Further Synthetic Attempts towards Calicene(1)

by **Ahmad Al-Dulayymi**(2), **Xiaoming Li**(3) and **Markus Neuenschwander***

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

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First synthetic attempts towards the so-far-unknown calicene (= 5-(cycloprop-2-en-1-ylidene)cyclopenta-1,3-diene) precursors 3-(cyclopenta-2,4-dien-1-ylidene)tricyclo[3.2.2.$2^{2,4}$]nona-6,8-diene (**4**; *Scheme 1*), 1,4-di(cyclopenta-2,4-dien-1-ylidene)cyclohexa-2,5-diene (**5**; *Scheme 2*), and (2-bromocycloprop-1-en-1-yl)cyclopentadiene (**6**; X = Br; *Scheme 5*) are reported, which would represent very attractive compounds for gas-phase pyrolysis (**4**), matrix photolysis (**5**), and low-temperature HBr eliminations in solution (**5**).

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1. Introduction(4). – Calicene (**1** = pentatriafulvalene = 5-(cycloprop-2-en-1-ylidene)cyclopenta-1,3-diene) is an attractive cross-conjugated molecule containing two rings of inverse electron demand, which are expected to support each other electronically and hence to increase π-delocalization(5)(6). Despite the fact that calicene has fascinated physical organic chemists for more than three decades while several synthetic attempts have been undertaken(4), **1** has not been isolated, trapped, or as yet spectroscopically identified.

Based on earlier work concerning reactions of 1-bromo-1-lithiocyclopropanes with cyclopent-2-en-1-one [6], we recently synthesized 7-bromo-7,8-dihydrocalicene (**2**) [1], which, to our knowledge, is the first precursor of parent calicene (**1**), containing a good leaving group. However, although HBr elimination from **2** is possible with bases such as Et_3N at room temperature or sodium cyclopentadienide at 0°, no cycloaddition products of calicene (**1**) could be isolated so far, when these reactions were run in the presence of trapping reagents. On the other hand, gas-phase pyrolysis experiments with the *RDA* precursor(7) **3** [7] were not very successful, even with elaborate equipment [8], mainly due to its reduced solubility and low volatility, although some anthracene could be trapped [9].

Here, we report first synthetic attempts towards the so-far-unknown calicene precursors **4**, **5**, and **6**, which would represent very attractive compounds for gas-phase

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(1) Fulvenes, Fulvalenes, Part 74. Part 73: [1].

(2) Postdoctoral Fellow 1997–1999.

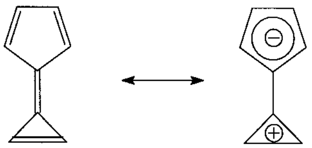
(3) Postdoctoral Fellow 1996–1999.

(4) For a more complete introduction into the topic and for extensive quotations of the literature, see [1].

(5) *Ab initio* calculations [2] show that bond lengths of formal C–C and C=C bonds of **1** are less alternating (and $\mu \approx 4.5$ D is increased) compared with triafulvene ($\mu = 1.9$ D [3]) or pentafulvene ($\mu = 0.424$ D [4]).

(6) According to our aromaticity plot for pentafulvenes and pentafulvalenes derived from ^3J(H,H) values [5], an aromaticity of *ca.* 30% may be estimated for calicene. This is perfectly in accord with the results of *ab initio* calculations [2], suggesting a 31% contribution for dipolar $\mathbf{1}^{\pm}$.

(7) *RDA* = *retro-Diels-Alder*.



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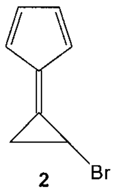

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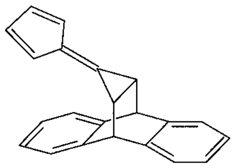

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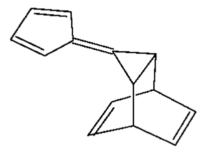

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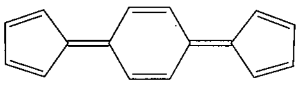

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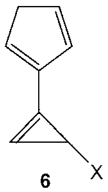

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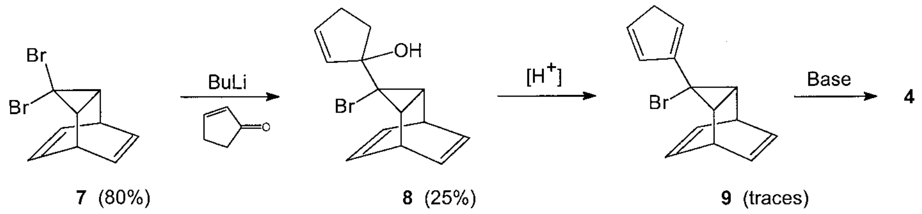
pyrolysis (**4**), matrix photolysis (**5**), and low-temperature HBr eliminations (**6**) in view of parent calicene (**1**)[8]).

2. Synthetic Attempts towards 4. – Compared with its dibenzo derivative **3**, **4** has several advantages in view of the foreseen *RDA* reaction[7]) **4** → **1**. First of all, due to the increased volatility and solubility of **4**, gas-phase-pyrolysis experiments should be much easier and straightforward. Then, *RDA* reaction[7]) of **4** is assumed to lead to calicene and benzene, which (contrary to anthracene formed from **3**) will be no more prone to cycloadditions with **1**. Furthermore, calicene could in principle be trapped in a matrix of frozen benzene. And finally, direct ^{1}H-NMR investigations of reaction products at low temperature should not be perturbed by appearance of the *singlet* of benzene at 7.26 ppm.

According to the synthetic plan (*Scheme 1*), 3,3-dibromotricyclo[3.2.2.0^{2,4}]nona-6,8-diene (**7**) was easily obtained by reaction of barrelene (prepared according to [10]) with $CHBr_3$/NaOH under phase-transfer conditions. Halogen/Li exchange of **7** in the presence of cyclopent-2-en-1-one gave the desired cyclopentenol **8**, albeit in moderate yields (25%). The structure of **8** was deduced from the spectroscopic data. In the ^{1}H-NMR spectrum, the most typical signals were the two *dt* of the vinylic cyclopentene

Scheme 1. *Planned Synthesis of* **4**



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[8]) The work presented here could not be completed due to the retirement of *M.N.*

H-atoms at 6.03 and 5.48 ppm (with $J = 5.5$ and 2.2 Hz, resp.), as well as the two *dd* at 1.73 and 1.51 ppm (with $J = 10.3$ and 4.4 Hz, resp.) of the diastereotopic cyclopropane H-atoms.

Although it is well-known that pentafulvenes[9]) are sensitive compounds and easily polymerize in the presence of strong acids [13], we so far did not have major problems with acid-catalyzed dehydrations of cyclopentenols (see **8** → **9**), followed by base-induced HBr eliminations (see **9** → **4**)[10]). In this case, however, treatment of **8** with small amounts of TsOH, followed by low-temperature chromatography over basic Al_2O_3 (according to the procedures used for the synthesis of **3** [7]), normally resulted in a nearly complete decomposition of the starting material[11]). It seems that strained fulvene **4** is more sensitive than its dibenzo analogue **3**. However, we still believe that the sequence depicted in *Scheme 1* can be completed under carefully controlled conditions at lower temperatures[8]).

3. Synthetic Attempts towards 5. – The so far unknown di(cyclopenta-2,4-dien-1-ylidene) compound **5** is an attractive fully conjugated molecule, which contains an essentially planar π-system. Similarly to pentafulvalene [14], **5** is assumed to be a quite unstable compound, which should, however, survive in solution at $-80°$ or in crystalline form around $-20°$. This makes **5** an appropriate candidate for low-temperature matrix photolysis, which could be an interesting route for generating calicene by [2 + 2] cycloaddition **5** → **10**, followed by cycloreversion **10** → 2 **1**[12]).

A straightforward plan for the synthesis of **5**[13]) is depicted in *Scheme 2*. 1,4-Dibromobenzene reacted with BuLi and cyclopent-2-en-1-one at $-80°$ to give cyclopentenol **11** in good yields[14]). By subsequent treatment of **11** with BuLi and cyclopent-2-en-1-one, the envisaged di(cyclopentenol) **12** was generated with a yield of 70%. Furthermore, acid-catalyzed dehydration **12** → **13** was possible, albeit so far in poor yields[15]).

The structure of compounds **11**, **12**, and **13** followed from spectroscopic data, where the cyclopentenol units of **11** and **12** are easily identified in the ^{1}H-NMR spectra. This is demonstrated by the ^{1}H-NMR spectrum of **11** (*Fig.*), which shows signals of vinylic H-atoms at 6.06 and 5.76 ppm (both as *dt* with $J = 5.5$ and $J' = 2.2$ Hz, resp.[16]), while

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[9]) For surveys, see [11][12].

[10]) For some typical examples, see [1][7].

[11]) In most experiments, traces of cyclopentadiene **9** could be spectroscopically identified.

[12]) The step **10** → 2 **1** is quite similar to the recently realized low-temperature matrix photolysis of pentalene dimers [15][16] (containing 2 pentafulvene moieties!), where 2 molecules of pentalene are generated by *hν*-induced cleavage of a cyclobutane ring [17].

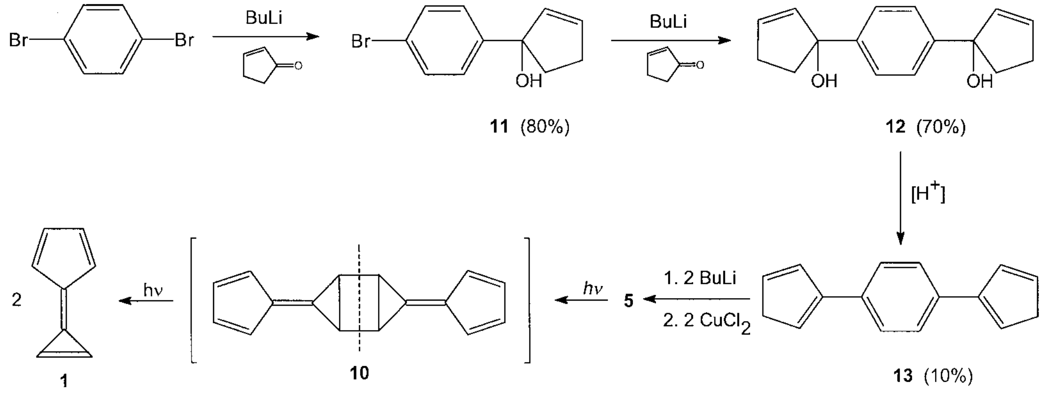
[13]) Other synthetic attempts such as Pd-catalyzed *Heck* coupling of 1,4-dibromobenzene with 2 mol-equiv. of sodium cyclopentadienide or bromination/elimination experiments of 1,4-di(cyclopenta-2,4-diene-1-ylidene)cyclohexane [18] (which represents the tetrahydroderivative of **5**) have failed so far.

[14]) Quite surprisingly, reaction of 1,4-dibromobenzene with 2.2 mol-equiv. of BuLi and 2.2 mol-equiv. of cyclopent-2-en-1-one gave mainly **11** and not **12**.

[15]) We believe that the yield of step **12** → **13** can be considerably improved if twofold dehydration can be achieved at lower temperature (see *Scheme 4*; 4,4′-di(cyclopentadienyl)biphenyl has been produced in a yield of 85% by chromatography of the corresponding di(cyclopentenol) over acidic silica gel at $-15°$).

[16]) It is impossible to assign these *multiplets* to H–C(2) and H–C(3) from the splitting pattern. Due to the fact that, in several other examples with confirmed assignment [9][1], H–C(2) absorbs in the range of 6.0–6.2 ppm, we tentatively assigned the *multiplet* at 6.06 ppm to H–C(2).

Scheme 2. *Planned Synthesis of Calicene* (**1**) via *Bis(pentafulvene)* **5**



nonequivalent $CH_2(4)$ H-atoms gave rise to complex *multiplets* at 2.56 and 2.40 ppm, and $CH_2(5)$ are nearly degenerate at 2.14 ppm. Additionally the *AA′BB′* system of the aromatic H-atoms was identified at 7.39 and 7.24 ppm, while the OH proton absorbs as a broad *singlet* at 1.84 ppm.

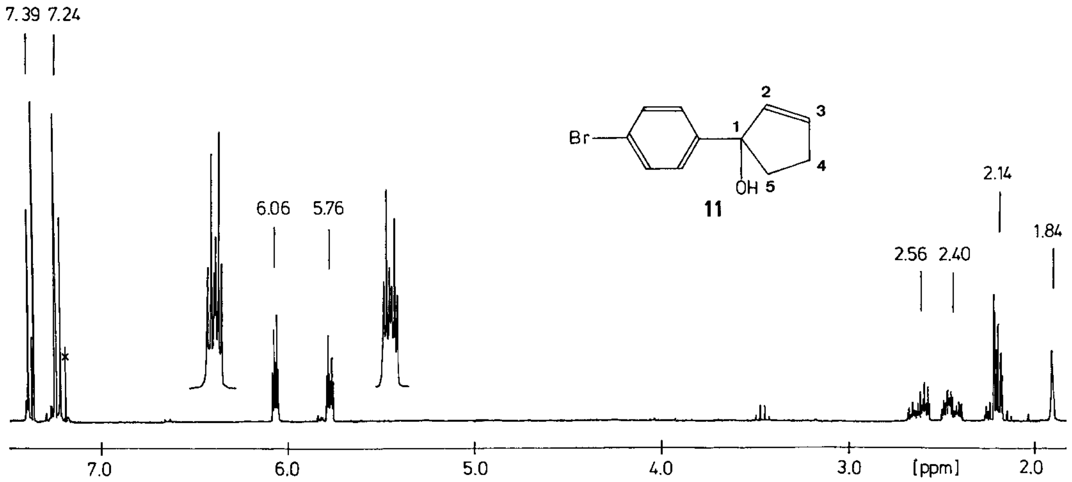
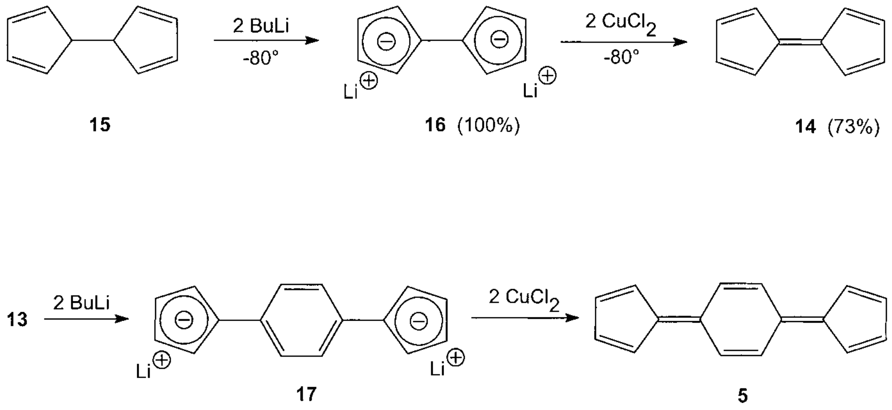


Figure. *^{1}H-NMR Spectrum* (300 MHz, $CDCl_3$) *of* **11**

Similarly to the synthesis of pentafulvalene (**14**) by deprotonation of 1,1′-bi(cyclopentadienyl) (**15** → **16**) and oxidation **16** → **14** by means of $CuCl_2$ (*cf. Scheme 3*, above [14]), the synthesis of bis(pentafulvene) **5** by twofold deprotonation of 1,4-di(cyclopentadienyl)benzene (**13** → **17**) and subsequent $CuCl_2$-induced oxidation of dianion **17** seemed to be easy and straightforward. It has to be kept in mind, however, that the target molecule **5** is considered to be such a thermally very unstable and oxygen-sensitive compound that all the steps **13** → **17** → **5**, as well as workup of **5**, should be performed at temperatures below – 50°. Due to insufficient amounts of **13**, we have not been able to optimize the sequence (*Scheme 3*, below).

Scheme 3. *Realized Synthesis of Pentafulvalene* (**14**) *and Planned Synthesis of* **5** *Starting* from **13**

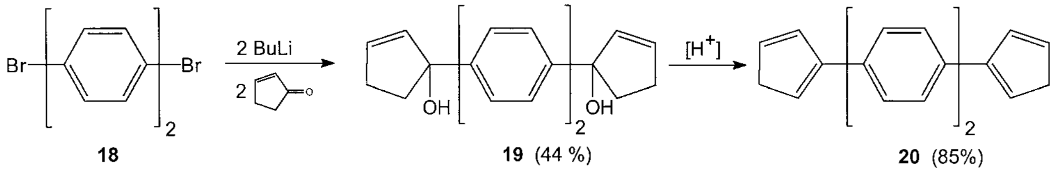


15 **16** (100%) **14** (73%)

17 **5**

Finally, it has to be mentioned that the synthesis depicted in *Scheme 2*, starting from 1,4-dibromobenzene, could be applied to 4,4′-dibromo-1,1′-biphenyl (**18**). Treatment of **18** with 2 mol-equiv. of BuLi and cyclopent-2-en-1-one at – 60° in THF directly gave, after protonation, bis(cyclopentenol) **19**, which could be easily dehydrated by chromatography over acidic silica gel at – 15° (**19** → **20**; *Scheme 4*).

Scheme 4



18 **19** (44 %) **20** (85%)

4. Synthetic Attempts towards 6[17]). – (2-Bromocycloprop-1-en-1-yl)cyclopentadiene (**6**; X = Br) is an outstanding calicene precursor in view of base-induced low-temperature HBr eliminations in solution. Compound **6** combines the acidity of a cyclopentadiene with the leaving-group qualities of Br placed in allylic position of the cyclopropene unit.

A surprisingly simple synthetic plan for the so far unknown calicene precursor **6** is summarized in *Scheme 5*; it is based on important work of *Baird et al.* [19], who showed that 1,1,2-tribromocyclopropanes react with 2 mole-equiv. of BuLi at low temperature to give 1-lithiocycloprop-1-enes, which can be used synthetically as nucleophiles. Starting with 1,1,2,3-tetrabromocyclopropane (**21**), halogen/Li exchange was expected

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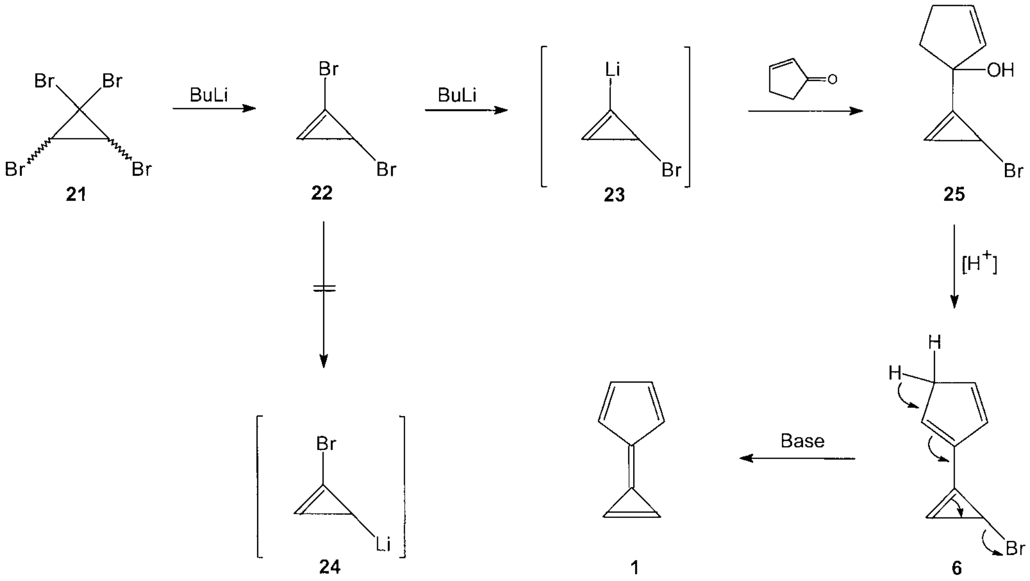
[17]) Note that alkyl- as well as alkenyl-cyclopentadienes normally exist as tautomeric mixtures, in which tautomers are interconverted by comparably fast 1,5-H shifts. The 1- and 2-substituted tautomers are predominant, but all three tautomers of **6** can easily undergo HBr elimination.

to take place at C(1), and subsequent β-elimination of one of the Br substituents would give **22**. We believe that further reaction of **22** with BuLi will produce 1-lithiocycloprop-1-ene **23** according to [19] (and not **24**[18])), and that subsequent reaction with cyclopent-2-en-1-one will generate **25** in a simple one-pot reaction starting from **21**. If acid-catalyzed dehydration **25** → **6** could be realized[19]) by low-temperature chromatography over acidic silica gel according to our methodology[15]), then the attractive calicene precursor **6** would be easily available.

Scheme 5. *Synthetic Plan for Calicene Precursor* **6**



So far, there exists no efficient synthesis of 1,1,2,3-tetrabromocyclopropane (**21**). While dibromocarbene addition to 1,2-dibromoethene according to *Makosza et al.* [20] and *Doering* and *Henderson* [21] failed, reaction of the olefin with (tribromomethyl)-(phenyl)mercury according to *Seyferth et al.* [22] gave impure **21** in a yield of only 2%. This prompted us to explore an alternative route to **21** (*Scheme 6*), starting from 2,2-dimethyl-1,3-dioxa-cyclohept-5-ene (**26**), which is available in high yields by acetalization of (*Z*)-but-2-ene-1,4-diol. Dibromocarbene addition under phase-transfer conditions [20] gave **27**, and subsequent hydrolysis **28** [23]. Our original plan was to prepare dicarboxylic acid **29** by $KMnO_4$ oxidation of **28** and to transform **29** to **21** by *Hunsdiecker* bromodecarboxylation [24]. Quite surprisingly, however, $KMnO_4$ oxida-

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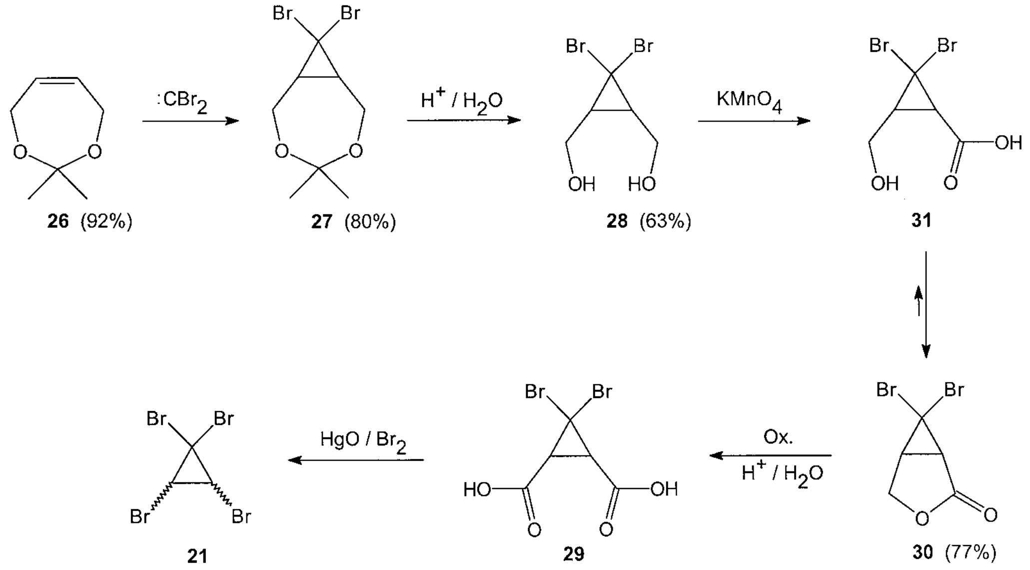
[18]) First of all, 1-bromocycloprop-1-enes react similarly to 1-bromoacetylenes as far as the easy halogen/Li exchange is concerned [19]. Then, the free energy of **24** will be considerably increased (compared to **22**) by any contribution of the antiaromatic cyclopropenylium anion, thus increasing the free activation enthalpy of the step **22** → **24**.

[19]) It will be interesting to see whether acid-catalyzed dehydration (giving a delocalized pentadienyl cation in the first step) will dominate over acid-catalyzed dehydrobromination of **25** (giving a substituted cyclopropenylium cation in the first step). According to HMO calculations, acid-catalyzed dehydration **25** → **6** should be favored.

tion of **28** directly gave high yields of lactone **30**, obviously by cyclization of the *ω*-hydroxycarboxylic acid **31**. First tentative experiments in view of an oxidation of lactone **30** under hydrolytic conditions (**30** → **31** → **29**) were promising[20]) so that we hope 1,1,2,3-tetrabromocyclopropane (**21**) will be obtained in acceptable over-all yields[8]).

Scheme 6. *Planned Synthesis of 1,1,2,3-Tetrabromocyclopropane* (**21**)



Additionally, we have successfully tested both the efficiency of 1-lithiocycloprop-1-enes as nucleophiles in reactions with cyclopent-2-en-1-one (which is crucial for realizing the synthetic plan of *Scheme 5*; see **23** → **25**), as well as *Hunsdiecker* reactions of 2,2-dibromocyclopropane-1-carboxylic acids (which is the important step in the synthesis of **21** according to *Scheme 6*). Addition of dibromocarbene to methyl methacrylate perfectly worked under phase-transfer conditions and gave 2,2-dibromocyclopropane-1-carboxylate **32**. After hydrolysis of the ester function (**32** → **33**), *Hunsdiecker* bromodecarboxylation of **33** afforded 1,1,2-tribromo-2-methylcyclopropane **34** in quite good yields, while subsequent treatment of **34** with 2 mol-equiv. of BuLi at – 80° obviously produced 1-lithio-2-methylcycloprop-1-ene **35**, which perfectly added to the C=O bond of cyclopent-2-en-1-one (**35** → **36**; *Scheme 7*).

5. Discussion. – In this paper, several novel synthetic pathways for so far unknown calicene precursors **4** (*Scheme 1*), **5** (*Scheme 2*), and **6** (*Scheme 5*) have been explored. While experimentally realized syntheses depicted in *Schemes 1* and *2* stopped short of the target molecules **4** and **5**, the synthesis of precursor **6** is as yet hampered by the unavailability of reasonable amounts of 1,1,2,3-tetrabromocyclopropane (**21**).

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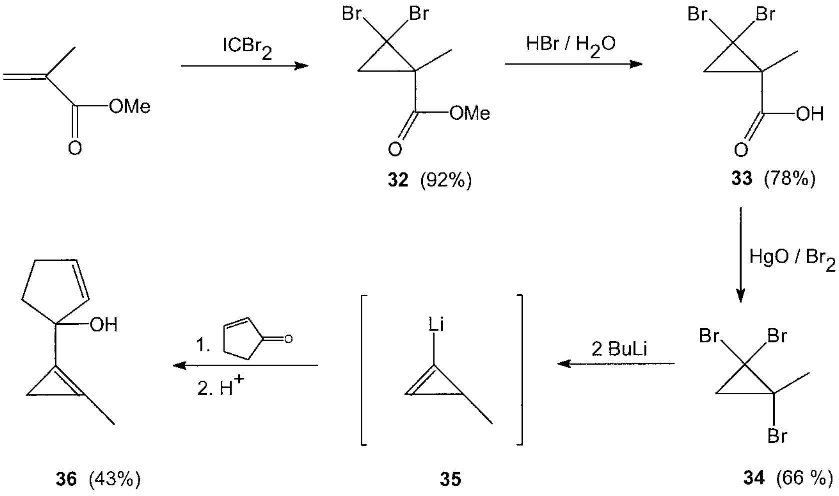
[20]) However, extraction of the H_2O phase did not give a pure enough sample of dicarboxylic acid **29** for the final step **29** → **21**.

Scheme 7



However, a very promising synthesis of **21** has been tested (*Scheme 6*), and it has been shown with model compounds (*Scheme 7*) that the central steps **21**$\rightarrow\rightarrow$**25** in *Scheme 5* seem to be promising. Since compounds **4**, **5**, and **6** are considered to be attractive precursors of calicene (**1**) for gas-phase pyrolysis (**4**), matrix photolysis (**5**), and low-temperature solution reactions (**6**), and that the synthetic sequences in *Schemes 1*, *2*, and *5* are simple and straightforward, we hope that this contribution will help to trap the so far eluding parent calicene (**1**) in the near future[8]).

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Experimental Part

General. Unless otherwise stated, all reactions were run under N_2 or Ar in two- or three-necked round-bottomed flasks equipped with a dropping funnel (or a septum), a magnetic stirrer, a N_2 inlet and, where needed, a thermometer with H_2O-free solvents and reagents. 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. A temp. of – 95° was reached by freezing toluene with liq. N_2. Spectra were recorded on the following instruments: UV. *Perkin-Elmer 554* and *Hewlett-Packard HP.8452 A*; λ_{max} (ε) in nm. IR: *Perkin-Elmer 399 B* and *1600*; $\tilde{\nu}$ in cm^{-1}. NMR: *Bruker AC-300*; δ in ppm rel. to TMS, *J* in Hz. MS: *Varian MAT CH-7A*, *m/z* (rel. %).

1. Synthetic Attempts towards 4 (*Scheme 1*). – 1.1. *Tricyclo[2.2.2]octa-2,5,7-triene* (= *Barrelene*): See [10].

1.2. *3,3-Dibromotricyclo[3.2.2.0^{2,4}]nona-6,8-diene* (**7**). In a 100-ml two-necked flask equipped with dropping funnel, septum, and magnetic stirrer, 10 ml of 50% aq. NaOH were slowly added at 0° to a vigorously stirred mixture of 500 mg (4.80 mmol) of barrelene, 1.34 g (5.3 mmol) of $CHBr_3$, and 500 mg (1.4 mmol) of cetrimide in 10 ml of CH_2Cl_2. The mixture was intensively stirred for 2 h at 0–5°, then overnight at r.t. (TLC showed complete conversion of barrelene). After adding *ca.* 20 ml of CH_2Cl_2, the mixture was transferred into a separatory funnel that contained 50 ml of H_2O. The org. layer was separated, washed with 2 × 50 ml of H_2O and concentrated *i.v.* The yellow oily residue was dissolved in 50 ml of Et_2O and dried ($MgSO_4$). Filtration and evaporation *i.v.* yielded 1060 mg (80%) of practically pure **7**. Anal. pure samples of **7** can be obtained by column chromatography (CC) at –20° over silica gel with pentane/Et_2O 10:1. ^1H-NMR (300 MHz, $CDCl_3$): 6.77 (*m*, 2 H); 6.22 (*m*, 2 H); 4.07 (*m*, 2 H); 2.10 (*m*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 138.6 (*d*); 131.7 (*d*); 42.7 (*s*);

38.7 (*d*); 37.7 (*d*). MS[21]): 278/276/274 (0.1/0.2/0.1, $M^{+\bullet}$), 116 (75), 115 (100), 91 (17), 89 (14), 78 (10), 65 (11), 63 (17), 51 (12), 50 (10), 39 (20).

1.3. *1-(3-Bromotricyclo[3.2.2.0^{2,4}]nona-6,8-dien-3-yl)cyclopent-2-en-1-ol* (**8**). In a 50-ml three-necked flask equipped with N_2-bubbler, septum, and magnetic stirrer, 1.0 g (3.6 mmol) of **7** and 0.8 g (9.7 mmol) of cyclopent-2-en-1-one were dissolved in 20 ml of THF, and the mixture was cooled to – 95°. To the stirred soln., 3.8 ml of 1.6M BuLi in hexane (6.1 mmol) were added dropwise during 1 h through the septum with a syringe. After stirring for 2 h at – 95°, warming to r.t., and stirring for 1 h at r.t., the reaction was quenched by adding 50 ml of Et_2O/50 ml of H_2O at 0°. The layers were separated, the aq. phase was extracted with Et_2O (3×20 ml), and the combined org. extracts were dried ($MgSO_4$) and evaporated *i.v.* The crude orange oil was purified by low-temp. (– 20°) CC (*ca.* 50 g of silica gel; pentane/Et_2O 10 : 2) to yield 253 mg (25.2%) of pale-yellow oil of **8**. R_f 0.14[22]). ^{1}H-NMR (300 MHz, $CDCl_3$): 6.81 (*m*, 2 H); 6.26 (*m*, 2 H); 6.03 (*dt*, *J* = 5.5, 2.2, 1 H); 5.48 (*dt*, *J* = 5.5, 2.2,1 H); 3.96 (*m*, 2 H); 2.46 (*m*,1 H); 2.28 (*m*, 3 H); 1.97 (*m*, 1 H); 1.73 (*dd*, *J* = 10.3, 4.4, 1 H); 1.51 (*dd*, *J* = 10.3, 4.4, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 141.35 (*d*); 141.31 (*d*); 137.6 (*d*); 136.0 (*d*); 135.5 (*d*); 132.0 (*d*); 90.7 (*s*); 39.3 (*d*); 39.0 (*d*); 37.3 (*t*); 34.69 (*d*); 34.66 (*d*); 30.8 (*t*). MS[21]): 280/278 (45/47, $M^{+\bullet}$), 262/260 (60/64), 182 (100), 167 (72), 144 (55), 132 (24). HR-MS: 278.0304 ($C_{14}H_{15}OBr$, $M^{+\bullet}$; calc. 278.0306).

2. Synthetic Attempts towards 5 (*Schemes 2* and *4*). – 2.1. *(1-(4-Bromophenyl)cyclopent-2-en-1-ol* (**11**). In a 250-ml flask, 28.8 ml of 1.6M BuLi (46.1 mmol) in hexane were added dropwise to a stirred soln. of 10 g (42.4 mmol) of 1,4-dibromobenzene in 70 ml of Et_2O at – 80° under N_2. After addition, the mixture was allowed to reach r.t. and stirred at r.t. for 30 min, then cooled again to – 80°. Then, 4.51 g (55 mmol) of cyclopent-2-en-1-one were added dropwise. The mixture was stirred for 1 h at – 80°, then allowed to reach r.t., and stirred for another h at r.t. before quenching by adding 40 ml of H_2O at – 40°. After extraction with Et_2O (3×20 ml) solvents were removed *i.v.* (14 Torr), and CC (silica gel; pentane/Et_2O 5 : 1) yielded 8.11 g (80%) of a pale-yellow oil of **11**. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.39 (*m*, 2 H); 7.24 (*m*, 2 H); 6.06 (*dt*, *J* = 5.5, 2.2, 1 H); 5.76 (*dt*, *J* = 5.5, 2.2, 1 H); 2.56 (*m*, 1 H); 2.40 (*m*, 1 H); 2.14 (*m*, 2 H); 1.84 (br. *s*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 145.9 (*s*); 136.1 (*d*); 135.2 (*d*); 131.0 (*d*); 126.6 (*d*); 120.5 (*s*); 86.5 (*s*); 41.9 (*t*); 31.3 (*t*). MS[21]): 240 (54, $M^{+\bullet}$), 238 (55, $M^{+\bullet}$), 185 (32), 183 (34), 160 (62), 159 (100), 145 (29), 144 (36), 142 (22), 141 (32), 131 (21), 115 (20), 105 (22), 83 (18), 77 (19).

2.2. *1,1′-(Benzene-1,4-diyl)di(cyclopent-2-en-1-ol)* (**12**). In a 100-ml flask, 15.5 ml of 1.6M BuLi (24.8 mmol) in hexane were added dropwise to a stirred soln. of 2.7 g (11.3 mmol) of **11** in 15 ml of Et_2O at – 40° under N_2. After addition, the mixture was allowed to reach r.t. and was stirred at r.t. for 30 min (formation of a white precipitate). After cooling the mixture to – 80°, 4.5 g (55 mmol) of cyclopent-2-en-1-one were slowly added, and the mixture was stirred at – 80° for 30 min, then for 1 h at r.t. before quenching by addition of 0.6 ml of H_2O at – 20°[23]). Subsequent filtration of the precipitate gave 1.92 g (70%) of NMR-pure pale-yellow solid **12**. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.32 (*s*, 4 H); 6.04 (*dt*, *J* = 5.5, 2.2, 2 H); 5.81 (*m*, 2 H); 2.58 (*m*, 2 H); 2.40 (*m*, 2 H); 2.19 (*m*, 4 H); 1.90 (br. *s*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 145.5 (*s*); 136.6 (*d*); 134.7 (*d*); 124.7 (*d*); 86.8 (*s*); 41.8 (*t*); 31.4 (*t*). MS[21]): 242 (68, $M^{+\bullet}$), 225 (39), 224 (50), 209 (22), 207 (19), 206 (22), 187 (27), 160 (86), 159 (100), 145 (22), 142 (20), 141 (27), 115 (20), 83 (96).

2.3. *1,4-Di(cyclopenta-1,4-dienyl)benzene* (**13**)[24]). In a 50-ml flask, 3.0 g (12.4 mmol) of **12** were dissolved in 15 ml of dry benzene under stirring. Acidic Al_2O_3 (3 g) was added, and the mixture was stirred for 1 h at r.t., then transferred into a column containing *ca.* 20 g of silica gel and eluted with benzene. Evaporation *i.v.* yielded 255 mg (10%)[25]) of a light-brown solid of **13**[24]). ^{1}H-NMR (300 MHz, $CDCl_3$): 7.42 (*s*, 4 H); 6.84 (*m*, 2 H); 6.55 (*m*, 2 H); 6.38 (*m*, 2 H); 3.33 (*m*, 4 H)[25]). ^{13}C-NMR (75 MHz, $CDCl_3$): 146.5 (*s*); 133.4 (*d*); 132.4 (*d*); 128.3 (*d*); 127.0 (*d*); 125.2 (*d*); 41.2 (*t*)[26]). MS[21]): 207 (72), 206 (100, $M^{+\bullet}$), 205 (29), 203 (24), 202 (24), 191 (30), 190 (30), 189 (25), 178 (24), 165 (25), 141 (28).

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[21]) Only the most important MS fragments are listed. In most cases, IR spectra have also been recorded, but they are not very relevant for the structure elucidation.

[22]) A first fraction (R_f 0.86) contained 14 mg (2.0%) of 'protonation product' (3-bromotricyclo[3.2.2.0^{2,4}]nona-6,8-diene).

[23]) Excess H_2O should be avoided because the product **12** is soluble in H_2O.

[24]) Tautomeric mixture with one predominant tautomer (*ca.* 90% according to ^{1}H-NMR).

[25]) Very probably, the yield of **13** will be considerably increased if the procedure for twofold dehydration of **19** → **20** will be applied (see *2.5*).

[26]) Signals of the major tautomer. Most signals of the minor tautomer are obscured.

2.4. *4,4′-Di(1-hydroxycyclopent-2-en-1-yl)-1,1′-biphenyl* (**19**). A 200-ml flask equipped with N_2 bubbler, septum, and magnetic stirrer was charged with 5.6 g (17.95 mmol) of 4,4′-dibromobiphenyl and 50 ml of dry THF. The soln. was stirred at − 60°, while 25 ml of 1.6м BuLi in hexane (40 mmol, 2.2 mol-equiv.) were added dropwise over 1 h with a syringe, followed by 3.0 g (36.5 mmol) of cyclopent-2-en-1-one in 20 ml of dry THF. The mixture was stirred for 2 h at − 60°, then for 20 h at r.t. After quenching with 20 ml of H_2O and 25 ml of sat. NH_4Cl at 0°, the mixture was extracted with CH_2Cl_2 (3 × 50 ml). The combined org. layers were washed with sat. aq. NaCl (3 × 50 ml), dried ($MgSO_4$), and concentrated *i.v.* to give 2.5 g (44%) of colorless oil of crude diol **19**. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.58 (*m*, 4 H); 7.51 (*m*, 4 H); 6.14 (*dt*, $J = 5.5$, 2.4, 2 H); 5.92 (*dt*, $J = 5.5$, 2.0, 2 H); 2.70 (*m*, 2 H); 2.50 (*m*, 2 H); 2.31 (*m*, 4 H); 2.00 (br. *s*, 2 H). MS[21]): 318 (28, $M^{+\bullet}$), 301 (22), 300 (44), 283 (36), 282 (100),141 (13). HR-MS: 318.1618 ($C_{22}H_{22}O_2$, $M^{+\bullet}$; calc.: 318.1620).

2.5. *4,4′-Di(cyclopentadienyl)-1,1′-biphenyl* **20**[27]). Diol **19** (2.0 g, 6.3 mmol) was dissolved in 5 ml of CH_2Cl_2 and added into a cooled (− 15°) column (length 20 cm) containing 100 g of acidic silica gel[28]) in CH_2Cl_2. Elution with CH_2Cl_2, evaporation of solvent *i.v.*, and recrystallization from Et_2O/CH_2Cl_2 5 : 3 yielded 1.5 g (85%) of yellow crystals of **20**. M.p. 154 – 156°. ^{1}H-NMR (300 MHz, $CDCl_3$)[27]): 7.8 – 7.4 (several *m*, 8 H); 7.00 (*m*); 6.95 (*m*); 6.73 (*m*); 6.62 (*m*); 6.48 (*m*, total 6 H); 3.43 (*m*); 3.24 (*m*, total 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$)[27]): 139.4 (*s*); 136.6 (*d*); 134.9 (*d*); 134.7 (*d*); 132.0 (*d*); 127.2 (*d*); 127.0 (*d*); 126.9 (*d*); 126.7 (*d*); 126.40 (*d*); 126.38 (*d*); 125.4 (*d*); 125.3 (*d*); 42.01 (*t*); 41.99 (*t*); 31.5 (*t*).

3. Planned Synthesis of 1,1,2,3-Tetrabromocyclopropane (**21**, *Scheme 6*) – 3.1. *5,7-Dihydro-2,2-dimethyl-2*H*-dioxepin* (**26**). 2,2-Dimethoxypropane (35.4 g, 0.34 mol) was added to a stirred soln. of 15 g (0.17 mol) of (*Z*)-but-2-ene-1,4-diol and 1.6 g (85 mmol) of TsOH in 100 ml of CH_2Cl_2 at r.t. After stirring the mixture for 2 h at r.t. (TLC showed complete conversion of starting material), the reaction was quenched with sat. aq. $NaHCO_3$. The aq. layer was extracted with CH_2Cl_2 (2 × 50 ml), the combined org. layers were dried ($MgSO_4$), and solvent was removed *i.v.:* 20.0 g (92%) of colorless oil of **26**. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.60 (br. *s*, 2 H); 4.20 (br. *s*, 4 H); 1.47 (*s*, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 129.4 (*d*); 102.0 (*s*); 61.4 (*t*); 23.9 (*q*).

3.2. *8,8-Dibromo-4,4-dimethyl-3,5-dioxabicyclo[5.1.0]octane* (**27**). In a 500-ml flask, a mixture of 70.7 g (0.28 mol) of $CHBr_3$, 3 g of cetrimide, 2 drops of Et_3N, and 50 ml of CH_2Cl_2 was stirred for 10 min at r.t. Then, 24 g (187 mmol) of **26** were added. Under vigorous stirring, a soln. of 75 g (1.875 mol) of NaOH in 75 ml of H_2O was slowly added at 0 – 10°. Stirring was continued at r.t. for 48 h. Then, the mixture was poured into 150 ml of H_2O and extracted with CH_2Cl_2 (3 × 100 ml). After evaporation *i.v.*, 150 ml of pentane were added, and the mixture was stirred for 15 min, while cetrimide was precipitating. After filtration, the soln. was dried ($MgSO_4$) and evaporated *i.v.* to give a yellow solid, which was purified by flash-CC (silica gel; pentane/AcOEt 4 : 1) to yield 45.0 g (80.2%) of **27**. Colorless solid. ^{1}H-NMR (300 MHz, $CDCl_3$)[29]): 4.23 (*m*, 2 H); 3.93 (*m*, 2 H); 2.07 (*m*, 2 H); 1.35 (*s*, 3 H); 1.28 (*s*, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 103.5 (*s*); 60.1 (*t*); 34.7 (*q*); 33.0 (*s*); 25.4 (*d*); 23.7 (*d*). MS[21]): 302/300/298 (0.3/0.7/0.3, $M^{+\bullet}$), 214 (14), 212 (27), 210 (14), 201 (10), 199 (22), 197 (11), 163 (11), 161 (12), 135 (22), 133 (48), 131 (27), 81 (26), 59 (49), 55 (16), 53 (49), 52 (23), 51 (48), 43 (100), 39 (22).

3.3. *[2,2-Dibromo-3-(hydroxymethyl)cycloprop-1-yl]methanol* (**28**). Compound **27** (20.0 g, 66.7 mmol) was added to 100 ml of 2N HCl, and the mixture was refluxed for 2 h under vigorous stirring. After addition of 50 ml of H_2O and cooling to r.t., the aq. phase was extracted with CH_2Cl_2 (1 × 100 ml, 3 × 50 ml). The combined org. layers were washed with 50 ml of sat. aq. $NaHCO_3$, decolorized with 2 g of charcoal, and dried ($MgSO_4$). Filtration and evaporation *i.v.* yielded 11.0 g (63.5%) of **28**. ^{1}H-NMR (300 MHz, $CDCl_3$)[29]): 4.11 (*m*, 2 H); 3.64 (*m*, 2 H); 2.35 (br. *s*, 2 H); 2.11 (*m*, 2 H).

3.4. *6,6-Dibromo-3-oxabicyclo[3.1.0]hexan-2-one* (**30**). $KMnO_4$ (24.3 g, 0.154 mol) was dissolved in 150 ml of H_2O by rapidly stirring at 0° for 10 min. Then, 0.99 g (3.07 mmol) of Bu_4NBr and a soln. of 4.0 g (15.4 mmol) of **28** in 20 ml of benzene were added, and the mixture was rapidly stirred at 0° for 16 h. After carefully adding sat. aq. $Na_2S_2O_5$ at 0° (until the brown coloration disappeared), acidifying to pH 1 with 10% of aq. H_2SO_4 and extracting with Et_2O (3 × 50 ml), the combined org. layers were dried ($MgSO_4$), and the solvent was removed *i.v.* to give 3.03 g (77%) of **30** as a colorless solid **30**, which was recrystallized from pentane. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.43 (*dd*, $J = 5.5$, 10.3, 1 H); 4.26 (*dt*, $J = 10.3$, 1.1, 1 H); 3.04 (*dd*, $J = 7.0$, 1.1, 1 H); 2.93 (*ddd*, $J = 7.0$, 5.5, 1.1, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 168.7 (*s*); 67.7 (*t*); 37.6 (*d*); 35.8 (*d*); 23.5 (*s*). MS[21]). 258/256/254 (2/4/2,

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[27]) Tautomeric mixture.

[28]) A round-bottomed 1-l flask was charged with 100 g of silica gel, 0.2 g of TsOH, and 150 ml of dry Et_2O. The slurry was thoroughly shaken, and solvent was removed *i.v.* in a rotatory evaporator.

[29]) Well-resolved *AA′MM′XX′* spectrum.

$M^{+\cdot}$), 228 (22), 226 (42), 224 (22), 214 (50), 212 (100), 210 (51), 199 (16), 133 (30), 131 (30), 119 (22), 117 (16), 51 (14), 39 (14).

4. Synthesis of 1-(2-Methylcycloprop-1-en-1-yl)cyclopent-2-en-1-ol (**36**, *Scheme 7*). – 4.1 *Methyl 2,2-Dibromo-1-methylcyclopropane-1-carboxylate* (**32**). A mixture of 187.0 g (0.74 mol) of $CHBr_3$, 5 g of cetrimide, and 50 g (0.5 mol) of methyl methacrylate in 150 ml of CH_2Cl_2 was stirred for 15 min at r.t. After cooling to 0°, a soln. of 200 g (5.0 mol) of NaOH in 200 ml of H_2O was slowly added. The mixture was rapidly stirred for 5 h at 20–25°, then poured into 300 ml of H_2O, and extracted with CH_2Cl_2 (3 × 150 ml). After evaporation of the combined org. layers, 200 ml of pentane were added, and the mixture was stirred for 15 min. After filtering off the precipitate of cetrimide, evaporation *i.v.* gave 125 g (92%) of **32** [25]. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.80 (*s*, 3 H); 2.43 (*d*, $J = 7.9$, 1 H); 1.61 (*s*, 3 H); 1.59 (*d*, $J = 7.9$, 1 H).

4.2. *2,2-Dibromo-1-methylcyclopropane-1-carboxylic Acid* (**33**). Ester **32** (30 g, 0.11 mol) was added to 118 ml of aq. HBr (48%), and the mixture was vigorously stirred under reflux (temp. of the oil bath 140–150°) for 4 h. After cooling to r.t., 200 ml of H_2O were added, and the mixture was extracted with Et_2O (3 × 50 ml). The combined org. layers were washed with sat. aq. NaCl, then the solvent was removed *i.v.* to give 22.0 g (77.5%) of colorless solid of **33**.

4.3. *1,1,2-Tribromo-2-methylcyclopropane* (**34**). To a stirred suspension of 6 g (23.26 mmol) of **33** and of 5.2 g (24 mmol) of red HgO in 30 ml of CCl_4, a soln. of 4.68 g (29.3 mmol) of Br_2 in 10 ml of CCl_4 was added dropwise at 85°. The mixture was refluxed for 3 h, then stirred at r.t. for 12 h, treated with 30 ml of pentane, stirred for another 5 min, and filtered over flash silica gel. The filtrate was evaporated *i.v.* to give 4.5 g (66%) of NMR-pure **34** [26]. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.09 (*s*, 3 H); 1.99 (*d*, $J = 9.2$, 1 H); 1.86 (*d*, $J = 9.2$, 1 H).

4.4. *1-(2-Methylcycloprop-1-en-1-yl)cyclopent-2-en-1-ol* (**36**). BuLi (1.6M; 4.69 ml, 7.5 mmol) in hexane was added dropwise to a stirred soln. of 1.0 g (3.41 mmol) of **34** in 10 ml of dry Et_2O under N_2 at −80°. After addition, the mixture was allowed to reach r.t. and stirred at r.t. for 15 min. Then, it was cooled to −95°, and 361 mg (4.4 mmol) of cyclopent-2-en-1-one were added dropwise. The mixture was stirred for 1 h at −95°, then for 1 h at −40°, before quenching with 3 ml of H_2O at −40°. After extraction with Et_2O (3 × 10 ml), the combined org. layers were dried ($MgSO_4$) and evaporated *i.v.* The crude product was purified by CC (silica gel; pentane/Et_2O 5:1) to give 0.20 g (43%) of a pale-yellow oil of **36**. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.90 (*dt*, $J = 5.6$, 2.2, 1 H); 5.70 (*dt*, $J = 5.6$, 2.2, 1 H); 2.51 (*m*, 2 H); 2.35 (*m*, 1 H); 2.28 (*m*, 1 H); 2.21 (*m*, 1 H); 2.05–1.92 (several *m*, 5 H) including 2.02 (*s*, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 134.1 (*d*); 133.9 (*d*); 112.2 (*s*); 107.2 (*s*); 82.9 (*s*); 37.3 (*t*); 31.0 (*t*); 11.0 (*q*); 8.6 (*t*). MS21): 136 (40, $M^{+\cdot}$), 121 (33), 93 (100), 91 (61), 83 (80), 77 (48), 55 (21), 43 (30).

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