Synthesis of Novel Precursors of Calicene and 7-Methylcalicene[1])

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Cyclopent-2-en-1-one is a versatile electrophilic cyclopentadiene equivalent in reactions with 1-bromo-1-lithiocyclopropanes. The synthetic sequence (outlined in *Scheme 1*) has been applied to the synthesis of functionalized 7-X-7,8-dihydrocalicenes **13c** (*Scheme 3*) and **13d** (*Scheme 4*). 7-Bromo-7,8-dihydrocalicene (**13d**) is considered to be a promising precursor of the so far unknown parent calicene (**2**). A similar sequence has been realized for 7-(chloromethyl)-7,8-dihydrocalicene (**21a**, *Scheme 5*) which, under appropriate conditions, could give 7-methylcalicene (**16**).

1. Introduction. – Triafulvene (**1**) and calicene (**2** = pentatriafulvalene) have fascinated experimental as well as physical organic chemists for more than three decades. During that time, the parent triafulvene has been generated in solution [2][3], as well as in the gas phase [4][5], so that its chemistry, and essential spectroscopic properties are well known today [4][5]. On the other hand, parent calicene **2** has not been isolated, trapped, or spectroscopically identified so far. Considering the fact that **2** contains two fully conjugated rings, which are expected to support each other electronically and hence to increase π-delocalization[4])[5]), this is at first sight quite surprising but could be explained with the higher reactivity of **2** due to the increased dipolar character[4]).

Most synthetic sequences for substituted calicenes start with highly substituted cyclopropenylium salts of the type **4**–**6**[6])[7]) or cyclopropenes such as **7**, which are reacted with (substituted) cyclopentadienides to give cyclopropenyl-cyclopentadienes. Provided that these intermediates contain additional leaving groups X in the three-membered ring (which is the case starting with **4**, **6**, and **7**), base-induced HX-elimination is usually straightforward and leads to substituted calicenes[6]). On the other hand, cyclopropenyl-cyclopentadienes prepared from **5** lack an additional leaving group and have to be subjected to hydride abstraction (followed by deprotonation)

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[1]) Fulvenes, Fulvalenes, Part 73. Part 72: [1].

[2]) Postdoctoral fellow 1997–1999.

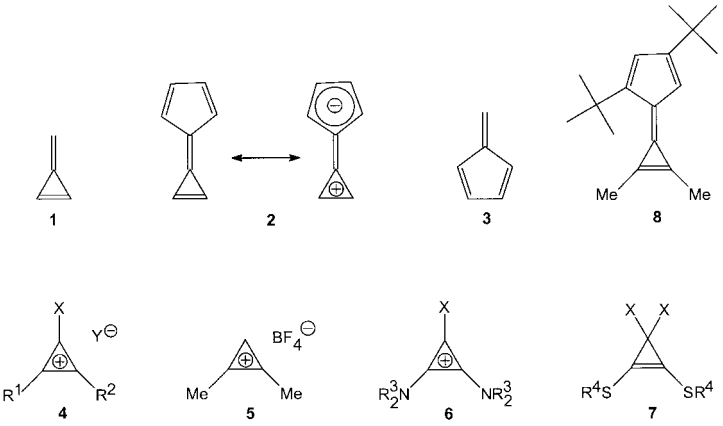
[3]) Postdoctoral fellow 1996–1999.

[4]) *Ab initio* calculations [6][7] show that bond lengths of formal single and double bonds of **2** are less alternating (and $\mu \approx 4.5$ D is increased) compared with **1** ($\mu = 1.9$ D [8]) or pentafulvene (**3**) ($\mu = 0.424$ D [9]).

[5]) According to our aromaticity plot for pentafulvenes and pentafulvalenes derived from ^3J(H,H) values [10], an aromaticity of *ca.* 30% may be estimated for calicene. This is perfectly in accord with the results of *ab initio* calculations [6], suggesting a 31% contribution of dipolar $\mathbf{2}^{\pm}$.

[6]) For typical examples, see [11–16] (from **4**), [17][18] (from **5**), [19][20] (from **6**), and [21] (from **7**).

[7]) Cyclopropenylium salts **4** (X = AcO) are supposed to be formed as intermediates in reactions of cyclopropenones with Ac_2O [22].



[17][18]. All these classical pathways fail in attempts to synthesize parent calicene **2**: while in reactions of unsubstituted cyclopropenylium salts **4** ($R^1 = R^2 = H$) with cyclopentadienide the leaving groups end up in vinylic position and cannot be eliminated later on [23], hydride abstractions from cyclopropenylcyclopentadienes (prepared from **5**) may be tedious even for relatively stable, substituted intermediates [17][18] and have always failed in cases with unsubstituted cyclopentadiene rings [13][24][25]. Furthermore, attempts to replace the amino groups of 7,8-diaminocalicenes (prepared from **6** [19][20]) or the alkylthio substituents of 7,8-bis(alkylthio)-calicenes (available from **7** [21]) have been undertaken [21][26] and did not result in formation of the parent calicene. Finally, it is interesting to note that **8** still represents the simplest alkyl-substituted calicene [17][18]. However, it is so highly substituted that it does not give much insight into spectroscopic and chemical properties of naked calicene (**2**)[8]).

Since the parent calicene (**2**) is expected to be an extremely reactive compound, it has to be generated either at very low temperature in dilute and O_2-free solutions [27], or by gas-phase pyrolysis followed by trapping **2** at low temperature. During the last ten years, we have made several attempts in both directions [28][29]. As far as low-temperature reactions in solutions are concerned, we planned to make use of the easy conversion of 1,1-dibromocyclopropanes **9** to 1-bromo-1-lithiocyclopropanes **10** [30] and the well-known reactivity of these carbenoids towards various electrophiles [31–34] and in reactions with cyclopent-2-en-1-one (**10** → **11**), which proceed at $-95°$ with reasonable yields [28]. The most tricky step of the sequence **10** → **13** (*Scheme 1*) is the acid-catalyzed dehydration of cyclopentenol **11** to give cyclopentadiene **12**, which, in some cases (with electron-donating substituents X), induced a ring-opening of the cyclopropyl unit of **11**. Although a small number of 7,8-dihydrocalicenes **13** has been prepared [28][29], no compounds **13** with good leaving groups X (*e.g.*, Br, Cl) nor with easily functionalizable substituents[9]) have been available so far, which would be a perequisite in view of a low-temperature synthesis of calicene (**2**) in solution.

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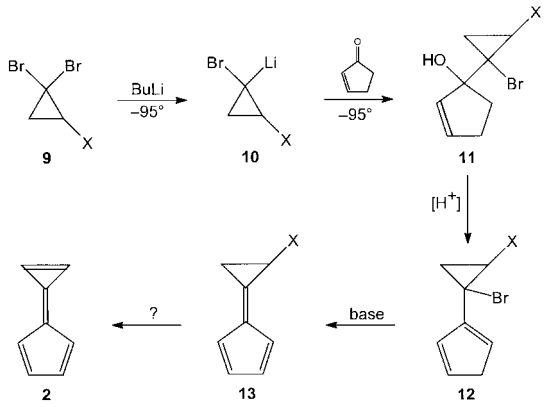
[8]) For instance, ^3J values are not available from the ^{1}H-NMR spectra of **8** [18], which would be important for deriving the extent of bond-length alternation in the five-membered ring of **8**.

[9]) For instance, substituents X such as COOR could be transformed into X = Br by the *Hunsdiecker* reaction [35].

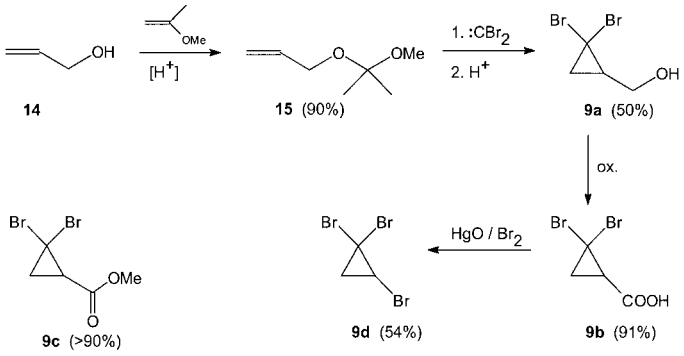
Scheme 1



In this paper, we report the synthesis of the first promising precursors of type **13** of calicene (**2**) and of 7-methylcalicene.

2. Synthesis of 1,1-Dibromocyclopropanes (9). – An easy access to functionalized 1,1-dibromocyclopropanes **9** is crucial in view of promising calicene precursors of type **13** (*Scheme 1*). Some years ago, we were thinking of allylic alcohol **14** as a versatile starting material but had to learn that the seemingly simple step **14** → **9a** (*Scheme 2*) cannot be directly realized by means of the available procedures [36–39] for dibromocarbene additions[10]). This problem can be solved by ketalization **14** → **15** [43], followed by dibromocarbene addition [37] and hydrolysis (**15** → **9a**). Permanganate oxidation of the alcohol **9a** gives the carboxylic acid **9b**, from which various carboxylic esters, such as **9c**, are prepared [44]. On the other hand, *Hunsdiecker* decarboxylation of **9b** provides a good access to 1,1,2-tribromocyclopropane (**9d**)[11]).

Scheme 2. *Synthesis of 1,1-Dibromocyclopropanes* **9**



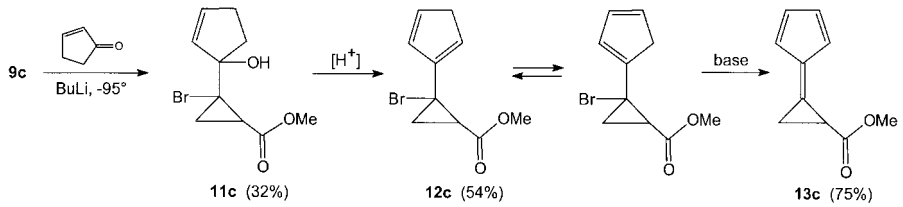
[10]) There exist, however, several multistep sequences for **9a** in the literature [40–42].

[11]) Direct dibromocarbene addition to bromoethene (according to phase-transfer procedures) gives only a 5% yield of **9d** [45].

3. Synthesis of Calicene Precursors 13c and 13d. – Our experiments show that the trickiest step of the synthesis of functionalized calicene precursors of type **13** is the alkylation of 1-bromo-1-lithio-2-X-cyclopropanes (**10** → **11**) with cyclopentenone. Although this step is normally fast enough at temperatures around −100° [28], alkylation **10** → **11** has to compete with intramolecular LiX elimination, which leads to the corresponding 1-bromocyclopropene [46]. On the other hand, BuLi is able to attack carbonyl groups of esters [47], so that the step **9c** → **11c** can turn out to be problematic as well. The best way to circumvent most of the problems is to slowly add BuLi to a mixture containing the 1,1-dibromocyclopropane **9** and cyclopentenone at very low temperature, so that the hereby generated carbenoid **10** is immediately trapped by cyclopentenone. Since in the course of the sequence **9** → **11** three centers of chirality are generated, diastereoisomeric mixtures of cyclopropylcyclopentenols **11** are isolated[12]), in which normally one or two diastereoisomers are dominating.

In fact, methyl-2,2-dibromocyclopropanecarboxylate (**9c**) reacts easily in Et_2O solution with cyclopentenone and BuLi at −95° to give a 60:40% mixture of two diastereoisomeric esters **11c** with moderate yields (*Scheme 3*). Acid-catalyzed dehydration of esters **11c** proceeds easily by reacting them with small amounts of TsOH in dry benzene to give two isomeric esters **12c** (which turn out to be tautomers, see later). Finally, base-induced HBr elimination **12c** → **13c** (77%) makes methyl 7,7-dihydrocalicene-7-carboxylate (**13c**) available.

Scheme 3



To transform the methoxycarbonyl group of **13c** into a good leaving group, we planned to carefully hydrolyze the ester **13c** and to replace COOH with Br through the well-known *Hunsdiecker* decarboxylation [35]. So far, however, hydrolysis of **13c** proved to be problematic due to the reactivity of the fulvene moiety of **13c**[13]).

Therefore, we tried to realize the tricky 'cyclopentadienylation' of 1,1,2-tribromocyclopropane (**9d**) which is very critical because the intermediary 1,2-dibromo-1-lithiocyclopropane **10d** will easily form 1-bromocyclopropene even at low temperature [46]. In fact, when BuLi is slowly added to a THF solution containing **9d** and cyclopentenone under routine conditions (−95°), the desired product **11d** cannot be detected. This prompted us to lower reaction temperatures as much as possible and to replace THF by Et_2O in order to still enable a reaction in solution at −110°. Under

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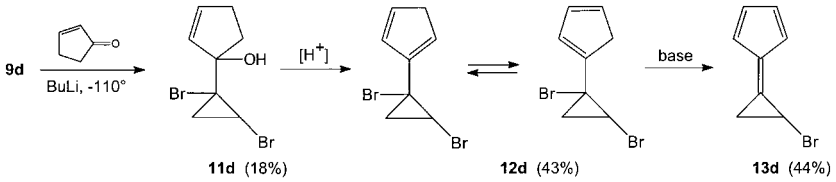
[12]) This is not as dramatic as it seems, since in the course of the sequence **11** → **12** → **13** → **2**, the chirality centers will be eliminated again. Furthermore, cyclopropyl protons of compounds **11**, **12**, and **13** display three sets of well-resolved *dd*s in the ^{1}H-NMR spectrum (see *Figs. 1* and *2*).

[13]) Pentafulvenes are known to be sensitive towards traces of strong acids, which induce polymerization [48][49]. On the other hand, they can be attacked by strong nucleophiles at C(6) [50][51].

these conditions, a diastereoisomeric mixture of cyclopropylcyclopentenol **11d** could be isolated in moderate yields (18%), which allowed us to complete the planned sequence (*Scheme 4*) and to generate 7-bromo-7,8-dihydrocalicene (**13d**). To our knowledge, **13d** is the first precursor of parent calicene (**2**) to contain a good leaving group[14]).

Scheme 4



The structures of the new compounds (*Schemes 3* and *4*) are consistent with the spectroscopic data, of which ^{1}H-NMR and ^{13}C-NMR data are very conclusive even for isomeric mixtures. This is demonstrated by the ^{1}H-NMR spectrum of the ester **12c** (*Fig. 1*), where two isomers (in a ratio of 2:1) are clearly identified. Each isomer produces three sets of *dd*s in the cyclopropane range at 2.17, 1.98, and 1.68 ppm (major isomer), and 2.13, 1.99, and 1.65 ppm (minor isomer) with typical *J* values. The narrow *multiplets* of the cyclopentadiene CH_2 units are localized at 3.07 and 3.13 ppm. In the vinylic range, which seems to be very complex at first sight, both *ABX* subspectra[15]) of the cyclopentadiene protons are visible, and the estimated coupling constants are typical for cyclopentadienes [52][15]).

4. Synthesis of a Precursor of 7-Methylcalicene (16). – Compared to calicene (**2**), 7-methylcalicene (**16**) is expected to display very similar electronic and spectroscopic properties. Its main advantage over **2** (besides minor stabilization) is the fact that, due to its reduced symmetry, the pairs of ring-H-atoms and ring-C-atoms are not equivalent anymore, which should allow a first-order analysis of the high-field ^{1}H-NMR spectra. On the other hand, the full set of coupling constants of the five-membered ring would be still available so that the extent of bond-length alternation could be derived from ^3J values[5]).

Making use of the same type of cyclopentadienylation reactions of 1-bromo-1-lithiocyclopropanes as explored previously (*Schemes 3* and *4*), a quite simple approach to 7-methylcalicene (**16**) can be conceived (*Scheme 5*): 1,1-dibromo-2-(halomethyl)cyclopropanes **18a** (X=Cl) and **18b** (X=Br) can be prepared from 3-halopropenes **17** by dibromocarbene addition, according to phase-transfer procedures [37]. Reaction with cyclopentenone and BuLi gives cyclopropylcyclopentenols **19** in good yields, and the synthesis of 7-(chloromethyl)-7,8-dihydrocalicene (**21a**) has been realized by acid-

[14]) First tentative experiments show that **13d** eliminates HBr in the presence of bases, such as Et_4N^+ Br^- at room temperature, or sodium cyclopentadienide (formation of NaBr at 0°). So far, however, neither parent **2** nor a cycloaddition product of **2** could be spectroscopically identified. These experiments will be continued at low temperature and under carefully controlled conditions.

[15]) They are labelled *ABX* (major isomer) and *A′B′X′* (minor isomer), the *A′B′* part being degenerate. For the major isomer with H–C(A) at 6.54, H–C(B) at 6.50, and H–C(X) at 6.31 ppm, $J_{AB} = 5.2$ Hz is typical for adjacent vinylic H-atoms of cyclopentadienes. H–C(A) displays a *dq*, because all its long-range couplings are *ca.* 1.5 Hz.

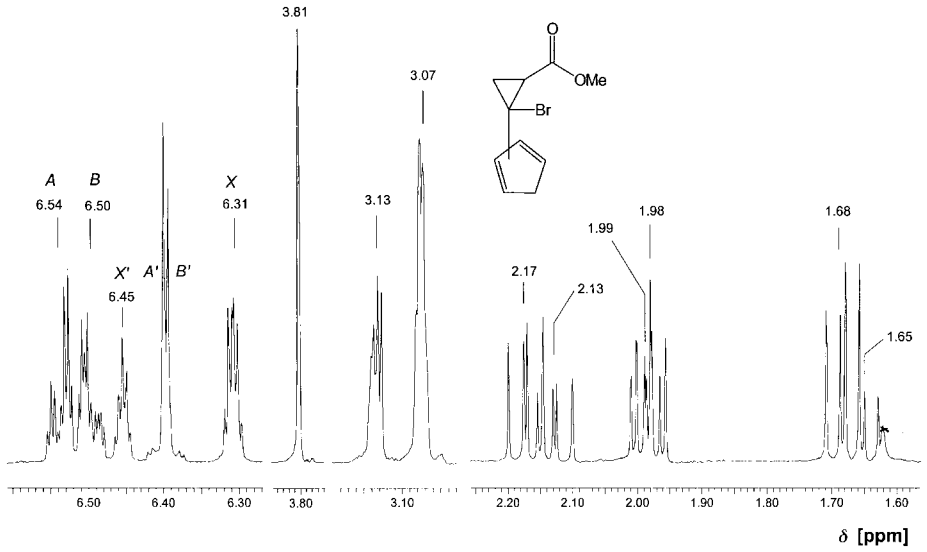
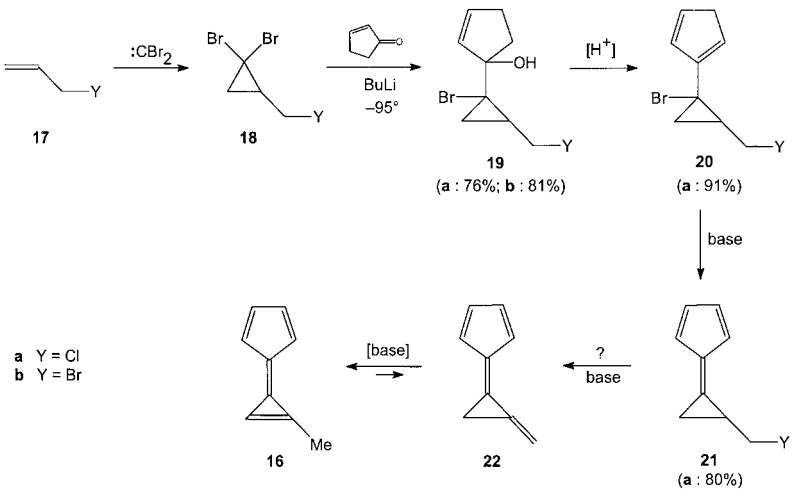


Fig. 1. *Sections of the* ^{1}*H-NMR Spectrum* (300 MHz, $CDCl_3$) *of* **12c** (tautomeric mixture)

Scheme 5



catalyzed dehydration of **19a** → **20a** followed by base-induced dehydrobromination **20a** → **21a**.

Spectroscopic data are consistent with the structures of **19a**, **19b**, **20a**, and **21a**[16]). Considerable structural information stems from ^{1}H-NMR spectra, which very often show a quite spectacular splitting pattern. In the ^{1}H-NMR spectrum of the predominant diastereoisomer of substituted cyclopropylcyclopentenol **19b** (*Fig. 2*), the *dxt* of both

[16]) Despite the presence of three centers of chirality, diastereoisomeric mixtures of **19a** and **19b** contain only two isomers in a ratio of *ca.* 3 :1. In the case of **20a**, one single isomer is predominant.

vinylic protons are found at 6.08 (H–C(2)) and 5.53 ppm (H–C(3)) with approximate coupling-constant values[17]) typical for cyclopentene moieties, while the diastereotopic protons of $CH_2(4)$ and $CH_2(5)$ produce complex *multiplets* at 2.6–2.3 and 2.00 ppm. On the other hand, all the H-atoms of the (bromomethyl)cyclopropane unit are not equivalent and display a first-order spectrum with the typical *dd* splittings of H-atoms of the exocyclic CH_2 unit at 3.75 and 3.50 ppm (with $J_{AB} = 10.3$ Hz), the *dd* of the cyclopropane ring at 1.40 and 0.99 ppm (with $J_{AB} = 6.6$ Hz), and the complex *m* of the cyclopropane-CH at 1.61 ppm. The only *s* of the spectrum, at 2.20 ppm, is generated by the OH group.

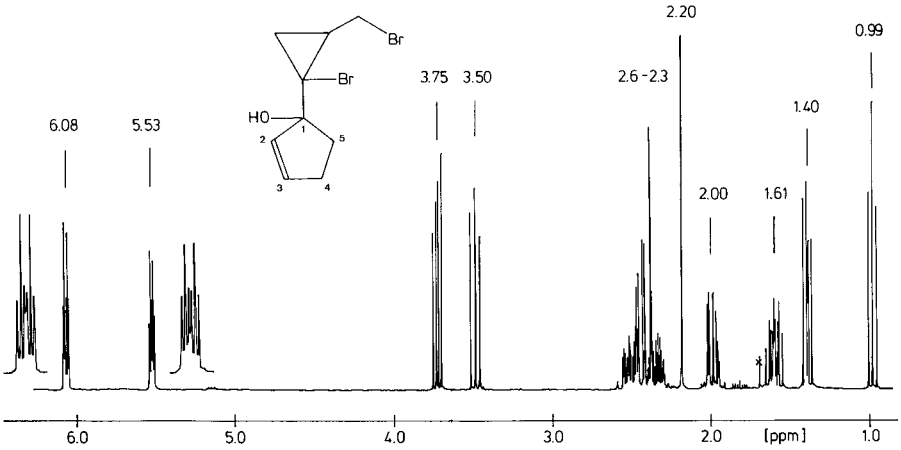


Fig. 2. *^{1}H-NMR Spectrum* (300 MHz, $CDCl_3$) *of* **19b**

5. Discussion. – Our results show that cyclopent-2-en-1-one can be applied as an electrophilic cyclopentadiene equivalent in reactions with 1-bromo-1-lithiocyclopropanes **10** at low temperature. Because nucleophiles such as **10** nearly exclusively attack the carbonyl group of cyclopentenone, no *Michael*-addition products have been isolated in the reactions outlined in *Schemes 3*, *4*, and *5*[18]). It is interesting to note that trapping of 1,2-dibromo-1-lithiocyclopropane **10d** with cyclopentenone can compete with intramolecular LiBr elimination at very low temperature, albeit with reduced yields (*Scheme 4*). The hereby formed compounds **11c** (*Scheme 3*), **11d** (*Scheme 4*), and **19a** (*Scheme 5*) can be transformed into functionalized 7,8-dihydrocalicenes **13c**, **13d**, and **21a** under appropriate conditions. As typical pentafulvenes, these compounds are reasonably stable in O_2-free solutions and allow experiments in the temperature range up to 0–20°. To our knowledge, 7-bromo-7,8-dihydrocalicene (**13d**) is the first promising precursor for parent calicene (**2**) containing a good leaving group in the three-membered ring.

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17) $J(2,3) \approx 5.75$; $J(2,4) \approx 2.2$; $J(3,4) \approx 2.0$ Hz. $J(2,3)$ is very typical for ^3J couplings of localized cyclopentene double bonds. The splittings are only approximate, because three of the four H-atoms of $CH_2(4)$ and $CH_2(5)$ at 2.6–2.3 and 2.00 ppm are close together, hence producing a high-order subspectrum.

18) Traces of *Michael*-addition products have been detected in other cases [28][29].

Experimental Part

General. Unless otherwise stated, all the reactions were performed under N_2 or Ar in two- or 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 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. Temp. of $-95°$ ($-110°$) were reached by freezing toluene (EtOH/MeOH 5:1) 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. Synthesis of Dibromocyclopropanes 9 and 18. – 1.1. *2,2-Dibromocyclopropane-1-methanol* (**9a**): [44].

1.2. *2,2-Dibromocyclopropanecarboxylic Acid* (**9b**). In a 750-ml flask, a soln. of 37.8 g (0.24 mol) of $KMnO_4$ in 300 ml of H_2O was vigorously stirred at 0°. 3.08 g (9.5 mmol) of $Bu_4N^+Br^-$ and a soln. of 11.0 g (47.8 mmol) of **9a** in 20 ml of benzene were added, and the reaction mixture was vigorously stirred for 16 h at 0°. Then, the mixture was carefully treated with sat. $NaHSO_3/H_2O$ until the brown color disappeared, acidified with 10% H_2SO_4, and then extracted with Et_2O (3×100 ml). The combined org. layers were dried ($MgSO_4$) and the solvent removed *i.v.* (14 mm Hg) to give 10.6 g (91%) of **9b** as a colorless solid, which was recrystallized from petroleum ether.

1.3. *Methyl 2,2-Dibromocyclopropanecarboxylate* (**9c**): [44].

1.4. *1,1,2-Tribromocyclopropane* (**9d**). To a suspension of 4.8 g (19.8 mmol) of **9b** and 4.26 g (19.7 mmol) of red HgO in 20 ml of CCl_4, a soln. of 3.7 g (23.1 mmol) of Br_2 in 10 ml of CCl_4 was added dropwise under stirring at 80°. The mixture was then refluxed for 3 h, stirred at r.t. for 4 h and, after adding 30 ml of petroleum ether, filtered through 'flash' silica gel. The filtrate was evaporated *i.v.* (14 mm Hg) and purified by column chromatography (CC) over silica gel with petroleum ether to give, after evaporation, 3 g (54%) of **9d** as a colorless oil [45][11]).

1.5. *1,1-Dibromo-2-(chloromethyl)cyclopropane* (**18a**). In a 250-ml flask, 50 ml of 50% aq. NaOH soln. were slowly added at 0° to a vigorously stirred mixture of 14.0 g (183 mmol) of *3-chloropropene* (**17a**), 16.8 ml (192 mmol) of $CHBr_3$, and 1.5 g (4.1 mmol) of cetrimide in 100 ml of CH_2Cl_2. The reaction mixture was vigorously stirred for 2 h at 5° and overnight at r.t. (TLC showed complete reaction). The mixture was then transferred into a separatory funnel containing 200 ml of H_2O, the org. layer separated, washed with H_2O (2×100 ml), and concentrated *i.v.* The residue was diluted with 150 ml of Et_2O, dried ($MgSO_4$), filtered, and evaporated to give 34.0 g (75%) of practically pure **18a** as a colorless oil. Analytically pure **18a** was obtained by distillation (7.6 Torr). ^{1}H-NMR (300 MHz, $CDCl_3$): 3.65 (*m*, 2 H); 2.04 (*m*, 1 H); 1.94 (*m*, 1 H); 1.49 (*m*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 46.1 (*t*); 32.2 (*d*); 28.9 (*t*); 25.7 (*s*).

1.6. *1,1-Dibromo-2-(bromomethyl)cyclopropane* (**18b**). In a 250-ml flask, 50 ml of 50% aq. NaOH soln. were slowly added to a vigorously stirred mixture of 15.0 g (124 mmol) of *3-bromopropene* (**17b**), 12.0 ml (137 mmol) of $CHBr_3$, and 1.5 g (4.1 mmol) of cetrimide ((hexadecyl)trimethylammonium bromide) in 50 ml of $CHCl_2$. The reaction mixture was vigorously stirred at 5° for 2 h, then overnight at r.t. (TLC showed incomplete reaction). After addition of another mol-equiv. of $CHBr_3$, stirring was continued for 10 h at r.t. Workup according to procedure *1.5* gave 23.6 g (65%) of practically pure **18b** as an orange-colored oil. Anal. pure **18b** was obtained by distillation (7.6 Torr). ^{1}H-NMR (300 MHz, $CDCl_3$): 3.47 (*m*, 2 H); 2.07 (*m*, 1 H); 1.95 (*m*, 1 H); 1.45 (*m*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 33.6 (*t*); 32.4 (*d*); 30.3 (*t*); 27.4 (*s*).

2. Synthesis of Calicene (= 5-(Cycloprop-2-enylidene)cyclopenta-1,3-diene) Precursors 13c (*Scheme 3*) **and 13d** (*Scheme 4*). – 2.1. *Methyl 2-Bromo-2-(1-hydroxycyclopent-2-enyl)cyclopropanecarboxylate* (**11c**). 1.33 ml of 1.6M BuLi in hexane (2.1 mmol) were added dropwise to a stirred soln. containing 0.5 g (1.94 mmol) of **9c** and 205 mg (2.5 mmol) of cyclopent-2-en-1-one in 15 ml of Et_2O under N_2 at $-95°$. The mixture was stirred for 1 h at $-95°$, allowed to warm to $-30°$, and stirred for another 30 min at $-30°$. After quenching the reaction by adding 3 ml of H_2O at $-30°$, the mixture was extracted with Et_2O (3×15 ml). The combined org. phases were evaporated (12 Torr) and the crude product purified by CC on *ca.* 30 g of silica gel with pentane/Et_2O 5:2 to give 0.16 g (32%) of a colorless oil (2:1 mixture of two isomers) of **11c**. IR ($CDCl_3$)[19]): 3476*m*, 2953*m*, 1732*s*, 1441*s*, 1384*m*–*s*, 1252*m*–*s*, 1202*m*–*s*, 1176*s*, 1089*m*–*s*, 1066*m*–*s*, 912*s*, 728*s*, 648*m*–*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): *major isomer:* 6.10 (*m*, 1 H); 5.52 (*m*, 1 H); 3.76 (*s*, 3 H); 2.6–2.3 (*m*, 4 H); 2.05 (*dd*, *J* = 9.2, 7.0, 1 H); 1.73 (*t*, *J* = 7.0, 1 H); 1.58 (*dd*, *J* = 9.2, 7.0, 1 H): signals of cyclopropane protons of *minor isomer*[19]): 2.21 (*dd*, *J* = 9.2, 7.0, 1 H); 1.70 (*dd*, *J* = 7.0, 6.6, 1 H); 1.45 (*dd*, *J* = 9.0, 6.6, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$; 2 isomers): 169.9 (*s*);

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[19]) Other signals of the minor isomer are obscured by those of the major isomer.

169.6 (*s*); 137.9 (*d*); 137.6 (*d*); 131.5 (*d*); 131.3 (*d*); 88.4 (*s*); 88.3 (*s*); 52.18 (*q*); 52.17 (*q*); 46.2 (*s*); 46.0 (*s*); 37.58 (*t*); 37.57 (*t*); 31.20 (*t*); 31.15 (*t*); 24.9 (*d*); 24.6 (*d*); 18.6 (*t*); 18.4 (*t*). MS[20]): 262 (1, $M^{+\bullet}$), 260 (1, $M^{+\bullet}$), 230 (67), 228 (70), 181 (31), 180 (33), 178 (32), 176 (100), 174 (99), 163 (46), 149 (58), 121 (56), 95 (46), 83 (59), 54 (29)[21]).

2.2. *Methyl 2-Bromo-2-(cyclopenta-1,4-dienyl)cyclopropanecarboxylate* (**12c**)[22]). A soln. of 1.0 g (3.8 mmol) of **11c** in 10 ml of dry benzene was stirred at r.t., and 140 mg (0.74 mmol) of TsOH were added. After 3 h of stirring at r.t. (TLC showed complete reaction), the solvent was removed *i.v.* (14 Torr), and the crude product was separated by CC over *ca.* 30 g of silica gel at $-10°$ with pentane/Et_2O 5 :2 to give 0.50 g (54%) of a mixture of 2 tautomers of **12c**. IR ($CDCl_3$)[20]): 2951*m*–*s*, 1738*s*, 1440*m*–*s*, 1385*m*–*s*, 1354*m*, 1196*m*–*s*, 1171*s*, 921*m*, 896*m*, 668*m*, 606*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): *major tautomer:* 6.54 (*dm*, $J = 5.2$, 1 *H*); 6.50 (*dm*, $J = 5.2$, 1 H); 6.31 (*m*, 1 H); 3.81 (*s*, 3 H); 3.07 (*m*, 2 H); 2.17 (*dd*, $J = 8.8$, 7.2, 1 H); 1.98 (*dd*, $J = 7.2$; 6.4, 1 H); 1.68 (*dd*, $J = 8.8$, 6.4, 1 H); *minor tautomer*: 6.45 (*m*, 1 H); 6.40 (*m*, 2 H); 3.81 (*s*, 3 H); 3.13 (*m*, 2 H); 2.13 (*dd*, $J = 8.8$, 7.2, 1 H); 1.99 (*dd*, $J = 7.2$, 6.4, 1 H); 1.65 (*dd*, $J = 8.8$, 6.4, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$)[22]): 169.3 (*s*); 169.2 (*s*); 148.8 (*s*); 147.8 (*s*); 135.2 (*d*); 133.4 (*d*); 132.0 (*d*); 131.6 (*d*); 130.0 (*d*); 128.8 (*d*); 52.4 (*q*); 42.2 (*t*); 41.1 (*t*); 33.5 (*s*); 32.5 (*s*); 29.8 (*d*); 28.5 (*d*); 22.9 (*t*); 21.9 (*t*). MS[20]): 244 (6, $M^{+\bullet}$), 242 (5, $M^{+\bullet}$), 185 (14), 183 (13), 163 (100), 135 (17), 131 (16), 104 (32), 103 (58), 77 (11)[21]).

2.3. *Methyl 7,8-Dihydrocalicene-7-carboxylate* (**13c**). A soln. of 0.20 g (0.82 mmol) of **12c** (tautomeric mixture) in 3 ml of Et_2O was transferred to a cooled ($-15°$) chromatography column containing 50 g of Al_2O_3 (basic with 3 drops of Et_3N) and eluted with Et_2O at $-15°$. The hereby formed intensely yellow fraction was collected. The solvent was evaporated *i.v.* to give 0.10 g (75%) of **13c** as a yellow oil. UV (hexane): 269 (21000), 358 (*ca.* 350). IR[20]): 3084*w*, 2961*w*, 2256*w*, 1734*s*, 1438*m*, 1200*m*, 1177*m*, 911*s*, 731*s*, 646*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.55–6.42 (*m*, 2 H); 6.33 (*dm*, $J = 5.2$, 1 H); 6.24 (*dm*, $J = 5.2$, 1 H); 3.72 (*s*, 3 H); 2.57 (*dd*, $J = 9.0$, 5.3, 1 H); 2.15 (*dd*, $J = 11.2$, 5.3, 1 H); 1.95 (*dd*, $J = 11.2$, 9.0, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 171.1 (*s*); 133.4 (*d*); 132.9 (*d*); 123.3 (*d*); 122.9 (*d*); 52.2 (*q*); 18.2 (*d*); 11.7 (*t*). MS[20]): 162 (85, $M^{+\bullet}$); 147 (36), 119 (44), 91 (100), 90 (14), 89 (17), 65 (31), 63 (16), 39 (17)[21]). HR-MS: 162.0682 ($M^{+\bullet}$, $C_{10}H_{10}O_2$; calc. 162.0680).

2.4. *1-(1,2-Dibromocyclopropyl)cyclopent-2-en-1-ol* (**11d**). In a 50-ml flask, a soln. containing 1.0 g (3.5 mmol) of **9d** and 380 mg (4.6 mmol) of cyclopent-2-enone in 12 ml of dry Et_2O was stirred at $-110°$. Then, 2.46 ml of 1.6M BuLi in hexane (3.94 mmol) were dropwise added through the septum with a syringe. The mixture was stirred at $-110°$ for 2 h, then quenched with 3 ml of H_2O, allowed to warm to r.t., and extracted with Et_2O (3×10 ml). The combined org. layers were evaporated *i.v.* (10°/14 Torr) to give a crude product whose ^{1}H-NMR spectrum shows the presence of three diastereoisomers **11d** in a ratio of 1 :0.5 :1. Careful chromatography on *ca.* 50 g of silica gel with pentane/Et_2O 5 :1 (containing a few drops of Et_3N) allowed separation of two isomers while the third remained impure. Total yield of all the fractions of **11d**: 180 mg (18%) as a colorless oil.

Data of Isomer 1: IR ($CDCl_3$)[20]): 3548*m*, 3460*m*, 3056*m*, 2936*m*, 2850*m*, 1361*m*, 1322*m*, 1252*m*, 1120*m*, 1060*s*, 1030*m*–*s*, 961*m*–*s*, 751*m*, 694*m*, 594*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.99 (*dm*, $J = 5.5$, 1 H); 5.83 (*dm*, $J = 5.5$, 1 H); 3.55 (*dd*, $J = 8.8$, 6.2, 1 H); 2.6–2.3 (*m*, 3 H); 2.27 (*s*, 1 H); 2.12 (*m*, 1 H); 1.73 (*dd*, $J = 8.5$, 6.2, 1 H); 1.67 (*dd*, $J = 8.8$, 8.5, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 136.2 (*d*); 133.7 (*d*); 88.4 (*s*); 42.4 (*s*); 38.4 (*t*); 30.9 (*t*); 26.8 (*d*); 23.0 (*t*). MS[20]): 266 (11, [$M^{+\bullet} - 18$]), 264 (22, [$M^{+\bullet} - 18$]), 262 (11, [$M^{+\bullet} - 18$]), 185 (23), 183 (22), 104 (100), 103 (48), 90 (11), 78 (12), 77 (24), 63 (11), 51 (22), 50 (11), 39 (10).

Data of Isomer 2: ^{1}H-NMR (300 MHz, $CDCl_3$): 6.05 (*dm*, $J = 5.5$, 1 H); 5.38 (*dm*, $J = 5.5$, 1 H); 3.20 (*dd*, $J = 9.2$, 5.9, 1 H); 2.55–2.20 (*m*, 3 H); 2.19 (*s*, 1 H); 1.91 (*m*, 1 H); 1.64 (*dd*, $J = 9.2$, 8.1, 1 H); 1.20 (*dd*, $J = 8.1$, 5.9, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 138.4 (*d*); 131.5 (*d*); 88.1 (*s*); 48.2 (*s*); 37.9 (*t*); 31.2 (*t*); 23.34 (*t*); 23.23 (*d*)[21]).

2.5. *1-(1,2-Dibromocyclopropyl)cyclopenta-1,3- and -1,4-diene* (**12d**)[22]). In a 50-ml flask, 67 mg (0.35 mmol) of $TsOH \cdot H_2O$ was added to a stirred soln. of 0.50 g (1.77 mmol) of **11d** in 10 ml of dry benzene at r.t. The mixture was stirred for 3 h (TLC showed complete reaction). Then, the solvent was removed *i.v.* (14 Torr) and the oily residue purified by CC on *ca.* 30 g of silica gel with pentane/Et_2O 5 :1. The pale-yellow fraction 1 was collected and gave, after evaporation *i.v.*, 0.20 g (43%) of **12d** as a yellow oil (1.5 :1 mixture of two tautomers). IR ($CDCl_3$)[20]): 3061*w*, 2958*m*, 2928*m*, 1420*m*, 1372*m*, 1357*s*, 1178*w*–*m*, 898*m*–*s*, 680*m*–*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): *major tautomer*[22]): 6.7–6.3 (*m*, 3 H); 3.56 (*dd*, $J = 8.5$, 5.5, 1 H); 3.08 (*m*, 2 H); 1.90 (*t*, $J = 8.5$); 1.61

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[23]) Only important IR absorptions and MS fragments are given.

[21]) For more spectroscopic data and illustrations of spectra, see [53], which is available on request from *M.N.*

[22]) Mixture of two tautomers.

(*dd*, *J* = 8.5, 5.5). ^{13}C-NMR (75 MHz, $CDCl_3$)[22]): 145.6 (*s*); 144.8 (*s*); 134.6 (*d*); 134.0 (*d*); 133.2 (*d*); 133.0 (*d*); 131.7 (*d*); 131.2 (*d*); 42.4 (*t*); 41.1 (*t*); 30.0 (*s*); 28.7 (*d*); 27.6 (*d*); 25.5 (*t*); 24.9 (*t*)[21]).

2.6. *7-Bromo-7,8-dihydrocalicene* (**13d**). A soln. of 200 mg (0.75 mmol) **12d** in 2 ml of Et_2O was transferred to a cooled (−20°) chromatography column containing 50 g of Al_2O_3 (basic, with 3 drops of Et_3N) and eluted with Et_2O at −20°. The hereby formed intensely yellow zone was collected. The solvent was evaporated *i.v.* (14 Torr, −25°) to give 60 mg (44%) of **13d** as an intensely yellow oil. IR ($CDCl_3$)[20]): 3071*w*, 2953*m*, 2922*m*–*s*, 2851*m*–*s*, 1214*m*–*s*, 910v*s*, 762*s*, 730*w*, 615*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.53 (*m*, 2 H); 6.40 (*m*, 1 H); 6.29 (*m*, 1 H); 3.86 (*dd*, *J* = 8.5, 4.4, 1 H); 2.24 (*dd*, *J* = 13.1, 8.5, 1 H); 1.85 (*dd*, *J* = 13.1, 4.4, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 134.3 (*d*); 133.2 (*d*); 123.1 (*d*); 122.3 (*d*); 15.8 (*t*); 12.1 (*d*). MS[20]): 184 (12, $M^{+\bullet}$), 182 (12, $M^{+\bullet}$), 103 (100), 102 (23), 77 (67), 63 (12), 51 (25), 50 (14)[21]). HR-MS: 181.973 ($M^{+\bullet}$, C_8H_7Br; calc. 181.988).

3. Synthesis of a Precursor 21a of 7-Methylcalicene (*Scheme 5*). – 3.1. *1-[1-Bromo-2-(chloromethyl)cyclopropyl]cyclopent-2-en-1-ol* (**19a**). A 100-ml flask was charged with 3.0 g (12 mmol) of **18a**, 1.4 g (18.3 mmol) of cyclopent-2-en-1-one, and 50 ml of THF. The soln. was cooled to −95°, and 15.0 ml of 1.6M BuLi in hexane (24 mmol) were added dropwise under stirring. After 2 h of stirring at −95°, warm-up, and 1 h of stirring at r.t., the mixture was quenched at 0° by adding 50 ml Et_2O and 50 ml H_2O and extracted with Et_2O (3 × 100 ml). The combined extracts were dried ($MgSO_4$) and evaporated *i.v.* The crude product was purified by low-temp. (−20°) CC on *ca*. 50 g of silica gel with pentane/Et_2O 10 : 4 to give colorless oils of two isomers **19a**[23]): 0.5 g (16.5%) of *isomer 1* (R_f 0.44) and 1.8 g (60%) of *isomer 2* (R_f 0.25). *Data of Isomer 1*[24]): ^{1}H-NMR (300 MHz, $CDCl_3$): 6.15 (*m*, 1 H); 5.57 (*m*, 1 H); 3.94 (*m*, 1 H); 3.69 (*m*, 1 H); 2.65–2.4 (*m*, 3 H); 1.95 (*m*, 1 H); 1.84 (*m*, 1 H); 1.30 (*m*, 1 H); 1.20 (*m*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 137.9 (*d*); 129.1 (*d*); 96.4 (*s*); 66.5 (*t*); 40.1 (*s*); 33.2 (*t*); 32.1 (*t*); 26.4 (*d*); 17.8 (*t*)[25]).

3.2. *1-[1-Bromo-2-(bromomethyl)cyclopropyl]cyclopent-2-en-1-ol* (**19b**). According to procedure *3.1*, with 3.0 g (10.2 mmol) of **18b**, 1.3 g (15.8 mmol) of cyclopent-2-en-1-one, 50 ml THF, and 14 ml of 1.6M BuLi in hexane (22.4 mmol). After low-temp. (−20°) CC of the crude product on *ca*. 50 g of silica gel with pentane/Et_2O 10 : 1, colorless oils of two isomers **19b**[23]) were obtained: 0.76 g (25%) of *isomer 1* (R_f 0.40) and 1.7 g (56%) of *isomer 2* (R_f 0.24). *Data of Isomer 2*[24]): 6.08 (*m*, 1 H); 5.53 (*m*, 1 H); 3.75 (*dd*, *J* = 10.3, 6.2, 1 H); 3.50 (*dd*, *J* = 10.3, 8.8, 1 H); 2.6–2.3 (*m*, 3 H); 2.20 (*s*, 1 H); 2.00 (*m*, 1 H); 1.61 (*m*, 1 H); 1.40 (*dd*, *J* = 9.9, 6.6, 1 H); 0.99 (*dd*, *J* = 7.0, 6.6, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 137.6 (*d*); 131.7 (*d*); 88.6 (*s*); 51.8 (*s*); 37.7 (*t*); 36.0 (*t*); 31.2 (*t*); 23.4 (*d*); 21.3 (*t*)[25]).

3.3. *2-[1-Bromo-2-(chloromethyl)cyclopropyl]cyclopenta-1,3-diene* (**20a**)[26]). A 50-ml flask was charged with 1.0 g (4 mmol) of **19a**, 20 ml of dry benzene, and 140 mg (0.8 mmol, cat. amount) of TsOH, the mixture was stirred for 3 h at r.t., and then evaporated *i.v.* The crude product was purified by low-temp. (−20°) CC over *ca*. 30 g of silica gel with pentane/Et_2O 20 : 1 to give 0.85 g (91%) of **20a**[26]) as a colorless oil. (R_f 0.85). ^{1}H-NMR (300 MHz, $CDCl_3$): 6.56 (*m*, 1 H); 6.50 (*m*, 1 H); 6.26 (*m*, 1 H); 3.92 (*dd*, *J* = 11.4, 6.2, 1 H); 3.76 (*dd*, *J* = 11.4, 8.1, 1 H); 3.07 (*m*, 2 H); 1.61 (*dd*, *J* = 9.6, 6.6, 1 H); 1.53 (*m*, 1 H); 1.24 (*dd*, *J* = 6.6, 6.2, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 148.4 (*s*); 134.9 (*d*); 132.5 (*d*); 128.2 (*d*); 47.6 (*t*); 41.1 (*t*); 36.3 (*s*); 27.0 (*d*); 22.9 (*t*)[25]).

3.4. *7-(Chloromethyl)-7,8-dihydrocalicene* (**21a**). The crude product obtained above (see *3.3*) was dissolved in *ca*. 2 ml of benzene, the soln. was transferred to a cooled (−20°) chromatography column containing 10 g of Al_2O_3 (basic) and eluted with pentane/Et_2O 20 : 1 at −20°. The hereby formed intensely yellow zone was collected. The solvent was evaporated *i.v.* to give 0.44 g (80% from **20a**) of **21a** as an orange oil, which is reasonably stable below −10°. UV (hexane): 270 (23200), 350 (430). IR[20]): 3060*w*, 2920*w*, 1627*m*–*s*, 1465*m*, 1370*m*, 1085*w*–*m*, 1007*w*–*m*, 875*w*–*m*, 800*w*–*m*, 760*s*, 595*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.59 (*m*, 2 H); 6.42 (*m*, 2 H); 3.62 (*m*, 2 H); 2.32 (*m*, 1 H); 1.89 (*dd*, *J* = 11.2, 9.6, 1 H); 1.48 (*dd*, *J* = 11.2, 5.5, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 139.6 (*s*); 137.3 (*s*); 133.3 (*d*); 132.5 (*d*); 123.5 (*d*); 123.2 (*d*); 47.0 (*t*); 18.5 (*d*); 11.0 (*t*). MS[20]): 154 (35, $M^{+\bullet}$), 152 (70, $M^{+\bullet}$), 117 (100), 104 (40), 86 (30), 74 (25). HR-MS: 152.0392 ($M^{+\bullet}$, C_9H_9Cl; calc. 152.0393)[25]).

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[24]) Mixture of two diastereoisomers.

[25]) NMR Spectra of *isomer 2* are very similar.

[26]) For more spectroscopic data and illustrations of spectra, see [54], which is available on request from *M.N.*

[27]) Quite surprisingly, only one isomer **20a** is isolated.

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