REVIEW

Low-Temperature Olefin Syntheses in View of Parent Fulvenes and Fulvalenes[1])

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Parent fulvenes and fulvalenes are thermally unstable cross-conjugated olefins for which low-temperature syntheses are indispensable. In this review 5 syntheses (in the temperature range between -100 and $-10°$) are discussed:

1. Reaction of sodium cyclopentadienide with 1-acetoxy-1-chloroalkanes or 1-acetoxy-1-bromoalkanes (**26**) gives acetoxy-alkyl-cyclopentadienes (**27**) which are easily converted to pentafulvenes (**2**) by low-temperature HOAc-elimination with NEt_3. This synthesis has been applied to parent pentafulvene (**2a**), heptafulvene (**3a**), nonafulvene (**4a**) and sesquifulvalene (**19a**) (*Schemes 8–11*).

2. Based on a nearly quantitative oxidative coupling of cyclononatetraenide (**8**) to give dihydrononafulvalene (**38**) (*Scheme 10*), a general synthetic plan for fulvalenes has been outlined (*Scheme 11*) and applied to the synthesis of pentafulvalene (**12**), nonapentafulvalene (**16**) and nonafulvalene (**14**). Several applications of oxidative couplings of *Hückel* anions are discussed (*Schemes 20* and *21*).

3. Trifunctional cyclopropanes **67** (in most cases 1,1-dibromo-2-X-cyclopropanes) are attractive precursors of parent triafulvene (**1a**) and calicene (**17**) (*Scheme 18*). Contrary to classical procedures they are transformed into nucleophiles (**67** → **68**) by halogen-lithium exchange, methylation (**68** → **69**) and HBr-elimination to give 1-methylidene-2-X-cyclopropanes of type **71**. By subsequent HX-elimination triafulvene (**1a**) has been synthesized and trapped as a [4 + 2]-cycloadduct **73** (*Scheme 20*). Furthermore, calicene precursors **77** are available by using cyclopentenone as an electrophilic cyclopentadiene equivalent.

4. Similarly, 1-lithio-1-bromo-2-X-cyclopropanes **68** are directly transformed into triafulvalene precursors **81** (*Scheme 26*) by a novel $CuCl_2$-catalyzed oxidative coupling.

5. In view of the synthesis of parent triafulvene (**1a**), triafulvalene (**11**) and calicene (**17**), *retro-Diels–Alder* reactions of stable precursors – prepared by low-temperature reactions (described in chapters **3** and **4**) – have been explored.

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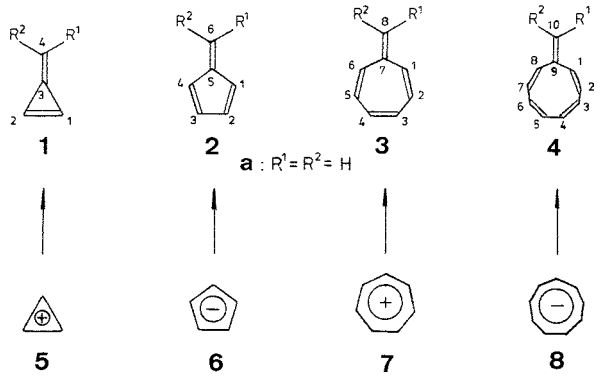
[1]) This and the subsequent review articles compile parts of the research work of the group of *M. N.* between 1964 and 2000, written for the collaborators. The chapters of the complete volume '*Research Topics*' are: I. *Low-Temperature Olefin Syntheses*; II. *Substituent Effects on π-Delocalization of Fulvenes and Fulvalenes*; III. *Fulvene Dimers*, *Trimers*, *and Polymers*; IV. *The Forgotten Carbonyl Reaction*; V. *Pentalene: Synthesis and First Spectroscopic Characterization*; VI. *Synthesis of 'Push-Pull' -Cyclobutadienes*; VII. *The Aminopropenal- and Aminopentadienal Rearrangement*; VIII. *'Push-Pull'-Diacetylenes*, *-Oligoacetylenes*, *-Polyacetylenes*; IX. *Sesquiterpenes of* Petasites hybridus *and* Petasites albus.

[2]) Deceased on May 7, 2015.

Introduction[3]**).** – **Fulvenes** are cyclic cross conjugated molecules with an odd number of C-atoms in the ring. According to the size of the ring skeleton they are named triafulvenes (**1**), pentafulvenes (**2**), heptafulvenes (**3**) and nonafulvenes (**4**). Pentafulvenes were the first fulvenes to be discovered in 1900 by *Thiele* [2], and the yellow color of these compounds (lat. *fulvus* = yellow) is responsible for the name of the whole family. After the first syntheses of substituted triafulvenes **1** [3] and of heptafulvenes **3** [4] it became usual to add the ring size as prefix to the name. The first simple member of the class of nonafulvenes **4** was isolated in 1969 [5].

Compared with cyclic aromatic and open-chain olefinic molecules, some typical features of fulvenes should be mentioned: First, fulvenes **1**–**4** were easily available from appropriate '*Hückel*'-type cations **5** [6][7] and **7** [8] and anions **6** and **8** [9][10]. Obviously, in principle, similar sequences may be applied for triafulvenes **1** and heptafulvenes **3**, starting with cations **5** and **7**. On the other hand, successful procedures for pentafulvenes (**6** → **2**) may have a good chance for nonafulvenes as well (**8** → **4**) (*Scheme 1*).

Scheme 1

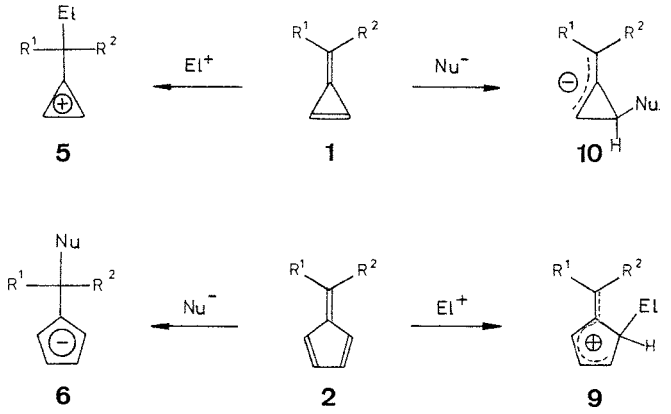


Then, it is remarkable that fulvenes are dipolar molecules. Today we know that the dipole moment is small for the parent molecules (see later), but it may be considerably larger for triafulvenes **1** and heptafulvenes **3** with electron-accepting substituents R^1 and R^2 (*e.g.*, CN) or for pentafulvenes **2** with electron-donating substituents (*e.g.*, $R^1 = R^2 = NR'_2$). At the same time electron-donating substituents are stabilizing **2** and **4**, while electron-accepting groups are stabilizing **1** and **3**.

Most fulvenes easily react with electrophiles and nucleophiles. Looking at the energy of the hereby formed reactive intermediates, and considering *Hammond*'s postulate, the reaction of pentafulvenes with nucleophiles (to give substituted cyclopentadienides) and that of triafulvenes with electrophiles (to give substituted cyclopropenylium salts) are easily understood. It is important to note, however, that electrophilic attack at C(1)/C(4) of pentafulvenes **2** may give delocalized cations **9**, while nucleophilic attack at C(1)/C(2) of triafulvenes **1** may give allylic anions of type

[3]) Parts of the introduction are identical with the introduction in [1], p. 1132–1135.

Scheme 2. *Reactions of Fulvenes with Electrophiles and Nucleophiles*



10. So reactions of type **1** → **10** and **2** → **9** are possible, too, especially, if **9** and **10** are stabilized by appropriate substituents R^1 and R^2 (*Scheme 2*).

Even more insight into the reactive behavior of fulvenes came from frontier orbital considerations [11][12]: Compared with benzene, its isomer pentafulvene (**2**) has a high-energy HOMO (**h**ighest **o**ccupied **m**olecular **o**rbital) and a comparably low-energy LUMO (**l**owest **u**noccupied **m**olecular **o**rbital). This accounted for the 'surprising' long-wavelength UV absorption of fulvenes, being responsible for the color of these compounds. Furthermore, one of the frontier orbitals of every fulvene had a nodal plane through the exocyclic double bond, so that the energy of that MO remained nearly uninfluenced by exocyclic substituents R^1 and R^2. This applied to the HOMO's of **2** and planar **4**, as well as the LUMO's of **1** and **3** (*Fig. 1*).

Considering the fact, that –*M*-substituents (like CN groups) are generally lowering the energy of the frontier orbitals while +*M*-substituents (like NMe_2 groups) are raising the energy of frontier orbitals [11][12], the consequences for fulvenes were the following: In pentafulvenes **2** and planar nonafulvenes **4**, NMe_2-groups are raising the energy of the LUMO, thus increasing the energy gap between HOMO and LUMO. On the other hand, CN-groups are expected to lower the energy of the LUMO, to decrease the energy gap and to induce a bathochromic shift of the longest-wavelength UV absorption. In heptafulvenes **3** and triafulvenes **1**, CN-groups are lowering the energy of

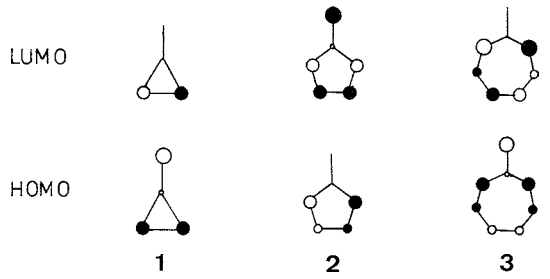


Fig. 1. Hückel *coefficients and frontier orbitals of fulvenes* **1**, **2**, *and* **3**

the HOMO, thus increasing the energy gap. On the other hand, NMe_2 groups were expected to raise the energy of the HOMO, to decrease the energy gap and to induce a bathochromic shift of the UV absorption (see *Figs. 2* and *3*).

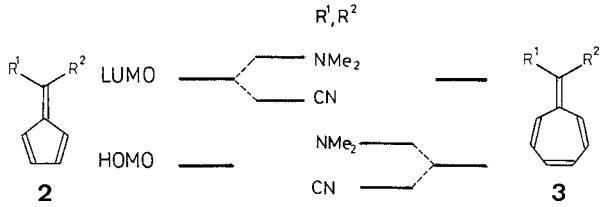


Fig. 2. *Influence of exocyclic substituents on the energy of frontier orbitals* (schematic)

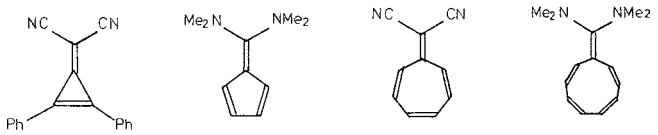


Fig. 3. *Examples of fulvenes with increased thermal stability*

The reactive behavior of fulvenes can be qualitatively explained by frontier orbital considerations [11][12]: *Nucleophiles* (with a high-energy HOMO) are expected to have a strong binding interaction with the LUMO of fulvenes. Looking at the LUMO of pentafulvenes **2** (see *Fig. 1*), it turned out that C(6) has the largest *Hückel* coefficient. So we could predict that nucleophiles would attack at C(6) of pentafulvenes **2** (and C(10) of planar nonafulvenes **4**). If any reaction with triafulvenes **1** or heptafulvenes **3** would take place, then, according to *Fig. 1*, it would be with the ring C-atoms.

On the other hand, *electrophiles* (being characterized by a low-energy LUMO) were expected to have a strong binding interaction with the HOMO of fulvenes. According to the *Hückel* coefficients, they were predicted to attack at the exocyclic C-atoms of triafulvenes and heptafulvenes, while pentafulvenes were expected to react predominantly at C(1)/C(4).

Frontier orbital considerations [11][12] gave very useful predictions concerning *cycloadditions* as well[4]). Since dienophiles with a low-energy LUMO (like maleic anhydride) were expected to have strong binding interactions with the HOMO of fulvenes, the preferred route of pentafulvenes should be a [4+2]-cycloaddition. Because the *Hückel* coefficients at C(1)/C(8) of heptafulvene are large, [8+2]-cycloadditions should be favored. Pentafulvenes are expected to undergo [6+4]-cycloadditions if the LUMO of **2** became important.

Hence we had *two classes of fulvenes* with respect to their synthesis, reactivity and spectroscopic properties (and especially substituent effects on spectra), namely triafulvenes **1**, heptafulvenes **3**, hendecafulvenes, … with 3-, 7-, 11-membered rings

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[4]) For the outstanding work of *Houk* about the periselectivity of fulvene cycloadditions see [12]. More examples about cycloadditions of fulvenes see [1].

and a total of 4,8,12 … π-electrons belonging to one class, and pentafulvenes **2**, nonafulvenes **4**, tridecafulvenes, … with 5-, 9-, 13-membered rings and a total of 6, 10, 14, … π-electrons belonging to another class.

Fulvalenes are cyclic cross-conjugated molecules with two fully conjugated rings being connected by a central double bond. *Fig. 4* shows all the combinations between 3-, 5-, 7- and 9-membered rings. There are fulvalenes with two identical rings (triafulvalene (**11**) till nonafulvalene (**14**)), fulvalenes **15** and **16** with rings of similar electron demand and fulvalenes (**17** till **20**) with rings of inverse polarization. Examples of that type are pentatriafulvalene (**17**) [synonym 'calicene'[5])] as well as heptapentafulvalene (**19**) [synonym 'sesquifulvalene'] whose dipolar forms (*Fig. 4*, right) are suggesting that both rings are supporting each other electronically.

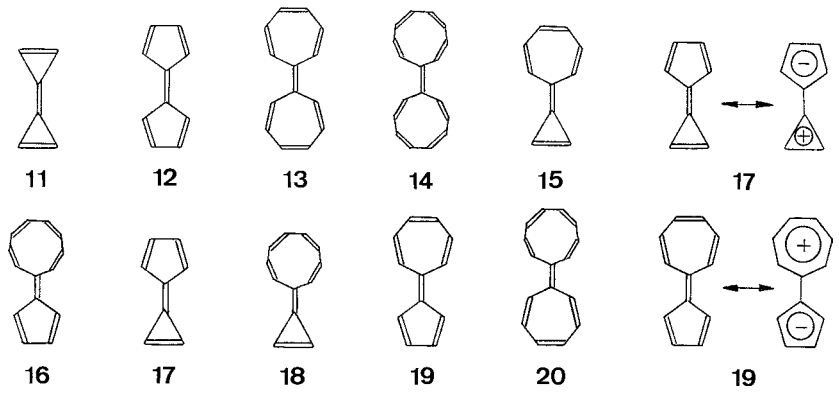

Fig. 4. *Fulvalenes* **11**–**20** (left) *and two examples of fulvalenes with rings of inverse electron demand* (right)

At the beginning of our work only the UV spectra of very dilute solutions (*ca.* 10^{-3} M) of pentafulvalene (**12**) [13], heptafulvalene (**13**)[6]) [8] and sesquifulvalene (**19**) [14] had been reported. All the other parent fulvalenes were unknown, and a complete spectroscopic characterization of **12**, **13** and **19** was missing.

My first contact with fulvenes happened during my dissertation: Around 1960 my supervisor Professor *H. Schaltegger* – an outstanding experimentalist and very motivating person – had explored the reaction of Na–CPD (**6**) with epichlorohydrin [16] which (surprisingly) resulted in the formation of 'spirodienol' **21**. The subsequent reaction of **21** with acetic anhydride gave the acetate **22** in high yields (*Scheme 3*)[7]). During distillation of the product mixture (and after separating AcOH and Ac_2O) the first droplets of the distillate of **22** had an orange

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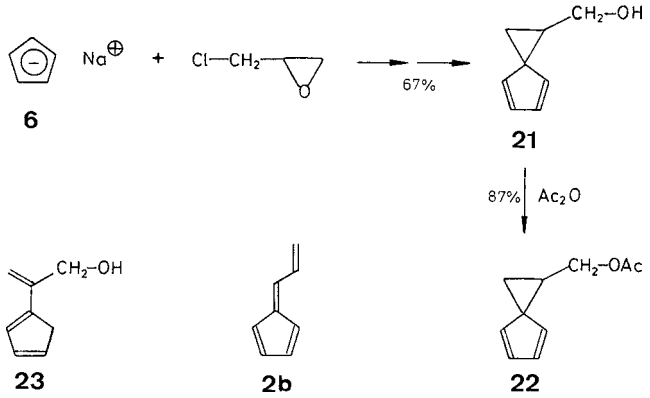
5) From lat. '*calix*' = cup.

6) It seems that parent heptafulvalene (**13**) has been isolated [15] by *Doering* and his group [7], but the synthesis of **13** has never been published.

7) The originally published structure **23** [16] was wrong (which didn't facilitate mechanistic speculations!); it was later corrected by *Barton* and *Woolsey* [17].

Scheme 3. *Reaction of Sodium Cyclopentadienide* (**6**) *with Epichlorohydrin*



color[8]). The main topic of my dissertation[9]) was the isolation and structure elucidation of this obviously volatile colored compound!

By systematic variation of the reaction parameters of the acid-catalyzed reaction **21** → **2b** the yield of pure 6-vinylfulvene (**2b**) could be increased to 10% which allowed the isolation and spectroscopic structure elucidation [18]. Furthermore, **2b** as well as its methyl derivatives were synthesized according to the *Thiele* procedure [19] which gave 6-vinylfulvenes only in low yields.

1. A New Fulvene Synthesis: Synthesis and Isolation of Pentafulvene, Heptafulvene, Nonafulvene and Sesquifulvalene. – 1.1. *Pentafulvene* (**2a**). The first pentafulvene synthesis found by *Thiele* [2] consisted in the condensation of carbonyl compounds with cyclopentadiene in ethanol in the presence of NaOEt. The base had two functions: To deprotonate cyclopentadiene (the pK_a of alcohols and cyclopentadiene being similar) and then to catalyze water elimination which was realized by deprotonation of substituted cyclopentadienes. The yields were good (around 50%)[10]) starting with ketones but in most cases quite low starting with aliphatic or α,β-unsaturated aldehydes (with yields usually lower than 3%)[11]). Solutions of parent pentafulvene (**2a**) had first been prepared by *Thiec* and *Wiemann* [21] according to *Thiele* [2], however attempts to isolate **2a** failed [22][12]). Finally parent **2a** could be separated from solvents by preparative GC (yield 0.6%!) [23]. – Because of the disappointing results of the *Thiele* synthesis and due to the fact that parent fulvenes and

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8) A later estimate showed that, based on 100 g of product **22** about 45 mg of 6-vinylfulvene (**2b**) are formed, which corresponds to a yield of 0.07% ! **2b** is very unstable and easily polymerizes at r.t. so that purification has to take place between -80 and $-20°$.

9) Obviously a high risk topic which I would not have dared to offer to a doctoral fellow even in 2000 (after a dramatic improvement of sensitivity and efficiency of NMR methods)!

10) Yields around 50% are quite good in fulvene syntheses.

11) Main side reactions are aldol condensations of the aldehyde, nucleophilic attack of cyclopentadienide at C(6) of the already formed pentafulvene as well as reaction of substituted cyclopentadienides with aldehydes or ketones [20].

12) Parent **2a** is extremely volatile and can't even be separated from Et_2O!

fulvalenes were of considerable theoretical interest, new pathways to parent **2a** were explored. In 1964 *Sturm* and *Hafner* [24] let 6-dimethylamino pentafulvene react with $LiAlH_4$ and obtained by thermolysis of the *Mannich* base Et_2O solutions of pentafulvene (**2a**) with yields around 30% [25].

A short time afterwards we realized the synthesis of spectroscopically pure pentafulvene (**2a**) with good yields: chloromethyl acetate (**26**) (X = Cl) could be prepared according to *Descudé* [26] by reaction of formaldehyde (**24**) with acetyl chloride (in the presence of $ZnCl_2$) to give, with sodium cyclopentadienide, a tautomeric mixture of (acetoxymethyl)-cyclopentadienes **27** which were reacted at $-10°$ with NEt_3 without solvent. After a simple workup, parent **2a** was isolated with good yields [27]. *Fig. 5* shows the purity of (acetoxymethyl)-cyclopentadienes **27** and of fulvene **2a**[13]). *Scheme 4* shows the similar reaction of bromomethyl acetate [28].

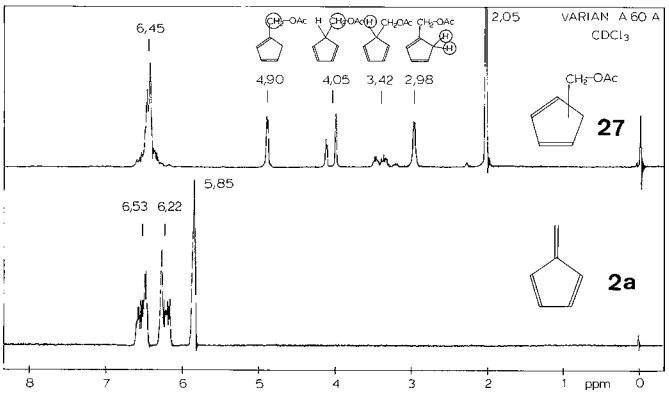
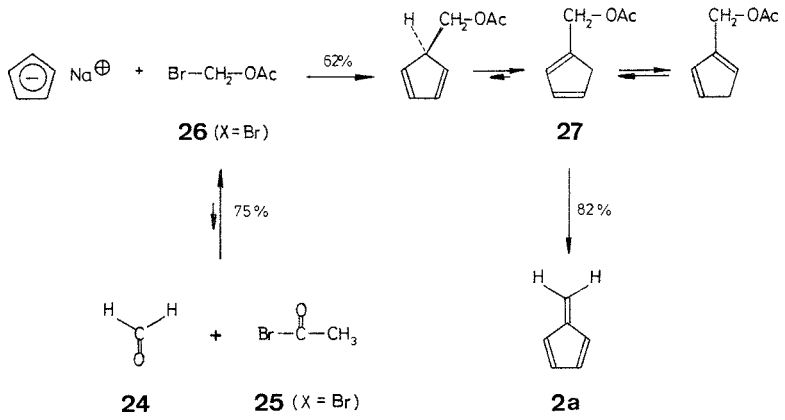


Fig. 5. *[1]H-NMR Spectra of pure acetoxymethyl cyclopentadienes* **27** *and of pentafulvene* (**2a**)

Scheme 4. *Synthesis of Spectroscopically Pure Pentafulvene* (**2a**)



[13]) Spectroscopic data of **2a** will be discussed later.

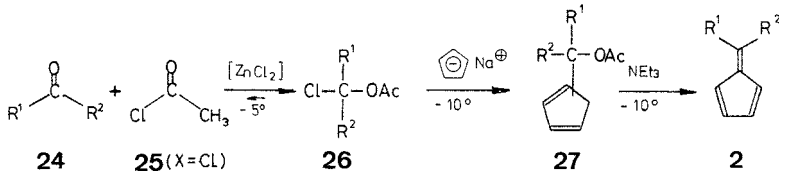
1.2. *A General Synthesis of Pentafulvenes.* After my postdoctoral time in Darmstadt we tried to explore a general pathway to pentafulvenes by reaction of sodium cyclopentadienide with chloromethyl acetate **26** (X = Cl). The first problem was the versatility of the synthesis of chloromethyl acetate like **24** + **25** → **26** (X = Cl).

Acetoxy-chloro-methane (**26**, $R^1 = R^2 = H$) was first prepared by *Descudé* [26] in 1901 by reaction of formaldehyde with acetyl chloride in the presence of $ZnCl_2$. The procedure was forgotten during decades and finally rediscovered by *Kirrmann* [29] and *Euranto* [30] with rather moderate success[14]).

Our re-investigation showed that chloromethyl acetates are available in high yields under proper conditions[15]), they were very versatile carbonyl derivatives with two different leaving groups [28][31]. Similarly, bromomethyl acetates (**26**, X = Br) were easily available as well [32]. There existed an equilibrium between starting materials **24**, **25** and product **26**, which was completely on the right side starting with aliphatic or aromatic aldehydes but is strongly dependent on the ring size in the case of alicyclic ketones.

Chloromethyl acetates (**26**) reacted easily with a slight excess of sodium cyclopentadienide at low temperatures (in most cases below −20°) to give tautomeric mixtures of cyclopenta-2,4-dien-1-ylmethyl acetates **27** which were subsequently treated with NEt_3 to give 6-alkyl- and 6-arylpentafulvenes **2** in good overall yields (*Scheme 5*)[16]).

Scheme 5. *Synthesis of Pentafulvenes* (**2**) *from Chloroalkanyl Acetates* (**26**, X = Cl). Average yields over all steps: 52% for 6-alkyl- and 6-arylfulvenes (17 examples).



The pentafulvene synthesis proceeding over chloromethyl acetates **26** worked well in many cases where the *Thiele* synthesis failed [25], because many side reactions like aldol-condensations did not occur. The main advantages were the low reaction temperature, the use of aprotic solvents and the simple aprotic workup conditions (if needed). This was the only method giving spectroscopically pure pentafulvene (**2a**) on a gram scale [27][28], and the method could be applied to 1,2-benzofulvenes and 1,2,3,4-dibenzofulvenes as well [33], if triethylamine was replaced by stronger bases in the last step. It has to be noted, however, that for 6,6-disubstituted pentafulvenes the *Thiele* sequence or its modifications have to be favored.

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14) Often the yields of products **26** were quite low, especially in cases where distillation took place in the presence of the catalyst. It is important to remove the catalyst before distillation.

15) The reaction will be discussed later in more detail (see *The Forgotten Carbonyl Reaction*).

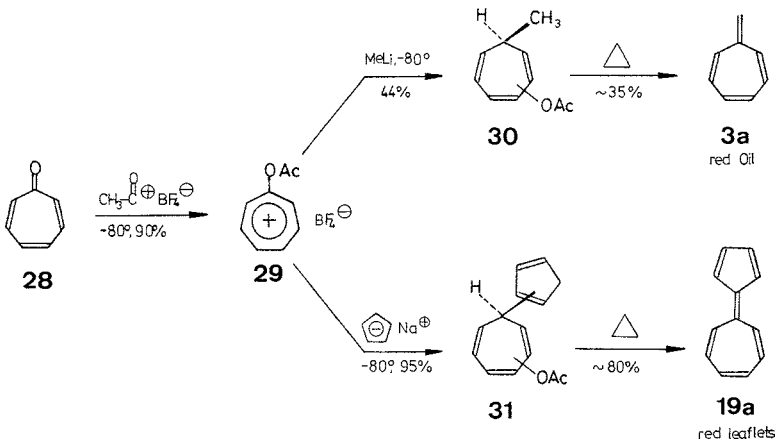
16) If the yields of chloromethyl acetates **26** are nearly quantitative, the whole sequence of *Scheme 5* can be realized as a simple 'one-pot-reaction'.

1.3. *Synthesis of Heptafulvene* (**3a**) *and Sesquifulvalene* (**19a**). With the synthesis of tropone (**28**) [34] and the structure elucidation of tropylium cation [35] by *Doering* and his group [36] the central requirements in view of the synthesis of heptafulvenes **3** and sesquifulvalenes **19** had been met around 1950. Nevertheless only UV spectra of very dilute solutions of parent heptafulvene (**3a**) [37] and sesquifulvalene (**19a**) [38] had been recorded before 1972. – At first sight one wouldn't believe that our synthesis of pentafulvene (**2a**) (with a negative polarization of the five-membered ring) could be applied to heptafulvene (**3a**) and sesquifulvalene (**19a**) (with a positive polarization of the seven-membered ring). Despite of that the synthesis of **3a** and **19a** was surprisingly simple (*Scheme 6*) [39][40].

So, acetylation of tropone [41] with acetyl fluoroborate [42] (**28** → **29**) proceeded at −80° to give acetoxytropylium fluoroborate (**29**) which was easily alkylated with methyl lithium (**29** → **30**) or cyclopentadienide (**29** → **31**) to give the appropriate acetoxyalkylcycloheptatrienes[17]) [39]. But the main problem was that in **30** and **31** the potential leaving group sat in vinylic position and could not be directly eliminated at low temperature. This problem was overcome by gas-phase pyrolysis (10^{-1} Torr, 360°, contact time *ca.* 20 s), because the AcO groups ended up in allylic position after a series of thermally allowed 1,5-H shifts and could be eliminated with NEt_3[18]). In this way spectroscopically pure heptafulvene (**3a**) and sesquifulvalene (**19a**) have been prepared [40].

Fig. 6 shows the ^{1}H-NMR-spectrum of sesquifulvalene (**19a**) at 270 MHz in C_6D_6 at −10° [43][19]). The interesting part was the *AA′BB′*-system of the protons of the five-membered ring at 6.32 and 6.27 ppm which could be analyzed to give vicinal coupling

Scheme 6



[17]) According to ^{1}H-NMR-spectroscopy, a mixture of 1-, 2- and 3-acetoxy-7-methyl-cycloheptatrienes was formed.

[18]) At the same time parent **3a** and **19a** are stabilized by NEt_3 and protected against acid-catalysed polymerisation.

[19]) Spectroscopic data of **3a** and **19a** will be discussed later.

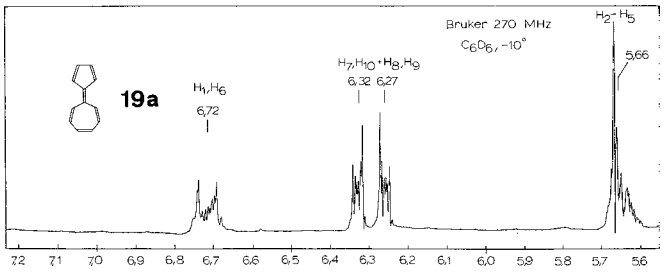


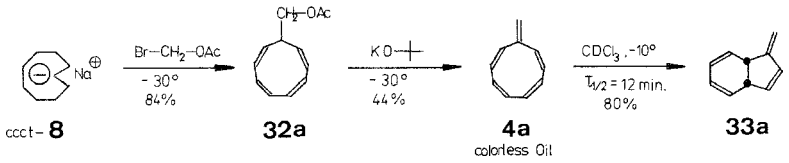
Fig. 6. *^{1}H-NMR Spectrum of sesquifulvalene* (**19a**) (270 MHz, C_6D_6, $-10°$)

constants of 5.2 and 2.2 Hz. This showed that in the five-membered ring of **19a** bond lengths were strongly alternating.

1.4. *Nonafulvene* (**4a**). With the successful synthesis of *all-cis*-cyclononatetraenide (*all-cis*-**8**) [9] and of the more nucleophilic *cis*,*cis*,*cis*,*trans*-cyclononatetraenide (*ccct*-**8**) [44][45], the most important nucleophiles in view of the synthesis of nonafulvenes had been made available around 1970. The first nonafulvene of type **4** to be synthesized was 10,10-bis(dimethylamino)nonafulvene [4] which beared two stabilizing amino groups at the exocyclic C-atom. In view of the synthesis of parent nonafulvene (**4a**) considerable problems could be foreseen: Although the synthesis outlined in *Scheme 7* looks simple and straightforward, one has to consider that both cyclononatetraenes of type **32** as well as nonafulvenes **4** are prone to easy 6π-valence isomerizations to give dihydroindenes (see **4a** → **33a**)[20]) even at temperatures below 0°. Furthermore, *all-cis*-**8** is less nucleophilic than cyclopentadienide **6**, probably due to delocalization of the negative charge over 9 C-atoms. Replacing *all-cis*-**8** by the more nucleophilic *ccct*-**8** may be an advantage but can give complex product mixtures [44][45]. And, last but not least, cyclononatetraenes are less acidic than cyclopentadienes so that eliminations of type **32a** → **4a** are more tricky. Despite of all these inconveniences, our attempts towards the synthesis of parent nonafulvene (**4a**) were successful (*Scheme 7*).

Reaction of *ccct*-CNT^- with bromomethyl acetate gave the substituted cyclononatetraene **32a** with surprisingly good yields, which, after purification by low-temperature chromatography, was reacted with ^{t}BuOK to give nonafulvene (**4a**). Nonafulvene is a colorless oil (M.p. $(-21°)-(-19°)$][21])[22]).

Scheme 7. *Synthesis of Nonafulvene* (**4a**) [47]



[20]) $\tau_{1/2}$ of cyclononatetraene : 16 min at 35° [46]; $\tau_{1/2}$ of nonafulvene (**4a**) : 12 min at $-10°$ [47].

[21]) Since pentafulvene (**2a**) is yellow and heptafulvene (**3a**) is red, we expected a colored compound.

[22]) Contrary to pentafulvenes, applications of the reaction of cyclononatetraenides with bromomethyl acetates were limited to the synthesis of 10-phenylnonafulvene [48], while several new nonafulvenes have been synthesized according to other procedures [49].

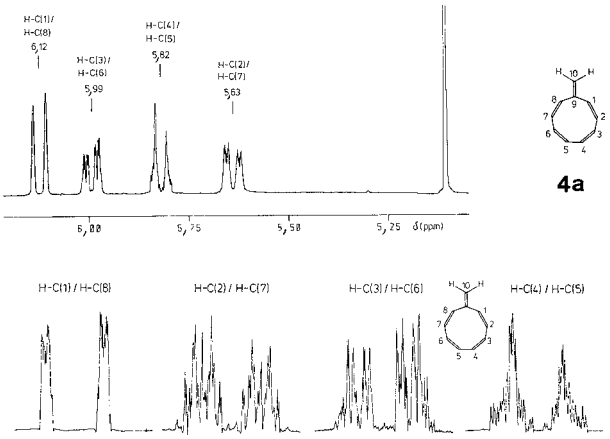


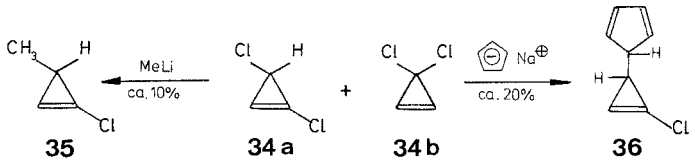
Fig. 7. *^{1}H-NMR Spectra of nonafulvene* (**4a**)*: Survey* (above)*, splitting pattern at 400 MHz* (below)

The survey-NMR spectrum is given in *Fig. 7* (above) [47], while the lower trace of *Fig. 7* displays the high-resolution ^{1}H-NMR spectrum at 400 MHz [48]. The protons of the nine-membered ring show an extremely complex *AA′MM′XX′YY′* splitting pattern which, after simulation and iteration, allows to extract the most important coupling constants (>1 Hz).

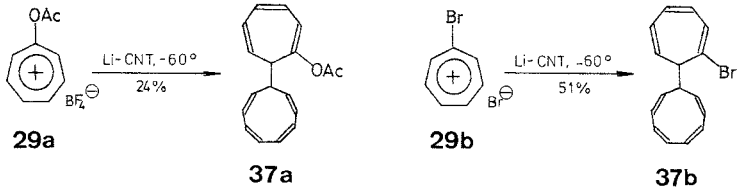
1.5. *First Attempts towards the Synthesis of Triafulvene, Calicene and Nonaheptafulvalene.* Similarly to the synthesis of heptafulvene (**3a**) and sesquifulvalene (**19**), triafulvene (**1a**) as well as calicene (**17**) could be made available by acylation of cyclopropenone [6], subsequent reaction with methyl lithium and cyclopentadienide, respectively, and final AcOH elimination. In fact, cyclopropenone reacted easily with acetyl fluoroborate at $-78°$, but the hereby formed acetoxy-cyclopropenylium fluoroborate underwent disproportionation into BF_3, acetyl fluoride and cyclopropenone. Although cyclopropenone precursors **34a** + **34b** reacted with methyl lithium or sodium cyclopentadienide (*Scheme 8*), elimination experiments **35** → **1a** and **36** → **17** were unsuccessful because the Cl-atom was in the vinylic position of **35** and **36**, respectively [50].

According to *Scheme 9*, possible precursors of nonaheptafulvalene (**20**) have been prepared by acylation of tropone with acetyl fluoroborate (to give **29a**) and oxalyl dibromide [51] (to give **29b**), however synthetic attempts towards nonaheptafulvalene (**20**) failed due to the easy valence isomerizations of the cyclononatetraene units of **37a**

Scheme 8. *First Synthetic Attempts towards Triafulvene* (**1a**) *and Calicene* (**17**)



Scheme 9. *Attempted Syntheses of Nonaheptafulvalene* (**20**)



and **37b**, while gas-phase pyrolysis experiments of the precursors **37a** and **37b** were unsuccessful as well [52].

Summary of Chapter 1. Chloro- as well as bromomethyl accetates (**26**) are versatile bifunctional carbonyl derivatives, bearing at C(1) two leaving groups of different leaving qualities. They have been widely applied to the low-temperature synthesis of a series of 6-alkyl- and 6-aryl pentafulvenes but, most importantly, to the isolation of spectroscopically pure pentafulvene (**2a**), heptafulvene (**3a**), nonafulvene (**4a**) and sesquifulvalene (**19**) (*Fig. 8*).

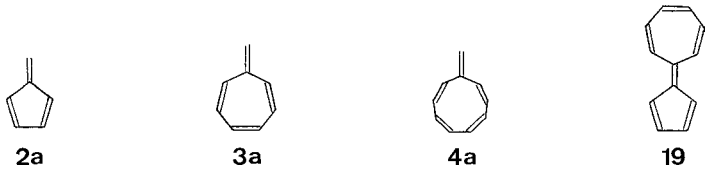
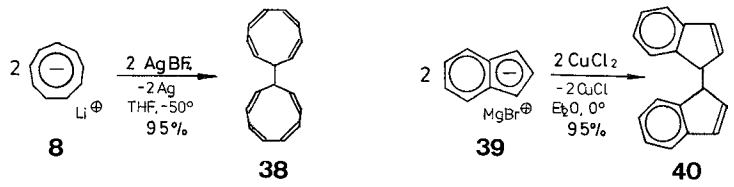


Fig. 8. *Isolated fulvenes and fulvalenes*

2. Oxidative Coupling of *Hückel* Anions. – In the course of our work with nonafulvenes [53] we found a surprisingly simple oxidative coupling reaction (*Scheme 10*, left): If equimolar amounts of Li-CNT (**8**) and $AgBF_4$[23]) were reacted in THF at $-50°$, silver was deposited and 1,1′-bi(cyclononatetraenyl) (**38**) was formed nearly quantitatively. In the literature [54] there is a similar oxidative coupling of indenide **39** in the presence of $CuCl_2$ to give high yields of 1,1′-biindenyl (**40**) (*Scheme 10*, right).

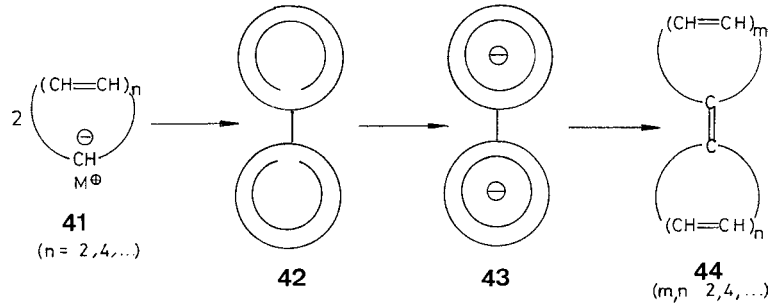
Scheme 10. *Oxidative Coupling of Cyclononatetraenide* (**8** [53]) *and of Indenide* (**39** [54])



[23]) CNT^- (**8**) and indenide (**39**) may both be coupled with $AgBF_4$ and $CuCl_2$, but it turns out that $AgBF_4$ works better in couplings of CNT^- while $CuCl_2$ gives higher yields in couplings of indenide or cyclopentadienide.

This surprisingly smooth coupling (*Scheme 10*) opend new possibilities in view of a general synthetic concept (*Scheme 11*) for fulvalenes of type **44**: A first oxidative coupling of *Hückel* anions **41** like cyclopentadienide (**41**, $n = 2$) or cyclononatetraenide (**41**, $n = 4$) gave dihydrofulvalene **42** and, after twofold deprotonation **42** → **43**, another oxidative coupling gave the fulvalene **44**.

Scheme 11. *General Synthetic Plan for Fulvalenes*

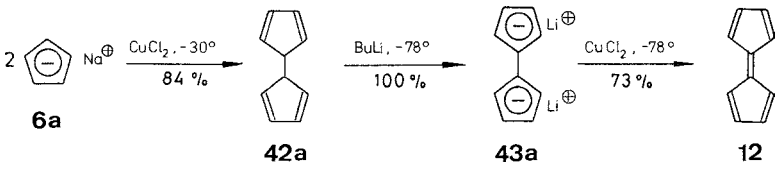


2.1. *Pentafulvalene* (**12**) [55]. Pentafulvalene (**12**) has been synthesized 1959 in *ca.* 10^{-3}-M solution [13] by reaction of cyclopentadienide with iodine, followed by deprotonation and a second oxidation by air (!), however it was spectroscopically never fully characterized.

According to *Scheme 12* the synthetic plan could easily be realized with surprisingly good yields. Pentafulvalene (**12**) is a very reactive deep-red compound. Its thermal stability is much lower than that of parent pentafulvene (**2a**), but by adding NMR-solvents at low temperature followed by partial evaporation, 0.3 – 0.4-M solutions were available which allowed ^{13}C- as well as ^{1}H-NMR investigations (*Fig. 9*). Even at $-80°$ dimerization (and polymerization) took place (*Scheme 13*) to give the expected *Diels–Alder* dimer **45** which later on rearranged stereoselectively to give a formal [2 + 2] dimer **46**.

2.2. *Nonapentafulvalene* (**16**) [56]. The synthesis of nonapentafulvalene (**16**) was quite tricky since it was complicated by the fact that two different *Hückel* anions **6** and **8** had to be coupled. If equal amounts of cyclopentadienide (**6**) and *ccct*-**8** were coupled, then dihydrofulvalenes **47a**, **42a**, and **48a** were formed in the ratio of 5 : 4 : 1 with a total yield of 85% (*Scheme 14*). If 5 mmols of Na-CPD (**6**) are coupled with 1 mmol of Na-CNT (**8**), then the product mixture contained only traces of **48a** besides **47a** and **42a**. If the mixture was then treated with Al_2O_3 at $-20°$, then tautomerizations **47a** → **47b** and

Scheme 12. *Synthesis of Pentafulvalene* (**12**)



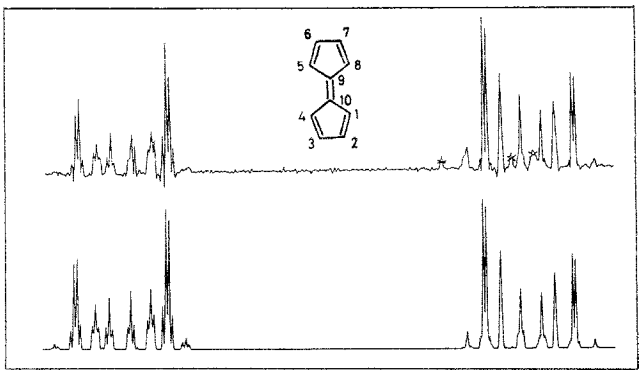
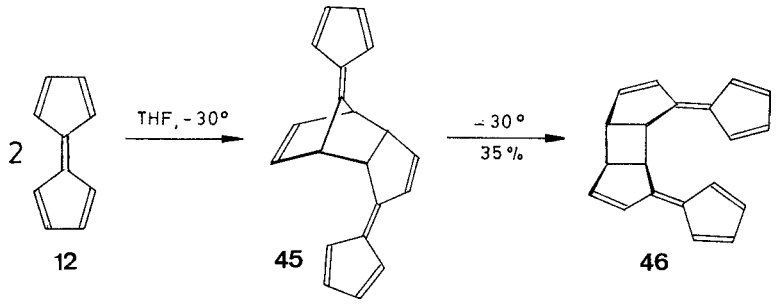
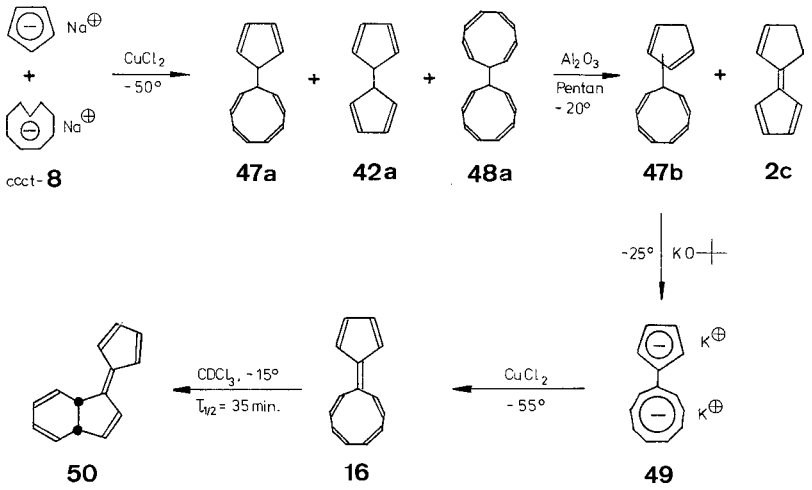


Fig. 9. *^{1}H-NMR Spectrum* (300 MHz) *of pentafulvalene* (**12**) *in CD_2Cl_2*. Top: Recorded spectrum (x = impurities); bottom: Spectrum after simulation and iteration with δ-values of 6.691 and 6.590 ppm and $J(1,2) = J(3,4) = 5.41$; $J(2,3) = 1.99$; $J(1,3) = J(2,4) = 1.32$; $J(1,4) = 1.98$; $J(2,6) = J(3,7) = 0.32$; $J(2,7) = J(3,6) = 0.17$ Hz.

Scheme 13. *Dimerization of Pentafulvalene* (**12**)



Scheme 14. *Synthesis of Nonapentafulvalene* (**16**)



42a → **2c** took place. This allowed the separation of the slow red zone of the fulvene **2c** from **47b**. Then twofold deprotonation of **47b** with ^{t}BuOK took place to give a precipitate of the dipotassium salt of **49**, and the final oxidative coupling with $CuCl_2$ gave nonapentafulvalene **16** (yield based on **47b**: *ca.* 30%).

Nonapentafulvalene (**16**) is a red hydrocarbon which can be crystallized at $-50°$ from concentrated solutions. It is very reactive so that even at low temperature valence isomerization to give dihydro pentafulvalene **50** easily takes place ($\tau_{1/2}$ *ca.* 35 min in $CDCl_3$ at $-15°$). That's why even carefully concentrated NMR solutions always contain small amounts of the valence isomer **50** (see *Fig. 10*).

2.3. *Nonafulvalene* (**14**) [57]. According to *Scheme 15* the general synthetic plan (*Scheme 11*) worked in the case of nonafulvalene (**14**) as well. As shown before, the oxidative coupling of CNT^- (**8**) proceeded nearly quantitatively in the presence of Ag^+. However, twofold deprotonation of bi(cyclononatetraenyl) (**48a**) was problematic (probably due to steric shielding) and only worked after base-induced tautomerization **48a** → **48b**. Deprotonation **48b** → **51** is possible, and the final oxidation of **51** with Ag^+ gave the desired nonafulvalene **14** in a yield of about 55%. Orange nonafulvalene **14** stayed stable during low-temperature chromatography at $-60°$ and could be crystallized at $-80°$, but due to the easy [$6\pi \rightarrow 4\pi + 2\sigma$] valence isomerization of the nine-membered rings it could not be isolated in spectroscopically pure form.

Nonafulvalene easily underwent valence isomerization of both nine-membered rings to give a stereoisomeric mixture of four isomers **52**, from which the predominant (*E-anti*)-isomer could be separated by low-temperature crystallization. *Fig. 11* (above) shows the ^{1}H-NMR-spectrum of (*E-anti*)-**52**, whose structure has been confirmed by an X-ray analysis (*Fig. 11*, below).

2.4. *More Applications of Oxidative Couplings of* Hückel *Anions.* The oxidative coupling of *Hückel* anions (and especially of cyclopentadienides) is not only important in view of the attractive parent fulvalenes **12**, **14**, and **16**, but it gives also access to rather

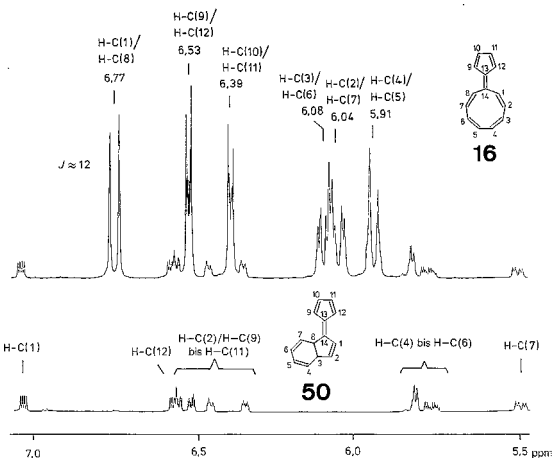
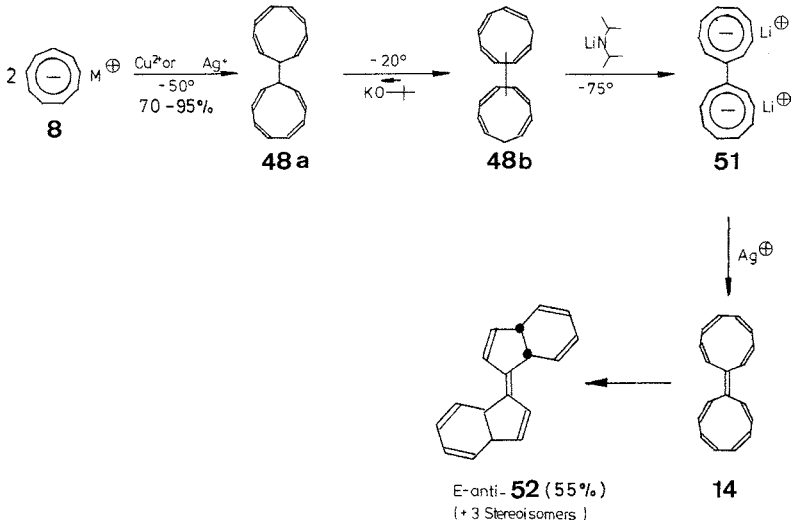


Fig. 10. *^{1}H-NMR Spectrum* (360 MHz, (D_6)acetone, $-40°$) *of nonapentafulvalene* (**16**, above) *as well as of its valence isomer* **50** (below)

Scheme 15. *Synthesis of Nonafulvalene* (**14**)[24])



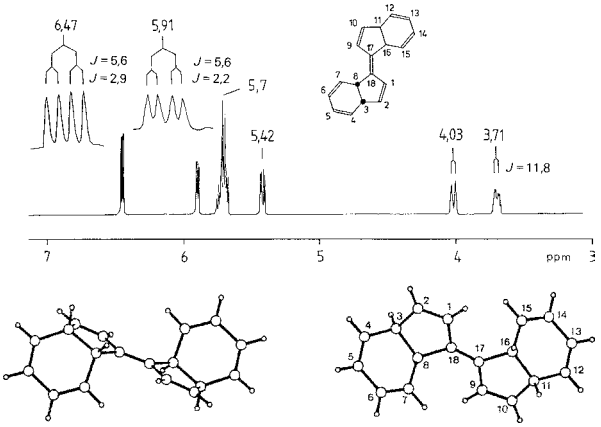


Fig. 11. *[1]H-NMR Spectrum* (400 MHz, $CDCl_3$, above) *and X-ray configuration* (below) *of* (E-anti)-**52**

unusual compounds, which are otherwise not easily available. In the following we describe some new applications[24]).

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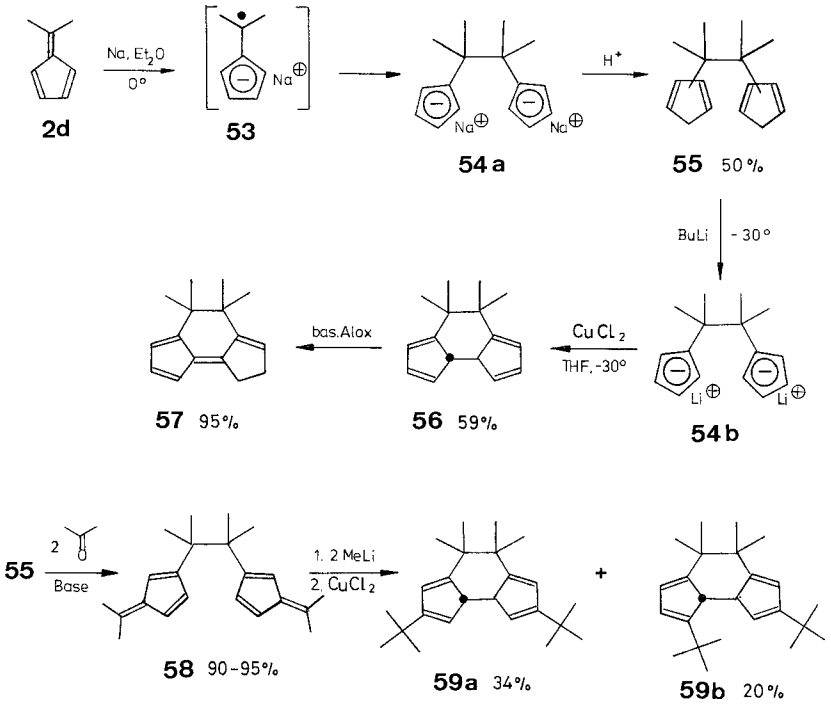
[24]) **48a** was prepared for the first time by *Hafner* and co-workers [58] by oxidative coupling of CNT^- (**8**) with iodine according to *Doering* [13]. The same authors [58] reported that reaction of **48a** with K gave dianion **51**, which is not correct: The reaction product is *ccct*-CNT^-K^+ [57].

[25]) Well-known applications: In 1958 *Doering & Matzner* [13] showed that cyclopentadienide (**6**) could be coupled by iodine to give bi(cyclopentadienyl) (**42a**). This reaction has been applied by *Hafner et al.* [58] to the synthesis of various *tert*-butyl-substituted pentafulvalenes. For the coupling of indenide by *Maréchal* [54], see *Scheme 10*.

Scheme 16 (top) starts with a reductive coupling described by *Rinehart et al.* [60]: 6,6-Dimethylpentafulvene (**2d**) could be reduced by Na in Et_2O to give the intermediary radical anion **53** whose SOMO[26]) had the largest *Hückel* coefficient at the exocyclic C(6). Therefore recombination of two **53** → **54a** is very reasonable, and after protonation the substituted 1,2-di(cyclopentadienyl)ethane **55** was isolated. After another deprotonation[27]) of **55** → **54b**, intramolecular oxidative coupling was induced to give **56** which easily isomerized to the substituted dihydrofulvalene **57** by acid or base catalysis[28]).

The second example of *Scheme 16* (bottom) shows an exceptionally high-yield *Thiele* synthesis **55** → **58**. Since nucleophiles like methyl lithium were known to attack at the exocyclic C(6) of pentafulvenes (see the introduction and survey articles [1][25]), the reaction of **58** with MeLi nearly quantitatively gave a di(cyclopentadienide) which – depending on the arrangement of the five-membered rings – had two options for an intramolecular oxidative coupling to give **59a** and **59b**. Similarly to the sequence **56** → **57**, compounds **59a** and **59b** nearly quantitatively tautomerized to give the corresponding bridged dihydropentafulvalenes (see **57**).

Scheme 16. *Examples of Intramolecular Oxidative Couplings of Cyclopentadienides* [59]



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[26]) **S**ingly **o**ccupied **m**olecular **o**rbital.

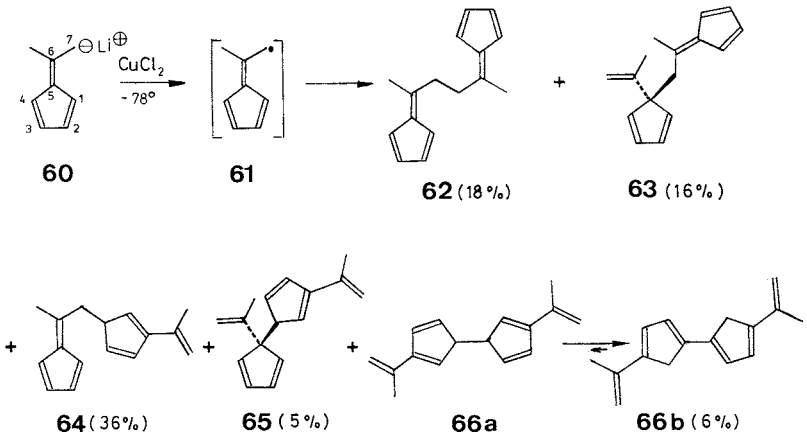
[27]) The sequence **54a** → **55** → **54b** is needed for purification.

[28]) The reaction **56** → **57** is elegantly completed by chromatography over basic Al_2O_3. In a similar way, **59** tautomerizes nearly quantitatively when kept in $CDCl_3$.

Dimethylfulvenyl anion **60** is a very attractive ambident anion for oxidative couplings, because the delocalized anion **60** as well as the fulvenyl radical **61** (which is formed after withdrawal of one electron from **60**) have several reactive sites. So, regioselectivity of the $CuCl_2$-induced coupling of **60** was very interesting, which could take place at C(1)–C(5) and C(7) (*Scheme 17*). If reactivity of all these C-atoms were the same, then a large number of reaction products would have to be expected, in addition to the tautomeric mixtures of cyclopentadienes that could be formed, too.

Anion **60** was easily prepared by reacting 6,6-dimethylfulvene (**2d**) at $-10°$ with 1.1 equiv. of LDA in THF [60]. Subsequently, the solution of anion **60** was dropwise added to the stirred brownish slurry of anhydrous $CuCl_2$ in THF at $-78°$. During the reaction, $CuCl_2$ dissolved to finally give a dark green-brown solution which was filtered over deactivated silica gel at $-30°$. After elution, the red solution was carefully concentrated (0°/0.2 mbar) to give a 92% yield of the crude mixture of dimers. Spectroscopic investigations showed that the reaction mixture was extremely complex, but it could be separated by low-temperature crystallization (**66b**), 'flash'-chromatography (**62**, **63**, and **65**) and HPLC or MPLC (**64**).

Scheme 17. *Oxidative Coupling of 6,6-Dimethylfulvenyl Anion*[29]) [61]



From the analytical yields of the reaction products (*Scheme 17*) reactivity indexes of the C-atoms of radical **61** were calculated [61] (*Table*, left) which qualitatively correspond with the size of the *Hückel* coefficients (*Table*, right), if one takes into account that C(5) is sterically strongly shielded[30]). Extended frontier orbital considerations [62] suggested that the reactive behavior of radical **61** was dominated by SOMO–SOMO interactions, while *Coulomb* interactions and loss of conjugation were secondary effects.

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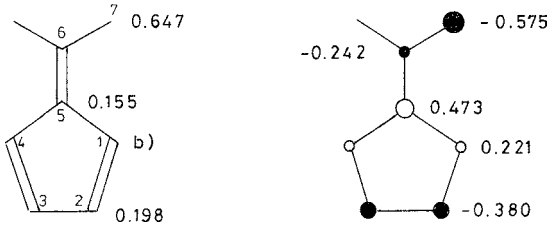
[29]) In *Scheme 17*, the primary products **64** and **65** form tautomeric mixtures, while **66b** is dominating in the equilibrium **66a** → **66b**.

[30]) For more extensive discussions see [62]. We are grateful to Prof. *H. Huber*, University of Basel, for theoretical calculations.

Table. *Reactivity Indexes Derived from Analytical Yields* (left) *and* Hückel *Coefficients of the SOMO of Radical* **61**[a])



[a]) Note that the *Hückel* coefficients of the SOMO of radical **61** are identical to those of the HOMO of anion **60**. [b]) Traces of a [7–1] coupling product have been identified.

2.5. *Summary of Chapter 2.* Based on the observation that $AgBF_4$ reacts with Li–cyclononatetraenide (**8**) nearly quantitatively to give bi(cyclononatetraenyl) **38**, a simple plan (*Scheme 11*) for the synthesis of fulvalenes by oxidative coupling of *Hückel* anions has been developed. This plan has been realized for pentafulvalene (**12**), nonapentafulvalene (**16**) and nonafulvalene (**14**) (*Fig. 12*). All these fulvalenes were very reactive and underwent dimerizations (**12**) and valence isomerizations (**14** and **16**) even at $-30°$. Despite of that, pentafulvalene (**12**) as well as nonapentafulvalene (**16**) have been characterized by ^{1}H- and ^{13}C-NMR spectroscopy. Some more oxidative couplings of substituted cyclopentadienides have been discussed.

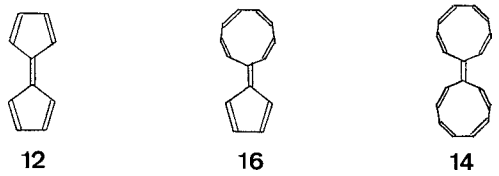


Fig. 12. *Fulvalenes prepared by oxidative coupling of* Hückel *anions*

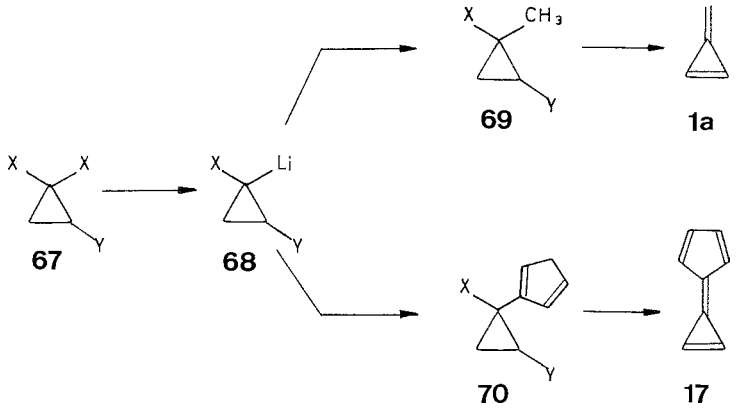
3. Syntheses with Trifunctional Cyclopropanes. – All well-known synthetic procedures for substituted (and sterically and/or electronically stabilized) triafulvenes (**1**) and calicenes (= pentatriafulvalenes **17**), such as *1*) reaction of cyclopropenones with CH-acidic methylenes (like malodinitrile) in the presence of acetic anhydride [3a] [3b] [63][31]), *2*) reaction of cyclopropenylium salts with carbanions [64], *3*) reaction of alkoxy cyclopropenylium salts with cyclopentadienides, followed by hydride abstraction [3d] [65], and *4*) *Wittig* reaction of cyclopropenones with phosphine methylenes [3c] [66], did not look very promising with respect to parent triafulvene (**1a**) or calicene (**17**) because at least one step of the sequences had to proceed at too high temperatures. A good synthetic plan for **1** or **17** had to take into account that the last step should have

[31]) For some typical examples, see [63], [64], [65], [66].

been carried out at low temperatures (−80°), or by gas-phase pyrolysis or 'flash'-photolysis, so that the products could be frozen in a matrix at low temperatures.

A promising synthetic plan (*Scheme 18*) [67] started with trisubstituted cyclopropanes **67** bearing three potential leaving groups. It could (at least in principle) be applied to the synthesis of triafulvene (**1a**) and calicene (**17**) as well: In analogy to other 1,1-dihalo cyclopropanes, metalation (**67** → **68**) as well as alkylation (**68** → **69**) should be proceeded at very low temperatures [68]. Contrary to the classical procedures, cyclopropanes were transformed into nucleophiles which had to be reacted with an electrophilic methyl or cyclopentadiene equivalent. This second case (see **68** → **70**) was supposed to be more problematic for calicene because electrophilic cyclopentadiene equivalents were unknown at the time.

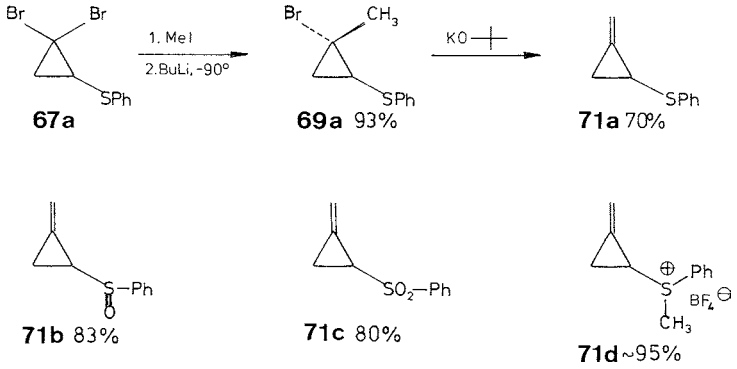
Scheme 18. *Synthetic Plan for* **1** *and* **17** *from Trisubstituted Cyclopropanes*



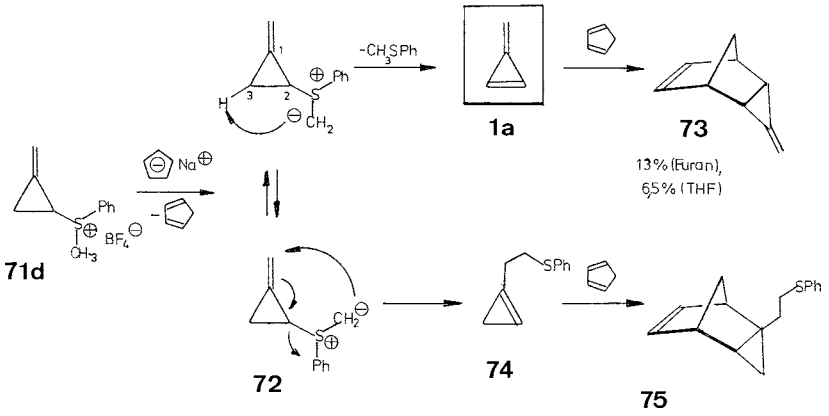
3.1. *Synthesis and Trapping of Triafulvene* (**1a**). In a first step a series of trihalogeno cyclopropanes **67** as well as of 1,1-dibromo-2-Y-cyclopropanes with potential leaving groups Y were prepared [69]. In that context it turned out that cyclopropanes with Y = AcO or Y = Cl did not survive under the conditions of the metallation-alkylation sequence **67** → **68** → **69**. On the other hand, 2,2-dibromocyclopropyl phenyl sulfide (**67a**) was metallated and methylated at −90° with high yields to give **69a**, and the following HBr elimination **69a** → **71a** was unproblematic. This allowed us to transform the phenylthio-substituent of **71a** into a better leaving group (see **71b**, **71c**, **71d**) (*Scheme 19*).

After a series of failed elimination experiments (with **71b**, **71c**, and **71d** as well) we finally reacted the sulfonium salt **71d** in the presence of an excess of sodium cyclopentadienide. The idea was to produce triafulvene (**1a**) in close proximity of cyclopentadiene and to trap it as a *Diels–Alder* product (*Scheme 20*). In fact, the cycloaddition product **73** could be isolated in moderate yields. Hints concerning the mechanism of the cycloaddition sequence stem from the isolation of a second cycloaddition product **75** which dominated if the reaction was carried out in THF (38% of **75** compared with 6.5% of **73**). Obviously, deprotonation of **71d** at first gave the ylide **72** which could either snap H–C(3) to form triafulvene (**1a**) or attack at the exocyclic C-atom to give cyclopropene **74**.

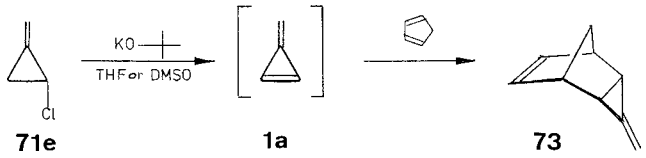
Scheme 19. *Synthesis of Triafulvene Precursors* **71** *from* **67a** [69]



Scheme 20. *Synthesis and Trapping of Triafulvene* (**1a**) [70]



Scheme 21. *Elegant Synthesis of Triafulvene* (**1a**) *According to Billups* [71]



Three years after we trapped triafulvene for the first time [70], *Billups et al.* [71] realized a very elegant synthesis[32]) of parent **1a** (*Scheme 21*) which was not only trapped as cycloaddition product **73** but spectroscopically fully characterized by *Staley* and *Norden* [72] after gas-phase pyrolysis and trapping it at low temperature.

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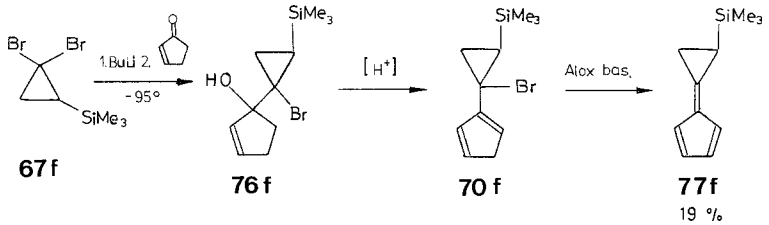
[32]) The starting material **71e** could not be prepared from 1,1-dibromo-2-chlorocyclopropane by Br-Li-exchange, methylation and HBr elimination [69]! It was prepared by reaction of CH_2Cl_2/CH_3Li with allene [71].

Scheme 22. *Synthesis of Calicene Precursor* **77f** (Y = $SiMe_3$)[33])

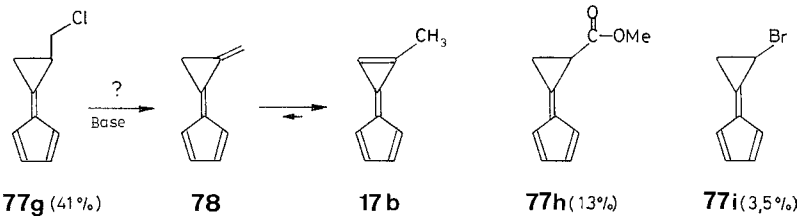


3.2. *Synthetic Attempts towards Calicene* (**17**). The synthetic plan for calicene (*Scheme 18*) started with a trifunctional cyclopropane **67** (normally X is Br) which was metallated with BuLi at $-95°$. Y was supposed to be a potential leaving group which can survive the halogen–lithium-exchange **67** → **68**. The central step of the sequence was the reaction of the functionalized Li–cyclopropane with an *electrophilic cyclopentadiene equivalent* **68** → **70**. It turned out that *cyclopentenone* fulfilled the requirements (*Scheme 22*).

A successful synthesis of a calicene precursor is shown in *Scheme 22* [73]. First of all we showed in five cases that cyclopentenone could survive metallation of the 1,1-dibromo-cyclopropane[34]) and was attacked at the carbonyl-C-atom by cyclopropyl-carbenoids (**68** → **76**, average yield around 35%), although the yields were not outstanding. Furthermore acid-catalyzed H_2O-elimination (**76f** → **70f**) as well as base-induced HBr elimination (**70f** → **77f**) were possible, although at that time [73] the trimethylsilyl derivative **77f** was the only available dihydro calicene with a potential (relatively bad) leaving group.

Only a couple of months before my retirement we synthesized three novel 7,8-dihydro calicenes with potential leaving groups [74] (*Scheme 23*). While **77g** was an interesting precursor of 7-methyl calicene (**17b**), 7-bromo-7,8-dihydro calicene **77i** represented the first precursor of parent calicene with a good leaving group. It would have been well suited for gas-phase pyrolysis[35]), however the bad overall-yields were preventing 'last-minute' pyrolysis experiments[36]).

Scheme 23. *Novel Attractive Precursors*[35]) *of Calicene* (**17**) *and 7-Methylcalicene* (**17b**) [74]



[33]) **76f** as well as **70f** have not been isolated but were directly converted to **77f** (yield 19% starting with **67f**).

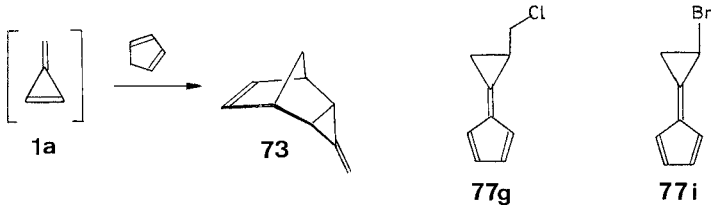
[34]) The important point is that cyclopentenone can be added *before* reaction of **67** with BuLi.

[35]) Promising seemed to be gas-phase pyrolysis of **77i** over a column containing $KOC(CH_3)_3$ while trapping the pyrolysate in liquid nitrogen.

[36]) Yields of **77g**, **77h**, and **77i** over all 4 steps starting with the corresponding 1,1-dibromo-cyclopropane **67**.

3.3. *Summary of Chapter 3.* Triafulvene (**1a**) has been trapped for the first time with cyclopentadiene to give the cycloaddition product **73**. – In view of the synthesis of calicene (**17**) it has been shown that cyclopentenone was a useful cyclopentadiene equivalent in reactions with lithium–cyclopropanes. – 7-Bromo-7,8-dihydrocalicene (**77i**) is the so far best calicene precursor with a good leaving group, while 7-chloromethyl-7,8-dihydrocalicene (**77g**) is an interesting precursor of 7-methyl-calicene (**17b**) (*Scheme 24*).

Scheme 24



4. $CuCl_2$-Induced Coupling of Cyclopropyl Carbenoids: An Attractive Way to Precursors of Triafulvalene (11). – Triafulvalene (**11**) is a highly strained cross-conjugated molecule and therefore very interesting both for spectroscopic as well as for theoretical reasons. According to *ab-initio* calculations [75][76] the parent compound **11** was characterized by strongly alternating bond lengths, and it was even higher in energy than 1,2-dehydrobenzene by 65 kJ/mol. It was not surprising therefore that triafulvalene is unknown and that no simple derivatives of **11** have been prepared so far. If one neglects speculative assignments of reactive intermediates [77], then there exists only one highly annulated and substituted triafulvalene in the literature [78] whose spectroscopic data don't allow any conclusions concerning the ground-state properties of parent triafulvalene. Parallel to our work a promising triafulvalene precursor has been prepared [79][37]), however the main product of 'flash'-vacuum pyrolysis [80] was triptycene besides traces of anthracene and hex-3-ene-1,5-diyne [76].

As we already showed in *Chapter 3*, substituted *1,1-dibromo-cyclopropanes are attractive synthetic building blocks.* They are easily metallated at $-100°$ with BuLi [81], and the formed 1-bromo-1-lithium cyclopropanes **68** are stable enough at temperatures below $-80°$ in order to be synthetically applied as nucleophiles. So they are excellent nucleophiles for low-temperature reactions!

In extension of the synthetic plan for fulvalenes (*Scheme 11*), 1-lithium-1-bromo-cyclopropanes (**68**) could be interesting precursors for the synthesis of substituted bi(cyclopropylidenes) **81** (*Scheme 25*): Oxidative coupling (2 equiv. **68** → **79**) followed by metallation (**79** → **80**) and LiBr elimination (**80** → **81**) should give the envisaged bi(cyclopropylidenes) **81**, and the whole sequence **67** →→ **81** could be applied in the temperature range between -100 and $-80°$. If any potential leaving group would

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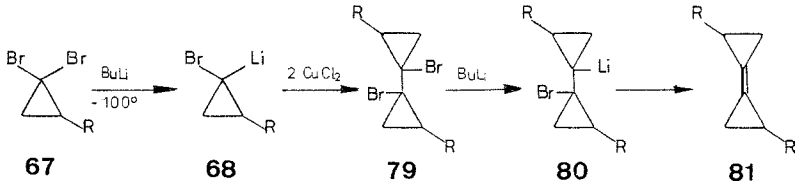
37) A formal 2:1-cycloaddition product of anthracene to the two 'cyclopropene'-double bonds of **11** [79].

Scheme 25. *Synthetic Plan for Triafulvalene Precursors*

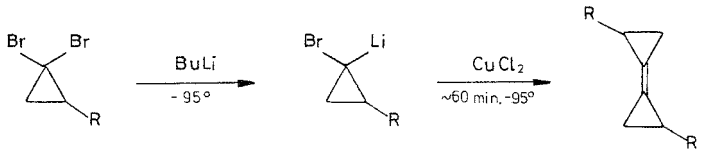


survive the sequence, then the door would be wide open for the synthesis of triafulvalene!

Preliminary experiments with 2,2-dibromocyclopropyl phenyl sulfide **67a** gave an extremely complex product mixture [82][83], but the sequence could be optimized and gave two surprising results: The main product was a *diastereoisomeric mixture of 1,1′-bi(cyclopropylidenes)* **81**, and the coupling reaction worked with *catalytic amounts of* $CuCl_2$ at $-95°$.

According to *Scheme 26*, substituted 1,1-dibromo-cyclopropanes[38]) **67** were transformed to substituted bi(cyclopropylidenes) **81** in a simple 'one-pot-reaction' at $-95°$. We investigated the new reaction in detail ([84]–[88]) and saw that it had a wide range and that stereoselectivity was small in so far that diastereomeric mixtures were formed[39]). The yields are usually high (around 65%) for alkyl- and phenyl-derivatives, medium for substituents R with hetero atoms (R = OR′, R = SR′) and small for typical leaving groups (like R = AcO, R = Br). Three typical examples are mentioned in *Scheme 26*.

Scheme 26. *Low Temperature Conversion of 1,1-Dibromo-cyclopropanes* **67** *to Bi(cyclopropylidenes)* **81** average yield **67** → **81**: 50% (30 examples)



The preparative yields of bi(cyclopropylidenes) **81** were strongly influenced by the reaction conditions so that it was worthwhile to optimize the reaction parameters. Generally, good yields of **81** could be obtained if 0.1 mol-equivalent of $CuCl_2$ were added to a 0.3-M THF-solution of the 1,1-dibromocyclopropane at $-95°$. Then BuLi

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[38]) Cyclopropanes **67** with 1 to 4 substituents were reacted, but in view of triafulvalene (**11**) only monosubstituted cyclopropanes were of interest.

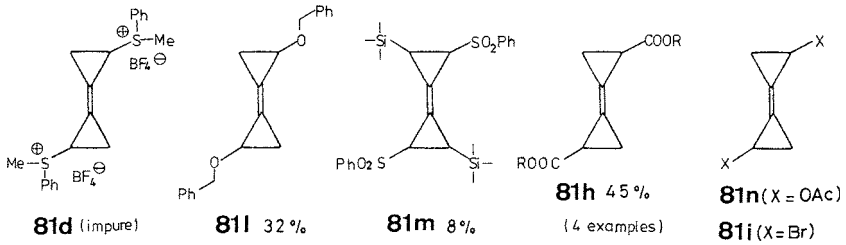
[39]) Starting with monosubstituted 1,1-dibromo-cyclopropanes **67**, normally, all four diastereoisomers are obtained. With respect to the synthesis of triafulvalene (**11**) this was of course no problem. The configuration of selected diastereomers had been confirmed by X-ray analysis [83].

was added[40]), the mixture was stirred for 1 h at $-95°$ and slowly warmed up to r.t. before workup took place, in most cases by 'flash'-chromatography over silica gel.

Several parameters were strongly influencing the success of the sequence **67** →→ **81** [84][85]: a) The optimum *reaction temperature* was in a small interval around $-95°$; at this temperature, a *reaction time* of 1 h was normally sufficient. b) *THF* was the *solvent of choice*, since carbenoids **68** were better stabilized by THF than by Et_2O [81]. A change to Et_2O was only recommended in case of slowly reacting stabilized carbenoids. c) Best yields were usually obtained with *high concentrations of starting material* **67** (*ca.* 0.3 M). d) *$CuCl_2$* was the *best catalyst*, however other catalysts like $CuBr_2$, CuCl and CuI worked as well. e) Under standard conditions (0.3-M solutions of **67** in THF, $-95°$) normally *no coupling products* **79** were observed. Their amount increased with high concentrations of $CuCl_2$ or if 1-bromo-1-chloro-cyclopropanes were reacted. f) In most reactions the catalyst was added before the halogen–lithium exchange was induced by BuLi ('*kinetic control*'). In some cases however, it was better to add $CuCl_2$ to the already formed Li-cyclopropane **68** ('*thermodynamic control*').

After an extensive investigation of the scope of the reaction **67** →→ **81** as well as of the parameters influencing the yields we tried to synthesize bi(cyclopropylidenes) **81** containing potential leaving groups [86][87]. Some examples are given in *Scheme 27*.

Scheme 27. *Possible Triafulvalene Precursors* **81** [86][87]



In analogy to the trapping experiment of triafulvene (*Scheme 20*) it was interesting to try the synthesis of the bis(sulfonium salt) **81d** by methylation of **81a** (*Scheme 26*). This worked, but, due to the low solubility of **81d**, purification was impossible and the attempted reaction of crude **81d** with cyclopentadienide failed. On the other hand, fluoride-induced elimination experiments with **81m** were not successful either. Furthermore, **81h** may be hydrolyzed to give the corresponding dicarboxylate, but the attempted Ag^+-induced decarboxylation (according to *Hunsdiecker–Borodin*) failed as well to give the 2,2′-dibromo-derivative **81i**, which would have been an outstanding triafulvalene precursor. The best precursor prepared so far (in a low yield) is 1,1′-bi(cyclopropylidene)-2,2′-diyl diacetate (**81n**). Even better would have been 1,1′-

[40]) We named that sequence 'under kinetic control', because the Li-cyclopropane **68** could be coupled immediately after formation. Sometimes, however, the yields were higher if the Li-cyclopropane **68** was prepared before $CuCl_2$ was added ('under thermodynamic control').

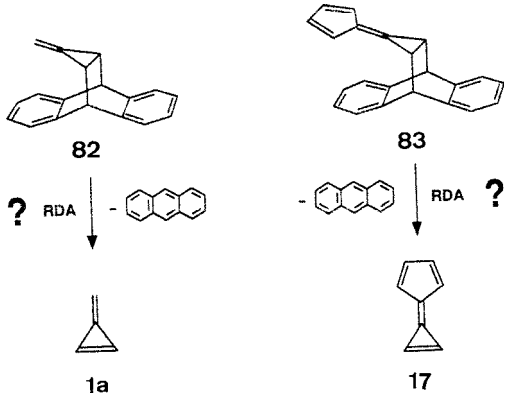
bi(cyclopropylidene)-2,2′-diyl bis(trifluoroacetate) (see **81n**, $X = CF_3COO$) whose synthesis has not been attempted.

Summary of Chapter 4. Reaction of 1-bromo-1-lithium cyclopropanes **68** at $-95°$ with catalytic amounts of $CuCl_2$ resulted in a low-temperature synthesis of 2,2′-disubstituted bi(cyclopropylidenes) **81** with overall yields around 50%. The scope of this new reaction as well as the reaction parameters (strongly influencing the yields) have been explored [84][85]. A series of triafulvalene precursors (with potential leaving groups in positions 2,2′ of **81**) have been prepared. However, so far the highly strained parent triafulvalene (**11**) could neither be isolated nor trapped as a cycloaddition product.

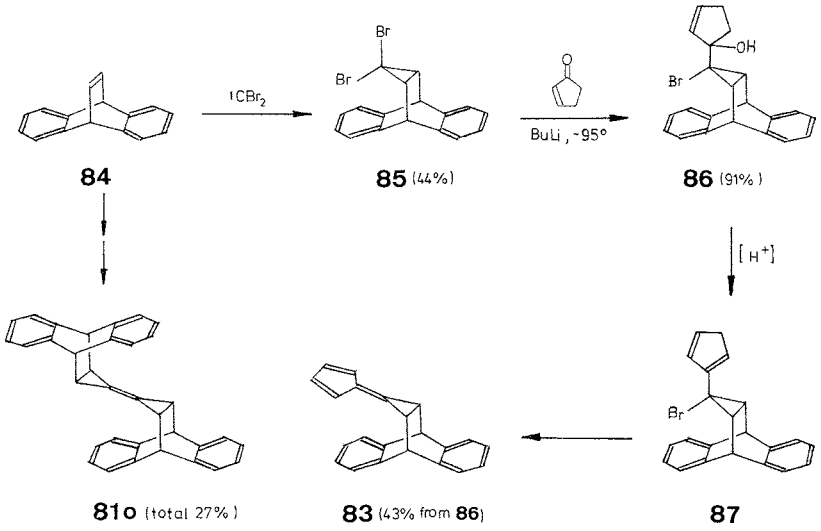
5. Triafulvene-, Calicene- and Triafulvalene Precursors for *retro-Diels–Alder* Reactions. – Despite of numerous synthetic attempts during the last 40 years, all parent cross conjugated fulvalenes containing cyclopropenylidene units remained elusive so far. While triafulvene (**1a**) has been prepared by 'flash'-pyrolysis of 1-methylidene-2-chlorocyclopropane [71] and spectroscopically characterized [72] in 1984, the parent compounds calicene (**17**) and triafulvalene (**11**) still were unknown in 2000. Problems involved in the synthesis of **1a** and **17** are not only based on their low thermal stability. They are also due to the fact that many synthetic sequences applied to substituted triafulvenes and calicenes can't be applied to the parent compounds. Furthermore, if the last step of the sequence results in product mixtures, spectroscopic identification (and even more so separation) of the unstable parent molecules **11** and **17** may be problematic.

A completely different synthetic plan for triafulvene (**1a**) and calicene (**17**) started with the then unknown *retro-Diels–Alder* (*RDA*) precursors **82** and **83** (*Scheme 28*) which could be available from dibenzobarrelene (=4a,9,9a,10-tetrahydro-9,10-ethenoanthracene; **84**). It was based on the assumption that the energy balance of the *RDA* reaction is improved by the formation of a 'low-energy' benzenoid besides a 'high-energy' nonbenzenoid compound. The preparative advantage was that precursors **82** and **83** were supposed to be quite stable at r.t. while fragmentation into **1a** and **17** was planned to be performed by 'flash' vacuum pyrolysis [89].

Scheme 28. *Synthetic Plan for Triafulvene* (**1a**) *and Calicene* (**17**)



Scheme 29. *Synthesis of* RDA *Precursors* **81o** [84] *and* **83** [90]



The synthesis of calicene precursor **83** [90] is summarized in *Scheme 29*. It makes use of our previous findings that cyclopentenone is attacked by Li-cyclopropanes at the carbonyl C-atom [73] (**85** → **86**). Acid-catalyzed elimination of water (**86** → **87**) was surprisingly simple while HBr elimination (**87** → **83**) was performed by chromatography over basic Al_2O_3. Similarly, the triafulvene precursor **82** was synthesized by metalation of the 1,1-dibromo-cyclopropane **85**, methylation of the carbenoid and HBr elimination [91].

If **85** was subjected to metalation and '$CuCl_2$-induced carbene dimerization' (see *Chapter 4*) then triafulvalene precursor **81o** was available.

Very unfortunately, various gas-phase pyrolysis experiments of **82**, **83**, and **81o** failed, although anthracene was detected in most cases and the MS spectra of calicene precursor **83** showed important peaks at $m/z = 178$ ($C_{14}H_{10}$) and $m/z = 102$ (C_8H_6) which were shown to be molecular ions according to *DADI-MIKES* experiments [90].

Final Remarks to Chapter 5. – The pyrolysis experiments of triafulvalene-, triafulvene- and calicene precursors **81o**, **82**, and **83** showed that formal cycloaddition products of anthracene to triafulvene and triafulvalenes underwent various undesired fragmentations and rearrangements under *RDA* conditions [90][91]. Additionally, fragmentation of precursor **81o** was hampered by the small solubility. Furthermore, even if the reactive parent compounds **1a**, **11**, and **17** should have been formed during gas-phase pyrolysis, there is the danger that they underwent cycloaddition to anthracene during workup.

Compared with their dibenzo-derivatives **81o** and **83** (*Scheme 29)*, precursors **81p** and **88** had big advantages. First of all, due to the better solubility and higher volatility of **81p** and **88**, gas-phase pyrolysis should have been easier to realize. Then, *RDA* reactions would have given, besides the target compounds **11** and **17**, benzene which (contrary to anthracene) was not prone to cycloaddition reactions. Furthermore, in case

of a clean *RDA* reaction, triafulvalene **11** as well as calicene **17** could have been frozen at low temperature in a benzene matrix. And finally, NMR-investigations of the olefinic reaction products would have been only slightly disturbed by the singlet of benzene.

In fact, triafulvalene precursor **81p** could be prepared (starting with barrelene [94], which is not easily available) with acceptable yields [92]. Unfortunately, we didn't have time for the gas-phase pyrolysis experiments before my retirement. – The sequence for the calicene precursor **88** was so far hampered by the fact that acid-catalyzed elimination of water (see **86** → **87** in *Scheme 29*) turned out to be problematic.

According to the symmetry of the molecule, the ^{1}H-NMR spectrum of **81p** (*Fig. 13*) displays four *multiplet*s at δ(H) 1.72, 3.90, 5.94, and 6.61 ppm. As expected, the signal of the 3-membered ring protons was at high field (1.72 ppm). The vinylic protons H–C(8)/H–C(9) at δ(H) 6.61 ppm and H–C(6)/H–C(7) at δ(H) 5.94 ppm [which were at higher field because of the anisotropy effect] showed a splitting pattern similar to *AA′XX′*[41]). Analysis of selectively decoupled spectra as well as simulation/iteration gave the essential coupling constants which fitted very well to the structure of **81p** [92].

First attempts towards the calicene precursors **89** and **90** ended at the level of preliminary work. The bis(fulvene) **89** was so far an unknown cross-conjugated molecule with a planar π-system. Being vinylog to pentafulvalene (**12**), **89** was supposed to be thermally quite unstable, but it should have survived in solution at $-80°$ or in crystalline form at $-20°$. This made it an interesting candidate for low-temperature matrix photolysis, during which calicene (**17**) could have been formed by an intramolecular [2 + 2]-cycloaddition-[2 + 2]-cycloreversion sequence [74][93].

On the other hand, 2-(3-bromocycloprop-1-en-1-yl)cyclopenta-1,3-diene (**90**) would be an excellent calicene precursor in view of an easy low-temperature HBr elimination: **90** combines the acidity of the cyclopentadiene unit with the leaving

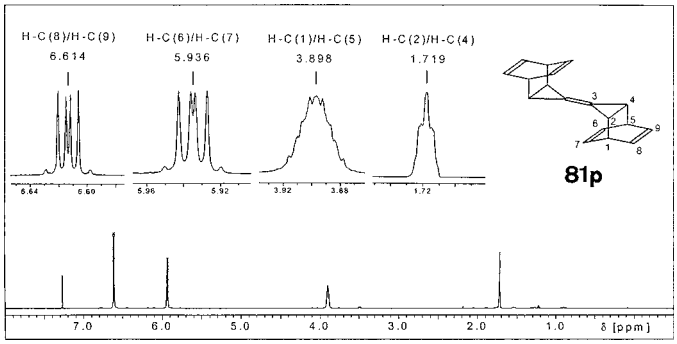


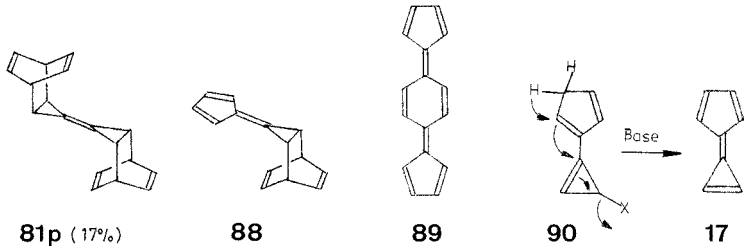
Fig. 13. *^{1}H-NMR Spectrum of the triafulvalene precursor* **81p** (500 MHz, $CDCl_3$, below)*;* above*: extensions of the multiplets*

41) The system was even more complex than *AAMM′XX′YY′* due to the long-range couplings through the central double bond. Simulation/iteration gave the coupling constants $J(1,2) = 3.8$; $J(1,4) = 0.3$; $J(1,5) = 0.3$; $J(1,6) = 1.7$; $J(1,7) = 6.1$; $J(1,8) = 6.0$; $J(1,9) = 1.2$; $J(2,4) = 10.7$; $J(6,7) = 7.0$; $J(8,9) = 7.1$ Hz.

qualities of a substituent in allylic position of the cyclopropene. First steps of a surprisingly simple synthetic plan have already been realized [74][93], but the synthesis of **90** has not been completed.

Summary of Chapter 5. By application of new reaction sequences the *retro-Diels–Alder* precursors **81o**, **82** and **83** of parent triafulvalene (**11**), triafulvene (**1a**) and calicene (**17**) have been prepared (*Scheme 29*). The mass spectra of calicene precursor **83** suggested that the envisaged *RDA* reaction worked in the gas phase, but the parent compounds could neither be isolated nor trapped. First attempts in view of the synthesis of 'ideal precursors' (*Scheme 30*) looked promising but could not be completed.

Scheme 30. *Novel Precursors of Triafulvalene* (**11**) *and Calicene* (**17**) [74][92][93]



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