Diphenyl- and Bis(phenylethynyl)semibullvalenes[1]

Helmut Quast* and **Jürgen Carlsen**

Institut für Organische Chemie der Universität Würzburg,
Am Hubland, W-8700 Würzburg

Received May 14, 1992

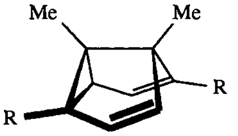
Key Words: Bicyclo[3.3.0]octadienes, derivatives of / Bromination, allylic, by *N*-bromosuccinimide / Zinc-copper couple / Semibullvalenes, 1,5-dimethyl-, 2,6- and 3,7-substituted

---

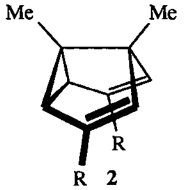
The 2,6- (**6b, c**) and 3,7-substituted 1,5-dimethylbicyclo[3.3.0]octadienes C_2- and C_S-**9b** and **c** are brominated by *N*-bromosuccinimide in the allylic positions to afford the dibromides **7b**, *exo,exo*-**7c**, **10b** and **c**, respectively. An excess of *N*-bromosuccinimide converts **10b** into the unsymmetrical tetrabromide **11**. On chromatography over silica gel, *exo,exo*-**7c** is epimerized to *endo,endo*-**7c**, while methanolysis occurs on reversed-phase chromatography yielding the dimethoxy compound **8**. Under ultrasonic irradiation, the zinc-copper couple converts the bromides **7b**, *exo,exo*-**7c**, **10c**, and **11** into the semibullvalenes **1b, c, 2c**, and **12** which are persistent in dilute solutions when atmospheric oxygen is strictly excluded. The UV/Vis spectra of **1b, c, 2c**, and **12** have been recorded during reversed-phase HPLC on a Bruker ChromScan detector. Notwithstanding the absence of a classical chromophor, **1c** does absorb at no less than 450 nm.

Consideration of the interaction between the antisymmetric component of the occupied degenerate Walsh orbital pair of cyclopropane and a low-lying acceptor orbital of a substituent resulted in the appreciation of changes of cyclopropane bonds[2−6], rate and equilibrium effects on cycloheptatriene ⇌ norcaradiene equilibria[2,3], related equilibria in the series of bridged annulenes[7], and the Cope rearrangement of semibullvalenes[8]. Eventually, the barriers to the latter have been calculated to be lowered or even abandoned by appropriately placed π-acceptor substituents[9]. The effect of ethynyl groups on cyclopropane bonds[10] and the cycloheptatriene ⇌ norcaradiene equilibrium **4** ⇌ **5** resembles that of a cyano group or is even greater. Thus, the equilibrium constants and hence the *stabilization* of the *opposite* cyclopropane bond increased in the order cyano (**4a, 5a**) < phenyl (**4b, 5b**) < phenylethynyl group (**4c, 5c**)[11]. The order of the *weakening* effects on *adjacent* cyclopropane bonds may be inferred hitherto only from the Cope rearrangement of 2,6-substituted barbaralanes **3**, the 2,6-diphenyl derivative **3b** of which rearranges more rapidly[12] than the 2,6-dicarbonitrile **3a**[13]. Except for the semibullvalenedicarbonitrile **1a**, no such semibullvalenes (**1b, c**) are known so far.

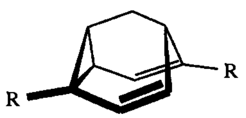
While an extremely low Cope barrier of **1a**[14] is in concordance with the predictions, the exceptional properties of **1a** did surprise, viz. a yellow colour and the fact that the colour faded reversibly at low temperatures[15]. Such light absorption in the absence of a classical chromophor and reversible thermochromism have later been found for 2,6-diphenylbarbaralane (**3b**)[12] and the semibullvalene-2,6-dicarboxylate **1d**[16]. Hence, both properties seem to emerge when two shallow minima on the potential energy hypersurface are separated by a tiny barrier. With the view of lowering this barrier further and shifting the thermally induced light absorption towards longer wavelengths, we have embarked on a study of semibullvalenes substituted by groups that extend π-conjugation. We report here on the synthesis of **1b** and **c**, and of its 3,7-substituted isomer **2c** as well. The 3,7-diphenylsemibullvalene **2b** is already known from the work of Askani[17] and Sauer et al.[18]. Besides the π-acceptor properties, the ethynyl groups in **1c** and **2c** exhibit the attractive feature of having effective rotational symmetry which, as in the case of a cyano group, obviates conformational ambiguities which may result from groups of lower symmetry.



1

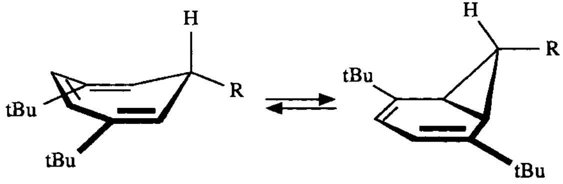


2



3

	R
1a – 5a	N≡C–
1b – 5b	Ph–
1c – 5c	Ph–C≡C–
1d – 3d	MeO_2C–

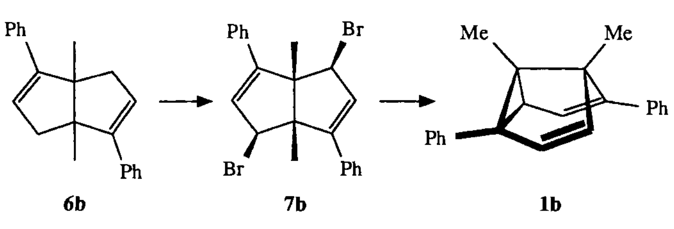


4 **5**

	4 : **5** (–120°C)[4]
4a, 5a	79.5 : 20.5
4b, 5b	77.8 : 22.2
4c, 5c	72.8 : 27.8

The precursors **6b, c** and C_2-, C_S-**9c** of the target molecules **1b, c** and **2c** have been synthesized recently from the corresponding ketones[19,20]. Cyclization of the bicyclo[3.3.0]octadienes **6** and **9** to the semibullvalenes was envisaged on the route pioneered by Askani[17] involving allylic bromination of 1,5-dimethylbicyclo[3.3.0]octadienes to the γ,γ'-dibromo derivatives followed by reductive cyclization. This seemingly straight route may be plagued by obstacles, however. Thus, the introduction of the bromine atoms into the *exo* position, which is necessary for a ring closure occurring on an extended W- or semi-W path[21], may become difficult or fail in the presence of encumbering substituents[22]. Furthermore, the allylic bromides are envisioned to be prone to rearrangements and decomposition if loss of bromide results in a highly stabilized allylic cation.

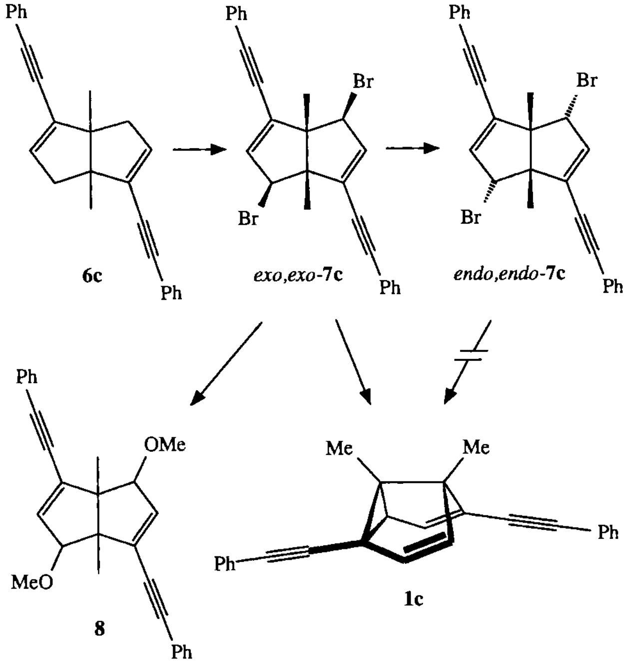
In the event, the diphenyl-2,6-diene **6b** was readily brominated by *N*-bromosuccinimide in refluxing tetrachloromethane under irradiation to afford almost quantitatively the *exo,exo*-dibromide **7b** as a pale yellow oil. Attempts at purification by chromatography on silica gel or aluminium oxide and by reversed-phase chromatography with methanol/water as eluent were frustrated, however, by decomposition with formation of molecular bromine. The structure **7b** of the bromination product is based on the apparent C_2-symmetry and the analogy to similar cases in which the bromine atoms exclusively have entered from the *exo* side of the *cis*-bicyclo[3.3.0]octadiene skeleton[14,16,23]. Debromination of **7b** by the zinc-copper couple in ether or tetrahydrofuran occurred very rapidly yielding a single product, as monitored by reversed-phase HPLC. While the reaction mixture could be filtered unchanged through a pad of kieselgur, decomposition resulted on flash chromatography over silica gel. Dilute solutions, which were golden yellow, persisted for several days at room temperature, but only when atmospheric oxygen was strictly excluded. Attempts to concentrate the solutions at low temperatures resulted in undefined decomposition. Similar observations have been reported for the 3,7-diphenylsemibullvalene **2b**[17] and 2,6-substituted semibullvalenes of type **1a** and **d** but devoid of the methyl groups at the bridgehead carbon atoms[16,23].



6b **7b** **1b**

In contrast to the bromination of **6b**, that of the phenylethynyl analogue **6c** is very slow as shown by monitoring the reaction with reversed-phase HPLC. Azodiisobutyronitrile does accelerate the reaction but leads to the formation of side products, however. In the event, prolonged heating of **6c** in the presence of an excess of *N*-bromosuccinimide afforded a high yield of *exo,exo*-**7c**, which was isolated as a yellow-orange solid. Its structure *exo,exo*-**7c** is inferred on the basis of the NMR spectra (Tables 3 and 4) and of the conversion to the semibullvalene **1c** on treatment with the zinc-copper couple (see below). Attempts at purification failed: Reversed-phase chromatography with methanol/water as eluent led to methanolysis. The product, obtained as an oil after chromatography, was the dimethoxy compound **8** of C_2 symmetry according to the proton and carbon-13 spectra (Tables 3 and 4). Chromatography of *exo,exo*-**7c** on silica gel or aluminium oxide with dichloromethane/methanol (99:1) as eluent induced complete epimerization yielding *endo,endo*-**7c**. Again, the NMR spectra indicated C_2 symmetry, but *endo,endo*-**7c** was *not* convertible to the semibullvalene **1c**. This observation supports the assignment of the *endo*-configuration to the bromine atoms. Both, the epimerization and the methanolysis of *exo,exo*-**7c**, probably follow an ion pair mechanism favoured by the formation of a highly stabilized delocalized carbenium ion.

While the dibromodiene *endo,endo*-**7c** was inert towards the zinc-copper couple, even under forcing conditions and ultrasonic irradiation, the epimer *exo,exo*-**7c** reacted very readily to yield a deep yellow-orange solution of **1c** which is persistent in a sealed NMR tube and in dilute solutions (HPLC) but decomposes even on very cautious partial removal of the solvent.



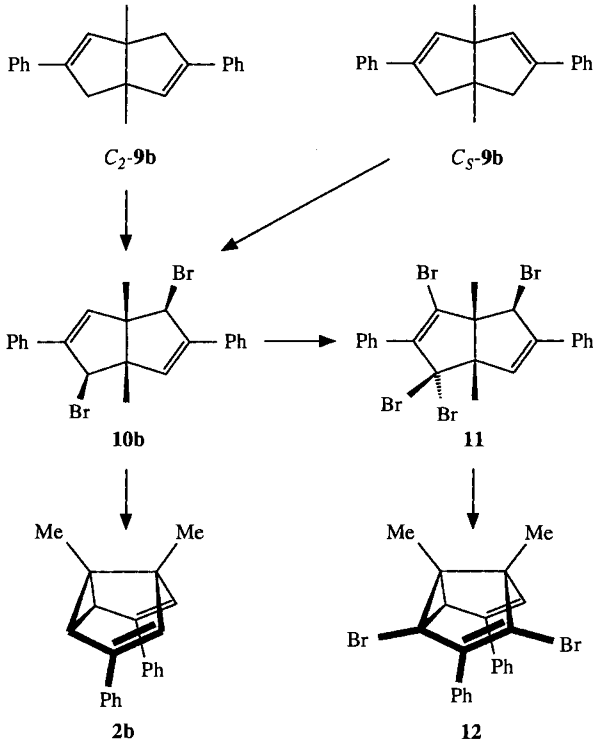
6c *exo,exo*-**7c** *endo,endo*-**7c** **8** **1c**

A 3:1 mixture of the 3,7-substituded dienes C_2- and C_S-**9b** has been brominated by *N*-bromosuccinimide in tetrachloromethane in the presence of azodiisobutyronitrile. The product was not characterized but immediately converted to the diphenylsemibullvalene **2b** which had to be kept in dilute solution because of its tendency to polymerize[17]. *N*-Bromosuccinimide in tetrachloromethane under irradiation rapidly converted a mixture of C_2- and C_S-**9b** to the *exo,exo* dibromo compound **10b** which was isolated as a pale yellow oil. No other products were detectable by reversed-phase HPLC and NMR spectroscopy. Further bromination of **9b** gave rise to the formation of a crystalline, unsymmetrical

Table 1. Yields, melting points and IR data of some 1,5-dimethylbicyclo[3.3.0]octa-2,6-diene derivatives

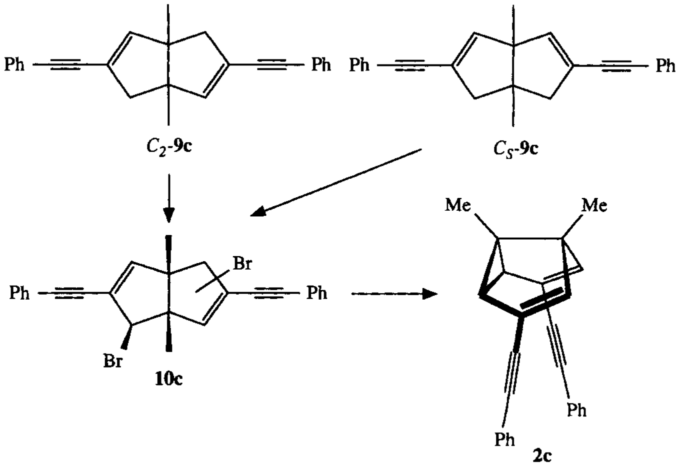
Cpd.	Yield [%]	M. p. [°C]	IR (KBr) [cm^{-1}] C≡C	IR (KBr) [cm^{-1}] C=C
7b	95	[a]		
exo,exo-**7c**	92	104–108	2205	1620 1595
endo,endo-**7c**	96	86–91	2205	1625 1598
8	84	[a]		
10b	93	[a]		
10c	82	50–60	2205	1612 1592
11	84	136–138		1635 1595

[a] Oil.



tetrabromo compound. Its structure **11** was assigned on the basis of the NMR spectra (Tables 3 and 4), the ready conversion to the 2,4-dibromosemibullvalene **12**, and the comparison with the tetrabromo dinitrile **11** (CN instead of Ph)[24]. Debromination of the tetrabromodiene **11** by the zinc-copper couple in tetrahydrofuran under ultrasonic irradiation afforded the 2,4-dibromodiphenylsemibullvalene **12** in quantitative yield. It survived under the conditions of reversed-phase HPLC and in concentrated solutions as well. Partial decomposition was observed on attempts at crystallization, however.

Bromination of the 2,6-bis(phenylethynyl)diene **6c** with *N*-bromosuccinimide was slow but yielded a single dibromo compound (*exo,exo*-**7c**). In contrast, an unseparable mixture of isomeric dibromo compounds **10c** was obtained from a mixture of C_2- and C_S-**9c** as a beige solid which was purified by flash chromatography. The zinc-copper couple converted this mixture to the bis(phenylethynyl)semibullvalene **2c** which persisted in a sealed NMR tube and on filtration of the reaction mixture through a pad of kieselgur followed by extraction with water. Though even solutions of higher concentration turned out to be reasonably stable, slow decomposition frustrated all attempts to obtain crystals.



NMR and UV/Vis Spectra of the Semibullvalenes

The proton (Table 3) and carbon-13 spectra (Table 4), taken from solutions at room temperature, of the semibullvalenes described here exhibit sharp signals that are indicative of very fast equilibrating degenerate valence tautomers. Line broadening was observed only of the signals of C-2/C-4 and C-6/C-8 in the carbon-13 spectrum of the 2,4-dibromosemibullvalene **12** which resembles the dibromosemibullvalene-3,7-dicarbonitrile **12** (CN instead of Ph)[24]. The retarding influence of bromine atoms at the termini of the allylic parts on the Cope rearrangement of semibullvalenes apparently does not depend on the nature of the central substituents[25].

The UV/Vis spectra of the phenyl- and phenylethynylsemibullvalenes are of particular relevance to the problem of colour and reversible thermochromism of semibullvalenes. Unfortunately, none of the new semibullvalenes could be crystallized nor survived purification procedures except for analytical reversed-phase HPLC which, therefore, was combined with rapid-scanning UV/Vis spectroscopy. Thus, not only a check of the peak homogeneity was possible but also recording the UV/Vis spectra of elusive species. The UV spectra of the corresponding phenyl- and phenylethynylbicyclo[3.3.0]octadienes were measured in the same way for comparison, besides their spectra in acetonitrile run on a conventional spectrometer. The data are compiled in Table 2.

Table 2. UV/Vis data of phenyl- and phenylethynylsemibullvalenes and bicyclo[3.3.0]octadienes; qualitative spectra from solutions in methanol/water (95:5) were run on a Bruker ChromScan UV/Vis detector during reversed-phase HPLC, quantitative spectra of solutions in acetonitrile on a conventional spectrometer (data given in square brackets)

Bicyclo[3.3.0]octadienes	λ_{max} [nm] (lg ε)	Semibullvalenes	λ_{max} [nm]
6b	246 [251 (4.310)]	**1b**	269
6c	274, 289 [275 (4.677), 291 (4.608)]	**1c**	253, 297, 310 (sh), 450 (w)
C_2-**9b**	258	**12**	253, 280 (sh)
C_S-**9b**	270		
C_2-**9c**	274, 291	**2c**	274, 309
C_S-**9c**	277, 290 (sh)		

The intense absorptions in the UV spectra of the semibullvalenes **1b**, **c** and **2c** resemble those of the corresponding bicyclo[3.3.0]octadiene precursors **6b**, **c** and **9c** observed at shorter wavelengths. These maxima apparently arise from similar chromophors present in both series. The search for absorptions of low intensity in the near UV and visible spectra uncovered a broad maximum at no less than 450 nm for the 2,6-bis(phenylethynyl)semibullvalene **1c** which resembles the temperature-dependent absorption of the semibullvalene-2,6-dicarbonitrile **1a** at 360 nm. Though an investigation of the temperature dependence of the visible absorption of **1c** has not been possible with the techniques available at present, there is hardly any doubt that **1c** ranges among the rare species of coloured semibullvalenes devoid of a classical chromophor.

Financial support by the *Fonds der Chemischen Industrie*, Frankfurt am Main, is gratefully acknowledged.

Experimental

Yields, physical data, IR: Table 1. – UV/Vis: Table 2. – ^{1}H NMR: Table 3. – ^{13}C NMR: Table 4. – Melting points: Determined in sealed capillary tubes on an apparatus from Büchi, Flawil, Switzerland, or on a Kofler apparatus from Reichert, Vienna, Austria. – IR: Perkin-Elmer 1420. – UV/Vis: Bruker ChromScan UV/Vis detector, connected to a Bruker HPLC system LC 21-C, and Hitachi U 3200, [ε] = [l mol^{-1} cm^{-1}]. – ^{1}H NMR: Bruker AC 200 (0.153 Hz/pt.) and AC 250 (0.305 Hz/pt.). – ^{13}C NMR: Bruker AC 200 and AC 250; the assignments were based on DEPT spectra. – MS (70 eV): Finnigan MAT 8200. – Flash chromatography: 40 × 4-cm glass column, connected to a Knauer UV detector 87.00 (λ = 254 or 280 nm), silica gel 32–63 μm (ICN Biomedicals), pentane/ether (95:5) or dichloromethane/methanol (99:1) as eluents, 1.8 bar. – Medium-pressure liquid chromatography (MPLC): 40 × 4-cm glass column, connected to a Knauer UV detector 87.00 (λ = 280 nm) and a Bischoff differential refractometer 8110, C18 reversed-phase silica gel Europrep 60–30, 20–45 μm (Knauer), 45 ml/min methanol/water (95:5), 15 bar. – High-performance liquid chromatography (HPLC): Bruker LC 21-C, equipped with a ChromScan UV/Vis detector and a Knauer UV detector 87.00 (λ = 254 or 280 nm), 250 × 4-mm stainless steel column containing C18 reversed-phase silica gel Europrep 60, 10 μm (Knauer), 2.0 ml/min methanol/water (95:5); retention times t_R [min]: 3.7 (**7b**), 3.8 (**10b**), 4.2 (**2c**), 4.6 (**12**), 4.7 (**8**), 4.9 (**1b**), 5.0 (**10c**), 5.7 (**1c** and **6b**), 5.6 and 5.9 (C_2- and C_S-**9c**), 5.8 and 5.9 (C_2- and C_S-**9b**), 6.1 (**6c**), 6.3 (*endo,endo*-**7c**), 6.4 (**11**), 9.1 (*exo,exo*-**7c**).

The following solvents were distilled under Ar (99.998%): Tetrachloromethane from diphosphorus pentoxide; pentane, ether, and tetrahydrofuran from sodium-potassium alloy. [D$_8$]-Tetrahydrofuran was stirred over sodium-potassium alloy and transferred into a high-vacuum line. – The dienes **6b**[19], **6c**[20], C_2-,C_S-**9b**[19], and C_2-,C_S-**9c**[20] were available from previous work. – Preparation and handling of semibullvalenes were carried out with strict exclusion of atmospheric oxygen under Ar (99.998%) by means of vacuum line techniques. Solvents, drying agents, and silica gel used for chromatography were carefully degassed and saturated with Ar. – Ultrasonic irradiation[26] was performed in a 120-W, 50-kHz ultrasonic cleaning bath RK 102 from Bandelin Electronic, Berlin.

Table 3. Chemical shifts (δ values) and absolute values of coupling constants [Hz] of ^{1}H-NMR spectra from [D]trichloromethane solutions of bicyclo[3.3.0]octadiene derivatives and from [D$_8$]tetrahydrofuran solutions of semibullvalenes

Cpd.	H_A	H_B	$^3J_{AB}$	Me (s)	Ph (m)
Bicyclo[3.3.0]octadiene Derivatives					
7b[a]	5.18	5.99	3.0	1.79	7.2–7.4
exo,exo-**7c**	5.35	6.16	2.9	1.57	7.3–7.5
endo,endo-**7c**	4.75	6.03	2.7	1.34	7.3–7.5
8	4.17 (d)	5.98 (d)		1.20 3.31	7.1–7.4
10b[a]	5.22	6.08		1.58	7.1–7.5
11	5.72	6.59		1.69 1.83	7.2–7.6
Semibullvalenes					
1b	4.60	5.40	4.1	1.05	7.1–7.5
1c	4.52	5.58	4.1	1.20	7.2–7.5
2c	4.35			1.10	7.2–7.5
12	4.70			1.42	7.1–7.5

[a] Solvent tetrachloromethane/[D$_{12}$]cyclohexane (5:3).

Allylic Bromination by N-Bromosuccinimide. – General Procedure: The bicyclo[3.3.0]octa-2,6-dienes **6b**, **c** or a mixture of bicyclo[3.3.0]octa-2,6- and -2,7-dienes, C_2-,C_S-**9b**, C_2-,C_S-**9c** were dissolved in tetrachloromethane (20 ml) under Ar. *N*-Bromosuccinimide was added and the suspension was heated under reflux and irradiation with a 250-W daylight lamp (Philips ML), which also served as the heat source, while the conversion was monitored by HPLC. After the reaction had run to completion, the mixture was cooled to 0°C and NMR spectra were recorded with 0.5-ml samples after the addition of 0.3 ml of [D$_{12}$]cyclohexane as an internal lock. The succinimide was removed by filtration and washed twice with tetrachloromethane. The yellow solutions were extracted with 0.5 M aqueous sodium hydroxide (2 × 100 ml) and water (2 × 100 ml), dried with sodium sulphate, and evaporated to dryness at 0°C/10^{-2} Torr.

Table 4. Chemical shifts (δ values) of ^{13}C-NMR spectra from [D]trichloromethane solutions of bicyclo[3.3.0]octadiene derivatives and from [D$_8$]tetrahydrofuran solutions of semibullvalenes. The chemical shift of carbon atoms that are equivalent in virtue of symmetry is given only once. Values of similar size that stem from carbon atoms, connected to the same number of hydrogen atoms, are printed in *italics* and may be exchanged

	quart. C				CH									
Cpd.	C-1 C-5	C-2 C-6	C-3 C-7	C-4 C-8	C-2 C-6	C-3 C-7	C-4 C-8	CH$_3$	C≡C		*ipso*-C	*o*-C, *m*-C		*p*-C
Bicyclo[3.3.0]octadiene Derivatives														
7b[a]	63.2	153.2	–	–	–	*128.46*	62.7	22.2			135.5	128.12	129.23	*128.91*
exo,exo-**7c**	61.5	134.68	–	–	–	134.58	63.2	20.3	83.4	96.7	122.2	128.4	131.8	129.0
endo,endo-**7c**	61.8	137.5	–	–	–	134.1	79.4	17.1	84.3	95.1	122.8	128.31	131.7	128.57
8	62.5	137.5	–	–	–	132.2	88.0	16.4	85.8	94.3	122.8	128.30	131.6	128.45
								58.0						
10b[a]	60.6	–	142.4	–	137.0	–	64.0	21.0			133.8	127.2	129.03	128.81
11	62.2	*133.1*	143.8	77.2	–	–	–	18.9			*132.6*	126.4	128.60	128.90
	66.5	–	140.9	–	137.1	–	63.3	19.3			*134.0*	127.8	129.72	
Semibullvalenes														
1b	66.0	109.2	–	–	–	123.3	94.7	14.0			139.4	128.8	129.3	127.2
1c	64.7	103.8	–	–	–	124.82	96.2	13.9	88.03	88.52	124.55	129.04	132.1	128.62
2c	60.2	–	115.6	–	95.6	–		15.3	87.6	89.8	124.4	129.00	132.0	128.68
12	62.3	92.4[b]	*136.35*		–	–	–	15.2			136.23	126.6	129.25	128.08
		–	*134.56*	–	96.0[c]	–					139.17	128.34	129.44	

[a] Solvent tetrachloromethane/[D$_{12}$]cyclohexane (5:3). — [b] Broad signal of a quaternary carbon atom. — [c] Broad signal of a methine carbon atom.

c-4,c-8-Dibromo-r-1,c-5-dimethyl-2,6-diphenylbicyclo[3.3.0]octa-2,6-diene (**7b**): Heating under reflux and irradiation for 0.5 h of a solution of **6b** (287 mg, 1.0 mmol) in tetrachloromethane and *N*-bromosuccinimide (375 mg, 2.1 mmol) afforded a pale yellow oil (420 mg, 95%), which slowly decomposed on standing at 20–25°C.

c-4,c-8-Dibromo-r-1,c-5-dimethyl-2,6-bis(phenylethynyl)bicyclo[3.3.0]octa-2,6-diene (*exo,exo*-**7c**): Heating under reflux and irradiation for 6 h of a solution of **6c** (335 mg, 1.0 mmol) in tetrachloromethane and *N*-bromosuccinimide (1.07 g, 6.0 mmol) produced a yellow-orange solid (455 mg, 92%), m.p. 104–108°C (dec.). — MS: *m*/*z* (%) = 495, 493, 491 (0.5, 1.0, 0.5) [M$^+$], 414, 412 (3, 3) [M$^+$ – Br], 413, 411 (7, 7) [M$^+$ – HBr], 333 (46) [M$^+$ – 2 Br], 332 (100) [M$^+$ – HBr – Br], 317 (45), 302 (41).

t-4,t-8-Dibromo-r-1,c-5-dimethyl-2,6-bis(phenylethynyl)bicyclo[3.3.0]octa-2,6-diene (*endo,endo*-**7c**): Flash chromatography of *exo,exo*-**7c** (247 mg, 0.5 mmol) on silica gel with dichloromethane/methanol (99:1) yielded yellow crystals (237 mg, 96%), m.p. 86–91°C. – MS: *m*/*z* (%) = 495, 493, 491 (0.7, 1.8, 0.7) [M$^+$], 414, 412 (6, 6) [M$^+$ – Br], 413, 411 (18, 17) [M$^+$ – HBr], 333 (45) [M$^+$ – 2 Br], 332 (100) [M$^+$ – HBr – Br], 317 (46), 302 (42).

4,8-Dimethoxy-r-1,c-5-dimethyl-2,6-bis(phenylethynyl)bicyclo[3.3.0]octa-2,6-diene (**8**): Medium-pressure liquid chromatography of *exo,exo*-**7c** (247 mg, 0.5 mmol) on reversed-phase silica gel with methanol/water (95:5) yielded a pale yellow oil (165 mg, 84%).

c-4,c-8-Dibromo-r-1,c-5-dimethyl-3,7-diphenylbicyclo[3.3.0]octa-2,6-diene (**10b**): Heating under reflux and irradiation for 0.5 h of a solution of a mixture of C_2- and C_S-**9b** (287 mg, 1.0 mmol) in tetrachloromethane and *N*-bromosuccinimide (375 mg, 2.1 mmol) gave rise to the formation of a pale yellow oil (390 mg, 93%).

2,4,4,c-8-Tetrabromo-r-1,c-5-dimethyl-3,7-diphenylbicyclo[3.3.0]octa-2,6-diene (**11**): Heating under reflux and irradiation for 2 h of a solution of a mixture of C_2- and C_S-**9b** (573 mg, 2.0 mmol) in tetrachloromethane and *N*-bromosuccinimide (1.56 g, 8.8 mmol) furnished a brown solid, which was purified by flash chromatography on silica gel with pentane/ether (95:5) to yield a beige solid (1.09 g, 84%), m.p. 136–138°C. – MS: *m*/*z* (%) = 606, 604, 602, 600, 598, (0.2, 0.8, 1.4, 0.9, 0.3) [M$^+$], 525, 523, 521, 519 (3, 8, 9, 3) [M$^+$ – Br], 444, 442, 440 (3, 6, 3) [M$^+$ – 2 Br], 443, 441, 439 (4, 4, 1) [M$^+$ – HBr – Br], 363, 361 (30, 27) [M$^+$ – 3 Br], 362, 360 (12, 5) [M$^+$ – 2 Br – HBr], 282 (100) [M$^+$ – 4 Br], 267 (18), 265 (25), 252 (17).

c-4,c-8-Dibromo-r-1,c-5-dimethyl-3,7-bis(phenylethynyl)bicyclo[3.3.0]octa-2,6-diene and Isomers (**10c**): Heating under reflux and irradiation for 6 h of a solution of a mixture of C_2- and C_S-**9c** (669 mg, 2.0 mmol) in tetrachloromethane and *N*-bromosuccinimide (783 mg, 4.4 mmol) afforded a beige solid, which was purified by flash chromatography on silica gel with pentane/ether (95:5) to yield a pale yellow solid (805 mg, 82%), m.p. 50–60°C (dec.). – MS: *m*/*z* (%) = 495, 493, 491 (2, 5, 3) [M$^+$], 494, 492, 490 (4, 4, 1) [M$^+$ – H], 414, 412 (16, 16) [M$^+$ – Br], 413, 411 (12, 8) [M$^+$ – HBr], 333 (100) [M$^+$ – 2 Br], 332 (21), 318 (38), 317 (36), 303 (34), 302 (33).

Solutions of the Semibullvalenes **1b**, **c**, **2c** *and* **12** *in [D$_8$]Tetrahydrofuran. – General Procedure:* An NMR sample tube which was connected to a high-vacuum line was charged with the brominated precursor (0.15 mmol) and the zinc-copper couple (50 mg), carefully degassed at 10^{-5} Torr, and refilled with Ar (4 ×). $[D_8]$-Tetrahydrofuran (0.7 ml) was transferred at 10^{-5} Torr into the sample tube which was cooled with liquid nitrogen and eventually sealed under high vacuum. After the reaction had run to completion (see below), the excess of the zinc-copper couple was transferred into the upper part of the NMR sample tube by means of a centrifuge whereupon the NMR spectra were recorded without delay.

1,5-Dimethyl-2,6-diphenyltricyclo[3.3.0.$0^{2,8}$]octa-3,6-diene (**1b**): a) In accordance with the general procedure, a suspension was prepared from **7b** and the zinc-copper couple in $[D_8]$tetrahydrofuran. The reaction started as soon as the solid suspension began to thaw and ran to completion within 5 min under ultrasonic irradiation at 20–25°C.

b) The zinc-copper couple (200 mg) was added to a solution of **7b** (200 mg, 0.45 mmol) in ether (10 ml). The suspension was kept under ultrasonic irradiation for 20 min at 20–25°C while the conversion was monitored by reversed-phase HPLC. The yellow suspension was filtered through a 7 × 2-cm pad of kieselgur which was eluted with ether (20 ml). Even at temperatures as high as 20–25°C, the semibullvalene **1b** persisted for weeks in the golden yellow, dilute solution (HPLC). Evaporation of the solvent, either in a stream of Ar or under vacuum, inevitably resulted in the disappearance of the HPLC signal without concomitant emergence of well-defined new signals.

1,5-Dimethyl-2,6-bis(phenylethynyl)tricyclo[3.3.0.$0^{2,8}$]octa-3,6-diene (**1c**): In conformity with the general procedure, a suspension was prepared from **7c** and the zinc-copper couple in $[D_8]$tetrahydrofuran. A pale yellow suspension resulted on thawing. Ultrasonic irradiation at 20–25°C for only 10 s gave rise to the formation of an orange-red suspension.

2,4-Dibromo-1,5-dimethyl-3,7-diphenyltricyclo[3.3.0.$0^{2,8}$]octa-3,6-diene (**12**): a) In compliance with the general procedure, a suspension was prepared from **11** and the zinc-copper couple in $[D_8]$tetrahydrofuran. After thawing, the reaction was induced by ultrasonic irradiation of the colourless suspension and monitored by ^{1}H-NMR spectroscopy. After 40 min, the mixture had turned yellow and exhibited only the ^{1}H-NMR signals of **12**.

b) The zinc-copper couple (1.0 g) was added to a solution of **11** (602 mg, 1.0 mmol) in tetrahydrofuran (15 ml), and the suspension was heated to 60–65°C under ultrasonic irradiation for 1 h, while the reaction was monitored by HPLC. The mixture was filtered through a 7 × 2-cm pad of kieselgur which was eluted with tetrahydrofuran (20 ml). After the solution had been concentrated to a volume of 5 ml by evaporation of the solvent at 0°C/10^{-2} Torr, it was diluted with ether (15 ml). Extraction with water (5 ml), drying with sodium sulphate and concentration of the solution in a stream of Ar to a volume of 5 ml yielded a yellow solution exhibiting a single HPLC signal. Attempts to induce crystallization by the addition of pentane (10 ml) and cooling to -20°C failed because of partial decomposition as shown by the emergence of new HPLC signals.

1,5-Dimethyl-3,7-bis(phenylethynyl)tricyclo[3.3.0.$0^{2,8}$]octa-3,6-diene (**2c**): a) In compliance with the general procedure, a suspension was prepared from **10c** and the zinc-copper couple in $[D_8]$tetrahydrofuran. After thawing, the reaction was induced by ultrasonic irradiation of the pale yellow suspension. After 5 min, the mixture had turned orange and exhibited only the ^{1}H-NMR signals of **2c**.

b) The procedure b), as described for **12**, was applied except that the mixture was allowed to react for only 0.5 h at 60–65°C under ultrasonic irradiation. Workup yielded an orange solution which showed a single HPLC signal. As in the case of **12**, attempts to obtain crystals led to partial decomposition.

---

[1] The results are part of the Dissertation by J. Carlsen, Universität Würzburg, **1992**.

[2] R. Hoffmann, *Tetrahedron Lett.* **1970**, 2907–2909.

[3] H. Günther, *Tetrahedron Lett.* **1970**, 5173–5176.

[4] For an electron density model of substituent-ring interactions in substituted cyclopropanes and a review see D. Cremer, E. Kraka, *J. Am. Chem. Soc.* **1985**, *107*, 3811–3819.

[5] For a classification of substituted cyclopropanes on the basis of the MO theory see T. Clark, G. W. Spitznagel, R. Klose, P. von Ragué Schleyer, *J. Am. Chem. Soc.* **1984**, *106*, 4412–4419.

[6] J. F. Liebman, A. Greenberg (Eds.), *Molecular Structure and Energetics, vol. 3, Studies of Organic Molecules*, VCH Publishers, Deerfield Beach, Florida, USA, **1986**.

[7] H. Günther, H. Schmickler, *Pure Appl. Chem.* **1975**, *44*, 807–828; D. Cremer, B. Dick, *Angew. Chem.* **1982**, *94*, 877–878; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 865–867; C. Gatti, M. Barzaghi, M. Simonetta, *J. Am. Chem. Soc.* **1985**, *107*, 878–887; L. Frydman, B. Frydman, I. Kustanovich, S. Vega, E. Vogel, C. Yannoni, *ibid.* **1990**, *112*, 6472–6476.

[8] R. Hoffmann, W.-D. Stohrer, *J. Am. Chem. Soc.* **1971**, *93*, 6941–6948.

[9] M. J. S. Dewar, W. W. Schoeller, *J. Am. Chem. Soc.* **1971**, *93*, 1481–1482; M. J. S. Dewar, D. H. Lo, *ibid.* **1971**, *93*, 7201–7207; M. J. S. Dewar, Z. Náhlovská, B. D. Náhlovský, *J. Chem. Soc., Chem. Commun.* **1971**, 1377–1378; L. S. Miller, K. Grohmann, J. J. Dannenberg, *J. Am. Chem. Soc.* **1983**, *105*, 6862–6865; M. J. S. Dewar, C. Jie, *Tetrahedron*, **1988**, *44*, 1351–1358.

[10] M. D. Harmony, R. N. Nandi, J. V. Tietz, J.-I. Choe, S. J. Getty, S. W. Staley, *J. Am. Chem. Soc.* **1983**, *105*, 3947–3951; T. T. Tidwell in *The Chemistry of the Cyclopropyl Group* (Eds.: S. Patai, Z. Rappoport), Wiley, New York, **1987**, part 1, p. 565–632; J. F. Liebman, A. Greenberg, *ibid.* part 2, p. 1083–1119.

[11] K. Takeuchi, Y. Senzaki, K. Okamoto, *J. Chem. Soc., Chem. Commun.* **1984**, 111–112; K. Takeuchi, H. Fujimoto, T. Kitagawa, H. Fujii, K. Okamoto, *J. Chem. Soc., Perkin Trans. 2,* **1984**, 461–467.

[12] H. Quast, E. Geissler, A. Mayer, L. M. Jackman, K. L. Colson, *Tetrahedron* **1986**, *42*, 1805–1813.

[13] L. M. Jackman, G. Ibar, A. J. Freyer, Y. Görlach, H. Quast, *Chem. Ber.* **1984**, *117*, 1671–1678.

[14] H. Quast, J. Christ, E.-M. Peters, K. Peters, H. G. von Schnering, *Chem. Ber.* **1985**, *118*, 1154–1175.

[15] H. Quast, J. Christ, *Angew. Chem.* **1984**, *96*, 606–607; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 631–632.

[16] H. Quast, A. Witzel, E.-M. Peters, K. Peters, H. G. von Schnering, *Chem. Ber.* **1992**, *125*, 2613–2623.

[17] R. Askani, *Tetrahedron Lett.* **1971**, 447–450; R. Askani, R. Kirsten, B. Dugall, *Tetrahedron* **1981**, *37*, 4437–4444.

[18] D. Paske, R. Ringshandl, I. Sellner, H. Sichert, J. Sauer, *Angew. Chem.* **1980**, *92*, 464–465; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 456–457; H. Schuster, H. Sichert, J. Sauer, *Tetrahedron Lett.* **1983**, *24*, 1485–1488; C. Schnieders, K. Müllen, C. Braig, H. Schuster, J. Sauer, *ibid.* **1984**, *25*, 749–752.

[19] H. Quast, J. Carlsen, T. Herkert, R. Janiak, H. Röschert, E.-M. Peters, K. Peters, H. G. von Schnering, *Liebigs Ann. Chem.* **1992**, 495–511.

[20] H. Quast, J. Carlsen, H. Röschert, E.-M. Peters, K. Peters, H. G. von Schnering, *Chem. Ber.* **1992**, *125*, 2591–2611.

[21] A. Nickon, N. H. Werstiuk, *J. Am. Chem. Soc.* **1967**, *89*, 3914–3915; W. H. Saunders, Jr., A. F. Cockerill, *Mechanisms of Elimination Reactions*, 1st ed., Wiley, New York, **1973**, p. 566–586.

[22] H. Quast, A. Mayer, E.-M. Peters, K. Peters, H. G. von Schnering, *Chem. Ber.* **1989**, *122*, 1291–1306.

[23] H. Quast, R. Janiak, E.-M. Peters, K. Peters, H. G. von Schnering, *Chem. Ber.* **1992**, *125*, 969–973.

[24] H. Quast, Y. Görlach, E.-M. Peters, K. Peters, H. G. von Schnering, L. M. Jackman, G. Ibar, A. J. Freyer, *Chem. Ber.* **1986**, *119*, 1801–1835.

[25] For the influence of bromine atoms on the degenerate Cope rearrangement of semibullvalenes see also D. Moskau, R. Aydin, W. Leber, H. Günther, H. Quast, H.-D. Martin, K. Hassenrück, L. S. Miller, K. Grohmann, *Chem. Ber.* **1989**, *122*, 925–931.

[26] T. J. Mason, *Practical Sonochemistry*, 1st ed., E. Horwood, New York, **1991**.

[213/92]

CAS Registry Numbers

1b: 142747-24-8 / **1c**: 142747-25-9 / **2c**: 142747-27-1 / **6b**: 142747-13-5 / **6c**: 142747-14-6 / **7b**: 142747-17-9 / *exo,exo*-**7c**: 142747-18-0 / *endo,endo*-**7c**: 142747-19-1 / **8**: 142747-20-4 / C_2-**9b**: 142747-15-7 / C_S-**9b**: 142747-28-2 / C_2-**9c**: 142747-16-8 / C_S-**9c**: 142484-40-0 / **10b**: 142747-21-5 / **10c** (*c*-4,*c*-8-Br_2): 142747-23-7 / **10c** (*c*-4,?-Br_2): 142747-29-3 / **11**: 142747-22-6 / **12**: 142747-26-0