

## Fortschrittsbericht · Progress Report

## Dehydroquadricyclanes [1]

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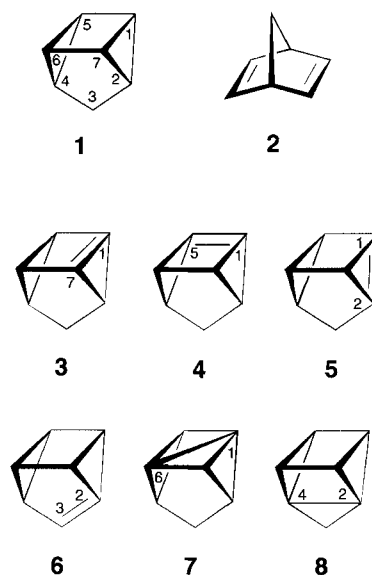
*Dedicated to Prof. Dr. K. B. Wiberg on the Occasion of his 70th Birthday*

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Tetracyclo[3.2.0.0<sup>2,7</sup>.0<sup>4,6</sup>]heptane (**1**, quadricyclane), a C<sub>7</sub>H<sub>8</sub> hydrocarbon with a strain energy of 78.7 kcal/mol [3] is easily accessible by photocyclization of norbornadiene **2** [4]. The enthalpy of isomerization to norbornadiene has been determined to be about 24 kcal/mol [5]. This molecular system has attained much attention by several groups of chemists. One particularly fascinating aspect is the ability of quadricyclane and its derivatives to act as storage for sun energy which can be released by rearrangement to the corresponding norbornadiene using transition metal ion catalysis [6].

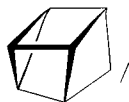
About 20 years ago we became interested in quadricyclane as a structurally rigid model compound which might allow the introduction of pyramidalized CC double bonds. In this overview we report on our results aiming at generating dehydroquadricyclanes **3–7** as reactive intermediates. Theoretical results concerning the stability of **8** are also included. In some cases, in which

trapping products could be isolated, the chemistry of these compounds is briefly presented [7].



Before the results of our experimental investigations are discussed, it is worth looking at the outcome of some ab initio MO calculations which were carried out for the dehydroquadricyclanes **3–8**, using the Gaussian 90 [8] and Gaussian 94 [9] program packages. The calculated  $E_{rel}$  are depicted in Table 1. The applied levels of theory have been Becke3LYP/6-31G\*\*/Becke3LYP/6-31G\*, TCSCF/6-31G\*\*/TCSCF/6-31G\*, and MP2/6-31G\*\*/MP2/6-31G\*. The numbers given in Table 1 are relative energies of the corresponding singlet states with respect to **3** in kcal/mol. The triplet states are high-

er in energy in all cases [10]. Vibrational analyses were carried out for the B3LYP/6-31G\* structures, giving positive frequencies for the model compounds indicating that these molecules are local minima on the  $C_7H_6$  energy hypersurface. There is one exception: the twisted bridgehead olefin **6** is a local energy minimum only at the TCSCF/6-31G\*//TCSCF/6-31G\* level of theory. The B3LYP/6-31G\* and MP2/6-31G\* calculations on **6** did not lead to a local energy minimum but to a rearranged framework of carbene structure **9**.



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In Figure 1, computer-generated B3LYP/6-31G\* structures including some interesting structural features are given for **3–5** and for **7** and **8**. The structure of **6** is based on TCSCF/6-31G\* calculations. Bond lengths are given in Å.

**Tab. 1**  $E_{rel}$  (kcal/mol) of dehydroquadricyclanes **3–8**

	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>
B3LYP/6-31G* <sup>a)</sup>	= 0.0	4.5	2.8	—	9.6	15.6
TCSCF/6-31G* <sup>b)</sup>	= 0.0	11.8	4.0	14.5	12.7	12.1
MP2/6-31G* <sup>c)</sup>	= 0.0	4.7	3.6	—	10.4	13.1

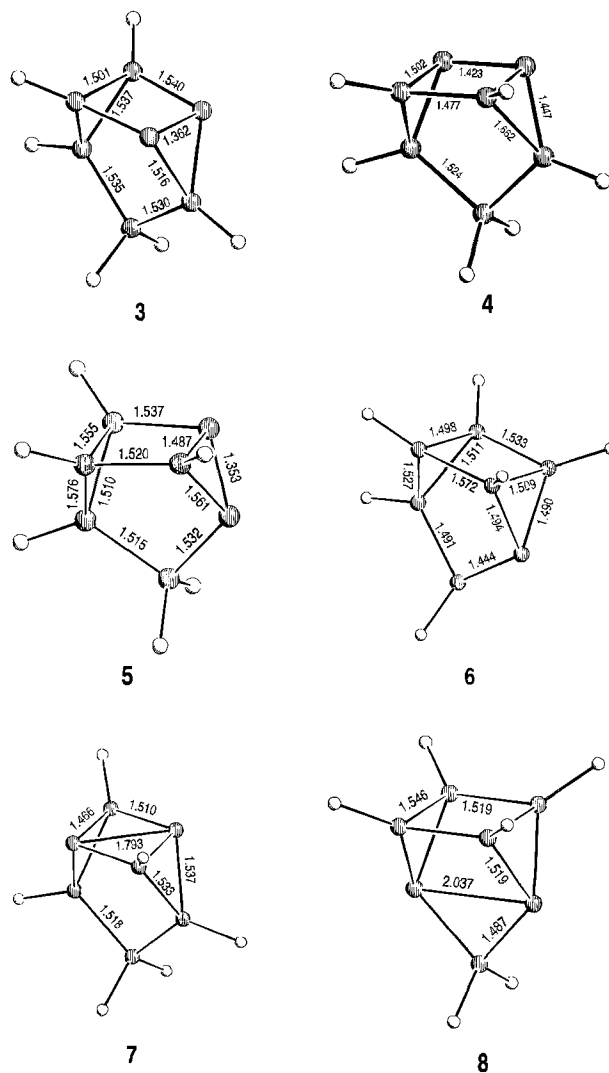
<sup>a)</sup> B3LYP/6-31G\*//B3LYP/6-31G\* energy of **3**: -270.1124892 a.u.; Zero-Point-energy (ZPE) of **3** 0.104470 a.u.; Scale factor for ZPE = 0.9804 [11].

<sup>b)</sup> Without ZPE correction.

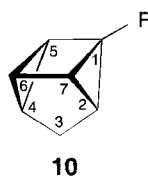
<sup>c)</sup> Without ZPE correction; MP2/6-31G\*//MP2/6-31G\* energy of **3**: -269.2267134 a.u.

## A. Metalation of Quadricyclane

The  $^{13}C$  NMR spectrum of **1** shows for the coupling constant  $^1J(^{13}C(1)-H) = 183$  Hz; therefore, metalation of this position by strong bases should be possible. Indeed, when **1** was treated with the butyllithium (BuLi)/tetramethylethylenediamine (TMEDA) complex at 20 °C for 48 hours in hexane, workup with deuterium oxide afforded [1-D]quadricyclane in 88% yield [12, 13]. Alternatively, metalation was also effected with BuLi/KO-*t*-Bu in hexane within 18 hours at 20 °C. 1-Quadricyclyllithium was treated with several electrophiles like acetone, tosyl bromide or tosyl chloride to give 1-quadricyclyl derivatives **10a**, **b** and **c** in yields of 77%, 26%, and 50% [12]. Following this route, 1-chloroquadricyclane **10c** is an easily accessible compound.



**Fig. 1** Computer generated structures of dehydroquadricyclanes **3–8**



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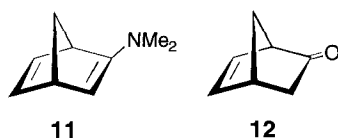
**Tab. 2** Yields of 1-substituted quadricyclanes **10**

<b>10</b>	R	Yield (%)	<b>10</b>	R	Yield (%)
<b>a</b>	C(CH <sub>3</sub> ) <sub>2</sub> OH	77	<b>g</b>	<i>t</i> -Bu	41
<b>b</b>	Br	26	<b>h</b>	Ph	32
<b>c</b>	Cl	50	<b>i</b>	(CH <sub>2</sub> ) <sub>2</sub> N	52
<b>d</b>	Me	36	<b>j</b>	Me <sub>2</sub> N	63
<b>e</b>	Bu	62	<b>k</b>	EtS	45

## B. 1,7-Dehydroquadricyclane 3

### 1. Trapping by Nucleophiles

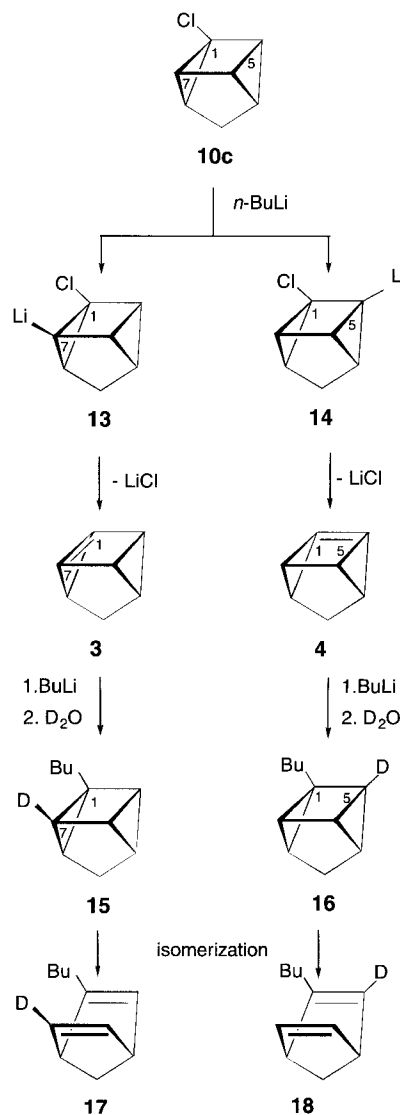
Our calculations indicate that 1,7-dehydroquadricyclane **3** is the most stable of the isomers under consideration. Based on our experience with bridgehead halo-substituted bicyclo[1.1.0]butanes [7], chloride **10c** seemed a particularly useful starting material for the generation of **3** by hydrogen chloride elimination. Indeed, reaction of **10c** with organolithium bases or lithium amides (at least 2.0 equivalents) gave rise to substituted quadricyclanes **10d** - **k** in reasonable yields (see Table 2). Whereas **10c** and lithium ethylthiolate did not give any **10k**, this thioether was formed in 45% yield when a mixture of LDA and LiSEt was used. Obviously, the presence of a strong base is a necessary condition for these substitution reactions to take place. 1-Dimethylaminoquadricyclane **10j** easily isomerized to the corresponding norbornadiene **11**, which was hydrolyzed to ketone **12** [12].



Some insight into the mechanism of these reactions was furnished by the reaction of **10c** with BuLi followed by workup with deuterium oxide and isomerization of the 1-butyl-[D]quadricyclane (35% yield) to the corresponding norbornandienes **17** and **18**. The ratio of these isomers was 83:17 [12]. A mechanistic rationalization of this result is given in Scheme 1:

The most important aspect of Scheme 1 is the formation of dehydroquadricyclanes **3** and **4**, which are formed by lithium chloride elimination of the metalated intermediates **13** and **14**. As the metalation step, in which **10c** is converted into **13** or **14** by BuLi, is certainly irreversible, the final ratio of 83:17 for products **17** and **18** is determined by the rates of metalation of C-7 versus C-5 in **10c**. The **17**:**18** (or **15**:**16**) ratio is not related to the differences in energy of **3** and **4**. **3** and **4** are pyramidalized bridgehead olefins, which in relation to unstrained alkenes, have high-lying HOMO's and low-lying LUMO's. The outstanding chemical property of pyramidalized olefins is, due to their low-lying LUMO, the ability to react with nucleophilic reagents.

A second set of experiments is also in accordance with Scheme 1. Optically active **10c\***, was obtained from ketone **12** (ee 50%) as indicated in Scheme 2. **12\*** was synthesized from norbornadiene by hydroboration with l-(–)-diisopinocampheylborane (obtained by diborane addition to (+)- $\alpha$ -pinene), followed by Jones oxidation of bicyclo[2.2.1]hept-5-ene-2-ol [12].

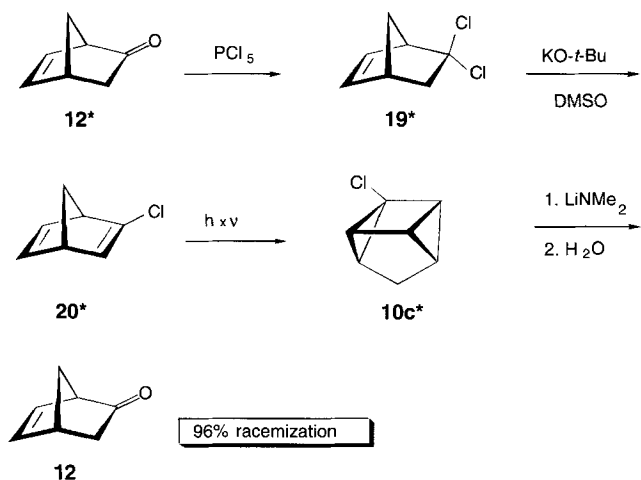


Scheme 1

The reaction of optically active **10c\*** with LiNMe<sub>2</sub> afforded after aqueous workup ketone **12**, which was nearly fully racemized. This result is well explained with the symmetrical structures of **3** and **4** as intermediates.

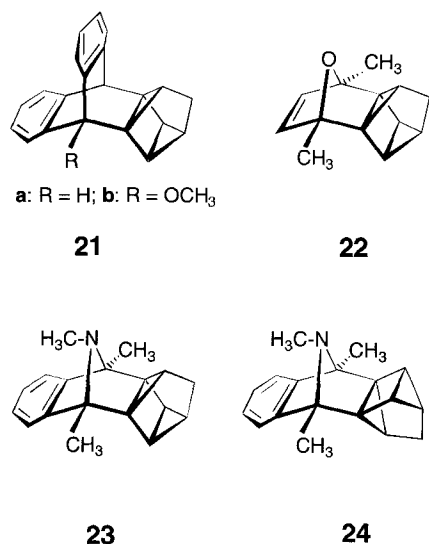
### 2. Trapping of 3 with Reactive 1,3-Dienes

Most convincing evidence for the existence of 1,7-dehydroquadricyclane is furnished by Diels-Alder trapping experiments. When **10c** was treated with lithium 2,2,6,6-tetramethylpiperidide or lithium diisopropylamide in THF in 60 °C bath in the presence of anthracene, 9-methoxyanthracene, 2,5-dimethylfuran, or 1,2,3-trimethylisoindole, the adducts **21a**, **21b**, **22**, and **23** were isolated in yields of 28%, 38%, 45%, and 63%. The structure of the adducts was based on their NMR spectra; for **21a**, the x-ray structure was determined.



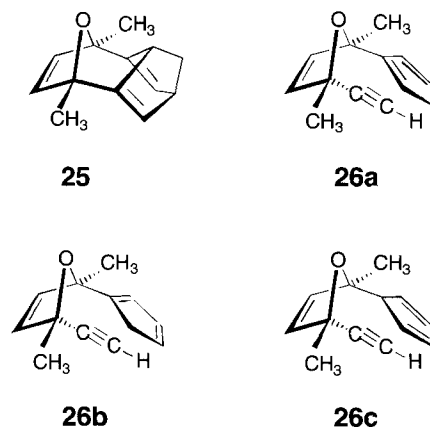
Scheme 2

Two aspects need further comment: a) From the structure of the adducts it is clear that only 1,7-dehydroquadricyclane **3** had been trapped. As the reaction of **10c** with organolithium bases had furnished evidence for the formation of 1,5-dehydroquadricyclane **4**, although only as minor component, an explanation for the lack



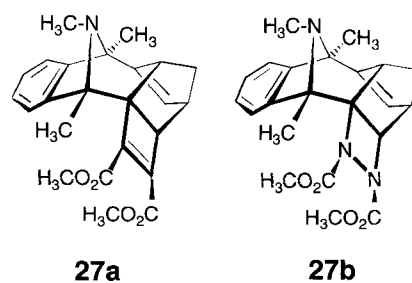
of its adducts seems necessary. b) 1,7-Dehydroquadricyclane **3** and 2,5-dimethylfuran and 1,2,3-trimethylisoindole could lead to two adducts of type **23** and **24**, as depicted for the isoindole case. Only one of these options was realized, probably for steric reasons. An answer to a) is more difficult. As the metalation reaction of **3** with lithium amides to give **13** and **14** is probably a reversible reaction, the competition between protonation of **13** and **14** by the free amine and elimination of lithium chloride might be responsible for the preferred formation of **3** over **4**.

Attempts to isomerize the adducts **21–23** to the corresponding isomers with norbornadiene substructure (*i.e.* for example **22**  $\rightarrow$  **25**) were unsuccessful and ended in the formation of polymeric material. Some evidence for this rearrangement was obtained by flash-vacuum pyrolysis at 410 °C. In 63% yield a mixture of acetylenes **26a–c** was isolated.



An obvious interpretation is the hypothesis of the formation of **25** as an intermediate which undergoes a *retro* Diels-Alder reaction to afford the observed products [15]. Following the principle of Wiseman [16], the strain energy of the two bridgehead CC double bonds of **25** should be similar to the strain energy of *trans,trans*-1,4-cyclooctadiene. Obviously, **25** is therefore not persistent at room temperature.

**22** and **23** were treated with electrophilic dienophiles which led to stable adducts of type **27a** and **b** [14, 15] in nearly quantitative yields.



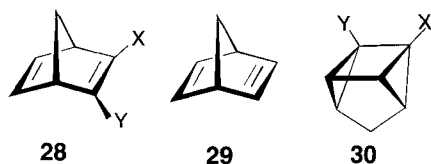
### C. 1,5-Dehydroquadricyclane **4**

#### 1. Synthesis of the Precursors

Although the formation of **4** as minor component was shown to take place in the reaction of **10c** with organolithium compounds, an alternative route had to be developed for its generation in a controlled fashion. This goal was achieved by the synthesis of 2-bromo-3-chlorobicyclo[2.2.1]hepta-2,5-diene (**28f**) and 2,3-

dibromobicyclo[2.2.1]hepta-2,5-diene (**28g**). We used the results of Schlosser [17] and Brandsma [18], who had shown independently that norbornadiene **28a** could be lithiated at the vinylic position by mixtures of BuLi and sodium or potassium *tert*-butoxide in THF at  $-78\text{ }^{\circ}\text{C}$  to give **28b**. **28b** was converted into bromide **28c** with 1,2-dibromoethane in 40% yield and into chloride **28d** with tosyl chloride in 34% yield [19]. The inductive effect of the halide at C-2 should enhance the acidity of the proton at C-3 in **28c** and **d**. Indeed, treatment of **28d** with *t*-BuLi in THF/pentane at  $-78\text{ }^{\circ}\text{C}$  followed by addition of 1,2-dibromoethane afforded **28f** in 44% yield [19]. Obviously, 2-chlorobicyclo[2.2.1]hept-3-yllithium **28e** is an intermediate in this reaction, which under the reaction conditions did not show any propensity to eliminate LiCl with formation of norbornenyne **29**.

The synthesis of the 2,3-dibromonorbornadiene **28g** was challenging, because starting from **28c**, most of the organolithium compounds effected a fast lithium bromine exchange with the formation of **28b**. Finally, this base proved to be the best choice for generating **28h**. This fact allowed a facile one-pot synthesis of dibromide **28g**: After metalation of norbornadiene with BuLi/KO-*t*-Bu in THF in the temperature range of  $-105$  to  $-30\text{ }^{\circ}\text{C}$ , 0.50 equiv. of 1,2-dibromoethane was added, the mixture kept for 1 h at  $-35\text{ }^{\circ}\text{C}$ . After addition of 0.50 equiv. of 1,2-dibromoethane at this temperature, standard workup afforded a 53% yield of **28g** [19].



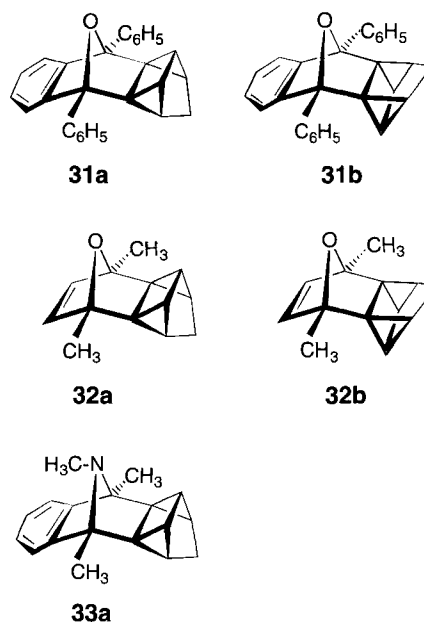
<b>28, 30</b>	<b>a</b>	<b>b</b>	<b>c</b>	<b>d</b>	<b>e</b>	<b>f</b>	<b>g</b>	<b>h</b>	<b>i</b>
X	H	Li	Br	Cl	Cl	Br	Br	Br	Br
Y	H	H	H	H	Li	Cl	Br	Li	SiMe <sub>3</sub>

**28f** and **g** were converted into the corresponding quadricyclanes **30f** and **g** in yields of 66% and 77% by irradiation with a high-pressure mercury lamp in the presence of 5 mol % of acetophenone [19].

## 2. Generation and Trapping of 1,5-Dehydroquadricyclane **4**

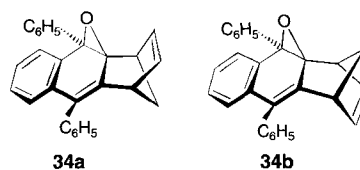
Reaction of **30f** and **30g** with 2.0 equiv. of *t*-BuLi in THF/pentane at  $-78\text{ }^{\circ}\text{C}$  led to **30e** and, respectively, **30h** which did not eliminate lithium halide below  $0\text{ }^{\circ}\text{C}$ . Addition of chlorotrimethylsilane to the mixture of **30g** and *t*-BuLi afforded a 60% yield of silane **30i**, indicating the persistency of **30h** at low temperature. However, when warmed to room temperature in the presence of diphenylisobenzofuran, both **30e** and **h** gave rise to

the formation of Diels-Alder adducts **31a** and **b** in the ratio of 83:17 (from **30e**) and 84:16 (from **30h**). The product ratios were determined by  $^1\text{H}$  NMR spectroscopy; within the usual error limits of this method, both ratios are identical. Identity of the product ratios is mandatory for the intermediacy of **4**, generated from different precursors. 2,5-Dimethylfuran instead of diphenylisobenzofuran as a trap resulted in the isolation of **32a** and **b** (yield 23%, ratio 3:1), whereas with 1,2,3-trimethylisindole only **33a** was produced in 65% yield. The structures of the adducts are based on their NMR spectra. The x-ray structure determination of **31a** confirmed the structural assignments [19].



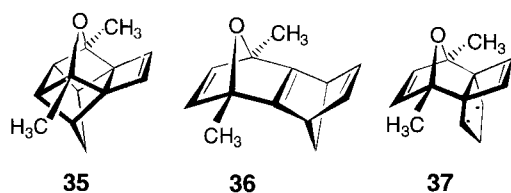
## 3. Rearrangements of **31** and **32**

Adducts **31a/b** showed a high propensity towards isomerization. After chromatography with a silica gel column, the isomers **34a** and respectively, **34b** were formed in high yield. **34a** was also produced when **31a** was heated under reflux in acetonitrile for 1 hour. The x-ray structure of **34a** has been determined. Although not investigated in detail, these isomerizations seem to follow a cationic route, probably catalyzed by traces of electrophiles [19].



Flash vacuum thermolysis of a 4:1 mixture of **32a/b** at  $340\text{ }^{\circ}\text{C}/0.001\text{ torr}$  led to an unexpected result. Where-

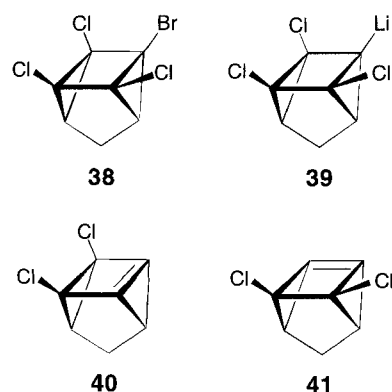
as the minor component **32b** had polymerized, **32a** was converted into one new isomer whose structure was determined to be **35**. The expected oxasesquinorbor-natriene **36** could be excluded [20]. Based on the results of B3LYP/6-31G\*\*/B3LYP/6-31G\* DFT calculations on structurally related model compounds carrying hydrogens instead of methyl groups, **35** is more stable by 28.0 kcal/mol than **32a** and more stable by 21.4 kcal/mol than **36** [21]. The formation of **35** takes place probably via diradical **37**, which according to DFT calculations is an intermediate.



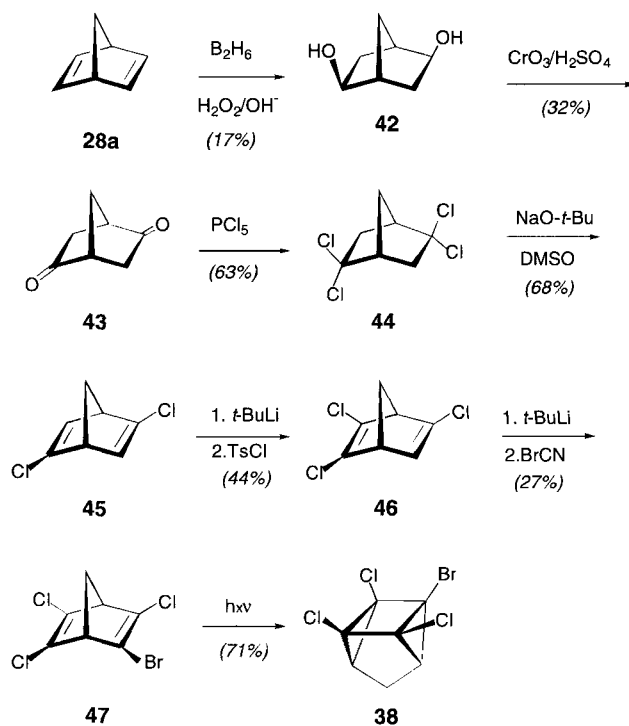
#### 4. 1,7- versus 1,5-Dehydroquadricyclane Formation

Although theory assigns a greater stability to 1,7-dehydroquadricyclane than to 1,5-dehydroquadricyclane, this prediction is not confirmed by any experimental results obtained so far. To attack this problem experimentally, 1-bromo-5,6,7-trichloro-quadricyclane **38** was needed as precursor, which after lithium bromine exchange with *t*-BuLi should lead to **39**. This intermediate has the choice of eliminating LiCl to give **40** or **41**. It is not unrealistic to expect that the difference in the energy of **40** and **41** is reflected in the difference of activation energies leading to **40** and **41**.

The synthesis of **38** is outlined in Scheme 3.

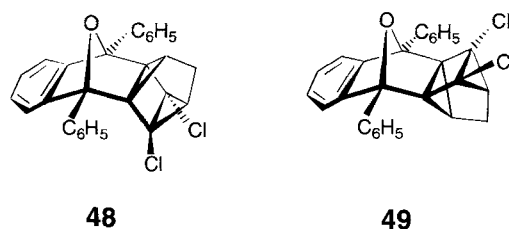


**38** in THF was treated at  $-78\text{ }^{\circ}\text{C}$  with *t*-BuLi in pentane, the solution charged with an excess of diphenylisobenzofuran and warmed to room temperature, and the excess of the trap removed with maleic anhydride and triethylamine. After the usual workup a nearly quantitative yield of 55:45 mixture of **48** and **49** was isolated.



Scheme 3

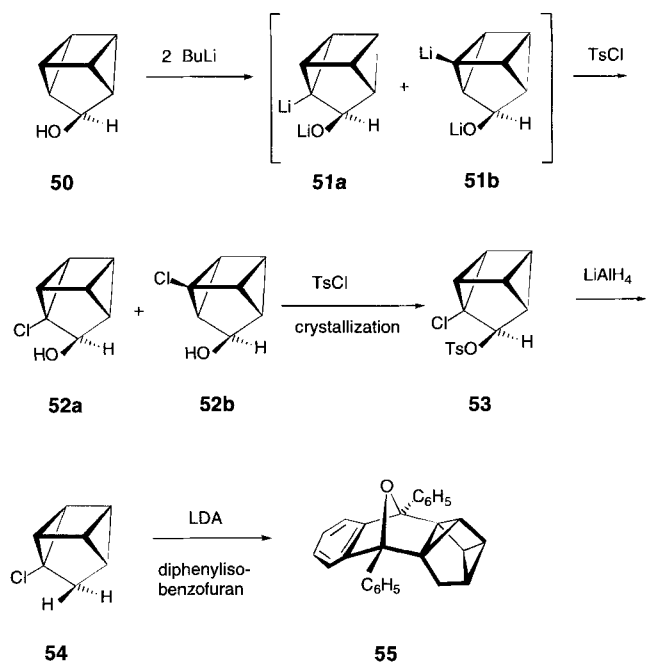
ed, which showed that only dichloro-1,7-dehydroquadricyclane **40** had been formed in the elimination process [15]. No evidence for the generation and trapping



of **41** could be deduced from the NMR spectra. Under the premises indicated above this result is in accordance with the calculation on the energies of **3** and **4**.

#### D. 1,2-Dehydroquadricyclane 5

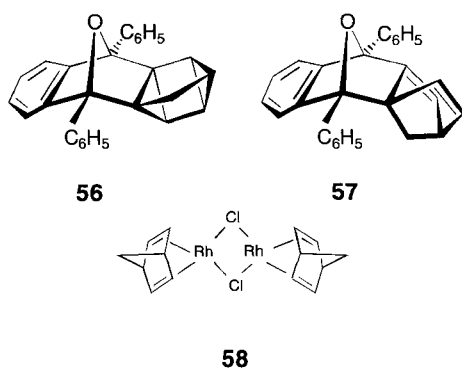
Again, dehydrohalogenation seemed the method of choice for generating 1,2-dehydroquadricyclane **5**. Using the pronounced acidity of C-1 (and C-7), an effective precursor for **5** could be 2-chloroquadricyclane **54**. The synthesis of **54** is outlined in Scheme 4. 3-Quadricyclanol **50** served as starting material. As shown for the first time by Klumpp and his group, its metalation with 2.0 equiv. of RLi takes place predominantly at C-2 [21]. Using BuLi as a base, the ratio of C-2 versus C-1 lithiation has been found to be 85:15 [22]. Reac-



Scheme 4

tion of the **51a/b** mixture with tosyl chloride gave rise to **52a/b** as a 85:15 mixture in a total yield of 25%. When the mixture of the chlorocarbinols was converted into the tosylates, **53** could be obtained pure by crystallization. Reduction of **53** with  $\text{LiAlH}_4$  furnished a 52% yield of **54** [10].

Convincing evidence for the generation of **5** was obtained by reaction of **54** with  $\text{LDA}$  in the presence of diphenylisobenzofuran, which furnished adduct **55** in 67% yield. In this Diels-Alder reaction, olefin **5** shows a pronounced "side selectivity": **5** approaches the diene in a way that the cyclopropane ring and the oxygen are located in one hemisphere. The stereoisomeric adduct **56** was not found [10].

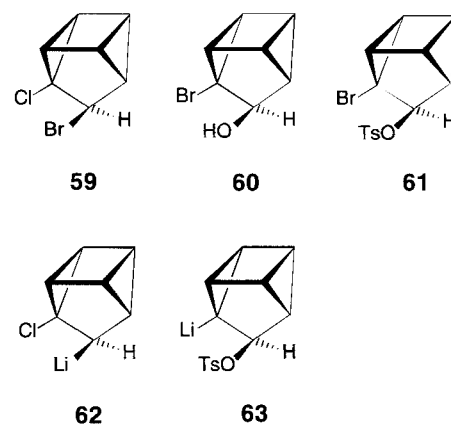


Adduct **55** could be isomerized to norbornadiene **57** by use of the complex **58** as a catalyst. **57** was stable in

solution at room temperature for several hours, but polymerized slowly within several days [10].

### E. 2,3-Dehydroquadricyclane **6**

2,3-Dehydroquadricyclane **6** differs from its counterparts **3–5**, because this olefin is the prototype of a twisted alkene, as depicted in Figure 1. Starting from 2-chloro-

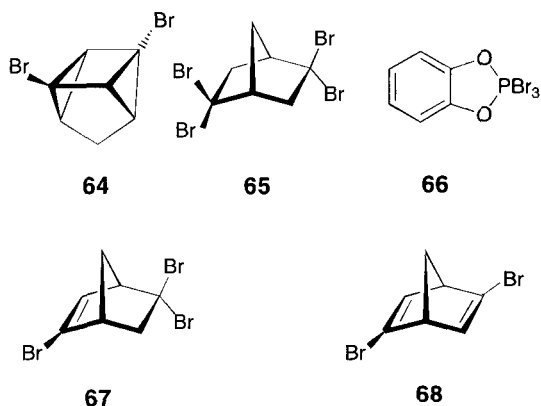


3-quadricyclanol **52a**, 3-bromo-2-chloroquadricyclane **59** could be synthesized in 71% yield [10]. Alternatively, bromide **60** was tosylated to give **61** in 84% yield. **59** and **61** served as starting materials for generating **6**.

Reaction of **59** with  $t\text{-BuLi}$  in the presence of 2,5-dimethylfuran or anthracene led, after aqueous workup, to **54**, indicating that the lithium bromine exchange of  $t\text{-BuLi}$  and **59** to give **62** had taken place, but that **62** did not show any propensity to eliminate  $\text{LiCl}$ . Similar results were obtained with **61** and  $t\text{-BuLi}$ , which were mixed at  $-78^\circ\text{C}$ . Warming of the solution of **63** in the presence of anthracene or 1,2,3-trimethylisindole did not give clear evidence for the formation of the corresponding Diels-Alder adducts. Although the possibility of formation of carbene **9** from **6** was envisioned, the reaction of **59** with  $t\text{-BuLi}$  in the presence of cyclopentene did not lead to the expected carbene adduct [10, 23].

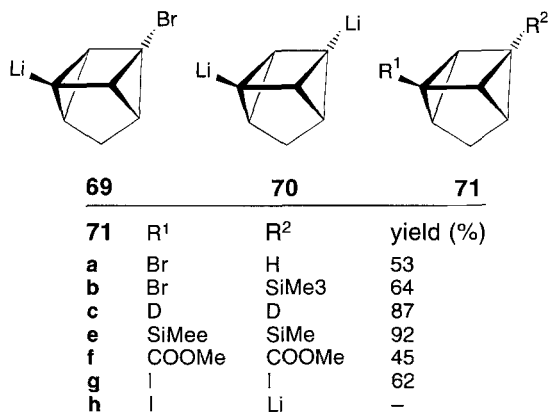
### F. 1,6-Dehydroquadricyclane **7**

1,6-Dibromoquadricyclane **64** seemed an appropriate precursor for the entry into the fleeting structure of 1,6-dehydroquadricyclane **7**. Again, bicyclo[2.2.1]heptane-2,5-dione **43** was used as starting material. The conversion into the tetrabromide **65** as achieved with tribromodioxaphosphole **66**. This reaction was accompanied by the formation of tribromide **67**. Separation of **65** and **67** was not necessary; treatment of the mixture with  $\text{KO-}t\text{-Bu/DMSO}$  furnished a 67% yield



of **68**. Photocyclization of **68** in the presence of 10% of acetophenone produced **64** in 81% yield [20].

Lithium bromine exchange of **64** with *t*-BuLi in ether at  $-78\text{ }^{\circ}\text{C}$  to give **69** was effective, however **69** did not eliminate lithium bromide up to room temperature. An excess of *t*-BuLi and **64** led to the formation of the dilithioquadricyclane **70**. **69** and **70** were observed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy and could be reacted with electrophilic reagents. In this way, **71b** was obtained by reaction of **69** with chlorotrimethylsilane, and **71g** by reaction of **70** with cyanogen iodide [20]. **71b** and **g** served as further precursors for generating **7**. **71b** was treated with CsF in DMSO, but was recovered unchanged. Mixing of the diiodide **71g** with 4.0 equiv. of *t*-BuLi afforded after addition of  $\text{D}_2\text{O}$  only **71c** [20]. Obviously, the intermediate **71h** is formed but Li elimination cannot compete with the second lithium iodine exchange.



### G. Concluding Remarks

Despite considerable efforts, 2,3-dehydroquadricyclane **6** and 1,6-dehydroquadricyclane **7** could not be generated with the precursors and methods reported in this overview. Looking at the calculated energies of **6** and **7** in comparison to **3**, **4**, and **5**, the unsuccessful attempts of formation of **6** and **7** are probably based

more on kinetic than on thermodynamic reasons. From the structural point of view, the lithium halide distance in the precursors **13**, **14**, and 1-lithio-2-chloroquadricyclane is somewhat shorter than in **62** and considerably shorter than in **69**. Metal halide elimination from **62** and **69** might be facilitated, if the lithium were *trans*-metalated against potassium or cesium.

In nearly all cases of this study, anionic leaving groups were halides. Gleiter has shown recently that completely different mechanisms are operative if quadricyclyl sulfones are treated with organolithium bases [24]. In this case, SET processes were involved which lead to fast ring opening of the quadricyclyl framework circumventing the formation of dehydroquadricyclanes.

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