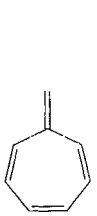
Exploring a New General Pathway to Parent Hydrocarbons Heptafulvene, Heptapentafulvalene, and Heptafulvalene[1])

by **Xiaoming Li**[2]) and **Markus Neuenschwander***

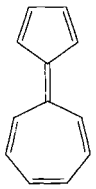
Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, CH-3012 Bern

A new general pathway to the parent cross-conjugated hydrocarbons heptafulvene (**1**) (*Scheme 3*), sesquifulvalene (**2**) (*Scheme 4*), and heptafulvalene (**3**) (*Scheme 5*) has been explored, starting with easily available 7,7-dibromobicyclo[4.1.0]hept-3-ene (**13**). Promising precursors have been synthesized by halo/lithio exchange of 1,1-dibromocyclopropane **13** → **14**, followed by methylation (→ **1**), cyclopentadienylation (→ **2**) and $CuCl_2$-induced 'carbene dimerization' (→ **3**) of the carbenoid **14**. So far, the main obstacle of all three sequences (*cf. Schemes 3*, *4*, and *5*) is the final base-induced dehydrobromination of precursors **17**, **24**, and **27**, which should be investigated in more detail.

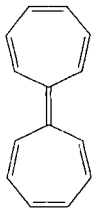
1. Introduction. – Although heptafulvene (**1**)[3]), sesquifulvalene (**2**)[4]) and heptafulvalene (**3**)[5]) have been known for quite a long time, these reactive parent cross-conjugated compounds are not so easily available and have to be synthesized by multistep sequences and/or from expensive starting materials.



1



2



3

So far, there exists only one general synthesis of parent fulvenes (and of fulvalenes with rings of inverse electron demand). It has been elaborated for parent pentafulvene [17], has a broad scope for 6-substituted pentafulvenes [18][19], and may be applied to the parent nonafulvene [20][21]. Keeping in mind the opposite polarization of pentafulvenes and heptafulvenes[6]), it is surprising to see that the same sequence may be applied to the synthesis of parent heptafulvene (**1**) and sesquifulvalene (**2**) as well (*Scheme 1*).

---

[1]) Fulvenes, Fulvalenes, Part 72. Part 71: [1].

[2]) Postdoctoral fellow 1996–1999.

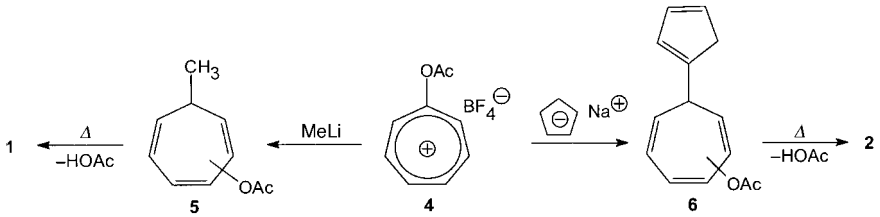
[3]) First synthesis (in solution): [2][3]; other prominent syntheses: [4–8]; experimental procedure for isolation: [8].

[4]) First synthesis (in solution): [9][10]; another prominent synthesis (including isolation procedure): [8]; the correct name of **2**, heptapentafulvalene, is only rarely used in the literature.

[5]) First synthesis and isolation: [11], quoted in [12]; other prominent syntheses: [13–16].

[6]) Note that pentafulvene has a dipole moment of 0.424 D [22] (with a negatively polarized five-membered ring), while heptafulvene (**1**) has a dipole moment of 0.477 D [23] (and a positively polarized seven-membered ring). For details, see [24][25].

Scheme 1



The synthetic plan is based on the fact that tropone may be acylated to give acetoxytropylium fluoroborate (**4**), which reacts with nucleophiles such as MeLi (**4** → **5**) and sodium cyclopentadienide (**4** → **6**) [7]. Parent hydrocarbons **1** and **2** are finally generated by gas-phase pyrolysis of **5** and **6** at 360°[7]) and trapped at low temperature [8].

As far as fulvalenes with identical rings (or with rings of similar electron demand) are concerned, there exists a quite general synthesis based on oxidative couplings of '*Hückel*'-anions[8]). This sequence has been successfully applied to the synthesis of parent pentafulvalene [27], nonapentafulvalene [28], and nonafulvalene [29], but of course has no application in the series of fulvalenes with three- and seven-membered rings[9]).

Due to the fact that a general approach to heptafulvalenes is still missing, while the synthesis of **1** and **2** (*Scheme 1*) is experimentally demanding[7]), we were exploring a new pathway to parent heptafulvalene (**1**) as well as to heptafulvalenes **2** and **3**. The synthetic plan (*Scheme 2*) is based on 1-bromo-1-lithiocyclopropanes (**7**), which are easily prepared at −90° from 1,1-dibromocyclopropanes [30] and alkylated (**7** → **8**) at low temperature [31–33]. Base-induced HBr elimination (**8** → **9**) allows introduction of the exocyclic C=C bond[10]). On the other hand, we have shown that cyclopent-2-en-1-one reacts with 1-bromo-1-lithiocyclopropanes (**7**) as an electrophilic cyclopentadiene equivalent (→ **10**) which makes 7,8-dihydrocalicenes **11** available [36][37]. Furthermore, $CuCl_2$-induced 'carbene dimerization' (**7** → **12**) [38][39] may be exploited for synthesizing substituted bi(cyclopropylidenes) **12**. Starting with appropriately substituted cyclopropanes (*e.g.*, $R^1,R^2 = CH_2-CH=CH-CH_2$), the three sequences of *Scheme 2* could be very useful for synthesizing heptafulvene (**1**), sesquifulvalene (**2**), and heptafulvalene (**3**) from cheap and easily available starting materials.

2. Attempted Synthesis of Heptafulvene (1) (*Scheme 3*). – 7,7-Dibromobicyclo[4.1.0]hept-3-ene (**13**) is easily available by dibromocarbene addition to cyclohexa-1,4-diene according to phase-transfer procedures [40][41]. As expected, Br/Li exchange (**13** → **14**) as well as methylation are fast at low temperature, so that one

---

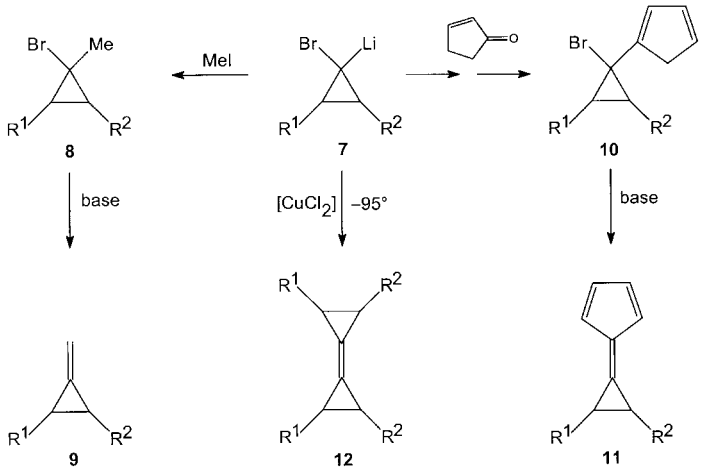
7) Although the sequence of *Scheme 1* seems to be simple and straightforward, its experimental applications are limited due to the fact that gas-phase pyrolysis and low-temperature trapping require special equipment and experimental skill of the operator.

8) For a short survey, see [26].

9) The true counterpart of the oxidative coupling of '*Hückel*' anions (like cyclopentadienide and cyclononatetraenide) would be a reductive coupling of '*Hückel*' cations (such as tropylium cation and cyclopropenylium cation). It has been tentatively tested by *Doering* in the early times of fulvalene chemistry [12].

10) For some typical examples, see [34][35].

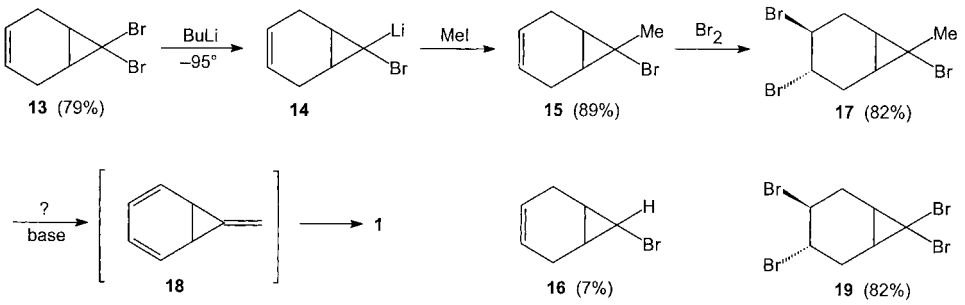
Scheme 2



predominant diasteroisomer **15**[11]) may be isolated after workup besides minor amounts of protonation products **16**. Subsequent bromination (**15** → **17**) gives the key precursor **17** with a yield of 82%.

A second pathway to **17** consists in reversing the bromination/methylation sequence: while bromination of **13** (→ **19**) proceeds with good yields (82%) as well, the subsequent reaction of **19** with BuLi and MeI gives a mixture of two diastereoisomers **17** [11]) with a total yield of 77%. This result clearly shows that formation of the corresponding cyclopropyl-carbenoid is much faster than HBr (or Br_2) elimination in the dibromocyclohexane moiety of **19**.

Scheme 3



So far, however, the attempted base-induced HBr elimination (**17** → **18** → **1**) has failed[12]) and needs to be reinvestigated.

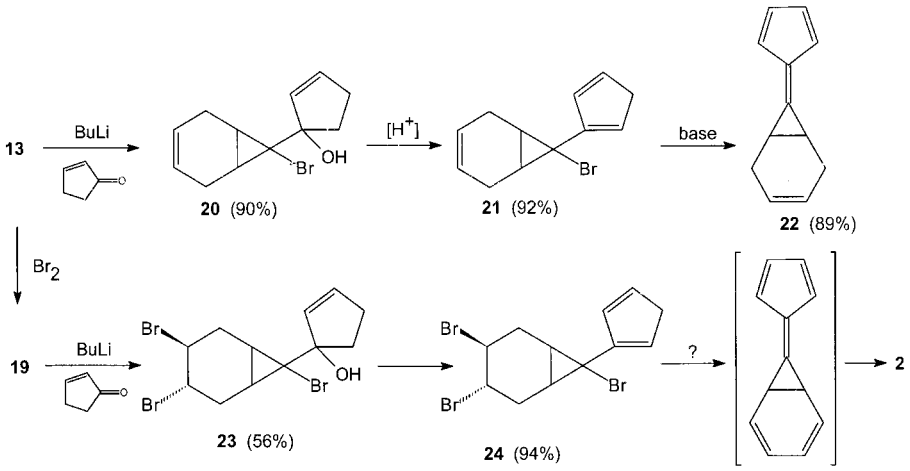
---

[11]) Since NOE experiments are often inconclusive, it is not easy to establish the configuration of cyclopropanes of type **15**, **17** *etc.* without an X-ray analysis. On the other hand, the structure of protonation products **16** *etc.* is easily derived from ^3J values ($^3J_{cis}$ *ca.* 7.5 Hz, $^3J_{trans}$ *ca.* 3.5 Hz) of H–C(7).

[12]) Quite surprisingly, reaction of **17** with 3 mol-equiv. of *t*-BuOK in THF for 1 h left **17** unchanged between –80° and 0°.

3. Synthetic Attempts towards Pentaheptafulvalene (2). – According to *Scheme 4*, 7,7-dibromobicyclo[4.1.0]hept-3-ene (**13**) might be an interesting starting material for the synthesis of sesquifulvalene (**2**). This is supported by the high-yielding reaction of cyclopropyl carbenoid **14** with cyclopent-2-en-1-one (**14** → **20**)[13]) as well as by the smooth conversion of cyclopentenol **20** to cyclopentadiene **21**[13]). Base-induced HBr elimination finally gives pentafulvene **22** in an overall yield of 74% starting from **13**.

Scheme 4



Unfortunately, so far, all attempts to introduce two potential leaving groups in the cyclohexene moiety of **22** failed[14]) so that the planned base-induced elimination (to give **25** and subsequently **2**) could not be tested.

An alternative sequence starts with bromination of **13** (→ **19**)[15]). It includes the tricky step **19** → **23**, where the question arises whether the planned Br/Li exchange (as well as the subsequent reaction of the corresponding cyclopropyl carbenoid with cyclopentenone to give **23**) is faster than side reactions of the 1,2-dibromocyclohexane moiety. Our results show that this is obviously the case at $-95°$ in THF, although the yields of **23**[13]) are considerably lower than those of the step **13** → **20**. Once again, acid-catalyzed dehydration of cyclopentenol **23** easily gives cyclopentadiene **24**[14])[15]). However, several attempts to generate sesquifulvalene by base-induced threefold HBr elimination (**24** → **25** → **2**) were unsuccessful and need further careful investigation.

The structures of all the new compounds of *Scheme 4* follow from the spectroscopic data, except for the configurations of the cyclopropane units of compounds **20**, **21**, **23**, and **24**[11]). The most conclusive structural evidence stems from ^{1}H-NMR results: due to the symmetry of molecules **20**, **21**, and **22**, the protons of the bicyclo[4.1.0]heptene moiety display a complex *AA′BB′XX′YY′* pattern in the ^{1}H-NMR spectrum, while the

---

[13]) According to ^{1}H- as well as ^{13}C-NMR data, one predominant diastereoisomer is formed.

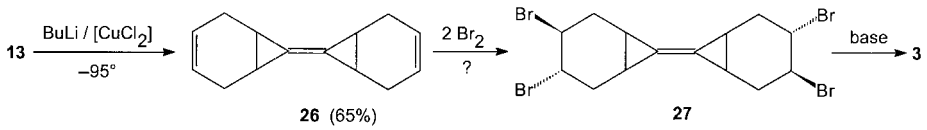
[14]) The attempted bromination of the cyclohexene unit of **22** obviously fails due to the well-known reactivity of the pentafulvene unit of **22** towards electrophiles. For typical examples, see [42–44].

[15]) Similarly, **13** is easily chlorinated by reaction with NCS/LiCl (96% yield), and the reaction product 7,7-dibromo-3,4-dichlorobicyclo[4.1.0]heptane can be converted to the corresponding cyclopentadiene (see **24**) or methyl derivative (see **17**) with similar yields.

H-atoms of the same moieties of structures **23** and **24** are non-equivalent so that J values can be derived. As expected, each of the vinylic protons of the cyclopentenol units of **20** and **23** shows *dt* splittings with $J_{AX} = 5.8$ Hz, while the splitting of the H-atoms of the cyclopentadienyl ring of **21** and **24** is of the type $ABXY_2$ with $J_{AB} = 5.5$ Hz for adjacent vinylic H-atoms. Additionally, the protons of the pentafulvene unit of **22** display the typical $AA'XX'$ splitting pattern of the *multiplets* at 6.35 and 6.55 ppm, and the resonances of the corresponding ring-C-atoms are in the expected range for fulvenes (131.5 and 122.4 ppm, resp.). Of course, the fulvene structure of **22** is additionally supported by characteristic UV and IR absorptions.

4. Synthesis of a Heptafulvalene Precursor. – 7,7-Dibromobicyclo[4.1.0]hept-3-ene (**13**) is a promising starting material for the synthesis of heptafulvalene, if $CuCl_2$-induced 'carbene dimerization' [38][39] may be applied to the carbenoid **14**, which can be prepared from **13** with BuLi at low temperature. In fact, reacting **13** with BuLi at $-95°$ in the presence of small amounts of anhydrous $CuCl_2$ gives a *cis/trans*-mixture of bi(cyclopropylidenes) **26** with a total yield of 65% [16]). However, so far, bromination/elimination experiments with bi(cyclopropylidene) **26** were not successful[17]).

Scheme 5



5. Discussion. – Three synthetic plans for heptafulvene (**1**, *Scheme 3*), sesquifulvalene (**2**, *Scheme 4*), and heptafulvalene (**3**, *Scheme 5*) have been explored starting with easily available 7,7-dibromobicyclo[4.1.0]hept-3-ene (**13**), and the promising precursors **17**, **22**, **24**, and **26** of all three parent non-benzenoid hydrocarbons have been synthesized. Our results show that the central Br/Li exchange (**13** → **14**) proceeds nearly quantitatively, while the subsequent methylation (**14** → **15**) or the introduction of cyclopentadiene units by reaction with cyclopent-2-enone (**14** → **20** → **21**) are high-yielding reactions. Last but not least, $CuCl_2$-induced 'carbene dimerization' (2 **14** → **26** + 2 LiBr) has been realized with good yields. Bromination problems of fulvene **22** (due to different competing double bonds) could be avoided by directly synthesizing **24** starting from **19** (*Scheme 4*). Similarly, it should be possible to make the diastereoisomeric mixture **27** available by reacting **19** with BuLi in the presence of traces of

---

16) ^{1}H- and ^{13}C-NMR data are in agreement with the structure **26**. Very typical for the bi(cyclopropylidene) unit are the signals of C-atoms of the three-membered ring at 116.2/10.6 ppm (major isomer) and 118.4/12.8 ppm (minor isomer). Due to the slight high-field shift of these C-atoms, as well as because of the higher melting point of the major isomer (126–128° *vs.* 106–108°), one can tentatively assign the major isomer to *trans*-**26**.

17) While careful bromination of **26** with two equiv. of Br_2 resulted in a crude product with the expected structural features of **27** according to ^{1}H-NMR spectra (the spectra are very similar to those of **19**), so far, no pure tetrabromo derivative of **26** could be isolated. On the other hand, low-temperature bromination/elimination experiments with **26** failed to give heptafulvalene (**3**) until now.

anhydrous $CuCl_2$, a side path which has not been attempted yet. It is quite surprising to note that the main obstacle in all three synthetic sequences (*Schemes 3*, *4*, and *5*) is the final base-induced dehydrobromination of precursors **17**, **24**, and **27**, which should be reinvestigated in more detail by variation of bases, reaction conditions, and leaving groups.

The authors thank the *Swiss National Science Foundation* (project No. 20-50331.97) for financial support.

Experimental Part

General. Unless otherwise stated, all the reactions were performed under N_2 or Ar in two- and three-necked round-bottomed flasks equipped with a dropping funnel (or a septum), a magnetic stirrer, an N_2-inlet and, where needed, a thermometer. Prior to the introduction of reagents, the vessels were thoroughly flame-dried and flushed with N_2 or Ar. Small amounts of sensitive liquids or solns. were injected into the reaction vessel through the septum with a syringe. Temp. of $-95°$ was reached by freezing part of toluene with liquid N_2. Spectra were recorded on the following instruments: UV: *Perkin-Elmer 554*; λ_{max} (ε) in nm. IR: *Perkin-Elmer 399B*; $\tilde{\nu}$ in cm^{-1}. NMR: *Bruker AC-300*; δ in ppm rel. to $SiMe_4$, *J* in Hz. MS: *Varian-MAT CH-7A*; *m/z* (rel. %).

1. Synthesis of Heptafulvene Precursors (*Scheme 3*). 1.1. *7,7-Dibromobicyclo[4.1.0]hept-3-ene* (**13**). In a 250-ml flask, 20 ml of 50% aq. NaOH were slowly added (10 min per 5 ml portion) at 0–5° to a vigorously stirred mixture containing 4.0 g (50 mmol) of cyclohexa-1,4-diene, 13.6 g (53.8 mmol) of $CHBr_3$ and *ca.* 1.5 g cetrimide (=(hexadecyl)trimethylammonium bromide) in 50 ml of CH_2Cl_2. The reaction mixture was stirred for 2 h at 0–5°, then overnight at r.t. (TLC showed complete reaction), then transferred to a separatory funnel containing 200 ml of H_2O. The org. layer was separated, washed with H_2O (2 × 100 ml) and concentrated *i.v.* to give an oily, yellow residue which was diluted with 150 ml of Et_2O and dried ($MgSO_4$). After evaporation of the filtrate *i.v.*, 10.0 g (79%) of colorless crystals of practically pure **13**. M.p. 36–38°. An anal. pure product was obtained by column chromatography (CC) on *ca.* 50 g of silica gel with pentane/Et_2O 10:1 (R_f 0.80). ^{1}H-NMR (300 MHz, $CDCl_3$): 5.52 (*s*, 2 H); 2.48 (*m*, 2 H); 2.10 (*m*, 2 H); 1.92 (*m*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 122.1 (*d*); 37.9 (*s*); 24.6 (*d*); 20.6 (*t*)[18]).

1.2. *7-Bromo-7-methylbicyclo[4.1.0]hept-3-ene* (**15**). In a 50-ml flask, 5.5 ml of 1.6M BuLi (8.8 mmol, 1.1 mol-equiv.) were added during 10 min at −95° to a stirred soln. containing 2 g (7.9 mmol) of **13** and 2.7 g (19 mmol, 2.4 mol-equiv.) of MeI in 10 ml of THF. After stirring for 30 min at −95° and warming to r.t. over 1 h, the mixture was quenched by adding 10 ml of H_2O at 0°. The layers were separated, and the aq. phase was then extracted with Et_2O (2 × 10 ml), and the combined org. extracts were dried ($MgSO_4$), filtered, and evaporated to dryness *i.v.* The resulting colorless, crystalline product was purified by CC with pentane/Et_2O 10:2 as eluent over 20 g of silica gel to give 1.3 g (88%) of **15** [11]) (second fraction, R_f 0.64, m.p. 59–61°), besides 0.1 g (7%) of trans-*7-bromobicyclo[4.1.0]hept-3-ene* (**16**) (first fraction, R_f 0.86).

Data of **15**: ^{1}H-NMR (300 MHz, $CDCl_3$): 5.53 (*s*, 2 H); 2.37 (*m*, 2 H); 2.10 (*m*, 2 H); 1.62 (*m*, 2 H); 1.57 (*s*, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 121.8 (*d*); 29.3 (*s*); 19.4 (*t*); 18.6 (*d*); 16.5 (*q*) [18]).

Data of **16**: ^{1}H-NMR (300 MHz, $CDCl_3$): 5.48 (*s*, 2 H); 2.82 (*t*, *J* = 3.5, 1 H); 2.38 (*m*, 4 H); 1.52 (*m*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 123.3 (*d*); 22.6 (*d*); 22.2 (*t*); 20.7 (*d*) [18]).

1.3. *3,4,7-Tribromo-7-methylbicyclo[4.1.0]heptane* (**17**). In a 100-ml flask, a soln. of 2.65 g (16.6 mmol) of Br_2 in 10 ml of CCl_4 was slowly added at 0° to a soln. of 3.09 g (16.5 mmol) of **15** in 10 ml of CCl_4. After stirring the mixture for 2 h at 0° and another 2 h at r.t., TLC showed complete reaction. The mixture was washed with 5% aq. Na_2CO_3, dried ($MgSO_4$), and concentrated *i.v.* to give 4.7 g (82%) of colorless crystals consisting of two diastereoisomers in a ratio of *ca.* 2:1 (^{1}H-NMR) which could be separated by CC over *ca.* 50 g of silica gel with pentane/Et_2O 10:1.

Data of the Major Isomer **17**: ^{1}H-NMR (300 MHz, $CDCl_3$): 4.23 (*m*, 1 H); 4.13 (*m*, 1 H); 2.84 (*m*, 1 H); 2.52 (*m*, 1 H); 2.35 (*m*, 1 H); 1.90 (*m*, 1 H); 1.82 (*s*, 3 H); 1.72 (*m*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 52.2 (*d*); 50.9 (*d*); 28.6 (*t*); 28.1 (*t*); 23.6 (*d*); 23.0 (*d*); 21.0 (*q*) [18]).

---

[18]) For more spectroscopic data and illustrations of spectra, see [45], which is available on request from *M.N.*

Data of the Minor Isomer **17**: ^{1}H-NMR (300 MHz, $CDCl_3$): 4.39 (*m*, 1 H); 4.13 (*m*, 1 H); 2.90 (*m*, 1 H); 2.60 (*m*, 2 H); 2.07 (*m*, 1 H); 1.77 (*s*, 3 H); 1.11 (*m*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 53.62 (*d*); 53.57 (*d*); 45.9 (*s*); 34.2 (*t*); 34.0 (*t*); 31.1 (*d*); 23.2 (*d*); 22.5 (*q*). HR-MS: 343.8413 ($C_8H_{11}Br_3$, $M^{+\bullet}$; calc.: 343.8411) [18]).

1.4. *3,4,7,7-Tetrabromobicyclo[4.1.0]heptane* (**19**) [15]). In a 100-ml flask, a soln. of 2.25 g of Br_2 (14 mmol) in 10 ml of CCl_4 was slowly added at 0° to a stirred soln. of 3.5 g (13.9 mmol) **13** in 10 ml of CCl_4. The resulting mixture was stirred for 2 h at 0° and for another 2 h at r.t. (TLC showed complete reaction), was then washed with 5% aq. Na_3CO_3-soln., and the org. layer was dried ($MgSO_4$) and evaporated *i.v.* The crude, crystalline product was purified by CC on *ca.* 50 g of silica gel with pentane/Et_2O 10:1 (R_f 0.74) to give 4.7 g (82%) of colorless crystals of **19**. M.p. 116–118°. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.25 (*m*, 1 H); 4.06 (*m*, 1 H); 3.00 (*m*, 1 H); 2.73–2.52 (*m*, 2 H); 2.11–0.97 (*m*, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 51.8 (*d*); 51.4 (*d*); 36.2 (*s*); 33.2 (*t*); 33.1 (*t*); 28.9 (*d*); 28.0 (*d*) [18]).

1.5. *Methylation* **19** → **17** [15]). In a 50-ml flask, 3.3 ml of 1.6M BuLi (5.2 mmol, 1.1 mol-equiv.) in hexane were added during 10 min to a stirred soln. containing 2 g (4.86 mmol) of **17** and 1.66 g (11.7 mmol, 2.4 mol-equiv.) of MeI in dry THF at −95°. After stirring for 30 min at −95° and warm-up to r.t. over 1 h, the mixture was quenched by adding 10 ml of H_2O at 0°. The layers were separated, then the aq. phase was extracted with Et_2O (2 × 10 ml), and the combined org. extracts were dried ($MgSO_4$) and evaporated *i.v.* The products were separated by CC over *ca.* 50 g of silica gel with pentane/Et_2O 10:2. The first fraction (R_f 0.64) yielded 1.0 g (59%) of colorless crystals of **17** [11]) with m.p. 59–61° (NMR data, see *Minor Isomer* of **17**). The second fraction (R_f 0.55) gave 0.3 g (15%) of colorless crystals of **17** [11]) with m.p. 48–50° (NMR data, see *Major Isomer* of **17**) [18]).

2. Synthesis of Sesquifulvalene Precursors. – 2.1. *1-(7-Bromobicyclo[4.1.0]hept-3-en-7-yl)cyclopent-2-en-1-ol* (**20**). In a 100-ml flask, 3.9 g (15.5 mmol) of **13**, and 2.5 g (30.45 mmol) of cyclopent-2-en-1-one were dissolved in 50 ml of THF and cooled to −95°. To the stirred soln., 17.6 ml of 1.6M BuLi in hexane (28.2 mmol) were dropwise added during 1 h at −95° through the septum with a syringe. After stirring for 2 h at −95° and subsequently 1 h at r.t., the mixture was quenched by adding 40 ml of H_2O/40 ml of Et_2O at 0°. The layers were separated, the aq. phase extracted with Et_2O (3 × 20 ml), and the combined org. extracts evaporated *i.v.* The crude product was purified by low-temp. (−20°) CC[19]) on *ca.* 50 g of silica gel with pentane/Et_2O 10:1 to give 3.55 g (90%) of a colorless oil of **20**. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.08 (*m*, 1 H); 5.59 (*s*, 2 H); 5.55 (*m*, 1 H); 2.6–2.2 (sev. *m*, 6 H); 2.03 (*m*, 3 H); 1.40 (*m*, 1 H); 1.18 (*m*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 137.5 (*d*); 131.6 (*d*); 123.5 (*d*); 123.3 (*d*); 90.1 (*s*); 61.7 (*s*); 38.4 (*t*); 31.0 (*t*); 21.6 (*t*); 21.1 (*t*); 14.77 (*d*); 14.74 (*d*). MS[20]): 256/254 (20/22, $M^{+\bullet}$), 237/235 (30/25), 175 (100), 163 (65), 128 (45), 52 (30). HR-MS: 254.0306 ($C_{12}H_{15}OBr$, $M^{+\bullet}$; calc.: 254.0308) [18]).

2.2. *7-Bromo-7-(cyclopenta-1,4-dienyl)bicyclo[4.1.0]hept-3-ene* (**21**). A 50-ml flask was charged with 2.0 g (7.84 mmol) of **20**, 10 ml of benzene, and 300 mg (1.7 mmol, cat. amount) of TsOH. The mixture was stirred at r.t. for 3 h, then evaporated *i.v.*, and the resulting crude product was then purified by low-temp. (−20°) CC [19]) on *ca.* 10 g of silica gel with pentane/Et_2O 20:1 (R_f 0.85) to give 1.7 g (91.5%) of colorless oil **21**. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.48 (*m*, 2 H); 6.22 (*m*, 1 H); 5.62 (br. *s*, 2 H); 3.05 (*s*, 2 H); 2.57 (*m*, 2 H); 2.14 (*m*, 2 H); 1.49 (*m*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 134.6 (*d*); 132.7 (*d*); 126.4 (*d*); 123.4 (*d*); 40.9 (*t*); 21.4 (*t*); 19.0 (*d*) [18]).

2.3. *7-(Cyclopenta-2,4-dienylidene)bicyclo[4.1.0]hept-3-ene* (**22**). The crude product obtained above (see *2.2*) was purified by low-temp. (−20°) CC over *ca.* 20 g of Al_2O_3 (basic) with pentane/Et_2O 20:1. The resulting intensely yellow zone was collected and evaporated *i.v.* to give 1.0 g (81% from **20**, 89% from **21**) of an orange-colored oil which crystallized around −40°. UV (hexane): 269 (21000), 358 (*ca.* 350). IR ($CDCl_3$): 3105*w*, 3040*w*, 2900*w*, 2810*w*, 1635*s*, 1460*m*–*s*, 1447*m*, 1375*s*, 1357*m*–*s*, 1095*m*, 1082*m*, 988*m*, 918*m*, 870*m*, 742*s*, 630*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.57 (*m*, 2 H); 6.37 (*m*, 2 H); 5.50 (*s*, 2 H); 2.49 (*m*, 4 H); 2.11 (*s*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 131.6 (*d*); 123.6 (*d*); 122.4 (*d*); 22.8 (*t*); 13.7 (*d*). MS [20]): 156 (100, $M^{+\bullet}$), 155 (77), 154 (50), 153 (44), 141 (77), 129 (38), 128 (63), 115 (70), 91 (33), 78 (32) [18]).

2.4. *1-(3,4,7-Tribromobicyclo[4.1.0]hept-7-yl)cyclopent-2-en-1-ol* (**23**)[21]). A 100-ml flask was charged with 3.0 g (7.29 mmol) of **19**, 0.6 g (7.31 mmol) of cyclopent-2-en-1-one, and 50 ml of THF. To the cooled (−95°) reaction mixture, 4.6 ml of 1.6M BuLi in hexane (7.36 mmol) were added dropwise during 1 h through the

---

19) For details, see [46], p. 1389.

20) Only the most important MS fragments and IR absorptions are listed.

21) 3,4-Dichloro-7-bromo derivatives corresponding to **23** and **24** have been isolated as well. For experimental procedures and spectra, see [45] [18]).

septum with a syringe under stirring. After 2 h of stirring at −95° and warming to r.t. during 1 h, the mixture was quenched by adding 50 ml of H_2O and 50 ml of Et_2O at 0°. The layers were separated, the aq. phase extracted with Et_2O (3 × 50 ml), and the combined extracts dried ($MgSO_4$) and evaporated *i.v.* The crude product was purified by low-temp. (−20°) CC [19]) on *ca.* 50 g of silica gel with pentane/Et_2O 10:1. The first two fractions with R_f 0.88 and R_f 0.80 contained minor amounts of protonation products (*trans/cis*-3,4,7-tribromobicyclo[4.1.0]-heptane[22]), yields of 6% and 3%, resp.). The last fraction (R_f 0.14) gave, after evaporation *i.v.*, 1.7 g (56%) of a colorless oil of **23**. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.09 (*m*, 1 H); 5.46 (*m*, 1 H); 4.41 (*m*, 1 H); 4.12 (*m*, 1 H); 2.90 (*m*, 1 H); 2.68–2.45 (sev. *m*, 3 H); 2.40–1.95 (sev. *m*, 5 H); 1.54 (*m*, 1 H); 1.35 (*m*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 138.1 (*d*); 131.4 (*d*); 89.7 (*s*); 60.3 (*s*); 53.5 (*d*); 53.3 (*d*); 38.6 (*t*); 33.9 (*t*); 33.8 (*t*); 31.0 (*t*); 19.2 (*d*); 18.4 (*d*) [18]).

2.5. *3,4,7-Tribromo-7-(cyclopenta-1,4-dienyl)bicyclo[4.1.0]heptane* (**24**). A 20-ml flask was charged with 1.0 g (2.41 mmol) of **23**, 10 ml of benzene, and *ca.* 90 mg (cat. amount, *ca.* 0.2 mol-equiv.) of TsOH. The mixture was stirred at r.t. for 3 h, then evaporated *i.v.*, and the resulting crude product was then purified by low-temp. (−20°) CC [19]) on *ca.* 20 g of silica gel with pentane/Et_2O 20:1 (R_f 0.64) to give 0.90 g (94%) of colorless crystals of **24**. M.p. 78–80°. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.47 (*m*, 2 H); 6.18 (*m*, 1 H); 4.46 (*m*, 1 H); 4.17 (*m*, 1 H); 3.04 (*s*, 2 H); 2.98 (*m*, 1 H); 2.70 (*m*, 2 H); 2.24 (*m*, 1 H); 1.56 (*m*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 135.0 (*d*); 132.4 (*d*); 127.3 (*d*); 53.5 (*d*); 53.3 (*d*); 41.0 (*t*); 33.9 (*t*); 33.7 (*t*); 22.8 (*d*); 22.2 (*d*). MS [20]): 399/97/95/93 (28/67/64/30, [$M^{+\cdot}$ − 1]), 319 (100), 318 (40), 315 (35), 236 (41), 157 (77), 156 (77), 155 (78), 141 (37), 129 (44), 128 (43), 115 (54), 91 (47), 80 (43), 79 (45), 77 (48). HR-MS: 393.8566 ($C_{12}H_{13}Br_3$, $M^{+\cdot}$ calc.: 393.8567) [18]).

2.6. *Attempted Dehydrobromination of* **24**. The resulting crude product (see *2.5*) was subjected to low-temp. (−20°) CC [19]) on Al_2O_3 (basic) with pentane/Et_2O 20:1. The hereby-formed intensely yellow zone was collected and evaporated *i.v.* to give, very surprisingly, 0.2 g (53%) of fulvene **22**.

3. Synthesis of a Heptafulvalene Precursor. – *7,7′-Bi(bicyclo[4.1.0]hept-3-enylidene)* (**26**). A 50-ml flask was charged with a soln. of 1.5 g (5.95 mmol) of **13** in 15 ml of THF and cooled to −95°. Under stirring at −95°, 3.9 ml of 1.6M BuLi (6.24 mmol) in hexane were slowly added during 30 min. After stirring the resulting mixture for 1 h at −95°, *ca.* 150 mg of dry $CuCl_2$ (*ca.* 0.2 mol-equiv., cat. amount) were added. The mixture was stirred at −95° for 1 h, then warmed to r.t., and quenched by adding 40 ml of 1N HCl. The mixture was extracted with Et_2O (3 × 40 ml), the combined org. extracts dried ($MgSO_4$), and evaporated *i.v.* The resulting orange-colored oil was purified by CC on *ca.* 50 g of silica gel with pentane/Et_2O 10:1 to give two isomers, *cis*-**26** and *trans*-**26** [16]). The first fraction (R_f 0.78) gave, after evaporation of solvents *i.v.*, 0.49 g (45%) of colorless crystals of **26** [16]) with m.p. 126–128°. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.36 (br. *s*, 4 H); 2.35 (*m*, 4 H); 2.25 (*m*, 4 H); 1.79 (br. *s*, 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 121.1 (*d*); 116.2 (*s*); 21.1 (*t*); 10.6 (*d*). MS [20]): 184 (58, $M^{+\cdot}$); 161 (80); 147 (100); 111 (35); 99 (25). HR-MS: 184.1253 ($C_{14}H_{16}$, $M^{+\cdot}$; calc.: 184.1252) [18]).

The second fraction (R_f 0.54) gave, after evaporation of solvents *i.v.*, 0.22 g (20%) of colorless crystals of **26** [16]) with m.p. 106–108°. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.41 (br. *s*, 4 H); 2.28 (br. *s*, 8 H); 1.65 (br. *s*, 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 123.3 (*d*); 118.4 (*s*); 23.3 (*t*); 12.8 (*d*) [18]).

REFERENCES

[1] M. Fischer, B. Aebi, P. Bönzli, S. Grillo, M. Neuenschwander, *Helv. Chim. Acta* **1999**, *82*, 1521.
[2] D. H. Wiley, Ph.D. Thesis, Yale University, 1954.
[3] W. E. von Doering, D. H. Wiley, *Angew. Chem.* **1955**, *67*, 429; W. E. von Doering, D. H. Wiley, *Tetrahedron* **1960**, *11*, 183.
[4] D. S. Matteson, J. J. Drysdale, W. H. Sharkey, *J. Am. Chem. Soc.* **1960**, *82*, 2853.
[5] C. Jutz, *Chem. Ber.* **1964**, *97*, 2050; C. Jutz, F. Voithenleitner, *Chem. Ber.* **1964**, *97*, 1337.
[6] H. E. Zimmermann, L. R. Sousa, *J. Am. Chem. Soc.* **1972**, *94*, 834.
[7] M. Neuenschwander, W. K. Schenk, R. Kyburz, *Chimia* **1971**, *25*, 361; *Chimia* **1972**, *26*, 194.
[8] W. K. Schenk, R. Kyburz, M. Neuenschwander, *Helv. Chim. Acta* **1975**, *58*, 1099.
[9] H. Prinzbach, W. Rosswog, *Angew. Chem.* **1961**, *73*, 543.
[10] H. Prinzbach, W. Rosswog, *Tetrahedron Lett.* **1963**, 1217.
[11] J. R. Mayer, Ph.D. Thesis, Yale University, 1955.
[12] W. E. von Doering, H. Krauch, *Angew. Chem.* **1956**, *68*, 661.

---

[22]) These protonation products give quite spectacular ^{1}H-NMR spectra which allow investigation of the configuration [11]). For spectroscopic data and illustrations of spectra, see [45].

[13] W. M. Jones, C. L. Ennis, *J. Am. Chem. Soc.* **1967**, *89*, 3069; W. M. Jones, C. L. Ennis, *J. Am. Chem. Soc.* **1969**, *91*, 6391.
[14] T. Mukai, T. Nakazawa, K. Isobe, *Tetrahedron Lett.* **1968**, 565.
[15] C. Wentrup, K. Wilczek, *Helv. Chim. Acta* **1970**, *53*, 1459.
[16] J. M. Myers, R. C. Joines, W. M. Jones, *J. Am. Chem. Soc.* **1970**, *92*, 4740.
[17] H. Schaltegger, M. Neuenschwander, D. Meuche, *Helv. Chim. Acta* **1965**, *48*, 955.
[18] K. Kyburz, H. Schaltegger, M. Neuenschwander, *Helv. Chim. Acta* **1971**, *54*, 1037.
[19] M. Neuenschwander, R. Iseli, *Helv. Chim. Acta* **1977**, *60*, 1061.
[20] M. Neuenschwander, A. Frey, *Chimia* **1974**, *28*, 117, 119.
[21] J. Furrer, P. Bönzli, A. Frey, M. Neuenschwander, P. Engel, *Helv. Chim. Acta* **1987**, *70*, 862.
[22] P. A. Baron, R. D. Brown, F. R. Burden, J. J. Domaille, R. Kent, *J. Mol. Spectrosc.* **1972**, *43*, 401.
[23] A. Bauder, C. Keller, M. Neuenschwander, *J. Mol. Spectrosc.* **1976**, *63*, 281.
[24] M. Neuenschwander, 'Fulvenes', in 'The Chemistry of Double-Bonded Functional Groups', Ed. S. Patai, John Wiley, New York, 1989, p. 1131 – 1268 and p. 1242 – 1246.
[25] A. P. Scott, I. Agranat, P. U. Biedermann, N. V. Riggs, L. Radom, *J. Org. Chem.* **1997**, *62*, 2026.
[26] M. Neuenschwander, *Pure Appl. Chem.* **1986**, *58*, 55.
[27] W. Rutsch, A. Escher, M. Neuenschwander, *Chimia* **1983**, *37*, 160; A. Escher, W. Rutsch, M. Neuenschwander, *Helv. Chim. Acta* **1986**, *69*, 1644.
[28] A. Escher, M. Neuenschwander, *Angew. Chem.* **1984**, *96*, 983; *Angew. Chem., Int. Ed.* **1984**, *23*, 973.
[29] A. Escher, M. Neuenschwander, P. Engel, *Helv. Chim. Acta* **1987**, *70*, 1623.
[30] G. Köbrich, *Angew. Chem.* **1972**, *84*, 557; *Angew. Chem., Int. Ed.* **1972**, *11*, 473.
[31] K. Kitatani, T. Hijama, H. Nozaki, *J. Am. Chem. Soc.* **1975**, *97*, 949; *idem Bull. Chem. Soc. Jpn.* **1977**, *50*, 3288.
[32] T. Hijama, A. Kanakura, H. Yamamoto, H. Nozaki, *Tetrahedron Lett.* **1978**, *33*, 3047.
[33] D. Seyferth, R. L. Lambert, *J. Organomet. Chem.* **1973**, *55*, C53; D. Seyferth, R. L. Lambert, M. Massol, *J. Organomet. Chem.* **1975**, *88*, 255.
[34] A. Weber, G. Sabbioni, R. Galli, U. Stämpfli, M. Neuenschwander, *Helv. Chim. Acta* **1988**, *71*, 2026.
[35] M. Mühlebach, M. Neuenschwander, *Chimia* **1992**, *46*, 382; M. Mühlebach, M. Neuenschwander, *Helv. Chim. Acta* **1993**, *76*, 2089.
[36] A. Weber, R. Galli, G. Sabbioni, U. Stämpfli, S. Walther, M. Neuenschwander, *Helv. Chim. Acta* **1989**, *72*, 41.
[37] M. Mühlebach, M. Neuenschwander, *Helv. Chim. Acta* **1994**, *77*, 1363.
[38] T. Loosli, M. Borer, I. Kulakowska, A. Minger, M. Neuenschwander, P. Engel, *Helv. Chim. Acta* **1995**, *78*, 1144; M. Borer, T. Loosli, A. Minger, M. Neuenschwander, P. Engel, *Helv. Chim. Acta* **1995**, *78*, 1311.
[39] M. Borer, M. Neuenschwander, *Helv. Chim. Acta* **1997**, *80*, 2486; R. Huwyler, X. Li, P. Bönzli, M. Neuenschwander, *Helv. Chim. Acta* **1999**, *82*, 1242; R. Huwyler, A. Al-Dulayymi, M. Neuenschwander, *Helv. Chim. Acta* **1999**, *82*, 2336.
[40] M. Makosza, A. Kacprowicz, M. Fedorynski, *Tetrahedron Lett.* **1975**, 2119; M. Makosza, in 'Modern Synthetic Methods 1976', Ed. R. Scheffold, Schweiz. Chemikerverband, 1976.
[41] M. Fedorynski, *Chem. Commun.* **1977**, 783.
[42] K. Hafner, *Angew. Chem.* **1962**, *79*, 499.
[43] P. T. Cheng, P. A. Gwinner, S. C. Nyburg, R. R. Stanford, P. Yates, *Tetrahedron* **1973**, *29*, 2699.
[44] C. Rentsch, M. Slongo, S. Schönholzer, M. Neuenschwander, *Makromol. Chem.* **1980**, *181*, 19; M. Slongo, S. Schönholzer, C. Rentsch, M. Neuenschwander, *Makromol. Chem.* **1980**, *181*, 31.
[45] X. Li, Research Report, University of Bern, 1999.
[46] S. Chai, M. Neuenschwander, *Helv. Chim. Acta* **1994**, *77*, 1377.

Received October 11, 1999