

Experiments Towards the Formation of 1,6-Dehydroquadricyclane and Density Functional Calculations on This and Related Molecules^[1]

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Received September 22, 1997

Keywords: Strained molecules / Quadricyclanes / Lithiation / Density functional calculations

1,6-Dibromoquadricyclane (**6**) was obtained from norbornadiene (**11**) by hydroboration, oxidation of the diol **12** to the diketone **14** and its conversion into 2,6-dibromonorbornadiene (**20**) using tribromodioxaphosphole **16b** followed by treatment of the mixture **17/18** with potassium *tert*-butoxide in DMSO and photocyclization of **20**. Reaction of **6** with *t*BuLi (2 equiv.) led to the formation of 1-bromo-6-lithioquadricyclane **7**, the NMR spectra of which were observed up to 0°C. **7** did not lose LiBr to give **4**, but could be trapped with H₂O and chlorotrimethylsilane to give **21e** (53 %) and **21f** (64 %). Reaction of **6** with *t*BuLi (> 4 equiv.) gave rise to 1,6-dilithio-

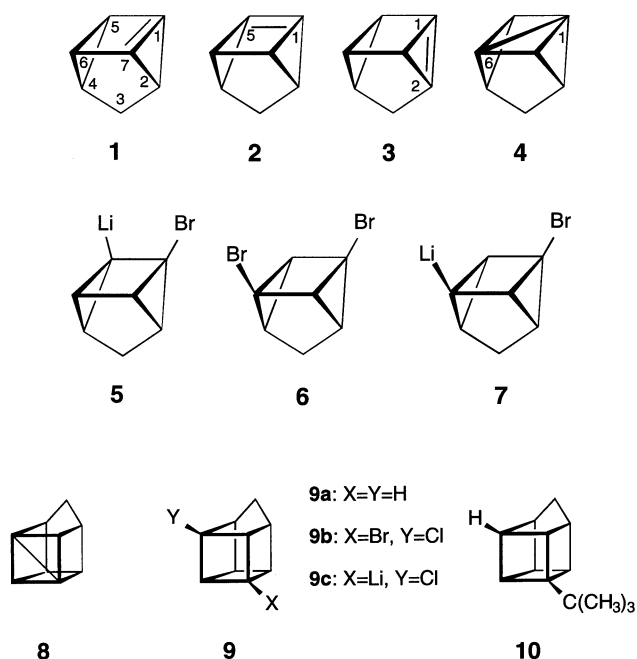
quadricyclane (**21c**), whose NMR spectra could also be recorded. **21c** was converted into the corresponding 1,6-disubstituted quadricyclanes with D₂O (87 %), chlorotrimethylsilane (92 %), dimethyl sulfate (55 %), methyl chloroformate (45 %), iodine monochloride (62 %), and *p*-toluenesulfonyl chloride (48 %). – Density functional calculations using the B3LYP/6-31G* level of theory showed that 1,6-dehydroquadricyclane (**4**) is a local energy minimum in its singlet electronic state. **4** contains a unique structure with 4 condensed cyclopropane units. The parent hydrocarbons **27** and **28**, hitherto unknown, are also local energy minima in their singlet electronic states.

Lithium halide elimination has proved as an efficient method for the generation of strained olefins^[2] and hydrocarbons^[3]. This reaction has furnished evidence for the formation of 1,7-dehydroquadricyclane (**1**)^{[4][5]}, 1,5-dehydroquadricyclane (**2**)^[6] and 1,2-dehydroquadricyclane (**3**)^[7], which could be trapped as Diels-Alder adducts. Ab initio MO calculations at the TCSCF level of theory using the 6-31G* basis set showed that **1**, **2**, and **3** were local energy minima on the C₇H₆ energy hypersurface, as was the non-olefinic 1,6-dehydroquadricyclane (**4**)^[7]. Taking **1** as reference model compound, **2**, **3**, and **4** were calculated to be less stable by 11.8, 4.0, and 12.7 kcal/mol. As **2** was formed by LiBr elimination from **5**, it seemed justified to synthesize dibromide **6** and convert it to **7**, to find out if **4** is experimentally accessible.

A molecule structurally related to 1,6-dehydroquadricyclane **4** is 2,4-dehydrohomocubane (**8**), which has been invoked as an intermediate in the reaction of dihalide **9b** with *tert*-butyllithium (*t*BuLi)^[8]. **8** was able to add *t*BuLi across the strained C–C single bond to afford **10** after aqueous workup. A similar behavior could be expected of **4**.

A. Synthesis of 1,6-Dibromoquadricyclane (**6**)

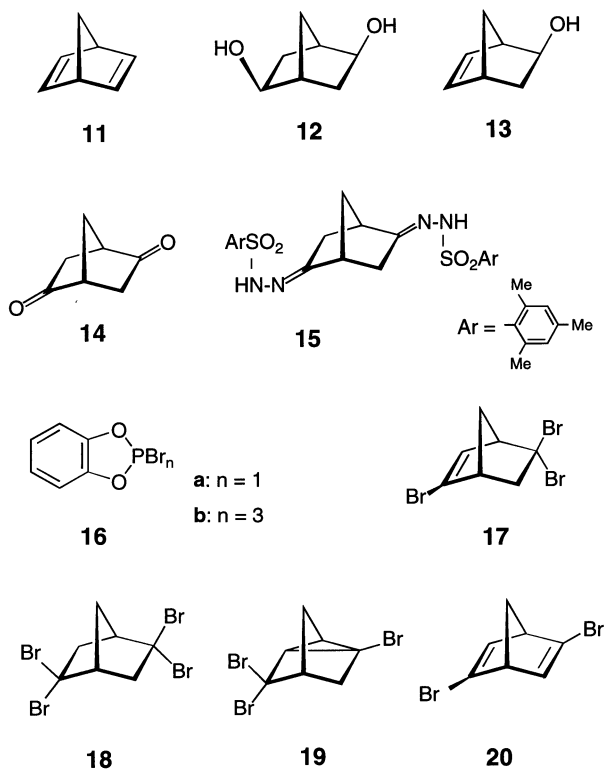
The synthetic procedure for the preparation of **6** started from norbornadiene (**11**). Its conversion to 2-*exo*-5-*syn*-bicyclo[2.2.1]heptanediol (**12**) by hydroboration in THF has been reported by Zweifel, Nagase, and Brown^[9]. In our hands, the yields of **12** did not exceed 35%. At a yield of 26%, the mono-alcohol **13** was a major side-product. Using



9-borabicyclo[3.3.1]nonane or the borane dimethyl sulfide complex as reducing agents did not lead to better results. 1,5-cyclooctanediol in the first and dimethyl sulfoxide in the second case could not be separated from **12** easily.

The conversion of **12** to bicyclo[2.2.1]heptane-2,5-dione (**14**) in 41 % yield by Jones oxidation has been reported by Hawkins, Hsu, and Wood^[10]. Although this yield could be

reached closely (39%), alternative methods for this oxidation were investigated. The procedure of Swern and Omura^[11] using DMSO/oxalyl chloride in CH₂Cl₂ furnished **14** in 35%, whereas the "oxon" method of Morimoto^[12] was not successful.

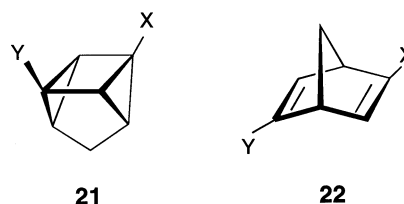


Two reaction paths were pursued to convert **14** into **20**. The Shapiro reaction^[13] with bis-hydrazone **15** and 4.0 equiv. of *n*-butyllithium (BuLi) followed by addition of 1,2-dibromoethane did not furnish any **20**. Alternatively, **14** was reacted with freshly prepared 2,2,2-tribromo-1,3,2-benzodioxaphosphole (**16b**)^[14] (from **16a** and Br₂) for 20 h in CH₂Cl₂ under reflux, which afforded 2,5,5-tribromobicyclo[2.2.1]hept-2-ene (**17**) in 61% yield and 2,2,5,5-tetrabromobicyclo[2.2.1]heptane (**18**) in 9% yield. In some experiments, a small amount of 2,2,5-tribromonortricyclane (**19**) (yield < 5%) was also observed. **17** and **18** could be separated by distillation, the traces of **19** accompanying **18** were hard to remove. The mixture of **17** and **18** was effectively converted into dibromide **20** in 67% yield by reaction with potassium *tert*-butoxide in DMSO. Photocyclization of **20** to **6** was accomplished in 81% yield by irradiating a solution of **20** in ether in the presence of 5% of acetophenone.

B. Reactions of **6** with Organolithium Bases

Under the premise that **4** could be generated from **6** and trapped by *t*BuLi, dibromide **6** was treated with an excess (5.0 equiv.) of *t*BuLi at –78°C for 2 hours, the mixture brought to 0°C and hydrolyzed with water. Besides some polymeric material, only quadricyclane (**21a**) could be isolated. There was no indication for the formation of **21b**,

the expected trapping product. This result implies that 1,6-dilithioquadricyclane (**21c**) was generated in the course of the reaction. Therefore, **6** was treated with 4.0 equiv. of *t*BuLi followed by addition of D₂O, which led to the isolation of 1,6-dideuterioquadricyclane (**21d**) in 87% yield and a D₂ content of > 90%. In a further experiment, **6** was reacted with only 2.0 equiv. of *t*BuLi at –78°C in ether; after 2.0 hours of reaction time at 0°C, aqueous workup resulted in the isolation of 1-bromoquadricyclane (**21e**) in 53% yield. To promote LiBr elimination from **7**, which is obviously present in the reaction mixture, the reaction was repeated by addition of tetramethylethylenediamine (TMEDA) in the first and by lithium bromide in the second modification, but in both cases only **21e** could be isolated.



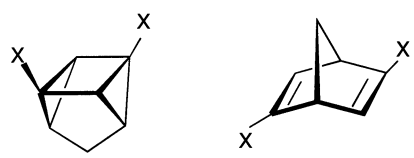
21, 22	a	b	c	d	e	f	g	h
X	H	H	Li	D	Br	Br	I	Cl
Y	H	C(CH ₃) ₃	Li	D	H	Si(CH ₃) ₃	Li	Li

The reported results indicated that 1-bromo-6-lithioquadricyclane (**7**) is persistent up to 0°C and does not eliminate LiBr. In the presence of *t*BuLi, a second lithium bromine exchange takes place under the formation of **21c**. This could be confirmed by ¹³C-NMR spectroscopy. For this purpose dibromide **6** in [D₈]THF was treated at –78°C with 2.0 equiv. of *t*BuLi, spectra of the solution were recorded at –80, –60, –40, and 0°C. At all temperatures clear signals were obtained for all C atoms of **7**. C-1 and C-6 appeared as singlets at δ = 34.50 and 11.58. At 25°C, the spectrum became unstable and many new signals appeared. When instead of 2.0 equiv. 4.0 equiv. of *t*BuLi were used, ¹³C-NMR spectra of **21c** in [D₈]THF were recorded at –80, –40, and 0°C, again showing intensive stable signals at these temperatures. The signal for C-1 and C-6 appeared at δ = 16.75; at 25°C, this signal faded quickly.

C. Synthesis of Some 1,6-Disubstituted Quadricyclanes

The persistency of **7** and **21c** below 0°C encouraged the reaction of these intermediates with some electrophiles. The reaction of **7** with chlorotrimethylsilane afforded **21f** in 64% yield. When chlorotrimethylsilane, dimethyl sulfate, methyl chloroformate, cyanogen iodide, or tosyl chloride were allowed to react with **21c**, the corresponding 1,6-disubstituted quadricyclanes **23a–e** were formed in reasonable yields.

After distillation, the diester **23c** was completely isomerized to dimethyl bicyclo[2.2.1]hepta-2,5-diene-2,5-dicarboxylate (**24c**). This compound was reconverted into **23c** in 78% yield by irradiation in ether in the presence of acetophenone. The isolated 1,6-diiodoquadricyclane (**23d**) con-



	23	24
X	Si(CH ₃) ₃	CH ₃
% Yield	92	55

tained 15% 2,5-diiodobicyclo[2.2.1]heptane (**24d**), which could be removed by preparative layer chromatography. **24d** was also formed in the reaction of **21c** with iodine, with *p*-tolylsulfonyl iodide and with iodine monochloride in yields of 34, 25 and 17%.

The access to 1-bromo-6-trimethylsilylquadricyclane (**21f**) and 1,6-diiodoquadricyclane (**23d**) prompted two further experiments aimed at reaching the goal of generating **4**. Compound **21f** was treated with 8.0 equiv. of CsF in DMSO^[15] for 24 h at room temperature, but only unreacted **21f** accompanied by some 2-bromo-5-trimethylsilylbicyclo[2.2.1]heptane (**22f**) could be isolated. **23d** and 4 equiv. of *t*BuLi afforded after reaction in ether at -78°C , warming to 0°C and addition of D₂O only 2,5-dideuteriobicyclo[2.2.1]heptane (**22d**) besides polymeric material. This result shows that **21g** is formed as an intermediate, which shares with **7** the inability to eliminate lithium halide.

Our experimental approach to generate 1,6-dehydroquadricyclane (**4**) did not succeed, because the activation energy for the LiBr elimination from **7** is energetically too costly. To overcome this problem, metal exchange of Li in **7** against a metal with lower bond energy to carbon like K, Cs, or Ag, might be the method of choice. This route will be followed in future activities in this field.

D. Ab Initio Calculations on 1,6-Dehydroquadricyclane and Related Molecules

In this section, the questions concerning the existence of 1,6-dehydroquadricyclane (**4**) as a short-lived reaction intermediate is approached by computational chemistry techniques. The Gaussian 94 program package^[16] has been used throughout. Specifically, the density-functional theory (DFT)^[17] with the Becke3LYP functional^[18] and the 6-31G* basis set has been applied preferentially in this investigation. This method has been used to calculate the energy difference between singlet and triplet carbenes^[19] and has been applied successfully to solve mechanistic problems in different areas of organic chemistry^[20].

1. Energies and Structures of Dehydroquadricyclanes

In Table 1 the B3LYP/6-31G**//B3LYP/6-31G* energies are given for dehydroquadricyclanes **1–4**, for quadricyclane (**21a**), 1-chloro-6-lithioquadricyclane (**21h**), for homocubane (**9a**), and 2-chloro-4-lithiohomocubane (**9c**).

The Becke3LYP results of Table 1 are consistent with our earlier calculations in which we used the TCSCF theory^[7]. Within these levels of theory, 1,7-dehydroquadricyclane (**1**) is the most stable of the four C₇H₆ isomers and **4** is the least stable. All molecules were local minima on the C₇H₆ energy hypersurface, as indicated by calculated real positive vibrational frequencies. However, at 0.9 kcal/mol the difference in energy between **2** and **4** is only marginal at the TCSCF/6-31G* level of theory, whereas within the B3LYP/6-31G* methodology the energy difference rises to 5.1 kcal/mol. This value indicates that formation of **4** by lithium halide elimination is energetically a more demanding process than the one of generating the olefinic dehydroquadricyclanes **1**, **2**, and **3**. If the 9.6 kcal/mol which **4** is higher in energy than **1** suffices to prevent its formation, is less clear.

Table 1. B3LYP/6-31G**//B3LYP/6-31G* energies for dehydroquadricyclanes **1–4**, **21a**, **21h**, **8**, **9a**, and **9c**

mole- cule	B3LYP energy [au]	ZPE ^[a] [au]	<i>E</i> _{rel} ^[b] [kcal/mol]	TCSCF ^[c] <i>E</i> _{rel} [kcal/mol]
1	−270.1124892	0.102422	0.0	0.0
2	−270.1047122	0.101815	4.5	11.8
3	−270.1076397	0.102053	2.8	4.0
4	−270.0961003	0.101359	9.6	12.7
21a	−271.4448293	0.126320	—	—
21h	−737.9381907	0.105912	—	—
8	−347.5212474	0.137185	—	—
9a	−348.8459265	0.161870	—	—
9c	−815.3380766	0.141148	—	—

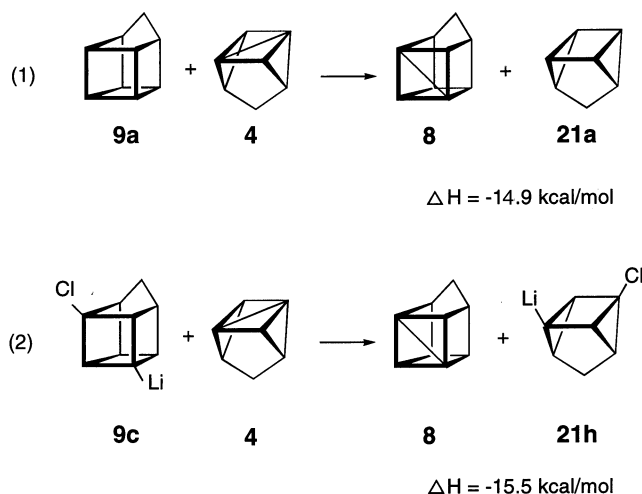
^[a] Scaled by a factor of 0.9804; see ref.^[21] — ^[b] B3LYP energy + ZPE, rel. to **1**. — ^[c] See ref.^[7].

The TCSCF/6-31G* structures of **1–3** differ only slightly from the B3LYP/6-31G* structures. For the “unsaturated center” of **1** the C1–C7 TCSCF distance was 1.3708 Å, the B3LYP distance was 1.3969 Å. The corresponding values for **2** (C1–C5) were 1.4292 Å and 1.4030 Å, and for **3** (C1–C2) 1.3656 Å and 1.3719 Å. A significant difference was found in the C1–C6 bond length of **4**. The TCSCF/6-31G* calculation showed a C–C distance of 1.9081 Å, whereas the B3LYP/6-31G* value amounted only to 1.7934 Å.

1,6-Dehydroquadricyclane (**4**) is structurally related to 1,7-dehydroquadricyclane (**1**) by hydrogen shift from C-1 to C-6. Furthermore, hydrogen shift from C-5 to C-6 would convert **4** into 1,5-dehydroquadricyclane (**2**). We have been able to locate the saddle points of these two reactions at $E = -270.016137142$ au (1 imaginary frequency at 1122.8i cm^{−1}, ZPE = 0.097297 au) and at $E = -270.0262276$ au (1 imaginary frequency at 1284.2i cm^{−1}, ZPE = 0.099400) using the B3LYP/6-31G* level of theory. IRC calculations on both saddle points assured that they connected **4** with **1** and, respectively, **4** with **2**. The transition structure of the **4** → **1** reaction showed a long C6–C7 bond of 2.0676 Å. For the **4** → **2** reaction, the C5–C6 bond length of the transition-state structure was calculated as 1.7479 Å. The unexpected structure of the first saddle point prompted us to recalculate the transition structure of the **4** → **1** reaction,

using the MP2/6-31G**//MP2/6-31G* level of theory. The result was in accord with the B3LYP/6-31G* calculation: The C6–C7 bond length amounted to 2.0036 Å ($E = -269.1206747$ au, one imaginary frequency at 1074.4i cm⁻¹, $ZPE = 0.099038$). From the above data, the B3LYP/6-31G* potential energy barrier (including ZPE correction) separating **4** from **1** is calculated to be 46.4 kcal/mol. At 41.4 kcal/mol, the energy barrier from **4** to **2** is somewhat lower. The MP2/6-31G* barrier of the **4** → **1** reaction is 52.3 kcal/mol and compares reasonably well with its B3LYP counterpart. The range of these barriers leaves no doubt that under low-temperature conditions the conversion of **4** to **1** and, respectively, to **2** by hydrogen migration will not be observed.

In the introductory section it was assumed that 2,4-dehydrohomocubane (**8**) might be a good model compound for comparison with 1,6-dehydroquadracyclane (**4**). However, two isodesmic reactions (1) and (2) show that this is not really true. Obviously, **4** has a considerably higher strain energy, which makes realistic comparisons between **4** and **8** hardly possible. The 15 kcal/mol in exothermicity which is shown by equations (1) and (2) should mainly originate from the difference in strain energy of **4** and **8**. If only parts of this energy enter the activation barrier between **21h** and **4**, the LiCl elimination from **21h** might be retarded to a point where it is not observed under the experimental conditions at 0°C.



1,6-Dehydroquadracyclane (**4**), still awaiting experimental birth, has a fascinating structure, which was calculated at the B3LYP/6-31G* level of theory. Selected structural data for the singlet as well as for the triplet are given in Table 2.

Atoms C1, C5, C6, and C7 form a bicyclo[1.1.0]butane subunit which is nearly planar (dihedral angle 5617 = 182.4° for the singlet and 179.7° for the triplet). At the side bonds C1–C7 and C5–C6 two three-membered rings are condensed to the central bicyclo[1.1.0]butane, for the singlet in the *exo* mode, leading to two additional bicyclo[1.1.0]butane subunits C1,C2,C7,C6 and C1,C5,C6,C4. The dihedral angles of these bicyclobutanes (1654 and 6172) amount to 108.2° for the singlet and 106.7° for the triplet. At 1.793 Å, the central bond C1–C6 of the singlet is

Table 2. B3LYP/6-31G* selected structural data of singlet and triplet **4**

bond	bond length		angle	bond angle	
	(singlet) [Å]	(triplet) [Å]		singlet [°]	triplet [°]
1–2	1.537	1.506	2–1–5	111.5	106.0
1–5	1.510	1.531	2–1–7	61.3	62.9
1–6	1.793	2.097	5–1–6	51.8	45.3
1–7	1.466	1.493	6–1–7	54.1	46.9
2–3	1.518	1.523	1–2–3	107.4	111.8
2–7	1.533	1.565	1–2–7	57.0	58.1
			3–2–7	114.1	109.9
			2–3–4	98.1	98.3
			1–5–4	97.7	103.0
			1–5–6	74.1	87.8
			6–5–4	61.6	59.0

strongly elongated. As expected, the C1–C6 bond for the triplet is considerably longer (2.097 Å).

The long C1–C6 bond of the singlet of **4** rises the question if the triplet state could be the ground state of **4**. The triplet energies of **1–4** have been calculated using the UB3LYP/6-31G**//UB3LYP/6-31G* level of theory. The results are given in Table 3, which also contains the singlet-triplet energy difference in kcal/mol.

Table 3 shows that the triplet state at the Becke3LYP/6-31G* level of theory is higher in energy by close to 20 kcal/mol for **1** and **2**, by 23 kcal/mol for **3** and by 10 kcal/mol for the non-olefinic 1,6-dehydroquadracyclane (**4**). This is in accordance with our earlier results^[7].

Table 3. Becke3LYP/6-31G* energies for dehydroquadracyclanes **1–4** triplets, and singlet-triplet energy differences

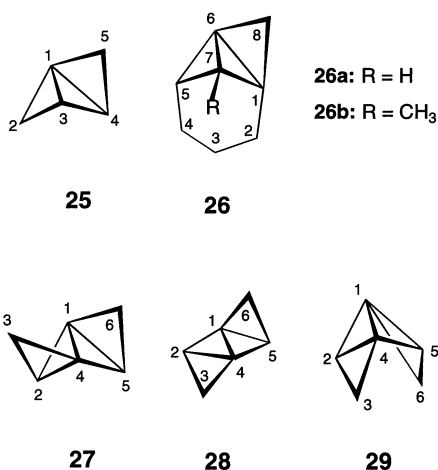
molecule	UB3LYP energy [au]	$ZPE^{[a]}$ [au]	ΔE_{T-S} [kcal/mol]
1	-270.0819443	0.100954	18.2
2	-270.0732200	0.100652	19.0
3	-270.0691118	0.100495	23.2
4	-270.0795599	0.100674	9.9

^[a] Scaled by a factor of 0.9804; see ref.^[21].

2. Some Three-Membered Ring-Condensed Structures

At this point it should be noted that condensation of a three-membered ring to a side-bond of bicyclo[1.1.0]butane has been achieved experimentally within model compounds **25**^[22] and **26b**^[23]. It seemed interesting to investigate theoretically if the parent of **4**, the tetracycle **27** and its stereoisomers **28** and **29** were minima on the corresponding energy hypersurface.

25 has been the subject of intensive ab initio MO calculations by Wiberg^[22]. The most interesting feature of these calculations on the structure of **25** at the HF/6-31G* and MP2/6-31G* level of theory was the finding that this molecule had C_1 symmetry with bond lengths of C1–C3 at 1.446 Å and of C1–C4 at 1.577 Å and a low energy barrier (0.9 kcal/mol) between an identical molecule with interchanged bond lengths of C1–C3 and C1–C4. We have approached this problem with the B3LYP/6-31G**//B3LYP/6-



31G* level of theory and found a similar result: **25** is a minimum on the C₅H₆ energy hypersurface in a C₁ structure. The bond lengths C1–C3 and C1–C4 were calculated as 1.454 Å and 1.519 Å, the dihedral angles 2–1–3–4 and 5–1–4–3 amounted to 122.4° and 136.4°. This result was also obtained using the QCISD/6-31G**/QCISD/6-31G* formalism. The corresponding structural parameters were 1.446 Å and 1.554 Å and 118.3° and 137.6°.

The calculations on the tetracycles **27–29** revealed that **27** and **28** were local minima on the C₆H₆ energy hypersurface. The central bicyclo[1.1.0]butane unit in **27** (C1–C2–C4–C5) is bent, the dihedral angle 2–1–4–5 was calculated as 161.9°, the bond length C1–C4 as 1.680 Å; this is considerably shorter than the C1–C6 bond in **4** (1.793 Å). The central bicyclo[1.1.0]butane unit in **28** (C1–C2–C4–C5) is planar, at a C1–C4 bond length of 1.911 Å. However, this unusually long bond does not severely destabilize the molecule, which is more stable by 25.5 kcal/mol than **27**. No local minimum with a structure related to **29** was found on the C₆H₆ energy hypersurface. The B3LYP/6-31G**/B3LYP/6-31G* results are given in Table 4.

Table 4. Singlet and triplet B3LYP/6-31G**/B3LYP/6-31G* energies for **25**, **27**, and **28** and singlet-triplet energy differences

molecule	B3LYP energy singlet [au]	ZPE singlet [au]	B3LYP energy triplet [au]	ZPE triplet [au]	ΔE _{TS} [kcal/mol]
25 ^[a]	–193.9576082	0.089649	–193.9295710	0.087648	16.3
27	–231.9856058	0.094862	–231.9610781	0.094529	14.4
28	–232.0260200	0.095036	–231.9809648	0.093343	28.0

^[a] QCISD/6-31G**/QCISD/6-31G* energy for **25**: E = –193.3206890.

27 and **28** have C₂ symmetry. The calculated structures of **27** and of **28** show some interesting features, which are collected in Table 5.

Table 5. Selected structural parameters of **27** and **28**, calculated by B3LYP/6-31G*

molecule	C1–C4 [Å]	C1–C2 [Å]	C2–C3 [Å]	C2–C4 [Å]	C3–C4 [Å]	<1–4–2–3 [°]	<2–1–4–5 [°]
27	1.680	1.522	1.524	1.441	1.525	113.9	161.9
28	1.911	1.459	1.555	1.506	1.476	116.9	180.0

The strongly elongated bond length C1–C4 of **27** and **28** opens the possibility for a triplet ground state. As seen from the data of Table 4, this is not the case. **25**, **27**, and **28** have singlet ground states, with triplet states energetically well above the singlet states.

Summing up, our calculations have revealed that 1,6-dehydroquadricyclane **4** is a molecule well in reach of experimental verification and that the parent hydrocarbons of **4**, the tetracycles **27** and **28**, are interesting targets for the synthetic chemist.

We thank the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* for financial support of this investigation.

Experimental Section

For analytical instruments and general procedures, see ref.^[17].

I. Starting Materials

Bicyclo[2.2.1]heptadiene (**11**), *N,N,N',N'*-tetramethylethylenediamine (TMEDA), *n*-butyllithium (BuLi), *tert*-butyllithium (*t*BuLi), potassium *tert*-butoxide (KO^{*t*}Bu), and chlorotrimethylsilane were commercial products.

2-Bromo-1,3,2-dioxaphoshole (16a)^[14]: Catechol (110.6 g, 1.004 mol) was mixed with PBr₃ (285.2 g, 1.05 mol) with stirring in an ice bath under nitrogen. Water (1.0 ml) was added as a catalyst, which caused a vigorous reaction with formation of gaseous HBr. As soon as the HBr formation slowed down, the mixture was heated in an oil bath to 120°C for 5 h. Purification of **16a** was carried out by distillation with a 15-cm Vigreux column, which led to a colorless oil (185.3 g, 84%) of b.p. 99–102°C/10 Torr (ref.^[14] b.p. 105–106/13 Torr). **16a** was stored under nitrogen at –15°C and converted with Br₂ into **16b** immediately prior to reaction.

II. Synthesis of 1,6-Dibromotetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane **6**

1. *2-exo-5-syn-Bicyclo[2.2.1]heptanediol (12)*^[9]. – *a. With the Borane–THF Complex*: A solution of borane in THF (225 ml, 1.80 M, 0.405 mol) was added dropwise to a solution of **11** (72.9 g, 0.791 mol) in THF (150 ml), cooled in an ice-bath. After stirring for 3 h at room temp., the colorless, gelatinous mixture was treated with 3 N NaOH (260 ml) and subsequently with H₂O₂ (30%, 150 ml), which were slowly added with stirring and cooling in an ice bath. The solution was then kept under reflux for 1 h and stirred for 16 h at room temperature. After addition of water (1.0 l) and ether (1.0 l), the ether layer was separated. It contained *exo*-bicyclo[2.2.1]hept-5-ene-2-ol (**13**) (23.0 g, 26%). The water layer was continuously extracted with ether for 3 d with a perforator. After removal of the solvent, **12** (35.0 g, 35%) was isolated as colorless crystals of m.p. 168–170°C^[24] (ref.^[10] 181–183°C).

b. With 9-Borabicyclo[3.3.1]nonane (9-BBN): A solution of **11** (9.20 g, 99.8 mmol) in THF (100 ml) was added dropwise to a solution of 9-BBN in THF (400 ml, 0.50 M, 200 mmol). After stirring for 2 h at room temperature, oxidative workup was carried out by addition of ethanol (160 ml), NaOH (6 N, 40 ml), and H₂O₂ (30%, 80 ml). Following the procedure as described in 1.a., the ether layer contained **13** (1.34 g, 12%), and the water layer a mixture of **12** (1.92 g, 15%) and cyclooctane-1,5-diol (3.10 g), which could not be separated by distillation or crystallization.

c. With the Borane–Dimethyl Sulfide Complex: The complex BH₃·SMe₂ (50 ml, 500 mmol), dissolved in hexane (250 ml), was added within 30 min to a solution of **11** (46.0 g, 499 mmol) which

was kept in an ice bath. The white suspension was stirred for 3 h at room temperature. After oxidation (500 ml of ethanol, 150 ml of 3 N NaOH, 168 ml of 30% H₂O₂), workup II.1.a. afforded **13** (10.3 g, 19%) and **12** (18.4 g, 29%). **12** was contaminated by dimethyl sulfoxide (DMSO, 15.0 g), which could not be removed by distillation or sublimation.

2. *Bicyclo[2.2.1]heptane-2,5-dione (14)*: Compound **14** was obtained by chromic acid oxidation of diol **12** following closely the procedure of Hawkins et al.^[10], which furnished **14** in 39% yield as a waxy white solid. The ¹H- and ¹³C-NMR spectra of **14** were similar to those reported in the literature^{[10][25]}.

3. *1,6-Dibromotetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (6)*. — *a. Reaction of 14 with 2,2,2-Tribromo-1,3,2-benzodioxaphosphol (16b)*: Bromine (21.6 g, 135 mmol) was added dropwise with stirring to a solution of **16a** (32.8 g, 149 mmol) in CH₂Cl₂ (40 ml) cooled in an ice bath and stirring was continued for 1 h at room temperature. The solution was again cooled in an ice bath and diketone **14** (8.12 g, 65.4 mmol) in CH₂Cl₂ (40 ml) was added and the mixture kept under reflux for 20 h. The developing gaseous HBr was carried into a 2 N NaOH solution with a slow nitrogen stream. The solution was diluted with CH₂Cl₂ (100 ml) and slowly pored into an ice-cooled 2 N soda solution. After separation of the organic phase, extraction of the water layer twice with 150 ml of CH₂Cl₂ and extraction of the combined CH₂Cl₂ phases twice with 100 ml of 2 N NaOH the solution was dried with MgSO₄, the solvent removed in vacuo and the residue analyzed by NMR spectroscopy from which the formation of a mixture of 2,5,5-tribromobicyclo[2.2.1]hept-2-ene (**17**) and 2,2,5,5-tetrabromobicyclo[2.2.1]heptane (**18**) could be deduced. Separation was achieved by distillation of **17**, which was removed at 40°C/0.001 Torr and condensed as a colorless liquid (13.2 g, 61%), whereas **18** was isolated by sublimation at 80°C/0.001 Torr and further purified by crystallization from hexane to give white crystals (2.43 g, 9%) of m.p. 148°C.

17: IR (film): $\tilde{\nu}$ = 2989 cm⁻¹, 1581, 1442, 1404, 1261, 1208, 959, 683. — ¹H NMR (400 MHz, CDCl₃): δ = 1.86 (m, 1 H, 7-H), 2.00–2.12 (m, 2 H, 2-, 6-H₂), 2.52 (m, 1 H, 7-H), 2.98 (m, 1 H, 1-H), 3.65 (m, 1 H, 4-H), 6.18 (m, 1 H, 3-H). — ¹³C NMR (100 MHz, CDCl₃): δ = 46.68 (t), 50.90 (t), 51.58 (d), 62.73 (d), 63.45 (s), 129.58 (s), 134.08 (d). — MS (70 eV); *m/z* (%): 335 (7), 333 (20), 331 (21) [M⁺], 329 (7), 253 (16), 251 (29), 249 (15), 171 (24), 169 (22), 79 (100).

18: IR (film): $\tilde{\nu}$ = 1463 cm⁻¹, 1432, 1264, 984, 875, 768, 685, 662. — ¹H NMR (400 MHz, CDCl₃): δ = 2.39 (m, 2 H, 7-H₂), 2.93 (m, 2 H, *endo*-2-, -6-H), 3.05 (m, 2 H, *exo*-2-, -6-H), 3.33 (m, 2 H, 1-, 4-H). — ¹³C NMR (100 MHz, CDCl₃): δ = 35.55 (t), 54.61 (t, 2 C), 58.22 (d, 2 C), 65.58 (s, 2 C). — MS (70 eV); *m/z* (%): 335 (28), 333 (95), 331 (100) [M⁺ – Br], 329 (31), 253 (8), 251 (15), 249 (7), 171 (26), 169 (22). — C₇H₈Br₄ (411.8): calcd. C 20.42, H 1.96; found C 20.70, H 2.01.

This reaction was repeated several times; in some experiments, the liquid **17** contained a small amount (< 5%) of 2,2,5-tribromonortricyclane (**19**), which could not be separated from **17**.

19: ¹³C NMR (100 MHz, CDCl₃): δ = 24.43 (d), 29.97 (s), 33.16 (t), 37.23 (d), 40.91 (t), 49.88 (d), 65.73 (s).

b. 2,5-Dibromobicyclo[2.2.1]hepta-2,5-diene (20): A solution of KO^tBu (22.9 g, 204 mmol) in DMSO (50 ml) was added dropwise with stirring to a solution of a mixture of **17** (14.5 g, 43.8 mmol) and **18** (5.00 g, 12.1 mmol) in DMSO (50 ml), cooled in an ice bath. After 20 h at room temperature, water (50 ml) was added and the mixture extracted five times with pentane. Separation of the phases was a slow process, even after addition of a saturated NaCl

solution. The combined pentane phases were extracted six times with water (500 ml) and dried with MgSO₄. After removal of the solvent, the oily residue was purified by distillation, affording **20** (9.37 g, 67%) as a pale yellow liquid of b.p. 30°C/0.001 Torr. — IR (film): $\tilde{\nu}$ = 2980 cm⁻¹, 2951, 1335, 1285, 1276. — ¹H NMR (400 MHz, CDCl₃): δ = 2.35 (m, 2 H, 7-H₂), 3.51 (m, 2 H, 1-, 4-H), 6.97 (m, 2 H, 3-, 6-H). — ¹³C NMR (100 MHz, CDCl₃): δ = 59.62 (d), 72.62 (t), 136.53 (s), 137.86 (d). — MS (70 eV), *m/z* (%): 171 (100), 169 (10), 146 (89), 90 (67). — C₇H₆Br₂ (249.9): calcd. C 33.64, H 2.42; found C 33.20, H 2.55.

c. Synthesis of 6: A solution of **20** (5.50 g, 22.0 mmol) and acetophenone (132 mg, 1.10 mmol) in ether (100 ml) with a 150-W mercury high-pressure lamp for 24 h in a glass apparatus. After removal of the solvent and distillation of the oily residue (25°C/0.001 Torr), the distillate was further purified by preparative layer chromatography (plc) (Merck, 2 mm, neutral Al₂O₃ 60 F₂₅₄) giving rise to **6** (4.46 g, 81%) as colorless liquid. — IR (film): $\tilde{\nu}$ = 2935 cm⁻¹, 2859, 1759, 1336, 1258, 1201. — ¹H NMR (400 MHz, CDCl₃): δ = 1.98 (dt, *J* = 5.3 Hz, *J* = 1.3 Hz, 2 H, 2-, 4-H), 2.13 (t, *J* = 1.3 Hz, 2 H, 3-H₂), 2.55 (d, *J* = 5.3 Hz, 2 H, 5-, 7-H). — ¹³C NMR (100 MHz, CDCl₃): δ = 30.93 (s), 31.43 [t, ¹*J*(¹³C¹H) = 135 Hz], 33.31 [d, ¹*J*(¹³C¹H) = 172 Hz], 36.70 [d, ¹*J*(¹³C¹H) = 195 Hz]. — MS (70 eV), *m/z* (%): 252 (18), 250 (33) [M⁺], 248 (15), 171 (100), 169 (92), 146 (85), 144 (88). — C₇H₆Br₂ (249.9): calcd. C 33.64, H 2.42; found C 33.40, H 2.60.

4. *Reactions of 6 with Organolithium Bases*. — *a. 6 and 5.0 equiv. of tBuLi*: A solution of *t*BuLi in pentane (5.2 ml, 8.4 mmol) was added dropwise with stirring to a solution of **6** (420 mg, 1.68 mmol) in ether (20 ml), which was kept at –78°C. The solution was stirred for 2 h at –78°C, warmed to 0°C, and carefully hydrolyzed with water. The ether phase was dried, the solvent removed and the residual oil analyzed by NMR spectroscopy which indicated the formation of polymeric material and of quadricyclane (**21a**).

b. 6 and 4.0 equiv. of tBuLi: A solution of *t*BuLi in pentane (10.6 ml, 16.9 mmol) was added dropwise with stirring to a solution of **6** (1.06 g, 4.24 mmol) in ether (10 ml), which was kept at –78°C. The solution was stirred for 1 h at –78°C and carefully hydrolyzed with 2 ml of D₂O. Distillative workup afforded [1,6-D₂]tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (**21d**) (349 mg, 87%) as colorless liquid, b.p. 25°C (bath)/12 Torr.

In the ¹H-NMR spectrum of **21d** the ratio of the signal areas of the multiplets at δ = 1.35–1.48 (2-, 4-, 5-, 7-H) and at δ = 2.02 (3-H₂) was 4.0:1, indicating a D₂ incorporation > 90%. — MS (70 eV); *m/z* (%): 94 (24) [M⁺], 93 (66), 92 (77), 57 (100).

c. 6 and 2.0 equiv. of tBuLi: A solution of *t*BuLi in pentane (6.85 ml, 11.0 mmol) was added dropwise with stirring to a solution of **6** (1.37 g, 5.48 mmol) in ether (10 ml), which was kept at –78°C. The solution was stirred for 2 h at –78°C, warmed to 0°C, and carefully hydrolyzed with water. The ether phase was dried, the solvent removed and the residual oil analyzed by NMR spectroscopy which indicated the formation of polymeric material and of 1-bromotetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (**21e**). Distillation of the oily residue afforded **21e** as a colorless liquid of b.p. 25°C (bath)/0.001 Torr, which was further purified by plc leading to 0.496 g (53%) of **21e**. — ¹H NMR (400 MHz, CDCl₃): δ = 1.54 (m, 1 H, 4-H), 1.77 (m, 1 H, 6-H), 1.85 (m, 1 H, 2-H), 1.95 (m, 1 H, 3-H), 2.05 (m, 1 H, 7-H), 2.09 (m, 1 H, 5-H), 2.21 (m, 1 H, 3-H). — ¹³C NMR (100 MHz, CDCl₃): δ = 15.03 (d), 24.50 (d), 25.11 (d), 27.16 (d), 31.58 (t), 32.38 (d), 34.28 (s).

The same experiment was repeated, but workup was carried out with deuterium oxide instead of water. In the ¹H-NMR spectrum

(CDCl₃) of the isolated [6-D]**21e** the signal at $\delta = 1.77$ was absent. Apart from minor chemical shift differences due to different concentrations, the ¹³C-NMR spectrum of [6-D]**21e** was identical to that of **21e** with the exception of the signal for C-6 which appeared at $\delta = 15.26$ as a low intensity triplet. – [6-D]**21e**: MS (70 eV); *m/z* (%): 173 (12), 171 (12) [M⁺], 146 (10), 144 (10), 92 (100), 57 (72). – C₇H₆D⁷⁹Br: calcd. 170.9793; found 170.9794 (HRMS).

d. **6**, 2.0 equiv. of *t*BuLi and TMEDA: A solution of *t*BuLi in pentane (3.7 ml, 5.9 mmol) was added dropwise with stirring to a solution of **6** (740 mg, 2.96 mmol) in ether (10 ml), which was kept at –78°C. The solution was stirred for 1 h at –78°C, charged at –50°C with *N,N,N',N'*-tetramethylethylenediamine (TMEDA, 347 mg, 2.97 mmol), warmed to 0°C and carefully hydrolyzed D₂O. Distillative workup afforded [6-D]**21e** (215 mg, 43%) of b.p. 10°C (bath)/0.01 Torr.

The same reaction with 1.0 equiv. of LiBr instead of TMEDA led also only to [6-D]**21e** and polymeric material.

In addition to these reactions, **6** was treated with BuLi (3.0 and 6.0 equiv.), and a mixture of BuLi and *t*BuLi. In all experiments considerable amounts of polymeric material and **21e** were formed.

e. *1-Bromo-6-lithiotetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (7)*: A solution of **6** (34.0 mg, 0.136 mmol) in [D₈]THF (1.5 ml) was transferred into a NMR tube, cooled to –78°C and carefully mixed with a solution of *t*BuLi (0.17 ml, 0.27 mmol) in pentane. All volatile parts were removed at –78°C/0.001 Torr. The residue was dissolved in [D₈]THF and the ¹³C-NMR spectrum of the solution recorded at –80°C, –60°C, –40°C, 0°C, and room temperature. – ¹³C NMR (100 MHz, CDCl₃): $\delta = 11.58$ (s, C-6), 30.49 (d, C-4), 30.71 (d, C-7), 31.95 (d, C-5), 32.05 (d, C-2), 33.54 (t, C-3), 34.50 (s, C-1).

In the spectrum taken at room temperature, the signals of **7** could not be recognized. Many new signals had appeared.

f. *1,6-Dilithiotetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (21c)*: Compound **6** (23.0 mg, 0.092 mmol) and *t*BuLi (0.368 mmol) were allowed to react as described under 4.d. The [D₈]THF solution of **21c** was again analyzed by ¹³C-NMR spectroscopy at –80°C, –60°C, –40°C, 0°C, and room temperature. – ¹³C NMR (100 MHz, CDCl₃): $\delta = 14.87$ (d, C-5, -7), 16.75 (s, C-1, -6), 23.08 (d, C-2, -4), 32.96 (t, C-3). – In the spectrum taken at room temperature, the signals of **21c** could not be recognized. Many new signals had appeared.

5. *Reactions of 7 and 21c*. – a. *1-Bromo-6-trimethylsilyltetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (21f)*: Compound **6** (1.08 g, 4.32 mmol) in ether (10 ml) was mixed at –78°C with *t*BuLi (5.40 ml, 8.64 mmol). The pale yellow solution was stirred for 1 h at –78°C and charged with chlorotrimethylsilane (428 mg, 3.94 mmol). The mixture was allowed to warm to room temperature and hydrolyzed with ice water. The organic material was extracted with ether. Distillative workup afforded **21f** [25°C(bath)/0.01 Torr], which was further purified by plc to give **21f** (610 mg, 64%) as colorless liquid. – IR (film): $\tilde{\nu} = 2956$ cm^{–1}, 2897, 2867, 1275, 1249, 1124, 852, 837, 751. – ¹H NMR (400 MHz, CDCl₃): $\delta = -0.05$ (s, 9 H, SiMe₃), 1.45 (m, 1 H, 5-H), 1.77 (m, 1 H, 7-H), 1.89–1.96 (m, 3 H, 3-H₂, 4-H), 2.29 (m, 1 H, 2-H). – ¹³C NMR (100 MHz, CDCl₃): $\delta = -2.24$ (q), 13.76 (s), 25.61 (d), 28.95 (d), 31.37 (d), 31.57 (d), 32.59 (t), 34.25 (s). – MS (70 eV); *m/z* (%): 244 (14), 242 (13) [M⁺], 146 (95), 144 (98), 83 (35), 73 (100). – C₁₀H₁₅⁷⁹BrSi: calcd. 242.0126; found 242.0096 (HRMS).

b. *1,6-Bistrimethylsilyltetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (23a)*: Compound **6** (1.30 g, 5.20 mmol) in ether (8.0 ml) was mixed at

–78°C with *t*BuLi (13.0 ml, 20.8 mmol). The yellow solution was stirred for 1 h at –78°C and charged with chlorotrimethylsilane (1.07 g, 9.85 mmol). The mixture was allowed to warm to room temperature, stirred for 16 h and hydrolyzed with ice water. The organic material was extracted with ether. Distillative workup afforded a colorless oil [b.p. 10°C (bath)/0.01 Torr], which was further purified by plc to give **23a** (1.07 g, 92%) as a colorless liquid. – IR (film): $\tilde{\nu} = 3044$ cm^{–1}, 2954, 2931, 2856, 1261, 1248. – ¹H NMR (400 MHz, CDCl₃): $\delta = -0.06$ (s, 18 H, SiMe₃), 1.22 (d, *J* = 4.0 Hz, 2 H, 5-, 7-H), 1.26 (dt, *J* = 4.0 Hz, *J* = 1.4 Hz, 2 H, 2-, 4-H), 2.08 (t, *J* = 1.4 Hz, 2 H, 3-H₂). – ¹³C NMR (100 MHz, CDCl₃): $\delta = -2.24$ (q), 12.13 (s), 18.58 (d), 27.11 (d), 33.76 (t). – MS (70 eV); *m/z* (%): 226 (2) [M⁺], 221 (7), 148 (42), 73 (100). – C₁₃H₂₄Si₂ (236.5): calcd. C 66.02, H 10.23; found C 66.16, H 10.27.

c. *1,6-Dimethyltetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (23b)*: Compound **6** (910 mg, 3.64 mmol) in ether (10 ml) was mixed at –78°C with *t*BuLi (8.5 ml, 14.4 mmol). The yellow solution was stirred for 1 h at –78°C, dimethyl sulfate (933 mg, 7.40 mmol) was added and stirring continued for 16 h at room temperature. After hydrolysis with 2 N ammonia, the ether layer was separated and dried with MgSO₄. Distillative workup afforded **23b** (240 mg, 55%) as a colorless liquid, b.p. 45°C (bath)/40 Torr. – ¹H NMR (400 MHz, CDCl₃): $\delta = 1.21$ (s, 6 H, Me), 1.30 (m, 4 H, 2-, 4-, 5-, 7-H), 1.88 (m, 2 H, 3-H₂). – ¹³C NMR (100 MHz, CDCl₃): $\delta = 15.13$ (q), 21.63 (s), 23.24 (d), 30.82 (d), 32.08 (t). – MS (70 eV); *m/z* (%): 120 (48) [M⁺], 105 (57), 91 (21), 80 (100). – C₉H₁₂: calcd. 120.0939; found 120.0934 (HRMS).

d. *Dimethyl Bicyclo[2.2.1]hepta-2,5-diene-2,5-dicarboxylate (24c) and Dimethyl Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane-1,6-dicarboxylate (23c)*: Compound **6** (1.40 g, 5.60 mmol) in ether (10 ml) was mixed at –78°C with *t*BuLi (14.0 ml, 22.4 mmol). The yellow solution was stirred for 1 h at –78°C, methyl chloroformate (1.04 g, 11.0 mmol) was added and stirring continued for 16 h at room temperature. After hydrolysis with 2 N ammonia, the ether layer was separated and dried with MgSO₄. Distillative workup afforded **24c** (510 mg, 45%) as a colorless liquid, b.p. 45°C (bath)/0.001 Torr. – IR (film): $\tilde{\nu} = 3010$ cm^{–1}, 2953, 1747, 1719, 1585, 1397, 1260, 1153, 1063, 986, 877, 770. – ¹H NMR (400 MHz, CDCl₃): $\delta = 2.27$ (m, 2 H, 7-H₂), 3.68 (s, 6 H, Me), 4.04 (m, 2 H, 1-, 4-H), 7.75 (m, 2 H, 3-, 6-H). – ¹³C NMR (100 MHz, CDCl₃): $\delta = 28.48$ (q), 51.53 (d), 73.36 (t), 148.32 (s), 155.14 (d), 164.74 (s). – MS (70 eV); *m/z* (%): 208 (50) [M⁺], 193 (51), 177 (75), 149 (91), 57 (100). – C₁₁H₁₂O₄: calcd. 208.0775; found 208.0735 (HRMS).

Photocyclization of 24c: Compound **24c** (100 mg, 0.480 mmol) was irradiated in 15 ml of ether with a mercury high-pressure lamp at –12°C for 24 h in the presence of acetophenone (2.88 mg, 0.0240 mmol). After removal of the volatile products in vacuo, **23c** (78.0 mg, 78%) was isolated as a colorless oil. – ¹H NMR (400 MHz, CDCl₃): $\delta = 2.43$ (dt, *J* = 4.7 Hz, *J* = 1.1 Hz, 2 H, 2-, 4-H), 2.61 (t, *J* = 1.1 Hz, 2 H, 3-H₂), 2.86 (d, *J* = 4.7 Hz, 2 H, 5-, 7-H), 3.67 (s, 6 H, Me). – ¹³C NMR (100 MHz, CDCl₃): $\delta = 26.88$ (s), 31.58 (t), 51.64 (q), 30.17 (d), 34.71 (d), 171.87 (s).

e. *1,6-Diiodotetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (23d)*: Compound **6** (1.00 g, 4.00 mmol) in ether (8 ml) was mixed at –78°C with *t*BuLi (10.0 ml, 16.0 mmol). The solution was stirred for 1 h at –78°C, iodine cyanide (1.20 g, 7.85 mmol, freshly crystallized from chloroform) was added, the mixture, which was protected against daylight, warmed to room temperature, and after stirring for 2 h hydrolyzed with water. 20 ml of a 2 N sodium thiosulfate solution was added, the ether layer separated, dried with MgSO₄ and the solvent removed in vacuo from a 0°C bath. According to NMR

spectroscopy, the residual oil (0.84 g, 62%) was a 85:15 mixture of **23d** and 2,5-diiodobicyclo[2.2.1]hepta-2,5-diene (**24d**). Further purification of **23d** was carried out with plc.

23d: ^1H NMR (400 MHz, CDCl_3): δ = 2.00 (dt, J = 4.9 Hz, J = 1.7 Hz, 2 H, 2-, 4-H), 2.20 (t, J = 1.7 Hz, 2 H, 3- H_2), 2.35 (d, J = 4.9 Hz, 2 H, 5-, 7-H). – ^{13}C NMR (100 MHz, CDCl_3): δ = 15.20 (s), 32.26 (t), 33.86 (d), 36.88 (d). – MS (70 eV); m/z (%): 344 (44) [M^+], 217 (53), 192 (47), 91 (100), 90 (49) 65 (85). – $\text{C}_7\text{H}_6\text{I}_2$: calcd. 343.8559; found 343.8573 (HRMS).

24d: ^1H NMR (400 MHz, CDCl_3): δ = 2.22 (m, 2 H, 7- H_2), 3.55 (t, 2 H, 1-, 4-H), 7.05 (m, 2 H, 3-, 6-H). – ^{13}C NMR (100 MHz, CDCl_3): δ = 63.77 (d), 72.95 (t), 104.59 (s), 146.84 (d).

The intended preparation of **23d** from **21c** was also carried out with iodine, iodine chloride, and 4-tolylsulfonyl iodide. In all cases the NMR spectra of the raw material indicated the formation of 2,5-diiodonorbornadiene (**24d**) in yields of 34%, 17%, and 25%.

f. 1,6-Dichlorotetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (23e): Compound **6** (1.03 g, 4.12 mmol) in ether (8 ml) was mixed at -78°C with $t\text{BuLi}$ (9.7 ml, 10.5 mmol). The solution was stirred for 1 h at -78°C , 4-tolylsulfonyl chloride (1.57 g, 8.23 mmol) was added, the mixture allowed to warm to room temperature, and after stirring for 20 h hydrolyzed with water. The ether layer was separated, dried with MgSO_4 and the solvent removed in vacuo. The oily residue was distilled at 25°C (bath)/0.01 Torr, the distillate further purified by plc to give **23e** (320 mg, 48%) as a colorless oil. – ^1H NMR (400 MHz, CDCl_3): δ = 2.02 (dt, J = 5.4 Hz, J = 1.4 Hz, 2 H, 2-, 4-H), 2.12 (t, J = 1.4 Hz, 2 H, 3- H_2), 2.54 (d, J = 5.4 Hz, 2 H, 5-, 7-H). – ^{13}C NMR (100 MHz, CDCl_3): δ = 30.95 (t), 32.75 (d), 36.17 (d), 43.55 (s).

6. Reactions of 23d and 21f Towards the Generation of 4. – a. 23d and $t\text{BuLi}$: Compound **23d** (0.860 g, 2.50 mmol) in ether (6 ml) was mixed at -78°C with $t\text{BuLi}$ in pentane (6.0 ml, 10.2 mmol). The solution was stirred for 1 h at -78°C , allowed to warm to room temperature, and hydrolyzed with D_2O . The ether layer was separated, dried with MgSO_4 and the solvent removed in vacuo. The oily residue was analyzed by NMR spectroscopy which showed besides polymeric material the presence of **21d**.

b. 21f and Cesium Fluoride: A solution of cesium fluoride (2.00 g, 13.2 mmol) in DMSO (20 ml) was added dropwise at room temperature to a solution of **21f** (400 mg, 1.64 mmol) in DMSO. After 24 h at room temperature, the reaction mixture was poured on ice/water, the organic material extracted with ether, and the ether layer extracted with water. After drying with MgSO_4 and removal of the solvent in vacuo, NMR analysis indicated the presence of unreacted **21f** accompanied by some 2-bromo-5-trimethylsilylbicyclo[2.2.1]heptane (**22f**).

7. Ab Initio Calculations: Ab initio calculations were performed with the GAUSSIAN 94 program package^[16]. Calculations employed the 6-31G* basis set. Spin unrestricted wave functions were used for triplets, spin restricted wave functions for singlets. DFT computations were carried out using the B3LYP keyword^[26]. Geometries were optimized by use of analytic gradients. The nature of the stationary points was investigated by calculation of the vibrational frequencies. Zero-point energies, calculated at the B3LYP/

6-31G* level of theory were corrected by a scaling factor of 0.9804^[18].

- [1] Taken in part from: S. Glück-Walther, Dissertation, Univ. München, 1993.
- [2] P. M. Warner, *Chem. Rev.* **1989**, 89, 1067–1093, and references therein.
- [3] G. Szeimies in *Advances in Strain in Organic Chemistry*, vol. 2 (Ed.: B. Halton), Jai Press, London, 1992, p. 1–55.
- [4] O. Baumgärtel, G. Szeimies, *Chem. Ber.* **1983**, 116, 2180–2204.
- [5] O. Baumgärtel, J. Harnisch, G. Szeimies, M. Van Meerse, G. Germain, J.-P. Declercq, *Chem. Ber.* **1983**, 116, 2205–2218.
- [6] J. Kennedoff, K. Polborn, G. Szeimies, *J. Am. Chem. Soc.* **1990**, 112, 6117–6118.
- [7] J. Podlech, K. Polborn, G. Szeimies, *J. Org. Chem.* **1993**, 58, 4113–4117.
- [8] J. Schäfer, G. Szeimies, *Tetrahedron Lett.* **1990**, 2263–2264.
- [9] G. Zweifel, K. Nagase, H. C. Brown, *J. Am. Chem. Soc.* **1962**, 84, 183–189.
- [10] R. T. Hawkins, R. S. Hsu, S. G. Wood, *J. Org. Chem.* **1978**, 43, 4648–4650.
- [11] K. Omura, D. Swern, *Tetrahedron* **1978**, 34, 1651–1660; see also: A. J. Mancuso, S. L. Huang, D. Swern, *J. Org. Chem.* **1978**, 43, 2480–2482.
- [12] M. Hirano, M. Oose, T. Morimoto, *Bull. Chem. Soc. Jpn.* **1991**, 64, 1046–1047.
- [13] R. H. Shapiro, *Org. React.* **1976**, 23, 405–507.
- [14] H. Gross, U. Karsch, *J. Prakt. Chem.* **1965**, 29, 315–318.
- [15] H.-G. Zoch, G. Szeimies, R. Römer, G. Germain, J.-P. Declercq, *Chem. Ber.* **1983**, 116, 2285–2310.
- [16] M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, *GAUSSIAN 94* (Revision D.3), Gaussian, Inc., Pittsburgh PA, 1995.
- [17] T. Ziegler, *Chem. Rev.* **1991**, 91, 651–667; J. Labanowski, J. Adzelm (Eds.), *Density Functional Methods in Chemistry*, Springer, Berlin, 1991; R. G. Parr, W. Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, New York, 1989.
- [18] M. J. Frisch, A. Frisch, J. B. Foresman, *GAUSSIAN 94 User's Reference*, Gaussian Inc., Pittsburgh, 1995, and references therein.
- [19] C. J. Cramer, F. J. Dulles, J. W. Storer, S. E. Worthington, *Chem. Phys. Lett.* **1994**, 218, 387–394; H. M. Sulzbach, E. Bolton, D. Lenoir, P. v. R. Schleyer, H. F. Schaefer III, *J. Am. Chem. Soc.* **1996**, 118, 9908–9914; P. R. Schreiner, W. L. Karney, P. v. R. Schleyer, W. T. Borden, T. P. Hamilton, H. F. Schaefer III, *J. Org. Chem.* **1996**, 61, 7030–7039.
- [20] See for example: E. Goldstein, B. Beno, K. N. Houk, *J. Am. Chem. Soc.* **1996**, 118, 6036–6043; J. Cioslowski, Y. Liu, M. Martinov, P. Piskorz, D. Moncrieff, *J. Am. Chem. Soc.* **1996**, 118, 5261–5264; J. C. Poutsma, J. J. Nash, J. A. Paulino, R. R. Squires, *J. Am. Chem. Soc.* **1997**, 119, 4686–4697.
- [21] J. B. Foresman, A. Frisch, *Exploring Chemistry with Electronic Structure Methods*, 2nd ed., Gaussian, Inc. Pittsburgh, 1996, p. 64.
- [22] K. B. Wiberg, N. McMurdie, J. V. McClusky, C. M. Hadad, *J. Am. Chem. Soc.* **1993**, 115, 10653–10657.
- [23] F. Alber, G. Szeimies, *Tetrahedron Lett.* **1994**, 4093–4096.
- [24] According to Hawkins et al.^[10] a small amount of the isomeric bicyclo[2.2.1]heptane-2,6-diol might be present and responsible for the melting point depression.
- [25] H. Ahlbrecht, M. Dietz, C. Schön, V. Baumann, *Synthesis* **1991**, 133–140.
- [26] A. D. Becke, *J. Chem. Phys.* **1993**, 98, 5648–5652.

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