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THE SYNTHESIS OF OCTAVALENE (TRICYCLO[5.1.0.0^{2,8}]OCTA-3,5-DIENE) AND SEVERAL SUBSTITUTED OCTAVALENES

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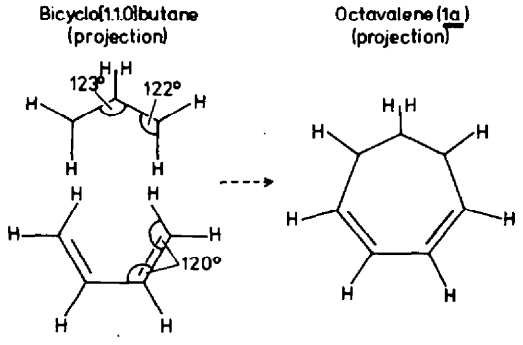
Abstract—The first synthesis of octavalene (**1a**) is reported. The starting material is homobenzvalene (**5**), to which monobromocarbene is added. The resulting compound **3a** takes up bromine across the central bicyclo[1.1.0]butane bond to form the tribromide **7a** which undergoes a cyclopropyl bromide–allyl bromide rearrangement on heating. From the product (**10a**) HBr is eliminated to give a 1,3-dibromocyclobutane with a 1,3-butadiene bridge across its 2- and 4-position (**11a**). Finally, t-butyllithium removes the two Br atoms from **11a** and converts it into a 4:1 mixture of **1a** and cyclooctatetraene. This reaction sequence represents the first application of protective group strategy in bicyclo[1.1.0]butane chemistry. Octavalene (**1a**) is shown to rearrange to cyclooctatetraene at 50°. Deuterium-labeled **1a** ([1,8-D_2] **1a**) is used to prove that a [1,5]-sigmatropic shift does not occur in **1a**. Utilizing the above methodology 4-bromooctavalene (**1b**) and 3-phenyl-5-bromooctavalene (**1c**) are synthesized from the dibromocarbene adducts **3b** and c of homobenzvalene (**5**) and 5-phenylhomobenzvalene (**6**), respectively. Surprisingly, **1c** was accompanied by a small quantity of 3-bromo-1-phenyloctavalene (**1d**). Possible mechanisms for the addition of bromine to the bicyclo[1.1.0]butane system of compounds **3** and for the formation of the octavalenes **1** are discussed. In the ^{13}C-NMR spectra of **1** and **11** chemical shifts at unexpectedly high field are observed for C-6 of the 1,3-cycloheptadiene moieties.

The unique properties of the $(CH)_8$ hydrocarbons[1a] have attracted the attention of many organic chemists. As a member of this family octavalene (**1a**) is of special interest, since a series of symmetry allowed [1,5]-sigmatropic shifts would make all the eight CH units equivalent.[1b,2a] Thus, **1a** could be the bullvalene analogue of the $(CH)_8$ series.

1a

Another important feature of **1a** is revealed by the molecular model. The angle between the two 3-membered rings of bicyclo[1.1.0]butane and that between one ring and the *endo*-CH bond have been determined to be 123° and 122°, respectively.[3] As shown in the projections below, these angles, as well as the bond angles of 1,3-butadiene have to be widened, when these units are formally tied together to give **1a**. The sum of the angles in the 7-membered ring in the projection of **1a** amounts to 900°, whereas the relevant angles of the fragments only total 847°. Thus, the strain



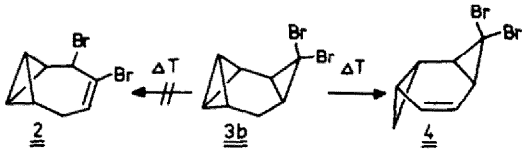
energy of **1a** should be larger than that expected based on those of bicyclo[1.1.0]butane (67.0 kcal mol^{-1})[4] and 1,3-cycloheptadiene (6.6 kcal mol^{-1}).[4] In addition, theoretical calculations[5] indicate, in agreement with experimental data,[5c,6] that the central bond of the bicyclo[1.1.0]butane system is lengthened, and hence weakened if the flap angle increases. Furthermore, an electronic interaction between the π system and the strained σ system should persist in **1a**. An interaction of this type causes the high reactivity and unusual spectroscopic properties of benzvalene.[7] The combination of steric and electronic effects leads one to anticipate that **1a** should exhibit interesting behaviour.

Previous attempts to synthesize octavalene

Attracted by such prospects, several research groups have undertaken to synthesize **1a**, unfortunately without success. These are reviewed briefly here. When 8,8-dibromobicyclo[5.1.0]octa-2,4-diene was treated with methyllithium the expected cyclopropylidene did not insert into the 6-*syn* C—H bond to give **1a** but rearranged to a mixture of dihydropentalenes.[2b,8] The tricarbonyliron complex of 8,8-dibromo[5.1.0]octa-2,4-diene could not be transformed into the tricarbonyliron complex of **1a**.[2] In analogy to the preparation of benzvalene via cyclopentadienylcarbene,[9] the intramolecular [2+1]- or [6+1]cycloaddition of cycloheptatrienylcarbene to form **1a** has been tried. However, the reactions of cycloheptatrienyldiazomethane proceeding with loss of nitrogen furnished cyclooctatetraene, heptafulvene, and benzene.[10] The disrotatory opening of the cyclobutene portion in tetracyclo[4.2.0.0^{2,4}.0^{3,5}]oct-7-ene, a valence isomer of **1a**, could not be achieved without rearrangement of the bicyclo[1.1.0]butane system.[11]

A straightforward strategy to construct the carbon skeleton of **1a** would be thermal ring enlargement of the dibromocarbene adduct **3b** of homobenzvalene to give

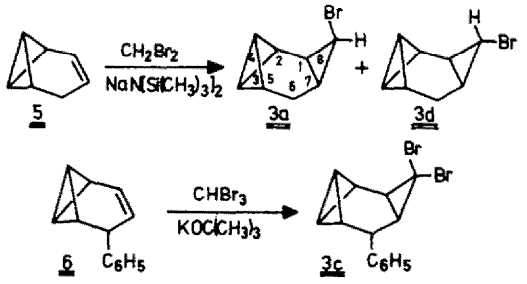
2. Model reactions, where the same ring size is involved, are the rearrangements of the dibromocarbene adducts of cyclohexene[12a] and bicyclo[3.2.1]oct-2-ene.[12b] However, all efforts inevitably led to the formation of dibromo-*trans*-bishomobenzene **4**.[13] Methyl substituents in different positions of **3b** did not alter the course of the reaction.[13a]



Protective group strategy

The thermally induced ring enlargement **3b** → **2** fails because traces of hydrogen bromide cannot be avoided if a bromohydrocarbon such as **3b** is heated. Similar to other bicyclo[1.1.0]butane derivatives,[14] **3b** is extremely sensitive to acid[13b] and therefore, undergoes the tricyclo[4.1.0.0^{2,7}]heptane–2-norcarene rearrangement[14a] to give **4** under the different conditions tried. Addition of base offers no remedy, since the traces of hydrogen bromide are either transformed to a weaker but still active acid[13a] or the base is not compatible with the dibromocyclopropane functionality.

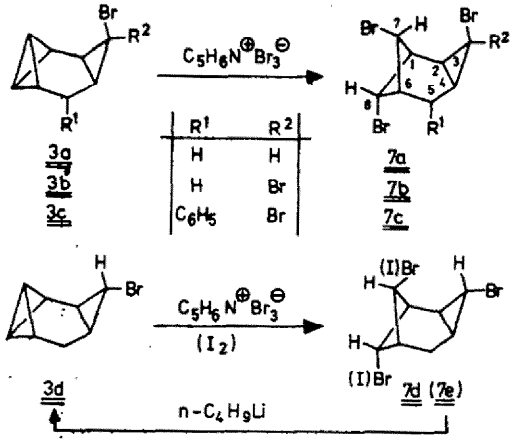
Preliminary experiments revealed that the monobromo compounds **3a,d**, which were prepared as a 1 : 1 mixture in 48% yield from homobenzvalene (**5**)[15] and monobromocarbene using the method of Martel and Hiriart,[16] behave analogously to **3b** on heating. This was also expected for the phenyl derivative **3c** obtained in 42% yield from 5-phenylhomobenzvalene (**6**)[15b] and



dibromocarbene. (The relative configuration at C-6 of **3c** is derived from the small interproton coupling $J_{6,7}$ = 0.8 Hz.) As bicyclo[1.1.0]butanes do not survive the conditions necessary to effect the desired cyclopropyl bromide–allyl bromide rearrangement, we looked for a reaction by means of which the bicyclo[1.1.0]butane system could be protected. The addition of bromine or iodine to the central bond of bicyclo[1.1.0]butane and some of its derivatives[17] and the formation of the bicyclo[1.1.0]butane moiety from 1,3-dihalocyclobutanes[17a–c,e,f,18] are well-known reactions. We have been able to use this bond breaking–bond reformation as a protection scheme.

In an earlier communication,[19] we reported its use for the first synthesis of octavalene (**1a**) starting from **3a**. This paper describes the details of this work as well as the preparation of 4-bromooctavalene (**1b**), 5-bromo-3-phenyloctavalene (**1c**), and 3-bromo-1-phenyloctavalene (**1d**).

Addition of bromine across the central bicyclo[1.1.0]butane bond of **3a–d**. Reaction of **3b** with elemental bromine as well as with iodine gave only intractable material. In contrast, the utilization of pyridine hydrobromide perbromide provided the desired adduct **7b** in 57% yield, and analogously, **3c** was converted to **7c** (36%). Similarly, the 1 : 1 mixture of **3a,d** led to the formation of **7a** and **d** in the ratio of 2 : 1. Crystallization of the mixture afforded the pure isomers **7a** and **d** in 52 and 18% yield, respectively. By treating the mixture of **3a,d** with iodine only **7e** (22%) was obtained, which obviously has its origin in **3d**. However, an addition product to **3a** was not found. n-Butyllithium converted **7e** back into **3d** (see the paragraph on the reconstruction of the central bicyclo[1.1.0]butane bond for this type of reaction).



The ^{1}H-NMR parameters of **7** are collected in Table 1. They contain the information necessary to determine the configuration of the carbon atoms carrying the newly introduced halogen atoms. In the spectra of **7a–c** a singlet (7-H) and a triplet (8-H, $J_{1,8} = J_{6,8}$ = 5.0–5.6 Hz) uniformly appear, while in those of **7d,e** 7-H also gives rise to a triplet (5.9, 4.5 Hz) or even a triple triplet. These splitting patterns caused by vicinal coupling indicate the stereochemistry in norpinane derivatives.[20] Since in the spectra of **7a–c** coupling constants between 7-H and 8-H on the one hand and 2-H through 5-H on the other are not resolved, the arrangement of C-7 and C-8 relative to C-3 has not been proved but seems plausible as shown on the basis of the most probable reaction course.

Although mechanistic investigations have not been carried out, the structures of **7** appear to support a radical pathway for the above halogen additions. Usually in addition reactions to bicyclo[1.1.0]butanes cyclopropylcarbinyl derivatives are formed, at least in part, if ionic intermediates are involved.[7a,14] On the contrary, cyclobutyl compounds are considered to be the result of radical chain reactions, for example the products of the addition of mercaptanes and disulfides,[21] and other similar cases.[22] Taking the orientation of the thiophenol addition to 1-substituted bicyclo[1.1.0]butanes[21] and annellated tricyclo[3.1.0.0^{2,6}]hexanes[23] as models, we assume that a halogen atom is added to the C-3—C-4 bond of **3** from the sterically less hindered side, i.e. to C-3, with inversion of its configuration. Because of the *trans* orientation of the dibromocyclopropane and phenyl

Table 1(a). ^{1}H-NMR parameters of tricyclo[4.1.1.0^{2,4}]octane, bicyclo[4.1.1]oct-3-ene, and bicyclo[4.1.1]octa-2,4-diene derivatives in $CDCl_3$. Chemical shifts (δ values) and multiplicities.

Compd	1-H	2-H	3-H	4-H	5-H$_{endo}$	5-H$_{exo}$	6-H	7-H	8-H
7a	q 3.20	ddd 1.62	t 3.52	qd 1.48	dt 2.19	ddd 2.50	qd 2.70	s 5.45	t 5.34
7b	q 3.30	dd 2.24	-	td 2.07	dt 2.17	ddd 2.50	qd 2.69	s 5.32	t 5.32
7c[a]	qd 3.37	dd 2.39	-	ddd 2.35	br.d 3.48	-	td 3.24	s 5.21	t 5.41
7d	dq 3.20	dddd 1.74	t 4.86	dddd 1.52	m 2.27	- 2.38	m 2.71	tt 4.22	t 4.19
7e	qui 3.01	b	t 4.95	b	m 2.17	- 2.37	m 2.60	br.t 4.47	t 4.43
10a	ddt 3.44	tq 4.83	ddq 5.84	dm 5.57	dtt 2.65[c]	dtt 2.38[c]	dqt 3.11	br.s 4.43	br.t 5.25
10b	dtd 3.48	br.d 4.80	-	ddt 6.19	dtd 2.61[c]	dddd 2.33[c]	dqt 3.10	q 4.43	br.t 5.23
10c[d]	m 3.44[e]	ddd 4.99	-	ddd 6.58	q 4.03	-	m 3.44[e]	q 4.53	td 5.19
11a	m 3.44	m 5.80	m 6.09	m 6.09	5-H: m 5.80		m 3.44	q 4.38	tq 5.33
11b	dddt 3.39	ddq 6.24	-	ddd 6.29	ddq 5.75		dddq 3.46	q 4.36	tq 5.32
11c[f]	br.t 3.91	-	t 6.46	-	dd 6.29		dddd 3.41	q 4.55	br.t 5.43

[a] C_6H_5: 7.25 (m; p-H), 7.36 (m; m-H), 7.43 (m; o-H). [b] m 1.35 - 1.83. [c] These assignments may be exchanged. [d] C_6H_5: 7.23 - 7.40 (m). [e] In C_6D_6 two signals appeared: 2.79 (dtd; 1-H) and 2.88 (m; 6-H). [f] Due to the systematic name the phenyl group is on C-2 in contrast to 10c, where it is on C-5. C_6H_5: 7.29 - 7.38 (m).

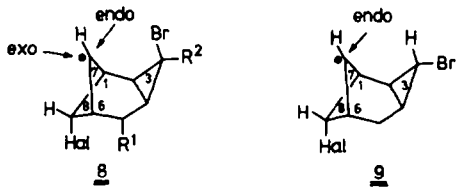
groups in 3c the attack at C-3 is also impeded. Fortunately, the reaction takes place in spite of the additional hindrance, but the yield of 7c is considerably diminished (36%) in comparison to that of 7b (57%).

Attack of the first halogen atom as discussed should generate the cyclobutyl radicals 8 and 9 from 3a–c and d, respectively. These intermediates may accept the second halogen atom in principle from both sides. In 8, however, the *endo*-bromine on the cyclopropane ring interferes, thus allowing only the formation of 7a–c with

Table 1(b). ^{1}H-NMR parameters of tricyclo[4.1.1.0^{2,4}]octane, bicyclo[4.1.1]oct-3-ene, and bicyclo[4.1.1]octa-2,4-diene derivatives in $CDCl_3$. Coupling constants (absolute values in Hz)

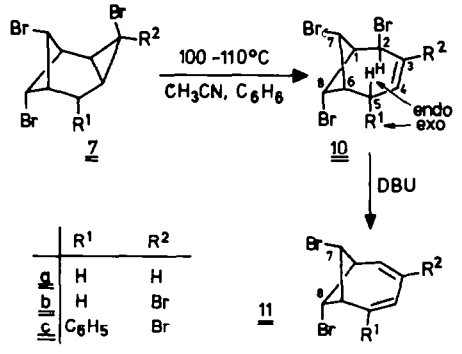
Compd	$J_{1,2}$	$J_{1,6}$	$J_{1,7}$	$J_{1,8}$	$J_{2,3}$	$J_{2,4}$	$J_{3,4}$	$J_{4,5endo}$	$J_{4,5exo}$	$J_{5,5}$	$J_{5endo,6}$	$J_{5exo,6}$	$J_{6,7}$	$J_{6,8}$	$J_{7,8}$
7a	6.0	5.7	a	5.1	8.1	9.0	8.1	1.5	9.0	15.0	2.0	4.5	a	5.1	a
7b	5.6	5.6	a	5.6	-	10.5	-	1.8	9.5	15.3	1.8	4.8	a	5.6	a
7c[b]	5.0	5.5	a	5.0	-	10.5	-	2.5	-	-	1.0	-	a	5.0	a
7d[c]	4.8	4.8	5.9	4.8	3.0	9.9	3.0	d	d	d	d	d	5.9	4.8	a
7e	4.8	4.8	4.5	5.4	3.0	d	3.0	d	d	d	d	d	4.5	5.4	a
10a[e]	4.0	4.5	1.0	7.8	4.0	2.0	12.3	3.6[f]	4.2[f]	19.7	3.6[f]	4.2[f]	1.0	7.8	0.7
10b[g]	4.8	4.8	1.3	7.8	-	9.8	-	4.0[f]	4.8[f]	19.5	4.0	4.0	1.0	7.8	0.7
10c[h]	5.2	5.0	1.1	7.8	-	0.6	-	3.0	-	-	2.4	-	1.1	7.8	0.7
11a[i]	d	d	0.6	7.1	d	d	d	$J_{4,5}$ =	d		$J_{5,6}$ =	d	0.6	7.1	0.6
11b[j]	9.4	5.4	0.6	7.0	-	1.8	-		11.7			9.0	0.6	7.0	0.6
11c[k]	-	5.0	0.6	7.2	-	-	-		-			9.4	0.6	7.2	0.6

[a] Not resolved. [b] $J_{1,4}$ = 0.8 Hz. [c] $J_{2,7}$ = $J_{5exo,7}$ = 0.9 Hz. [d] Not determined. [e] $J_{1,3}$ = $J_{2,5endo}$ = $J_{2,5exo}$ = $J_{3,5endo}$ = $J_{3,5exo}$ = 2.0, $J_{4,6}$ = 1.4 Hz. [f] These values may be exchanged. [g] $J_{2,5endo}$ = 2.0 or 1.4, $J_{2,5exo}$ = 1.4 or 2.0 Hz. [h] $J_{2,5}$ = 1.9, $J_{4,6}$ = 1.4 Hz. [i] $J_{2,8}$ = $J_{5,8}$ = 0.6 Hz. [j] $J_{1,5}$ = $J_{2,5}$ = $J_{2,6}$ = $J_{2,8}$ = $J_{4,6}$ = $J_{5,8}$ = 0.6 Hz. [k] $J_{1,3}$ = $J_{3,5}$ = 1.5 Hz.



an *exo*-bromine at C-7. Since we could not obtain iodine adducts of **3a,b**, it seems reasonable that in these cases the steric crowding becomes prohibitive even at the *exo*-face of C-7. With respect to the cyclobutane ring of **8** the hydrogen atom at C-8 occupies a *syn*-axial position relative to an *exo*-approaching reagent and thus may place too high a barrier for iodine, but not for the smaller bromine. Because of the presence of a hydrogen atom at the *endo*-side (C-3) the cyclopropane ring in **9** demands less space. Therefore, the approach of bromine as well as iodine from the *endo*-face of C-7, giving rise to **7d,e**, is feasible. The *exo* side of C-7 cannot compete probably due to the steric hindrance of 8-H. The formation of **7d,e** is in accord with the known stereochemical course of the iodination of tricyclo-[4.1.0.0^{2,7}]heptane[17e] and a tricyclo[3.1.0.0^{2,6}]hexane derivative.[17f]

The butadiene - bridged trans - 1,3 - *dibromocyclobutanes* **11a–c**. With **7a–c** in hand the next step towards the octavalene skeleton was the cyclopropyl bromide–allyl bromide rearrangement. This ring opening proceeds under mild conditions in the bicyclo[3.1.0]hexane series, and the mechanism has been investigated thoroughly.[15a,24] Drastically elevated temperatures are necessary to effect the ring enlargement in norcarane derivatives,[12,24] to which **7** belongs. Since the rate determining step generates a bromide ion and an allyl cation, use of polar solvents is preferred. Accordingly, we observed the formation of **10a–c** from **7a–c** at 100–110° in mixtures of acetonitrile and benzene, the latter being unavoidable for reasons of solubility. The isolated yields were 82, 81 and 31% for **10a–c**, respectively. The tribromide **7a** rearranged about ten times as fast as the tetrabromides **7b,c**



providing evidence for allyl cation intermediates. Those formed from **7b,c** are destabilized by the inductive effect of the additional bromine substituent, and therefore, should be generated more slowly than the intermediate derived from **7a**. That an *endo*-bromine at C-3 of **7** is mandatory for the ring enlargement follows from the behaviour of **7d**. It was shown to be stable up to 150° and decomposed to tar at 170°.

The structures of compounds **10** are supported by the ^{1}H-NMR spectra (Tables 1(a) and (b)). In particular, the coupling constants between 5-H and the proton of the bromine-bearing allylic carbon (1.4–2.0 Hz) prove that these are homoallylic and not vicinal. Consequently, the double bond must be located between C-3 and C-4 and not between C-2 and C-3. As in **7**, the *exo,syn*-orientation of the bromines at the cyclobutane moiety is indicated by the characteristic difference between the vicinal coupling interactions of 8-H (7.8 Hz) and 7-H (*ca* 1 Hz). Decoupling experiments were used to determine the origin (1-, 6-, 8-H) of the narrow splitting of the 7-H absorption. The spectra gave no information regarding the configuration of C-2. In the 6,6-dichlorobicyclo[3.1.0]hexane series it has been shown that the leaving chloride ion is recaptured by the allyl cation on the same face of the ring, and that a slow interconversion of product stereoisomers may occur.[25] On the basis of these results kinetic as well as thermodynamic control strongly favour the configuration given in formula **10** with the 2-Br on the less congested *endo* side.

To complete the butadiene bridge across the *trans*-1,3-dibromocyclobutane unit a 1,4-elimination of HBr from **10** was required. This was achieved by the treatment of **10** with the 1,8-diazabicyclo[5.4.0]undec-7-ene(DBU)[26] in benzene affording **11a–c** in 74, 95 and 65% yield, respectively.

In the ^{13}C-NMR spectra of **11** (Table 2) the big difference (15.1, 17.5 ppm) between the chemical shifts of C-7 and C-8 is striking. The signals of these carbons were distinguished from the C-1, C-6 absorptions by means of the magnitude of the one-bond ^{13}C—H coupling constants, which are larger for C-7, C-8 (164–177 Hz) than for C-1, C-6 (151, 153 Hz) because of the electronegative bromines. As revealed by a comparison with the chemical shifts of **7** and **10**, one of the signals arising from C-7 and C-8 has moved upfield by 13–18 ppm as a consequence of the completion of the butadiene bridge, while the other absorption is changed only by a few ppm. Unusual highfield absorptions of this type seem to be characteristic of rigid 1,3-cycloheptadiene derivatives such as **11** and the octavalenes **1** (see below).

The specific assignment of the C-7, C-8 signals has been made tentatively on the basis of long-range CH coupling constants under the reasonable assumption that the interactions transmitted by three bonds are the largest ones.[27] In the spectrum of **11a**, the absorption at δ 26.78 shows a 13 Hz doublet, which establishes the assignment to C-8, since only 7-H qualifies as a coupling nucleus with its antiperiplanar arrangement relative to C-8. Based on the Karplus equation the coupling constant $J_{C\text{-}7,8\text{-}H}$ should be smaller because of the synclinal relationship between these nuclei. In fact, the signal at δ 44.31 shows no splitting and consequently it is assigned to C-7. Using the rules governing long-range CH couplings[27] we have also tried to distinguish between the two resonances of the olefinic carbons and to assign specifically the signals of **11b** as given in Table 2.

We note that we are not the first to synthesize the bicyclo[4.1.1]octa-2,4-diene system via compounds of type **7**. The 3-bromo-2,7,7-trimethyl derivative has been prepared by the reaction of dibromocarbene with α-pinene followed by thermolysis of the resulting adduct.[28] Other approaches to this class of compounds are also known.[29]

Table 2. ^{13}C-NMR chemical shifts (δ values), multiplicities, and one-bond ^{13}C—H coupling constants (in Hz) of tricyclo[4.1.1.0^{2,4}]octane, bicyclo[4.1.1]oct-3-ene, and bicyclo[4.1.1]octa-2,4-diene derivatives in $CDCl_3$. Footnotes to coupling constants give couplings caused by remote protons

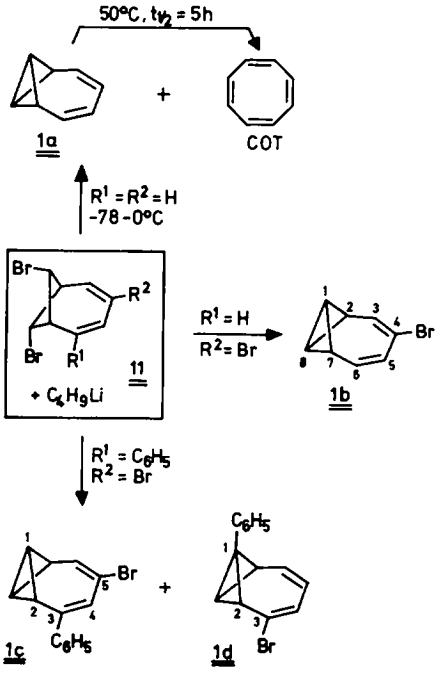
Compd	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
7a	48.63[a] d 157	22.97 d 167	34.96 d 185	10.95 d 169	25.79 t 133	48.01[a] d 154	52.11[b] d 168	46.26[b] d 171
7b	48.31[a] d	36.81 d	38.17 s	25.47 d	27.16 t	47.89[a] d	50.77[b] d	44.54[b] d
7c[c]	48.42[a] d	36.80 d	37.78 s	31.89 d	45.53 d	48.60[a] d	52.90[b] d	45.32[b] d
7d	47.28 d 153	27.69 d 170	23.30 d 195	16.49 d 170	23.30 t 130	43.58 d 155	44.83[a] d 160	41.74[a] d 160
10a	57.59 d 152	51.12 d 164	126.13 d 156	128.00 d 160	31.17 t 128	49.85 d 156	45.05[a] d 169	43.93[a] d 161
10b	57.53[a] d	56.82[a] d	121.56 s	131.99 d	33.04 t	49.41 d	44.15[b] d	43.14[b] d
10c[d]	57.53[a] d	57.36[a] d	122.91 s	134.55 d	49.85 d	55.57[a] d	45.50[b] d	40.34[b] d
11a	52.59 d 151	129.33 d 165	127.18[e] d 160[e]	127.18[e] d 160[e]	129.33 d 165	52.59 d 151	44.31 d 177	26.78[f] d 164[f]
11b	52.76[g] d 151[g]	130.01[h] d 170[h]	120.69[i] s	132.67[j] d 165[j]	130.76[k] d 165[k]	52.01[l] d 153[l]	42.13 d 176	27.03[m] d 166[m]
11c[n]	57.32 d	n	n	120.87 s	n	52.92 d	42.73 d	27.63 d

[a,b] These assignments may be exchanged. [c] C_6H_5: 126.88 (d; p-C); 128.09 (d), 128.45 (d)(o-, m-C); 141.48 (s; ipso-C). [d] C_6H_5: 127.24 (d; p-C); 128.34 (d), 129.24 (d) (o-, m-C); 138.72 (s; ipso-C). [e] t, $J_1 = J_5 = 11$ Hz. [f] d, $J_7 = 13$ Hz. [g] d, $J_6 = 6$ Hz. [h] t, $J_4 = J_8 = 5$ Hz. [i] Quintet, $J_1 = J_2 = J_4 = J_5 = 9$ Hz. [j] t, $J_2 = J_6 = 8$ Hz. [k] d, $J_8 = 5$ Hz. [l] t, $J_1 = J_4 = 7$ Hz. [m] d, $J_7 = 13$ Hz. [n] Due to the systematic name the phenyl group of 11c is on C-2 in contrast to 10c, where it is on C-5. C-2, C-3, C-5, C_6H_5: 125.91 (d), 128.66 (d)(o, m-C); 128.48 (d), 129.58 (d), 129.70 (d)(C-3, C-5, p-C); 141.67 (s), 143.30 (s)(C-2, ipso-C).

Reconstruction of the central bicyclo[1.1.0]*butane bond and some properties of the octavalenes* **1a** *and* **b**. 1,3-Dihalocyclobutanes have been converted into bicyclo[1.1.0]butanes by means of different reagents.[17,18] However, application of these methods to **11b** did not succeed. Lithium aluminium hydride[17b,c] for example did not react with **11b**, whereas metallic sodium[17a,18] or Na–K alloy led to extensive decomposition. MeLi in ether or n-BuLi in hexane did not affect **11b**, but by using n-BuLi in ether at −78° and then warming up to 0° we obtained a 45% yield of 4-bromooctavalene (**1b**). No isomers of **1b** were found. In contrast, treatment of **11a** with n-BuLi under these conditions gave rise to a mixture (3 : 1) of unsubstituted octavalene (**1a**) and cyclooctatetraene (COT). Compound **11c** behaved differently and afforded a 5 : 1 mixture of the two octavalene derivatives **1c** and **d** in 42% yield. Bromooctavalene **1b** was purified by distillation, whereas the purification, of **1a**,**c**,**d** under a variety of different conditions failed. Attempted separation of **1a** from COT by preparative VPC led to rearrangement to COT; **1c**,**d** decomposed when submitted to distillation or chromatography. It was not even possible to get rid of n-BuBr, the coproduct in the case of **1a**, because an effective distillation was not feasible with the small quantities available. However, utilization of t-BuLi instead of n-BuLi circumvented this problem. The coproduct t-BuBr either codistilled with ether used as solvent or it lost HBr under the influence of t-BuLi. Another advantage of this reagent was the more favourable ratio (4 : 1) of the mixture of **1a** and COT and an improved yield of 50%.

In contrast to the parent hydrocarbon 4-bromooctavalene (**1b**) turned out to be sensitive to air. Probably a polymeric peroxide is formed by radical addition of oxygen. Calculations[5] suggest that this could be due to the weakness of the central bicyclo[1.1.0]butane bond as a consequence of the large flap angle.

Proof for the structure of the octavalenes (1) was provided by the NMR data, which are summarized in Tables 3 and 4. According to the C_{2v} symmetry of **1a** its ^{1}H- and ^{13}C-NMR spectra consist of four signals each. In $CDCl_3$ 1,8-H absorb as a triplet at δ 1.27 showing



$J_{1,2}$ = 3.0 Hz. Other coupling constants could not be measured directly, since 2,7-H (δ 2.97), 3,6-H (6.13), and 4,5-H (5.72) constitute an AA'MM'XX' system. However, from the spectra of the substituted compounds **1b–d** all the coupling constants of the octavalene skeleton have been obtained on a first-order basis except $J_{1,8}$, which was determined to be 9.0 Hz by observing the ^{13}C satellites of the 1,8-H resonance. The interactions $J_{1,2}$, $J_{1,8}$, and $J_{2,7}$ have the characteristic magnitude for bicyclo[1.1.0]butane derivatives; cf. the corresponding parameters of unsubstituted bicyclo[1.1.0]butane[30] and homobenzvalene.[15a] In the spectrum of **1d** the integral of the triplet (J = 3.3 Hz) at δ 1.90 indicates only one proton (8-H), thus establishing that C-1 carries a substituent. Further, the position of the second substituent in **1d**, the position of the bromine in **1b**, and the arrangements of the substituents in **1c** follow unambiguously from the multiplicities of the signals and the magnitude of the coupling constants.

In the ^{13}C-NMR spectra of **1a–c** the absorptions at δ −13.41, −11.72, and −10.39, respectively, represent the most upfield chemical shifts of all bicyclo[1.1.0]butane derivatives to date.[31a] The corresponding one-bond ^{13}C—H coupling constants in **1a** (207 Hz) and **1b,c** (213 Hz) are characteristic of carbons located at the central bond of the bicyclo[1.1.0]butane system.[30] The comparison of these chemical shifts with those of benzvalene (δ 48.3)[31b] and benzobenzvalene (δ 42.4)[31a] is of special interest. In order to rationalize these values we have proposed an orbital interaction model,[31] which also accommodates the big difference with respect to the chemical shift of octavalene (**1a**). The values of the carbons at the central bond of the bicyclo[1.1.0]butane system in the Diels–Alder adduct of **1a** and 4-phenyl-4H-1,2,4-triazole-3,5-dione (δ 20.2, 11.5)[32] illustrate that the high-field absorptions of C-1, C-8 in **1** are not simply a consequence of the 4-membered bridge spanning the bicyclo[1.1.0]butane

Table 3. ^1H-NMR chemical shifts (δ values), multiplicities, and coupling constants of octavalenes

Compd	Solvent	1-,8-H	2-H	3-H	4-H	5-H	6-H	7-H
1a[a]	$CDCl_3$[b]	1.27 t	2.97 m	6.13 m	5.72 m	5.72 m	6.13 m	2.97 m
	C_6D_6[c]	0.96	2.68	6.11	5.79	5.79	6.11	2.68
1b[d]	$CDCl_3$[b]	1.38 t	2.82 dq	6.48 ddd	-	5.84 ddd	6.00 ddd	2.90 dqd
	C_6D_6[c]	0.88	2.31	6.44	-	6.01	5.74	2.41
1c[e,f]	$CDCl_3$[b]	1.56 t	3.44 qd	-	6.14 t	-	6.54 dd	2.96 dq
1d[g,f]	$CDCl_3$[b]	1.90 t	3.92 td	-	6.33 ddd	5.57 ddd	6.24 ddd	3.56 dtd

[a] $J_{1,2}$ = 3.0 Hz; the AA'MM'XX' spectrum of 2-H through 7-H has not been analyzed. [b] Determined relative to internal tetramethylsilane. [c] Determined relative to C_6D_5H taken to absorb at 7.26. [d] $J_{1,2} = J_{1,7} = J_{2,7}$ = 3.0, $J_{2,3}$ = 7.0, $J_{3,5}$ = 2.4, $J_{3,6}$ = 0.6, $J_{5,6}$ = 12.0, $J_{5,7}$ = 1.1, $J_{6,7}$ = 6.6 Hz. [e] $J_{1,2} = J_{1,7} = J_{2,7}$ = 3.1, $J_{2,4}$ = 1.8, $J_{4,6}$ = 2.2, $J_{6,7}$ = 7.0 Hz. [f] C_6H_5: 7.25 - 7.45 (m). [g] $J_{2,7} = J_{2,8} = J_{7,8}$ = 3.3, $J_{2,4}$ = 2.2, $J_{4,5}$ = 7.8, $J_{4,6}$ = 0.8, $J_{5,6}$ = 11.5, $J_{5,7}$ = 0.8, $J_{6,7}$ = 6.5 Hz.

Table 4. ^{13}C-NMR chemical shifts (δ values), multiplicities, and one-bond ^{13}C—H coupling constants (in Hz) of octavalenes. Footnotes to coupling constants give couplings caused by remote protons

Compd	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
1a[a]	-13.41 d 207	45.26 d 147	137.59[b] d 155[b]	124.46[c] d 155[c]	124.46[c] d 155[c]	137.59[b] d 155[b]	45.26 d 147	-13.41 d 207
1b[d]	-11.72[e] d 213[e]	44.82[f] d 153[f]	138.45[g] d 159[g]	115.86[h] s[h]	129.25[i] d 163[i]	137.87 d 155	44.22[j] d 151[j]	-11.72[e] d 213[e]
1c[d,k]	-10.39[l] d 213[l]	49.61[m] d 151[m]	149.79 s	126.74[n] d 161[n]	115.63[o] s[o]	137.47[p] d 161[p]	45.34[q] d 153[q]	-10.39[l] d 213[l]
1d[d,r]	4.50[s] s[s]	55.00[s] d 158[s]	r	r	122.17[t] d 160[t]	135.79[s] d 157[s]	44.83[s] d 155[s]	4.00[s] d 211[s]

[a]Solvent C_6D_6. [b]d, J_5 = 9 Hz. [c]dd, J_6 = 12, J_2 = 7 Hz. [d]Solvent $CDCl_3$. [e]Sext., $J_2 = J_3 = J_6 = J_7 = J_8$ = 4 Hz. [f]dq, J_7 = 15, $J_1 = J_3 = J_8$ = 5 Hz. [g]d, J_5 = 7 Hz. [h]Quint., $J_2 = J_3 = J_5 = J_6$ = 10 Hz. [i]t, $J_3 = J_7$ = 8 Hz. [j]tq, $J_2 = J_5$ = 12, $J_1 = J_6 = J_8$ = 5 Hz. [k]C_6H_5: 126.23 (d, 158 Hz; t, $J_{p} = J_{o'}$ = 6 Hz; o-C), 127.63 (d, 161 Hz; t, $J_{o} = J_{o'}$ = 7 Hz; p-C), 128.32 (d, 159 Hz; d, J_{m} = 7 Hz; m-C), 143.16 (s; qd, $J_{m} = J_{m'}$, J_4 = 6, J_2 = 3 Hz; ipso-C). [l]Quint., $J_2 = J_6 = J_7 = J_8$ = 4 Hz. [m]ddt, J_7 = 14, J_4 = 10, $J_1 = J_8$ = 5 Hz. [n]dd, J_6 = 9, J_2 = 6 Hz. [o]ddd, J_7 = 12, J_4 and J_6 = 4 and 8 Hz. [p]d, J_4 = 7 Hz. [q]dq, J_2 = 14, $J_1 = J_6 = J_8$ = 5 Hz. [r]C_6H_5: 126.10 (d, 158 Hz; t; $J_{p} = J_{o'}$ = 6 Hz; o-C), 128.39 (d, 159 Hz; d, J_{m} = 7 Hz; m-C). The signals of C-3, C-4, ipso-C, and p-C are either superimposed by absorptions of 1c or have not been found because of low intensity. [s]Additional splitting not determined. [t]d, J_7 = 7 Hz.

system. Rather, a special high-field effect of the rigid 1,3-cycloheptadiene moiety fixed in the envelope conformation appears to be operative, as reported previously[33] (see also the ^{13}C-NMR spectra of **11**).

The evidence for the arrangement of the phenyl group and the bromine atom shown in the formula of **1d** is derived from the ^{13}C-NMR data for 1-bromo-[34a] and 1-phenyltricyclo[4.1.0.0^{2,7}]heptane[34b] with respect to the parent hydrocarbon.[34c] Although there the substituents exert similar α effects (Br, 17.5 ppm; C_6H_5, 17.0 ppm), their β effects on the other carbon at the central bond (C-7) (Br, 8.1 ppm; C_6H_5, 15.9 ppm) and on the lateral bicyclo[1.1.0]butane carbons (Br, 7.3 ppm; C_6H_5, 1.4 ppm) are very different. Provided that these substituent effects can be applied to octavalene (**1a**), the compound formed along with **1c** should have structure **1d** and not its isomer with exchanged substituents.

In the ^{13}C-NMR spectra of **1a–d** only a few signals can be assigned specifically on the basis of chemical shifts and one-bond coupling constants. For example, the distinction between the C-3 and C-4 resonances of **1a** is uncertain. Similarly, in the case of **1b**, the assignments of C-2 and C-7 as well as of C-3, C-5, and C-6 are not unambiguous. Again, as in the bicyclo[4.1.1]octa-2,4-diene series above, reference is made to the diagnostic value of long-range CH coupling constants.[27] Since the analysis has been carried out only on a first-order basis, misinterpretations are possible. However, the data in Table 4 present a self-consistent pattern.

The mass spectrum of the mixture of **1a** and COT resembles that of pure COT[35] with the exception of two additional lines appearing at *m/e* 91 and 92 with an intensity of 15 and 12%, respectively, relative to the base peak at *m/e* 104. This indicates clearly a different fragmentation mode of **1a** as compared to COT in accordance with the structure of **1a**, which suggests a rather easy extrusion of one CH group on electron impact to generate the favourable tropylium ion.

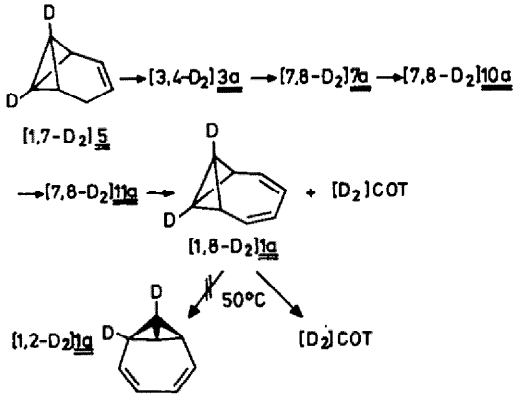
Unambiguous support for the structure of **1a** was provided by reaction of **1a** with 4-phenyl-4H-1,2,4-triazole-3,5-dione furnishing the Diels–Alder adduct, which has been subjected to X-ray structure analysis. The results of which have already been published.[32]

Questions regarding the automerization of octavalene (**1a**) *and the formation of rearranged octavalene* **1d**

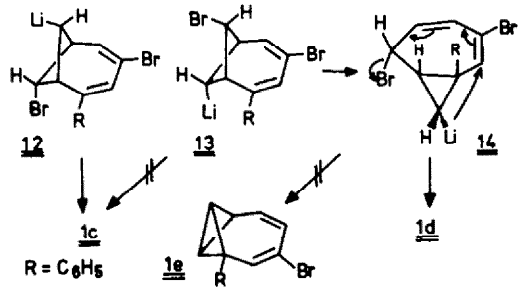
The possibility that **1a** could undergo a degenerate rearrangement was certainly the strongest motivation for its synthesis. However, the NMR spectra of **1a** and its derivatives **1b–d** do not indicate any dynamics, and a spectrum of **1a** taken at 60° remained unchanged with respect to that recorded at 24°. The possibility of measurements at more elevated temperatures is only very small, since **1a** was found to rearrange to COT with a half-life of about 5 h at 50°.

In order to observe the anticipated automerization,

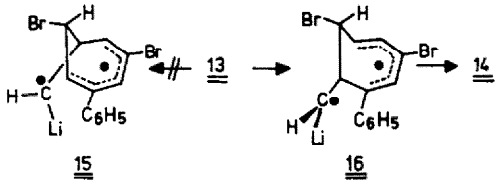
even if it were very slow in the available temperature range, we synthesized [1,8-D_2]**1a** via the sequence [1,7-D_2]**5** → [3,4-D_2]**3a** → [7,8-D_2]**7a** → [7,8-D_2]**10a** → [7,8-D_2]**11a**. The product, which was a 1.2:1 mixture of doubly labeled **1a** and COT, gave a ^{1}H-NMR spectrum with no signal at δ 0.96 in C_6D_6, thus proving that the deuterium atoms occupied positions 1 and 8 of **1a**. Warming the sample to 50° caused the slow increase of the COT singlet, but an absorption at δ 0.96 did not appear. Obviously, [1,5]-C *migrations*, which would produce [1,2-D_2]**1a** with a proton at C-8 in the first step, *do not occur*; the rearrangement to COT is more facile.



The above experiment suggests that the surprising formation of **1d** is not due to two subsequent [1,5]-C migrations starting from the major isomer **1c**. This is supported by the fact that the ratio **1c**:**1d** remained constant at 20°. If the 5:1 mixture represented the thermodynamic equilibrium, the interconversion of **1c** and **d** would have to be fast at 20°. This would result in NMR coalescence phenomena, which were not observed. Consequently, a partitioning of the reaction pathways has to be rationalized by



means of intermediates produced from the stable precursor **11c**. Octavalane **1c** would be expected, if butyllithium converts **11c** into **12** which would then undergo an intramolecular alkylation with inversion at the electrophilic centre. In contrast, **1c** would not be formed if the bromine–lithium exchange from **11c** led to **13** having the wrong configuration at the electrophilic centre. The simplest way from **13** to **1d** involves [1,5]-C migration of the lithiated carbon to produce **14** followed by nucleophilic displacement with a pentadienyl rearrangement. Based on the high acceleration of pericyclic reactions in anionic systems,[36] it is conceivable that the [1,5]-sigmatropic shift in **13** occurs under mild conditions. The necessary configuration of the lithiated carbon in **14** would occur, if the rearrangement of **13** took place with inversion, a result which has already been observed in processes of this type.[37] For a direct S_N reaction in **14**, which would lead to octavalene **1e**, the configuration of the electrophilic centre is still unfavourable, but should not be critical for the proposed substitution with pentadienyl rearrangement, since even in the S_N2' reaction examples for both stereochemical possibilities are known.[38]



The fact that we observe a product originating only from one out of the two possible sigmatropic shifts of **13** could arise from the relative stability of **15** and **16**, which we consider either as intermediates or as resonance structures contributing to the transition states. Whereas in **15** the phenyl group should have hardly an effect on the energy of the pentadienyl radical moiety, in **16** it should cause a substantial stabilization. Thus, structure **16** would rationalize the formation of **14** from **13**. In addition, the corresponding structures derived from tribromide **11b** would be less favoured than **16** explaining the failure to detect a rearranged bromooctavalene along with **1b**. It should be noted that the intermediacy of diradicals in [1,5]-C migrations is still a matter of debate.[37]

EXPERIMENTAL

M.ps were determined on a Reichert (Vienna) apparatus by the Kofler method and are uncorrected. The ^{1}H-NMR spectra were recorded on Varian EM 390 and Bruker WM400 instruments; the ^{13}C-NMR spectra were recorded on Bruker WH 90 and WM400 instruments; chemical shifts (δ values) are expressed in ppm downfield from TMS. Mass spectra were obtained from a Varian MAT CH 7 spectrometer. IR spectra were recorded using Beckman AccuLab 4 and Perkin–Elmer 157 G instruments. UV spectra were measured on a Beckman DB-GT spectrophotometer. Microanalytical determinations were performed using Heraeus equipment, a Perkin–Elmer 240 Elemental Analyzer, or a Carlo Erba Strumentatione Elemental Analyzer Model 1106.

*8-endo- (**3a**) and 8-exo-Bromotetracyclo[5.1.0.0^{2,4}.0^{3,5}]octane (**3d**)*

Homobenzvalene (**5**)[15] (5.00 g, 54.3 mmol), NaN[Si(CH_3)$_3$]$_2$ (13.3 g, 72.6 mmol), and 30 ml of pentane were admixed under N_2. The slurry was stirred at 0–5° while CH_2Br_2 (17.0 g, 97.8 mmol), dissolved in 5 ml of pentane, was introduced from a dropping funnel within 20 min. Stirring was continued for 3 h at 0–5° and then for 15 h at 20°. After cooling with ice, the light brown soln was cautiously hydrolyzed with ice-cold water. Extractions of the mixture with ether (4 × 30 ml), drying of the combined organic layers over K_2CO_3/Na_2SO_4, concentration *in vacuo*, and distillation of the yellow liquid residue gave HN[Si(CH_3)$_3$]$_2$ at 60° (bath)/14 Torr and 4.82 g (48%) of a yellowish liquid at 85–100° (bath)/14 Torr, which has been characterized as a nearly pure 1:1 mixture of **3a,d**. Repeated distillation of the second fraction gave good material b.p. 30°/0.1 Torr. MS (70 eV) *m/e* 186, 184 (1, 1%, M$^+$), 105 (100, M$^+$ – Br). The specific assignment of the absorptions in the NMR spectra of the mixture was possible when isomerically pure **3d** became available from **7e** (see below). ^{1}H-NMR ($CDCl_3$) **3a**: δ 0.89 (br. ddd, $J_{1,7}$ = 10.3, $J_{6exo,7}$ = 8.7, $J_{7,8}$ = 7.8 Hz, 7-H), 1.03 (br. ddd, $J_{1,2}$ = 4.2, $J_{1,8}$ = 6.9 Hz, 1-H), 1.45 (br. dt, $J_{3,4}$ = 10.8, $J_{2,3}$ = $J_{3,5}$ = 2.4 Hz, 3-

H), 1.46 (m, 6-H$_{endo}$), 1.79 (br. ddd, $J_{6,6}$ = 14.4, $J_{5,6exo}$ = 2.4 Hz, 6-H$_{exo}$), 1.90 (br. dt, $J_{2,4}$ = $J_{4,5}$ = 3.0 Hz, 4-H), 2.27 (≈ sext., $J_{2,5}$ ≈ $J_{5,6endo}$ ≈ 2.7 Hz, 5-H), 2.59 (≈ quint., 2-H), 3.16 (dd, 8-H); **3d**: δ 1.04 (m, 7-H), 1.32 (dddd, $J_{1,7}$ = 10.2, $J_{1,2}$ = 3.6, $J_{1,8}$ = 2.4, $J_{1,4}$ = 0.8 Hz, 1-H), 1.47 (br. dt, $J_{3,4}$ = 11.2, $J_{2,4}$ = $J_{4,5}$ = 3.2 Hz, 4-H), 1.51 (br. dt, $J_{2,3}$ = $J_{3,5}$ = 2.8 Hz, 3-H), 1.61 (br. d, $J_{6,6}$ = 14.2 Hz, 6-H$_{endo}$), 1.64 (br. dd, $J_{6exo,7}$ = 7.5 Hz, 6-H$_{exo}$), 2.25 (≈ br. sext., $J_{2,5}$ ≈ $J_{5,6endo}$ ≈ $J_{5,6exo}$ ≈ 2.5 Hz, 5-H), 2.63 (dd, $J_{7,8}$ = 3.3 Hz, 8-H), 2.82 (≈ quint., 2-H). ^{13}C-NMR ($CDCl_3$) **3a**: δ −0.66 (d, 205 Hz, C-3), 8.78 (d, 209 Hz, C-4), 7.74 and 8.03 (each d, 170 Hz, C-1, C-7), 14.20 (t, 125 Hz, C-6), 33.66 (d, 187 Hz, C-8), 35.48 and 35.78 (each d, 156 Hz, C-2, C-5); **3d**: δ 3.35 (d, 201 Hz) and 4.49 (d, 204 Hz) (C-3, C-4), 15.70 and 17.19 (each d, 162 Hz, C-1, C-7), 16.18 (t, 128 Hz, C-6), 25.15 (d, 190 Hz, C-8), 36.62 (d, 156 Hz, C-5), 40.03 (d, 159 Hz, C-2). The assignment is based on the spectra of the parent hydrocarbon and the 8,8-dibromo derivative.[39] (Found: C, 52.49; H, 5.01. Calc for C_8H_9Br (185.1): C, 51.92; H, 4.90%.)

Compound [3,4-D_2]**3a,d**. According to the procedure described above a 1:1 mixture of [3,4-D_2]**3a,d** (3.50 g, 22%) was obtained from [1,7-D_2]**5**[15] (8.00 g, 85.0 mmol, 95% D). In comparison to that of **3a,d** the 60 MHz ^{1}H-NMR spectrum of the deuterated product showed some simplifications upfield from δ 2.00.

8,8 - *Dibromo* - 6 - exo - *phenyltetracyclo*[5.1.0.0^{2,4}.0^{3,5}]*octane* (**3c**)

5-Phenylhomobenzvalene (**6**)[15b] (2.00 g, 11.9 mmol), t-BuOK (5.33 g, 47.6 mmol), and 30 ml of petroleum ether (b.p. 30–50°) were stirred under N_2 at −15 to −20° as $CHBr_3$ (6.69 g, 26.4 mmol) was added by means of a dropping funnel over 30 min. The mixture was allowed to warm up to 20°, and stirring was continued for an additional 30 min at that temp. Sufficient water was cautiously introduced to dissolve the ppt completely. The organic phase was separated, and the water phase was extracted with petroleum ether. After washing with water the combined organic layers were dried over Na_2CO_3/Na_2SO_4 and concentrated *in vacuo*. On trituration with 10 ml of petroleum ether, the brown semicrystalline residue furnished 1.72 g (42%) of **3c** as yellowish crystals, m.p. 97–98°. MS (70 eV) *m/e* 342, 340, 338 (0.2, 0.4, 0.2%, M^+), 180 (100, M^+ − 2Br). ^{1}H-NMR ($CDCl_3$) δ 1.59 (dq, $J_{1,7}$ = 11.0, $J_{2,7}$ = $J_{5,7}$ = $J_{6,7}$ = 0.8 Hz, 7-H), 1.67 (dtd, $J_{3,4}$ = 10.5, $J_{2,3}$ = $J_{3,5}$ or $J_{2,4}$ = $J_{4,5}$ = 2.5, $J_{3,6}$ or $J_{1,4}$ = 0.8 Hz, 3-H or 4-H), 1.84 (ddd, $J_{1,2}$ = 4.5 Hz, 1-H), 2.15 (dtd, $J_{2,4}$ = $J_{4,5}$ or $J_{2,3}$ = $J_{3,5}$ = 3.2, $J_{1,4}$ or $J_{3,6}$ = 0.8 Hz, 4-H or 3-H), 2.34 (m, 5-H), 2.69 (narrow m, 6-H), 2.93 (m, wider than m of 5-H, 2-H), 7.20–7.35 (m, C_6H_5). ^{13}C-NMR ($CDCl_3$) δ 0.21 (d, 207 Hz, C-3), 9.02 (d, 209 Hz, C-4), 21.96 (d, 166 Hz, C-1), 29.42 (d, 166 Hz, C-7), 31.12 (d, 133 Hz, C-6), 37.46 (d, 160 Hz, C-2), 37.88 (s, C-8), 43.31 (d, 158 Hz, C-5), C_6H_5: 126.52 (d, *p*-C), 127.94 (d) and 128.61 (d) (*o*- and *m*-C), 146.28 (s, *ipso*-C). (Found: C, 49.58; H, 3.44. Calc for $C_{14}H_{12}Br_2$ (340.1): C, 49.45; H, 3.56%.)

3,3,7-exo,8-syn-*Tetrabromotricyclo*[4.1.1.0^{2,4}]*octane* (**7b**)

Pyridinium hydrobromide perbromide ($C_5H_6N^+Br_3^-$) (3.00 g, 9.38 mmol) was added in small portions to a stirred soln of **3b**[13b] (2.00 g, 7.58 mmol) in 30 ml of anhyd pyridine at −25 to −30° under N_2. The brown–red reagent was decolourized immediately and a colourless solid precipitated. After additional stirring of the slightly yellow suspension for 2 h at −20 to −30°, it was poured into 300 ml of ice–water. The solid dissolved and another solid started to separate. After 15 h at 0° the crystals were collected by filtration and thoroughly washed with cold water. Recrystallization from MeOH afforded 1.83 g (57%) of **7b** as colourless rectangular prisms, m.p. 110–111°. MS (70 eV) *m/e* 347, 345, 343, 341 (4, 12, 12, 4%, M^+ − Br), 199 (83), 104 (62), 103 (67), 51 (100). ^{1}H-NMR, see Table 1. ^{13}C-NMR, see Table 2. (Found: C, 22.88; H, 1.92; Br, 75.49. Calc for $C_8H_8Br_4$ (423.8): C, 22.67; H, 1.90; Br, 75.43%.)

3-endo,7-exo,8-syn-(**7a**) *and* 3-exo,7-endo,8-syn-*Tribromotricyclo*[4.1.1.0^{2,4}]*octane* (**7d**)

According to the procedure described for **7b** the 1:1 mixture of **3a,d** (11.2 g, 60.5 mmol) was treated with $C_5H_6N^+Br_3^-$ (19.4 g, 60.5 mmol). The workup of the mixture gave 9.80 g (47%) of a crystalline 2:1 mixture of **7a,d**, which was dissolved in 70 ml of hot MeOH. After 15 h at −30° the crystalline material was collected by filtration, and a second crop was obtained by evaporating the mother liquor *in vacuo* to dryness and recrystallization of the residue as above from 40 ml of MeOH to give a combined yield of 5.50 g (52% with respect to **3a**) of **7a** as colourless crystals, m.p. 85–86°. After evaporation of the mother liquor *in vacuo* a brown oil remained, which was dissolved in the minimum quantity of ether. After addition of pentane to a point where a slight turbidity could be observed, the mixture was kept at −35° for 2 days to afford 1.88 g (18% with respect to **3d**) of **7d** as colourless crystals, m.p. 87–88°. MS (70 eV) **7a**, *m/e* 267, 265, 263 (12, 25, 13%, M^+ − Br), 104 (100); **7d**, almost identical with that of **7a**. ^{1}H-NMR, see Table 1. ^{13}C-NMR, see Table 2. (Found: **7a**: C, 27.61; H, 2.61; Br, 69.57; **7d**: C, 27.56; H, 2.70; Br, 68.78. Calc for $C_8H_9Br_3$ (344.9): C, 27.86; H, 2.63; Br, 69.51%.)

Compound [7,8-D_2]**7a**. According to the procedure described above 1.82 g (56% with respect to [3,4-D_2]**3a**) of [7,8-D_2]**7a** was obtained from the [3,4-D_2]**3a,d** mixture (3.50 g, 18.7 mmol). In comparison to the ^{1}H-NMR spectrum of **7a** the absorptions at δ 5.34 and 5.45 (7-H, 8-H) were almost completely absent in that of [7,8-D_2]**7a**, and the multiplicities of the signals at 2.70 and 3.20 (6-H, 1-H) were correspondingly reduced.

3,3,7 - exo,8 - syn - *Tetrabromo* - 5 - exo - *phenyltricyclo*[4.1.1.0^{2,4}]*octane* (**7c**)

According to the procedure described for **7b** compound **3c** (1.40 g, 4.12 mmol) was treated with $C_5H_6N^+Br_3^-$ (2.81 g, 8.79 mmol). The workup of the mixture gave crude **7c** as a colourless solid, which was treated with 30 ml of $CHCl_3$. Some insoluble material was removed by filtration; the volume of the filtrate was then reduced *in vacuo* to 5 ml. Filtration through a pad of Al_2O_3 (activity grade III, $CHCl_3$), evaporation of the eluate *in vacuo*, and treatment of the residual liquid with 2 ml of petroleum ether provided 735 mg (36%) of pure **7c** as colourless crystals, m.p. 139–140°. MS (70 eV) *m/e* 423, 421, 419, 417 (8, 23, 23, 8%, M^+ − Br), 179 (100). ^{1}H-NMR, see Table 1. ^{13}C-NMR, see Table 2. (Found: C, 33.77; H, 2.29; Br, 64.21. Calc for $C_{14}H_{12}Br_4$ (499.9): C, 33.64; H, 2.42; Br, 63.94%.)

3 - exo - *Bromo* - 7 - endo,8 - syn - *diiodotricyclo*-[4.1.1.0^{2,4}]*octane* (**7e**)

The 1:1 mixture of **3a,d** (690 mg, 3.73 mmol), dissolved in 3 ml of anhyd pyridine, was added dropwise over 40 min to a stirred soln of I_2 (947 mg, 3.73 mmol) in 10 ml of pyridine kept at −35 to −40°. The mixture was allowed to warm to 20°, and stirring was continued for an additional hour. The resulting brown–red soln was poured into 60 ml of ice–water, and the brown solid thus ppt was isolated by filtration. The solid was extracted with hot MeOH. Concentration of the resulting extracts gave a brown solid which was recrystallized from MeOH to give 180 mg (22% with respect to **3d**) of **7e** as colourless needles, m.p. 120–121°. MS (70 eV) *m/e* 359 (0.3%, M^+ − Br), 313, 311 (2, 2, M^+ − I), 105 (100). ^{1}H-NMR, see Table 1.

8 - exo - *Bromotetracyclo*[5.1.0.0^{2,4}.0^{3,5}]*octane* (**3d**)

To a soln of **7e** (300 mg, 0.68 mmol) in 30 ml of anhyd ether at −78° was syringed n-BuLi (0.72 ml of 1.9 M in hexane, 1.36 mmol) over 15 min under N_2. With continued stirring, the soln was kept at −78° for 1 h and then allowed to warm to −5°. After hydrolysis, the aqueous layer was removed by means of a pipette, and the organic layer was dried over anhyd Na_2SO_4 and concentrated *in vacuo*. From the residue a colourless oil was obtained by means of evaporation at 20°/0.01 Torr into a trap kept at −78°. This material contained some n-BuOH (from n-BuLi), which was removed by addition of NaH and repetition of the evaporation process. In the cooled trap 23 mg

(45%) of a liquid was collected consisting mainly of **3d** as shown by the NMR spectra.

2,7 - exo, 8 - syn - *Tribromobicyclo*[4.1.1]*oct* - 3 - *ene* (**10a**)

In a thick-walled tube **7a** (5.70 g, 16.5 mmol) was dissolved in 20 ml of anhyd benzene and 50 ml of anhyd acetonitrile was added. The tube was sealed and heated at 100–110° for 7 h. The black ppt formed was removed by filtration, and the solvents were evaporated *in vacuo*. From the residual, dark brown, highly viscous liquid, 5.00 g of a yellowish oil was obtained by distillation at 70–80° (bath)/0.001 Torr. On treatment with a small quantity of MeOH this liquid was transformed into colourless crystals. Recrystallization from MeOH yielded 4.62 g (82%) of a 12 : 1 mixture of **10a** and **11a**, m.p. 57–58°. IR (KBr) 1660 (C=C) cm^{-1}. MS (70 eV) *m/e* 348, 346, 344, 342 (0.6, 2.1, 2.1, 0.7%, M^+), 267 (14), 185 (62), 183 (63), 104 (100). ^{1}H-NMR, see Table 1. ^{13}C-NMR, see Table 2. (Found: C, 28.40; H, 2.77; Br, 69.82. Calc for $C_8H_9Br_3$ (344.9): C, 27.86; H, 2.63; Br, 69.51%.)

Compound [7,8-D_2]**10a**. According to the procedure described above [7,8-D_2]**7a** (1.82 g, 5.24 mmol) was transformed into [7,8-D_2]**10a** (1.50 g, 82%). In comparison to the ^{1}H-NMR spectrum of **10a** the absorptions at δ 4.43 and 5.25 were reduced to 5% intensity, and the multiplicities of the signals at 3.11 and 3.44 were simplified.

2,3,7 - exo,8 - syn - *Tetrabromobicyclo*[4.1.1]*oct* - 3 - *ene* (**10b**)

In a thick-walled tube **7b** (800 mg, 1.89 mmol) was dissolved in 5 ml of anhyd benzene. After addition of 8 ml of anhyd acetonitrile the tube was sealed and heated at 100–110° in an oil bath for 96 h. The black ppt formed was removed by filtration and the solvents were evaporated *in vacuo*. The residual light brown solid was recrystallized twice from MeOH to give 645 mg (81%) of **10b** as colourless needles, m.p. 121–122°. IR (KBr) 1642 (C=C) cm^{-1}. MS (70 eV) *m/e* 428, 426, 424, 422, 420 (1, 4, 6, 4, 1%, M^+), 104 (100). ^{1}H-NMR, see Table 1. ^{13}C-NMR, see Table 2. (Found: C, 23.03; H, 2.05; Br, 75.54. Calc for $C_8H_8Br_4$ (423.8): C, 22.67; H, 1.90; Br, 75.43%.)

2,3,7 - exo,8 - syn - *Tetrabromo* - 5 - exo - *phenylbicyclo*[4.1.1]*oct* - 3 - *ene* (**10c**)

In a thick-walled tube **7c** (560 mg, 1.12 mmol) was dissolved in 10 ml of anhyd benzene and 40 ml of anhyd acetonitrile was added. The tube was sealed and heated at 110° for 72 h. Evaporation of the solvents *in vacuo*, dissolution of the black residue in $CHCl_3$, filtration of this soln through Al_2O_3 (activity grade III, column 10 × 2 cm), and again evaporation of the solvent *in vacuo* gave a yellowish oil, which was treated with 5 ml of petroleum ether to furnish 173 mg (31%) of **10c** as colourless crystals, m.p. 132–133°. MS (70 eV) *m/e* 504, 502, 500, 498, 496 (0.1, 0.4, 0.6, 0.4, 0.1%, M^+), 179 (100). ^{1}H-NMR, see Table 1. ^{13}C-NMR, see Table 2. (Found: C, 33.91; H, 2.29; Br, 63.74. Calc for $C_{14}H_{12}Br_4$ (499.9): C, 33.64; H, 2.42; Br, 63.94%.)

7 - exo,8 - syn - *Dibromobicyclo*[4.1.1]*octa* - 2,4 - *diene* (**11a**)

1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (3.80 g, 25.0 mmol) was added to a soln of **10a** (5.50 g, 15.9 mmol) dissolved in 16 ml of anhyd benzene. Under N_2 the mixture was warmed to 35–40° for 48 h. To this mixture 50 ml of water and 20 ml of 2 N HCl were added to dissolve the ppt and to remove excess DBU, respectively. The mixture was extracted with two 60 ml portions of ether and 40 ml of CH_2Cl_2, the combined organic layers were washed with $NaHCO_3$ aq and dried over Na_2SO_4. Evaporation of the solvents *in vacuo* and distillation of the residual yellow oil at 40–50° (bath)/0.001 Torr gave a colourless liquid, which solidified rapidly. Recrystallization from i-propanol afforded 3.11 g (74%) of **11a**, m.p. 63–64°. The residue from the distillation consisted mainly of unchanged starting material **10a**, which was resubmitted to the elimination with DBU to give a second crop of **11a**. IR (KBr) 1598 (C=C) cm^{-1}. UV (n-hexane) λ_{max} (log ε) 305 (3.21), 291 (3.50), 279 (3.54), 268 (3.46), 260 (sh, 3.36), 251 (sh, 3.25), 212 nm (sh, 3.65). MS (70 eV) *m/e* 266, 264, 262 (1.2, 2.5, 1.3%, M^+), 104 (100). ^{1}H-NMR, see Table 1. ^{13}C-NMR, see Table 2. (Found: C, 36.34; H, 3.27; Br, 60.74. Calc for $C_8H_8Br_2$ (264.0): C, 36.40; H, 3.05; Br, 60.55%.)

Compound [7,8-D_2]**11a**. According to the procedure described above [7,8-D_2]**10a** (1.50 g, 4.32 mmol) was converted into [7,8-D_2]**11a** (720 mg, 63%). In comparison to the ^{1}H-NMR spectrum of **11a** the absorptions at δ 4.38 and 5.33 were virtually missing, and the multiplicities of the signals at 3.44 and 5.80 were correspondingly reduced.

3,7 - exo,8 - syn - *Tribromobicyclo*[4.1.1]*octa* - 2,4 - *diene* (**11b**)

DBU (450 mg, 2.96 mmol) was added to the soln of **10b** (500 mg, 1.18 mmol) in 6 ml of anhyd benzene under N_2. After 4 d at 20° a suspension of a colourless solid in the yellow soln was formed. Water (10 ml) and 5 ml of 2 N HCl were added to dissolve the solid and remove the excess DBU. The mixture was extracted with four 20 ml portions of ether; the combined organic layers were washed with $NaHCO_3$ aq and dried over Na_2SO_4. Evaporation of the solvents *in vacuo* gave 384 mg (95%) of pure **11b** as a yellowish solid, m.p. 79–80°, which after sublimation at 45° (bath)/0.001 Torr gave a colourless solid, m.p. 80–81°. IR (KBr) 1617 (C=C), 1592 (C=C) cm^{-1}. UV (n-hexane) λ_{max} (log ε) 317 (2.98), 304 (3.28), 293 (3.29), 284 (sh, 3.16), 271 (sh, 2.85), 234 nm (3.36). MS (70 eV) *m/e* 346, 344, 342, 340 (0.8, 2.2, 2.3, 0.8%, M^+), 103 (100). ^{1}H-NMR, see Table 1. ^{13}C-NMR, see Table 2. (Found: C, 28.41; H, 2.21; Br, 69.80. Calc for $C_8H_7Br_3$ (342.9): C, 28.02; H, 2.06; Br, 69.92%.)

4,7 - exo,8 - syn - *Tribromo* - 2 - *phenylbicyclo*[4.1.1]*octa*-2,4-*diene* (**11c**)

A soln of DBU (522 mg, 3.43 mmol) in 5 ml of anhyd benzene was added to **10c** (1.41 g, 2.82 mmol) dissolved in 15 ml of benzene. After stirring for 1 d at 20°, a colourless ppt was formed which was dissolved by addition of water. The organic layer was separated, and the water phase was extracted with three 25 ml portions of ether. The combined organic phases were washed with 20 ml of 2 N HCl and then with $NaHCO_3$ aq and dried over Na_2SO_4. Evaporation of the solvents *in vacuo*, filtration of the brown residue through Al_2O_3 (activity grade III, column 10 × 2 cm, $CHCl_3$), and concentration of the filtrate *in vacuo* gave a light yellow oil, which was treated with a few ml of n-pentane to afford 770 mg (65%) of **11c** as colourless crystals, m.p. 85–86°. IR (KBr) 1605, 1570 (C=C) cm^{-1}. UV (n-hexane) λ_{max} (log ε) 316 (3.91), 237 (sh, 3.91), 228 (3.96), 222 nm (sh, 3.94). MS (70 eV) *m/e* 422, 420, 418, 416 (1.4, 4.0, 4.0, 1.2%, M^+), 179 (100). ^{1}H-NMR, see Table 1. ^{13}C-NMR, see Table 2. (Found: C, 40.43; H, 3.03. Calc for $C_{14}H_{11}Br_3$ (419.0): C, 40.13; H, 2.65%.)

Tricyclo[5.1.0.$0^{2,8}$]*octa*-3,5-*diene* (**1a**)

To a soln of **11a** (500 mg, 1.89 mmol) in 7 ml of anhyd ether at −78° was syringed t-BuLi (1.50 ml of 1.25 M in n-pentane, 1.88 mmol) over 20 min under N_2. The soln was stirred at −78° for an additional period of 30 min and then allowed to warm up to 0°. After cautious hydrolysis of the mixture with a minimum quantity of water, the aqueous layer was removed by means of a pipette at 20° and the organic layer was dried over anhyd K_2CO_3. The solvent was evaporated at 0° *in vacuo* (20 Torr) to yield a residual yellow liquid, from which a colourless liquid (98 mg, 50%) was obtained by distillation at 20° *in vacuo* (0.01 Torr) into a trap kept at −78°. This liquid was a 4 : 1 mixture of **1a** and COT along with 1% of ether and an impurity causing a singlet absorption (intensity 10% in relation to the singlet of COT) at δ 1.07 in the ^{1}H-NMR spectrum. Attempts to purify **1a** by VPC (5% NaOH and 20% carbowax 20M on chromosorb P) failed, since under these conditions **1a** rearranged to COT. Utilization of n-BuLi instead of t-BuLi gave a 3 : 1 mixture of **1a** and COT along with n-BuBr, which could not be removed. MS (70 eV) *m/e* 104 (100%, M^+), 103 (76), 102 (13), 92 (12), 91 (15), 78 (95), 77 (50), 63 (13), 52 (17), 51 (45), 50 (25), 39 (28). ^{1}H-NMR, see Table 3. ^{13}C-NMR, see Table 4. Dissolved in C_6D_6 **1a** rearranged to COT at 50°, the

half-life being approximately 5 h. In contrast to the behaviour of **1b** (see below), the parent hydrocarbon **1a** did not change when oxygen was bubbled through its soln at 0°.

Compound [1,8-D_2]**1a**. According to the procedure described above [7,8-D_2]**11a** was treated with t-BuLi to give a 1.2:1 mixture of [1,8-D_2]**1a** and [D_2]COT (neither the deuterium content of COT nor the positions of the labels were investigated). In comparison to the ^{1}H-NMR spectrum of **1a**, in that of [1,8-D_2]**1a** the signal of 1,8-H (δ 0.96, C_6D_6) was almost completely missing, and the multiplicity of the 2,7-H absorption had changed to a broad doublet. On warming up to 50° in C_6D_6 the intensities of the three signals of [1,8-D_2]**1a** decreased and that of the COT absorption increased. No additional signal at δ 0.96 appeared.

4-*Bromotricyclo*[5.1.0.0^{2,8}]*octa*-3,5-*diene* (**1b**)

To a soln containing **11b** (500 mg, 1.46 mmol) in 10 ml of anhyd ether at −78° was syringed n-BuLi (1.32 ml of 1.1 M in ether, 1.46 mmol) over 10 min under N_2. The slightly yellow soln was stirred at −78° for 20 min and then allowed to warm up to 0°. After cautious hydrolysis with the minimum quantity of water, the aqueous layer was removed by means of a pipette, and the organic layer was dried over anhyd K_2CO_3 at 20°. Sometimes, the mixture turned black suddenly at −20° indicating an excess of n-BuLi, although this reagent was initially introduced stoichiometrically. In these cases immediate hydrolysis gave the usual yield of **1b** after the workup. However, allowing the black soln to warm up led to complete decomposition. After drying, the ether soln was concentrated *in vacuo* and from the residual viscous yellow oil, 120 mg (45%) of colourless crystalline **1b**, m.p. 30–32°, was obtained by means of distillation at 20–25° (bath)/0.001 Torr. When **11b** was utilized in excess with respect to n-BuLi, the remaining **11b** in part codistilled with **1b**. Then a second distillation at 40–60° (bath)/0.2 Torr was performed to furnish pure **1b**. Since the crystals of **1b** were transformed by air within minutes into a colourless liquid, which showed only broad absorptions in the ^{1}H-NMR spectrum, **1b** must be handled strictly in an atmosphere of N_2. Solns of **1b** were found to be less sensitive, but bubbling oxygen through a sample in $CDCl_3$ caused complete decomposition within 2 h at 20°. In contrast to C_6D_6 solns, those in $CDCl_3$ were found to decompose in a few days at −20°, probably due to the sensitivity of **1b** towards traces of acid. Samples of pure **1b** which had been sealed *in vacuo* were stable over an extended period of time at −20°. IR (film) 1635 (C=C) cm^{-1}. UV (n-pentane) λ_{max} (log ε) 327 (sh, 2.71), 321 (sh, 2.93), 312 (sh, 3.21), 306 (sh, 3.29), 299 (3.36), 294 (3.36), 289 (sh, 3.34), 282 (sh, 3.29), 226 (sh, 3.51), 204 nm (3.78). MS (70 eV) *m/e* 184, 182 (1, 1%, M^+), 103 (100), 102 (21), 77 (76), 76 (10), 51 (40), 50 (24), 39 (12). ^{1}H-NMR, see Table 3. ^{13}C-NMR, see Table 4. (Found: C, 52.84; H, 3.99. Calc for C_8H_7Br (183.1): C, 52.49; H, 3.85%.)

5 - *Bromo* - 3 - *phenyl* - (**1c**) *and* 3 - *bromo* - 1 - *phenyltri* - *cyclo*[5.1.0.0^{2,8}]*octa*-3,5-*diene* (**1d**)

To a soln of **11c** (720 mg, 1.72 mmol) in 10 ml of anhyd ether at −78° was syringed n-BuLi (1.38 ml of 1.3 M in hexane, 1.80 mmol) over 20 min under N_2. After continuous stirring for 30 min at −78°, the soln was allowed to warm to 0°. Cautious hydrolysis, separation of the layers, extraction of the aqueous layer with ether, drying of the combined ether layers over Na_2SO_4, and evaporation of the solvent *in vacuo* gave 410 mg of a viscous, brown oil, which was shown by NMR spectroscopy to be a 5:1 mixture of **1c,d** containing only a few impurities. Using mesitylene as an internal standard, the yield of **1c,d** was determined to be 172 mg (42%). Attempts to purify and to separate the mixture by distillation or chromatography failed because **1c,d** decomposed under the conditions employed. ^{1}H-NMR, see Table 3. ^{13}C-NMR, see Table 4.

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