *m*/*z* (%) = 268 (83) [M^+]. $C_{12}H_{10}F_6$ (268.2): calcd. C 53.77, H 3.76; found C 54.18, H 3.58.

1,5-Dimethyl-3,7-diphenylsemibullvalene (11f): This compound was obtained by General Procedure (1). Compounds **7f** (800 mg, 3.40 mmol) and **8** (700 mg, 6.50 mmol) in $CHCl_3$ (20 mL), after stirring at 60 °C for 18 h and purification by FC (CH_2Cl_2/PE = 1:5), yielded **11f** (700 mg, 2.50 mmol, 74%) as a yellow oil. IR (KBr): $\tilde{\nu}$ = 3040, 2880, 1601, 1490, 1450, 835, 770, 700 cm^{-1}. ^1H NMR (90 MHz, CD_3OD): δ = 1.07 (s, 6 H, 1a-CH_3, 5a-CH_3), 4.43 (s, 4 H, 2-H, 4-H, 6-H, 8-H), 6.99−7.45 (m, 10 H, Ar-H). ^{13}C NMR (22.63 MHz, $CDCl_3$): δ = 15.8 (−CH_3, 2 C, 1a-CH_3, 5a-CH_3), 58.5 (quat. C, 2 C, C-1, C-5), 88.7 (=CH, 4 C, C-2, C-4, C-6, C-8), 125.3 (=CH, 4 C, Ar-C), 126.4 (=CH, 2 C, Ar-C), 128.2 (=CH, 4 C, Ar-C), 133.3 (quat. C, 2 C, C-3, C-7), 137.3 (quat. C, 2 C, Ar-C). MS (EI, 70 eV): *m*/*z* (%) = 284 (100) [M^+]. MS (HR): calcd. 284.15649; found 284.15615. UV/Vis (1,4-dioxane): λ_{max} (ε) = 297 (15600), 258 (18000).

1,5-Dimethyl-3,7-di-*p*-tolylsemibullvalene (11g): This compound was obtained by General Procedure (1). Compounds **7g** (1.00 g, 3.80 mmol) and **8** (700 mg, 6.50 mmol) in $CHCl_3$ (20 mL), after stirring at 70 °C for 1 d and purification by FC (acetone/PE = 1:10 → CH_2Cl_2/PE = 1:8), yielded **11g** (1.00 g, 3.20 mmol, 84%) as colourless crystals, m.p. 86−88 °C. IR (KBr): $\tilde{\nu}$ = 3020, 2950, 2920, 1510, 1450, 810, 800 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): δ = 1.18 (s, 6 H, 1a-CH_3, 5a-CH_3), 2.25 (s, 6 H, Ar-CH_3), 4.38 (s, 4 H, 2-H, 4-H, 6-H, 8-H), 7.02−7.44 (m, 8 H, Ar-H). ^{13}C NMR (22.63 MHz, $CDCl_3$): δ = 15.9 (−CH_3, 2 C, 1a-CH_3, 5a-CH_3), 21.0 (−CH_3, 2 C, Ar-*C*H$_3$), 58.4 (quat. C, 2 C, C-1, C-5), 88.4 (=CH, 4 C, C-2, C-4, C-6, C-8), 125.7 (=CH, 4 C, Ar-C), 128.9 (=CH, 4 C, Ar-C), 133.0 (quat. C, 2 C, C-3, C-7), 134.6 (quat. C, 2 C, Ar-C), 136.0 (quat. C, 2 C, Ar-C). MS (HR): calcd. 312.18779; found 312.18812. UV/Vis (1,4-dioxane): λ_{max} (ε) = 301 (15100), 260 (19500).

3,7-Bis(3-methoxyphenyl)-1,5-dimethylsemibullvalene (11h): This compound was obtained by General Procedure (1), as a by-product in the synthesis of **9h**. Compounds **7h** (1.10 g, 3.74 mmol) and **8** (2.00 g, 18.8 mmol) in CCl_4 (20 mL), after stirring at 60 °C for 4 h and purification by FC (acetone/PE = 1:5) followed by recrystallization (methanol), yielded **11h** (400 mg, 1.16 mmol, 31%) as colourless crystals, m.p. 97−99 °C. IR (KBr): $\tilde{\nu}$ = 3030, 2960, 2840, 1610, 1495, 1280, 1040, 775 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): δ = 1.20 (s, 6 H, 1a-CH_3, 5a-CH_3), 3.70 (s, 6 H, −OCH_3), 4.36 (s, 4 H, 2-H, 4-H, 6-H, 8-H), 6.92−7.41 (m, 8 H, aryl-H). ^{13}C NMR (22.63 MHz, $CDCl_3$): δ = 15.8 (−CH_3, 2 C, 1a-CH_3, 5a-CH_3), 55.1 (−CH_3, 2 C, −O*C*H$_3$), 58.5 (quat. C, 2 C, C-1, C-5), 88.9 (=CH, 4 C, C-2, C-4, C-6, C-8), 111.6 (=CH, 2 C, Ar-C), 112.0 (=CH, 2 C, Ar-C), 118.5 (=CH, 2 C, Ar-C), 129.2 (=CH, 2 C, Ar-C), 133.3 (quat. C, 2 C, C-3, C-7), 138.8 (quat. C, 2 C, Ar-C), 159.6 (quat. C, 2 C, Ar-C). MS (EI, 70 eV): *m*/*z* (%) = 344 (100) [M^+]. MS (HR): calcd. 344.17762; found 344.17763. UV/Vis (1,4-dioxane): λ_{max} (ε) = 300 (12900), 261 (12900).

3,7-Bis(4-methoxyphenyl)-1,5-dimethylsemibullvalene (11i): This compound was obtained by General Procedure (1). Compounds **7i** (1.01 g, 3.43 mmol) and **8** (1.20 g, 11.3 mmol) in $CHCl_3$ (10 mL), after stirring under reflux for 3 h and purification by FC (CH_2Cl_2/PE = 1:1) followed by recrystallization (methanol), yielded **11i** (1.10 g, 3.19 mmol, 93%) as colourless crystals, m.p. 111−113 °C. IR (KBr): $\tilde{\nu}$ = 3040, 2815, 1609, 1510, 1463, 1250, 1180, 1028, 810 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): δ = 1.24 (s, 6 H, 1a-CH_3, 5a-CH_3), 3.73 (s, 6 H, −OCH_3), 4.34 (s, 4 H, 2-H, 4-H, 6-H, 8-H), 6.69−7.23 (m, 8 H, Ar-H). ^{13}C NMR (22.63 MHz, CD_2Cl_2): δ = 15.9 (−CH_3, 2 C, 1a-CH_3, 5a-CH_3), 55.4 (CH_3, 2 C, −O*C*H$_3$), 58.6 (quat. C, 2 C, C-1, C-5), 88.3 (=CH, 4 C, C-2, C-4, C-6, C-8), 113.9 (=CH, 4 C, Ar-C), 127.1 (=CH, 4 C, Ar-C), 130.4 (quat. C,

2 C, Ar-C), 132.5 (quat. C, 2 C, C-3, C-7), 158.9 (quat. C, 2 C, Ar-C). MS (EI, 70 eV): *m/z* (%) = 344 (100) [M$^+$]. MS (HR): calcd. 344.17762; found 344.17763. UV/Vis (1,4-dioxane): λ_{max} (ε) = 305 (17100), 264 (22900).

3,7-Bis(3-chlorophenyl)-1,5-dimethylsemibullvalene (11j): This compound was obtained by General Procedure (1). Compounds **7j** (740 mg, 2.44 mmol) and **8** (380 mg, 3.56 mmol) in CH_2Cl_2 (5 mL), after stirring at 60 °C for 12 h and purification by bulb tube distillation (200 °C/0.01 Torr), yielded **11j** (285 mg, 0.81 mmol, 33%) as a yellow oil. IR (KBr): $\tilde{\nu}$ = 3040, 2960, 2930, 1600, 1560, 1480, 1095, 790, 780 cm^{-1}. ^{1}H NMR (60 MHz, $CDCl_3$): δ = 1.20 (s, 6 H, 1a-CH_3, 5a-CH_3), 4.43 (s, 4 H, 2-H, 4-H, 6-H, 8-H), 7.05−7.34 (m, 8 H, Ar-H). ^{13}C NMR (22.63 MHz, $CDCl_3$): δ = 15.7 (−CH_3, 2 C, 1a-CH_3, 5a-CH_3), 59.0 (quat. C, 2 C, C-1, C-5), 89.2 (=CH, 4 C, C-2, C-4, C-6, C-8), 124.0 (=CH, 2 C, Ar-C), 125.9 (=CH, 2 C, Ar-C), 126.6 (=CH, 2 C, Ar-C), 129.6 (=CH, 2 C, Ar-C), 132.3 (quat. C, 2 C, C-3, C-7), 134.3 (quat. C, 2 C, Ar-C), 139.1 (quat. C, 2 C, Ar-C). MS (EI, 70 eV): *m/z* (%) = 352 (100) [M$^+$]. UV/Vis (1,4-dioxane): λ_{max} (ε) = 300 (12800), 263 (15400).

1,5-Dimethyl-3,7-bis(3-trifluoromethylphenyl)semibullvalene (11k): This compound was obtained by General Procedure (1). Compounds **7k** (1.00 g, 2.60 mmol) and **8** (500 mg, 4.64 mmol) in CCl_4 (20 mL), after stirring at 60 °C for 30 h and purification by FC ($CHCl_3$/PE= 1:4), yielded **11k** (900 mg, 2.14 mmol, 82%) as a yellow oil. IR (KBr): $\tilde{\nu}$ = 3050, 2970, 1330, 1170, 1130, 1075, 800, 700 cm^{-1}. ^{1}H NMR (60 MHz, $CDCl_3$). δ = 1.20 (s, 6 H, 1a-CH_3, 5a-CH_3), 4.40 (s, 4 H, 2-H, 4-H, 6-H, 8-H), 7.13−7.41 (m, 8 H, Ar-H). ^{13}C NMR (22.63 MHz, $CDCl_3$). δ = 15.6 (−CH_3, 2 C, 1a-CH_3, 5a-CH_3), 59.1 (quat. C, 2 C, C-1, C-5), 89.4 (=CH, 4 C, C-2, C-4, C-6, C-8), 122.5 (quat. C, 2 C, Ar-C), 123.3 (=CH, 2 C, Ar-C), 123.9 (quat. C, 2 C, -CF_3), 128.9 (=CH, 4 C, Ar-C), 131.9 (=CH, 2 C, Ar-C), 132.4 (quat. C, 2 C, C-3, C-7), 138.0 (quat. C, 2 C, Ar-C). MS (EI, 70 eV): *m/z* (%) = 420 (100) [M$^+$]. MS (HR): calcd. 420.13113; found 420.13008. UV/Vis (1,4-dioxane): λ_{max} (ε) = 298 (6460), 259 (10500).

1,5-Dimethyl-3,7-bis(2-thiazolyl)semibullvalene (11l): This compound was obtained by General Procedure (1). Compounds **7l** (128 mg, 0.516 mmol) and **8** (199 mg, 1.88 mmol) in CH_2Cl_2 (10 mL), after stirring under reflux for 65 min and purification by bulb tube distillation (175 °C/0.05 Torr) followed by recrystallization (CH_2Cl_2/*n*-hexane), yielded **11l** (70.0 mg, 0.235 mmol, 46%) as colourless crystals, m.p. 173−174 °C. IR (CH_2Cl_2): $\tilde{\nu}$ = 3100, 3065, 3020, 2955, 2920, 2860, 1575, 1465, 1290, 1120, 1040, 855, 825, 720, 685, 645 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.25 (s, 6 H, 1a-CH_3, 5a-CH_3), 4.79 (s, 4 H, 2-H, 4-H, 6-H, 8-H), 7.14 (d, ^3J = 3.2 Hz, 2 H, Ar-H), 7.68 (d, ^3J = 3.2 Hz, 2 H, Ar-H). ^{13}C NMR (63 MHz, $CDCl_3$): δ = 15.4 (−CH_3, 2 C, 1a-CH_3, 5a-CH_3), 59.9 (quat. C, 2 C, C-1, C-5), 90.2 (=CH, 4 C, C-2, C-4, C-6, C-8), 118.0 (=CH, 2 C, Ar-C), 128.2 (quat. C, 2 C, C-3, C-7), 143.1 (=CH, 2 C, Ar-C), 164.9 (quat. C, 2 C, Ar-C). MS (EI, 70 eV): *m/z* (%) = 298 (100) [M$^+$]. UV/Vis (1,4-dioxane): λ_{max} (ε) = 282 (15240), 326 (13900). $C_{16}H_{14}N_2S_2$ (298.4): calcd. C 64.40, H 4.73, N 9.39; found C 63.87, H 4.88, N 9.24.

1,5-Dimethyl-3,7-bis(2-methyl-1,3,4-oxadiazol-5-yl)semibullvalene (11m): This compound was obtained by General Procedure (1). Compounds **7m** (160 mg, 0.650 mmol) and **8** (199 mg, 1.88 mmol) in CH_2Cl_2 (10 mL), after stirring under reflux for 1 h and purification by recrystallization (CH_2Cl_2/*n*-hexane), yielded **11m** (117 mg, 0.395 mmol, 61%) as colourless crystals, m.p. 163−165 °C. IR (CH_2Cl_2): $\tilde{\nu}$ = 3020, 2960, 2920, 2860, 1600, 1560, 1495, 1440, 1355, 1250, 1225, 1195, 1175, 960, 810, 720 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.24 (s, 6 H, 1a-CH_3, 5a-CH_3), 2.48 (s, 6 H, Ar-CH_3), 4.87 (s, 4 H, 2-H, 4-H, 6-H, 8-H). ^{13}C NMR (63 MHz, $CDCl_3$): δ = 10.9 (−CH_3, 2 C, Ar-*C*H_3), 15.0 (−CH_3, 2 C, 1a-CH_3, 5a-CH_3), 60.7 (quat. C, 2 C, C-1, C-5), 91.5 (=CH, 4 C, C-2, C-4, C-6, C-8), 118.7 (quat. C, 2 C, C-3, C-7), 162.4 (quat. C, 2 C, Ar-C), 162.9 (quat. C, 2 C, Ar-C). MS (EI, 70 eV): *m/z* (%) = 296 (100) [M$^+$]. UV/Vis (1,4-dioxane): λ_{max} (ε) = 240 (17600), 326 (13000). $C_{16}H_{16}N_4O_2$ (296.3): calcd. C 64.86, H 5.44, N 18.91; found C 64.07, H 5.54, N 18.76.

1,5-Dimethyl-3,7-bis(2-pyridyl)semibullvalene (11n): This compound was obtained by General Procedure (1). Compounds **7n** (248 mg, 1.05 mmol) and **8** (199 mg, 1.88 mmol) in CH_2Cl_2 (15 mL), after stirring under reflux for 24 h and purification by bulb tube distillation (160 °C/0.01 Torr) and FC (CH_2Cl_2/EtOAc = 1:9), yielded **11n** (49.5 mg, 0.173 mmol, 16%) as a yellow oil. IR (CH_2Cl_2): $\tilde{\nu}$ = 3060, 3015, 2960, 2920, 2860, 1700, 1585, 1460, 1425, 1215, 1150, 780 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.25 (s, 6 H, 1a-CH_3, 5a-CH_3), 4.82 (s, 4 H, 2-H, 4-H, 6-H, 8-H), 6.99−7.04 (m, 2 H, Ar-H), 7.35−7.39 (m, 2 H, Ar-H), 7.49−7.56 (m, 2 H, Ar-H), 8.47−8.50 (m, 2 H, Ar-H). ^{13}C NMR (63 MHz, $CDCl_3$): δ = 15.6 (−CH_3, 2 C, 1a-CH_3, 5a-CH_3), 59.3 (quat. C, 2 C, C-1, C-5), 89.9 (=CH, 4 C, C-2, C-4, C-6, C-8), 120.5 (=CH, 2 C, Ar-C), 121.4 (=CH, 2 C, Ar-C), 134.0 (quat. C, 2 C, C-3, C-7), 136.0 (=CH, 2 C, Ar-C), 149.2 (=CH, 2 C, Ar-C), 155.3 (quat. C, 2 C, Ar-C). MS (EI, 70 eV): *m/z* (%) = 286 (84) [M$^+$]. UV/Vis (1,4-dioxane): λ_{max} (ε) = 240 (10150), 284 (8890).

1,5-Dimethyl-3,7-bis(4-pyridyl)semibullvalene (11o): This compound was obtained by General Procedure (1). Compounds **7o** (251 mg, 1.06 mmol) and **8** (199 mg, 1.88 mmol) in CH_2Cl_2 (15 mL), after stirring under reflux for 2 h and purification by bulb tube distillation (165 °C/0.01 Torr), FC (CH_2Cl_2/EtOH = 15:1 → 20:1) followed by recrystallization (CH_2Cl_2/*n*-hexane), yielded **11o** (94.5 mg, 0.33 mmol, 31%) as colourless crystals, m.p. 162−163 °C. IR (KBr): $\tilde{\nu}$ = 3020, 2960, 2920, 2865, 1585, 1530, 1405, 1285, 1210, 980, 895, 805, 640 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.25 (s, 6 H, 1a-CH_3, 5a-CH_3), 4.59 (s, 4 H, 2-H, 4-H, 6-H, 8-H), 7.22−7.24 (m, 4 H, Ar-H), 8.45−8.48 (m, 4 H, Ar-H). ^{13}C NMR (63 MHz, $CDCl_3$): δ = 15.5 (−CH_3, 2 C, 1a-CH_3, 5a-CH_3), 59.3 (quat. C, 2 C, C-1, C-5), 90.0 (=CH, 4 C, C-2, C-4, C-6, C-8), 120.3 (=CH, 4 C, Ar-C), 131.8 (quat. C, 2 C, C-3, C-7), 144.0 (quat. C, 2 C, Ar-C), 149.9 (=CH, 4 C, Ar-C). MS (EI, 70 eV): *m/z* (%) = 286 (100) [M$^+$]. UV/Vis (1,4-dioxane): λ_{max} (ε) = 264 (16000), 284 (14100). $C_{20}H_{18}N_2$ (286.4): calcd. C 83.88, H 6.34, N 9.78; found C 83.13, H 6.57, N 9.63.

1,5-Dimethyl-3,7-bis(2-pyrazinyl)semibullvalene (11p): This compound was obtained by General Procedure (1). Compounds **7p** (291 mg, 1.22 mmol) and **8** (214 mg, 2.02 mmol) in CH_2Cl_2 (10 mL), after stirring at room temperature for 19 h and purification by FC (twice; CH_2Cl_2/EtOAc = 2:1 → 2:3), yielded **11p** (93.0 mg, 0.323 mmol, 27%) as a yellow oil. IR (KBr): $\tilde{\nu}$ = 3060, 2960, 2930, 2870, 1725, 1585, 1510, 1460, 1390, 1305, 1140, 1060. 1010, 825, 730, 690 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.28 (s, 6 H, 1a-CH_3, 5a-CH_3), 4.91 (s, 4 H, 2-H, 4-H, 6-H, 8-H), 8.25−8.26 (m, 2 H, Ar-H), 8.38−8.40 (m, 2 H, Ar-H), 8.66−8.67 (m, 2 H, Ar-H). ^{13}C NMR (63 MHz, $CDCl_3$): δ = 15.6 (−CH_3, 2 C, 1a-CH_3, 5a-CH_3), 60.2 (quat. C, 2 C, C-1, C-5), 90.8 (=CH, 4 C, C-2, C-4, C-6, C-8), 132.1 (quat. C, 2 C, C-3, C-7), 142.4 (=CH, 2 C, Ar-C), 142.6 (=CH, 2 C, Ar-C), 144.2 (=CH, 2 C, Ar-C), 151.0 (quat. C, 2 C, Ar-C). MS (EI, 70 eV): *m/z* (%) = 288 (100) [M$^+$]. UV/Vis (1,4-dioxane): λ_{max} (ε) = 240 (13900), 310 (13600).

Acknowledgments

We are grateful to the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and the BASF AG for the financial support of the research.

[1] A. C. Cope, E. M. Hardy, *J. Am. Chem. Soc.* **1940**, *62*, 441−444.
[2] S. J. Rhoads, in: *Molecular Rearrangements*, vol 1 (Ed.: P. de Mayo), John Wiley & Sons, New York, **1963**, pp. 684−696.
[3] S. J. Rhoads, N. R. Raulins, *Org. React.* **1975**, *22*, 1−252.
[4] J. J. Gajewski, in: *Hydrocarbons Thermal Rearrangements*, Academic Press, New York, **1981**, pp. 166−176.
[5] R. B. Woodward, R. Hoffmann, *The Conservation of Orbital Symmetry*, Academic Press, New York, **1970**.
[6] An excellent review was presented quite recently by: H. Hopf, *Classics in Hydrocarbon Chemistry*, Wiley-VCH Verlag GmbH, Weinheim, **2000**.
[7] W. v. E. Doering, W. R. Roth, *Tetrahedron* **1963**, *19*, 715−737.
[8] J. Sauer, P. Bäuerlein, W. Ebenbeck, R. Dyllick-Brenzinger, C. Gousetis, H. Sichert, T. Troll, U. Wallfahrer, *Eur. J. Org. Chem.* **2001**, 2639−2657.
[9] G. Schröder, J. F. M. Oth, *Angew. Chem.* **1967**, *79*, 458−467; *Angew. Chem. Int. Ed. Engl.* **1967**, *6*, 438−447.
[10] W. v. E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr, G. Klumpp, R. M. Rubin, M. Saunders, *Tetrahedron* **1967**, 3943−3963.
[11] H. Quast, C. Becker, E. M. Peters, H. G. v. Schnering, *Liebigs Ann./Recueil* **1997**, 1733−1738 and earlier references cited therein.
[12] L. M. Jackman, E. Fernandes, M. Heubes, H. Quast, *Eur. J. Org. Chem.* **1998**, 2209−2227 and earlier references cited therein.
[13] H. Quast, M. Seefelder, *Angew. Chem.* **1999**, *111*, 1132−1136; *Angew. Chem. Int. Ed.* **1999**, *38*, 1064−1067.
[14] M. Seefelder, H. Quast, *Angew. Chem.* **1999**, *111*, 1136−1139; *Angew. Chem. Int. Ed.* **1999**, *38*, 1068−1071.
[15] D. Paske, R. Ringshandl, J. Sellner, H. Sichert, *Angew. Chem.* **1980**, *92*, 464−465; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 456−457.
[16] J. Sellner, H. Schuster, H. Sichert, J. Sauer, H. Nöth, *Chem. Ber.* **1983**, *116*, 3751−3761.
[17] H. Schuster, H. Sichert, J. Sauer, *Tetrahedron Lett.* **1983**, 1485−1488.
[18] C. Schnieders, K. Müllen, C. Braig, H. Schuster, J. Sauer, *Tetrahedron Lett.* **1984**, 749−752.
[19] H. E. Zimmerman, G. L. Grunewald, *J. Am. Chem. Soc.* **1966**, *88*, 183−184.
[20] H. E. Zimmerman, R. W. Binkley, R. S. Givens, M. A. Sherwin, *J. Am. Chem. Soc.* **1967**, *89*, 3932−3933.
[21] H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, M. A. Sherwin, *J. Am. Chem. Soc.* **1969**, *91*, 3316- 3323.
[22] H. E. Zimmerman, H. Iwamura, *J. Am. Chem. Soc.* **1970**, *92*, 2015−2022 and references cited therein.
[23] N. J. Turro, J.-M. Liu, H. E. Zimmerman, R. E. Factor, *J. Org. Chem.* **1980**, *45*, 3511−3512.
[24] J. Meinwald, D. Schmidt, *J. Am. Chem. Soc.* **1969**, *91*, 5877−5878.
[25] H. E. Zimmerman, J. D. Robbins, J. Schantl, *J. Am. Chem. Soc.* **1969**, *91*, 5878−5879.
[26] J. Meinwald, H. Tsurata, *J. Am. Chem. Soc.* **1969**, *91*, 5877−5878.
[27] R. Askani, *Tetrahedron Lett.* **1970**, 3349−3350.
[28] R. Askani, T. Hornykiewytsch, W. Schwertfeger, M. Jansen, *Chem. Ber.* **1980**, *113*, 2154−2174 and references cited therein.
[29] D. R. James, G. H. Birnberg, L. A. Paquette, *J. Am. Chem. Soc.* **1974**, *96*, 7465−7477 and references cited therein.
[30] R. K. Russel, R. E. Wingrad, Jr., L. A. Paquette, *J. Am. Chem. Soc.* **1971**, *93*, 3085−3086.
[31] D. Moskau, R. Aydin, W. Leber, H. Guenther, H. Quast, H. D. Martin, K. Hassenrueck, L. S. Miller, K. Grohmann, *Chem. Ber.* **1989**, *122*, 925−931.
[32] J. Sauer, "1,2,4,5-Tetrazines", in: *Comprehensive Heterocyclic Chemistry II* (Eds.: A. R. Katritzky, C. W. Rees, E. F. Scriven), Pergamon Press, Oxford, **1996**, vol. 6, pp. 901−957.
[33] F. Bickelhaupt, W. H. de Wolf, *Tetrahedron Lett.* **1972**, 3509−3511.
[34] J. Sauer, P. Bäuerlein, W. Ebenbeck, C. Gousetis, H. Sichert, T. Troll, F. Utz, U. Wallfahrer, *Eur. J. Org. Chem.* **2001**, 2629−2638.
[35] A. Steigel, J. Sauer, D. A. Kleier, G. Binsch, *J. Am. Chem. Soc.* **1972**, 2770−2779.
[36] G. Maier, *Valenzisomerisierungen*, Chemische Taschenbücher 17 (Eds.: W. Foerst, H. Grünewald), Verlag Chemie, Weinheim, **1972**.
[37] G. Maier, U. Heep, *Chem. Ber.* **1968**, *101*, 1371−1380.
[38] R. M. Moriarty, C.-L. Yeh, N. Ishibi, *J. Am. Chem. Soc.* **1971**, *93*, 3085−3086.
[39] J. Schuster, Dissertation, Universität Regensburg, **1983**.
[40] H. Stimmelmayr, Dissertation, Universität Regensburg, **1992**.
[41] G. L. Closs, K. D. Krantz, *J. Org. Chem.* **1966**, *31*, 638.

Received August 8, 2001
[O01389]